ANIONIC EQUILIBRIA IN MAJOR SOIL TYPES OF KERALA

By

RESHMA M. R.

(2015- 21-032)

THESIS

Submitted in partial fulfilment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY IN AGRICULTURE

Faculty of Agriculture

Kerala Agricultural University

DEPARTMENT OF SOIL SCIENCE AND AGRICULTURAL CHEMISTRY

COLLEGE OF HORTICULTURE

VELLANIKKARA, THRISSUR - 680 656
KERALA, INDIA

DECLARATION

I hereby declare that this thesis entitled **"ANIONIC EQUILIBRIA IN MAJOR SOIL TYPES OF KERALA"** is a bonafide record of research work done by me during the course of research and the thesis has not previously formed the basis for the award to me of any degree, diploma, associateship, fellowship or other similar title, of any other University or Society.

Reshma M. R.
(2015-21-032)

Vellanikkara,
27-10-2020

CERTIFICATE

Certified that this thesis entitled **"ANIONIC EQUILIBRIA IN MAJOR SOIL TYPES OF KERALA"** is a record of research work done independently by Ms. Reshma M. R. under my guidance and supervision and that it has not previously formed the basis for the award of any degree, diploma, fellowship or associateship to her.

Vellanikkara,

27-10-2020

Dr. P. Sureshkumar

(Major Advisor, Advisory Committee)
Professor and Head (Retd.)
(Radiological Safety Officer)
Radiotracer Laboratory
College of Horticulture
Vellanikkara

CERTIFICATE

We, the undersigned members of the advisory committee of Ms. Reshma, M. R., a candidate for the degree of **Doctor of Philosophy in Agriculture** with major in Soil Science and Agricultural Chemistry, agree that the thesis entitled **"Anionic equilibria in major soil types of Kerala"** may be submitted by Ms. Reshma M. R., in partial fulfillment of the requirement for the degree.

27.10.2020

Dr. P. Sureshkumar

(Major advisor, Advisory Committee)
Professor and Head (Retd.)
(Radiological Safety Officer)
Radiotracer Laboratory
College of Horticulture
Vellanikkara

27.10.2020

Dr. Jayasree Sankar S.

(Member, Advisory Committee)
Professor and Head
Department of Soil Science
and Agricultural Chemistry
College of Horticulture
Vellanikkara

27/10/2020

Dr. K. M. Durga Devi

(Member, Advisory Committee)
Professor
Department of Soil Science
and Agricultural Chemistry
College of Horticulture
Vellanikkara

27/10/2020

Dr. A. Latha

(Member, Advisory Committee)
Professor (Agronomy) and Head
Agricultural Research Station
College of Horticulture
Vellanikkara

27/10/2020

Mr. Ayyoob K. C.

(Member, Advisory Committee)
Assistant Professor
Department of Agricultural Statistics
College of Horticulture
Vellanikkara

27/10/2020

Dr. M. P. Sujatha

(External Examiner)
Senior Principal Scientist & Head
Soil Science Department
Kerala Forest Research Institute
Peechi

Acknowledgement

Towards the end of this great voyage in the quest for knowledge and wisdom, which makes the beginning of a new horizon, it gives me an insurmountable task to mention all of them who planted and nurtured the spirit of faith and help in accomplishing this task. I take this opportunity to look back on the path traversed during the course of this endeavour and to remember the guiding faces behind the task with a sense of gratitude.

Firstly I would like to express my deep sense of gratitude and indebtedness to ***Dr. P. Sureshkumar****, Professor and Head (Retd.), Radiological Safety Officer, Radiotracer Laboratory, College of Horticulture for giving me the wonderful opportunity to complete my PhD thesis under his supervision, it is truly an honor. He has been there providing his heartfelt support and guidance at all times and has given me invaluable guidance, inspiration and suggestions in my quest for knowledge. During this journey I could realize his words are true that freedom of thinking and freedom of working without any prejudice is the success of any research work. I value his knowledge and wisdom which nurtured this research in right direction without which this thesis would not have been possible and I shall eternally be greatful to him for his assistance.*

It is with immense pleasure, I express my whole hearted gratitude and never ending indebtedness to ***Dr. Jayasree Sankar S.****, Professor and Head, Department of Soil Science and Agricultural Chemistry and member of my Advisory Committee for her expert guidance, patient hearing, constructive criticisms, valuable suggestions and above all her support and encouragement throughout the course of study.*

I take pride in acknowledging the insightful guidance of ***Dr. K. M. Durga Devi****, Professor, Department of Soil Science and Agricultural Chemistry and member of my Advisory Committee for her critical evaluation of manuscript, constant encouragement, sincere help and support in times of need especially in the preparation of this thesis.*

I thankfully acknowledge ***Dr. A. Latha****, Professor & Head, Agricultural Research Station, Mannuthy, and member of my Advisory Committee for her esteemed advice, timely help, and valuable suggestions throughout this programme.*

I express my gratitude to ***Sri. Ayyoob K. C.****, Assistant Professor, Department of Agricultural Statistics and member of my Advisory Committee for his valuable suggestions and help in doing the statistical analysis and interpretation of data.*

I wish to express my sincere thanks to ***Dr. P. K. Sushama****, Former Professor& Head, Department of Soil Science and Agricultural Chemistry for her inspiring attitude and sincere help during preparation of technical programme.*

It is my privilege to express my heartfelt thanks to ***Dr. Sandeep S.*** *Senior Scientist, Department of Soil Science, Kerala Forest Research Institute, Peechi, Thrissur, for his esteemed advice, timely help and valuable suggestions throughout this programme.*

My heartfelt thanks to ***Dr. P. K. Rajeevan,*** *(Former Registrar, Kerala Agricultural University),* ***Dr. Laly John*** *(Professor & Head, Department of Agricultural Statistics) and* ***Dr. V.I. Beena*** *(Assistant Professor and Head, Radiotracer Laboratory) for their love and support which helped me to achieve this goal. I would like to thank* ***Dr. Bhindu P. S.*** *(Assistant Professor, ARS, Chalakkudy) for her help during the work and thesis preparation.*

I thankfully acknowledge ***Dr. Betty Bastian, Dr. Rajalakshmi. K., Dr. Divya Vijayan and Dr. Smitha John*** *of the Department of Soil Science and Agricultural Chemistry for their ever-willing help rendered at various phases of my study. I do gratefully acknowledge the services provided by Central and College library for the preparation of the thesis. I express my sincere gratitude to* ***Dr. A. T. Francis****, Librarian, all the teachers and non-teaching staff of College of Horticulture, Vellanikkara.*

I express my gratitude to my friends and colleagues ***Soniya, Silpa, Unnikrishnan, Nideesh ettan, Rajakumar, Irene, Sophiya and Nisha****. I would like to express special thanks to* ***Geetha chechi*** *for her timely help and encouragement. No words can truly potray my indebtedness to* ***Upasana chechi*** *and* ***Sam*** *for their paryers, support and immense help which made me more bold during this journey. I would like to record my sincere thanks to Barathy chechi, Sugandhi chechi and Sabreesh ettan.*

I owe my special thanks to ***Narayanan chettan*** *for his immense help during course of sample collection and field experiment.*

__Jawaharlal Nehru Memorial Fund for Doctoral studies__ is gratefully acknowledged.

I am forever behold to my loving __Achan__ and __Amma__ without whose support, prayers, blessings and sacrifices I would not have completed this work. No words can express my sincere gratitude towards my sister __Chakkara, brother-in-law Bibin__ and ***Lachu vava** for their love, personal sacrifices, incessant inspiration and constant prayers which helped me to complete this venture successfully.*

Words fail when I express my feelings to my **Mother-in-law** *whose support helped me to complete this venture successfully.*

To my best half __Vineeshettan__ and Son __Jagannath__, I am unable to express my feelings by words for their affectionate encouragement, patience, support and sacrifices during the course of the study.

One last word; since it is practically impossible to list all the names who contributed contributions to my work, it seems proper to issue a blanket of thanks for those who helped me directly or indirectly during the course of study.

Finally, I thank God for bestowing me with divine spirit, essential strength and necessary support to find my way towards a glorious career amidst several hurdles and struggles.

.....any omission in this small manuscript does not mean lack of gratitude.

Reshma M. R.

***“Dedicated to Amma,
Achan, Vineesh ettan,
Kannamon and
Chakkara”***

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

Introduction

1. INTRODUCTION

Ion exchange is an important process in soil. The process of ion exchange represents a transfer of ions between a solid phase and an ion in liquid phase. The process follows law of mass action. Sum of exchangeable cations that can be adsorbed by a soil colloidal system which can be exchanged with the cations in soil solution in equivalent basis is called cation exchange capacity (CEC). Anion exchange capacity (AEC) can be defined as the sum of exchangeable anions that can be adsorbed by soil colloidal system which can be exchanged with anions in soil solution on equivalent basis. Adsorption of ions on soil colloid includes different mechanisms like electrostatic force of attraction, isomorphus replacement and formation of chemical bonds. Adsorbed ions with electrostatic force of attraction are exchangeable. So ion exchange capacity is just a part of adsorption of ions in soil. Nature and behavior of cations in soil are well-studied, whereas studies about anionic nutrients in soil are less. Extensive study about anionic nutrients in soil is needed especially in tropical soils to unravel the different fractions of anionic nutrients, quantity-intensity relations, strength of binding of these anions in soil and to know about their preferential adsorption. Highly weathered condition in tropical soils is more conducive for anion exchange and anion adsorption. Moreover the role of anion exchange if any with respect to availability of these nutrient anions to plants is also studied under such soil environment.

Charge development in soil occurs by two processes. Permanent charge development through isomorphous substitution and pH dependent charge development. The pH at which net surface charge of the soil colloids is zero is known as ‘zero-point of charge’ (ZPC). Formation of negative charges in soil solid phase mainly occurs through isomorphous substitution and these charges will not change with change in pH. However the positive charge development through isomorphous replacement is very rare. Positive or negative charges are developed as a result of change in pH. Positive charges are developed, when pH is less than ZPC of the minerals. Negative charges are formed if the soil pH is greater than the ZPC of minerals (Sparks, 2003).

Soils with amphoteric surface reactive groups are called variable charge soils, which includes Oxisols, Ultisols, Alfisols, Spodosols and Andisols. The variable charge component is usually developed on surfaces of organic soil constituents with carboxyl, phenolic, or amino reactive groups, as well as on surfaces of inorganic soil constituents with hydroxyl reactive groups (Qafoku *et al.,* 2004). Highly weathered tropical soils are rich in kaolinite mineral, oxides and hydroxides of Fe and Al (Khawmee *et al.,* 2013), hematite and goethite. These minerals are responsible for the development of pH dependent positive charges in tropical soils. ZPC of these minerals are relatively high, hence they can provide pH dependent positive charge under acidic soil pH. ZPC of other important soil components like organic matter and silica is 2 (Gu and Schulz, 1991), hence formation of pH dependent positive charges is not possible at normal soil pH (5-7.5).

The essential nutrients like N, P, S, B, Mo, Cl and the beneficial element Si are absorbed by plants in their anionic forms. Availability of anionic nutrients in soils depends on pH, ionic strength, organic matter content, silica content, oxides and hydrous oxides of iron and aluminium. Different fractions of anions and competition of anions in soil also contribute to available pool.

The interaction between anions and the surface of the soil solid phase involves the mechanisms of non-specific adsorption and specific adsorption. Non-specific adsorption includes both negative and positive adsorption which is due to the electrostatic force of attraction and outer-sphere complexation. In the outer sphere complex, the ion retains its hydration sphere and attaches to the surface via electrostatic forces, whereas the inner sphere complex is partially dehydrated and directly bound to the surface.The anions are expelled from the diffuse double layer formed on negatively charged surfaces which is negative adsorption or anion exclusion (Tan, 2011). In positive adsorption anions get adsorbed to the positively charged surface or edges. It mainly depends on change in pH and electrolyte concentration. Lyotropic series of anions for adsorption is as follows: SiO_4^{4-} > PO_4^{3-} >> SO_4^{2-} > NO_3^- = Cl^- (Bolt, 1976). Specifically adsorbed anions form mono-dentate or bi-dentae inner-sphere complexes by the displacement of O or OH groups in lattice. If the complex formed is mono-dentate it can be somewhat labile and if it is bi-dentate it will not be available. If the outer-sphere complexes are formed, adsorption will be reversible.

Kerala is a slender strip of land in the southern tip of Indian subcontinent, lies along the coastline of Arabian Sea on the west and the mountains of the Western Ghats on the east, sloping down the hills to the coastal belt. Kerala is located between 8°18' and 12°48' N latitude and 74°52' and 77°22' E longitude. Low land (below 7.5 m MSL), mid land (between 7.5 m and 75m MSL) and high land (above 75 m MSL) are the three parallel physiographic zones in Kerala. The geographical area of Kerala is 38,864 km^2, out of which 10.2 per cent is low land region, 41.8 per cent mid land region and 48 per cent high land region. (KSHIS, 2020). The dominant soil forming process is laterisation under tropical humid climate of Kerala. The factors of soil formation are affected by local variations in climate, relief and vegetation and it leads to the development of a variety of soils ranging from potential acid sulphate soils to black cotton soils; clay soils to sandy soils with wide variation in physico-chemical properties and available nutrient status. Sixty eight per cent of the soil samples were reported with high available phosphorus status in Kerala (KSHIS, 2020), which is uncommon in tropical soils where the possibility of fixation is very high.

High rainfall during monsoon season leads to leaching of bases and accumulation of iron, aluminium and manganese. Black cotton soils are seen in low rainfall areas of eastern parts of Palakkad district. Soils developed by deltaic deposition and tidal influence of Arabian Sea are acid saline/potentially acid sulphate soil with very low pH. The soils of *Kuttanad, Pokkali, Kole* and *Kaipad* come under this category (Nair *et al.,* 2013). The dominant mineral in Kerala soil is kaolinite (Sureshkumar, 1993) and high content of sesquioxides is also reported

(Santhosh, 2013). Soils of Kerala are one of the best to study about the chemistry of anions in soil because of the acidic soil pH with dominance of kaolinite mineral and oxides and hyrous oxides of Fe and Al.

In the above scenario, it is necessary to unravel the chemistry of anionic nutrients in soil and their quantity-intensity relations, with respect to major soil types of Kerala. The present study was undertaken with the following objectives:

- To study the relative adsorption of selected anions (nitrate, phosphate, sulphate, silicate, molybdate and borate)
- To study the competitive interaction of fractions of these anions with respect to their adsorption behavior and bio availability
- To study the relative intensities of each of these anions

Review of literature

2. REVIEW OF LITERATURE

Soil is a dynamic natural complex consisting of solid, liquid and gas phases. During the process of soil formation under the influence of different soil forming factors, it acquires electric charges (positive or negative) which confer specific thermodynamic and physico-chemical properties. These charges are of different origin and different scales. Some occur during the deterioration and formation of secondary substances like clays, alumino silicates, oxides and humified organic matter. The negative charges on soil colloid results in cation exchange and positive charges lead to anion exchange properties.

Anion exchange reactions are not studied as cation exchange. It is more relevant in variable charge soil. Variable charge soils are seen in the Oxisols, Ultisols, Alfisols, Spodosols and Andisols. Surface reactive groups with amphoteric nature are high in these soils. Hence thery are considered as variable charge soils. In general, highly weathered tropical soils, sub-tropical and soils from volacanic ash parent materials are coming under this category. The mineralogical, physical and chemical characteristics of these soils are different from soils of temperate regions. The variable charge component in inorganic soil component is mainly hydroxyl reactive groups, whereas carboxyl, phenolic, or amino reactive groups are seen in organic soils.

2.1 MINERALOGY OF HIGHLY WEATHERED TROPICAL SOIL

The most important mineralogical components in variable charge soil are: kaolinite, iron oxides, gibbsite, anatase and maghemite in Oxisols (Fonte and Weed, 1991); poorly crystalline kaolinite, small amount of irregular interstratified hydroxy-interlayered illitic vermiculite and iron oxides in Ultisols (Koch *et al.*,1992); illite, vermiculite, smectite, kaolinite and kaolinite interstratified minerals in Alfisols (Zhang *et al.*, 2016); minor amounts of mica, chlorite, kaolinite and vermiculite in the clay fraction of Spodosols (Righi and De Coninck, 1977).

The dominance of kaolinite mineral in Oxisols and Ultisols of Thailand soils were also reported by Khawmee *et al.* (2013). Iron oxide mineralogy of well-drained Ultisols and Oxisols were studied by Bigham *et al.* (1978) and reported the dominance of goethite and hematite.

2.2. ANIONIC NUTRIENTS AND THEIR FRACTIONS IN SOIL

Nitrogen, phosphorous, sulphur, boron, molybdenum, chlorine and silicon are the anionic nutrients in soil, because they are absorbed by plants in their anionic forms. Except silicon all other elements among this are considered as essential elements. Silicon is considered as beneficial element.

2.2.1. Nitrogen

Essentiality of nitrogen was discovered by Theodore de Saussure in 1804. Nitrogen is the first limiting nutrient in crop production. The plant usable forms of nitrogen are NO_3^- and NH_4^+. More than 95 per cent of the total N in most of the surface soil is organically combined. According to Young and Aldag (1982), the inorganic N compounds detected in soils includes NO_3^-, NO_2^-, exchangeable NH_4^+, nonexchangeable (mineral-fixed) NH_4^+, dinitrogen gas (N_2), and nitrous oxide (N_2O). Other chemical or biological intermediates are nitric oxide (NO), nitrogen dioxide (NO_2), hydroxylamine (NH_2OH), hyponitrous acid (HON = NOH), azide (N_3^-), and some cyano compounds.

2.2.2. Phosphorous

Essentiality of P was discovered by C. Sprengel in 1839. $H_2PO_4^-$ and HPO_4^{2-} are the plant usable forms of P in soil. The sequential extraction scheme proposed by Peterson and Corey (1966) partitioned inorganic P into four pools, aluminium phosphate, iron phosphate, reductant soluble phosphate and calcium phosphate. Krishnakumar (1991) and Deepa (1995) reported low available P status in laterite soil, in spite of continuous application of fertilizer P. The presence of high amounts of clay, Al, Fe and sesquioxides is responsible for fixation of applied P (Doddamani and Rao, 1996).

2.2.3. Sulphur

Essentiality of S was discovered by Sachs and Knop in 1860. SO_4^{2-} is the plant usable form of S in soil. Williams and Steinbergs (1959) studied soil sulphur fractions as indices of available sulphur in Australian soil. They found that sulphate sulphur, total water-soluble sulphur, and heat-soluble sulphur were all correlated with the amount of sulphur taken up by the plants. They could also observe that major fraction of S in soil is organic. Sequential extraction of S was carried out by Xiao-quan *et al.* (1992) and sulfur constituents were fractionated into water-soluble, adsorbed, dilute-HCl-volatile and dilute-HCl-soluble, pyrite-associated, HI-reducible, ester-bound and carbon-bonded sulfur.

2.2.4. Boron

Warington (1923) proved the essentiality of B plant nutrition. H_3BO_3, $H_2BO_3^-$, HBO_3^{2-} and BO_3^{3-} are the plant usable forms of B in soil. Readily soluble B, specifically adsorbed B, oxide bound B, organically bound B and residual B were the five B fractions that can be extracted by the sequential extraction procedure proposed by Hou *et al.* (1994, 1996). Relationships of individual B fractions with physico-chemical properties of the experimental soils confirmed the validity of the proposed fractionation scheme. According to Hou *et al.* (1994) the readily soluble and specifically adsorbed B fractions accounted for less than 2 per cent of the total soil B in the sequential extraction procedure.

2.2.5. Chlorine

Broyer *et al.* (1954) discovered the essentiality of chlorine in plant nutrition and Cl^- is the plant usable form. According to Oberg (1998), organic chlorine and inorganic chloride forms are the major forms of chlorine in soil. Chloride concentration in soils is usually low (0.5 to less than 35 ppm) but can accumulate in saline soils to substantial levels (possibly more than 6000 ppm) (Tisdale *et al.,* 1985).

2.2.6. Molybdenum

Arnon and Stout (1939) discovered the essentiality of Mo in soil. The plants take up Mo in the form of the molybdate anions (MoO_4^{2-} and $HMoO_4^{-}$) which are the predominant species in soil solution. For strongly acidic (pH < 4.5) and acidic soils (pH 4.6-5.5), Mo concentration in the soil solution was lower than 0.02 µmol L^{-1} (Rutkowska *et al.,* 2017). Above pH 4.2, MoO_4^{2-} is the common anion followed in decreasing order by $MoO_4^{2-} > HMoO_4^{-} > H_2MoO_4^{0} > MoO_2(OH)_2^{+} > MoO_2^{2+}$ (Lindsay 1979). Lang and Kaupenjohann (1999) studied different fractions of Mo in acid forest soil. Free plus non-specifically bound Mo ranged between 5 and 28 µg kg^{-1}. Specifically bound Mo ranged from 44 to 407 µg kg^{-1}. Molybdenum extracted by ammonium oxalate and ascorbic acid ranged from 135 to 1071 µg kg^{-1}.

2.2.7. Silicon

Silicon (Si) is the second most abundant element in the earth's crust and plays a number of important roles in the mineral nutrition of plants and it is considered as beneficial element. Monomeric form (H_4SiO_4) is the plant-available form of soil Si. Polymerization of monomeric form results in formation of polysilicic acid which is not shown to be plant-available (Williams and Crerar, 1985). Georgiadis *et al.* (2013) partitioned silicon in soil into five pools: mobile Si, Si in adsorbed silicic acid, Si in soil organic matter, Si in pedogenic oxides and hydroxides, amorphous silica of biogenic and minerogenic origin.

2.3 FACTORS AFFECTING AVAILABILITY OF ANIONS IN SOIL

2.3.1. pH

The bioavailability of P is strongly tied to soil pH. P fixation occurs at very low and very high pH. As the pH increases from below 5 to 6, iron and aluminium phosphates become somewhat soluble, as pH drops from greater than 8 to below 6, calcium phosphate compounds increase in solubility (Weil and Brady, 2017). According to Cerozi and Fitzsimmons (2019) pH in aquaponics systems is maintained at a 5.5-7.2 range for optimal availability and uptake of P by plants. High pH values resulted in the formation of insoluble calcium phosphate species.

Boron adsorption by soils increased as a function of solution pH in the range of pH 3 to 9 (Barrow, 1989; Bingham *et al.,* 1971) and decreased in the range of pH 10 to 11.5 (Goldberg and Glaubig, 1986)**.** A green house study was conducted by Peterson and Newman (1976) at 5 different pH levels (4.7, 5.3, 5.8, 6.3, 7.4) to study the effect of pH on B availability. They observed a 2.5-fold drop in B uptake occurred at pH 7.4 as compared with the other soil pH levels indicating substantial fixation of B. The highly significant negative partial correlation between pH and available boron showed that increasing pH decreases the amount of available boron, and the effect is due to fixation (Berger and Truog, 1946).

Since most of the total soluble Si below pH 8.0 consists of uncharged $Si(OH)_4$, changes in ionic strength would not significantly alter the total soluble Si in most soils (Elgawhary and Lindsay, 1972).

Increasing soil pH from 5.0 through the use of $CaCO_3$ resulted in large increases of sulfate-S in the soil solution. The large increase in soil solution sulfate S was probably due to a sharp decline in retention of adsorbed sulfate at higher pH values **(**Elkins and Ensminger, 1971).

According to Rutkowska *et al.* (2017), the most important factor that influencing Mo concentration in soil solution is pH. Regular liming can improve the availability of molybdenum to plants in acid soils.

2.3.2. Organic matter

Several scientists worked on effect of green manure addition on P availability (Randhawa *et al.,* 2005 and Silva *et al.,* 2012). Randhawa *et al.,* (2005) could observe 5-fold increase in organic P mineralisation rate in green manure amended soil compared to the corresponding unamended soil. The mobilization of phosphorus occurs by conversion of insoluble Ca, Al and Fe forms of P to soluble forms through action of organic acids and chelates that are produced during decomposition of manures (El-Baruni and Olsen, 1979).

Silicon accumulates in plants as silica deposits particularly in the shoots. This silica is returned to the soil mainly in plant litter. As the organic matter (OM) is decomposed the silica is released. Wang *et al.* (2018) studied the dissolution kinetics of silicon on biochar application. The mechanism of silicon release is suggested to be controlled by a protective carbon-silicon interaction, as accompanied by carbon release. They suggested that Si-rich biochar could serve as a source of Si with slow release, while Si-deficient biochar could serve as an extra Si sink in agricultural paddy soil.

The study conducted by Berger and Truog (1946) revealed that organic matter influences the availability of boron to a greater extent than pH. The incorporation of FYM proved beneficial in improving available B and exchangeable Ca contents in soils and enhancing the B and Ca uptake by cauliflower (Chander *et al.*, 2007).

Positive correlations were found between soil solution Mo concentration and organic carbon in soil. The increase in soil solution Mo was under the influence of increased soil organic carbon contents from below 5 to more than 15 g kg^{-1} (Rutkowska *et al.*, 2017).

Saren *et al.* (2016) found that addition of organic matter decreased non-sulphate sulphur in soils. This is because of the activities of S-oxidizing organisms which not only releases sulphate sulphur from the added organic source but also from native source present in the soil.

2.3.3. Release from minerals

At pH 4.5, $AlPO_4$ $2H_2O$ (variscite) and $FePO_4$ $2H_2O$ (strengite) control the concentration of $H_2PO_4^-$ in solution. Dissolution of these minerals increases when pH increases. At pH 4.8 both strengite and fluorapatite can exist in soil. As pH increases, the $H_2PO_4^-$ concentration decreases as the Ca-P precipitate (Tisdale *et al.*, 1985).

Adsorption of water molecules on the surface of quartz and amorphous silica leading to the formation of four silanol groups around the silicon atom and the detachment of orthosilicic acid from the surface from surface lead to the dissolution of quartz and amorphous silica (Sokolova, 2013). The release of alkali metals and calcium from the surface feldspars causes the dissolution of feldspar. Adsorbed Mo can be released into the solution by the reductive dissolution of Mn and Fe oxides (Smedley and Kinniburgh, 2017).

2.4. ADSORPTION OF ANIONS IN SOIL

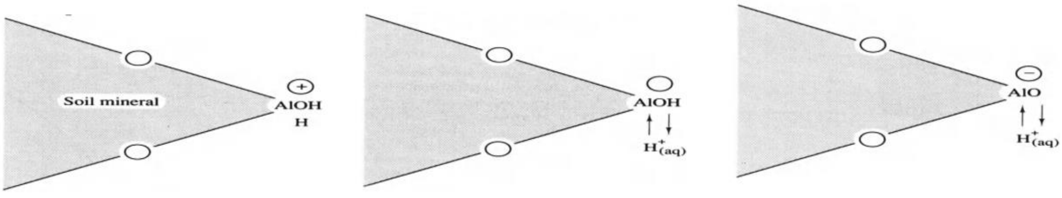
Adsorption can be defined as the accumulation of a substance or material at an interface between the solid surface and bathing solution. Adsorption can include the removal of solute (substance dissolved in solvent) molecules from the solution and of solvent (continuous phase of solution, in which solute is dissolved) molecules from the solid surface and attachment of solute molecule to the surface (Stumm, 1992). Adsorption does not include surface precipitation or polymerization process (Sparks, 2003). It is one of the most important processes in soil. It determines the quantity of plant nutrients, metal, pesticides and other organic chemicals retained on soil surface and therefore is one of the primary processes that affect transport of nutrients and contaminants.

2.4.1. Mechanism of adsorption

Adsorption of ions on soil colloid includes different mechanisms like electrostatic force of attraction, isomorphus replacement and formation of chemical bonds. Both physical and chemical forces are involved in adsorption of solute from solution. Physical forces include Van der Waals forces (eg. Partitioning) and electrostatic outersphere complexes (eg. Ion exchange). Chemical forces resulting from short range interactions include inner-sphere complexation that involves a ligand exchange mechanism, covalent bonding and hydrogen bonding (Stumm and Morgan, 1981).

Sparks (2003) described inner-sphere and outer-sphere complexation during adsorption on soil surface. Outer-sphere complexes are weaker than inner-sphere complexes because of the electrostatic coulombic interactions, whereas covalent or ionic bonds are involved in outer-shpere complex formation. Hence the process is rapid and reversible in case of outer-sphere complexation and the adsorption occurs between surface and adsorbate which are opposite in charge. In case of inner-sphere complexation, the process is irreversible and slow. The original charge of the adsorbent can be increased, reduced, neutralized or reversed due to inner-sphere complexation. Outer and inner-sphere complexation can occur simultaneously.

Two important processes for anion adsorption in soil is the development of positive charge and specific adsorption/ligand exchange which are detailed as below. Figure 1 describes surface charge development on Fe and Al oxides and hydroxides. Figure 2 describes specific adsorption of phosphate on the surface of the minerals by replacing OH groups (Pansu and Gautheyrou, 2007)



a) Low pH b) ZPC c) High pH

Fig. 1. Variation in surface charge on iron and aluminum hydroxides as a function of pH

At lower pH than ZPC, soil surface adsorb H^+ ion from solution and becomes positive charge (Fig.1a). When pH increases and reaches ZPC, the adsorbed H^+ dissociate into soil solution leaving the surface with no net charge (Fig.1b). At higher pH than ZPC, an additional H^+ dissociate into soil, leaving the surface negatively charged (Fig.1c) (Schlesinger and Bernhardt, 2013). The displacement reaction in specific adsorption is as follows (Tan, 2011).

$$\text{-Al-OH} + H_2PO_4^- \rightarrow \text{-Al-}H_2PO_4 + OH^-$$

Mono and bidentate iron-phosphorous complexes are formed as a result of specific adsorption as shown in Figure 2. Only a part of this phosphorous is recovered by desorption analysis. Monodentate complex is somewhat labile, whereas bidentate complex is irreversible (Hingston *et al.,* 1974).

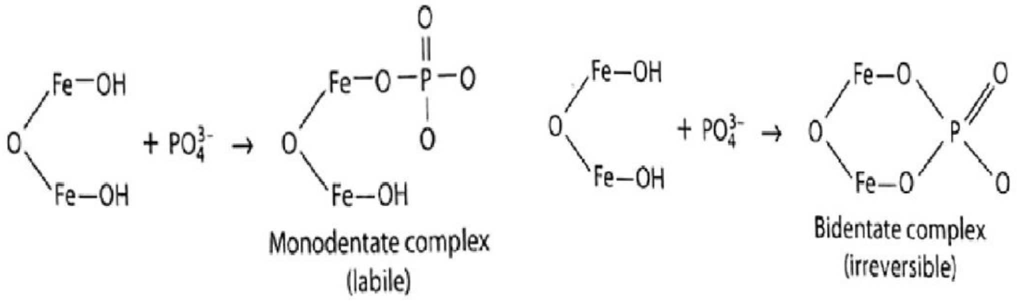


Fig .2. Mono and bidentate iron-phosphorous complex formation

Bolt (1976) reported a decreasing order of preferential adsorption among anions as $SiO_4^{4-} > PO_4^{3-} >> SO_4^{2-} > NO_3^- = Cl^-$. Young (2000) also suggested this lyotropic series, and that adsorption process was physical in nature.

2.4.2. Adsorption isotherms

Adsorption isotherm, which describes the relation between the activity or equilibrium concentration of the adsorbate and the quantity of adsorbate on the surface at constant temperature, is usually employed to describe adsorption. Freundlich and Langmuir adsorption isotherms are most commonly used models to study about the adsorption process in soil.

2.4.2.1. Langmuir adsorption isotherm

Langmuir (1918) developed Langmuir equation to describe the adsorption of gas molecules on a planar surface. Olsen and Watanabe (1957) used Langmuir adsorption isotherm to describe phosphate sorption on soils. They used the following equation and explained the parameters as follows:

$$x/m = kbc/(1 + kc)$$

where x/m = mg of P adsorbed per 100 g soil, b = the adsorption maximum, c = equilibrium P concentration in moles per liter, and k = a constant related to the bonding energy of the absorbent for the adsorbate. In linear form, the equation becomes

$$c/(x/m) = (1/kb) + (c/b)$$

Another useful form of the equation is $k = \theta/(1-\theta)*c$, where θ = the fraction of the adsorption maximum at a given equilibrium phosphorus concentration, or c. When $\theta = 0.5$, or one-half saturation, then $k = 1/c$. The constant, k, which is related to the bonding energy of the soil for phosphate, is equal to the reciprocal of the equilibrium concentration of phosphorus at one-half saturation. Most of the assumptions of Langmuir adsorption isotherm are not followed in heterogenous soil system. Hence, Sparks (2003) suggested the use of Langmuir equation for qualitative and descriptive purposes. Sposito (1982) studied about the use of Langmuir equation in interpreting two surface adsorption and concluded that, any sorption reaction for which the distribution coefficient is a finite, decreasing function of the amount sorbed, q, and extrapolates to zero at a finite value of q, can be represented mathematically by a two-surface Langmuir equation. Some researchers have proposed the a two-site or two-surface Langmuir equation to describe adsorption process as an evidence of two sites of different affinities on the adsorbent surface. The plots of multiple site adsorptions show multiple linear parts in the isotherm (Shuman, 1975).

2.4.2.2. Freundlich adsorption isotherm

The Freundlich equation was first used to describe gas phase adsorption and solute adsorption. Adsorption data at low concentrations can be well explained by Freundlich adsorption isotherm equation (Sposito, 1984). It is an empirical adsorption model and expressed as

$q = K_dC^{1/n}$, where q and C are quantity adsorbed per unit quantity of adsorbent and equilibrium concentration of solute respectively.

Linear form is, $\log q = 1/n \log C + \log K_d$

K_d is a partition coefficient, and n is a correction factor. The single K_d term in the Freundlich equation implies that the energy of adsorption on a homogeneous surface is independent of surface coverage (Sparks, 2003). There are opposite interpretations also which states that adsorption decreases exponentially as the surface coverage increases.

Elrashidi and O'Connor (1982) explained Zn sorption in soil using Freundlich equation. Linear plot was obtained at lower concentrations whereas nonlinear part of plot was observed at higher concentration. They suggested that the deviations from this equation indicate the presence of more than one type of site or mechanism for Zn sorption in the soils. The sites responsible for Zn sorption at lower concentrations were characterized by much higher energies than those at higher solution concentrations. Sparks (2003) opined that these types of conclusions from Freundlich adsorption constants are wrong. An adsorption experiment of dye on activated carbon was done by Inam *et al.* (2017), where they explained K and n as adsorption capacity and adsorption intensity respectively. They suggested that the slope ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity; it becomes more heterogeneous as its value gets closer to zero; value of 1/n greater than unity is indication of cooperative adsorption. Salahi and Ghorbani (2014) used K value as an indication of nature and strength of adsorption process and n as the distribution of active sites. If $n < 1$, bond energy increases with surface density; if $n > 1$, bond energies decrease with surface density and when $n = 1$, all surface sites are equivalent.

2.4.3. Factors affecting adsorption of anions and anion exchange capacity in soil

2.4.3.1. Soil reaction (pH)

The effect of pH on surface charge properties were studied by Shamshuddin and Ismail (1995). When pH increases the net surface charge becomes more negative and cation exchange capacity increases. While the decrease in pH increases the positive charges and hence the anion exchange capacity also increased. Karak *et al.* (2005) also observed the decrease in positive charge and increase in negative charge with increase in pH for all experimental soils. Moghimi *et al.* (2013) observed the dominance of 2:1 silicate clay minerals and alkaline pH in arid soils. Presence of permanent negative charge was recorded high. They also suggested that anion adsorption capacities of these soils are less due to a shortage of materials having variable charge. Bolland *et al.* (1976) found out that, as the pH of the suspension decreased, the positive surface charge on the kaolinites was increased. Positively charged sites and negatively charged sites on the surface of the clays are independent of one another.

2.4.3.2. Ionic strength

It has been observed that a characteristic pH usually occurs above which adsorption of phosphate by goethite and variable charge soils increases with the increase in ionic strength and below this a reverse trend occurs (Barrow *et al.*, 1980; Bolan *et al.*, 1986). Anions are coordinated nearer to the surface than electrolyte in suspension during specific adsorption and they posess high binding constant. As a result, specific adsorption of anions on variable-charge soils occurred in a separate plane (Xu *et al.*, 2010). Charge of the surface became more negative with the increase of ionic strength. Phosphate and arsenate adsorption on variable charge soils was found increased with increasing concentration of $NaNO_3$ and it was attributed to the change of the potential in the adsorption plane induced by the change of ionic strength (Wang *et al.*, 2009).

2.4.3.3. Point of Zero Charge (PZC) or Zero point Charge (ZPC) of soil

The PZC can be defined as the suspension pH at which surface has a net charge of zero (Sparks, 2003). If the measured pH of a colloid is lower than PZC, the surface is net positively charged; if pH > PZC, the surface is net negatively charged. PZC of different components in soil are given in Table 1 (Sparks, 2003; Gu and Schulz, 1991). A strong correlation was found between amounts of Fe and Al oxides and ZPC of the strongly weathered soils.

Table 1. ZPC of different soil components

Material	ZPC
α-Al_2O_3	9.1
α-$Al(OH)_3$	5.0
γ-AlOOH	8.2
CuO	95
Fe_3O_4	6.5
α-FeOOH	7.8
α-Fe_2O_3	6.7
“$Fe(OH)_3$” (amorphous)	8.5
MgO	12.4
δ-MnO_2	2.8
β-MnO_2	7.2
SiO_2	2.0
$ZrSiO_4$	5.0
Feldspars	2-2.4
Kaolinite	4.6
Montmorillonite	2.5
Albite	2.0
Chrysotile	>10
Organic matter	2

2.4.3.4. Surface area

Skjemstordand and Koppi (1983) found an increase in anion exchange capacity with increase in specific surface area which accounted for 70 per cent of variance. The trend was visible in soils with dominance of kaolin, hematite/goethite and mica, more prominent in soils with dominance of hematite/goethite.

2.4.3.5. Clay content and type of clay

A significant positive correlation of AEC and clay (0.67**) content was recorded by McVay *et al.* (2004). In contrast to soils with a clay mineralogy dominated by crystalline layer silicates, which have very little positive charge or very low anion exchange capacity (AEC), soils containing the amorphous clay allophane and imogolite had a noticeable amount of AEC, especially in acidic pH ranges (Gu and Schulz, 1991). Kaolinite, coexisting with crystalline Fe oxides were considered to be the dominant components of the variable charge in the strongly weathered soils, and amorphous alumino-silicates. Allophane and other materials like allophane were the dominant variable charge components in volcanic ash soils, whereas kaolinite and iron and aluminium oxides are the dominant components in highly weathered tropical soils (Sakurai *et al.,* 1990). Possibility of development of permanent positive charge on imogolite surface was observed by Theng *et al.* (1982) which occurred at neutral-alkaline pH.

Kaolinite carries no permanent negative charge and relatively high ZPC. Kaolinite can sorb anions onto their positive sites (Mott, 1981). Illite of various kinds also appears to have some anion sorption capacity. No measurable amount of AEC was found in large quantities of halloysite and monmorillonite (Okamura and Wada, 1983). Smectites have been shown to have an almost negligible capacity for anions adsorption, and indeed negative adsorption has been observed (Gu and Schulz, 1991).

2.4.3.6. Silica content

Desilication process is important in determining surface charge properties, because, the presence of silica always renders the system more negative, regardless of whether the silica forms an integral part of the structure of the soil colloids or whether it is chemically adsorbed onto their surface. Soils with high content of silica were recorded with low PZC values (Gonzales-Batista *et al.*, 1982). Silica can provide pH dependent positive charge only if the pH is less than 2.

2.4.3.7. Fe and Al oxide

Poorly crystalline forms of Fe and Al possessed higher anion adsoption capacity than crystalline forms beacuse of the greater surface area. Poorly crystalline forms are oxalate-extractable, whereas crystalline forms are dithionate-extractable (Parfitt and Smart 1978; Chorover *et al.*, 2004). Positive correlation was found between oxalate extractable Al content and potential adsorption of various anions in different types of soil (Harrison *et al.*, 1989). Sakurai *et al.* (1990) found a shift in ZPC to a higher pH value, caused by the coating of Fe and Al oxides. Hence the possibility of providing positive charge increased. Hendershot and Lavkulich (1983) suggested that, effect of sesquioxide coatings on the PZSE (Point of Zero Salt Effect) is dependent on (i) the material being coated and (ii) the type of coating material.

2.4.3.9. Organic matter

Anion adsorption capacity was inhibited by soil organic matter, especially organic anions, which tend to bind to the reactive surfaces of Fe and Al minerals (Karltun and Gustafsson, 1993; Gu *et al.*, 1995). Xu *et al.* (2007) studied adsorption of organic acids on variable charge soils and they found that: (i) variable charge soils have a great adsorption capacity for low-molecular-weight organic acids which are adsorbed greatly on variable charge soils. (ii) Adsorption through electrostatic force of attraction and specific adsorption are the two main mechanisms of adsorption of organic acids in these soils. (iii) Adsorption of organic acids were decreased in the presence of phosphate and sulphate. It is due to the competitive adsorption of phosphate and sulphate towards the adsorption site. The effect of phosphate was more prominent than the effect of sulphate. (iv) The adsorption is greatly influenced by the change in pH, since dissociation of inorganic acids and chemical properties of soil are dependent on pH.

2.4.4. Adsorption of different anions in soil

2.4.4.1. Adsorption of nitrate in soil

The amount of nitrate adsorbed onto soils increased in the order of clay>loam> sand and the adsorption was consistently suited to fit with Freundlich adsorption isotherm (Akosman and Ozdemir, 2010). Effect of contact time, dosage and pH to the adsorption of nitrate in red soil was studied by Mise and Bashetty (2013). They found that the extent of nitrate adsorption increased with increase in time and attain equilibrium, and the increase in amount of adsorbent added, increases the removal of nitrate from the solution and the removal efficiency of adsorbent increases with decrease in pH. Mohsenipour *et al.* (2015) found that kaolin particles are capable of adsorbing nitrate and retaining it in soils and the mean percentage of reduction of nitrate concentration in solution was 25 per cent of initial concentration. The quantity of nitrate sorption was increased with depth in soil profile (Hamdi *et al.,* 2013).

Kinetic studies of nitrate adsorption conducted by Toner *et al.* (1989) in middle Atlantic soil revealed that nitrate adsorption in soil is rapid and reversible as a result of van der Waals type interactions or outersphere complexation mechanism and they found that adsorbed and desorbed quantity is equal. On contrary, Qafoku *et al.* (2000) explained the adsorption as an overlapping or interpenetration of double layers around positively charged Al-polymers and negatively charged silicate minerals. Shivasharanappa *et al.* (2013) found that lateritic soils in Karnataka are good adsorbent for nitrate. Adsorption data of nitrate was found well explained by Freundlich and Langmuir adsorption isotherm (Mohsenipour *et al.,* 2015; Shivasharanappa *et al.,* 2013).

2.4.4.2. Adsorption of phosphate in soil

Phosphorus deficiency is often reported in well-weathered Oxisols and Ultisols because of their strong acidic reactions and abundance of Al^{3+} and Fe^{3+} ions that form complex with P (Tisdale *et al.,* 1985). Adsorption of phosphate by variable charge soils was found increasing with increasing concentration of electrolyte ($NaNO_3$), was attributed to the change of the potential in the adsorption plane induced by the change of ionic strength (Xu *et al.,* 2010). A rapid increase in adsorption of P was found initially, and then the adsorption was slowly increased, followed by a plateau with increased exogenous application of P (Wang *et al*., 2017). Wang *et al*. (2017) also suggested that P adsorption in soil is a spontaneous process.

High P adsorption by aluminium-peat complex was due to the adsorption of complex Al-phosphate cations by the peat and by the precipitation of amorphous Al-hydroxy-phosphate, likely $AlH_2P0_4(OH)_2$ (Bloom, 1981). Nuclear magnetic resonance study of phosphate adsorption on boehmite revealed that the complex formed is innersphere and it was relatively immobile (Bleam *et al.,* 1991). Inner-sphere monodentate complex formation of P on goethite surface was confirmed by (Persson *et al.,* 1996). Protonated and non-protonated bridging bidentate as well as a non-protonated monodentate, between orthophosphate ions and surface of goethite particles in aqueous suspensions were confirmed by Tejedor-Tejedor and Anderson (1990). The ATR-FTIR investigation on phosphate adsorption mechanisms at the ferrihydrite - water interface showed that inner-sphere surface complexes were non-protonated, bidentate binuclear species (Fe_2PO_4) at pH 7.5, whereas protonated innersphere complexes were formed at pH 4 to 5 (Arai and Sparks, 2001).

At higher temperature, P adsorption was increased indicating that P is strongly held on the surface (Mehadi and Taylor, 1988). The content of amorphous and free iron in soil showed significant positive correlation with isotherm constants of Freundlich. Langmuir, Tempkin and Van Huay adsorption isotherms (Tamungang *et al.,* 2016). Gunary (1970) found that phosphate sorption does not always obey the Langmuir equation and he developed an extension of Langmuir equation which provides better fit than either of the Langmuir and Freundlich equations and which also provides a means of calculating a unique phosphate adsorption maximum. He included a square-root term in the Langmuir equation to imply that the soil would adsorb a little phosphate firmly, a slightly greater amount of phosphate less firmly, and so on until a limiting value was reached when all the components of the phosphate adsorption system were saturated. Syers *et al.* (1973) suggested the presence of two populations of sites which have a widely differing affinity for P since two linear relationships were obtained while plotting of data in a conventional Langmuir equation. He also found that "Eadie-Hofstee" equation (rearranged Langmuir form) described adsorption of low equilibrium P concentration in a better way.

2.4.4.3. Adsorption of sulphate in soil

Nor (1981) found a linear increase in sulphate S adsorbed with a doubling of the concentration added in the soils. Sulphate adsorption was found in the decreasing order: lateritic > red > alluvial soils regardless of the concentration of sulphate solution employed (Dolui and Nandi, 1989). Subsurface horizon adsorbed more sulphate than surface soil (Williams and Steinbergs, 1962). Gokila *et al.* (2017) suggested that the main reason for S deficiency was the irreversible nature of sulphate sorption capacity and largely depends on the pH, amorphous and crystalline Fe and Al content, available phosphorus, organic carbon content, clay, Ca and Mg. They also suggested that the available sulphate content of these soils further moderated the adsorption processes of sulphur in soil.

Wijnja and Schulthess (2000) studied sulfate adsorption mechanisms on goethite surfaces using Raman spectroscopy and ATR-FTIR, indicated that predominantly monodentate inner-sphere surface complexes were formed at $pH < 6$, while at $pH > 6$ outer-sphere surface complexes were formed. In contrast, predominantly outer-sphere surface complexes were formed with Al_2O_3 but a small fraction is also present as an inner-sphere complex at $pH<6$. They concluded that complexation of these anions with Al oxide is weaker than with Fe oxide. Formation of monodentate sulphate surface complexes were noticed on the surface of hematite between pH 3 and 5 (Hug, 1997).

At low concentrations of dissolved sulphate, the amount adsorbed was in accordance with the Langmuir equation. At higher concentrations this relationship broke down and it is postulated that this is due to differing adsorption sites (Haque and Walmsley, 1973). Haque and Walmsley (1973) observed that sulphate adsorption was related to the percentage of NaOH-extractable aluminium in the soil and no correlation was found with Fe_2O_3 content. On contrary, Biswas *et al.* (2003) reported that Fe and Al oxides were the key factors contributing to the retention of sulphate in soil and they also reported that Freundlich equation provided good fit to describe sulphate adsorption in soil.

2.4.4.4. Adsorption of boron in soil

Adsorption of added B was found in the order: Vertisols > Inceptisols > Alfisols, in which Freundlich adsorption isotherm appeared the best fit for Vertisols and Inceptisols, and Langmuir for Alfisols which showed lowest B adsorption. Freundlich and Langmuir adsorption constants were positively correlated with free $CaCO_3$, CEC and clay content (Dey *et al.*, 2013). Singh (1971) also reported better fit of Freundlich adsorption isotherm for B adsorption in soil. Boron adsorption was found decreasing with increasing temperature for kaolinite, montmorillonite, gibbsite, goethite, calcite (reaction temperatures: 10, 25, and 40 ^{0}C) (Goldberg *et al.*, 1993). Montmorillonite adsorbed boron with more energy than kaolonite at lower temperature but at higher temperature kaolinite adsorbed more B (Singh, 1971).

Goldberg (1997) reported that boron adsorbing surfaces in soils are aluminium and iron oxides, magnesium hydroxide, clay minerals, calcium carbonate and organic matter. He also suggested that chemical models such as the constant capacitance model, the triple layer model, and the Stern VSC-VSP model can be used to describe B adsorption over changing conditions of solution pH and B concentration. Majidi *et al*. (2010) studied the adsorption of B in calcareous soil. They found that increase in pH increased B adsorption in soil and adsorption maximum was found increased with increased electrolyte concentration.

Majidi *et al*. (2010) suggested that outer-sphere complexation is the major binding mechanism for B adsorption in calcareous soils. Boron adsorption lowered the point of zero charge of amorphous aluminum and iron hydroxides, allophane, and kaolinite, implying specific adsorption (inner-sphere complexation) of B on theses adsorbent (Su and Suarez, 1995). If an increase in temperature increases the amount of products formed, it is chemical adsorption. But the adsorption of B as a function of temperature was found inconclusive in suggesting a specific mechanism (Biggar and Fireman, 1960).

2.4.4.5. Adsorption of molybdenum in soil

Molybdenum forms monodentate, mononuclear bidentate and binuclear bidentate surface complexes with oxides of Fe and Al (Xu *et al.,* 2013). Molybdenum adsorption exhibited a maximum near pH 4 - 5 and decreased with increasing pH above 5. There was wide applicability of the regression model prediction equation for describing Mo adsorption as a function of solution pH (Goldberg *et al.,* 2008). ZPC of kaolinite was shifted towards lower pH value by the adsorption of Mo. This is due to the inner-sphere complex formation during the adsorption process (Xu *et al.,* 2013). The relative adsorption on the clay minerals increased in the order: illite < kaolinite< kaolinite and montmorillonite < nontronite < meta halloysite (Motta and Miranda, 1989). Adsorption of Mo was found highest in kaolinite followed by illite and montmorillonite (Goldberg et *al.*, 1996). On the basis of X-ray Absorption Near Edge Structure (XANES) analysis, Arai (2010) studied the molybdenum surface speciation on goethite and found that tetrahedral coordination changes to octahedral coordination with decrease in pH.

Molybdenum can be adsorbed by soil organic matter. The mechanism of complex formation during adsorption process is still unknown. Mo is strongly to bonded to humic acids and fulvic acids (Pendias and Pendias, 2001)

Molybdate and sulphate is getting adsorbed on goethite. But the mechanism of adsorption is different. Outer-sphere complex formation occur in case of sulphate while inner-sphere adsorption complex formation occur in case of phosphate. Hence sulphate does not show competition towards the adsorption site on goethite (Xu *et al.,* 2006). Wu *et al.* (2000; 2001) observed that the adsorption of SO_4^{2-} was significantly inhibited by MoO_4^{2-}. Goldberg and Forster (1998) reported that there was no competition between molybdate and phosphate for adsorption, even at phosphate-molybdate ration of 2:1. They suggested the presence of heterogeneous adsorption sites on clay minerals in soil, in which some site were showing preference for molybdenum adsorption. Roy *et al.* (1986) demonstrated that the adsorption of molybdate was noticeably reduced by the competitive adsorption of phosphate. Sun and Selim (2018) observed that adsorption isotherms for Mo were strongly nonlinear. The values for Freundlich adsorption constant (K_F) continued to increase over time and there was a significantly negative relation with solution pH.

2.4.4.6. Adsorption of silicon in soil

Haynes and Zhou (2018) reported the increase in silicon adsortption with increasing pH. Adsorption is favored most strongly near the pKa values of the acids because the proportion of negatively charged ions increases rapidly near the pKa values. pKa for H_4SiO_4 is at 9.8. Since typical soil pH ranges from 5 to 7, silicon is present as uncharged H_4SiO_4 at this pH. Silicon is mainly adsorbed as the oxyanion $H_3SiO_4^-$ (Hingston *et al.*, 1972). Repulsion between silicate and the negatively charged surfaces and the competitive nature of hydroxyl anions is more in soil pH above the pKa value of silicic acid. Hence adsorption was found decreased above this pH (Haynes and Zhou, 2018). Silicon adsorption was reported on reagent grade iron oxides and aluminium oxides (Jones and Handreck, 1967). High silicon adsorption was reported on aluminium and iron oxides, whereas moderate silicon adsorption was recorded on hematite and goethite. Very less silicon adsorption was recorded on silicate minerals, alkaline earth carbonates and reagent grade aluminium oxides and hydroxides. Herbillion and Vinhan (1969) suggested two important processes of silicon adsoprion, which were chemisorption and polymerization. Siever and Woodford (1973) reported little silicon adsorption on the surface of secondary clay minerals. Silicon comes into soil solution due to disintegration of clay minerals by acidification. It is a common process in acid soils (Podzols) present in temperate regions and acidic topsoils present in Luvisols (Sommer *et al.*, 2006). Mc-Keague and Cline (1963a) described Si adsorption using Freundlich adsorption isotherm.

2.5. Interference of Si in molybdenum blue reaction of orthophosphate determination

Molybdenum blue (MB) reaction can be used for the spectrometric estimation of orthophosphate, silicate, arsenate and germanate. Since soil extract may contain enough quantity of silicate, the chances of overestimation of both phosphate and silicate are more. In MB reaction, Keggin ion formed around the particular analyte anion as first step. In next step, a blue colured product is formed by the reduction of this heteropoly acid (Nagul *et al.*, 2015).

$$PO_4^{3-} + 12MoO_4^{2-} + 27H^+ \rightarrow H_3PO_4(MoO_3)_{12} + 12H_2O$$

$$H_3PMo(VI)_{12}O_{40} + \text{Reductant} \rightarrow [H_4PMo(VI)_8Mo(V)_4O_{40}]^{3-}$$

A strong acid, a source of Mo(VI) and a reductant, are common in molybdenum blue reaction. The concentrations of acid and molybdate are most important for the formation of the heteropoly acid and controlling its reduction. Keggin structure formed in the case of orthophosphate, is known as 12-molybdophosphoric acid (12-MPA), and in case of silicate this compound is called 12-molybdosilicic acid (12-MSP).

The MB reaction for orthophosphate is usually performed between pH 0 and 1. This pH is suitable for the formation of stable reduced product without excessive direct reduction of Mo(VI). A combination of acid concentration and molybdate concentration determines Mo speciation. It is determined by the average number of protons bound to molybdate in solution (Cruywagen *et al.*, 2002).

It had been shown via Raman spectroscopy that each anionic molybdate species in the presence of orthophosphate favours the formation of one particular molybdophosphoric acid (Murata and Ikeda, 1983). The α-molybdosilicic acid is formed at pH between 3.8 and 4.8 and the β-acid at pH between 1.0 and 1.8 (Truesdale and Smith, 1975). Zhang *et al*. (1999) found that too lower acidity leads to silicate interference in phosphorous estimation. This is due to two separate phenomena; 12-MSA is only stable at higher pH than 12-MPA. At low pH, orthosilicic acid (H_4SiO_4) exists in equilibrium with polysilicic acids which form 12-MSA much more slowly than orthosilicic acid (Weitz, 1950). Weitz (1950) also found that higher reaction temperatures favour the decomposition of polysilicic acids into orthosilicic acid which leads interference due to formation of 12-MSA. Silicate interference can be effectively controlled by using a sufficiently high acidity and by avoiding heating.

In a widely used method proposed for the determination of orthophosphate in natural waters (Murphy and Riley, 1962), the interference of silica was partially reduced by the use of a comparatively high concentration of sulfuric acid, and by taking the spectrophotometric readings 10 min exactly after the addition of the reagents (Ciavatta *et al.*, 1990).

Materials and methods

3. MATERIALS AND METHODS

The present study entitled "Anionic equilibria in major soil types of Kerala" was carried out at the Radiotracer laboratory, CoH, KAU during 2016-2019. Five experiments were conducted to achieve the objectives of the project using the collected soil samples from different agro-ecological units: 1. Initial characterization was done to know the availability indices of nutrients in collected soils. 2. Fractionation of selected anions was carried out to understand the dominant fractions and their contribution to the available pool. 3. Adsorption studies were done to assess the Q-I relationship and to know the best fit adsorption isotherm. 4. Studies on anion exchange property were conducted to understand the drawbacks of existing method if any. 5. Interference of silicon in phosphorous estimation was studied to know the possibility of over estimation. The materials used and the methods adopted are summarized here.

3.1. COLLECTION AND CHARACTERIZATION OF SOIL SAMPLES

3.1.1 Collection of soil samples

Representative surface soil samples (0-20 cm) were collected from 7 agro-ecological units of Kerala, and the details of sampling locations are presented in Table 2. Altogether 22 samples with variation in texture and organic matter content, were collected from seven different AEUs of Kerala.

3.1.2. Characterization of soil samples

The soil samples were air dried under shade, ground and sieved through 2 mm sieve and used for characterization. The samples were characterized with respect to texture, bulk density, pH, EC, OC, CEC, AEC, total N, nitrate N, ammoniacal N, available nutrients (N, P, K, Ca, Mg, S, Fe, Mn, Cu, Zn, B, Mo and Si). XRD analysis was done to know the dominant minerals present in the soil. The standardized procedures adopted for the characterization of soil samples are detailed hereunder.

3.1.2.1. Physico-chemical properties

Soil pH

The pH of the soils was determined in a 1:2.5 soil water suspension, potentiometrically using pH meter (Jackson, 1958).

Electrical conductivity (EC)

Soil water suspension was prepared in a ratio of 1: 2.5. EC was estimated in the supernatant using a conductivity meter (Jackson, 1958).

Organic carbon (OC)

Wet digestion method proposed by Walkley and Black (1934) was followed for the determination of OC content of soil. Correction for incomplete oxidation was also carried out.

Bulk density

Dry bulk density of the soils was determined following the core method (Carter and Gregorich, 2007).

Soil texture

Texture of the soils was determined by international pipette method (Robinson, 1922). Soil (20 g) was taken in a 500 mL beaker. For the destruction of organic matter, 10 mL of 30 per cent hydrogen peroxide solution was added to that and heated on hot plate. To ensure the dispersion of soil particles, 8 mL of 1N NaOH was added. After stirring it was transferred into a spoutless cylinder of 1000 mL capacity and kept undisturbed. 20 mL of suspension was pipetted out from the undisturbed cylinder according to the sedimentation time. After oven drying, the weight of clay and silt particle was found out. The sediments were washed and oven dried to findout the weight of sand particle.

Cation exchange capacity (CEC)

Barium chloride extractable cations were determined by following the procedure of Hendershot and Duquette (1986). The cations present in the exchangeable sites in the soil were replaced by Barium. Forty millilitres of 0.1M $BaCl_2$ was added to 4 g of soil in centrifuge tube. After a shaking period of 2hrs, it was filtered through Whatman No.42 filter paper for the determination of CEC. Estimation of cations in the extract (Ca, Mg, Al, Fe, Mn, Cu, Zn, Na and K) was done using ICP-OES (Model: Perkin Elmer-Optima 8000).

Since the lowland soils are high in water soluble cations, deduction of water soluble fraction from barium chloride extractable cations was carried out to avoid over estimation. Water soluble cations were estimated by the modified procedure of Baruah *et al.* (2011). Deionised water (25 mL) water was added to 5g soil in centrifuge tube. The supernatant was decanted after centrifugation at 4000 rpm for 30 minutes. Using 25 mL deionized water the residue was washed, shaken, centrifuged and filtered. Estimation of cations was done using ICP-OES (Model: Perkin Elmer-Optima 8000). CEC was expressed as cmol(+) kg^{-1}.

Anion exchange Capacity

Ten grams of the soil samples were taken and leached with 100 mL $BaCl_2$ -TEA (90 mL triethanolamine diluted to 1 L and and adjusted pH to 8.1 with HCl. Diluted to 2 L and mixed with 2 L of water containing 100g $BaCl_2.2H_2O$). The soil samples were again leached with 100 mL $CaCl_2.2H_2O$ solution (50g $CaCl_2.2H_2O$ adjusted to pH 8 with saturated $Ca(OH)_2$ solution and washed again. The calcium saturated soil was dried at 45°C and weighed into a centrifuge tube sufficient to give 0.2 m.e. CEC. Shaking period of 30 min was given after adding 20 mL of 0.01M H_3PO_4. After shaking it was allowed to stand for 24 hours and shaken again for 30 minutes. Supernatant was decanted after centrifugation (Hesse, 1971). P content was estimated using ICP-OES (Model: Perkin Elmer-Optima 8000).

Table 2. Sampling locations

Agro ecological unit (AEU)	**Sample No.**	**GPS coordinates**	**Location**
Pokkali lands (AEU-5)	1	N 10^{0}03.333' , E 76^{0}14.986'	Varapuzha 1
	2	N 10^{0}03.454', E 76^{0}14.929'	Varapuzha 2
	3	N 10^{0}03.639', E 76^{0}14.858'	Varapuzha 3
*Kole*lands (AEU-6)	4	N 10^{0}29.089', E 76^{0}07.678'	Manalurthazham
	5	N 10^{0}30.554', E 76^{0}06.403'	Vadakkekonchira
	6	N 10^{0}29.089' , E 76^{0}07.678'	Thekkekonchira
Northern coastal plain (AEU-2)	7	N 10^{0}33.576 ', E 76^{0}00.973 '	Chavakkad
	8	N 10^{0}29.575 ' , E 76^{0}02.868 '	Engandiyur
	9	N 10^{0}18.401 ' , E 76^{0}02.868 '	Perinjanam
Onattukara sandy plain (AEU-3)	10	N 09^{0}10.588 ', E 76^{0}31.009'	Kayamkulam
	11	N 09^{0}10.244 ', E 76^{0}30.653'	Cheravally I
	12	N 09^{0}10.190', E 76^{0}30.672'	Cheravally II
Kuttanad (AEU-4)	13	N 09^{0}29.410 ', E 76^{0}26.629'	RajapuramKayal
	14	N 09^{0}30.395', E 76^{0}26.116'	Thekkearayaram
	15	N 09^{0}32.061', E 76^{0}26.131'	Pathepathinalayiram
North central Laterite (AEU-10)	16	N 10^{0}48.767', E 76^{0}07.461'	Pattambi
	17	N 10^{0}33.018', E 76^{0}15.988'	Madakkathara
	18	N 10^{0}32.311', E 76^{0}15.401'	Vellanikkara
Palakkad eastern plain (AEU-23)	19	N 10^{0}42.343', E 76^{0}46.975'	Chitoor
	20	N 10^{0}43.278', E 76^{0}47.523'	Nallepilly
	21	N 10^{0}43.720', E 76^{0}47.736'	Nallepilly
	22	N 10^{0}42.570', E 76^{0}46.605'	Thekedesam

Plate 1. Sample collection

Northern coastal plain

Kole land

Palakkad eastern plain

Onattukara sandy plain

3.1.2.2. Available nutrients

Available Nitrigen (Av.N)

Available N in the soil was determined by following alakaline permagnate method (Subbiah and Asija, 1956) using 0.32 per cent $KMnO_4$ and 2.5 per cent NaOH. Released ammonia was absorbed in 2.5 per cent boric acid. It was titrated against 0.02N H_2SO_4 after complete distillation.

Available phosphorus (Av.P)

Available phosphorus in the collected soil samples were extracted using Bray No.1 reagent (Bray and Kurtz, 1945) for soils with pH below 6.5 and by Olsen's method (Olsen *et al.*, 1954) for soils with pH above 6.5 and its content in the extract was estimated using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES;Model: Perkin Elmer-Optima 8000).

Available potassium (Av.K), calcium (Av.Ca), magnesium (Av.Mg)

Available potassium, calcium and magnesium in the soil samples were extracted using neutral normal ammonium acetate. Potassium content in the extract was estimated by flamephotometry (Jackson, 1958). Calcium and magnesium content was estimated in Atomic Absorption Spectrophotometer (Model: Perkin Elmer-PinAAcle 500).

Available sulphur (Av.S)

Available S was extracted by using 0.15% $CaCl_2$ (Williams and Steinberg, 1959; Tabatabai, 1982) and estimated by turbidimetry (Massoumi and Cornfield, 1963) using spectrophotometer (Model: Systronics169).

Available micronutrients (Av.Fe, Av.Cu, Av.Mn and Av.Zn)

Available micronutrients in soil samples were extracted using 0.1M HCl (Sims and Johnson, 1991) for soils with pH below 6.5 and with 0.005M DTPA and 0.01M $CaCl_2.2H_2O$ buffered at pH 7.3 by 0.1M triethanolamine (TEA) for soils with pH above 6.5 (Lindsay and Norvell, 1978). The filtrate was collected and analysed for Fe, Cu, Mn and Zn using Atomic Absorption Spectrophotometer (Model: Perkin Elmer-PinAAcle 500).

Available boron (Av.B)

Available boron in soil samples were extracted with hot water (Berger and Truog, 1939) and estimated using ICP-OES (Model: Perkin Elmer-Optima 8000).

Available Molybdenum (Av.Mo)

Soil sample (15g) was weighed into 250 mL Erlenmeyer flask.150 mL of buffered (pH=3) 0.2 M ammonium oxalate solution was added to the sample and shaken for 16 h at room temperature. After filtration through Whatman No. 42 filter paper, it was estimated using ICP-OES (Model: Perkin Elmer-Optima 8000) (Carter and Gregorich, 2007).

Available silicon (Av.Si)

Available Si in soil was extracted using 0.5 M acetic acid following 1:2.5 ratio (Korndorfer *et al.,* 2001). Estimation was done using ICP-OES (Model: Perkin Elmer-Optima 8000).

3.1.2.3. Exchangeable ammoniacal N and Nitrate N Total N

The soil samples were extracted with 2 M KCl in a 1:10 soil to KCl ratio by shaking for 1 h and filtered off using Whatman No. 42 filter paper. Leachate was collected and an aliquot of this was distilled with 0.2 g dry magnesium oxide and the distillate was collected in boric acid with mixed indicator. It was titrated against standard acid to estimate the ammoniacal nitrogen. 0.2 g Devarda’s alloy was added to the distillation flask to convert nitrate nitrogen to ammoniacal nitrogen. After distillation, it was titrated against standard acid (Keeney and Nelson, 1982). Total N content was estimated using CHNS analyser (Model: Elementar’s vario EL cube)

3.1.2.4. Citrate -Bicarbonate- Dithionate extractable Fe

Forty mL of 0.3M sodium citrate was added to 4 g soil. 5 mL of 1M $NaHCO_3$ was added to that and kept in water bath (80^0C). One g $Na_2S_2O_4$ was added and stirred continuously for 1 min and occasionally for 15 min. 10 mL saturated NaCl and 10mL acetone was added at the end of 15 min digestion period (Mehra and Jackson, 2013). Iron content was estimated using AAS (Model: Perkin Elmer-PinAAcle 500).

3.1.2.15. Mineralogy

Clay, silt and fine sand was separated from the seven representative soil samples following the standard procedure (Jackson, 1979). Dominant minerals present in the soils were identified using PXRD (Model; Bruker, D8 advance). Preparation of diagram of X-ray difftarction pattern and smootherning of the curve were done in Origin Pro 8.5.0.

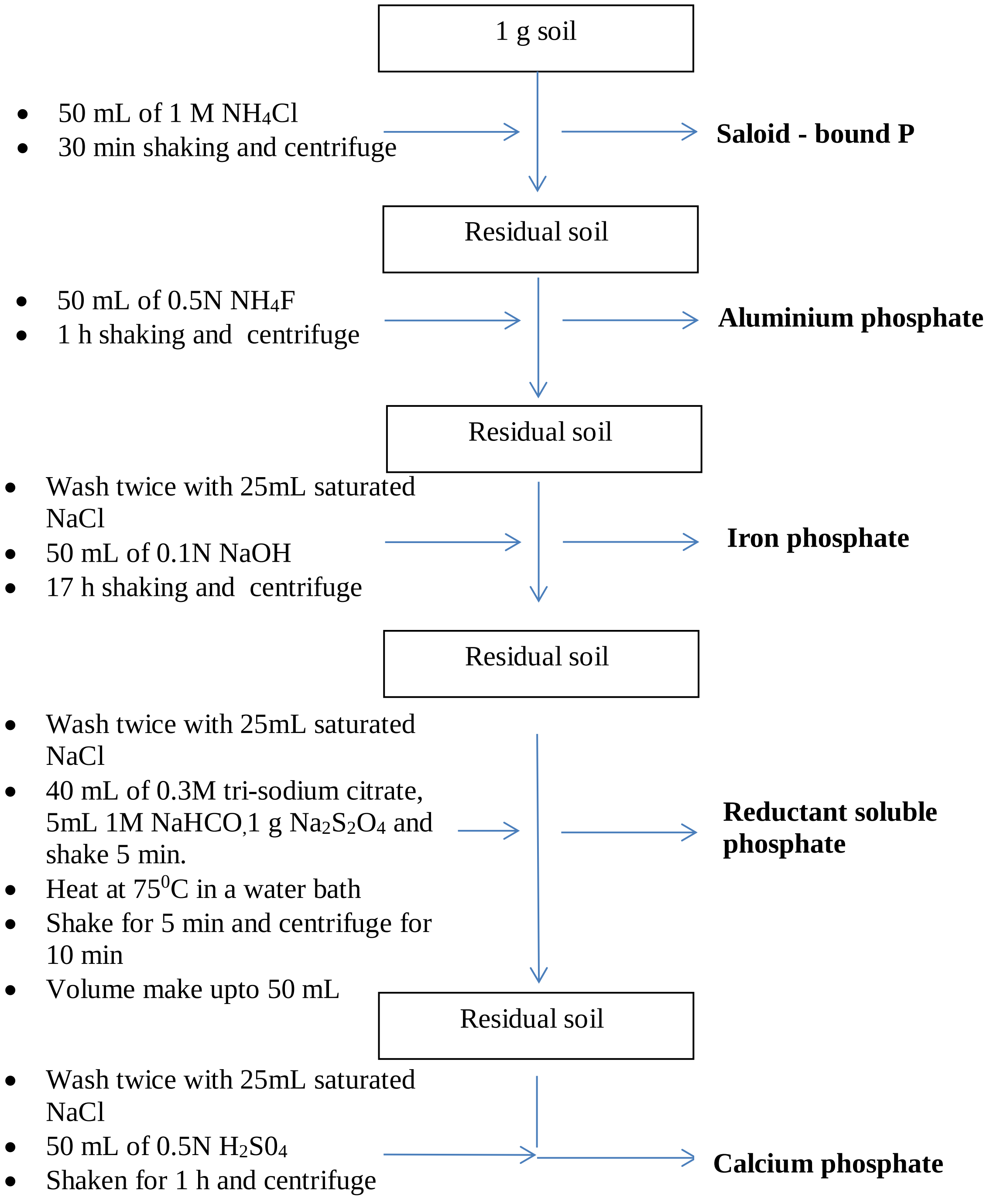
3.2. FRACTIONATION

Different fractions of P, S, Si and B were estimated. Whatman No.42 filterpaper was used for filtration.

3.2.1. Phosphorous

The inorganic fractions of soil P was extracted by the method proposed by (Peterson and Corey, 1966), which include sequential extraction of soluble and loosely bound phosphorus, aluminum phosphate, iron phosphate, reductant soluble phosphate and calcium phosphate (Fig. 3). The organic P fraction was estimated following ignition method (Saunders and Williams, 1955) and total P content was estimated following perchloric acid digestion method (Carter and Gregorich, 2007). Estimation of P in all the extract was done in ICP-OES (Model: Perkin Elmer-Optima 8000).

Fig. 3. Flow diagram of fractionation of inorganic P in soil



Residual P = Total P – (Inorganic P fractions + Organic P)

Saloid-bound P

Soil sample was weighed (1 g) in a 100 mL centrifuge tube, added 50 mL of 1N NH_4Cl. It was shaken for 30 min and centrifuged at 2000 rpm for 10 min to remove the easily soluble and loosely bound phosphorus ("saloid-bound" P).

Aluminium phosphate

To the soil residue, 50 mL of 0.5N NH_4F (pH 8.2) was added and shaken for 1 h. After shaking, it was centrifuged for 10 min at 2000 rpm to extract aluminium phosphate.

Iron phosphate

The soil residue was washed twice with 25 mL of saturated NaCl by centrifugation at 2000 rpm for 5 min. It was shaken for 17 h after adding 50 mL of 0.1N NaOH. The suspension was centrifuged for15 min at 2400 rpm to remove iron phosphate.

Reductant soluble phosphate

The soil residue was washed twice with successive centrifuge washings with 25 mL of saturated NaCl and it was suspended in 40 mL of 0.3M tri-sodium citrate, and added 5mL of 1M $NaHCO_3$, 1 g of solid $Na_2S_2O_4$ and shaken for 5 min. The suspension was heated in a water bath at 75^0C to 80^0C. The suspension was shaken for 5 min and centrifuged at 2000 rpm for 10 min to remove reductant soluble phosphate. The volume was made upto 50 mL.

Calcium phosphate

The remaining soil residue was washed with two successive centrifuge washings with saturated NaCl (25 mL) and 50 mL of 0.5N H_2SO_4 was added. The suspension was centrifuged for 10 min at 2000 rpm after a shaking period of 1 h to remove calcium phosphate.

Organic P

Soil sample was weighed (2g) into a porcelain crucible. It was ignited in a muffle furnace at a temperature of 550°C for one hour. The samples were cooled and transferred to centrifuge tubes. A duplicate set of 2 g of soils were taken in centrifuge tubes. 100 mL of 0.2N H_2SO_4 was added to both sets of soil samples, and shaken for 16 and 30 min. Then the samples were centrifuged and supernatant solution was decanted.

Total P

Concentrated HNO_3 (20 mL) was added into soil sample (2 g) and heated approximately 130 ^{0}C to oxidize organic matter. 30 mL of $HClO_4$ was added and allowed to digest in fume hood at 200^{0}C for 20 min. After adding 2 mL of $HClO_4$ to wash down the particles, the sample was heated for another 10-15 minutes.

3.2.2. Sulphur

The S fractions included in this study are sulphate sulphur, total water soluble sulphur, sulphur released by heating, sulphate soluble after ignition, total organic sulphur and total sulphur. Total sulphur was estimated using CHNS analyser. The other fractions were determined by following the procedure of Williams and Steinbergs (1959) and S in the extracts was estimated by turbidimetry (Massoumi and Cornfield, 1963) using a spectrophotometer (Model: Systronics169).

Sulphate sulphur

Soil sample (5 g) was weighed into 50 mL centrifuge tubes, 25 mLof 0.15 per cent $CaCl_2$ was added, and shaken for 30 min. After filtration, sulphur in the extract was estimated using suitable aliquot.

Total water soluble sulphur

The soil (5 g) was extracted with 33 mL of 1.0 per cent sodium chloride. After centrifuging and filtering, a 25 mL aliquot was pipetted into a silica basin and evaporated to dryness with 2 mL of 3 per cent hydrogen peroxide. The basins were then heated in a hot-air oven at 102 °C for 60 min to ensure the removal of excess peroxide. After cooling, the residue was taken up in 25 mL of water, transferred to a centrifuge tube, and centrifuged to remove suspended matter. Sulphur was then determined from a suitable aliquot.

Sulphur released by heating (Heat-soluble sulphur)

Soil (5 g) was weighed into a silica basin and 20 mL of water was added. The basin was then placed on a gently boiling water-bath and evaporated to dryness. It was then heated for 60 min in a hot-air oven at 102 ^{0}C. After cooling the soil was transferred to a 50 mL centrifuge tube and extracted with 33 mL of 1.0 per cent sodium chloride. Sulphur was then estimated using suitable aliquot.

Sulphate soluble after ignition

Soil was weighed (1 g) into a silica basin and gently ignited over a burner flame for 15 min. After cooling, the soil was transferred to a 50 mL centrifuge tube and sulphate extracted with 1.0 per cent sodium chloride and estimated using suitable aliquot.

Total organic sulphur

Five or 10 g soil samples, depending on the amount of organic matter, of finely ground soil were leached with distilled water, then with 1 per cent hydrochloric acid and finally with distilled water until no chloride was present in the leachate. The soil was transferred to a beaker and oxidised with hydrogen peroxide and extracted with 1 per cent sodium chloride. Estimation was done from suitable aliquot.

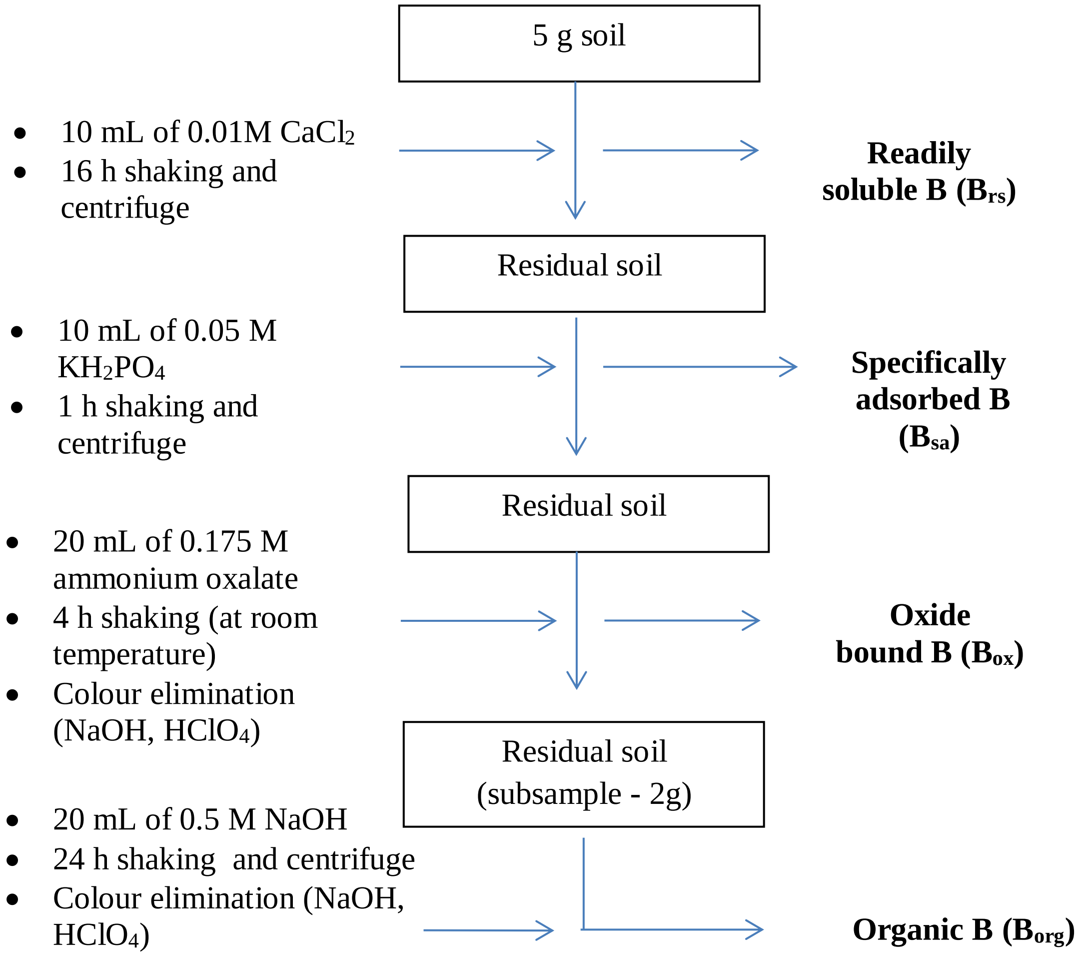
Total sulphur

Total sulphur content of the soil was estimated by direct combustion using CHNS analyzer (Model: Elementar'svario EL cube).

3.2.3. Boron

Sequential extraction procedure of Hou *et al*. (1994, 1996) and Datta *et al.* (2002) was followed to extract readily soluble B, specifically adsorbed B, oxide bound B and organically bound B (Fig. 4).

Fig. 4. Flow diagram of fractionation of B in soil



Residual B= Total B – (B_{rs} +B_{sa} + B_{ox} + B_{org})

Readily soluble B

Soil sample (5g) was weighed into 50 mL polythene centrifuge tubes. Ten millilitres of 0.01M $CaCl_2$ was added. It was shaken for 16 hours (Hou *et al.*, 1994, 1996). Supernatant solution was filtered after centrifugation at 10000 rpm for a period of 30 minutes.

Specifically adsorbed B

To extract specifically adsorbed B, 10 mL of 0.05 M KH_2PO_4 was added to the soil residue. It was shaken for one hour and centrifuged at 10000 rpm for 30 minutes to extract specifically adsorbed B.

Oxide bound B

Oxide bound boron was extracted by adding 20 mL of 0.175M ammonium oxalate (pH 3.25) to the residue and shaken for a period of 4 hours. Supernatant was filtered after centrifugation. The yellowish or reddish colour of the extracts was eliminated by the treatment of NaOH and $HClO_4$.

An aliquot of 14 mL was transferred into 50 mL teflon beaker, and to this 2 mL 5 N NaOH solution was added. The weight of beaker with extract was recorded. For the complete precipitation of dissolved iron, it was heated on a hot plate. The beaker was weighed again after precipitation of dissolveed iron. The loss on weight due to heating was made up with distilled water. The suspension was then fitered using Whatman no. 42 filter paper, to remove the precipitated iron. Nine mL of aliquot was transferred to another 50 mL teflon beaker, to which 4 mL of concentrated H_2SO_4 and 1 mL of 60 per cent $HClO_4$ were added. To destroy organic matter, it was then heated on a hot plate at 135 ^{0}C till the volume was reduced to about 6 mL. Percholric acid was added in an increment of 0.5 mL until the solution became colourless. Finally the volume was reduced to 4 or 5 mL. After transferring into graduated polyethylene centrifuge tube (15 mL), final volume was made up to 6 mL.

Organically bound B

A subsample of two grams of the residue from the ammonium oxalate extraction was treated with 20 mL of 0.5 M NaOH and shaken for 24 h. Red colour of the extract due to the dissolution of organic matter was eliminated by following the same procedure as described in colour elimination procedure of oxide bound B.

Total B

Aqua regia (3 mL) was added to 0.2 g soil in a 50 mL teflon beaker. It was kept overnight for wet digestion. After that it was digested at 135 ^{0}C for 2 h. After complete digestion, the extract was diluted with distilled water.

Residual B

The residual boron was estimated by subtracting the sum of all fractions of B from total B.

3.2.4. Silicon

Soil samples were subjected to sequential extraction of different silicon (Si) fractions in soils. The procedure followed for the extraction of Si in soil as given by Georgiadis *et al*. (2013) is presented in figure 5. Total Si was determined following HF digestion (Tan, 2000). The Si in the extract was estimated using ICP-OES (Model: Perkin Elmer-Optima 8000).

Mobile silicon

Silicon from the mobile silica fraction was extracted with 0.01 M $CaCl_2$ solution using a soil to solution ratio of 1:5. The samples were shaken on a horizontal shaker for 24 h, only for 1 min h^{-1} in order to accelerate the extraction, but at the same time to avoid Si abrasion from mineral grains.

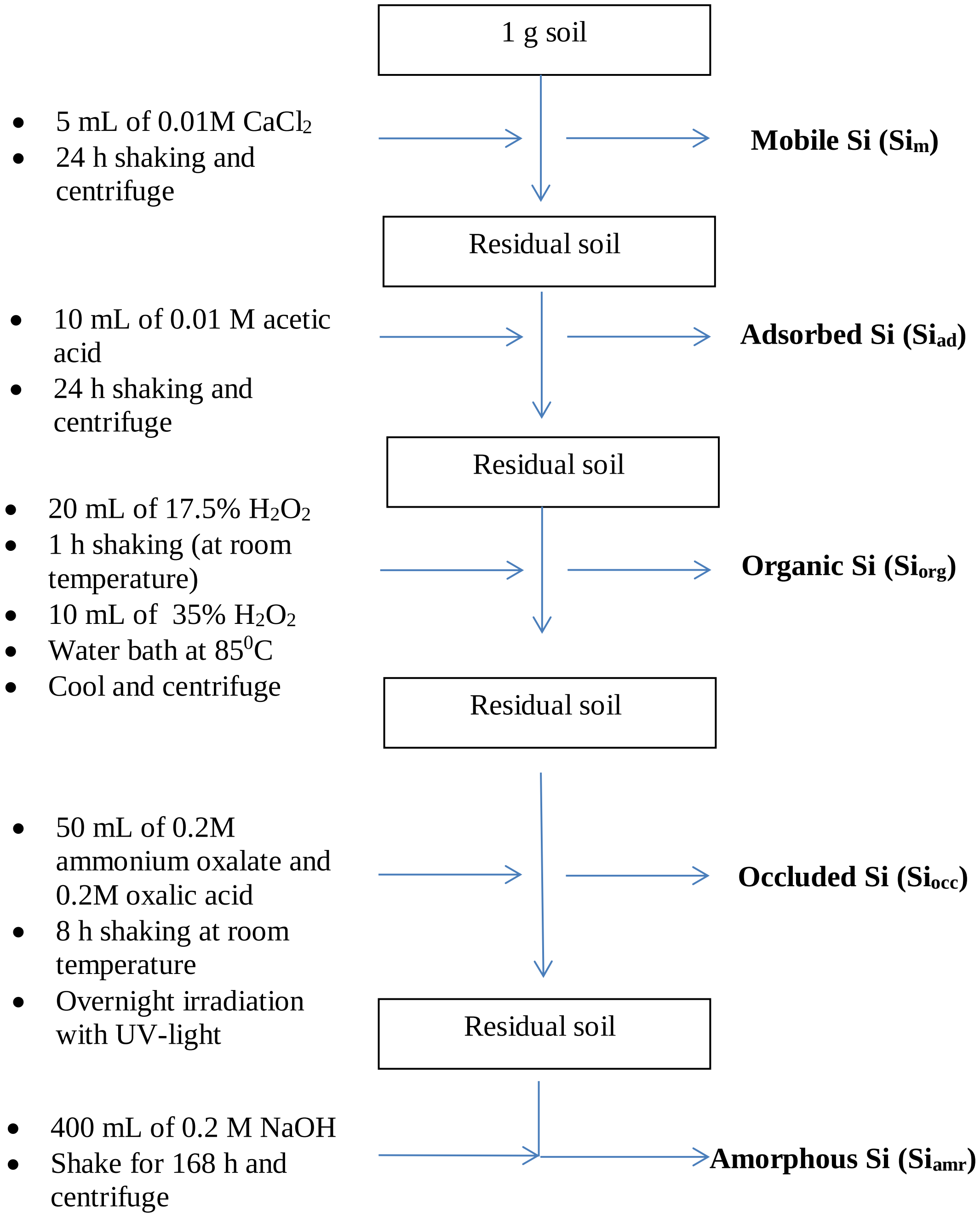
Adsorbed silicon

The samples were rinsed with distilled water, after extracting Si from mobile silica fraction. To extract Si from adsorbed silica 10 ml of 0.01 M acetic acid were added to the soil and the samples were then shaken for 24 h.

Silicon in soil organic matter

The samples were treated with 20 mL 17.5% H_2O_2, manually shaken 4–6 times and kept for 1 h at room temperature. Then, 10 mL of 35% H_2O_2 were added, and the samples were kept in a water bath at 85 °C, until the reaction is completed. It was filtered after cooling.

Fig. 5. Flow diagram of fractionation of Si in soil



$$\textbf{Residual Si} = \textbf{Total Si} - (Si_m + Si_{ad} + Si_{org} + Si_{occ} + Si_{amr})$$

Silicon occluded in pedogenic oxides and hydroxides

To extract Si occluded in pedogenic oxides and hydroxides, 50 mL 0.2 M ammonium oxalate and 0.2 M oxalic acid were added. The extractant was applied at daylight and room temperature for 8 h and shaken the samples horizontally for 1 min h^{-1}. Then, the suspensions were irradiated with UV light overnight.

Amorphous silicon

Amorphous Si was extracted with 0.2 M NaOH solution by shaking slowly for 168 h at room temperature, using a sample to solution ratio of 1:400. This step provided the amount of total (minerogenic and biogenic) amorphous Si.

Total Si and Residual Si

To extract total Si content in soil, 2 mL aqua regia and 12mL HF was added to 0.2 g soil sample. After complete digestion, the total Si content was estimated. Residual Si was estimated by subtracting the sum of all the fractions from total Si.

3.3. ADSORPTION STUDY

3.3.1. Adsorption experiment

3.3.1.1. Single anion system

Adsorption studies of individual anions viz., phosphorous, sulphur, silicon, nitrate, boron, and molybdenum were conducted at two temperatures (25^0C and 40^0C) with the collected 22 soil samples. After equilibration, the soil solution was filtered through filter paper (Whatman No. 42). pH of the equilibrium solution was noted.

3.4.1.1.1. Nitrate

Five gram soil samples were equilibrated with 20 mL different concentrations of NO_3 - N. Equilibration was assumed to have occurred after the mixture was shaken for 1 h (Strahm and Harrison, 2006). The concentrations used were 0, 10, 20, 40, 80, 120, 160 mg L^{-1}. The solutions were prepared using

$NaNO_3$. Nitrate content in the equilibrium solution was estimated colorimetrically using spectrometer (model: systronics 169) (Cataldo *et al.*, 1975).

3.3.1.1.2. Phosphorous

Five gram soil was weighed out in to 250 mL conical flasks. 50 mL of different P concentrations (0, 10, 20, 40, 80 and 100 mg L^{-1}) were added to the flask. The solutions were prepared using KH_2PO_4 in 0.01M $CaCl_2$. Shaking period of 1 h was given for equilibration (Geetha, 2008). The concentration of P in the equilibrium solution was estimated using ICP-OES (Model: Perkin Elmer-Optima 8000).

3.3.1.1.3. Sulphur

Soil samples (5g) were equilibrated with 25 mL different concentration of sulphur solutions (0, 5, 25, 50, 100 and 200 mg L^{-1}). The solutions were prepared using K_2SO_4. The soil suspensions were shaken for one hour at normal speed, left standing overnight and shaken for another hour the next morning (Chao *et al.*, 1962). Sulphur content in equilibrium solution was estimated by turbidimetry using spectrometer (model: systronics169) (Massoumi and Cornfield, 1963).

3.3.1.1.4. Boron

Soil samples (2.5g) were equilibrated with 25 mL of different levels of B concentration (0, 0.5, 1.0, 2.0, 4.0, 8.0, 12 and 16 mg L^{-1}). The solutions were prepared in 0.01 M $CaCl_2$ using boric acid as B source. Soil samples were shaken for 24 hours to achieve steady state condition (Shafiq *et al.,* 2008). The concentration of B in the equilibrium solution was estimated using ICP-OES (Model: Perkin Elmer-Optima 8000).

3.3.1.1.5. Molybdenum

The soil samples (2.5 g) were equilibrated with 25 mL of different concentrations of Mo (0, 10, 20, 40, 60, 80 and 100 ppm). Soil samples were shaken for 6 hours to achieve steady state condition. Na_2MoO_4 was used to prepare the solutions (Karimian and Cox, 1978). The concentration of Mo in the equilibrium solution was estimated using ICP-OES (Model: Perkin Elmer-Optima 8000).

3.3.1.1.6. Silicon

One gram of soil was equilibrated with different concentrations of silicon (0, 5, 20, 40, 80, 100 and 200 mg L^{-1}) in 20 mL solution of 0.01 M $NaNO_3$. Si standard by Merck (NH_4SiF_6 in water, made in Germany) was used as Si source. The soil samples were shaken for 24 hours to achieve steady state condition (Qiu *et al.,* 2010). The concentration of Si in the equilibrium solution was estimated using ICP-OES (Model: Perkin Elmer-Optima 8000).

3.3.1.2. Binary systems of anions

Competitive adsorption of phosphorous and boron was carried out using 6 different concentrations (0, 0.1, 0.25, 0.5, 1, 2, 4 millimol L^{-1}) of each anion. A total of 36 combinations were tried. The experiment was conducted at 25 ^{0}C. An equilibration period of 24 h was provided. The solutions were prepared in 0.01 M $CaCl_2$ using KH_2PO_4 as P source and boric acid as B source. The concentration of both anions in equilibrium solution was estimated using ICP-OES (Model: Perkin Elmer-Optima 8000).

3.3.2. Quantity (Q) – Intensity (I) relations

The Q (amount of adsorbate adsorbed per unit quantity of adsorbent) and I (equilibrium concentration) parameters were calculated from the data of adsorption experiments conducted with the increasing concentration of particular element added to the soil. Q-I curves were prepared for each soil by plotting the amount of adsorbate adsorbed (q_e) on Y axis and the equilibrium concentration (C_e) in the soil solution on X axis. Slope of the Q-I curve was considered as buffer power. Maximum amount adsorbed/desorbed was also recorded. Intercepts and slopes were computed from the best fit curves using regression analysis. The slope of the curve is the parameter which explains the buffer power (nutrient supplying power of soil). The simple linear equation $\Delta Q = bC + K$ was used to obtain the best curve, where b is the buffer power (slope of the curve) and K is the intercept.

3.3.3. Adsorption isotherms

The isotherm usually describes the adsorption system with some important information from which we can develop an equation representing the results and we can use the equation for interpreting some parameters of adsorption. Adsorption data was fitted into three isotherms via. Langmuir, Freundlich and Tempkin.

3.3.3.1. Langmuir adsorption isotherm

$q_e = q_m K_L C_e/(1+K_L C_e)$

Linear form can be expressed as

$C_e/q_e = (1/(q_{max}*K_L))+((1/q_{max})*C_e)$

Where q_e(mg kg^{-1}) is the quantity adsorbed at equilibrium, C_e(mg L^{-1}) is the equilibrium concentration of solute, q_m(mg kg^{-1}) is the maximum amount of adsorbate that can be adsorbed, K_L(L mg^{-1}) is constant related to binding strength. While plotting the Langmuir adsorption isotherm for P adsorption, q_e was converted into mg of P adsorbed per one gram of soil inorder to get more precise linear equation.

3.3.3.2. Freundlich adsorption isotherm

$q_e = K_F C_e^{1/n}$

Linear form can be expressed as

$\log q_e = \log K_F + (1/n) \log C_e$

where q_e(mg kg^{-1}) is the quantity adsorbed at equilibrium,C_e(mg L^{-1}) is the equilibrium concentration of solute, K_F and 1/n are empirical constants. K_F (mg kg^{-1}) (L kg^{-1})$^{1/n}$ is the Freundlich adsorption constant, the amount adsorbed at unit concentration. It is characteristic for the adsorbent and the adsorbate adsorbed.

3.3.3.3. Tempkin adsorption isotherm

$q_e = (RT/b) \ln (K_T C_e)$

A linear form of the Tempkin isotherm can be expressed as

$q_e = (RT/b) \ln K_T + (RT/b) \ln C_e$

where q_e (mg kg^{-1}) is the quantity adsorbed at equilibrium, C_e (mg L^{-1}) is the equilibrium concentration of solute, K_T (L kg^{-1}) is Tempkin adsorption constant and b (J mol^{-1}) is constant related to heat of adsorption.

Constants of different adsorption isotherms were calculated from the slope and intercept values of respective linear equations of isotherm.

3.3.4. Thermodynamic parameters

Thermodynamic parameters were calculated from the variation of the thermodynamic equilibrium constant, K^0 (Biggar and Cheung, 1973).

$K^0 = as/ae = \gamma s\ Cs/\gamma e Ce$ …………………………………………………. (1.1)

Where,

as = activity of adsorbed solute
ae = activity of solute in equilibrium
Cs = µg of solute adsorbed per mL of solvent in contact with the adsorbed surface
Ce = µg of solute adsorbed per mL of solvent in equilibrium
γs = activity coefficient of adsorbed solute
γe = activity coefficient of solute in equilibrium solution
Cs was calculated according to the following equation (Fu *et al.,* 1948)

$Cs = ((\rho_1/M_1)\ A_1)/\ (S/N(x/m)) - (A_2/M_2 x 10^6)$……………………………. (1.2)

ρ1 = density of solvent (density of water g cc^{-1})

M_1 and M_2 molecular weights of solvent and solute respectively (g mol^{-1})
A_1 and A_2 = respective cross sectional areas of solvent and solute molecule (cm^2 $molecule^{-1}$)
N = Avogadro‘s number (6.023 x 10^{23} molecules mol^{-1})
S = surface area of adsorbent (cm^2 g^{-1})
x/m = specific adsorption (μg g^{-1})
The cross sectional areas (cm^2) of the solvent and solute molecules were estimated from the following equation (Kodera and Onishi, 1959)

$A = 1.091 \times 10^{-16} [(M \times 10^{24})/ (N \times \rho)]^{2/3}$ ……………………………….(1.3)

Where, M and ρ represent the molecular weight and density respectively

Surface area of soils

About 1.1 g of calcium saturated soil samples were taken in shallow small weighing cans and dried to a constant weight over P_2O_5 in evacuated dessiccator. Approximately 3 ml of ethylene glycol monoethyl ether (EGME) was added to each of the dried sample to form mineral absorbate slurry. The slurry was allowed to equilibrate for at least one hour and then kept in evacuated desiccators. The samples were first weighed one hour after the evacuation, then at successively longer time intervals until a constant weight was attained (Carter *et al.*, 1965). 2.86 x 10^{-4} g of EGME was required to form a monolayer of 1 m^2. The surface area of the soil was then calculated based on the amount of EGME retained using the following equation:

$S(m^2g^{-1})=(1\ m^2/ 2.86 \times 10^{-4})$ x amount of EGME retained(g)/weight of soil taken (g) ……………………………………………………………………(1.4)

In equation (1.2) since S/N (x/m) >> $A_2/M_2 \times 10^6$, the equation is reduced to

$Cs = (\rho_1/M_1)\ A_1/\ (S/N(x/m))$ ……………………………………………(1.5)

This can be used to calculate microgram of solute adsorbed per mL of solvent in contact with the adsorbed surface, ie., Cs in g mL^{-1}.

At lower concentration, activity coefficient approaches unity and hence Cs/Ce = K^0

Values of K^0 were obtained by plotting log (Cs/Ce) Vs Cs and extrapolating to zero.

The standard free energy (ΔG^0) was calculated from

$\Delta G^0 = -RT \ln K^0$ …………………………………………………………(1.6)

The standard enthalpy (ΔH^0) was obtained from the integrated form of the Vant Hoff equation,

$\ln K^0_2 / K^0_1 = -\Delta H^0/R\,[(1/T_2) - (1/T_1)]$ ……………………………………(1.7)

The standard entropy (ΔS^0) was calculated from

$\Delta S^0 = (\Delta H^0 - \Delta G^0)/T$ ……………………………………………………..(1.8)

3.4. STUDIES ON ANION EXCHANGE

3.4.1. Determination of anion exchange capacity

Ten grams of the soil samples were taken and leached with 100 mL $BaCl_2$ -TEA (90 mL triethanolamine diluted to 1 L and and adjusted pH to 8.1 with HCl. Diluted to 2 L and mixed with 2 L water containing 100 g $BaCl_2.2H_2O$). The soil samples were again leached with 100 mL $CaCl_2.2H_2O$ solution (50g $CaCl_2.2H_2O$ adjusted to pH 8 with saturated $Ca(OH)_2$ solution and washed again. The calcium saturated soil was dried at 45 °C and weighed into a centrifugetube sufficient to give 0.2 m.e. CEC. Afterwards 20 mL 0.01M phosphoric acid was added and shaken for 30 minutes, and allowed to stand for 24 hours and again shaken for 30 minutes. The suspension was centrifuged and the supernatant solutions were decanted (Hesse, 1971). P content was estimated using ICP-OES (Model: Perkin Elmer-Optima 8000).

The remaining soil was washed, dried at 40 ^{0}C, and added 0.02 M KCl to the soil maintaining soil: solution ratio of 1:10 to exchange the P in exchange sites with high concentration of Cl^-. Extractant was filtered after 60 min shaking and P content was estimated using ICP-OES (Model: Perkin Elmer-Optima 8000).

Using H_3PO_4, 250 ppm P solution was prepared and 30 mL of 250 ppm P the solution was added to 3 g soil in centrifuge tube. It was shaken shaken for 60 min. All the anions in the extract were determined. Water soluble anions were determined following the procedure for determination of water soluble cations as described in 3.1.2.1.

3.4.2. Determination of ZPC

Different concentrations of indifferent electrolytes were prepared (NaCl - 0.001M, 0.01M, 0.05M and 0.2M). 40 mL of 0.001M NaCl was added to 2 g soil sample in beaker. Agitated with a bar magnet for 5 min without stopping, then the initial pH was measured. Using an automatic titrimeter (Model; Metrohm 877 titrino plus) connected to a combined electrode, titration was done with 0.1M HCl solution by regulating the additions to one drop every 2 min. Titration was continued until the pH became 3.0. The same procedure was carried out for another sample titrated against 0.1M NaOH until the pH became 9.5-10.0. The remaining titrations were conducted with additions of indifferent electrolyte 0.01, 0.05 and 0.2M NaCl. Graphs were prepared. pH at the intersecting point is considered as ZPC (Pansu and Gautheyrou, 2007).

3.5. STUDIES ON PHOSPHOROUS - SILICON INTERFERENCE

3.5.1. Extractability of different extracts used for P and Si extraction

Four extractants were used to study the extracting ability of P and Si.

a. 0.5M acetic acid: 25 mL of 0.5 M acetic acid was added to 10 g soil and shaken for 1 hr (Korndorfer *et al.*, 2001).

b. 0.1M HCl: 30 mL of 0.1 M HCl was added to 3 g soil and shaken for 5 min (Sims and Johnson, 1991).

c. Citrate -Bicarbonate- Dithionate: 40 mL of 0.3M sodium citrate was added to 4 g soil. 5 mL of 1M $NaHCO_3$was added to that and kept in water bath (80^0C). 1 g of $Na_2S_2O_4$ was added and stirred continuously for 1 min and occasionally for 15 min. 10 mL saturated NaCl and 10mL acetone was added at the end of 15 min digestion period (Mehra and Jackson, 2013).

d. Bray No. 1 reagent: 50 mL of Bray No.1 reagent was added to 5 g soil and shaken for exactly 5 minutes (Bray and Kurtz, 1945).

Content P and Si in the extract were estimated using ICP-OES (Model: Perkin Elmer-Optima 8000).

3.5.2. Interference of Silicon in colorimetric estimation of P

Twenty phosphorous standards (0.1 to 2 mg L^{-1}) were prepared and estimated using standard procedure of P estimation (Watanbe and Olsen, 1965). The absorbance was measured at eight different wavelength (500, 630, 660, 700, 750, 800, 882, 950 nm). Twenty silicon standards (0.1 to 2 mg L^{-1}) were also prepared and estimated using standard colorimetric procedure for Si estimation and absorbance were measured at eight different wave length (500, 630, 660, 700, 750, 800, 882, 950 nm).

Twenty four silicon standards were prepared (0.5, 1, 2.5, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110,120, 130, 140, 150, 160, 170, 180, 190 and 200 mg L^{-1}). These standards were estimated using standard procedure for P estimation (Watanbe and Olsen, 1965). The absorbance were measured at eight different wavelengths (500, 630, 660, 700, 750, 800, 882, 950 nm).

Twenty one solutions were prepared with different Si:P ratio. Phosphorous concentration was fixed as 0.1 mg L^{-1}. Increasing concentration of Si was added to maintain Si:P ratio as P alone, 1, 10, 20, 40, 80, 100, 120, 160, 200, 250, 500, 1000, 1500, 2000, 2500, 3000, 3500, 4000, 4500 and 5000. Solutions were estimated following standard procedure for colorimetric estimation of P.

Absorbance were measured at eight different wave lengths (500, 630, 660, 700, 750, 800, 882, 950 nm).

3.7. Statistical analysis

Correlation studies were carried out using using IBM SPSS statistics version 20. Path analysis was done in OPSTAT package (Sheoran *et al.*, 1998). Linear form adsorption isotherms were prepared in micosoft excel.

Results

4. RESULTS

The data generated from the various experiments conducted to realise the objectives of the study are presented in this chapter.

4.1. CHARACTERISATION OF SOIL SAMPLES

Representative soil samples (22 Nos.) collected from 7 agro ecological units of Kerala as detailed as detailed in Table 2 in materials and methods, were analysed to study the physico-chemical properties and nutrient status of the soils. The analysis was done with triplicate samples.

4.1.1. Physico-chemical properties

The physico-chemical properties of the 22 collected soil samples are shown in Table 3.

4.1.1.1. Soil pH

The pH of the soils ranged from 3.17 to 7.52 with an average of 5.1. The lowest pH was recorded in the *Pokkali* soils (Sample No. 10) and highest in the soil collected from Palakkad eastern plain (sample No. 21). Ultra acidic pH (<3.5) was recorded in all the three *Pokkali* soils. Two soils collected from *Onattukara* sandy plain (Sample No. 10 and 12) and three soils from Palakkad eastern pain showed pH value above 6.5.

4.1.1.2. Electrical conductivity (EC)

The lowest electrical conductivity of 0.05 dS m^{-1} (Sample No. 17) was recorded in north central laterite soil and the highest value of 15.02 dS m^{-1} was recorded in *Pokkali* soil (Sample No. 3). The remaining two *Pokkali* soils also showed high electrical conductivity of 7.85 dS m^{-1}(Sample No. 1) and 13.83 dS m^{-1} (Sample No. 2). All the three soils (Sample No. 13, 14 and 15) collected from *Kuttanad* were recorded with EC greater than 1 dS m^{-1}. (1.58, 1.13 and 3.91 dS m^{-1} repectively). The remaining collected soils showed EC value less than one.

4.1.1.3. Organic carbon (OC)

Organic carbon content of collected soils ranged from 0.32 to 6.74 per cent. The highest value was recorded in *Pokkali* (Sample No. 3) soil and the lowest recorded in northern coastal plain (Sample No. 9). All the soils collected from northern coastal plain and *Onattukara* sandy plain showed low organic carbon status (<0.75 per cent). All the soils collected from *Pokkali, Kole* and *Kuttanad* showed high organic carbon status (>1.5 per cent).

4.1.1.4. Bulk density (Bd)

Bulk density of the soils ranged from 0.6 to 1.93 Mg m^{-3} with an average value of 1.30 Mg m^{-3}. The lowest value was recorded in the soils collected from *Pokkali* (Sample No. 2) and *Kuttanad* (Sample No. 14). Lowland soils showed low bulk density. The highest value was recorded in soils collected from Palakkad eastern plain.

4.1.1.5. Texture

Sand content of the collected soil varied from 12.76 per cent to 90.24 per cent with a mean value of 48.06 per cent. Soil collected form *Kuttanad* showed lowest sand content (Sample No. 14) and the soil collected from northern coastal plain showed the highest sand content (Sample No. 8). All the soils collected from northern coastal plain and *Onattukara* sandy plain were recorded with more than 50 per cent sand content. The soils collected from *Kuttanad* showed <20 per cent sand content.

The silt content of the soil ranged from 5.76 to 42.50 per cent. The mean value of silt content of the collected samples was found as 23.96 per cent. The lowest value was recorded in soils of northern coastal plain (Sample No. 9) and the highest was recorded in soil collected from *Kole* (Sample No. 4). All the soils collected from northern coastal plain showed less than 15 per cent silt content.

The clay content of the soil varied from 3.43 to 57.23 per cent. The soil from *Kuttanad* (Sample No. 15) showed highest clay content whereas the soil from northern coastal plain (Sample No. 8) showed the lowest. All the soils collected from *Kuttanad* were recorded with more than 50 per cent clay content.

Out of the twenty two collected soil samples three soils were loamy in nature. Four samples were clayey in texture which includes all the soils collected from *Kuttanad* and one from *Kole.* All the three soils collected from *Onattukara* sandy plain and one soil sample collected from Palakkad eastern plain were coming under sandy loam textural class. Four soil samples were sandy clay loam in texture. Out of the three samples from northern coastal plain two samples were sandy and the other one was loamy sand in texture. Two soils collected from north central laterite were sandy clay and the other one was sandy clay loam. Two samples collected from *Kole* were clay loam in texture.

4.1.1.6. Cation exchange capacity

Cation exchange capacity of the soils under study ranged from 1.39 cmol(+) kg^{-1} to 27.38 cmol(+) kg^{-1}. Lowest value was recorded in soil from northern coastal plain (Sample No. 8) and the highest was recorded in soil from Palakkad eastern plain (Sample No. 21). Out of the twenty two collected soil samples, six samples were recorded with more than 10 cmol(+) kg^{-1} CEC and all the three samples collected from northern coastal plain were recorded with CEC less than 2 cmol(+) kg^{-1}.

4.1.1.7. Anion exchange capacity

Highest AEC of 34.49 cmol(-) kg^{-1} was recorded in *Pokkali* soil (Sample No. 3) and the lowest value of 3.91 cmol(-) kg^{-1} in soil from *Onattukara* sandy plain (Sample No. 12). All the low land soils of *Pokkali, Kole* and *Kuttanad* were recorded with high AEC, whereas sandy soils from northern coastal plain and *Onattukara* sandy plain and soils from Palakkad eastern plain were with low AEC.

Table 3. Physico-chemical properties of soil from different AEUs of Kerala

Sample No.	pH	EC (dS m^{-1})	OC (%)	Bd (Mg m^{-3})	CEC (cmol(+) kg^{-1})	AEC (cmol(-) kg^{-1})	Sand (%)	Silt (%)	Clay (%)	Textural class
1	3.38	7.85	5.3	0.6	8.31	30.96	50.8	26	23.2	sandy clay loam
2	3.17	13.83	5.74	0.64	5.69	33.09	47.1	30.2	22.7	Loam
3	3.34	15.02	6.74	1.3	6.06	34.49	41	34	25	Loam
4	4.53	0.39	3.44	1.18	8.85	23.68	24.5	42.5	33	clay loam
5	4.02	0.54	3.06	1.33	5.7	17.39	28.73	25.3	45.98	Clayey
6	4.00	0.67	2.57	1.83	4.57	15.69	25.24	36.24	38.52	clay loam
7	5.17	0.06	0.35	1.91	1.66	4.14	80.25	11.43	8.32	loamy sand
8	4.28	0.12	0.43	1.91	1.39	4.57	90.24	6.33	3.43	Sandy
9	6.23	0.09	0.32	1.74	1.52	4.33	89.33	5.76	4.91	Sandy
10	6.82	0.22	0.49	1.38	3.79	7.04	70.87	15.2	13.93	sandy loam
11	5.18	0.08	0.53	1.62	4.05	5.41	60.43	32.2	7.37	sandy loam
12	6.98	0.16	0.36	0.89	7.45	3.91	60.6	20	19.4	sandy loam
13	4.01	1.58	4.18	0.6	7.05	18.07	14	34.5	51.5	Clayey
14	4.21	1.13	4.8	0.63	10.65	26.38	12.76	32.24	55	Clayey

Table 3. Continued

Sample No.	pH	EC (dS m^{-1})	OC (%)	Bd (Mg m^{-3})	CEC (cmol(+) kg^{-1})	AEC (cmol(-) kg^{-1})	Sand (%)	Silt (%)	Clay (%)	Textural class
15	3.4	3.91	6.48	1.59	12.46	29.15	18	24.77	57.23	Clayey
16	5.49	0.16	1.91	1.22	6.88	12.54	51.6	18.2	30.2	sandy clay loam
17	4.47	0.05	1.43	1.37	2.81	20.56	48.23	12.43	42.97	sandy clay
18	5.94	0.14	1.43	1.16	6.95	18.14	49.2	13.75	37.05	sandy clay
19	7.24	0.48	1.38	1.93	21.42	10.56	34.26	40.21	25.53	Loam
20	6.9	0.18	0.83	1.49	13.84	7.45	47.44	25.1	27.46	sandy clay loam
21	7.52	0.3	1.22	1.5	27.38	8.88	57.22	18.34	24.44	sandy loam
22	5.96	0.1	0.78	0.6	11.68	5.8	55.62	22.34	22.04	sandy clay loam
Min.	**3.17**	**0.05**	**0.32**	**1.93**	**1.39**	**3.91**	**12.76**	**5.76**	**3.43**	**-**
Max.	**7.52**	**15.02**	**6.74**	**0.6**	**27.38**	**34.49**	**90.24**	**42.5**	**57.23**	**-**

4.1.2. Available nutrient status

Available nutrients status of the collected soils was estimated using standard procedure and the data is shown in Table 4.

4.1.2.1. Available nitrogen (Av.N)

The available nitrogen content of the soil ranged from 85.05 kg ha^{-1} to 730.80 kg ha^{-1}. The highest value was recorded in soils collected from *Kuttanad* (Sample No. 14) and the lowest value in soil from northern coastal plain (Sample No. 9). Out of 22 collected samples only 2 samples of *Kuttanad* (Sample No. 14 and 15) were recorded with high fertility status of available N. Thirteen soils showed low available nitrogen status (<280 kg ha^{-1}).

4.1.2.2. Available phosphorous (Av.P)

The lowest available phosphorus (7.32 kg ha^{-1}) content was found in soil from *Kuttanad* (Sample No. 14) whereas the highest (219.25 kg ha^{-1}) in the soil from *Pokkali* (Sample No.1). Out of the 22 samples analysed, low status (<10 kg ha^{-1}) available phosphorous status was found only in 4 samples. Fourteen samples were recorded with high level of (>24 kg ha^{-1}) available phosphorous, out of which 8 samples were with >100 kg ha^{-1}. The remaining 4 samples were found in medium category with respect to available P.

4.1.2.3. Available potassium (Av.K)

The available K status in collected soils ranged from 17.92 kg ha^{-1} to 855.62 kg ha^{-1}. Soil from northern coastal plain (Sample No. 9) showed lowest level of available K and soil from Palakkad eastern plain (Sample No.19) with highest value. Out of the collected samples, 6 samples were with low K status (<115 kg ha^{-1}) and 9 samples with high available K (>275 kg ha^{-1}). The remaining 7 samples were coming under medium category (115-275 kg ha^{-1}).

4.1.2.4. Available calcium (Av.Ca)

Available Ca content in the soil ranged from 74.45 to 4976.65 mg $kg^{-1.}$ The lowest value was found in the soil from northern coastal plain (Sample No. 8) and the highest value in the soil from Palakkad eastern plain (Sample No. 21). Out of 22 samples collected, only 6 samples were deficient (<300 mg kg^{-1}). The remaining soils were sufficient. Eight samples were with greater than 1000 mg kg^{-1} available Ca, which includes all the four samples collected from Palakkad eastern plain (Sample No. 19, 20, 21 and 22), all the three *Pokkali* soils (Sample No. 1, 2 and 3) and one sample from north central laterite (Sample No. 18).

4.1.2.5. Available magnesium (Av.Mg)

Highest content of available magnesium (2269.50 mg kg^{-1}) was observed in *Pokkali* soil (Sample No. 3), and the lowest (29.11 mg kg^{-1}) in *Onattukara* sandy plain (Sample No. 10). Ten samples were deficient in available magnesium (<120 mg kg^{-1}), which includes all the samples from northern coastal plain, *Onattukara* sandy plain, northern central laterite and the two soils from *Kole* land. All the three *Pokkali* soils were with very high Mg content (>1000 mg Kg^{-1}).

4.1.2.6. Available sulphur (Av.S)

Highest level of available sulphur (8291.67 mg kg^{-1}) was found in *Pokkali* soil (Sample No. 3), and the lowest (3.82 mg kg^{-1}) in northern coastal plain (Sample No. 9). All the three *Pokkali* soils were very high in available sulphur status (>5000 mg kg^{-1}). Out of 22 collected soils, only two samples of northern coastal plain (Sample No. 7 and 9) were coming under deficient category (<5 mg kg^{-1}).

4.1.2.7. Available iron (Av.Fe)

Lowest content of available iron (22.20 mg kg^{-1}) was observed in the soil from north central laterite (Sample No. 17), while the highest value of 1370 mg kg^{-1} recorded in *Kuttanad* soil (sample 15). All the soils were sufficient in available Fe status (>5 mg kg^{-1}). All the soils from *Pokkali, Kole* and *Kuttanad* region showed very high status of available Fe (>500 mg kg^{-1}).

4.1.2.8. Available manganese (Av.Mn)

Soil from northern coastal plain (Sample No. 9) was with lowest content of available Mn (2.72 mg kg^{-1}) and the highest (92.23 mg kg^{-1}) was in the soils of Palakkad eastern plain (Sample No. 21). All the collected soils exhibited sufficient status of available Mn (>1 mg kg^{-1}). Six soil samples exhibited comparatively very high available Mn content (>100 mg kg^{-1}), which include all the soils from north central laterite (Sample No. 16, 17 and 18), one soil from *Kole* (Sample No. 4), and two soils from Palakkad eastern plain (Sample No. 19 and 21).

4.1.2.9. Available copper (Av.Cu)

Lowest value for available Ca (0.46 mg kg^{-1}) was observed in the soils of northern coastal plain (Sample No. 8), and the highest (8.83 mg kg^{-1}) in *Pokkali* soils (Sample No. 3). Out of the 22 collected soil samples, four were deficient in available Ca (<1 mg $kg^{-1}$for acidic soil and <0.12 mg $kg^{-1}$for neutral to alkaline soils). The deficient samples are from northern coastal plain (Sample No. 7, 8 and 9) and *Onattukara* sandy plain (Sample No.11).

4.1.2.10. Available Zn (Av.Zn)

Soil from *Onattukara* sandy plain (Sample No. 11) showed lowest available Zn content of 1.20 mg kg^{-1} whereas *Pokkali* soil (Sample No. 3) showed the highest available Zn content of 246.80 mg kg^{-1}. None of the sample were deficient in zinc content (<1 mg kg^{-1} for acidic soil and <0.6 mg kg^{-1} for neutral and alkaline soil). All the three *Pokkali* soils showed comparatively very high available Zn status (>150 mg kg^{-1}).

Table 4. Available nutrients status and CBD-Fe content of soils from different AEUs of Kerala

Sample No.	N	P	K	Ca	Mg	S	Fe	Mn	Cu	Zn	B	Si	CBD-Fe
	kg ha^{-1}			mg kg^{-1}									%
1	387.45	219.25	205.33	1084.95	1977.38	6463.54	1130	35.36	8.76	189.95	2.37	4.24	0.831
2	409.5	127.76	116.11	1106.65	2162.5	7017.36	1015	25.01	6.87	196.35	2.63	3.42	1.172
3	384.3	151.95	400.96	1002.34	2269.5	8291.67	1090	24.17	8.83	246.8	1.7	3.93	1.055
4	327.6	9.06	387.15	980.75	226.72	45.66	810	134.75	8.1	8.56	5.42	6.29	1.519
5	431.55	14.04	154.93	679.83	107.65	111.98	750	30.06	6.11	4.37	3.08	3.03	1.354
6	396.9	13.63	162.77	573.35	91.9	172.05	765	26.08	4.56	5.32	1.52	3.15	1.221
7	110.25	134.85	22.03	157.15	32.39	4.51	133.2	3.79	0.57	1.73	0.28	1.84	0.192
8	138.6	42.27	36.59	74.45	47.51	8.85	73.2	3.96	0.46	1.31	0.41	1	0.133
9	85.05	201.71	17.92	178.4	37.34	3.82	64.4	2.72	0.52	2.36	0.04	2.15	0.116
10	116.55	46.68	129.17	617.67	29.11	7.47	114.8	13.83	1.95	2.9	0.88	15.37	0.156
11	122.85	119.83	89.97	279.4	30.25	6.25	33.7	4.19	0.84	1.2	0.25	5.36	0.098
12	94.5	33.13	50.03	619.35	46.49	6.6	95.3	9.34	1.36	3.38	0.1	16.93	0.100
13	548.1	10.49	324.24	297.3	274.78	332.81	1085	77.35	3.94	5.35	3.5	2.76	1.259
14	730.8	7.32	505.51	526.5	595.5	259.55	895	31.27	4.04	6.26	0.44	6.04	2.012
15	677.25	8.89	570.58	386.75	721.88	822.74	1370	26.46	3.27	9.58	1.9	4.1	2.080
16	220.5	35.8	356.44	701.16	191.77	15.1	37.4	137.63	1.69	6.41	0.08	10.64	0.850
17	258.3	8.29	230.33	165.78	38.99	6.77	22.2	125.88	5.48	2.25	0.22	4.01	1.167
18	204.75	160.99	608.22	1287.5	99.48	13.54	65.3	106.75	5.13	2.88	1.11	13.45	1.066

Table 4. Continued

Sample No.	N	P	K	Ca	Mg	S	Fe	Mn	Cu	Zn	B	Si	CBD-Fe
	kg ha^{-1}			mg kg^{-1}									%
19	211.05	144.32	855.62	2694.6	307.5	36.11	93.7	119.75	3.04	10.65	0.42	54.58	0.827
20	138.6	32.28	357.17	2190.85	147.77	9.55	100.9	79.25	2.17	12.03	2.09	41.85	1.167
21	151.2	20.16	105.28	4976.65	316.75	15.45	185.8	192.23	3.6	8.55	1.3	23.28	0.555
22	119.7	79.83	223.78	1472.5	284.45	5.03	130.8	49.1	3.78	23.71	2.93	18.43	0.790
Minimum	**85.05**	**7.32**	**17.92**	**74.45**	**29.11**	**3.82**	**22.2**	**2.72**	**0.46**	**1.2**	**0.04**	**1**	**0.098**
Maximum	**730.8**	**219.25**	**855.62**	**4976.65**	**2269.5**	**8291.67**	**1370**	**192.23**	**8.83**	**246.8**	**5.42**	**54.58**	**2.080**

Table 5. Exchangeable cations and water soluble plus exchangeable Al content in the soils from different AEUs of kerala

Sample No.	Exchangeable cations (mg kg^{-1})									CEC (cmol(+) kg^{-1})	WS+Ex.Al (mg kg^{-1})
	Ca	Mg	Na	K	Fe	Mn	Cu	Zn	Al		
1	528.38	348	278.05	5.85	258.33	2.86	0.67	14.1	54.5	8.31	695.1
2	438.88	31.5	662.5	13.37	138.1	1.9	0.64	80.95	20.9	5.69	874.9
3	1125.25	92.5	136.25	6.86	114.25	2.69	0.53	131.65	28.75	6.06	671.75
4	979.28	230.53	161.2	76.11	20.65	106.58	0.43	5.33	59.02	8.85	59.015
5	544.32	95.39	154.1	70.35	26.23	22.39	0.53	3.76	102.95	5.70	102.95
6	410.85	72.93	152.09	25.88	30.1	16.93	0.55	4.66	89.55	4.57	89.55
7	159.6	39.82	111.89	2.66	4.19	2.44	0.32	1.57	2.61	1.66	2.61
8	71.09	47.59	118.75	10.59	5.34	3.59	0.32	1.22	7.69	1.39	7.685
9	158.28	37.32	101.61	5.37	3.09	1.43	0.29	1.06	nd	1.52	nd
10	596.21	32.86	101.45	27.86	3.06	2.24	0.31	0.97	nd	3.79	nd
11	254.52	28.45	100.17	12.51	3.66	2.65	0.29	1.06	1.33	4.05	1.33
12	521.07	39.97	107.44	9.24	3.09	1.9	0.3	0.98	nd	7.45	nd
13	267.2	274.5	294.3	56.92	34.85	34.86	0.55	3.8	156.7	7.05	156.7

Table 5. Continued

Sample No.	Exchangeable cations(mg kg^{-1})									CEC (cmol(+) kg^{-1})	WS+Ex.Al (mg kg^{-1})
	Ca	**Mg**	**Na**	**K**	**Fe**	**Mn**	**Cu**	**Zn**	**Al**		
14	591.9	528.23	332.7	128.49	33.5	21.55	0.33	3.42	117.4	10.65	117.4
15	243.4	389.73	328.65	95.45	178.9	11.02	0.31	6.35	633.33	12.46	687.1
16	779.69	231.61	104.29	105.97	9.41	75.25	0.29	1.5	1.15	6.88	1.145
17	165.77	30.79	103.65	55.5	9.44	106.35	0.35	1.86	63.17	2.81	63.165
18	964.83	111.86	108.46	202.03	9.36	42.97	0.2	0.99	1.04	6.95	1.04
19	3394.67	363.79	143.46	281.67	9.35	6.55	0.21	0.93	0.86	21.42	0.86
20	2403.68	153.32	109.29	117.54	9.35	7.54	0.19	0.96	0.9	13.84	0.9
21	4748.4	353.28	134.02	21.45	9.35	3.14	0.18	0.9	0.74	27.38	0.74
22	1739.67	281.34	118.27	73.75	9.35	18.03	0.14	2.08	0.93	11.68	0.93
Minimum	**71.09**	**28.45**	**100.17**	**2.66**	**3.06**	**1.43**	**0.14**	**0.9**	**nd**	**1.39**	**nd**
Maximum	**4748.4**	**528.23**	**662.5**	**281.67**	**258.33**	**106.58**	**0.67**	**131.65**	**633.33**	**27.38**	**874.90**

*nd not in detectable limit

4.1.2.11. Available boron (Av.B)

Available B content of the soils ranged from 0.04 to 5.42 mg kg^{-1}. Lowest content was found in the soil from northern coastal plain (Sample No. 9) and the highest in the soil from *Kole* land (Sample No. 4). Out of the 22 collected samples, nine were deficient in available boron (<0.5 mg kg^{-1}).

4.1.2.12. Available silicon (Av.Si)

Available silicon content of the soil ranged from 1 to 54.58 mg kg^{-1}. The lowest value was observed in the soil from northern coastal plain (Sample No. 8) and the highest in the soil from Palakkad eastern plain (Sample No. 19). Except the sample No. 19 from Palakkad eastern plain all other soils were deficient in the status of available silicon (<47mg kg^{-1}). All the collected samples from *Pokkali, Kole* and *Kuttanad* were with less than 10 mg $kg^{-1}$of available Si.

4.1.2.13. Available molybdenum (Av.Mo)

None of the samples were with detectable amount of available Mo.

4.1.3. Citrte-Bicarbonate-Dithionate extractable Fe (CBD-Fe)

The content of CBD extractable Fe in the collected soil samples is given in Table 4. Highest value of CBD-Fe (2.08 per cent) was recorded in *Kuttanad* soil (Sample No. 15), and the lowest value of 0.098 per cent in the soil from *Onattukara* sandy plain (Sample No. 11). Two soils from *Kuttanad* (Sample No. 14 and 15) were recorded with greater than 2 per cent of CBD-Fe. All the soils from northern coastal plain and *Onattukara* sandy plain were with low CBD-Fe content.

4.1.4. Exchageable cations and water soluble plus exchangeable Al

The data on Exchangeable cations present in the collected soil samples are presented in Table 5. Water soluble plus exchangeable Al content were taken under consideration, since solubility of Al is high under acidic pH.

4.1.4.1. Exchangeable calcium (Ex.Ca)

Exchangeable calcium in the soil ranged from 71.09 to 4748.40 mg kg^{-1}. The highest value was recorded in the soil from Palakkad eastern plain (Sample No. 21) and the lowest in the soils of northern coastal plain (Sample No. 8). All the four soils collected from Palakkad eastern plain showed comparatively higher content of exchangeable Ca.

4.1.4.2. Exchangeable magnesium (Ex.Mg)

Lowest exchangeable magnesium content of 28.45 mg kg^{-1} was observed in soil from *Onattukara* sandy plain (Sample No. 11). Highest content of 528.23 mg kg^{-1} was observed in *Kuttanad* soil (Sample No. 14). Comparatively low content of exchangeable Mg was found in the northern coastal plain and *Onattukara* sandy plain.

4.1.4.3. Exchangeable sodium (Ex.Na)

Exchangeable Na content of the soils under study ranged from 100.17 mg kg^{-1} to 662.5 mg kg^{-1}. The lowest value was recorded in the soils of *Onattukara* sandy plain (Sample No. 11) and the highest in *Pokkali* soil (Sample No. 2).

4.1.4.4. Exchangeable pottasium (Ex.K)

Soil from northern coastal plain (Sample No.7) was with the lowest value of 2.66 mg kg^{-1} for exchangeable K and the soil from Palakkad eastern plain (Sample No. 19) with the highest value of 281.67 mg kg^{-1}.

4.1.4.5. Exchangeable iron (Ex.Fe)

Exchangeable iron content in the soils ranged from 3.06 to 258.33 mg kg^{-1}. The highest content was recorded from *Pokkali* soil (Sample No. 1) and the lowest from northern coastal plain (Sample No. 10). Exceptionally higher content of exchangeable Fe was found in *Pokkali* soils. All the soils except *Kole* and *Kuttanad* were with less than 10 mg kg^{-1} exchangeable iron.

4.1.4.6. Exchangeable manganese (Ex.Mn)

Soil from northern coastal plain (Sample No. 9) showed the lowest exchangeable manganese content of 1.43 mg kg^{-1} whereas the soil from *Kole* land (Sample No. 4) showed the highest exchangeable Mn content of 106.58 mg kg^{-1}. Exceptionally very high content exchangeable Mn (>100 mg kg^{-1}) was observed in the soils from *Kole* land (Sample No. 4) and north central laterite (Sample No. 17).

4.1.4.7. Exchangeable copper (Ex.Cu)

Exchangeable copper content in the soils varied from 0.14 to 0.67 mg kg^{-1}. Lowest exchangeable Cu was observed in the soil from Palakkad eastern plain (Sample No. 22) and the highest from *Pokkali* soil (Sample No. 1). There is no much variation in the content of exchangeable Cu among the collected soils.

4.1.4.8. Exchangeable zinc (Ex.Zn)

Lowest content of exchangeable Zn (0.90 mg kg^{-1}) was noted in the soil of Palakkad eastern plain (Sample No. 21). The highest value of 131.65 mg kg^{-1} followed by 80 mg kg^{-1}, were recorded in the two *Pokkali* soils (Sample No. 3 and 2 respectively). The exchangeable Zn content of the other soils (except *Pokkali* soils) ranged from 0.90 mg kg^{-1} to 5.33 mg kg^{-1}.

4.1.4.9. Exchangeable Al and exchangeable plus water soluble aluminium (Ex.Al and Ex.+WS.Al)

Exchangeable aluminium content was not in a detectable limit in three soils (Sample No. 9 and 10 of northern coastal plain and Sample No. 12 from *Onattukara* sandy plain). Exceptionally high exchangeable aluminium content (633.33 mg kg^{-1}) was observed in *Kuttanad* soil (Sample No. 15). Highest value of water soluble plus exchangeable Al (874.9 mg kg^{-1}) was found in *Pokkali* soil (Sample No. 3). Water soluble plus exchangeable Al was also not in detectable limit in three soils (Sample No. 9 and 10 of northern coastal plain and Sample No. 12 from *Onattukara* sandy plain).

4.1.5. N pools (Exchangeable ammoniacal N, nitrate and total N)

Table 6. Exchangeable ammoniacal N, nitrate and total N content in the soils (mg kg^{-1}) from different AEUs of Kerala

Sample No.	NH_4^+ - N	NO_3^- - N	Total N
1	44.8	14.2	3900
2	56	10.2	4300
3	72.8	11.4	4600
4	84	11.8	3100
5	67.2	12.6	2200
6	50.4	12	2300
7	12.4	4.8	800
8	10.8	5.6	1200
9	11.2	5	800
10	16.2	12.4	1100
11	15.8	16.8	1000
12	15.5	11.2	900
13	72.8	4.6	3400
14	67.2	5.6	4000
15	56	5.1	4800
16	11	16.8	2100
17	11.4	5.6	1700
18	16.8	10.2	1400
19	22.4	11	1600
20	11.3	11.2	1400
21	10.2	16.8	1400
22	11.2	10.8	1400
Minimum	**10.8**	**5**	**800**
Maximum	**72.8**	**16.8**	**4800**

Exchageable ammonical N, nitrate N and total N content of the collected soils are given in Table 6. Highest value for ammonical N (72.8 mg kg^{-1}) was found in the soil from *Pokkali* (Sample No. 3) and *Kuttanad* (Sample No. 13) and the lowest value (10.2 mg kg^{-1}) in the soil from Palakkad eastern plain (Sample No. 21).

Low land soils of *Pokkali*, *Kole* and *Kuttanad* were noted with high value of ammonical N. All the soils from northern coastal plain were with low value of both ammoniacal and nitrate N. Highest nitrate N content (16.8 mg kg^{-1}) was found in the soils from *Onattukara* sandy plain (Sample No. 11), north central laterite (Sample No. 16) and Palakkad eastern plain (Sample No. 21) and the lowest value (4.6 mg kg^{-1}) in the soil from *Kuttanad* (Sample No. 13).

Highest value for total N (4800 mg kg^{-1}) was noted in *Kuttanad* soil (Sample No. 15), and lowest (800 mg kg^{-1}) in the soil from northern coastal plain (Sample No. 7 and 9). All the sandy soils from northern coastal plain and *Onattukara* sandy plain were recorded with low total N content.

4.1.6. Mineralogy

X-ray diffractograms of clay, silt and sand content of seven representative soils from seven agro-ecological units revealed the dominance of kaolinite in all clay fractions of soils except in the soil from Palakkad eastern plain. The peak of mixed layer mineral was dominant in X-ray diffraction pattern of clay and silt fractions of Palakkad eastern plain. The presence of calcite was unique to the soil from Palakkad eastern plain. Dominance of quartz or kaolinite was observed in silt fraction. Sand fraction of all soils was dominated by quartz. Other than this, gibbsite was a common mineral present in all the soils. Different minerals present in clay, silt, sand fractions of representative soils are given in Table 7.

Table 7. Minerals present in clay, silt and sand fractions of representative soils from different AEUs of Kerala

AEUs	Clay	Silt	Sand
Pokkali	Kaolinite, gibbsite, quartz, hematite	Mixed layer minerals, mica, kaolinite, gibbsite, quartz, goethite	Mixed layer minerals, kaolinite, gibbsite, quartz, goethite
Kole land	Kaolinite, gibbsite, quartz	Kaolinite, gibbsite, quartz, feldspar	Quartz, feldspar,
Northern coastal plain	Kaolinite, mixed layer minerals, quartz	Kaolinite, mixed layer minerals, quartz	Quartz, feldspar
Onattukara sandy plain	Kaolinite, mixed layer minerals	Kaolinite, quartz	Quartz, goethite
Kuttanad	Kaolinite, mixed layer minerals, gibbsite, hematite	Kaolinite, mixed layer minerals, gibbsite	Quartz, feldspar, hematite, gibbsite
North central laterite	Kaolinite, quartz, hematite	Kaolinite, quartz, hematite, gibbsite	Quartz, hematite
Palakkad eastern plain	Mixed layer minerals, hydroxyl interlayered vermiculite, gibbsite, quartz, calcite	Mixed layer minerals, gibbsite, quartz, calcite	Hdroxyl interlayered vermiculite, gibbsite, quartz, calcite feldspar

4.1.7. Correlation study

4.1.7.1. Relationship between physico-chemical properties and available nutrients

Correlation coefficients between soil properties and available nutrient status are presented in Table 8 and the correlation of exchangeable cations is given in Table 9. Water soluble plus exchangeable Al was also included in correlation study since most of the soils were extremely acidic with more solubility of Al.

pH was significantly and positively correlated with CEC (0.451*), Av.Si (0.723**) and negatively correlated with EC (-0.581**), OC (-0.771**), AEC (-0.754**), Av.N (-0.711**), Av.Mg (-0.563**), Av.S (-0.553**), Av.Fe (-0.779**), Av.Cu (-0.559**), Av.Zn (-0.504*), CBD-Fe (-0.518*). EC was significantly and positively correlated with OC (0.763**), AEC (0.754**), Av.Mg

(0.966**), Av.S (0.974**), Av.Fe (0.632**), Av.Cu (0.633**) and Av.Zn (0.959**).

Table 8. Correlation between physico-chemical properties and available nutrients

	pH	EC	OC	AEC	CEC	Sand	Silt	Clay
EC	-0.581**							
OC	-0.771**	0.763**						
AEC	-0.754**	0.749**	0.944**					
CEC	0.451*							
Sand			-0.661**	-0.627**				
Silt			0.534*	0.474*		-0.776**		
Clay			0.573**	0.576**		-0.896**		
Av.N	-0.711**		0.852**	0.779**		-0.821**	0.511*	0.820**
Av.K					0.466*	-0.619**	0.476*	0.556**
Av.Ca					0.902**			
Av.Mg	-0.563**	0.966**	0.790**					
Av.S	-0.553**	0.974**	0.706**	0.716**				
Av.Fe	-0.779**	0.632**	0.943**			-0.679**	0.563**	0.575**
Av.Cu	-0.559**	0.633**	0.722**			-0.540**	0.514*	0.428*
Av.Zn	-0.504*	0.959**	0.666**					
Av.B			0.460*	0.434*		-0.517*	0.542**	
Av.Si	0.723**							
CBD-Fe	-0.518*		0.721**	0.731**		-0.884**	0.528*	0.904**

** Correlation is significant at the 0.01 level (2- tailed).

* Correlation is significant at the 0.05 level (2-tailed).

Organic carbon (OC) had significant negative correlation with sand content (-0.661**) and positively correlated with AEC (0.944**), silt (0.534*), clay (0.573**), Av.N (0.852**), Av.Mg (0.790**), Av.S (0.7063**), Av.Fe (0.943**), Av.Cu (0.722**), Av.Zn (0.666*), Av.B (0.460*) CBD-Fe (0.721**). AEC showed significant positive correlation with silt (0.474*), clay (0.576**), Av.N (0.779**), Av.S (0.716**), Av.B (0.434*), CBD-Fe (0.731**) and negative correlation with sand (-0.627**). CEC had significant positive correlation with Av.K (0.466*) and Av.Ca (0.902**).

4.1.7.2. Relationship between exchangeable cations and soil properties

Table 9. Correlation between exchangeable cations and soil properties

	Ex.Ca	**Ex.Mg**	**Ex.Na**	**Ex.K**	**Ex.Fe**	**Ex.Cu**	**Ex.Zn**	**WS+Ex.Al**
pH	0.614**		-0.564**		-0.635**	-0.789**	-0.463*	-0.697**
EC			0.625**		0.728**	0.634**	0.926**	0.904**
OC			0.697**		0.795**	0.673**	0.623**	0.865**
CEC	0.916**	0.685**		0.471*				
Sand		-0.575**						
Silt								
Clay		0.538**						
Av.N		0.556**	0.632**		0.542**	0.528*		0.563**
Av.K		0.599**		0.887**				
Av.Ca	0.972**							
Av.Mg			0.643**		0.821**	0.620**	0.831**	0.912**
Av.S			0.545**		0.764**	0.661**	0.874**	0.871**
Av.Fe			0.677**		0.763**	0.739**	0.467*	0.788**
Av.Cu					0.590**	0.637**	0.556**	0.613**
Av.Zn			0.497*		0.732**	0.622**	0.874**	0.833**
Av.B						0.425*		
Av.Si	0.770**			.658**		-0.556**		

** Correlation is significant at the 0.01 level (2- tailed).

* Correlation is significant at the 0.05 level (2-tailed).

Sand content had significant negative correlation with Av.N (-0.821**), Av.K (-0.619**), Av.Fe (-0.679**), Av.Cu (-0.540*), Av.B (-0.517*), CBD-Fe (-0.884**). Silt content was positively correlated with Av.N (0.511*), Av.K (0.476*), Av.Fe (0.563**), Av.Cu (0.514*), Av.B (0.542**), CBD-Fe (0.528*). Clay content was significantly and positively correlated with Av.N (0.820**), Av.K (0.556**), Av.Fe (0.575*), Av.Cu (0.428*) and CBD-Fe (0.904**).

Correlation coefficient between exchangeable cations and other soil properties are given in Table 9. Ex.Ca had significant positive correlation with pH (0.614**), CEC (0.916**), Av.Ca (0.972**) and Av.Si (0.770**). Ex.Mg had significant positive correlation with CEC (0.685**), clay (0.538**), Av.N (0.556**), Av.K (0.599**) and negative correlation with sand content (-0.575**). Ex.Na had significant positive correlation with EC (0.625**). Ex.K was significantly and positively correlated with CEC (0.471*) and Av.K (0.887**).

Significant positive correlation of Ex.Fe with EC (0.728**), OC (0.795**) and negative correlation with pH (-0.635**) was observed. The same trend was followed by Ex.Cu, Ex.Zn and WS+Ex.Al. Ex.Fe, Cu and Zn had significant positive correlation with their available pool.

4.2. FRACTIONATION

Sequential fractionation of inorganic phosphorous, boron, silicon and non-sequential fractionation of sulphur were carried out in order to understand the dominant fractions of these elements in soil and their contribution to the available pool.

4.2.1. Fractionation of phosphorous

4.2.1.1. Different fractions of phosphorous

The data on various fractions as well as total phosphorous in the collected soils is given in the Table 10 and 11.

Saloid bound P (SB-P) includes soluble and loosely bound forms. SB-P content of the soils ranged from 0.50 to 38.58 mg kg^{-1}. The lowest value was found in the soil from northern coastal plain (Sample No. 8) and the highest in the soil from *Onattukara* sandy plain (Sample No. 12). Relatively higher amount of saloid bound P was found in *Onattukara* sandy plain and *Pokkali* soil.

Table 10. Different fractions of P in the soils from different AEUs of Kerala

Sample No.	**SB-P**	**Al-P**	**Fe-P**	**RS-P**	**Ca-P**	**Org-P**	**Res-P**	**Tot-P**
	mg kg^{-1}							
1	24.50	278.80	393.85	78.99	21.90	146.25	11.21	955.50
2	15.20	90.80	373.05	42.13	8.65	453.38	22.04	1005.25
3	14.68	95.85	405.35	58.24	13.30	436.38	8.47	1032.25
4	2.18	35.65	260.50	85.93	10.65	527.50	60.10	982.50
5	1.00	35.70	157.60	72.63	14.05	358.13	134.15	773.25
6	0.63	37.95	218.30	58.85	14.45	312.88	33.20	676.25
7	4.75	54.50	21.40	58.33	68.25	95.38	48.15	350.75
8	0.50	20.30	34.40	43.75	58.05	61.71	101.29	320.00
9	32.60	11.20	53.60	78.04	39.75	37.00	101.31	353.50
10	12.03	85.80	41.60	29.97	39.20	19.00	34.90	262.50
11	10.60	68.75	36.10	31.49	10.05	22.65	20.11	199.75
12	38.58	63.40	41.85	35.58	12.80	12.25	13.30	217.75
13	1.45	46.95	170.85	77.19	8.55	261.25	135.01	701.25
14	2.15	35.95	216.90	54.82	6.75	515.38	62.81	894.75
15	5.45	28.70	294.25	91.77	5.95	359.50	180.13	965.75
16	0.83	25.25	235.10	91.20	7.40	249.88	183.10	792.75
17	1.45	9.70	270.85	75.62	9.55	225.86	19.47	612.50
18	1.00	34.20	230.30	101.75	10.45	222.00	8.81	608.50
19	32.90	45.50	147.00	74.01	32.60	63.50	147.25	542.75
20	11.08	42.25	104.45	69.59	43.05	83.13	433.21	786.75
21	9.05	61.55	49.70	49.59	100.60	115.25	242.76	628.50
22	3.70	92.85	134.15	65.22	50.85	137.13	154.61	638.50
Minimum	**0.50**	**9.70**	**21.40**	**29.97**	**5.95**	**12.25**	**8.47**	**199.75**
Maximum	**38.58**	**278.80**	**405.35**	**101.75**	**100.60**	**527.50**	**433.21**	**1032.25**

Highest content of aluminium phosphate (278.80 mg kg^{-1}) was extracted from *Pokkali* soil (Sample No. 1). The lowest content of 9.70 mg kg^{-1} was recorded in the soil from north central laterite (Sample No. 17).

The iron bound phosphate (Fe-P) in the soils under study was ranged from 21.40 to 405.35 mg kg^{-1}. The lowest value was found in the soil of northern coastal plain (Sample No. 7), and the highest value in the *Pokkali* soil (Sample No. 3). Comparatively less content of Fe-P was observed in the soils of northern coastal plain and *Onattukara* sandy plain.

There was not much variation in the reductant soluble (sesquioxide occluded) phosphate in the soils. The lowest value of 29.97 mg kg^{-1} was recorded in *Onattukara* sandy soil (Sample No. 10) and the highest value (101.75 mg kg^{-1}) in the soil from north central laterite (Sample No. 18).

The calcium phosphate (Ca-P) in the soils ranged from 5.95 to 100.60 mg kg^{-1} with a mean value of 26.68 mg kg^{-1}. The lowest value was observed in *Kuttanad* soil (Sample No. 15) and the highest in the soils from Palakkad eastern plain (Sample No. 21). All the *Kuttanad* soils and soils from northern central laterite showed low values of calcium phosphate.

The content of organic phosphate (Org-P) in the soils showed a wide range. The lowest value of 12.25 mg kg^{-1} was observed in the *Onattukara* sandy soil (Sample No. 12) and the highest value of 527.50 mg kg^{-1} in the soil collected from *Kole* land (Sample No. 4). Soils from northern coastal plain and *Onattukara* sandy plain were with comparatively less organic phosphate content than other soils.

The residual phosphate (Res-P) content of the soil ranged from 8.47 to 433.21 mg kg^{-1}. The lowest value of 8.47 mg kg^{-1} was noted in the *Pokkali* soil (Sample No. 3) and the highest (433.21 mg kg^{-1}) in the soil of Palakkad eastern plain (Sample No. 20).

Table 11. Percentage distribution of fractions of P in soil

Sample No.	SB-P	Al-P	Fe-P	RS-P	Ca-P	Org-P	Res-P
1	2.56	29.18	41.22	8.27	2.29	15.31	1.17
2	1.51	9.03	37.11	4.19	0.86	45.10	2.19
3	1.42	9.29	39.27	5.64	1.29	42.27	0.82
4	0.22	3.63	26.51	8.75	1.08	53.69	6.12
5	0.13	4.62	20.38	9.39	1.82	46.31	17.35
6	0.09	5.61	32.28	8.70	2.14	46.27	4.91
7	1.35	15.54	6.10	16.63	19.46	27.19	13.73
8	0.16	6.34	10.75	13.67	18.14	19.29	31.65
9	9.22	3.17	15.16	22.08	11.24	10.47	28.66
10	4.58	32.69	15.85	11.42	14.93	7.24	13.30
11	5.31	34.42	18.07	15.77	5.03	11.34	10.07
12	17.72	29.12	19.22	16.34	5.88	5.63	6.11
13	0.21	6.70	24.36	11.01	1.22	37.25	19.25
14	0.24	4.02	24.24	6.13	0.75	57.60	7.02
15	0.56	2.97	30.47	9.50	0.62	37.22	18.65
16	0.10	3.19	29.66	11.50	0.93	31.52	23.10
17	0.24	1.58	44.22	12.35	1.56	36.88	3.18
18	0.16	5.62	37.85	16.72	1.72	36.48	1.45
19	6.06	8.38	27.08	13.64	6.01	11.70	27.13
20	1.41	5.37	13.28	8.84	5.47	10.57	55.06
21	1.44	9.79	7.91	7.89	16.01	18.34	38.63
22	0.58	14.54	21.01	10.21	7.96	21.48	24.21
Minimum	**0.09**	**1.58**	**6.10**	**4.19**	**0.62**	**5.63**	**0.82**
Maximum	**17.72**	**34.42**	**44.22**	**22.08**	**19.46**	**57.60**	**55.06**

Among the soils, relatively lower content of total phosphate (199.75 mg kg^{-1}) was seen in *Onattukara* sandy soil (Sample No.11) and the highest (1032.25 mg kg^{-1}) was observed in *Pokkali* soil (Sample No. 3). Northern coastal sandy soils and *Onattukara* sandy soils exhibited relatively less content of total phosphate whereas soils of *Pokkali, Kole* and *Kuttanad* were with high total phosphate.

4.2.1.2. Percentage distribution of fractions of P

The data on percentage distribution of fractions of P in soil are presented in Table 11.The contribution of SB-P was to the tune of 0.09 to 17.72 per cent. *Onattukara* sandy soil (Sample No. 12) was with highest per cent of SB-P. The contribution of Al-P ranged from 1.58 to 34.42 per cent. Iron bound phosphate contributed to the total P in the tune of 6.10 to 44.22 per cent. The content of RS-P ranged from 4.19 to 22.08 per cent.

The lowest per cent contribution of Ca-P (0.62 per cent) towards total P is recorded in *Kuttanad* soil (Sample No. 15) and the highest (19.46 per cent) in the northern coastal plain (Sample No. 7). The contribution of Org-P ranged from 5.63 to 57.60 per cent of total P in soil. Relatively higher amount of Org-P was reported in *Pokkali, Kole* and *Kuttanad* soil. Per cent contribution of Res-P towards total P ranged from 0.82 to 55.06 per cent. The per cent of this fraction is high in soils of Palakkad eastern plain and low in *Pokkali* soils.

4.2.1.3. Contribution of different fractions of P to the available pool

The correlation coefficients between available P and different fractions of P in soils are given in Table 12. The data revealed that only four fractions were significantly correlated to the available pool. Saloid-bound P and aluminium phosphate showed significant positive correlation with available P, whereas organic P and residual P showed significant negative correlation.

The path coefficient analysis of the fractions with the available pool depicts a clearer picture. The path coefficients showing the direct and indirect effects of different fractions on available P in soil are presented in Table12. The direct effect of SB-P on available P is high and positive as indicated by the path coefficient of 0.333. The direct effect of Al-P on available P is positive and high with a path coefficient of 0.330. The direct effect of residual P on available P is negative and moderate (-0.243).

4.2.1.4. Relationship among different fractions of P in soil

Correlation coefficients of different fractions of P in soil are given in Table 13. Saloid-bound P which is readily available in soil had significant negative correlation with Org-P (-0.446**). Iron phosphate showed significant positive correlation with RS-P, Org-P and Tot-P (0.434*, 0.726** and 0.859** respectively) and significant negative correlation with Ca-P (-0.587**). Reductant soluble P had significant positive correlation with Tot-P (0.488**). Calcium phosphate showed a significant negative correlation with Org-P (-0.529*). There was significant and high positive correlation between Org-P and Tot-P (0.825**). Al-P and Res-P did not show any significant correlation with other fractions of P in soil.

4.2.1.5. Relationship between different fractions of P and physico-chemical properties

Correlation coefficients of fractions of P with physico-chemical properties of soil are presented in Table 14. Saloid-bound P had significant negative correlation with clay content of the soil (-0.430*). Aluminium phosphate was significantly and positively correlated with EC (0.493*). Iron phosphate showed significant positive correlation with EC (0.733**), OC (0.851**), AEC (0.941**), silt (0.435*) and clay (0.498*). Fe-P was significantly and negatively correlated with pH and sand content with correlation coefficient of -0.693** and -0.551** respectively.

Reductant soluble phosphate showed significant positive correlation only with clay content (0.507*). Calcium phosphate content of the soil was significantly and positively correlated with pH (0.535*) and sand content (0.575**) whereas significant and negative correlation was found with OC (-0.510*), AEC (-0.563**), silt content (-0.445*) and clay content (-0.524*). Significant positive correlation was found between Org-P with EC (0.461*), OC (0.785**), AEC (0.813**), silt content (0.532*) and clay content (0.667**).

Whereas significant negative correlation was found between Org-P and pH (-0.686**), sand content (-0.722**).

Table 12. Correlation coefficients and path coefficients of different fractions of P to available P

	SB-P	Al-P	Org-P	Res-P	Correlation coefficients
SB-P	**0.333**	0.108	0.063	0.025	0.529**
Al-P	0.109	**0.330**	0.013	0.060	0.512**
Org-P	-0.148	-0.029	**-0.142**	0.042	-0.278*
Res-P	-0.034	-0.082	0.024	**-0.243**	-0.335*

(Values on diagonal are direct effects and values on horizontal lines are indirect effects)

Table 13. Correlation coefficients among the fractions of P in soil

	SB-P	Fe-P	RS-P	Ca-P	Org-P
RS-P		0.434*			
Ca-P		-0.587**			
Org-P	-0.446*	0.726**		-0.529*	
Res-P					
Tot-P		0.859**	0.488*		0.825**

Table 14. Correlation coefficients of fractions of P with physico-chemical properties of soil

	pH	EC	OC	AEC	CEC	Sand	Silt	Clay
SB-P								-0.430*
Al-P		0.493*						
Fe-P	-0.693**	0.733**	0.851**	0.941**		-0.551**	0.435*	0.498*
RS-P								0.507*
Ca-P	0.535*		-0.510*	-0.563**		0.575**	-0.445*	-0.524*
Org-P	-0.686**	0.461*	0.785**	0.813**		-0.722**	0.532*	0.667**
Res-P					0.560**			
Tot-P	-0.582**	0.589**	0.846**	0.860**		-0.685**	0.518*	0.621**

**Correlation is significant at the 0.01 level (2-tailed)
*Correlation is significant at the 0.05 level (2-tailed)

Table 15. Correlation coefficients of fractions of P with available nutrients

	N	K	Ca	Mg	S	Fe	Mn	Cu	Zn	B	Si
SB-P											
Al-P				0.641**	0.645**			0.461*	0.664**		
Fe-P	0.626**			0.774**	0.730**	0.709**		0.846**	0.713**		
RS-P		0.571**					0.453*				
Ca-P	-0.550**		0.571**			-0.448*					
Org-P	0.785**			0.451*		0.733**		0.692**		0.541**	
Res-P			0.504*								0.568**
Tot-P	0.707**	0.451*		0.655**	0.555**	0.756**		0.783**	0.548**	0.606**	

Table 16. Correlation coefficients of fractions of P with exchangeable cations

	Ex.Ca	Ex.Mg	Ex.Na	Ex.K	Ex.Fe	Ex.Mn	Ex.Cu	Ex.Zn	WS +Ex. Al
SB-P						-0.461*			
Al-P					0.705**		0.450*		0.520*
Fe-P			0.547**		0.741**		0.616**	0.607**	0.785**
RS-P				0.518*		0.530*			
Ca-P	0.575**						-0.459*		
Org-P			0.549**				0.508*	0.456*	0.496*
Res-P	0.562**						-0.447*		
Tot-P		0.497*	0.557**		0.625**		0.475*	0.482*	0.664**

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

WS: water soluble, Ex: exchangeable

Residual phosphate content showed significant positive correlation only with CEC (0.560**). Significant negative correlation was found between Tot-P and pH (-0.582**) and sand content (-0.685**). Total phosphate content of the soil was significantly and positively correlated with EC (0.589**), OC (0.846**), AEC (0.860**), silt content (0.518**) and clay content (0.621**).

4.2.1.6. Relationship between different fractions of P and available nutrients

Correlation coefficients of different fractions of P with available nutrients in soil are shown in Table 15. Saloid bound P was significantly and positively correlated only with Av.P (0.529**). Aluminium bound phosphate had significant positive correlation with Av.P (0.512**), Av.Mg (0.641**), Av.S (0.645**), Av.Cu (0.461*) and Av.Zn (0.664**). A high significant positive correlation was found between Fe-P with Av.N (0.626**), Av.Mg (0.774**), Av.S (0.730**), Av.Fe (0.709**), Av.Cu (0.846**) and Av.Zn (0.713**). Reductant soluble phosphate had positive correlation with Av.K (0.571**) and Av.Mn (0.453**).

Calcium bound phosphate showed significant negative correlation with Av.N (-0.550**), Av.Fe (-0.448**) and positive correlation with Av.Ca (0.571**). Significant negative correlation was observed between Org-P and Av.P (-0.278*). Significant positive correlation of Org-P was observed with Av.N (0.785**), Av.Mg (0.451*), Av.Fe (0.733**), Av.Cu (0.692**) and Av.B (0.541**).

Residual phosphate had a significant negative correlation with Av.P (-0.335*) and positive correlation with Av.Ca (0.504*) and Av.Si (0.568**). Total phosphate content of the soil was significantly and positively correlated with Av.N (0.707**), Av.K (0.451*), Av.Mg (0.655**), Av.S (0.555**), Av.Fe (0.756**), Av.Cu (0.783**), Av.Zn (0.548**) and Av.B (0.606**).

4.2.1.7. Relationship between different fractions of P and exchangeable cations

Correlation coefficients of different fractions of P with exchangeable cations in soil are given in Table 16. A significant negative correlation was found between SB-P and Ex.Mn (-0.461*). Aluminium phosphate had significant positive correlation with Ex.Fe (0.705**), Ex.Cu (0.450*) and WS+Ex.Al (0.520*). The content of iron phosphate in soil was found to be positively and significantly correlated with Ex.Na (0.547**), Ex.Fe (0.741**), Ex.Cu (0.616**), Ex.Zn (0.607**) and WS+Ex.Al (0.785**). Reductant soluble phosphate had significant positive correlation with Ex.K (0.518*) and Ex.Mn (0.530*).

Calcium phosphate content of the soil showed significant positive correlation with Ex.Ca (0.575**) and negative correlation with Ex.Cu (-0.459*). Organic phosphate content of the soil was significantly and positively correlated with Ex.Na (0.549**), Ex.Cu (0.508*), Ex.Zn (0.456*) and WS+Ex.Al (0.496*). Residual phosphate had significant positive correlation with Ex.Ca (0.562**) and negative correlation with Ex.Cu (-0.447*). Total phosphate content of the soil was significantly and positively correlated with Ex.Mg (0.497*), Ex.Na (0.557**), Ex.Fe (0.625**), Ex.Cu (0.475*), Ex.Zn (0.482*) and WS+Ex.Al (0.664**).

4.2.2. Fractionation of sulphur

4.2.2.1. Different fractions of sulphur in soil

The data on various fractions as well as total phosphorous in the collected soils are given in the Table 17.

The lowest value (3.82 mg kg^{-1}) of sulphate sulphur content was noted in the soil from northern coastal plain (Sample No. 9), and the highest (8291.67 mg kg^{-1}) in the *Pokkali* soil (Sample No. 3). All the three *Pokkal i*soils showed >5000 mg kg^{-1} of sulphate sulphur. Low lands of *Kole* and *Kuttanad* also had higher values of sulphate sulphur than other soils.

The total water soluble sulphur in the soils except *Pokkali* soils ranged from 10.04 to 364.17 mg kg^{-1}. The lowest value of 10.04 mg kg^{-1} was observed in the northern coastal sandy soil (Sample No. 7). The highest value of 7433.77 mg kg^{-1} was noted in the *Pokkali* soil (Sample No. 3).

Table 17. Different fractions of S in the soils from different AEUs of Kerala

Sample No.	Suphate S	Total water soluble S	Heat soluble S	Sulphate soluble after ignition	Total organic S	Total S
	mg kg^{-1}					
1	6463.54	5432.25	5532.00	11666.67	20564.33	24790.00
2	7017.36	6232.45	6250.24	15468.75	20378.43	28330.00
3	8291.67	7433.77	7558.92	5468.75	19854.23	27590.00
4	45.66	113.35	127.70	929.35	1139.13	1520.00
5	111.98	182.22	154.96	366.85	846.34	1020.00
6	172.05	193.70	195.13	603.26	898.70	1190.00
7	4.51	10.04	15.78	67.93	261.96	320.00
8	8.85	12.91	22.96	59.78	347.39	400.00
9	3.82	17.22	21.52	114.13	214.91	260.00
10	7.47	15.34	23.46	157.61	295.65	340.00
11	6.25	14.35	41.61	92.39	282.61	320.00
12	6.60	22.96	20.09	127.72	260.87	300.00
13	332.81	246.78	470.61	831.52	1463.04	1640.00
14	259.55	364.17	427.13	888.59	1576.09	1890.00
15	822.74	348.65	660.00	2168.48	3911.96	4440.00
16	15.10	20.09	31.57	160.33	278.65	330.00
17	6.77	35.87	21.52	149.46	210.22	250.00
18	13.54	30.13	40.17	133.15	198.91	230.00
19	36.11	37.43	54.52	168.48	285.43	350.00
20	9.55	18.65	43.04	222.83	275.24	370.00
21	15.45	22.96	43.04	336.96	265.17	350.00
22	5.03	25.83	27.26	141.30	258.43	350.00
Minimum	**3.82**	**10.04**	**15.78**	**59.78**	**198.91**	**230.00**
Maximum	**8291.67**	**7433.77**	**7558.92**	**15468.75**	**24378.43**	**28330.00**

The lowest content (15.78 mg kg^{-1}) of heat soluble sulphur was noted in the soil from northern coastal plain (Sample No. 7), and the highest (7558.92 mg kg $^{-1}$) in the *Pokkali* soil (Sample No. 3). All the three *Pokkali* soils showed very high heat soluble sulphur content (>5000 mg kg^{-1}). Almost all the soils other than low land soils of *Pokkali*, *Kuttanad* and *Kole* were with <15 mg kg^{-1} heat soluble S.

The lowest content of sulphate soluble after ignition was observed (59.78 mg kg^{-1}) in the northern coastal sandy soil (Sample No. 8), and the highest (15468 mg kg^{-1}) in the *Pokkali* soil (Sample No. 2). Two *Pokkali* soils showed >10000 mg kg^{-1}of sulphate soluble after ignition. Soils from northern coastal plain were with lower content of sulphate soluble after ignition.

Total content organic sulphur content was low (61.96 mg kg^{-1}) in northern coastal sandy soil (Sample No. 7) and the highest (16902.17 mg kg^{-1}) was noted in *Pokkali* soil (Sample No. 1). Among other soils comparatively higher values were observed in *Kole* and *Kuttand* soils. Total content of organic sulphur was lower in the soils of northern coastal sandy plain and *Onattukara* sandy plain.

Total sulphur content of the soils varied from 230.00 to 28330.00 mg kg^{-1}. Highest content was recorded in *Pokkali* soil (Sample No. 2). All the *Pokkali* soils recorded with >20000 mg kg^{-1}of total S. The lowest value was seen in the soil from northern central laterite (Sample No. 18). Comparatively higher total sulphur content was observed in *Kole* and *Kuttand* soils.

4.2.2.2. Contribution of different fractions of S to the available pool

The correlation coefficients and path coefficients of different fractions of S on available pool are given in Table 18. Since sulphate sulphur is considered as the available S, this fraction was excluded from correlation study and path analysis. All the fractions showed high significant positive correlation with available S.

Total water soluble S had very high significant positive correlation with available S (0.999**). The direct effect of total water soluble S (0.321) on available S was high and positive. The indirect effect of water soluble S on available S through total S (0.246), heat soluble (0.283) S and total organic S (0.224) was moderate and positive.

Heat soluble S was significantly and positively correlated with available S (0.999**). The direct effect of heat soluble S (0.284) on available S was moderate and positive. The indirect effect of heat soluble S on available S through total water soluble S (0.321) was positive and high; through total S (0.247) and total organic S (0.220) was positive and moderate.

Significant positive correlation was found between sulphate soluble after ignition and available S (0.880**). The indirect effect of sulphate soluble after ignition on available S through total water soluble S (0.280); through heat soluble S (0.247); total organic S (0.207) and through total S (0.229) was positive and moderate.

Total organic S had significant positive correlation with available S (0.990**). The direct effect of total organic S on available was moderate and positive (0.223). The indirect effect of total organic S on available S through total water soluble S (0.316) was high and positive; through heat soluble S (0.280); through total organic S (0.223) and through total S (0.248) was moderate and positive.

Total S showed significant positive correlation with available S (0.995**). The direct effect of total S on available S was moderate and positive (0.248). The indirect effect of total S on available S through total water soluble S (0.357) was high and positive; through heat soluble S (0.281) and total organic S (0.222) was moderate and positive.

4.2.2.3. Relationship among different fractions of S

All the fractions of S had very high significant and positive correlation among them (Table 19). Sulphate S showed significant positive correlation with total water soluble S (0.997**), heat soluble S (0.999**), sulphate soluble after ignition (0.880**), total organic S (0.982**) and total S (0.995**). Total water soluble S was significantly and positively correlated with heat soluble S (0.999**), sulphate soluble after ignition (0.871**), total organic S (0.978**), and total S (0.989**).

Heat soluble S was significantly and positively correlated with sulphate soluble after ignition (0.870**), total organic S (0.977**) and total S (0.993**). Sulphate soluble after ignition had significant positive correlation with total organic S (0.917**) and total S (0.921**). Total organic S had significant positive correlation with total S (0.988**).

4.2.2.4. Relationship between different fractions of S and physico-chemical properties of soil

Correlation coefficients of different fractions of S with physico-chemical properties of soil are given in Table 20. All the S fractions had significant negative correlation with pH and positive correlation with EC, OC and AEC. Sulphate S showed significant positive correlation with EC (0.974**), OC (0.706**), AEC (0.716**) and negative correlation with pH (-0.553**). Significant and positive correlation was found between total water soluble S with EC (0.974**), OC (0.695**), AEC (0.709**) and negative correlation with pH (-0.545**). Heat soluble S had significant positive correlation with EC (0.977**), OC (0.713**), AEC (0.721**) and negative correlation with pH (-0.557**).

Table 18. Correlation coefficients and path coefficients of different fractions of S on available pool

	Total water soluble S	**Heat soluble S**	**Sulphate soluble after ignition**	**Total organic S**	**Total S**	**Correlation coefficients**
Total water soluble S	**0.321**	0.283	-0.071	0.219	0.246	0.999**
Heat soluble S	0.321	**0.284**	-0.071	0.220	0.247	0.999**
Sulphate soluble after ignition	0.280	0.247	**-0.082**	0.207	0.229	0.880**
Total organic S	0.316	0.280	-0.076	**0.223**	0.248	0.990**
Total S	0.318	0.281	-0.0.75	0.222	**0.248**	0.995**

** Correlation is significant at the 0.01 level (2-tailed)
* Correlation is significant at the 0.05 level (2-tailed)

Table 19. Correlation coefficients among the fractions of S

	Sulphate S	Total water soluble S	Heat soluble S	Sulphate soluble after ignition	Total organic S
Total water soluble S	0.999**				
Heat soluble S	0.999**	0.999**			
Sulphate soluble after ignition	0.880**	0.871**	0.870**		
Total organic S	0.990**	0.985**	0.986**	0.927**	
Total S	0.995**	0.992**	0.993**	0.921**	0.997**

Table 20. Correlation coefficients of different fractions of S with physico-chemical properties of soil

	pH	EC	OC	AEC
Suphate S	-0.553**	0.974**	0.706**	0.716**
Total water soluble S	-0.545**	0.974**	0.695**	0.709**
Heat soluble S	-0.557**	0.977**	0.713**	0.721**
Sulphate soluble after ignition	-0.541**	0.853**	0.647**	0.679**
Total organic S	-0.582**	0.955**	0.728**	0.739**
Total S	-0.575**	0.971**	0.723**	0.735**

Table 21. Correlation coefficients of different fractions of S with available nutrient contents

	Av.P	Av.Mg	Av.Fe	Av.Cu	Av.Zn
Suphate S	0.498*	0.977**	0.582**	0.666**	0.995**
Total water soluble S	0.494*	0.972**	0.566**	0.669**	0.996**
Heat soluble S	0.487*	0.976**	0.587**	0.669**	0.995**
Sulphate soluble after ignition	0.437*	0.894**	0.571**	0.594**	0.860**
Total organic S	0.495*	0.981**	0.621**	0.677**	0.981**
Total S	0.485*	0.982**	0.607**	0.672**	0.986**

** Correlation is significant at the 0.01 level (2-tailed)

* Correlation is significant at the 0.05 level (2-tailed)

Table 22. Correlation coefficients of different fractions of S with exchangeable cations

	Ex.Na	**Ex.Fe**	**Ex.Cu**	**Ex.Zn**	**WS+Ex.Al**
Suphate S	0.545**	0.764**	0.663**	0.874**	0.871**
Total water soluble S	0.537**	0.734**	0.661**	0.888**	0.852**
Heat soluble S	0.546**	0.749**	0.664**	0.887**	0.865**
Sulphate soluble after ignition	0.785**	0.799**	0.687**	0.628**	0.871**
Total organic S	0.608**	0.828**	0.695**	0.806**	0.901**
Total S	0.612**	0.793**	0.686**	0.843**	0.895**

** Correlation is significant at the 0.01 level (2-tailed)
* Correlation is significant at the 0.05 level (2-tailed)

Sulphate soluble after ignition showed significant and positive correlation with EC (0.853**), OC (0.647**), AEC (0.679**) and negative correlation with pH (-0.541**). There was significant and positive correlation of organic S with EC (0.924**), OC (0.681**), AEC (0.708**) and negative correlation with pH (-0.554**). Total S was significantly and positively correlated with EC (0.971**), OC (0.723**), AEC (0.735**) and negatively correlated with pH (-0.575**).

4.2.2.5. Relationship between different fractions of S and available nutrients

Correlation coefficients of different fractions of S with available nutrient contents in soil were given in Table 21.

Sulphate S showed significant and positive correlation with Av.P (0.498*), Av.Mg (0.977**), Av.Fe (0.582**), Av.Cu (0.666**) and Av.Zn (0.995**). Total water soluble S had significant and positive correlation with Av.P (0.494*), Av.Mg (0.972**), Av.Fe (0.566**), Av.Cu (0.669**) and Av.Zn (0.996**). Significant and positive correlation was found between heat soluble S with Av.P (0.487*), Av.Mg (0.976**), Av.Fe (0.587**), Av.Cu (0.669**) and Av.Zn (0.995**).

Sulphate soluble after ignition had significant and positive correlation with Av.P (0.437*), Av.Mg (0.894**), Av.Fe (0.571**), Av.Cu (0.594**) and Av.Zn (0.860**). Total organic S was significantly and positively correlated with Av.P (0.524*), Av.Mg (0.962**), Av.Fe (0.579**), Av.Cu (0.695**) and Av.Zn (0.979**). Significant and positive correlation was found between total S and Av.P (0.485*), Av.Mg (0.982**), Av.Fe (0.607**), Av.Cu (0.672**), Av.Zn (0.986**).

4.2.2.6. Relationship between different fractions of S and exchangeable cations

Correlation coefficients of different fractions of S with exchangeable cations in soil were given in Table 22. Sulphate S had significant positive correlation with Ex.Na (0.545**), Ex.Fe (0.764**), Ex.Cu (0.663**), Ex.Zn (0.874**), WS+Ex.Al (0.871**). Total water soluble S was significantly and positively correlated with Ex.Na (0.537**), Ex.Fe (0.734**), Ex.Cu (0.661**), Ex.Zn (0.888**), WS+Ex.Al (0.852**). Heat soluble S showed significant and positive correlation with Ex.Na (0.546**), Ex.Fe (0.749**), Ex.Cu (0.664**), Ex.Zn (0.887**) and WS+Ex.Al (0.867**).

Significant and positive correlation was found between sulphate soluble after ignition and Ex.Na (0.785**), Ex.Fe (0.799**), Ex.Cu (0.687**), Ex.Zn (0.628**) and WS+Ex.Al (0.871**). Total organic S showed significant and positive correlation with Ex.Na (0.552**), Ex.Fe (0.808**), Ex.Cu (0.704**), Ex.Zn (0.776**) and WS+Ex.Al (0.857**). Total S showed significant and positive correlation with Ex.Na (0.612**), Ex.Fe (0.793**), Ex.Cu (0.686**), Ex.Zn (0.843**) and WS+Ex.Al (0.895**).

4.2.3. Fractionation of boron

4.2.3.1. Different fractions of B in soil

The data on various fractions as well as total B in the collected soils are given in Table 23. Readily soluble B in the soil ranged from 0.180 to 1.980 mg kg^{-1}. Lowest value was recorded in coastal sandy soil (Sample No. 8) and the highest value in the soil from *Kole* land (Sample No. 4). All the *Pokkali* soil samples also had higher values of readily soluble B content.

Table 23. Different fractions of B in the soils from different AEUs of Kerala

Sample No.	**Readily soluble B**	**Specifically adsorbed B**	**Oxide bound B**	**Organically bound B**	**Residual B**	**Total B**
	mg kg^{-1}					
1	0.972	0.415	0.799	2.720	29.343	34.250
2	1.246	0.532	0.482	2.330	24.910	29.500
3	1.434	0.489	0.423	1.620	21.783	25.750
4	1.980	0.062	0.629	1.970	25.359	30.000
5	0.330	0.097	0.690	1.400	17.233	19.750
6	0.236	0.121	0.322	1.390	11.931	14.000
7	0.254	0.107	0.618	0.130	11.891	13.000
8	0.180	0.075	0.368	0.330	16.547	17.500
9	0.194	0.084	0.403	0.861	12.208	13.750
10	0.238	0.120	0.439	0.879	14.824	16.500
11	0.180	0.065	0.520	0.801	13.184	14.750
12	0.202	0.103	0.548	0.402	15.495	16.750
13	0.344	0.111	0.391	1.400	13.504	15.750
14	0.458	0.205	0.785	2.560	16.742	20.750
15	0.744	0.198	0.567	3.100	12.391	17.000
16	0.380	0.119	0.728	0.983	11.791	14.000
17	0.234	0.076	1.013	1.113	13.064	15.500
18	0.224	0.081	0.725	0.978	10.992	13.000
19	0.396	0.297	1.022	1.469	16.316	19.500
20	0.234	0.159	0.547	1.263	14.547	16.750
21	0.212	0.256	1.059	0.970	14.752	17.250
22	0.210	0.127	0.851	1.670	13.891	16.750
Minimum	**0.180**	**0.062**	**0.322**	**0.130**	**10.992**	**13.000**
Maximum	**1.980**	**0.532**	**1.059**	**3.100**	**29.343**	**34.250**

Table 24. Percentage distribution of different fractions of B in the soils from different AEUs of Kerala

Sample No.	Readily soluble B	Specifically adsorbed B	Oxide bound B	Organically bound B	Residual B
1	2.838	1.213	2.334	7.942	85.674
2	4.224	1.803	1.633	7.898	84.442
3	5.569	1.900	1.644	6.291	84.595
4	6.600	0.207	2.097	6.567	84.530
5	1.671	0.489	3.495	7.089	87.256
6	1.686	0.867	2.298	9.929	85.221
7	1.954	0.826	4.752	1.000	91.469
8	1.029	0.427	2.103	1.886	94.556
9	1.411	0.611	2.934	6.262	88.782
10	1.442	0.727	2.663	5.325	89.842
11	1.220	0.438	3.525	5.433	89.382
12	1.206	0.613	3.272	2.402	92.508
13	2.184	0.705	2.482	8.889	85.741
14	2.207	0.986	3.784	12.337	80.685
15	4.376	1.165	3.338	18.235	72.886
16	2.714	0.848	5.198	7.021	84.219
17	1.510	0.490	6.536	7.181	84.283
18	1.723	0.626	5.574	7.523	84.555
19	2.031	1.521	5.242	7.535	83.671
20	1.397	0.949	3.265	7.539	86.849
21	1.229	1.484	6.142	5.625	85.520
22	1.254	0.760	5.083	9.970	82.933
Minimum	**1.029**	**0.207**	**1.633**	**1.000**	**72.886**
Maximum	**6.600**	**1.900**	**6.536**	**18.235**	**94.556**

The lowest value of specifically adsorbed B (0.062 mg kg^{-1}) was noted in soil from *Kole* land (Sample No. 4) followed by *Onattukara* sandy soil (Sample No. 11), and the highest value of 0.532 mg kg^{-1} in the *Pokkali* soil (Sample No. 2). All the *Pokkali* soils had comparatively higher values of specifically adsorbed B. Oxide bound boron content in the soil ranged from 0.322 to 1.059 mg kg^{-1}. Lowest value was observed in the soil from *Kole* land (Sample No. 6) and the highest value in the soil from Palakkad eastern plain (Sample No. 21).

Lowest value of organically bound boron (0.130 mg kg^{-1}) was recorded in coastal sandy soil (Sample No. 7) and the highest value (3.10 mg kg^{-1}) in *Kuttanad* soil (Sample No. 15). Low lands soils of *Pokkali, Kole* and *Kuttanad* showed higher values of organically bound boron content.

Residual B content in the soil ranged from 10.992 to 29.343 mg kg^{-1}. Lowest value of residual B was recorded in the laterite soil (Sample No. 18) and the highest value in *Pokkali* soil (Sample No. 1). All the *Pokkali* soils were with higher values of residual B content. Lowest value for total boron (13 mg kg^{-1}) was seen in the coastal sandy soil (Sample No. 7) and the laterite soil (Sample No. 18). Highest value of total B (34.250 mg kg^{-1}) content was recorded in *Pokkali* soil (Sample No. 1).

The lowest value of specifically adsorbed B (0.062 mg kg^{-1}) was noted in soil from *Kole* land (Sample No. 4) followed by *Onattukara* sandy soil (Sample No. 11), and the highest value of 0.532 mg kg^{-1} in the *Pokkali* soil (Sample No. 2). All the *Pokkali* soils had comparatively higher values of specifically adsorbed B. Oxide bound boron content in the soil ranged from 0.322 to 1.059 mg kg^{-1}. Lowest value was observed in the soil from *Kole* land (Sample No. 6) and the highest value in the soil from Palakkad eastern plain (Sample No. 21).

Lowest value of organically bound boron (0.130 mg kg^{-1}) was recorded in coastal sandy soil (Sample No. 7) and the highest value (3.10 mg kg^{-1}) in *Kuttanad* soil (Sample No. 15). Low lands soils of *Pokkali, Kole* and *Kuttanad* showed higher values of organically bound boron content.

Residual B content in the soil ranged from 10.992 to 29.343 mg kg^{-1}. Lowest value of residual B was recorded in the laterite soil (Sample No. 18) and the highest value in *Pokkali* soil (Sample No. 1). All the *Pokkali* soils were with higher values of residual B content. Lowest value for total boron (13 mg kg^{-1}) was seen in the coastal sandy soil (Sample No. 7) and the laterite soil (Sample No. 18). Highest value of total B (34.250 mg kg^{-1}) content was recorded in *Pokkali* soil (Sample No. 1).

4.2.3.2. Percentage distribution of fractions of B in soil

Percentage distribution of fractions of B in the soils is given in Table 24. Readily soluble B in the soils ranged from 1.029 to 6.6 per cent. Lowest value was recorded in the coastal sandy soil (Sample No. 8), and the highest in the soil from *Kole* land (Sample No. 4). All the *Pokkali* soils and *Kuttanad* soils were with higher per cent contribution of readily soluble B to total B content. The per cent contribution of specifically adsorbed B to total B ranged from 0.207 to 1.90 per cent. Lowest value was in the soil from *Kole* land (Sample No. 4) and the highest in the *Pokkali* soil (Sample No. 3). The percentage contribution of oxide bound B content ranged from 1.633 to 6.536 per cent. Lowest value was in the *Pokkali* soil (Sample No. 2) and the highest in the laterite soil (Sample No. 17).

Highest contribution of organically bound B to total B content (18.235 per cent) was seen in the *Kuttanad* soil (Sample No. 15) and the lowest (1 per cent) in the coastal sandy soil (Sample No. 7). The highest per cent contribution to total B was by the residual B (72.886 - 94.556 per cent), the lowest in *Kuttanad* soil (Sample No. 15), and the highest in the coastal sandy soil (sampke No. 7). The dominance of different fractions of B in the soil was in the order, Residual B>> organically bound B> oxide bound B≈ readily soluble B>specifically adsorbed B.

4.2.3.3. Contribution of different fractions of B to the available pool

Correlation coefficients and path coefficients of different fractions of B to the available pool are given in Table 25. Available B was significantly and positively correlated with readily soluble B (0.635**), organically bound B (0.497*), residual B (0.525*) and total B (0.559**).

The direct effect of readily soluble boron on available B was positive and very high (0.831). The indirect effect of readily soluble B on available B through organically bound B (0.548) and residual B (3.542) was very high and positive; through total B (-4.286) was very high and negative. The direct effect of organically bound boron to the available B was positive and very high (0.962). The indirect effect of organically bound B to the available pool through readily soluble B (0.473) and residual B (2.319) was positive and very high; through total B was very high and negative (-3.258).

The direct effect of residual B on available B was very high and positive (4.493). The indirect effect of residual B on available pool through readily soluble B (0.655) and organically bound B (0.497) was positive and very high; through total B was very high and negative (-5.120). The direct effect of total B on available B was very high and negative (-5.177). The indirect effect of total B on available pool through readily soluble B (0.688), organically bound B (0.606) and residual B (4.443) was positive and very high.

4.2.3.4. Relationship among different fractions of B

Correlation coefficients among different fraction of B in soil are given in Table 26. Readily soluble B was significantly and positively correlated with specifically adsorbed B (0.524**), organically bound B (0.569**), residual B (0.788**) and total B (0.828**). Specifically adsorbed B had significant positive correlation with organically bound B (0.531*), residual B (0.654**) and total B (0.688**). Organically bound B had significant positive correlation with residual B (0.516*) and total B (0629**). Significant positive correlation was found between residual B and total B (0.989**).

Table 25. Correlation coefficients and path coefficients of fractions of B to available B

	Readily soluble B	Organically bound B	Residual B	Total B	Correlation coefficient
Readily soluble B	**0.831**	0.548	3.542	-4.286	0.635**
Organically bound B	0.473	**0.962**	2.319	-3.258	0.497*
Residual B	0.655	0.497	**4.493**	-5.120	0.525*
Total B	0.688	0.606	4.443	**-5.177**	0.559**

Table 26. Correlation coefficients among the B fractions in soil

	Readily soluble B	Specifically adsorbed B	Organically bound B	Residual B
Specifically adsorbed B	0.524*			
Organically bound B	0.569**	0.531*		
Residual B	0.788**	0.654**	0.516*	
Total B	0.828**	0.688**	0.629**	0.989**

Table 27. Correlation coefficients of fractions of B with physico-chemical properties of soil

	pH	EC	OC	AEC	CEC	Sand	Silt	Clay
Readily soluble B	-0.514*	0.648**	0.692**	0.728**			0.547**	
Specifically adsorbed B		0.898**	0.669**	0.652**				
Oxide bound B					0.627**			
Organically bound B	-0.550**	0.492*	0.831**	0.805**		-0.684**	0.542**	0.602**
Residual B	-0.432*	0.649**	0.559**	0.607**			0.423*	
Total B	-0.473*	0.676**	0.647**	0.692**			0.479*	

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

Table 28. Correlation coefficients of different fractions of B with available nutrients

	Av.N	Av.P	Av.K	Av.Ca	Av.Mg	Av.S	Av.Fe	Av.Mn	Av.Cu	Av.Zn	Av.Si
Readily soluble B					0.658**	0.629**	0.635**		0.741**	0.624**	
Specifically adsorbed B		0.426*			0.935**	0.896**	0.527*		0.567**	0.896**	
Oxide bound B				0.574**				0.673**			0.446*
Organically bound B	0.788**		0.468*		0.607**	0.462*	0.801**		0.629**	0.438*	
Residual B					0.739**	0.726**	0.535*		0.725**	0.734**	
Total B					0.774**	0.737**	0.610**		0.772**	0.742**	

Table 29. Correlation coefficients of fractions of B with exchangeable cations

	Ex.Ca	Ex.Mg	Ex.Na	Ex.K	Ex.Fe	Ex.Cu	Ex.Zn	Ex.Al	WS+Ex.Al
Readily soluble B			0.440*		0.533*	0.530*	0.603**		0.623**
Specifically adsorbed B			0.625**		0.706**	0.471*	0.777**		0.814**
Oxide bound B	0.592**	0.507*		0.473*					
Organically bound B		0.642**	0.670**		0.756**			0.606**	0.711**
Residual B			0.482*		0.636**	0.629**	0.496*		0.618**
Total B			0.539**		0.692**	0.622**	0.510*		0.677**

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

4.2.3.5. Relationship between different fractions of B and physico-chemical properties of soil

Correlation coefficients of different fractions of B with physico-chemical properties of soil are given in Table 27. Readily soluble B was significantly and negatively correlated with pH (-0.514*); positively correlated with EC (0.648**), OC (0,692**), AEC (0.728**) and silt content (0.547**). Specifically adsorbed B had significant positive correlation with EC (0.898**), OC (0.669**) and AEC (0.652**). Oxide bound B was significantly and positively correlated with CEC (0.627**).

Organically bound B was significantly and positively correlated with EC (0.492*), OC (0.831**), AEC (0.805**), silt (0.542**), clay (0.602**); negatively correlated with pH (-0.550**), sand (-0.684**). Residual B was significantly and positively correlated with EC (0.649**), OC (0.559**), AEC (0.607**) and silt (0.423*); negatively correlated with pH (-0.432*). Total B was significantly and positively correlated with EC (0.676**), OC (0.647**), AEC (0.692**) and silt; negatively correlated with pH (-0.473*).

4.2.3.6. Relationship between different fractions of B and available nutrients

Correlation coefficients of different fractions of B with available nutrient status in soil are given in Table 28. Readily soluble B had significant positive correlation with Av.Mg (0.6588**), Av.S (0.629**), Av.Fe (0.635**), Av.Cu (0.741**) and Av.Zn (0.624**). Specifically adsorbed B showed significant positive correlation with Av.P (0.426*), Av.Mg (0.935**), Av.S (0.896**), Av.Fe (0.527*), Av.Cu (0.567**) and Av.Zn (0.896**). Oxide bound B was significantly and positively correlated with Av.Ca (0.574**), Av.Mn (0.673**) and Av.Si (0.446*).

Organically bound B had significant positive correlation with Av.Mg (0.607**), Av.S (0.462*), Av.Fe (0.801**), Av.Cu (0.629**) and Av.Zn (0.438**). Residual B showed significant positive correlation with Av.Mg (0.739**), Av.S (0.726**), Av.Fe (0.535*), Av.Cu (0.725**) and Av.Zn

(0.734**). Total B content was significantly and positively correlated with Av.Mg (0.774**), Av.S (0.737**), Av.Fe (0.610*), Av.Cu (0.772**) and Av.Zn (0.742**).

4.2.3.7. Relationship between different fractions of B with exchangeable cations

Correlation coefficients of different fractions of B with exchangeable cations present in soil are given in Table 29. Readily soluble B was significantly and positively correlated with Ex.Na (0.440*), Ex.Fe (0.533*), Ex.Cu (0.530*), Ex.Zn (0.603**) and WS+Ex.Al (0.623**). Specifically adsorbed B had significant and positive correlation with Ex.Na (0.625**), Ex.Fe (0.706**), Ex.Cu (0.471*), Ex.Zn (0.777**) and WS+Ex.Al (0.814**). Oxide bound B had significant positive correlation with Ex.Ca (0.592**), Ex.Mg (0.507*) and Ex.K (0.473*).

Organically bound B was significantly and positively correlated with Ex.Mg (0.642**), Ex.Na (0.670**), Ex.Fe (0.756**) and WS+Ex.Al (0.711**). Residual B had significant and positive correlated with Ex.Na (0.482*), Ex.Fe (0.636*), Ex.Cu (0.629*), Ex.Zn (0.496*) and WS+Ex.Al (0.677**). Total B was significantly and positively correlated with Ex.Na (0.539**), Ex.Fe (0.692**), Ex.Cu (0.622**), Ex.Zn (0.510*) and WS+Ex.Al (0.677**).

4.2.4. Fractionation of silicon

4.2.4.1. Different fractions of silicon

The data on various fractions as well as total silicon in the collected soils are given in the Table 30. Mobile Si in the soil ranged from 1.93 to 52.50 mg kg^{-1}. The lowest value was recorded in the soil from northern coastal plain (Sample No.9), and the highest in the soil from Palakkad eastern plain (Sample No. 19). All the collected soils from northern coastal plain showed comparatively lower mobile Si content.

The lowest value for adsorbed Si (23.51 mg kg^{-1}) was recorded in the northern coastal sandy soil (Sample No. 7) and the highest (196.40 mg kg^{-1}) in the soil from Palakkad eastern plain (Sample No. 20). Comparatively higher values of adsorbed silicon were noted in the soils from Palakkad eastern plain and *Pokkali* soils.

Content of organic silicon in the soils ranged from 116.13 to 1746.90 mg kg^{-1}. The lowest value was found in the northern coastal sandy soil (Sample No. 9), and the highest value was found in *Pokkali* soil (Sample No. 1). All the soils were with higher content of organic Si than mobile and adsorbed silicon.

The content of occluded silicon in the soils ranged from 71.64 to 1134.40 mg kg^{-1}. The lowest value was in the northern coastal sandy soil (Sample No. 9), and the highest in the soil from *Kole* land (Sample No. 4). Comparatively lower content of occluded silicon was observed in the northern coastal sandy soil and *Onattukara* sandy soil.

The lowest content of amorphous silicon (2552.80 mg kg^{-1}) was observed in northern coastal sandy soil (Sample No. 8). The highest value (32056 mg kg^{-1}) was observed in *Pokkali* soil (Sample No. 3). Comparatively lower content of amorphous silicon was observed in the soils from northern coastal sandy soil and *Onattukara* sandy soil.

Residual Si content of the soils varied from 77058.48 to 190401.7 mg kg^{-1}. The lowest content was observed in the soil from *kole* land (Sample No. 5) and the highest in the soil from *Kuttanad* (Sample No. 13). The highest content of total Si (212.9 g kg^{-1}) was noted in *Kuttanad* soil (Sample No. 13) and the lowest (97.6 g kg^{-1}) in the laterite soil (Sample No. 18).

4.2.4.2. Percentage distribution of fractions of Si in soil

The percentage contribution of each fraction of Si to total Si is given in Table 31.

Table 30. Different fractions of Si in the soils from different AEUs of Kerala

Sample No	Mobile Si	Adsorbed Si	Organic Si	Occluded Si	Amorphous Si	Residual Si	Total Si
	mg kg^{-1}						g kg^{-1}
1	25.20	85.42	1746.90	1083.60	28876	156382.9	188.2
2	31.50	83.30	1512.30	904.80	27516	167452.1	197.5
3	30.33	86.70	1637.70	958.00	32056	164831.3	199.6
4	38.11	49.57	548.40	1134.40	13180	94949.52	109.9
5	20.75	31.68	498.30	822.80	20168	77058.48	98.6
6	17.87	25.27	543.90	591.60	11336	130985.4	143.5
7	4.93	23.51	165.63	174.56	3559.6	172571.8	176.5
8	2.82	39.74	146.13	104.68	2552.8	161453.8	164.3
9	1.93	32.41	116.13	71.64	5368	172709.9	178.3
10	13.82	50.35	223.38	178.20	5184	146850.3	152.5
11	3.31	90.15	154.74	86.12	6080	182785.7	189.2
12	13.50	42.78	257.79	138.96	6372	157775	164.6
13	29.06	34.92	703.50	886.80	20844	190401.7	212.9
14	41.16	49.11	864.90	1088.00	17196	168060.8	187.3
15	40.15	45.54	1521.30	950.40	19208	123034.6	144.8
16	20.40	78.86	438.30	554.40	18520	87588.05	107.2
17	9.95	39.79	176.07	747.20	9272	99054.99	109.3
18	11.84	75.23	274.89	889.60	9624	86724.44	97.6
19	52.50	164.40	874.80	960.40	10592	86055.9	98.7
20	39.07	196.40	740.70	809.60	17364	79750.23	98.9
21	21.57	53.13	370.50	972.00	4888	102194.8	108.5
22	32.69	105.50	1067.10	550.40	12596	131048.3	145.4
Minimum	**1.93**	**23.51**	**116.13**	**71.64**	**2552.80**	**77058.48**	**97.6**
Maximum	**52.50**	**196.40**	**1746.90**	**1134.40**	**32056.00**	**190401.70**	**212.9**

Table 31. Percentage distribution of fractions of Si in the soils from different AEUs of Kerala

Sample No	Mobile Si	Adsorbed Si	Organic Si	Occluded Si	Amorphous Si	Residual Si
1	0.013	0.05	0.93	0.58	15.34	83.09
2	0.016	0.04	0.77	0.46	13.93	84.79
3	0.015	0.04	0.82	0.48	16.06	82.58
4	0.035	0.05	0.50	1.03	11.99	86.40
5	0.021	0.03	0.51	0.83	20.45	78.15
6	0.012	0.02	0.38	0.41	7.90	91.28
7	0.003	0.01	0.09	0.10	2.02	97.77
8	0.002	0.02	0.09	0.06	1.55	98.27
9	0.001	0.02	0.07	0.04	3.01	96.86
10	0.009	0.03	0.15	0.12	3.40	96.30
11	0.002	0.05	0.08	0.05	3.21	96.61
12	0.008	0.03	0.16	0.08	3.87	95.85
13	0.014	0.02	0.33	0.42	9.79	89.43
14	0.022	0.03	0.46	0.58	9.18	89.73
15	0.028	0.03	1.05	0.66	13.27	84.97
16	0.019	0.07	0.41	0.52	17.28	81.71
17	0.009	0.04	0.16	0.68	8.48	90.63
18	0.002	0.08	0.28	0.91	9.86	88.86
19	0.053	0.17	0.89	0.97	10.73	87.19
20	0.040	0.20	0.75	0.82	17.56	80.64
21	0.020	0.05	0.34	0.90	4.51	94.19
22	0.022	0.07	0.73	0.38	8.66	90.13
Min	**0.001**	**0.01**	**0.07**	**0.04**	**1.55**	**78.15**
Max	**0.053**	**0.20**	**1.05**	**1.03**	**20.45**	**98.27**

The contribution of residual Si to the total Si was more than 80 per cent in all the soils. It was followed by amorphous Si, which ranged from 1.55 to 20.45 per cent. The contribution of other fractions to the total Si was very less, the least contribution by mobile Si was found to be the least (0.001 to 0.053 per cent). The percentage contribution of amorphous and occluded Si was less in *Onattukara* sandy soil and northern coastal sandy soil.

4.2.4.3. Contribution of different fractions of Si to the available pool

The correlation coefficients between available Si and different fractions of Si in the soil are given in Table 32. The data revealed that four fractions were significantly correlated to the available pools. Mobile and adsorbed Si had significant positive correlation with available Si (0.504* and 0.798** respectively). Residual and total Si showed significant and negative correlation with available Si (-0.513* and -0.526* respectively). The path coefficients showing the direct and indirect effects of different fractions on available Si in soil are presented in Table 32.

The direct effect of mobile Si (0.414) on the available Si was positive and very high. The indirect effect of mobile Si on available Si through adsorbed Si (0.356) and total Si (0.387) was positive and high; through residual Si was very high and negative (-0.653). The direct effect of adsorbed Si on available Si was found positive and very high (0.665). The indirect effect of adsorbed Si on available Si through total Si (0.648) was very high and positive; through mobile Si was found positive and moderate (0.221) and, through residual Si was negative and very high (-0.737).

The direct effect of residual Si (2.053) on available Si was found positive and very high. The indirect effect of residual Si on available Si through total Si was negative and very high (-2.195), and through adsorbed Si (-0.239) was negative and moderate. The direct effect of total Si (-2.259) on available Si was negative and very high. The indirect effect of total Si on available Si through residual Si (1.994) was positive and very high.

Table 32. Correlation coefficients and path coefficients of fractions of Si to available Si

	Mobile Si	Adsorbed Si	Residual Si	Total Si	Correlation coefficients
Mobile Si	**0.414**	0.356	-0.653	0.387	0.504*
Adsorbed Si	0.221	**0.665**	-0.737	0.648	0.798**
Residual Si	-0.132	-0.239	**2.053**	-2.195	-0.513*
Total Si	-0.071	-0.191	1.994	**-2.259**	-0.526*

Table 33. Correlation coefficients between the Si fractions in soil

	Mobile Si	Organic Si	Occluded Si	Residual Si
Adsorbed Si	0.534*			
Organic Si	0.671**			
Occluded Si	0.765**	0.636**		
Amorphous Si	0.550**	0.858**	0.662**	
Residual Si				
Total Si				0.972**

Table 34. Correlation coefficients of fractions of Si with physico-chemical properties of soil

	pH	EC	OC	AEC	CEC	Sand	Silt	Clay
Mobile Si			0.542**	0.479*	0.632**	-0.723**	0.711**	0.538**
Adsorbed Si					0.472*			
Organic Si	-0.526*	0.786**	0.837**	0.764**		-0.468*	0.497*	
Occluded Si			0.702**	0.762**	0.534*	-0.775**	0.587**	0.707**
Amorphous Si	-0.635**	0.782**	0.865**	0.827**		-0.559**	0.508*	0.446*
Residual Si					-0.447*			
Total Si	-0.462*	0.495*						

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

Table 35. Correlation coefficients of fractions of Si with available nutrients

	Av.N	Av.K	Av.Ca	Av.Mg	Av.S	Av.Fe	Av.Mn	Av.Cu	Av.Zn	Av.B
Mobile Si	0.533*	0.729**				0.493*		0.427*		0.481*
Adsorbed Si		0.476*	0.463*							
Organic Si	0.578**			0.864**	0.774**	0.761**		0.644**	0.771**	0.424*
Occluded Si	0.658**	0.645**		0.486*		0.623**	0.530*	0.775**		0.568**
Amorphous Si	0.634**			0.819**	0.775**	0.768**		0.732**	0.766**	0.480*
Residual Si		-0.455*	-0.459*				-0.682**			
Total Si			-0.446*	0.470*	0.493*		-0.665**		0.462*	

Table 36. Correlation coefficients of fractions of Si with exchangeable cations

	Ex.Ca	Ex.Mg	Ex.Na	Ex.K	Ex.Fe	Ex.Mn	Ex.Cu	Ex.Zn	WS+Ex.Al
Mobile Si	0.442*	0.718**		0.572**					
Adsorbed Si	0.537**			0.527*					
Organic Si		0.463*	0.626**		0.852**		0.471*	0.608**	0.864**
Occluded Si		0.656**	0.445*	0.441*	0.476*				0.458*
Amorphous Si			0.583**		0.735**		0.657**	0.660**	0.792**
Residual Si	-0.491*			-0.608**		-0.469*			
Total Si	-0.491*		0.434*	-0.580**		-0.451*	0.483*		0.453*

4.2.4.4. Relationship among different fractions of Si in soil

Correlation coefficients among different fractions of Si in soil are given in table 33. Mobile Si had significant positive correlation with adsorbed Si (0.534*), organic Si (0.671**), occluded Si (0.765**), and amorphous Si (0.550**). Organic Si was significantly and positively correlated with occluded Si (0.636**) and amorphous Si (0.858**). Occluded Si had significant positive correlation with amorphous Si (0.662**). Residual Si had significant positive correlation with total Si (0.972**).

4.2.4.5. Relationship between different fractions of Si and physico-chemical properties of soil

Correlation coefficients of different fractions of Si with physico-chemical properties of soil are presented in Table 34.

Mobile Si had significant positive correlation with OC (0.542**), AEC (0.479*), CEC (0.632**), silt (0.711**) and clay (0.538**). It showed significant negative correlation with sand (-0.723**). Adsorbed Si had significant positive correlation only with CEC (0.472*). Organic Si was significantly and positively correlated with EC (0.786**), OC (0.837**), AEC (0.764**) and silt content (0.497*); whereas significant negative correlation was found with pH (-0.526*) and sand (-0.468*).

Occluded Si was significantly and positively correlated with OC (0.702**), AEC (0.762**), CEC (0.534*), silt (0.587**) and clay (0.707**) whereas the negative correlation was found only with sand (-0.775**). Significant and positive correlation was found between amorphous Si with EC (0.782**), OC (0.865**), AEC (0.827**), silt (0.508*) and clay (0.446*). Amorphous Si had significant negative correlation with pH (-0.635**) and sand (-0.559**). Residual Si had negative significant correlation only with CEC (-0.447*). Total Si had significant positive correlation with EC (0.495*) and negative correlation with pH (-0.462*).

4.2.4.6. Relationship between different fractions of Si and available nutrients

Correlation coefficients of different fractions of Si with available nutrients in soil are shown in Table 35. Mobile Si was significantly and positively correlated with Av.N (0.533*), Av.K (0.729**), Av.Fe (0.493*), Av.Cu (0.427*) and Av.B (0.481*). Adsorbed Si showed significant positive correlation only with Av.K (0.476*) and Av.Ca (0.463*). Organic Si was significantly and positively correlated with Av.N (0.578**), Av.Mg (0.864**), Av.S (0.774**), Av.Fe (0.761**), Av.Cu (0.644*), Av.Zn (0.771**) and Av.B (0.424*).

Occluded Si had significant positive correlation with Av.N (0.658**), Av.K (0.645**), Av.Mg (0.486*), Av.Fe (0.632*), Av.Mn (0.530*), Av.Cu (0.775**) and Av.B (0.568**). Significant and positive correlation was found between amorphous Si with Av.N (0.634**), Av.Mg (0.819**), Av.S (0.775**), Av.Fe (0.768**), Av.Cu (0.732**), Av.Zn (0.766**) and Av.B (0.480**). Residual Si had significant negative correlation with Av.K (-0.455*), Av.Ca (-0.459*) and Av.Mn (-0.682**). Total Si had significant positive correlation with Av.Mg (0.470*), Av.S (0.493*), Av.Zn (0.462*) and negative correlation with Av.Ca (-0.446*), Av.Mn (-0.665**).

4.2.4.7. Relationship between different fractions of Si and exchangeable cations

Correlation coefficients of different fractions of Si with exchangeable cations in soil are given in Table 36.

Mobile Si was significantly and positively correlated with Ex.Ca (0.442*), Ex.Mg (0.718**) and Ex.K (0.572**). Adsorbed Si had significant positive correlation only with Ex.Ca (0.537**) and Ex.K (0.527*). Organic Si was significantly and positively correlated with Ex.Mg (0.463*), Ex.Na (0.626**), Ex.Fe (0.852**), Ex.Cu (0.471*), Ex.Zn (0.608**) and WS+Ex.Al (0.864**).

Occluded Si had significant positive correlation with Ex.Mg (0.656**), Ex.Na (0.445*), Ex.K (0.441*), Ex.Fe (0.476*) and WS+Ex.Al (0.458*). Amorphous Si was significantly and positively correlated with Ex.K (0.583**), Ex.Fe (0.735**), Ex.Cu (0.657**), Ex.Zn (0.660**) and WS+Ex.Al (0.792**). Residual Si had showed significant negative correlation with Ex.Ca (-0.491*), Ex.K(-0.608**) and Ex.Mn (-0.469*). Total Si had significant positive correlation with Ex.Na (0.434*), Ex.Cu (0.483*), WS+Ex.Al (0.453*) and negative correlation with Ex.Ca (-0.491*), Ex.K (-0.580**), Ex.Mn (-0.451*).

4.3. ADSORPTION STUDY

4.3.1. Adsorption study of single anions

4.3.1.1. Adsorption study of nitrate

Quantity –intensity relation

Soil samples were equilibrated with different concentrations of NO_3 – N as detailed in the section 3.1.1.1. Concentration of nitrate in equilibrium solution after equilibration period was considered as intensity factor and the amount adsorbed per unit weight of the soil was considered as quantity factor. The Q-I curves were fitted with this data by plotting concentration of nitrate in equilibrium solution in X axis and quantity adsorbed per unit weight of the soil in Y axis. The intercept and slope were computed from the best fit curve using regression analysis. The slope of the curve explains the buffer power. The parameters of the Q-I curve and maximum quantity adsorbed per unit weight of the soil from the added concentration of nitrate are given in Table 37. R^2 value ranged from 0.470 to 0.903. More than 50 per cent of the adsorption data were fitted to the respective Q-I curve in all soils at both temperatures (25 ^{0}C and 40 ^{0}C) except for soil from Palakkad eastern plain (Sample No. 20) at 25 ^{0}C.

Highest buffer power of 1.165 L kg^{-1} (at 25 ^{0}C) and 1.141 L kg^{-1} (at 40 ^{0}C) were recorded in *Pokkali* soil (Sample No. 3). Lowest buffer power of 0.17 L kg^{-1} (at 25 ^{0}C) and 0.155 L kg^{-1} (at 40 ^{0}C) was recorded in soil from *Onattukara* sandy plain (Sample No. 12). All the *Pokkali* soils were with high buffer at both temperatures. Sandy soils from coastal sandy plain and *Onattukara* sandy plain had lower buffer power at both temperatures. All the soils collected from low lands of *Pokkali, Kole* and *Kuttanad* were recorded with buffer power greater than

0.5 L kg^{-1}. Buffer power was found decreasing with increase in temperature in all the soils except in sample No. 1 and 19.

Table 37. Parameters of Q-I curve for nitrate adsorption

Sample No.	Temp.	Linear equation	Buffer power (L kg^{-1})	Intercept (mg kg^{-1})	Max. quantity adsorbed (mg kg^{-1})	R^2
1	25 ^{0}C	$q_e = 1.122\ C_e + 2.43$	1.122	2.43	138.90	0.848
	40 ^{0}C	$q_e = 1.119\ C_e + 2.17$	1.119	2.17	137.45	0.853
2	25 ^{0}C	$q_e = 1.131\ C_e + 4.26$	1.131	4.26	150.57	0.807
	40 ^{0}C	$q_e = 0.935\ C_e + 7.08$	0.935	7.08	120.30	0.842
3	25 ^{0}C	$q_e = 1.165\ C_e + 14.13$	1.165	14.13	178.60	0.671
	40 ^{0}C	$q_e = 1.141\ C_e + 11.88$	1.141	11.88	176.67	0.676
4	25 ^{0}C	$q_e = 0.623\ C_e + 12.16$	0.623	12.16	98.61	0.639
	40 ^{0}C	$q_e = 0.52\ C_e + 9.79$	0.520	9.79	75.34	0.611
5	25 ^{0}C	$q_e = 0.588\ C_e + 10.67$	0.588	10.67	92.19	0.681
	40 ^{0}C	$q_e = 0.569\ C_e + 8.86$	0.569	8.86	88.43	0.688
6	25 ^{0}C	$q_e = 0.893\ C_e + 6.30$	0.893	6.30	107.16	0.827
	40 ^{0}C	$q_e = 0.878C_e + 8.37$	0.878	8.37	110.23	0.786
7	25 ^{0}C	$q_e = 0.24\ C_e - 9.97$	0.240	-9.97	23.99	0.819
	40 ^{0}C	$q_e = 0.230\ C_e - 11.14$	0.230	-11.14	22.40	0.821
8	25 ^{0}C	$q_e = 0.350\ C_e - 11.49$	0.350	-11.49	37.60	0.892
	40 ^{0}C	$q_e = 0.317\ C_e - 9.89$	0.317	-9.89	32.45	0.851
9	25 ^{0}C	$q_e = 0.242\ C_e - 9.93$	0.242	-9.93	24.37	0.816
	40 ^{0}C	$q_e = 0.196\ C_e - 7.14$	0.196	-7.14	19.09	0.667
10	25 ^{0}C	$q_e = 0.241\ C_e - 9.75$	0.241	-9.75	25.55	0.873
	40 ^{0}C	$q_e = 0.221\ C_e - 7.17$	0.221	-7.17	22.56	0.777
11	25 ^{0}C	$q_e = 0.188\ C_e - 8.28$	0.188	-8.28	16.14	0.727
	40 ^{0}C	$q_e = 0.176\ C_e - 8.56$	0.176	-8.56	15.73	0.707
12	25 ^{0}C	$q_e = 0.170\ C_e - 5.65$	0.170	-5.65	16.00	0.731
	40 ^{0}C	$q_e = 0.155\ C_e - 4.81$	0.155	-4.81	15.00	0.717
13	25 ^{0}C	$q_e = 0.735\ C_e + 10.64$	0.735	10.64	93.87	0.785
	40 ^{0}C	$q_e = 0.73\ C_e + 9.8$	0.73	9.8	87.43	0.800

Table 37. Continued

Sample No.	Temp.	Linear equation	Buffer power (L kg^{-1})	Intercept (mg kg^{-1})	Max. quantity adsorbed (mg kg^{-1})	R^2
14	25 ^{0}C	$q_e = 0.789\ C_e + 10.65$	0.789	10.65	98.13	0.806
	40 ^{0}C	$q_e = 0.763\ C_e + 9.80$	0.763	9.80	94.60	0.810
15	25 ^{0}C	$q_e = 1.033\ C_e + 8.73$	1.03	8.73	136.10	0.766
	40 ^{0}C	$q_e = 0.999\ C_e + 9.30$	0.999	9.30	125.25	0.785
16	25 ^{0}C	$q_e = 0.835\ C_e - 4.50$	0.835	-4.50	95.39	0.889
	40 ^{0}C	$q_e = 0.810\ C_e - 2.96$	0.81	-2.96	92.34	0.903
17	25 ^{0}C	$q_e = 0.499\ C_e + 0.65$	0.499	0.65	74.45	0.802
	40 ^{0}C	$q_e = 0.472\ C_e + 2.01$	0.472	2.01	75.56	0.728
18	25 ^{0}C	$q_e = 0.630\ C_e - 4.87$	0.63	-4.87	89.23	0.834
	40 ^{0}C	$q_e = 0.614\ C_e - 5.04$	0.614	-5.04	84.02	0.858
19	25 ^{0}C	$q_e = 0.290\ C_e - 0.84$	0.29	-0.84	61.19	0.513
	40 ^{0}C	$q_e = 0.302\ C_e - 1.68$	0.302	-1.68	60.80	0.538
20	25 ^{0}C	$q_e = 0.298\ C_e - 1.23$	0.298	-1.23	65.56	0.470
	40 ^{0}C	$q_e = 0.288\ C_e + 0.60$	0.288	0.60	64.20	0.480
21	25 ^{0}C	$q_e = 0.338\ C_e - 2.95$	0.338	-2.95	53.35	0.701
	40 ^{0}C	$q_e = 0.332\ C_e - 1.74$	0.332	-1.74	55.32	0.703
22	25 ^{0}C	$q_e = 0.333\ C_e - 1.01$	0.333	-1.01	68.27	0.522
	40 ^{0}C	$q_e = 0.282\ C_e + 0.80$	0.282	0.80	56.62	0.538

Intercept of Q-I curves were positive for all the low land soils of *Pokkali, Kole* and *Kuttanad* at both temperatures. Other than that, laterite soil (Sample No. 17) at both temperature and soils from Palakkad eastern plain (Sample No. 20 and 22) at 40 ^{0}C were recorded with positive intercept values. The Q-I curves of remaining soils were with negative value of intercept. The highest value of intercept (14.125 mg kg^{-1}at 25 ^{0}C, 11.876 mg kg^{-1} at 40 ^{0}C) was recorded in the soil from *Kole* land (Sample No. 3) and the lowest value of intercept at 25 ^{0}C (-11.494 mg kg^{-1}) were held in Sample No. 8 and Sample No. 7 of coastal sandy soil respectively.

The maximum quantity adsorbed (178.6 mg kg^{-1} at 25 ^{0}C, 176.67 mg kg^{-1} at 40 ^{0}C) was higher P*okkali* soil (Sample No. 3) at both temperatures and the lowest value adsorbed (16 mg kg^{-1} at 25 ^{0}C, 15 mg kg^{-1} at 40 ^{0}C) in the *Onattukara* sandy soil (Sample No. 12). All the sandy soils from northern coastal plain and *Onattukara* sandy plain were with low value of maximum quantity adsorbed. Maximum quantity of nitrate adsorbed was more than 100 mg kg^{-1} in all the *Pokkali* soils at both temperatures, and it was decreasing with increase in temperature in all the soils except in one laterite soil (Sample No. 17) and the soil from Palakkad eastern plain (Sample No. 21).

Correlation coefficients of parameters of Q-I curve with soil properties are given in Table 38. Buffer power at 25 ^{0}C was significantly and positively correlated with buffer power at 40 ^{0}C (0.992**), maximum quantity adsorbed at 25 ^{0}C (0.957**) and 40 ^{0}C (0.947**). Maximum quantity adsorbed at 25 ^{0}C had significant positive correlation with buffer power at 40 ^{0}C (0.947**) and maximum quantity adsorbed at 40 ^{0}C (0.985**). Buffer power at 40 ^{0}C was significantly and positively correlated with maximum quantity adsorbed at 40 ^{0}C (0.956**).

Buffer power at 25 ^{0}C had significant positive correlation with EC (0.736**), OC (0.916**), AEC (0.914**), clay (0.522*), CBD-Fe (0.675**), Av.N (0.749**), Av.Mg (0.764**), Av.S (0.710**), Av.Fe (0.831**), Av.Cu (0.720**), Av.Zn (0.675**), WS+Ex.Al (0.821**), total N (0.908**) and negative correlation with pH (-0.790**) and sand (-0.562**).

Maximum quantity adsorbed at 25 ^{0}C was significantly and positively correlated with EC (0.761**), OC (0.918**), AEC (0.896**), clay (0.549*), silt (0.490*), CBD-Fe (0.725**), Av.N (0.712**), Av.Mg (0.785**), Av.S (0.725**), Av.Fe (0.811**), Av.Cu (0.817**), Av.Zn (0.708**), WS+Ex.Al (0.805**), total N (0.905**) and negatively correlated with pH (-0.715**) and sand (-0.624**).

Table 38. Correlation between parameters of Q-I curve and soil properties for nitrate adsorption

	Buffer power at 25 ^{0}C	Max. quantity adsorbed at 25 ^{0}C	Buffer power at 40 ^{0}C	Max. quantity adsorbed at 40 ^{0}C
Max. quantity adsorbed at 25 ^{0}C	0.957**			
Buffer power at 40 ^{0}C	0.992**	0.947**		
Max. quantity adsorbed at 40 ^{0}C	0.947**	0.985**	0.956**	
pH	-0.790**	-0.715**	-0.771**	-0.687**
EC	0.736**	0.761**	0.700**	0.729**
OC	0.916**	0.918**	0.906**	0.894**
AEC	0.914**	0.929**	0.896**	0.903**
Sand	-0.562**	-0.624**	-0.579**	-0.627**
Silt		0.490*		0.471*
Clay	0.522*	0.554**	0.549**	0.572**
CBD - Fe	0.675**	0.725**	0.655**	0.706**
Av.N	0.749**	0.712**	0.757**	0.706**
Av.Mg	0.764**	0.785**	0.737**	0.760**
Av.S	0.710**	0.725**	0.684**	0.707**
Av.Fe	0.831**	0.811**	0.824**	0.784**
Av.Cu	0.720**	0.817**	0.703**	0.796**
Av.Zn	0.675**	0.708**	0.650**	0.691**
WS+Ex.Al	0.821**	0.805**	0.789**	0.765**
Total N	0.908**	0.905**	0.893**	0.874**

**Correlation is significant at the 0.01 level (2-tailed)
*Correlation is significant at the 0.05 level (2-tailed)

Buffer power at 40 ^{0}C showed significant positive correlation with EC (0.700**), OC (0.906**), AEC (0.896**), clay (0.549**), CBD-Fe (0.655**), Av.N (0.757**), Av.Mg (0.737**), Av.S (0.684**), Av.Fe (0.824**), Av.Cu (0.703**), Av.Zn (0.650**), WS+Ex.Al (0.821**), total N (0.893**) and negative correlation with pH (-0.771**) and sand (-0.579**).

Maximum quantity adsorbed at 40 ^{0}C was significantly and positively correlated with EC (0.729**), OC (0.894**), AEC (0.903**), clay (0.572*), silt (0.471*), CBD-Fe (0.706**), Av.N (0.706**), Av.Mg (0.760**), Av.S (0.707**), Av.Fe (0.784**), Av.Cu (0.796**), Av.Zn (0.691**), WS+Ex.Al (0.765**), total N (0.874**) and negatively correlation with pH (-0.687**) and sand (-0.627**).

Adsorption isotherm

Soils with minimum four points with positive slopes in the Q-I curves were used for fitting in adsorption isotherm. All the soils collected from northern coastal plain (Sample No. 7, 8, 9) and one sample from *Onattukara* sandy plain (Sample No. 10) showed dominance of desorption at 40 ^{0}C. Hence these soils were not included in adsorption isotherms. Nitrate adsorption in soil was well explained by Freundlich adsorption isotherm followed by Tempkin isotherm. Only few samples were fitted into Langmuir adsorption isotherm.

Freundlich adsorption isotherm

The linear form of Freundlich adsorption isotherm was fitted by plotting logarithmic value of equilibrium concentration on X axis and logarithmic value of quantity adsorbed per unit weight of soil on Y axis. Slope of the linear equation of Freundlich adsorption isotherm ($\log q_e = \log K_F + (1/n) \log C_e$) is the constant 1/n which indicates adsorption intensity. The intercept on Y axis represents the logarithmic value of Freundlich constant $K_{F,}$ indicating the strength of adsorption.

More than 60 per cent of variation could be explained by Freundlich adsorption isotherm for all soils in case of nitrate adsorption. The parameters of Freundlich adsorption isotherms for nitrate adsorption are given in Table 39. All the soils except laterite soil at 25 ^{0}C showed 1/n value less than 2. The highest 1/n value at 25 ^{0}C (2.264) was held in laterite soil (Sample No. 16). The highest 1/n value at 40 ^{0}C (1.181) was recorded in *Kuttanad* soil (Sample No. 15). The lowest 1/n value (0.286 at 25 ^{0}C; 0.222 at 40 ^{0}C) at both temperatures was observed in *Onattukara* sandy soil (Sample No. 12). An increase in 1/n value with increase in temperature was observed in eleven samples.

Table 39. Parameters of Freundlich adsorption isotherm for nitrate adsorption

Sample No.	Temp.	Linear equation	1/n	K_F (mg kg^{-1}) (L kg^{-1})$^{1/n}$	R^2
1	25 ^{0}C	log q_e = 1.066 log C_e - 0.032	1.066	0.929	0.896
	40 ^{0}C	log q_e = 1.163 log C_e - 0.209	1.163	0.619	0.895
2	25 ^{0}C	log q_e = 0.939 log C_e + 0.207	0.939	1.611	0.864
	40 ^{0}C	log q_e = 0.943 log C_e + 0.161	0.943	1.448	0.838
3	25 ^{0}C	log q_e = 0.969 log C_e + 0.238	0.969	1.728	0.851
	40 ^{0}C	log q_e = 0.961 log C_e + 0.226	0.961	1.682	0.901
4	25 ^{0}C	log q_e = 1.029 log C_e - 0.114	1.029	0.769	0.696
	40 ^{0}C	log q_e = 1.168 log C_e - 0.273	1.168	0.533	0.895
5	25 ^{0}C	log q_e = 0.876 log C_e + 0.151	0.876	1.414	0.757
	40 ^{0}C	log q_e = 0.985 log C_e - 0.081	0.985	0.830	0.737
6	25 ^{0}C	log q_e = 1.168 log C_e - 0.273	1.168	0.533	0.895
	40 ^{0}C	log q_e = 1.242 log C_e - 0.4	1.242	0.398	0.848
7	25 ^{0}C	log q_e = 1.724 log C_e - 2.288	1.724	0.005	0.908
8	25 ^{0}C	log q_e = 1.662 log C_e - 1.978	1.662	0.011	0.827
9	25 ^{0}C	log q_e = 0.503 log C_e + 0.199	0.503	1.579	0.681
10	25 ^{0}C	log q_e = 0.444 log C_e + 0.374	0.444	2.368	0.884
11	25 ^{0}C	log q_e = 0.297 log C_e + 0.542	0.297	3.487	0.704
	40 ^{0}C	log q_e = 0.314 log C_e + 0.456	0.314	2.854	0.633
12	25 ^{0}C	log q_e = 0.286 log C_e + 0.582	0.286	3.822	0.91
	40 ^{0}C	log q_e = 0.222 log C_e + 0.685	0.222	4.841	0.988
13	25 ^{0}C	log q_e = 1.0777 log C_e - 0.1524	1.078	0.704	0.863
	40 ^{0}C	log q_e = 1.063 log C_e - 0.135	1.063	0.733	0.885
14	25 ^{0}C	log q_e = 1.043 log C_e - 0.058	1.043	0.876	0.879
	40 ^{0}C	log q_e = 1.120 log C_e - 0.223	1.120	0.599	0.869
15	25 ^{0}C	log q_e = 1.251 log C_e - 0.371	1.251	0.426	0.884
	40 ^{0}C	log q_e = 1.181 log C_e - 0.254	1.181	0.558	0.858
16	25 ^{0}C	log q_e = 2.264 log C_e - 2.495	2.264	0.003	0.864
	40 ^{0}C	log q_e = 1.677 log C_e - 1.383	1.677	0.041	0.894

Table 39. Continued

Sample No.	Temp.	Linear equation	1/n	K_F (mg kg^{-1}) (L kg^{-1})$^{1/n}$	R^2
17	25 ^{0}C	$\log q_e = 1.618 \log C_e - 1.464$	1.618	0.034	0.905
	40 ^{0}C	$\log q_e = 1.421 \log C_e - 1.094$	1.421	0.081	0.891
18	25 ^{0}C	$\log q_e = 1.417 \log C_e - 1.064$	1.417	0.086	0.963
	40 ^{0}C	$\log q_e = 1.595 \log C_e - 1.404$	1.595	0.039	0.946
19	25 ^{0}C	$\log q_e = 0.896 \log C_e - 0.343$	0.896	0.455	0.69
	40 ^{0}C	$\log q_e = 0.992 \log C_e - 0.526$	0.992	0.298	0.73
20	25 ^{0}C	$\log q_e = 0.758 \log C_e - 0.080$	0.758	0.831	0.601
	40 ^{0}C	$\log q_e = 0.661 \log C_e + 0.138$	0.661	1.372	0.585
21	25 ^{0}C	$\log q_e = 0.832 \log C_e - 0.157$	0.832	0.697	0.809
	40 ^{0}C	$\log q_e = 0.852 \log C_e - 0.195$	0.852	0.638	0.819
22	25 ^{0}C	$\log q_e = 0.740 \log C_e + 0.02$	0.740	1.047	0.627
	40 ^{0}C	$\log q_e = 0.659 \log C_e + 0.156$	0.659	1.431	0.623

Table 40. Parameters of Langumuir adsorption isotherm for nitrate adsorption

Sample No.	Temp.	Linear equation	q_m (mg kg^{-1})	K_L (L mg^{-1})	R^2
9	25 ^{0}C	$C_e/q_e = 0.0424 C_e + 1.972$	23.59	0.022	0.823
10	25 ^{0}C	$C_e/q_e = 0.0348 C_e + 1.880$	28.74	0.019	0.919
11	25 ^{0}C	$C_e/q_e = 0.0631 C_e + 1.833$	15.85	0.034	0.871
	40 ^{0}C	$C_e/q_e = 0.0505 C_e + 2.111$	19.80	0.024	0.904
12	25 ^{0}C	$C_e/q_e = 0.0583 C_e + 1.447$	17.15	0.040	0.995
	40 ^{0}C	$C_e/q_e = 0.0509 C_e + 1.751$	19.65	0.029	0.977

All the samples from *Onattukara* sandy plain showed high K_F value at both the temperatures (Sample No. 10, 11, and 12). The highest K_F value at both temperatures (3.822 at 25 ^{0}C and 4.841 at 40 ^{0}C) was observed in *Onattukara* sandy soil (Sample No. 12). The lowest K_F value of 0.003 at 25 ^{0}C was recorded in laterite soil (Sample No. 16), and the lowest value at 40 ^{0}C (0.039) was also in laterite soil (Sample No. 18). Adecrease in K_F value with increase in temperature was observed in eleven samples.

Constant related to adsorption intensity (1/n) value at 25 ^{0}C was significantly and positively correlated with 1/n at 40 ^{0}C (0.928**) and negatively with K_F (-0.778** at 25 ^{0}C and -0.737** at 40 ^{0}C). K_F at 25 ^{0}C showed significant positive correlation with K_F at 40 ^{0}C (0.946**) and negative correlation with 1/n at 40 ^{0}C (-0.847**). Significant negative correlation was found between 1/n at 40 ^{0}C and K_F at 40 ^{0}C (-0.858**).

Langumuir adsorption isotherm

Linear form of Langmuir adsorption isotherm was fitted by plotting equilibrium concentration (C_e) on X axis and C_e/q_e on Y axis. Linear equation of Langmuir adsorption isotherm is $C_e/q_e= (1/(q_m*K_L))+((1/q_m)*C_e)$. The parameters of Langmuir isotherm are q_m and K_L, which was derived from the slope and intercept of the graph. q_m is the maximum amount of adsorbent that can be adsorbed (monolayer) and K_L is constant related to the binding strength. The parameters of Langmuir adsorption isotherm is given in Table 40.

Only four samples were with R^2 value greater than 0.5 for Langmuir adsorption isotherm, which included *Onattukara* sandy soils (Sample No. 10 at 25 ^{0}C; Sample No.11 and 12 at both temperatures) and coastal sandy soil (Sample No. 9 at 25 ^{0}C). Maximum quantity that can be adsorbed (q_m) ranged from 5.85 to 28.74 mg kg^{-1}. K_L value was found very less for the soils (<0.05 L mg^{-1}) studied.

Tempkin adsorption isotherm

Linear form of Tempkin adsorption isotherm was fitted by plotting natural logarithm of equilibrium concentration ($\ln C_e$) on X axis and quantity adsorbed per unit weight of the soil (q_e) on Y axis. A linear form of the Temkin isotherm can be expressed as

$$q_e = (RT/b) \ln K_T + (RT/b) \ln C_e$$

It is also assumed that the heat of adsorption of all molecules in the layer decreases linearly as a result of increase in surface coverage, and that adsorption is characterized by uniform distribution to maximum binding energy. Tempkin adsorption constant K_T is the equilibrium binding energy constant related to maximum binding energy, which indicates the adsorbent-adsorbate interaction. The constant b is related to heat of adsorption. These constants were derived from slope and intercept of the linear plot of Tempkin adsorption isotherm.

Tempkin adsorption isotherm could explain the adsorption process only in 19 samples. The parameters of Tempkin adsorption isotherm is given in Table 41. Three soils from Palakkad eastern plain were not fitted into Tempkin isotherm. The highest K_T value was recorded in *Onattukara* sandy soil (0.317 L kg^{-1} at 25 ^{0}C in Sample No. 11 and 0.424 L kg^{-1} in Sample No.12). The lowest K_T value at 25 ^{0}C (0.030 L kg^{-1}) was held in coastal sandy soil (Sample No.7) and the lowest value at 40 ^{0}C (0.072 L kg^{-1}) in soil from Palakkad eastern plain (Sample No. 21). Ten samples had an increase in K_T value with increase in temperature.

The highest b value (870.27 J mol^{-1} at 25 ^{0}C and 675.25 J mol^{-1} at 40 ^{0}C) was observed in *Onattukara* sandy soil (Sample No. 12) and the lowest (48.51 j mol^{-1} at 25 ^{0}C and 51.79 at 40 ^{0}C) in the *Pokkali* soil (Sample No. 3). Higher b value was recorded in all the sandy soils from northern coastal plain and *Onattukara* sandy plain. Twelve samples showed an increase in b value with increase in temperature.

K_T at 25 ^{0}C showed significant positive correlation with b at 25 ^{0}C (0.865**), K_T at 40 ^{0}C (0.871**) and b at 40 ^{0}C (0.786**). The constant (b) is related to heat of adsorption at 25 ^{0}C was significantly and positively correlated with K_T at 40 ^{0}C (0.926**) and b at 40 ^{0}C (0.985**). Significant positive correlation was found between K_T at 40 ^{0}C and b at 40 ^{0}C (0.904**).

Table 41. Parameters of Tempkin adsorption isotherm for nitrate adsorption

Sample No.	Temp.	Linear equation	K_T (L kg^{-1})	b (J mol^{-1})	R^2
1	25 ^{0}C	$q_e = 48.83 \ln C_e - 109.5$	0.106	50.74	0.895
	40 ^{0}C	$q_e = 47.49 \ln C_e - 104.17$	0.112	54.79	0.852
2	25 ^{0}C	$q_e = 39.18 \ln C_e - 78.70$	0.134	63.23	0.885
	40 ^{0}C	$q_e = 45.85 \ln C_e - 95.42$	0.125	56.76	0.772
3	25 ^{0}C	$q_e = 51.07 \ln C_e - 101.43$	0.137	48.51	0.75
	40 ^{0}C	$q_e = 50.25 \ln C_e - 102.73$	0.129	51.79	0.74
4	25 ^{0}C	$q_e = 42.24 \ln C_e - 93.85$	0.108	58.65	0.954
	40 ^{0}C	$q_e = 28.99 \ln C_e - 53.22$	0.159	89.77	0.705
5	25 ^{0}C	$q_e = 26.18 \ln C_e - 49.34$	0.152	94.64	0.782
	40 ^{0}C	$q_e = 26.6 \ln C_e - 47.67$	0.167	97.83	0.772
6	25 ^{0}C	$q_e = 42.24 \ln C_e - 93.85$	0.108	58.65	0.954
	40 ^{0}C	$q_e = 17.83 \ln C_e -38.21$	0.117	145.95	0.98
7	25 ^{0}C	$q_e = 16.28 \ln C_e - 57.37$	0.030	152.15	0.926
8	25 ^{0}C	$q_e = 21.75 \ln C_e - 73.95$	0.033	113.93	0.903
9	25 ^{0}C	$q_e = 6.29 \ln C_e - 12.46$	0.138	394.07	0.649
10	25 ^{0}C	$q_e = 7.1605 \ln C_e - 14.28$	0.136	346.01	0.84
11	25 ^{0}C	$q_e = 3.5775 \ln C_e - 4.11$	0.317	692.54	0.557
	40 ^{0}C	$q_e = 3.8967 \ln C_e - 4.06$	0.353	667.82	0.7
12	25 ^{0}C	$q_e = 2.847 \ln C_e + 0.43$	1.163	870.27	0.979
	40 ^{0}C	$q_e = 3.854 \ln C_e - 3.31$	0.424	675.25	0.894
13	25 ^{0}C	$q_e = 35.82 \ln C_e - 76.53$	0.118	69.16	0.924
	40 ^{0}C	$q_e = 36.20 \ln C_e - 76.54$	0.121	71.88	0.923
14	25 ^{0}C	$q_e = 37.52 \ln C_e - 80.81$	0.116	66.04	0.948
	40 ^{0}C	$q_e = 37.94 \ln C_e - 79.54$	0.123	68.59	0.944
15	25 ^{0}C	$qe = 50.43 \ln Ce - 114.89$	0.102	49.13	0.879
	40 ^{0}C	$qe = 47.93 \ln Ce - 106.56$	0.108	54.30	0.897
16	25 ^{0}C	$q_e = 41.07 \ln C_e - 105.89$	0.076	60.33	0.94
	40 ^{0}C	$q_e = 39.3 \ln C_e - 98.89$	0.081	66.22	0.955
17	25 ^{0}C	$q_e = 26.44 \ln C_e - 66.55$	0.081	93.70	0.862
	40 ^{0}C	$q_e = 25.19 \ln C_e - 61.61$	0.087	103.32	0.81
18	25 ^{0}C	$q_e = 29.77 \ln C_e - 77.54$	0.074	83.24	0.819
	40 ^{0}C	$q_e = 30.36 \ln C_e - 78.86$	0.074	85.71	0.775
21	25 ^{0}C	$q_e = 17.41 \ln C_e - 45.00$	0.075	142.35	0.644
	40 ^{0}C	$q_e = 17.95 \ln C_e - 47.17$	0.072	144.97	0.63

Thermodynamics of nitrate adsorption/desorption in soil

The surface area and the parameters of thermodynamics of adsorption/desorption of nitrate in the soils are given in Table 42.

Table 42. Thermodynamic parameters of nitrate adsorption/desorption

Sample No.	**surface area (m^2 g^{-1})**	**K^0**		**ΔG^0 (kcal mol^{-1})**		**ΔH^0 (kcal mol^{-1})**	**ΔS^0 (cal mol^{-1} K^{-1})**	
		25 ^{0}C	**40 ^{0}C**	**25 ^{0}C**	**40 ^{0}C**		**25 ^{0}C**	**40 ^{0}C**
Adsorption								
1	62.24	3.84	3.9	-0.797	-0.847	0.2	3.35	3.35
2	59.23	4.24	4.25	-0.855	-0.901	0.04	3.01	3.01
3	67.45	4.26	4.25	-0.858	-0.901	-0.01	2.86	2.86
4	79.66	2.92	2.75	-0.636	-0.629	-0.76	-0.42	-0.42
5	112.44	3.02	2.9	-0.655	-0.662	-0.51	0.48	0.48
6	89.48	3.35	3.24	-0.715	-0.731	-0.39	1.08	1.08
7	6.34	3.53	-	-0.746		-		
8	8.21	3.6	-	-0.759		-		
9	6.11	4.99	-	-0.952		-		
10	8.39	5.43	-	-1.002		-		
11	15.66	4.91	4.28	-0.942	-0.904	-1.71	-2.56	-2.56
12	18.65	4.5	5.42	-0.890	-1.051	2.31	10.75	10.75
13	84.32	3.43	3.47	-0.731	-0.774	0.12	2.87	2.87
14	94.07	3.5	3.3	-0.742	-0.743	-0.71	0.10	0.10
15	124.78	2.98	3.04	-0.647	-0.691	0.23	2.94	2.94
16	38.92	2.18	3.04	-0.460	-0.692	4.15	15.48	15.48
17	40.33	2.73	2.95	-0.594	-0.673	0.98	5.28	5.28
18	53.56	2.86	2.63	-0.623	-0.602	-1.02	-1.35	-1.35
19	33.42	3.09	3.03	-0.668	-0.690	-0.25	1.41	1.41
20	40.73	2.95	3.13	-0.641	-0.709	0.7	4.51	4.51
21	29.78	3.6	3.57	-0.759	-0.792	-0.11	2.18	2.18
22	39.69	3.19	3.53	-0.686	-0.785	1.26	6.54	6.54
Desorption								
7	6.34	-	5.05	-	-1.007	-	-	-
8	8.21	-	4.06	-	-0.871	-	-	-
9	6.11	-	4.68	-	-0.959	-	-	-
10	8.39	-	4.12	-	-0.881	-	-	-

Largest surface area of 124.78 m^2g^{-1} was noted in *Kuttanad* soil (Sample No. 15). Lowland soils of *Pokkali, Kole* and *Kuttanad* were with large surface area. The lowest surface area of 6.11 m^2g^{-1} was seen in the northen coastal sandy soil (Sample No 9).

The highest value of thermodynamic equilibrium constant (K^0) for nitrate adsorption (5.43 at 25 ^{0}C in Sample No.10 and 5.42 at 40 ^{0}C in Sample No. 12) was recorded in *Onattukara* sandy soils. Thermodynamic equilibrium constants with dominance of desorption at 40 ^{0}C ranged from 4.12 to 5.05. The lowest value K^0 (2.18 at 25 ^{0}C in Sample No.16 and 2.63 at 40 ^{0}C in Sample No. 18) at both temperatures were observed in laterite soil.

Change in free energy of adsorption and desorption was found negative for all the soils at both the temperatures. The highest value of change in free energy was observed in laterite soil at both temperatures (-0.46 kcal mol^{-1} at 25 ^{0}C in Sample No. 16 and -602 kcal mol^{-1} at 40 ^{0}C in Sample No. 18). The lowest value of change in free energy was observed in *Onattukara* sandy soil at both temperatures (-1.002 kcal mol^{-1} at 25^{0}C in Sample No. 10 and -1.051 kcal mol^{-1} at 40 ^{0}C in Sample No. 12). Change in free energy of desorption was ranged from -1.007 to 0.871 kcal mol^{-1}.

Change in enthalpy was negative for nitrate adsorption in nine soils and positive for the remaining nine soils. Change in entropy for nitrate adsorption was positive for all the soil except Sample No. 4, 11 and 18.

4.3.1.2. Adsorption study of phosphorous

Quantity – intensity relation

Adsorption study of P in the collected soil was carried out at 25 ^{0}C and 40 ^{0}C following the procedure described in 3.3.1.2. Five gram soil was equilibrated with 0, 10, 20, 40, 80 and 100 mg $L^{-1}$of P solution. The concentration of P in the equilibrium solution was estimated.

The parameters of the Q-I curve and maximum P adsorbed per unit weight of the soil from the added concentration of P are given in Table 43. L-shaped curve was obtained for low land soils of *Pokkali*, *Kole* and *Kuttanad*. Most of the soils collected from northern coastal sandy plain and *Onattukara* sandy plain had a maximum adsorption, after which increasing added concentration of P resulted in decreasing the quantity adsorbed. All the collected soils except coastal sandy soil (Sample No. 7) were with R^2 value > 0.5 for the linear fit of quantity - intensity curve at both 25 ^{0}C and 40 ^{0}C. High R^2value was for the low land soils of *Pokkali, Kole* and *Kuttanad.*

Highest buffer power of 159.95 (at 25 ^{0}C) and 214.82 L kg^{-1} (at 40 ^{0}C) was recorded in *Kuttanad* soil (Sample No. 15) and the lowest buffer power of 0.6 (at 25 ^{0}C) and 0.81 L kg^{-1} (at 40 ^{0}C) in coastal sandy soil (Sample No. 8). Buffer power of sandy soils ranged from 0.6 to 1.29 L kg^{-1}. Out of the 22 samples, nine samples showed a decrease in buffer power with increase in temperature, which was more prominent in the soils collected from Palakkad eastern plain. In other soils, a general trend of increase in buffer power with increase in temperature was observed.

Highest value of maximum quantity of adsorbed P at 25 ^{0}C (982.85 mg kg^{-1}) and 40 ^{0}C (1061.43 mg kg^{-1}) were noted in *Kuttanad* soil (Sample No. 15), where highest buffer power was also reported. The lowest value of maximum quantity of adsorbed P (59.10 mg kg^{-1}) at 25 ^{0}C was seen in coastal sandy soil (Sample No. 10), whereas the higher value of 55.60 mg kg^{-1} in the soil from Palakkad eastern plain (Sample No. 21) at 40 ^{0}C. A decrease in maximum quantity adsorbed with increase in temperature was observed in laterite soils, and also the soils collected from Palakkad eastern plain. For other soils, maximum quantity adsorbed was increasing with increase in temperature was observed.

Q-I curve of all soils except coastal sandy soil at 40 ^{0}C had positive intercept for P adsorption. Low land soils of *Kole* and *Kuttanad* were with high positive intercept. Sandy soils from northern coastal plain and *Onattukara* sandy soils were reported with lower value of intercept. Highest value of intercept (140.54 mg kg^{-1} at 25 ^{0}C in Sample No. 5 and 160.58 mg kg^{-1} at 40 ^{0}C in Sample No. 6) at both temperatures was noted in soil from *Kole* land. Lowest value of intercept (0.28 mg kg^{-1} at 25 ^{0}C and -0.37 mg kg^{-1} at 40 ^{0}C) at both temperatures was recorded in coastal sandy soil (Sample No. 9).

Correlation between parameters of Q-I curve of P adsorption and soil properties are given in Table 44. Buffer power at 25 ^{0}C had significant positive correlation with buffer power at 40 ^{0}C (0.991**), maximum quantity adsorbed at 25 ^{0}C (0.658**) and 40 ^{0}C (0.678**). Maximum quantity adsorbed at 25 ^{0}C had significant positive correlation with maximum quantity adsorbed at 40 ^{0}C (0.994**) and buffer power at 40 ^{0}C (0.607**). Buffer power at 40 ^{0}C had significant positive correlation with maximum quantity adsorbed at 40 ^{0}C (0.630**).

Iron bound P fraction was significantly and positively correlated with buffer power (0.482* at 25 ^{0}C, 0.449* at 40 ^{0}C) and maximum quantity adsorbed (0.803** at 25 ^{0}C, 0.752** at 40 ^{0}C). Calcium bound P fraction had significant negative correlation with maximum quantity adsorbed at 25 ^{0}C (-0.633**) and 40 ^{0}C (-0.606**). Organic P fraction was significantly and positively correlated with buffer power (0.563** at 25 ^{0}C, 0.528* at 40 ^{0}C) and maximum quantity adsorbed (0.857** at 25 ^{0}C, 0.841** at 40 ^{0}C). Total P had significant positive correlation with buffer power (0.568** at 25 ^{0}C, 0.522* at 40 ^{0}C) and maximum quantity adsorbed (0.797** at 25 ^{0}C, 0.758** at 40 ^{0}C). CBD extractable Fe content had significant positive correlation with buffer power (0.734** at 25 ^{0}C and 0.718** at 40 ^{0}C) and maximum quantity adsorbed (0.795** at 25 ^{0}C and 0.770** at 40 ^{0}C).

pH showed significant negative correlation with buffer power (-0.536* at 25 ^{0}C, -0.513* at 40 ^{0}C) and maximum quantity adsorbed at both 25 ^{0}C (-0.828**) and 40 ^{0}C (-0.847**). EC had significant positive correlation with maximum quantity adsorbed at both 25 ^{0}C (0.544**) and 40 ^{0}C (0.529*). OC content in soil showed positive correlation with buffer power (0.751** at 25 ^{0}C, 0.701** at 40 ^{0}C) and maximum quantity adsorbed (0.903** at 25 ^{0}C, 0.897** at 40 ^{0}C). The same trend was observed in case of available N.

Table 43. Parameters of Q-I curve for P adsorption

Sample No.	Temp.	Linear equation	Buffer power (L kg^{-1})	Intercept (mg kg^{-1})	Max. quantity adsorbed (mg kg^{-1})	R^2
1	25 ^{0}C	$q_e = 36.34\ C_e + 45.4$	36.34	45.4	935.2	0.881
	40 ^{0}C	$q_e = 38.18\ C_e + 14.44$	38.18	14.44	951.13	0.966
2	25 ^{0}C	$q_{e\,=}\ 27.85\ C_e + 53.22$	27.85	53.22	934	0.959
	40 ^{0}C	$q_{e\,=}\ 32.94\ C_e + 59.45$	32.94	59.45	965.19	0.966
3	25 ^{0}C	$q_{e\,=}\ 35.40\ C_e + 32.40$	35.40	32.40	944.8	0.975
	40 ^{0}C	$q_{e\,=}\ 36.15\ C_e + 37.46$	36.15	37.46	944.78	0.968
4	25 ^{0}C	$q_{e\,=}\ 31.94\ C_e + 109.41$	31.94	109.41	895.6	0.889
	40 ^{0}C	$q_{e\,=}\ 31.17\ C_e + 124$	31.17	124	922.15	0.787
5	25 ^{0}C	$q_{e\,=}\ 20.32\ C_e + 140.54$	20.32	140.54	883.76	0.854
	40 ^{0}C	$q_{e\,=}\ 21.1\ C_e + 158.61$	21.1	158.61	913.35	0.809
6	25 ^{0}C	$q_{e\,=}\ 16.27\ C_e + 138$	16.27	138.00	922.95	0.845
	40 ^{0}C	$q_{e\,=}\ 16.24\ C_e + 160.58$	16.24	160.58	953.54	0.771
7	25 ^{0}C	$q_{e\,=}\ 0.81\ C_e + 18.13$	0.81	18.13	89.1	0.415
	40 ^{0}C	$q_{e\,=}\ 0.93\ C_e + 18.28$	0.93	18.28	117.6	0.424
8	25 ^{0}C	$q_{e\,=}\ 0.6\ C_e + 14.32$	0.6	14.32	107.6	0.634
	40 ^{0}C	$q_{e\,=}\ 0.81\ C_e + 13.84$	0.81	13.84	181.6	0.574
9	25 ^{0}C	$q_{e\,=}\ 0.91\ C_e + 0.281$	0.91	0.28	92.5	0.704
	40 ^{0}C	$q_{e\,=}\ 0.82\ C_e - 0.37$	0.82	-0.37	84.7	0.997
10	25 ^{0}C	$q_{e\,=}\ 1.19\ C_e + 16.39$	1.19	16.39	59.1	0.843
	40 ^{0}C	$q_{e\,=}\ 1.29\ C_e + 19.88$	1.29	19.88	74.3	0.700
11	25 ^{0}C	$q_{e\,=}\ 1.06\ C_e + 21.63$	1.06	21.63	102.8	0.888
	40 ^{0}C	$q_{e\,=}\ 1.25\ C_e + 34.86$	1.25	34.86	125.1	0.619

Table 43. Continued

Sample No.	Temp.	Linear equation	Buffer power (L kg^{-1})	Intercept (mg kg^{-1})	Max. quantity adsorbed (mg kg^{-1})	R^2
12	25 ^{0}C	$q_e = 1.20 C_e + 22.51$	1.20	22.51	148.2	0.577
	40 ^{0}C	$q_e = 1.07 C_e + 13.11$	1.07	13.11	164.2	0.554
13	25 ^{0}C	qe = 41.81 Ce + 101.53	41.81	101.53	965.08	0.963
	40 ^{0}C	qe = 41.00 Ce + 110.19	41.00	110.19	1051.28	0.947
14	25 ^{0}C	$q_e = 78.00 C_e + 132.09$	78.00	132.09	976	0.897
	40 ^{0}C	$q_e = 103.47 C_e + 124.77$	103.47	124.77	1058.33	0.915
15	25 ^{0}C	$q_e = 159.95 C_e + 84.07$	159.95	84.07	982.85	0.891
	40 ^{0}C	$q_e = 214.82 C_e + 58.42$	214.82	58.42	1061.43	0.950
16	25 ^{0}C	$q_e = 5.38 C_e + 62.63$	5.38	62.63	309.9	0.913
	40 ^{0}C	$q_e = 5.39 C_e + 74.23$	5.39	74.23	257.4	0.880
17	25 ^{0}C	$q_e = 1.20 C_e + 22.51$	1.20	22.51	502.9	0.577
	40 ^{0}C	$q_e = 19.20 C_e + 157.53$	19.20	157.53	481.2	0.794
18	25 ^{0}C	$q_e = 12.87 C_e + 60.26$	12.87	60.26	358.8	0.872
	40 ^{0}C	$q_e = 9.8 C_e + 75.34$	9.8	75.34	228.2	0.751
19	25 ^{0}C	$q_e = 6.97 C_e + 8.68$	6.97	8.68	236.2	0.558
	40 ^{0}C	$q_e = 2.23 C_e + 61.71$	2.23	61.71	169.6	0.784
20	25 ^{0}C	$q_e = 2.68 C_e + 56.51$	2.68	56.51	109.6	0.792
	40 ^{0}C	$q_e = 2.63 C_e + 54.58$	2.63	54.58	65.8	0.823
21	25 ^{0}C	$q_e = 3.78 C_e + 75.23$	3.78	75.23	65.3	0.827
	40 ^{0}C	$q_e = 3.62 C_e + 84.73$	3.62	84.73	55.6	0.791
22	25 ^{0}C	$q_e = 3.5 C_e + 28.52$	3.5	28.52	199.5	0.914
	40 ^{0}C	$q_e = 1.77 C_e + 51.47$	1.77	51.47	164.6	0.744

Table 44. Correlation between parameters of Q-I curve and soil properties for P adsorption

	Buffer power at 25 ^{0}C	**Max. quantity adsorbed at 25 ^{0}C**	**Buffer power at 40 ^{0}C**	**Max. quantity adsorbed at 40 ^{0}C**
Max. quantity adsorbed at 25 ^{0}C	0.658**		0.607**	0.994**
Buffer power at 40 ^{0}C	0.991**	0.607**		0.630**
Max. quantity adsorbed at 40 ^{0}C	0.678**	0.994**	0.630**	
Fe-P	0.482*	0.803**	0.449*	0.752**
Ca-P		-0.633**		-0.606**
Org-P	0.563**	0.857**	0.528*	0.841**
Tot-P	0.568**	0.797**	0.522*	0.758**
pH	-0.536*	-0.828**	-0.513*	-0.847**
EC		0.544**		0.529*
OC	0.751**	0.903**	0.701**	0.897**
AEC	0.632**	0.885**	0.597**	0.857**
Sand	-0.616**	-0.784**	-0.573**	-0.763**
Silt		0.600**		0.586**
Clay	0.659**	0.709**	0.651**	0.687**
Av.N	0.833**	0.898**	0.804**	0.910**
Av.Mg		0.567**		0.549**
Av.S		0.501*		0.481*
WS+Ex.Al	0.584**	0.672**	0.554**	0.668**
Av.Fe	0.763**	0.926**	0.702**	0.941**
Av.Cu		0.757**		0.708**
Av.Zn		0.459*		0.435*
Av.B		0.565**		0.555**
Av.Si		-0.435*		-0.477*
CBD-Fe	0.734**	0.795**	0.718**	0.770**

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

Sand showed significant negative correlation with buffer power (-0.616** at 25 ^{0}C, -0.573** at 40 ^{0}C) and maximum quantity adsorbed (-0.784** at 25 ^{0}C,

-0.763** at 40 ^{0}C). An opposite trend was observed in case of clay. Clay had significant positive correlation with buffer power (0.659** at 25^{0}C, 0.651** at 40 ^{0}C) and maximum quantity adsorbed (0.709** at 25 ^{0}C, 0.687** at 40 ^{0}C). AEC was significantly and positively correlated with buffer power (0.632** at 25 ^{0}C, 0.597** at 40 ^{0}C) and maximum quantity adsorbed (0.885** at 25 ^{0}C, 0.857** at 40 ^{0}C). Silt content had significant positive correlation with maximum quantity adsorbed at 25 ^{0}C (0.600**) and 40 ^{0}C (0.586**).

Available S had significant positive correlation with maximum quantity adsorbed at 25 ^{0}C (0.501*) and 40 ^{0}C (0.481*). Available B was significantly positively correlated with maximum quantity adsorbed at 25 ^{0}C (0.565**) and 40 ^{0}C (0.555**). Available Si was significantly and negatively correlated with maximum quantity adsorbed at 25 ^{0}C (-0.435*) and 40 ^{0}C (-0.477*). Available Fe was significantly and positively correlated with buffer power (0.763** at 25 ^{0}C, 0.702** at 40 ^{0}C), and maximum quantity adsorbed (0.926** at 25 ^{0}C, 0.941** at 40 ^{0}C). Exchangeable plus water soluble Al had significant positive correlation with buffer power (0.584** at 25 ^{0}C, 0.554** at 40 ^{0}C) and maximum quantity adsorbed (0.672** at 25 ^{0}C, 0.668** at 40 ^{0}C).

Adsorption isotherm

Freundlich adsorption isotherm was the best to explain P adsorption in soil followed by Tempkin adsorption isotherm and Langmuir adsorption isotherm.

Freundlich adsorption isotherm

Parameters of Freundlich adsorption isotherm is given in Table 45. All samples at both temperatures showed R^2 values of greater than 0.5. 1/n value of all the soils followed the theoretical value (<1). The highest value of 1/n at 25 ^{0}C (0.942) and 40 ^{0}C (0.930) was observed in soils from coastal sandy plain (Sample No. 9). The lowest value of 1/n at 25 ^{0}C (0.269) and 40 ^{0}C (0.275) was observed in the soil from Palakkad eastern plain (Sample No. 19). Any general trend of increase or decrease in 1/n value with temperature was not observed. *Kole* land soils were with 1/n value varying from 0.377 to 0.398 at both the temperatures.

Pokkali soils were with high 1/n values ranging from 0.763 to 0.932 at both the temperatures.

Out of the 22 samples collected, 17 samples had an increase in K_F value with increase in temperature. The highest value of constant related to adsorption strength (K_F) at 40 ^{0}C was noted as 311.32 in *Kuttanad* soil (Sample No. 15) whereas 268.41 was recorded at 25 ^{0}C in *Kuttanad* soil (Sample No.14). The lowest K_F value at 25 ^{0}C (1.079) and 40 ^{0}C (1.084) was recorded in coastal sandy soil (Sample No. 9). Soils from *Kole* and *Kuttanad* were recorded with high K_F values. Sandy soils from coastal sandy plain and *Onattukara* sandy plain had showed lower K_F values.

Correlation between parameters of Freundlich adsorption isotherm and soil properties are given in Table 46. Significant and positive correlation was found between 1/n value at 25 ^{0}C and 1/n value at 40 ^{0}C (0.966**). K_F value at 25 ^{0}C had significant positive correlation with K_F value at 40 ^{0}C (0.989**). The correlation between 1/n and K_F was negative but not significant. pH showed significant negative correlation with 1/n (-0.442* at 25 ^{0}C, -0.522* at 40 ^{0}C) and K_F values (-0.493* at 25 ^{0}C, -0.497* at 40 ^{0}C) at both the temperature.

Saloid - bound P fraction had significant negative correlation with K_F value at 25 ^{0}C (-0.495*) and 40 ^{0}C (-0.496*). Significant positive correlation was found between aluminium bound P wih 1/n value at 25 ^{0}C (0.488*). Iron bound P had significant positive correlation with K_F at both the temperatures (0.457* at 25 ^{0}C, 0.445* at 40 ^{0}C) and 1/n at 40 ^{0}C (0.436*). Reductant soluble phosphate had significant positive correlation with K_F at 25 ^{0}C (0.450*) and 40 ^{0}C (0.454*). Calcium bound P was significantly and negatively correlated with K_F at 25 ^{0}C (-0.516*) and 40 ^{0}C (-0.503*). Organic P had significant positive correlation with K_F at 25 ^{0}C (-0.734*) and 40 ^{0}C (0.741*). Total P was significantly and positively correlated with K_F at 25 ^{0}C (0.557**) and 40 ^{0}C (0.575**).

Table 45. Parameters of Freundlich adsorption isotherm for P adsorption

Sample No.	**Temp.**	**Linear equation**	**1/n**	**K_F (mg kg^{-1}) (L kg^{-1})$^{1/n}$**	**R^2**
1	25 ^{0}C	$\log q_e = 0.932 \log C_e + 1.71$	0.932	51.67	0.955
	40 ^{0}C	$\log q_e = 0.921 \log C_e + 1.70$	0.921	50.35	0.993
2	25 ^{0}C	$\log q_e = 0.763 \log C_e + 1.82$	0.763	65.48	0.987
	40 ^{0}C	$\log q_e = 0.775 \log C_e + 1.87$	0.775	73.27	0.983
3	25 ^{0}C	$\log q_e = 0.837 \log C_e + 1.79$	0.837	61.55	0.988
	40 ^{0}C	$\log q_e = 0.855 \log C_e + 1.79$	0.855	61.24	0.98
4	25 ^{0}C	$\log q_e = 0.398 \log C_e + 2.32$	0.398	207.54	0.957
	40 ^{0}C	$\log q_e = 0.397 \log C_e + 2.33$	0.397	211.4	0.933
5	25 ^{0}C	$\log q_e = 0.391 \log C_e + 2.28$	0.391	191.12	0.996
	40 ^{0}C	$\log q_e = 0.394 \log C_e + 2.32$	0.394	207.30	0.979
6	25 ^{0}C	$\log q_e = 0.38 \log C_e + 2.25$	0.380	176.73	0.992
	40 ^{0}C	$\log q_e = 0.377 \log C_e + 2.29$	0.377	193.42	0.976
7	25 ^{0}C	$\log q_e = 0.509 \log C_e + 0.92$	0.509	8.31	0.579
	40 ^{0}C	$\log q_e = 0.496 \log C_e + 0.98$	0.496	9.43	0.579
8	25 ^{0}C	$\log q_e = 0.442 \log C_e + 0.94$	0.442	8.64	0.736
	40 ^{0}C	$\log q_e = 0.504 \log C_e + 0.9$	0.504	7.94	0.69
9	25 ^{0}C	$\log q_e = 0.942 \log C_e + 0.032$	0.942	1.08	0.861
	40 ^{0}C	$\log q_e = 0.93 \log C_e + 0.035$	0.930	1.08	0.995
10	25 ^{0}C	$\log q_e = 0.565 \log C_e + 0.96$	0.565	9.11	0.921
	40 ^{0}C	$\log q_e = 0.566 \log C_e + 0.998$	0.566	9.96	0.858
11	25 ^{0}C	$\log q_e = 0.461 \log C_e + 1.14$	0.461	13.82	0.974
	40 ^{0}C	$\log q_e = 0.52 \log C_e + 1.16$	0.520	14.45	0.789
12	25 ^{0}C	$\log q_e = 0.416 \log C_e + 1.22$	0.416	16.68	0.517
	40 ^{0}C	$\log q_e = 0.33 \log C_e + 1.24$	0.330	17.19	0.955
13	25 ^{0}C	$q_e = 0.473 \log C_e + 2.31$	0.473	203.15	0.989
	40 ^{0}C	$q_e = 0.459 \log C_e + 2.33$	0.459	214.14	0.983

Table 45. Continued

Sample No.	Temp.	Linear equation	1/n	K_F (mg kg^{-1}) (L kg^{-1})$^{1/n}$	R^2
14	25 ^{0}C	$q_e = 0.54 \log C_e + 2.43$	0.54	268.41	0.977
	40 ^{0}C	$q_e = 0.600 \log C_e + 2.45$	0.6	284.38	0.943
15	25 ^{0}C	$q_e = 0.821 \log C_e + 2.41$	0.821	259.42	0.961
	40 ^{0}C	$q_e = 0.822 \log C_e + 2.49$	0.822	311.32	0.956
16	25 ^{0}C	$q_e = 0.457 \log C_e + 1.74$	0.457	55.4	0.982
	40 ^{0}C	$q_e = 0.433 \log C_e + 1.81$	0.433	64.3	0.991
17	25 ^{0}C	$q_e = 0.349 \log C_e + 2.34$	0.349	218.88	0.982
	40 ^{0}C	$q_e = 0.405 \log C_e + 2.26$	0.405	181.01	0.722
18	25 ^{0}C	$q_e = 0.329 \log C_e + 2.1$	0.329	125.57	0.813
	40 ^{0}C	$q_e = 0.313 \log C_e + 2.13$	0.313	133.81	0.786
19	25 ^{0}C	$q_e = 0.269 \log C_e + 1.818$	0.269	65.13	0.813
	40 ^{0}C	$q_e = 0.275 \log C_e + 1.807$	0.275	64.12	0.815
20	25 ^{0}C	$q_e = 0.412 \log C_e + 1.62$	0.412	41.49	0.956
	40 ^{0}C	$q_e = 0.393 \log C_e + 1.64$	0.393	43.41	0.959
21	25 ^{0}C	$q_e = 0.363 \log C_e + 1.83$	0.363	67.38	0.986
	40 ^{0}C	$q_e = 0.347 \log C_e + 1.87$	0.347	74.23	0.984
22	25 ^{0}C	$q_e = 0.535 \log C_e + 1.40$	0.535	25.18	0.937
	40 ^{0}C	$q_e = 0.342 \log C_e + 1.62$	0.342	41.2	0.955

OC showed significant positive correlation with 1/n (0.530* at 25 ^{0}C, 0.570** at 40 ^{0}C) and K_F (0.546** at 25 ^{0}C, 0.578** at 40 ^{0}C) values at both temperatures. AEC was significantly and positively correlated with 1/n (0.440* at 25 ^{0}C, 0.502* at 40 ^{0}C) and K_F (0.580** at 25 ^{0}C, 0.576** at 40 ^{0}C) values at both temperature. Clay had significant positive correlation with K_F values at 25 ^{0}C (0.927**) and at 40 ^{0}C (0.934**). Reverse trend was seen in the case of sand. Sand was significantly and negatively correlated with K_F values at 25 ^{0}C (-0.838**) and at 40 ^{0}C (-0.854**).

Table 46. Correlation between parameters of Freundlich adsorption isotherm and soil properties for P adsorption

	1/n at 25 ^{0}C	**K_F 25 ^{0}C**	**1/n at 40 ^{0}C**	**K_F 40 ^{0}C**
1/n at 40 ^{0}C	0.966**			
K_F 40 ^{0}C		0.989**		
SB-P		-0.495*		-0.496*
Al-P	0.488*			
Fe-P		0.457*	0.436*	0.445*
RS-P		0.450*		0.454*
Ca-P		-0.516*		-0.503*
Org-P		0.734**		0.741**
Tot-P		0.557**		0.575**
pH	-0.442*	-0.493*	-0.522*	-0.497*
EC	0.641**		0.655**	
OC	0.530*	0.546**	0.570**	0.578**
AEC	0.440*	0.580**	0.502*	0.576**
Sand		-0.838**		-0.854**
Silt				0.424*
Clay		0.927**		0.934**
Av.N		0.824**		0.855**
Av.P	0.517*	-0.549**	0.488*	-0.549**
Av.K		0.453*		0.466*
Av.Ca				
Av.Mg	0.667**		0.668**	
Av.S	0.658**		0.664**	
Av.Fe	0.505*	0.581**	0.529*	0.626**
Av.Mn	-0.504*		-0.501*	
Av.Cu		0.433*		
Av.Zn	0.634**		0.627**	
Av.Si	-0.423*		-0.476*	
WS+Ex.Al	0.713**		0.727**	
CBD-Fe		0.88**		0.898**

**Correlation is significant at the 0.01 level (2-tailed)
*Correlation is significant at the 0.05 level (2-tailed)

Available P had significant positive correlation with 1/n values at 25 ^{0}C (0.517*) and 40 ^{0}C (0.488*). Available P was significantly and negatively correlated with K_F values at 25 ^{0}C (-0.549**) and 40 ^{0}C (-0.549**). Available S had significant positive correlation with 1/n value at 25 ^{0}C (0.658**) and at 40 ^{0}C (0.664**). Available Si was significantly and negatively correlated with 1/n values at 25 ^{0}C (-0.423*) and 40 ^{0}C (-0.476*). Water soluble plus exchangeable Al showed significant positive correlation with 1/n (0.713** at 25 ^{0}C and 0.727** at 40 ^{0}C). CBD extractable Fe content showed significant positive correlation with K_F (0.880** at 25 ^{0}C and 0.898** at 40 ^{0}C).

Langmuir adsorption isotherm

The parameters of Langmuir adsorption isotherm are given in Table 47. Adsorption of P in one coastal sandy soil (Sample No. 9) and *Onattukara* sandy soil (Sample No. 12) was not fitted into Langmuir adsorption isotherm. While plotting the graph, q_e was converted to mg of P adsorbed per gram of soil in order to get more precise linear equation.

The highest value of adsorption maxima (q_m) was recorded in *Pokkali* (Sample No. 1) soil at 25 ^{0}C (2680.25 mg kg^{-1}) and 40 ^{0}C (3523.61 mg kg^{-1}). The lowest value of q_m was observed in coastal sandy soil (Sample No. 7) at 25 ^{0}C (69.27 and mg kg^{-1}) and 40 ^{0}C (81.19 mg kg^{-1}). Low land soils of *Pokkali, Kole, Kuttanad* and laterite soils were recorded with high q_m. Ten samples had an increase in q_m with increase in temperature, while a decrease in q_m with increase in temperature was observed in other ten samples.

The highest value of bonding energy constant (K_L) at 25 ^{0}C (0.545 L mg^{-1}) was noted in laterite soil (Sample No. 17), while at 40 ^{0}C it was highest (0.446 L mg^{-1}) in the soil from *Kole* land (Sample No. 5). Higher values of K_L were noted in low lands of *Kole* and *Kuttanad,* while lower value in the sandy soils from coastal sandy plain and *Onattukara* sandy plain. Lowest values of K_L (0.02 L mg^{-1} at 25 ^{0}C and 0.014 L mg^{-1} at 40 ^{0}C) were observed in *Pokkali* soil (Sample No. 1). An increase in K_L value with increase in temperature was observed in tweleve samples.

Table 47. Parameters of Langmuir adsorption isotherm for P adsorption

Sample No.	Temp.	Linear equation	q_m (mg kg^{-1})	K_L (L mg^{-1})	R^2
1	25 ^{0}C	$C_e/q_e = 0.373\ C_e + 18.87$	2680.25	0.020	0.586
	40 ^{0}C	$C_e/q_e = 0.284\ C_e + 20.48$	3523.61	0.014	0.703
2	25 ^{0}C	$C_e/q_e = 0.69\ C_e + 17.35$	1450.54	0.040	0.973
	40 ^{0}C	$C_e/q_e = 0.65\ C_e + 14.82$	1539.17	0.044	0.965
3	25 ^{0}C	$C_e/q_e = 0.477\ C_e + 17.69$	2095.56	0.027	0.895
	40 ^{0}C	$C_e/q_e = 0.462\ C_e + 17.26$	2164.50	0.027	0.835
4	25 ^{0}C	$C_e/q_e = 1.317\ C_e + 3.7$	759.13	0.356	0.913
	40 ^{0}C	$C_e/q_e = 1.381\ C_e + 3.12$	723.96	0.442	0.901
5	25 ^{0}C	$C_e/q_e = 1.331\ C_e + 4.2$	751.26	0.317	0.989
	40 ^{0}C	$C_e/q_e = 1.332\ C_e + 2.99$	750.75	0.446	0.998
6	25 ^{0}C	$C_e/q_e = 1.438\ C_e + 4.79$	695.60	0.300	0.989
	40 ^{0}C	$C_e/q_e = 1.450\ C_e + 3.27$	689.56	0.444	0.998
7	25 ^{0}C	$C_e/q_e = 14.44\ C_e + 153.73$	69.27	0.094	0.63
	40 ^{0}C	$C_e/q_e = 12.32\ C_e + 181.41$	81.19	0.068	0.622
8	25 ^{0}C	$C_e/q_e = 14.24\ C_e + 288.42$	70.24	0.049	0.75
	40 ^{0}C	$C_e/q_e = 11.23\ C_e + 308.39$	89.07	0.036	0.622
10	25 ^{0}C	$C_e/q_e = 6.27\ C_e + 258.05$	159.49	0.024	0.814
	40 ^{0}C	$C_e/q_e = 6.58\ C_e + 204.76$	151.92	0.032	0.744
11	25 ^{0}C	$C_e/q_e = 7.20\ C_e + 197.49$	138.87	0.036	0.972
	40 ^{0}C	$C_e/q_e = 6.36\ C_e + 130.58$	157.25	0.049	0.906
13	25 ^{0}C	$C_e/q_e = 1.00\ C_e + 4.35$	998.90	0.23	0.911
	40 ^{0}C	$C_e/q_e = 1.032\ C_e + 3.77$	969.37	0.28	0.918
14	25 ^{0}C	$C_e/q_e = 0.926\ C_e + 2.28$	1079.8	0.406	0.986
	40 ^{0}C	$C_e/q_e = 0.847\ C_e + 2.16$	1180.92	0.392	0.984
15	25 ^{0}C	$C_e/q_e = 0.489\ C_e + 3.12$	2047.08	0.157	0.818
	40 ^{0}C	$C_e/q_e = 0.449\ C_e + 2.57$	2229.65	0.175	0.759

Table 47. Continued

Sample No.	Temp.	Linear equation	q_m (mg kg^{-1})	K_L (L mg^{-1})	R^2
16	25 ^{0}C	$C_e/q_e = 2.17\ C_e + 37.4$	460.19	0.058	0.94
	40 ^{0}C	$C_e/q_e = 2.26\ C_e + 28.50$	443.5	0.079	0.973
17	25 ^{0}C	$C_e/q_e = 1.43\ C_e + 2.62$	701.21	0.545	0.997
	40 ^{0}C	$C_e/q_e = 1.28\ C_e + 5.5$	781.31	0.233	0.966
18	25 ^{0}C	$C_e/q_e= 1.82\ C_e + 17.56$	548.79	0.104	0.599
	40 ^{0}C	$C_e/q_e = 1.83\ C_e + 16.47$	546.66	0.111	0.65
19	25 ^{0}C	$C_e/q_e = 4.28\ C_e + 41.97$	233.74	0.102	0.864
	40 ^{0}C	$C_e/q_e = 3.96\ C_e + 49.15$	252.67	0.081	0.91
20	25 ^{0}C	$C_e/q_e = 3.67\ C_e + 50.09$	272.67	0.073	0.95
	40 ^{0}C	$C_e/q_e = 3.70\ C_e + 51.97$	270.22	0.071	0.951
21	25 ^{0}C	$C_e/q_e = 2.90\ C_e + 28.68$	344.64	0.101	0.979
	40 ^{0}C	$C_e/q_e = 2.98\ C_e + 22.11$	335.22	0.135	0.997
22	25 ^{0}C	$C_e/q_e = 2.67\ C_e + 97.10$	374.66	0.027	0.743
	40 ^{0}C	$C_e/q_e = 5.11\ C_e + 51.27$	195.89	0.1	0.969

Correlation between parameters of Langmuir adsorption isotherm and soil properties are given in Table 48. A significant positive correlation was found between q_m at 25 ^{0}C and q_m at 40 ^{0}C (0.987**). K_L at 25 ^{0}C was significantly and positively correlated with $K_L$at 40 ^{0}C (0.840**). Saloid-bound P was significantly and negatively correlated with K_L at 25 ^{0}C (-0.474*) and at 40 ^{0}C (-0.546**).

Aluminium bound P had significant positive correlation with q_m at 25 ^{0}C (0.578**) and at 40 ^{0}C (0.645**). Iron bound P showed significant positive correlation with q_m at 25 ^{0}C (0.860**) and at 40 ^{0}C (0.817**). Organic P fraction was significantly and positively correlated with q_m (0.560** at 25 ^{0}C, 0.466* at 40 ^{0}C) and K_L (0.537** at 25 ^{0}C, 0.644** at 40 ^{0}C). Total P had significant positive correlation with q_m (0.764** at 25 ^{0}C, 0.699* at 40 ^{0}C).

Table 48. Correlation between parameters of Langmuir adsorption isotherm and soil properties for P adsorption

	q_m at 25 ^{0}C	**K_L at 25 ^{0}C**	**q_m at 40 ^{0}C**	**K_L at 40 ^{0}C**
K_L at 25 ^{0}C				0.840**
q_m at 40 ^{0}C	0.987**			
K_L at 40 ^{0}C		0.840**		
SB-P		-0.474*		-0.546**
Al-P	0.578**		0.645**	
Fe-P	0.860**		0.817**	
RS-P				
Ca-P				
Org-P	0.560**	0.537**	0.466*	0.644**
Res-P				
Tot-P	0.764**		0.699**	
pH	-0.722**		-0.684**	
EC	0.755**		0.715**	
OC	0.912**		0.852**	
AEC	0.892**		0.843**	
Sand	-0.459*	-0.587**		-0.714**
Silt				0.467*
Clay		0.692**		0.704**
Av.N	0.692**	0.499*	0.633**	0.579**
Av.P		-0.599**		-0.623**
Av.Mg	0.830**		0.811**	
Av.S	0.772**		0.760**	
Av.Fe	0.854**		0.802**	
Av.Cu	0.733**		0.692**	
Av.Zn	0.742**		0.730**	
Ex.Na	0.564**		0.533*	
WS+Ex.Al	0.892**		0.866**	
CBD-Fe	0.554*	0.606**	0.475*	0.661**

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

pH was significantly and negatively correlated with adsorption maxima (q_m) at 25 ^{0}C (-0.722**) and at 40 ^{0}C (-0.684**). EC was significantly and positively correlated with q_m at 25 ^{0}C (0.755**) and at 40 ^{0}C (0.715**). OC had significant positive correlation with q_m at 25 ^{0}C (0.912**) and at 40 ^{0}C (0.852**).

AEC was significantly and positively correlated with q_m at 25 ^{0}C (0.892**) and at 40 ^{0}C (0.843**). Sand was significantly and negatively correlated with q_m at 25 ^{0}C (-0.459*) and with K_L (-0.587** at 25 ^{0}C, -0.714** at 40 ^{0}C). Clay had significant positive correlation with K_L at 25 ^{0}C (0.692**) and at 40 ^{0}C (0.704**).

Available P was significantly and negatively correlated with K_L (-0.599** at 25 ^{0}C and -0.623** at 40 ^{0}C). Available Fe had significant positive correlation with q_m at 25 ^{0}C (0.854**) and at 40 ^{0}C (0.802**). Available Zn was significantly and positively correlated with q_m at 25 ^{0}C (0.742**) and at 40 ^{0}C (0.730**). Exchangeable plus water soluble Al also there with same trend, significant positive correlation with q_m at 25 ^{0}C (0.892**) and at 40 ^{0}C (0.866**). CBD extractable Fe content had significant positive correlation with q_m (0.554** at 25 ^{0}C and 0.475* at 40 ^{0}C) and K_L (0.606** at 25 ^{0}C and 0.661** at 40 ^{0}C).

Tempkin adsorption isotherm

The parameters of Tempkin adsorption isotherm is given in Table 49. Out of the 22 samples collected, 18 samples were recorded with an increase in constant related to strength of bonding (K_T) with increase in temperature. This trend was more prominent in soil from *Kole* land. The highest value of K_T at 40 ^{0}C (8.29 L kg^{-1}) and 25 ^{0}C (11.44 L kg^{-1}) was recorded in soil from *Kole* land (Sample No. 4) and laterite soil (Sample No. 17) respectively. Sandy soils from northern coastal plain and *Onattukara* sandy plain were recorded with low K_T values at both temperatures.

The highest value of constant related to heat of adsorption (b) at both temperatures (132.19 J mol^{-1} at 25 ^{0}C, 100.39 J mol^{-1} at 40 ^{0}C) was observed in coastal sandy soil (Sample No. 8), whereas the lowest value (7.56 J mol^{-1} at 25 ^{0}C, 7.82 J mol^{-1}at 40 ^{0}C) was recorded in *Kuttanad* soil (Sample No.15). Fifteen samples had an increase in K_T with increase in temperature.

Table 49. Parameters of Tempkin adsorption isotherm for P adsorption

Sample No.	Temp.	Linear equation	K_T (L kg^{-1})	b (J mol^{-1})	R^2
1	25 ^{0}C	$q_e = 299.7 \ln C_e - 165.65$	0.575	8.27	0.956
	40 ^{0}C	$q_e = 290.98 \ln C_e - 162.06$	0.573	8.94	0.95
2	25 ^{0}C	$q_e = 244.2 \ln C_e - 93.66$	0.681	10.15	0.974
	40 ^{0}C	$q_e = 256.3 \ln C_e - 67.567$	0.768	10.15	0.977
3	25 ^{0}C	$q_e = 276.26 \ln C_e - 122.03$	0.643	8.97	0.966
	40 ^{0}C	$q_e = 282.45 \ln C_e - 121.83$	0.650	9.21	0.983
4	25 ^{0}C	$q_e = 130.61 \ln C_e + 264.37$	7.57	18.97	0.869
	40 ^{0}C	$q_e = 130.35 \ln C_e + 275.69$	8.29	19.96	0.814
5	25 ^{0}C	$q_e = 125.61 \ln C_e + 234.12$	6.45	19.72	0.956
	40 ^{0}C	$q_e = 129.66 \ln C_e + 261.38$	7.51	20.07	0.988
6	25 ^{0}C	$q_e = 117.09 \ln C_e + 207.93$	5.91	21.16	0.965
	40 ^{0}C	$q_e = 117.83 \ln C_e + 238.21$	7.55	22.09	0.98
7	25 ^{0}C	$q_e = 28.23 \ln C_e - 39.18$	0.250	87.76	0.579
	40 ^{0}C	$q_e = 30.54 \ln C_e - 41.67$	0.255	85.22	0.568
8	25 ^{0}C	$q_e = 18.75 \ln C_e - 20.38$	0.337	132.11	0.573
	40 ^{0}C	$q_e = 25.92 \ln C_e - 36.29$	0.247	100.39	0.585
9	25 ^{0}C	$q_e = 33.82 \ln C_e - 76.48$	0.104	73.26	0.621
	40 ^{0}C	$q_e = 28.69 \ln C_e - 63.24$	0.110	90.70	0.913
10	25 ^{0}C	$q_e = 36.28 \ln C_e - 52.04$	0.238	68.29	0.828
	40 ^{0}C	$q_e = 39.85 \ln C_e - 55.59$	0.248	65.31	0.683
11	25 ^{0}C	$q_e = 30.06 \ln C_e - 29.74$	0.372	82.41	0.965
	40 ^{0}C	$q_e = 38.4 \ln C_e - 34.34$	0.409	67.77	0.732
12	25 ^{0}C	$q_e = 34.54 \ln C_e - 36.97$	0.343	71.74	0.539
	40 ^{0}C	$q_e = 26.42 \ln C_e - 26.15$	0.372	98.49	0.502
13	25 ^{0}C	$q_e = 171.94 \ln C_e + 261.98$	4.59	14.41	0.892
	40 ^{0}C	$q_e = 167.7 \ln C_e + 282.84$	5.40	15.52	0.896

Table 49. Continued

Sample No.	Temp.	Linear equation	K_T (L kg^{-1})	b (J mol^{-1})	R^2
14	25 ^{0}C	$q_e = 207.45 \ln C_e + 363$	5.75	11.943	0.972
	40 ^{0}C	$q_e = 238.71 \ln C_e + 388.25$	5.09	10.901	0.996
15	25 ^{0}C	$q_e = 327.85 \ln C_e + 355.15$	2.18	7.557	0.97
	40 ^{0}C	$q_e = 332.97 \ln C_e + 430.37$	3.64	7.815	0.995
16	25 ^{0}C	$q_e = 89.76 \ln C_e - 21.05$	0.79	27.602	0.911
	40 ^{0}C	$q_e = 86.58 \ln C_e + 4.74$	1.06	30.057	0.941
17	25 ^{0}C	$q_e = 112.61 \ln C_e + 274.41$	11.44	22.001	0.98
	40 ^{0}C	$q_e = 140.68 \ln C_e + 206.63$	4.34	18.498	0.903
18	25 ^{0}C	$q_e = 84.94 \ln C_e + 119.19$	4.07	29.168	0.589
	40 ^{0}C	$q_e = 89.34 \ln C_e + 137.18$	4.64	29.127	0.538
19	25 ^{0}C	$q_e = 38.92 \ln C_e + 40.29$	2.82	63.663	0.711
	40 ^{0}C	$q_e = 39.44 \ln C_e + 39.35$	2.71	65.976	0.786
20	25 ^{0}C	$q_e = 58.62 \ln C_e - 17.05$	0.75	42.262	0.888
	40 ^{0}C	$q_e = 55.01 \ln C_e - 8.75$	0.85	47.304	0.899
21	25 ^{0}C	$q_e = 65.07 \ln C_e + 24.94$	1.47	38.073	0.941
	40 ^{0}C	$q_e = 62.03 \ln C_e + 42.55$	1.99	41.951	0.995
22	25 ^{0}C	$q_e = 76.66 \ln C_e - 82.32$	0.34	32.32	0.789
	40 ^{0}C	$q_e = 39.54 \ln C_e + 5.67$	1.15	65.812	0.912

The constant related to strength of bonding (K_T) at 25 ^{0}C was significantly and positively correlated with K_T at 40 ^{0}C (0.841**), negatively correlated with b (-0.442* at 25 ^{0}C, -0.510* at 40 ^{0}C). Constant related to heat of adsorption (b) at 25 ^{0}C showed significant positive correlation with b at 40 ^{0}C (0.925**) and negative correlation with K_T at 40 ^{0}C (-0.513*). K_T at 40 ^{0}C was significantly and negatively correlated with constant related to heat of adsorption (b) at 40 ^{0}C (-0.557**).

Saloid-bound P had significant negative correlation with K_T (-0.445* at 25^{0}C, -0.495* at 40 ^{0}C). Iron bound P had significant negative correlation with b (-0.800** at 25 ^{0}C, -0.841**at 40 ^{0}C). Reductant soluble P was significantly and positively correlated with K_T at 40 ^{0}C (0.432*), negatively correlated with b (-0.478* at 25 ^{0}C, -0.438* at 40 ^{0}C). Calcium bound P had significant positive correlation with b (0.500* at 25 ^{0}C, 0.529* at 40 ^{0}C). Organic P was significantly and positively correlated with K_T (0.512* at 25 ^{0}C, 0.630** at 40 ^{0}C), negatively correlated with b (-0.740** at 25 ^{0}C, -0.803** at 40 ^{0}C). Total P content had significant negative correlation with b (-0.856** at 25 ^{0}C, -0.873** at 40 ^{0}C).

pH was significantly and positively correlated with b at both temperatures (0.456* at 25 ^{0}C, 0.623** at 40 ^{0}C). EC had a significant negative correlation with b (-0.442* at 25 ^{0}C, -0.483* at 40 ^{0}C). OC also showed the same trend, significant negative correlation with b (-0.749** at 25 ^{0}C, -0.817** at 40 ^{0}C). AEC was significantly and positively correlated with b (-0.793** at 25 ^{0}C, -0.878** at 40 ^{0}C).

Sand was significantly and positively correlated with b (0.781** at 25 ^{0}C and 0.786** at 40 ^{0}C), negatively correlated with K_T (-0.576** at 25 ^{0}C and -0.746** at 40 ^{0}C). An opposite trend was observed in the case of silt and clay. Silt was significantly and positively correlated with K_T at 40 ^{0}C (0.480*), negatively correlated with b (-0.513*at 25 ^{0}C, -0.519* at 40 ^{0}C). Clay content had significant positive correlation with K_T (0.672** at 25 ^{0}C, 0.742** at 40 ^{0}C) and negative correlation with b (-0.769** at 25 ^{0}C, -0.774** at 40 ^{0}C).

Available P had significant negative correlation with K_T (-0.481* at 25^{0}C, -0.507* at 40 ^{0}C). Available S had significant negative correlation with constant related to heat of adsorption (b) at 40 ^{0}C (-0.450*). Significant positive correlation of available B with K_T at 40 ^{0}C (0.522*) and negative correlation with b (-0.539** at 25 ^{0}C, -0.506* at 40 ^{0}C) was observed. Av. Fe had significant negative correlation with b (-0.688** at 25 ^{0}C, -0.740** at 40 ^{0}C). Water soluble plus exchangeable Al was significantly and negatively correlated with b (-0.537** at

25 ^{0}C, -0.589** at 40 ^{0}C). CBD extractable Fe had significant positive correlation with K_T (0.580** at 25 ^{0}C and 0.684** at 40 ^{0}C) and negative correlation with b (-0.805** at 25 ^{0}C and -0.836** at 40 ^{0}C.

Table 50. Correlation between parameters of Tempkin adsorption isotherm and soil properties for P adsorption

	K_T at 25 ^{0}C	**b at 25 ^{0}C**	**K_T at 40 ^{0}C**	**b at 40 ^{0}C**
b at 25 ^{0}C	-0.442*			
K_T at 40 ^{0}C	0.841**	-0.513*		
b at 40 ^{0}C	-0.510*	0.925**	-0.557**	
SB-P	-0.445*		-0.495*	
Fe-P		-0.800**		-0.841**
RS-P		-0.478*	0.432*	-0.438*
Ca-P		0.500*		0.529*
Org-P	0.512*	-0.740**	0.630**	-0.803**
Tot-P		-0.856**		-0.873**
pH		0.456*		0.623**
EC		-0.442*		-0.483*
OC		-0.749**		-0.817**
AEC		-0.793**		-0.878**
Sand	-0.576**	0.781**	-0.746**	0.786**
Silt		-0.513*	0.480*	-0.519*
Clay	0.672**	-0.769**	0.742**	-0.774**
Av.N	0.423*	-0.696**	0.555**	-0.783**
Av.P	-0.481*		-0.507*	
Av.Mg		-0.500*		-0.528*
Av.S				-0.450*
Av.Cu		-0.767**	0.439*	-0.784**
Av.Zn				-0.423*
Av.B		-0.539**	0.522*	-0.506*
Av.Fe		-0.688**		-0.743**
WS+Ex.Al		-0.537**		-0.589**
CBD-Fe	0.580**	-0.805**	0.684**	-0.836**

**Correlation is significant at the 0.01 level (2-tailed)
*Correlation is significant at the 0.05 level (2-tailed)

Table 51. Thermodynamic parameters of P adsorption

Sample No.	surface area (m^2 g^{-1})	K^0		ΔG^0 (kcal mol^{-1})		ΔH^0 (kcal mol^{-1})	ΔS^0 (cal mol^{-1} K^{-1})	
		25 ^{0}C	40 ^{0}C	25 ^{0}C	40 ^{0}C		25 ^{0}C	40 ^{0}C
1	62.24	7.92	7.91	-1.225	-1.286	-0.017	4.06	4.06
2	59.23	8.18	8.33	-1.245	-1.318	0.22	4.92	4.92
3	67.45	8.01	8.02	-1.232	-1.295	0.027	4.22	4.22
4	79.66	10.02	9.94	-1.365	-1.429	-0.098	4.25	4.25
5	112.44	9.75	9.99	-1.348	-1.431	0.301	5.53	5.53
6	89.48	9.88	10.16	-1.357	-1.442	0.342	5.7	5.7
7	6.34	6.68	6.78	-1.125	-1.19	0.181	4.38	4.38
8	8.21	6.72	6.55	-1.128	-1.169	-0.322	2.71	2.71
9	6.11	6.04	6.25	-1.065	-1.14	0.431	5.02	5.02
10	8.39	7.36	7.24	-1.182	-1.231	-0.198	3.3	3.3
11	15.66	7.44	7.05	-1.189	-1.215	-0.673	1.73	1.73
12	18.65	6.21	5.72	-1.081	-1.085	-1	0.27	0.27
13	84.32	9.67	9.83	-1.343	-1.422	0.207	5.2	5.2
14	94.07	10	9.92	-1.363	-1.427	-0.092	4.27	4.27
15	124.78	9.08	9.32	-1.307	-1.389	0.323	5.47	5.47
16	38.92	8.22	8.59	-1.248	-1.337	0.533	5.98	5.98
17	40.33	11.4	10.16	-1.441	-1.442	-1.421	0.07	0.07
18	53.56	8.76	8.68	-1.285	-1.344	-0.107	3.95	3.95
19	33.42	8.5	8.72	-1.267	-1.347	0.317	5.32	5.32
20	40.73	7.76	7.89	-1.213	-1.285	0.212	4.78	4.78
21	29.78	9.08	9.52	-1.306	-1.402	0.586	6.35	6.35
22	39.69	7.92	7.91	-1.143	-1.297	1.916	10.26	10.26

Thermodynamics of P adsorption in soil

The thermodynamic parameters of P adsorption are given in Table 51. The thermodynamic equilibrium constant of the soil ranged from 6.04 to 11.4 at 25 ^{0}C and from 5.72 to 10.16 at 40 ^{0}C. The highest value at both temperatures was seen in the laterite soil (Sample No. 17) and lowest at 25 ^{0}C was in coastal sandy soil (Sample No. 9) and at 40 ^{0}C in *Onattukara* sandy soil (Sample No. 12).

The change in free energy was recorded as negative values for adsorption of P in soil at both the temperatures. An increase in negative value of free energy change with increase in temperature in all the soil was observed. Nine soils had negative value for change in enthalpy, whereas the other soils were recorded with positive values. Change in entropy for all the soils were with positive value at both temperatures.

4.3.1.3. Adsorption study of sulphur

Quantity - intensity relation

Quantity - intensity relationship of S in the collected soil samples were studied at two temperatures *viz.* 25 and 40 ^{0}C as described in section 3.3.1.1.3. Q-I curves were plotted from the data obtained with amount of S adsorbed or desorbed on Y axis and equilibrium concentration on X axis.

All the collected soils except laterite soil (Sample No. 17) at 40 ^{0}C had dominance of desorption at both the temperatures. The characteristics of the desorption curves at 25 ^{0}C and 40 ^{0}C are given in Table 52. In most of the soils, adsorption was observed at high concentration of added S and hence the slope of those soils was with a positive value. *Pokkali* soils didn’t show any trend in desorption of S especially at 40 ^{0}C. R^2 value of linear form of best fit curve was >0.5 for all the soils except, *Kuttanad* soil (Sample No. 15 at both temperatures), *Pokkali* soil (Sample No. 1 and 3 at 40 ^{0}C), *Kole* soil (Sample No. 6 at 25 ^{0}C), *Onattukara* sandy soil (Sample No. 11 at 25 ^{0}C) and soils from Palakkad eastern plain (Sample No. 19 and 21 at 40 ^{0}C).

Table 52. Parameters of Q-I curve for S adsorption

Sample No.	Temp	Linear equation	Buffer power (L kg^{-1})	Intercept (mg kg^{-1})	Max. quantity desorbed (mg kg^{-1})	R^2
1	25 ^{0}C	q_e= -3.45C_e - 409.71	-3.45	-409.71	3788.1	0.989
	40 ^{0}C	q_e = -2.02C_e – 3043	-2.02	-3043	5670.65	0.368
2	25 ^{0}C	q_e= -3.41C_e - 625.16	-3.41	-625.16	4255.45	0.997
	40 ^{0}C	q_e= -19.63C_e - 2047	-19.63	-2047	7084.78	0.5
3	25 ^{0}C	q_e= -9.29C_e - 947.7	-9.29	-947.7	4245.91	0.678
	40 ^{0}C	q_e = -0.65C_e - 5738.4	-0.65	-5738.4	6840.22	0.087
4	25 ^{0}C	q_e = 1.14C_e - 159.46	1.14	-159.46	134.78	0.894
	40 ^{0}C	q_e= 1.50C_e - 173.81	1.5	-173.81	135.87	0.99
5	25 ^{0}C	q_e= 1.33C_e - 241.06	1.33	-241.06	203.26	0.958
	40 ^{0}C	q_e= 1.63C_e - 263.01	1.63	-263.01	204.26	0.961
6	25 ^{0}C	q_e= 2.35C_e - 404.24	2.35	-404.24	286.95	0.418
	40 ^{0}C	q_e= 1.935C_e - 388.93	1.93	-388.93	261.96	0.746
7	25 ^{0}C	q_e= 0.49C_e - 72.87	0.49	-72.87	84.25	0.524
	40 ^{0}C	q_e= 0.52C_e - 20.63	0.52	-20.63	18.48	0.927
8	25 ^{0}C	q_e= 1.37C_e - 78.98	1.37	-78.98	62.82	0.943
	40 ^{0}C	q_e= 1.21C_e - 47.25	1.21	-47.25	33.7	0.729
9	25 ^{0}C	q_e= 1.584C_e - 78.05	1.58	-78.05	79.34	0.799
	40 ^{0}C	q_e= 1.25C_e - 63.07	1.25	-63.07	55.43	0.735
10	25 ^{0}C	q_e= 1.15C_e - 94.13	1.15	-94.13	108.70	0.531
	40 ^{0}C	q_e= 0.69C_e - 81.94	0.69	-81.94	95.65	0.567
11	25 ^{0}C	q_e= 0.845C_e - 53.5	0.85	-53.5	121.74	0.103
	40 ^{0}C	q_e= 0.61C_e - 52.13	0.61	-52.13	69.57	0.713
12	25 ^{0}C	q_e= -1.59C_e + 18. 9	1.59	18.9	468.5	0.732
	40 ^{0}C	q_e= 1.63C_e - 167.18	1.63	-167.18	153.26	0.719
13	25^{0}C	q_e= 0.55C_e -498.18	0.55	-498.18	511.95	0.525
	40 ^{0}C	q_e= 2.18C_e – 741.63	2.18	-741.63	513.04	0.919

Table 52. Continued

Sample No.	Temp.	Linear equation	Buffer power (Lkg^{-1})	Intercept (mg kg^{-1})	Max. quantity desorbed (mg kg^{-1})	R^2
14	25 ^{0}C	q_e= 1.38C_e -592.08	1.38	592.08	496.74	0.566
	40 ^{0}C	q_e= 0.77C_e – 573.84	0.77	-573.84	548.91	0.597
15	25 ^{0}C	q_e = 1.87C_e - 1507.6	1.87	-1507.6	1360.87	0.081
	40 ^{0}C	q_e = 0.84C_e - 1117.4	0.84	-1117.4	1138.04	0.007
16	25 ^{0}C	q_e = -1.26C_e - 26.61	-1.26	-26.605	184.78	0.778
	40 ^{0}C	q_e = 0.85C_e - 64.71	0.85	-64.71	75.00	0.726
17	25 ^{0}C	q_e = -1.05C_e - 2.69	-1.05	-2.69	119.55	0.72
	40 ^{0}C	q_e = 1.12C_e + 13.72	1.12	13.72	8.7	0.783
18	25 ^{0}C	q_e = -1.22C_e - 1.44	-1.22	-1.4	146.73	0.641
	40 ^{0}C	q_e = 1.95C_e - 31.49	1.95	-31.49	31.52	0.676
19	25 ^{0}C	q_e = -1.13C_e - 53.92	-1.13	-53.92	153.26	0.693
	40 ^{0}C	q_e = 1.34C_e - 174.58	1.34	-174.58	171.74	0.355
20	25 ^{0}C	q_e = -1.04C_e - 26.64	-1.04	-26.64	154.34	0.634
	40 ^{0}C	q_e = 0.95C_e - 78.93	0.95	-78.93	75.00	0.671
21	25 ^{0}C	q_e = -1.71C_e - 20.64	-1.71	-20.64	257.61	0.813
	40 ^{0}C	q_e = 0.63C_e - 119.49	0.63	-119.49	177.17	0.23
22	25 ^{0}C	q_e = -1.85C_e + 21.29	-1.85	21.29	560.86	0.817
	40 ^{0}C	q_e = 1.27C_e - 86.05	1.27	-86.05	82.61	0.669

Negative value of buffer power was observed in all the *Pokkali* soils (Sample No.1, 2 and 3) at both the temperatures. It was also observed in laterite soils (Sample No. 16, 17 and 18) and soils from Palakkad eastern plain (Sample No. 19, 20, 21 and 22) at 25 ^{0}C. Highest buffer power at 25 ^{0}C (2.35 L kg^{-1}) was observed in the soil from *Kole* land (Sample No. 6), whereas the highest value of 2.18 L kg^{-1} at 40 ^{0}C was observed in *Kuttanad* soil (Sample No. 13). An increase in buffer power with increase in temperature was observed in fourteen samples.

Highest value of maximum quantity desorbed was observed in *Pokkali* soil (Sample No. 2) at both 25 ^{0}C (4255.45 mg kg^{-1}) and 40 ^{0}C (7084.78 mg kg^{-1}). Increase in maximum quantity desorbed with increase in temperature was observed in three soils of *Pokkali* (Sample No. 1, 2 and 3), *Kole* (Sample No. 4 and 5), *Kuttanad* (Sample No. 13 and 14). Lowest value of maximum quantity desorbed at 40 ^{0}C (8.7 mg kg^{-1}) was observed in the laterite soil (Sample No. 17). Lowest value of maximum quantity desorbed at 25 ^{0}C (79.34 mg kg^{-1}) was observed in coastal sandy soil (Sample No. 9). Very high values of maximum quantity desorbed was recorded in *Pokkali* soils at both temperatures. Coastal sandy soils were with low values of maximum quantity desorbed.

Correlation coefficients of the parameters of Q-I curve of S adsorption/desorption with soil properties is given in Table 53. Maximum quantity desorbed at 25 ^{0}C was significantly and negatively correlated with buffer power at 25^{0}C (-0.745**). Buffer power at 40 ^{0}C had significant negative correlation with maximum quantity desorbed at 25 ^{0}C (-0.681**). Maximum quantity desorbed at 40 ^{0}C showed significant positive correlation with maximum quantity desorbed at 25 ^{0}C (0.992**); negative correlation with buffer power at 25 ^{0}C (-0.757**) and 40 ^{0}C (-0.713**).

Buffer power at both temperatures had significant negative correlation with all the S fractions. Maximum quantity desorbed at both temperatures had significant positive correlation with all the S fractions. Available P showed significant negative correlation with buffer power at 25 ^{0}C (-0.464*); positive correlation with maximum quantity desorbed at 25 ^{0}C (0.453*) and 40 ^{0}C (0.473*). Available Cu was with the same trend of available P, negative correlation with buffer power and positive correlation with maximum quantity desorbed. Available S was significantly and positively correlated with maximum quantity desorbed (0.986** at 25 ^{0}C, 0.994** at 40 ^{0}C); negatively correlated with buffer power (-0.796** at 25 ^{0}C, -0.647**40 ^{0}C). Available Mg and available Zn also had same trend. Ex.Na had significant positive correlation with maximum quantity desorbed at 25 ^{0}C (0.630**) and at 40 ^{0}C (0.626**) and negative correlation with buffer power at 40 ^{0}C (-0.822**). WS+Ex.Al showed significant positive correlation with maximum quantity desorbed (0.924** at 25 ^{0}C and 0.897** at 40 ^{0}C) and negative correlation with buffer power (-0.531* at 25 ^{0}C and -0.663** at 40 ^{0}C).

Table 53. Correlation between parameters of Q-I curve and soil properties for S desorption/adsorption

	Buffer power at 25 ^{0}C	Max. quantity desorbed at 25 ^{0}C	Buffer power at 40 ^{0}C	Max. quantity desorbed at 40 ^{0}C
Maxi.quantity desorbed at 25 ^{0}C	-0.745**			
Buffer power at 40 ^{0}C		-0.681**		
Max. quantity desorbed at 40 ^{0}C	-0.757**	0.992**	-0.713**	
Suphate S	-0.796**	0.986**	-0.647**	0.994**
Total water soluble S	-0.804**	0.980**	-0.650**	0.992**
Heat soluble S	-0.801**	0.983**	-0.643**	0.993**
Sulphate soluble after ignition	-0.539**	0.910**	-0.852**	0.917**
Total organic S	-0.735**	0.990**	-0.676**	0.993**
Total S	-0.752**	0.991**	-0.700**	0.999**
Av.P	-0.464*	0.453*		0.473*
Av.Mg	-0.766**	0.988**	-0.661**	0.983**
Av.S	-0.796**	0.986**	-0.647**	0.994**
Av.Fe		0.640**		0.606**
Av.Cu	-0.569**	0.656**		0.657**
Av.Zn	-0.833**	0.976**	-0.624**	0.985**
Ex.Na		0.630**	-0.822**	0.626**
WS+Ex.Al	-0.531*	0.924**	-0.663**	0.897**

**Correlation is significant at the 0.01 level (2-tailed)
*Correlation is significant at the 0.05 level (2-tailed)

Adsorption isotherm

Soil sample with minimum four points of adsorption with increasing concentration of added S was considered for adsorption isotherm fitting. It was observed only in laterite soil (Sample No. 17) at 40 ^{0}C. For all other soils dominance of desorption was observed. So isotherms were fitted only for laterite soil (Sample No. 17) at 40 ^{0}C. Parameters of three different adsorption isotherm of Sample No. 17 at 40 ^{0}C are given in Table 54. Data were fitted well with all the three isotherms. Comparing the R^2 value, It was found that linear fit of Tempkin adsorption isotherm was the best to explain S adsorption in laterite soil (Sample No. 17) followed by Langmuir adsorption isotherm and Freundlich adsorption isotherm.

The value of 1/n value of Freundlich adsorption isotherm was 0.624 and K_F was recorded as 7.83. Adsorption maxima (q_m) and K_L of Langmuir adsorption isotherm was 222.22 mg kg^{-1} and 0.015 L mg^{-1} respectively. Value of consatnt related to heat of adsorption (b) and constant related to adsorption strength (K_T) of Tempkin isotherm was 47.29 J mol^{-1} and 0.137 L kg^{-1} respectively.

Table 54. Parameters of different adsorption isotherm for S adsorption in laterite soil (17) at 40 ^{0}C

Freundlich adsorption isotherm			
Linear equation	**1/n**	**K_F (mg kg^{-1}) (L kg^{-1})$^{1/n}$**	**R^2**
$\log q_e = 0.62 \log C_e + 0.89$	0.624	7.83	0.848
Langmuir adsorption isotherm			
Linear equation	**q_m (mg kg^{-1})**	**K_L(L mg^{-1})**	**R^2**
$C_e/q_e = 0.0045\ C_e + 0.298$	222.22	0.015	0.896
Tempkin adsorption isotherm			
Linear equation	**b(J mol^{-1})**	**K_T (L kg^{-1})**	**R^2**
$q_e = 52.39 \ln C_e - 104.3$	47.29	0.137	0.945

Thermodynamics of S adsorption/desorption in soil

Table 55. Thermodynamic parameters of S adsorption/desorption

Sample No.	surface area (m^2g^{-1})	K^0		ΔG^0 (kcal mol^{-1})		ΔH^0 (kcal mol^{-1})	ΔS (cal mol^{-1} K^{-1})	
		25 ^{0}C	40 ^{0}C	25 ^{0}C	40 ^{0}C		25 ^{0}C	40 ^{0}C
Desorption								
1	62.24	4.52	4.57	-0.893	-0.945	0.15	3.50	3.50
2	59.23	4.58	4.63	-0.901	-0.953	0.13	3.47	3.47
3	67.45	3.63	4.50	-0.763	-0.936	2.66	11.49	11.49
4	79.66	3.69	2.82	-0.773	-0.644	-3.33	-8.57	-8.57
5	112.44	3.51	3.08	-0.743	-0.699	-1.61	-2.92	-2.92
6	89.48	3.72	3.65	-0.778	-0.804	-0.25	1.77	1.77
7	6.34	5.72	5.50	-1.033	-1.06	-0.50	1.79	1.79
8	8.21	4.99	4.45	-0.952	-0.929	-1.42	-1.56	-1.56
9	6.11	5.00	5.00	-0.953	-1.001	0.01	3.24	3.24
10	8.39	5.58	5.36	-1.018	-1.044	-0.49	1.76	1.76
11	15.66	4.13	4.48	-0.84	-0.933	1.01	6.21	6.21
12	18.65	4.14	4.60	-0.841	-0.949	1.31	7.21	7.21
13	84.32	3.65	3.62	-0.766	-0.8	-0.10	2.23	2.23
14	94.07	3.55	3.65	-0.75	-0.806	0.35	3.68	3.68
15	124.78	3.53	3.31	-0.746	-0.744	-0.79	-0.14	-0.14
16	38.92	3.89	4.14	-0.805	-0.884	0.76	5.25	5.25
17	40.33	3.22	-	-0.693	-	-	-	-
18	53.56	3.97	2.46	-0.816	-0.559	-5.92	-17.12	-17.12
19	33.42	4.48	4.20	-0.888	-0.892	-0.80	0.31	0.31
20	40.73	3.94	3.68	-0.811	-0.81	-0.84	-0.08	-0.08
21	29.78	4.53	4.83	-0.895	-0.979	0.79	5.64	5.64
22	39.69	3.93	3.94	-0.81	-0.853	0.04	2.85	2.85
Adsorption								
17	40.33	-	3.95	-	-0.855	-	-	-

Thermodynamic parameters of S adsorption in laterite soil (Sample No. 17 at 40 ^{0}C) and S desorption in the remaining 21 samples are given in Table 55. The value of thermodynamic equilibrium constant (K^0) for S adsorption in laterite soil (Sample No. 17) was recorded as 3.22 at 25 ^{0}C and 3.95 at 40 ^{0}C. Change in free energy for S adsorption/desorption at both the temperatures were negative. Change in enthalpy and entropy was found as positive for S adsorption in laterite soil (Sample No. 17) at 40 ^{0}C.

K^0 for S desorption at 25 ^{0}C ranged from 3.51 to 5.7. Lowest value was recorded in soil from *Kole* land (Sample No. 5) and the highest value was recorded in coastal sandy soil (Sample No. 7). Highest K^0 at 40 ^{0}C (5.36) was recorded in *Onattukara* sandy soil (Sample No. 10) and the lowest K^0 (2.46) was recorded in laterite soil (Sample No. 18). Change in free energy was negative for S desorption at both temperatures. Eleven soils were recorded with negative value for enthalpy change with regard to S desorption. Six samples were recorded with negative value for change in entropy and the remaining was positive.

4.3.1.4. Adsorption study of boron

Quantity- intensity relationship

Adsorption study of B was carried out as described in section 3.3.1.4. The Q-I curves were fitted with the adsorption data.The parameters of the Q-I curve and maximum B adsorbed per unit weight of the soil from the added concentration of B are given in Table 56. More than 50 per cent of variation in Q-I relation could be explained in all soils except in *Pokkali* soil (sample 1, 3), laterite soil (Sample No. 17), soil from Palakkad eastern plain (Sample No. 19, 20) at 40 ^{0}C and coastal sandy soil (Sample No. 9) at 25 ^{0}C. Dominance of desorption was observed at 40 ^{0}C. Complete desorption was observed in coastal sandy soil (Sample No. 9) at 40 ^{0}C. No other soils had complete desorption and hence only the coastal sandy soil (Sample No.9) at 40 ^{0}C was recorded with negative slope (buffer power).

Highest buffer power at 25 ^{0}C (2.42 L kg^{-1}) and 40 ^{0}C (2.37 L kg^{-1}) was observed in the soil from *Kole* land in Sample No. 4 and 6 respectively. Lowest buffer power at 25 ^{0}C (0.21 L kg^{-1}) was observed in *Onattukara* sandy soil (Sample No.12) whereas the lowest buffer power at 40 ^{0}C (-0.79 L kg^{-1}) was observed in coastal sandy soil (Sample No. 9).

Table 56. Parameters of Q-I curve for B adsorption

Sample No.	Temp	Linear equation	Buffer power (L kg^{-1})	Intercept (mg kg^{-1})	Max. quantity adsorbed (mg kg^{-1})	R^2
1	25 ^{0}C	$q_e= 2.17\ C_e - 2.99$	2.17	-2.99	28.7	0.909
	40 ^{0}C	$q_e = 0.62C_e - 1.55$	0.62	-1.55	14.98	0.403
2	25 ^{0}C	$q_e= 1.1\ C_e - 2.41$	1.1	-2.41	12	0.942
	40 ^{0}C	$q_e= 0.61\ C_e - 2.52$	0.61	-2.52	10.23	0.472
3	25 ^{0}C	$q_e = 0.616C_e - 1.00$	0.616	-1	6.5	0.808
	40 ^{0}C	$q_e = 0.621C_e - 2.41$	0.621	-2.41	9.67	0.486
4	25 ^{0}C	$q_e = 2.42C_e - 4.90$	2.42	-4.9	36	0.824
	40 ^{0}C	$q_e = 1.24C_e - 0.41$	1.24	-0.41	18.9	0.996
5	25 ^{0}C	$q_e = 0.89C_e + 0.14$	0.89	0.14	11.9	0.946
	40 ^{0}C	$q_e = 2.37C_e - 4.95$	2.37	-4.95	16.47	0.747
6	25 ^{0}C	$q_e = 0.9C_e - 0.19$	0.9	-0.19	13.5	0.957
	40 ^{0}C	$q_e = 0.42C_e + 0.37$	0.42	0.37	6.2	0.59
7	25 ^{0}C	$q_e = 0.23C_e - 0.41$	0.23	-0.41	3.3	0.82
	40 ^{0}C	$q_e = 1.55C_e - 2.61$	1.55	-2.61	9.045	0.776
8	25 ^{0}C	$q_e = 0.35C_e - 0.67$	0.35	-0.67	5	0.983
	40 ^{0}C	$q_e = 0.36C_e - 0.87$	0.36	-0.87	2.88	0.519
9	25 ^{0}C	$q_e= 0.97\ C_e + 0.82$	0.97	0.82	17.24	0.158
	40 ^{0}C	$q_e= -0.79\ C_e - 0.58$	-0.79	-0.58	desorption	0.942
10	25 ^{0}C	$q_e= 0.30C_e - 0.33$	0.30	-0.33	4.6	0.788
	40 ^{0}C	$q_e = 0.39\ C_e - 1.35$	0.39	-1.35	1.9	0.653
11	25 ^{0}C	$q_e = 0.34\ C_e - 0.42$	0.34	-0.42	4.9	0.874
	40 ^{0}C	$q_e = 0.41\ C_e - 1.43$	0.41	-1.43	1.93	0.668
12	25 ^{0}C	$q_e= 0.21\ C_e + 0.21$	0.21	0.21	3.6	0.734
	40 ^{0}C	$q_e= 1.94\ C_e - 2.42$	1.94	-2.42	9.22	0.712
13	25 ^{0}C	$q_e = 0.63C_e - 0.33$	0.63	-0.33	4.35	0.712
	40 ^{0}C	$q_e = 0.66C_e - 1.37$	0.66	-1.37	4.3	0.921
14	25 ^{0}C	$q_e = 0.85C_e + 0.15$	0.85	0.15	5.87	0.88
	40 ^{0}C	$q_e = 0.56C_e - 0.67$	0.56	-0.67	5.36	0.908

Table 56. Continued

Sample No.	Temp	Linear equation	Buffer power (L kg^{-1})	Intercept (mg kg^{-1})	Max. quantity Adsorbed (mg kg^{-1})	R^2
15	25 ^{0}C	$q_e = 0.94C_e + 0.03$	0.94	0.03	12.4	0.866
	40 ^{0}C	$q_e = 0.78C_e - 0.86$	0.78	-0.86	10.4	0.801
16	25 ^{0}C	$q_e = 1.09C_e + 0.17$	1.09	0.17	16	0.97
	40 ^{0}C	$q_e = 0.7C_e - 0.49$	0.7	-0.49	9.6	0.701
17	25 ^{0}C	$q_e = 1.16C_e + 0.44$	1.16	0.44	16.7	0.966
	40 ^{0}C	$q_e = 0.84C_e + 1.72$	0.84	1.72	18.34	0.117
18	25 ^{0}C	$q_e = 0.94C_e + 2.57$	0.94	2.57	17.6	0.646
	40 ^{0}C	$q_e = 1.10x - 0.07$	1.10	-0.07	17.4	0.914
19	25 ^{0}C	$q_e = 0.59C_e + 0.94$	0.59	0.94	9.95	0.468
	40 ^{0}C	$q_e = 0.23C_e + 1.13$	0.23	1.13	5.15	0.37
20	25 ^{0}C	$q_e = 0.58C_e + 0.3$	0.58	0.3	8.8	0.953
	40 ^{0}C	$q_e = 0.16C_e - 0.39$	0.16	-0.39	4.36	0.169
21	25 ^{0}C	$q_e = 1.03C_e - 0.13$	1.03	-0.13	14.7	0.98
	40 ^{0}C	$q_e = 0.36C_e + 0.47$	0.36	0.47	6.31	0.477
22	25 ^{0}C	$q_e = 0.87C_e - 0.96$	0.87	-0.96	12	0.962
	40 ^{0}C	$q_e = 0.14C_e - 0.62$	0.14	-0.62	2.68	0.205

Positive intercept was noted in one sample from laterite soil (Sample No. 17) and in one sample from Palakkad eastern plain (Sample No. 19) at both temperatures. Soil from Palakkad eastern plain (Sample No. 21) was noted with positive intercept at 40 ^{0}C. All the remaining soils were with negative value of intercept at 40 ^{0}C. Highest value of maximum quantity adsorbed at both temperatures (36 mg kg^{-1} at 25 ^{0}C, 18.9 mg kg^{-1} at 40 ^{0}C) was observed in the soil from *Kole* land (Sample No. 4) and the lowest value at 25 ^{0}C (3.3 mg kg^{-1}) in coastal sandy soil (Sample No. 7). Coastal sandy soil (Sample No. 9) didn’t show any adsorption with added concentration of B at 40 ^{0}C. All the soils except five samples had a decrease in the value of maximum quantity adsorbed with increase in temperature. A decrease in buffer power with increase in temperature was noted in thirteen soil samples showed.

Table 57. Correlation between parameters of Q-I curve and soil properties for B adsorption

	Buffer power at 25 ^{0}C	**Max. quantity adsorbed at 25 ^{0}C**	**Buffer power at 40 ^{0}C**	**Max. quantity adsorbed at 40 ^{0}C**
Buffer power at 25 ^{0}C		0.957**		0.602**
Max. quantity adsorbed at 40 ^{0}C				0.601**
EC			0.600**	
AEC	0.548**			0.554**
Clay				0.437*
RS-B	0.648**	0.551**		0.475*
SA-B			0.574**	
OR-B	0.579**			
Res-B	0.614**	0.481*		
Total-B	0.660**	0.515*		
Av.Mg			0.538**	
Av.S			0.523*	
Av.Mn		0.460*		
Av.Cu	0.689**	0.571**		0.670**
Av.Zn			0.498*	
Av.B	0.591**	0.500*		
Ex.Fe	0.464*			
Ex.Mn	0.535*	0.557**		0.614**
WS+Ex.Al			0.566**	
CBD-Fe	0.437*		0.442*	

**Correlation is significant at the 0.01 level (2-tailed)
*Correlation is significant at the 0.05 level (2-tailed)

Correlation coefficients of parameters Q-I curve of B adsorption with soil properties are given in Table 57. Buffer power at 25 ^{0}C had significant positive correlation with AEC (0.548**), RS-B (0.648**), OR-B(0.579**), Res B (0.614**), total B (0.660**), Av.Cu (0.689**), Av.B (0.591**), Ex.Fe (0.464*), Ex. Mn (0.535*) and CBD-Fe (0.437*). Maximum quantity adsorbed at 25 ^{0}C had significant positive correlation with buffer power at 25 ^{0}C (0.957**), RS-B (0.551**), Res-B (0.481*), total B (0.515*), Av.Mn (0.460*), Av.Cu (0.571**), Av.B (0.500*) and Ex. Mn (0.557**).

Buffer power at 40 ^{0}C had significant positive correlation with EC (0.600**),SA-B (0.574**), Av.Mg (0.538**), Av.S (0.523*), Av.Zn (0.498*), WS+Ex. Al (0.566**) and CBD- Fe(0.442*). Maximum quantity adsorbed at 40^{0}C had significant positive correlation with buffer power at 25 ^{0}C (0.602**), maximum quantity adsorbed at 25 ^{0}C (0.601**), AEC (0.554**), clay (0.437*), RS-B (0.475*), Av.Cu (0.670**) and Ex.Mn (0.614**).

Adsorption isotherms

Only the samples which got minimum four points with positive slope in quantity-intensity curve was used for adsorption isotherm fitting, remaining samples were having dominance of desorption. Dominance of desorption was observed in all the samples from *Onattukara* sandy plain (Sample No. 10, 11 and 12), coastal sandy plain (Sample No. 7 and 8), two samples from *Pokkali* (Sample No. 2 and 3), one sample from Palakkad eastern plain (Sample No. 22) at 40^{0}C and one sample from northern coastal plain (Sample No. 9) at both 25 ^{0}C and 40 ^{0}C. Adsorption data of remaining soils were used for isotherm fitting. None of the samples followed Langmuir adsorption isotherm. Data of adsorption of B in laterite soil (Sample No. 17) and soil from Palakkad eastern plain (Sample No. 20) at 40 ^{0}C were not fitted in any of the adsorption isotherm. Most of the soils collected from low lands of *Pokkali and Kole* had better fitting of data in Tempkin adsorption isotherm than Freudlich isotherm. Reverse trend was observed in case of soils collected from Palakkad eastern plain. Comparing the total number of samples with R^2 value >0.5, it was found that Freundlich adsorption isotherm explains B adsorption in the collected soil samples.

Freundlich adsorption isotherm

Kuttanad soil (Sample No. 14) at 25 ^{0}C was not fitted into Freundlich adsorption isotherm. The parameters of Freundlich adsorption isotherm for B adsorption are given in Table 58. Highest value of 1/n at 25 ^{0}C (1.782) was observed in the soil from Palakkad eastern plain (Sample No. 22) and the lowest value at 25 ^{0}C (0.582) in *Onattukara* sandy soil (Sample No. 10). Highest value of 1/n at 40 ^{0}C (1.779) was noted in the soil from *Kole* land (Sample No. 5) and the lowest value (0.524) in the soil from Palakkad eastern plain (Sample No. 21).

Highest value of constant related to adsorption strength (K_F) at 25 ^{0}C (13.67) was observed in the soil from Palakkad eastern plain (Sample No. 21) and the lowest value at 25 ^{0}C (0.13) in the soil from Palakkad eastern plain (Sample No. 22). Highest value of K_F at 40 ^{0}C (9.94) was in the laterite soil (Sample No. 18) and the lowest value (0.088) in the soil from *Pokkali* soil (Sample No. 1).

Tempkin adsorption isotherm

Soil from Palakkad eastern plain (Sample No. 21) at 40 ^{0}C was not fitted into Tempkin adsorption isotherm. The parameters of Tempkin adsorption isotherm is given in Table 59. Highest value (2.068 L kg^{-1} at 25 ^{0}C) of K_T at both temperatures was seen in the soil from Palakkad eastern plain. The lowest value (0.424 L kg^{-1} at 25 ^{0}C) of K_T was observed in *Pokkali* soil (Sample No. 2) and that at 40 ^{0}C (0.794 L kg^{-1}) in *Kuttanad* soil (Sample No. 15). Highest value of b at 25 ^{0}C (2574.90 J mol^{-1}) was observed in *Onattukara* sandy soil (Sample No. 12), and the lowest (201 J mol^{-1}) in the *Pokkali* soil (Sample No. 1). Highest value of b at 40 ^{0}C (2614.57 J mol^{-1}) was recorded in soil from *Kuttanad* (Sample No. 14) and the lowest value (463.47 J mol^{-1}) in the soil from *Kole* land (Sample No. 4).

Table 58. Parameters of Freundlich adsorption isotherm for B adsorption

Sample No.	**Temp**	**Linear equation**	**1/n**	**K_F (mg kg^{-1}) (L kg^{-1})$^{1/n}$**	**R^2**
1	25 ^{0}C	$\log q_e = 0.893 \log C_e + 0.3$	0.893	1.995	0.5
	40 ^{0}C	$\log q_e = 1.613 \log C_e - 1.053$	1.613	0.088	0.643
2	25 ^{0}C	$\log q_e = 1.611 \log C_e - 0.695$	1.611	0.202	0.939
3	25 ^{0}C	$\log q_e = 1.075 \log C_e - 0.303$	1.075	0.497	0.816
4	25 ^{0}C	$\log q_e = 1.186 \log C_e - 0.252$	1.186	0.560	0.462
	40 ^{0}C	$\log q_e = 1.076 \log C_e - 0.006$	1.076	0.986	0.996
5	25 ^{0}C	$\log q_e = 1.352 \log C_e - 0.280$	1.352	0.526	0.827
	40 ^{0}C	$\log q_e = 1.779 \log C_e - 0.660$	1.779	0.221	0.541
6	25 ^{0}C	$\log q_e = 1.111 \log C_e - 0.128$	1.111	0.744	0.931
	40 ^{0}C	$\log q_e = 1.592 \log C_e - 0.769$	1.592	0.170	0.610
7	25 ^{0}C	$\log q_e = 0.619 \log C_e - 0.376$	0.619	0.420	0.500
8	25 ^{0}C	$\log q_e = 1.281 \log C_e - 0.844$	1.281	0.143	0.974
10	25 ^{0}C	$\log q_e = 0.582 \log C_e - 0.188$	0.582	0.648	0.428
11	25 ^{0}C	$\log q_e = 0.818 \log C_e - 0.332$	0.812	0.465	0.767
12	25 ^{0}C	$\log q_e = 1.198 \log C_e - 0.751$	1.198	0.177	0.758
13	25 ^{0}C	$\log q_e = 0.907 \log C_e - 0.310$	0.907	0.490	0.704
	40 ^{0}C	$\log q_e = 0.595 \log C_e - 0.130$	0.595	0.743	0.756
14	40 ^{0}C	$\log q_e = 0.683 \log C_e - 0.408$	0.683	0.390	0.547
15	25 ^{0}C	$\log q_e= 1.084 \log C_e - 0.050$	1.084	0.893	0.944
	40 ^{0}C	$\log q_e = 0.856 \log C_e + 0.062$	0.856	1.152	0.18
16	25 ^{0}C	$\log q_e = 1.053 \log C_e + 0.042$	1.053	1.100	0.971
	40 ^{0}C	$\log q_e = 0.890 \log C_e + 0.070$	0.890	1.015	0.736
17	25 ^{0}C	$\log q_e = 0.902 \log C_e + 0.200$	0.902	1.585	0.970
18	25 ^{0}C	$\log q_e = 0.858 \log C_e + 0.302$	0.858	2.003	0.788
	40 ^{0}C	$\log q_e = 0.997 \log C_e + 0.030$	0.997	9.94	0.870
19	25 ^{0}C	$\log q_e = 0.737 \log C_e + 0.173$	0.737	1.488	0.650
	40 ^{0}C	$\log q_e = 0.841 \log C_e - 0.190$	0.841	0.652	0.598
20	25 ^{0}C	$\log q_e = 1.002 \log C_e - 0.156$	1.002	0.697	0.969
21	25 ^{0}C	$\log q_e = 1.136 \log C_e - 0.090$	1.136	13.67	0.982
	40 ^{0}C	$\log q_e = 0.524 \log C_e + 0.190$	0.524	1.533	0.50
22	25 ^{0}C	$\log q_e = 1.782 \log C_e - 0.890$	1.782	0.130	0.888

Table 59. Parameters of Tempkin adsorption isotherm for B adsorption

Sample No.	**Temp**	**Linear equation**	**K_T (L kg^{-1})**	**b (J mol^{-1})**	**R^2**
1	25 ^{0}C	$q_e = 12.33 \ln C_e - 8.325$	0.508	201.00	0.683
2	25 ^{0}C	$q_e = 6.55 \ln C_e - 5.606$	0.424	378.47	0.906
3	25 ^{0}C	$q_e = 3.09 \ln C_e - 1.119$	0.695	802.58	0.921
4	25 ^{0}C	$q_e = 11.7 \ln C_e - 8.158$	0.497	211.85	0.547
	40 ^{0}C	$q_e = 5.62 \ln C_e - 0.502$	0.914	463.47	0.827
5	25 ^{0}C	$q_e = 3.74 \ln C_e + 0.8$	1.238	662.19	0.935
	40 ^{0}C	$q_e = 3.97 \ln C_e + 1.565$	1.483	656.08	0.892
6	25 ^{0}C	$q_e = 3.63 \ln C_e + 0.658$	1.198	681.98	0.824
	40 ^{0}C	$q_e = 2.14 \ln C_e + 0.813$	1.461	1214.03	0.754
7	25 ^{0}C	$q_e = 1.07 \ln C_e - 0.336$	0.730	2314.84	0.553
8	25 ^{0}C	$q_e = 2.23 \ln C_e - 1.891$	0.428	1109.03	0.857
10	25 ^{0}C	$q_e = 1.43 \ln C_e - 0.269$	0.828	1737.79	0.505
11	25 ^{0}C	$q_e = 1.79 \ln C_e - 0.693$	0.678	1388.23	0.741
12	25 ^{0}C	$q_e = 0.96 \ln C_e + 0.059$	1.063	2574.90	0.476
13	25 ^{0}C	$q_e = 1.31 \ln C_e + 0.708$	1.715	1887.53	0.624
	40 ^{0}C	$q_e = 1.24 \ln C_e + 0.280$	1.254	2101.67	0.615
14	25 ^{0}C	$q_e = 2.35 \ln C_e + 1.114$	1.608	1056.35	0.976
	40 ^{0}C	$q_e = 1 \ln C_e + 0.251$	1.287	2614.57	0.332
15	25 ^{0}C	$q_e = 4.78 \ln C_e - 0.418$	0.916	517.85	0.946
	40 ^{0}C	$q_e = 4.18 \ln C_e - 0.961$	0.794	622.30	0.985
16	25 ^{0}C	$q_e = 4.51 \ln C_e + 1.165$	1.294	549.18	0.9
	40 ^{0}C	$q_e = 3.59 \ln C_e - 0.105$	0.971	724.91	0.873
17	25 ^{0}C	$q_e = 6.94 \ln C_e - 2.707$	0.676	357.02	0.985
18	25 ^{0}C	$q_e = 4.91 \ln C_e + 2.488$	1.660	504.79	0.737
	40 ^{0}C	$q_e = 4.70 \ln C_e + 0.216$	1.046	553.38	0.731
19	25 ^{0}C	$q_e = 2.62 \ln C_e + 1.906$	2.068	944.41	0.733
	40 ^{0}C	$q_e = 1.19 \ln C_e + 1.275$	2.920	2186.97	0.595
20	25 ^{0}C	$q_e = 2.57 \ln C_e + 0.735$	1.331	965.05	0.937
21	25 ^{0}C	$q_e = 4.33 \ln C_e + 0.714$	1.179	572.57	0.890
22	25 ^{0}C	$q_e = 4.57 \ln C_e - 2.026$	0.641	542.54	0.853

Table 60. Thermodynamic parameters of B adsorption/desorption

Sample No.	Surface area (m^2 g^{-1})	K^0		ΔG^0 (kcal mol^{-1})		ΔH^0 (K cal mol^{-1})	ΔS^0 (cal mol^{-1} K^{-1})	
		25 ^{0}C	40 ^{0}C	25 ^{0}C	40 ^{0}C		25 ^{0}C	40 ^{0}C
Adsorption								
1	62.24	3.12	1.99	-0.674	-0.426	-5.59	-16.49	-16.49
2	59.23	2.52	-	-0.548	-	-	-	-
3	67.45	2.35	-	-0.505	-	-	-	-
4	79.66	2.17	2.90	-0.459	-0.662	3.58	13.54	13.54
5	112.44	1.47	2.71	-0.229	-0.62	7.55	26.09	26.09
6	89.48	2.33	2.36	-0.501	-0.534	0.16	2.23	2.23
7	6.34	3.82	-	-0.794	-	-	-	-
8	8.21	5.17	-	-0.973	-	-	-	-
10	8.39	3.66	-	-0.768	-	-	-	-
11	15.66	3.40	-	-0.725	-	-	-	-
12	18.65	2.52	-	-0.547	-	-	-	-
13	84.32	1.98	1.49	-0.405	-0.248	-3.52	-10.46	-10.46
14	94.07	1.64	1.04	-0.291	-0.024	-5.60	-17.82	-17.82
15	124.78	2.38	2.16	-0.513	-0.479	-1.19	-2.26	-2.26
16	38.92	3.68	3.44	-0.772	-0.768	-0.85	-0.25	-0.25
17	40.33	3.81	3.71	-0.792	-0.815	-0.33	1.54	1.54
18	53.56	3.80	3.45	-0.791	-0.77	-1.20	-1.37	-1.37
19	33.42	3.54	2.85	-0.749	-0.652	-2.68	-6.47	-6.47
20	40.73	3.11	1.87	-0.671	-0.389	-6.27	-18.80	-18.80
21	29.78	3.57	3.43	-0.753	-0.766	-0.51	0.83	0.83
22	39.69	2.06	-	-0.428	-	-	-	-
Desorption								
2	-	-	3.56	-	-0.79	-	-	-
3	-	-	3.15	-	-0.713	-	-	-
7	-	-	5.34	-	-1.042	-	-	-
8	-	-	5.05	-	-1.008	-	-	-
9	6.11	5.57	4.83	-1.017	-0.979	-1.76	-2.49	-2.49
10	-	-	5.15	-	-1.02	-	-	-
11	-	-	4.77	-	-0.972	-	-	-
12	-	-	2.55	-	-0.583	-	-	-
22	-	-	3.05	-	-0.694	-	-	-

Thermodynamics of B adsorption/desorption in soil

Dominance of desorption was observed in coastal sandy soil (Sample No. 9) at both temperatures. Hence all thermodynamic parameters of B desorption was worked out in this soil. Dominance of desorption was observed in all the samples from *Onattukara* sandy plain (Sample No. 10, 11 and 12), northern coastal plain (7 and 8), two samples from *Pokkali* (2, 3), one sample from Palakkad eastern plain (Sample No. 22) at 40 ^{0}C. Thermodynamic parameters of B adsorption/desorption is given in Table 60.

Highest value of thermodynamic equilibrium constant (K^0) for B adsorption at 25 ^{0}C (3.57) was noted in the soil from Palakkad eastern plain (Sample No. 21) and the lowest value (1.47) in the soil from *Kole* land (Sample No. 5). Highest value of K^0 for B adsorption at 40 ^{0}C (3.71) was recorded in laterite soil (Sample No. 17) and the lowest value (1.04) in the soil from *Kuttanad* (Sample No. 14). Highest value of K^0 for B desorption at 40 ^{0}C (5.05) was noted in coastal sandy soil (Sample No. 8) and, the lowest value (2.55) in the *Onattukara* sandy soil (Sample No. 12).

Adsorption and desorption of B in the soil had negative value for change in free energy. Change in enthalpy was positive for adsorption of B in *Kole* land (Sample No. 4, 5 and 6). Remaining soils had negative value of change in enthalpy for adsorption of B. Change in entropy was positive for adsorption of B in all the soil from *Kole* land (Sample No. 4, 5 and 6), one laterite soil (Sample No. 17) and one soil from Palakkad eastern plain (Sample No. 21). Remaining soils were with negative value for change in entropy.

4.3.1.5. Adsorption study of molybdenum

Quantity- intensity relationship

Soil samples were equilibrated with different concentrations of Mo as described in 3.3.1.1.5. The parameters of Q-I curve is given in Table 61. All the soils except four samples were reported (Sample No. 7, 12 and 16 at 40 ^{0}C, Sample No.19 and 20 at 25 ^{0}C) with R^2 values > 0.5 at both temperatures.

Maximum quantity of Mo adsorbed per unit weight of soil at 25 ^{0}C ranged from 59.1 to 982.85 mg kg^{-1}. The lowest value was noted in the soil from northern coastal plain (Sample No. 10) and the highest value in the *Kuttanad* soil (Sample No. 15). The lowest value of maximum quantity adsorbed per unit weight of soil at 40^{0}C (55.6 mg kg^{-1}) was recorded in the soil from Palakkad eastern plain (Sample No. 21). Highest value was recorded at both the temperature (1061.43 mg kg^{-1} at 40 ^{0}C and 982.85 mg kg^{-1}) was in the *Kuttanad* soil (Sample No. 15). Increase in maximum quantity adsorbed was found with increase in temperature in 14 soils. The decrease in the amount of maximum quantity adsorbed with increase in temperature was observed in all laterite soils, and the soils from Palakkad eastern plain. Low land soils of *Pokkali, Kole* and *Kuttanad* had higher values of maximum quantity adsorbed at both temperatures. Sandy soils from northern coastal plain and *Onattukara* sandy plain were with lower values of maximum quantity of adsorbed Mo.

The highest values of buffer power at both temperatures (9497.8 L kg^{-1} at 25 ^{0}C, 14748 L kg^{-1} at 40 ^{0}C) were recorded in *Kuttanad* soil (Sample No. 15).The lowest buffer power at 25 ^{0}C (0.522 L kg^{-1}) was in the coastal sandy soil (Sample No. 10). The lowest buffer power at 40 ^{0}C (0.436 L kg^{-1}) was recorded in soil from Palakkad eastern plain (Sample No. 21). Low land soils of *Pokkali, Kole* and *Kuttand* were with higher buffer power, whereas other soils with low buffer power. Q-I curve of all soils were with positive intercept except soil from *Onattukara* sandy plain at 25 ^{0}C (Sample No. 12) and the soil from Palakkad eastern plain at 40 ^{0}C (Sample No. 19). Q-I curves of lowland soils of *Pokkali, Kole* and *Kuttanad* were with high positive intercept values.

Correlation coefficients of parameters of Q-I curve with soil properties are given in the Table 62. Maximum quantity adsorbed at 25 ^{0}C was significantly and positively correlated with maximum quantity adsorbed at 40 ^{0}C (0.994**). Buffer power at 25 ^{0}C had significant positive correlation with buffer power at 40 ^{0}C (0.996**).

Table 61. Parameters of Q-I curve for Mo adsorption

Sample No.	Temp	Linear equation	Max. quantity adsorbed (mg kg^{-1})	Buffer power (L kg^{-1})	Intercept (mg kg^{-1})	R^2
1	25 ^{0}C	q_e= 325.16C_e + 221.9	935.2	325.16	221.9	0.819
	40 ^{0}C	q_e = 220.17C_e + 300.17	951.13	220.17	300.17	0.69
2	25 ^{0}C	q_e = 319.73C_e + 208.52	934	319.73	208.52	0.822
	40 ^{0}C	q_e = 438.57C_e + 176.79	965.19	438.57	176.79	0.919
3	25 ^{0}C	q_e = 621C_e + 120.22	944.68	621	120.22	0.854
	40 ^{0}C	q_e = 186.56C_e + 288.64	944.78	186.56	288.64	0.693
4	25 ^{0}C	q_e = 106C_e + 216.85	895.6	106	216	0.903
	40 ^{0}C	q_e = 117.11C_e + 264.16	922.15	117.11	264.16	0.842
5	25 ^{0}C	q_e = 82.74C_e + 293.06	883.76	82.74	293.06	0.683
	40^{0}C	q_e = 85.17C_e + 228.63	913.35	85.17	228.63	0.839
6	25^{0}C	q_e = 154.65C_e + 243.18	922.95	154.65	243.18	0.833
	40^{0}C	q_e = 256.24C_e + 255.65	953.54	256.24	255.65	0.853
7	25^{0}C	q_e = 0.817C_e + 28.82	88.9	0.817	28.82	0.875
	40 ^{0}C	q_e = 0.597C_e + 40.68	117.6	0.597	40.68	0.398
8	25 ^{0}C	q_e = 1.11C_e + 23.66	107.6	1.11	23.66	0.908
	40^{0}C	q_e = 1.46C_e + 29.55	181.6	1.46	29.55	0.805
9	25 ^{0}C	q_e = 0.97C_e + 7.60	92.5	0.97	7.63	0.859
	40 ^{0}C	q_e = 0.93C_e + 8.59	84.7	0.93	8.59	0.787
10	25 ^{0}C	q_e = 0.522C_e + 7.72	59.1	0.522	7.72	0.79
	40 ^{0}C	q_e = 0.834C_e + 2.982	74.3	0.834	2.982	0.835
11	25^{0}C	q_e = 1.06C_e + 23.478	102.8	1.06	23.48	0.902
	40 ^{0}C	q_e = 1.22C_e + 9.54	125.1	1.22	9.54	0.983
12	25^{0}C	q_e = 1.96C_e - 22.29	148.2	1.96	-22.29	0.919
	40 ^{0}C	q_e = 1.09C_e + 23.65	164.2	1.09	23.65	0.444
13	25 ^{0}C	q_e = 429.21Ce + 225.85	965.08	429.21	225.85	0.906
	40 ^{0}C	q_e = 756.11Ce + 243.05	1051.28	756.11	243.05	0.885
14	25 ^{0}C	q_e = 993.78Ce + 226.6	976	993.78	226.6	0.882
	40 ^{0}C	q_e = 2466.9Ce + 233.19	1058.33	2466.9	233.19	0.880
15	25 ^{0}C	q_e = 9497.8Ce + 13.75	982.85	9497.8	13.75	0.97
	40 ^{0}C	q_e = 14748Ce + 182.14	1061.43	14748	182.14	0.95

Table 61. Continued

Sample No	Temp	Linear equation	Max. quantity adsorbed (mg kg^{-1})	Buffer power (L kg^{-1})	Intercept (mg kg^{-1})	R^2
16	25 ^{0}C	q_e = 2.54Ce + 65.29	309.9	2.54	65.29	0.71
	40 ^{0}C	q_e = 1.87Ce + 90.13	257.4	1.87	90.13	0.394
17	25 ^{0}C	q_e = 7.65Ce + 148.73	502.9	7.65	148.73	0.862
	40 ^{0}C	q_e = 7.54Ce + 152.32	481.2	7.54	152.32	0.857
18	25 ^{0}C	q_e = 3.80Ce + 35.26	358.8	3.80	35.26	0.816
	40 ^{0}C	q_e = 2.36Ce + 58.41	228.2	2.36	58.41	0.933
19	25 ^{0}C	q_e = 1.49Ce + 20.07	236.2	1.49	20.07	0.273
	40 ^{0}C	q_e = 1.68Ce - 16.18	169.6	1.68	-16.18	0.746
20	25 ^{0}C	q_e = 0.747Ce + 12.10	109.6	0.747	12.10	0.396
	40 ^{0}C	q_e = 0.688Ce + 3.21	65.8	0.688	3.21	0.91
21	25 ^{0}C	q_e = 0.708Ce + 5.16	65.3	0.708	5.16	0.795
	40 ^{0}C	q_e = 0.436Ce + 11.58	55.6	0.436	11.58	0.506
22	25 ^{0}C	q_e = 1.01Ce + 46.18	199.5	1.01	46.18	0.989
	40 ^{0}C	q_e = 1.84Ce + 8.63	164.6	1.84	8.63	0.995

pH had significant negative correlation with maximum quantity adsorbed (-0.828** at 25 ^{0}C, -0.847** at 40 ^{0}C). EC was significantly and positively correlated with maximum quantity adsorbed (0.544** at 25 ^{0}C, 0.529* at 40 ^{0}C). Organic carbon had significant positive correlation with maximum quantity adsorbed (0.903** at 25 ^{0}C, 0.897** at 40 ^{0}C) and buffer power (0.505* at 25 ^{0}C, 0.487* 40 ^{0}C).

AEC was significantly and positively correlated with maximum quantity adsorbed (0.885** at 25 ^{0}C, 0.857** at 40 ^{0}C). Sand content had significant negative correlation with maximum quantity adsorbed (-0.784** at 25 ^{0}C, -0.763** at 40 ^{0}C) whereas silt content had significant positive correlation with maximum quantity adsorbed (0.600** at 25 ^{0}C, 0.586** at 40 ^{0}C). Clay content showed significant positive correlation with maximum quantity adsorbed

(0.709** at 25 ^{0}C, 0.687** at 40 ^{0}C) and buffer power (0.467* at 25 ^{0}C, 0.492* at 40 ^{0}C).

Table 62. Correlation between parameters of Q-I curve and soil properties for Mo adsorption

	Max. quantity adsorbed at 25 ^{0}C	**Buffer power at 25 ^{0}C**	**Max. quantity adsorbed at 40 ^{0}C**	**Buffer power at 40 ^{0}C**
Buffer power at 25 ^{0}C				
Max. quantity adsorbed at 40 ^{0}C	0.994**			
Buffer power at 40 ^{0}C		0.996**		
pH	-0.828**		-0.847**	
EC	0.544**		0.529*	
OC	0.903**	0.505*	0.897**	0.487*
AEC	0.885**		0.857**	
Sand	-0.784**		-0.763**	
Silt	0.600**		0.586**	
Clay	0.709**	0.467*	0.687**	0.492*
Av.N	0.898**	0.554**	0.910**	0.575**
Av.Mg	0.567**		0.549**	
Av.S	0.501*		0.481*	
Av.Fe	0.926**	0.515*	0.941**	0.502*
Av.Cu	0.757**		0.708**	
Av.Zn	0.459*		0.435*	
Av.B	0.565**		0.555**	
Av.Si	-0.435*		-0.477*	
WS+Ex.Al	0.671**	0.474*	0.668**	0.437*
CBD-Fe	0.795**	0.512*	0.770**	0.531*

**Correlation is significant at the 0.01 level (2-tailed)
*Correlation is significant at the 0.05 level (2-tailed)

Available S had significant positive correlation with maximum quantity adsorbed at both temperature (0.501* at 25 ^{0}C, 0.481* at 40 ^{0}C). Available B also had the same trend. Available B was significantly and positively correlated with maximum quantity adsorbed (0.565** at 25 ^{0}C, 0.555** at 40 ^{0}C). A significant and negative correlation was found between available Si and maximum quantity adsorbed (-0.435* at 25 ^{0}C, -0.477* at 40 ^{0}C). Available Fe showed significant positive correlation with maximum quantity adsorbed (0.926** at 25 ^{0}C, 0.941** at 40 ^{0}C) and buffer power (0.515* at 25 ^{0}C, 0.502 at 40 ^{0}C). Available Zn showed significant positive correlation with maximum quantity adsorbed (0.459* at 25 ^{0}C, 0.435* at 40 ^{0}C). Water soluble plus exchangeable Al was significantly and positively correlated with maximum quantity adsorbed (0.671** at 25 ^{0}C, 0.668** at 40 ^{0}C), and buffer power (0.474* at 25 ^{0}C, 0.437* at 40 ^{0}C). CBD-Fe had significant positive correlation with maximum quantity adsorbed (0.795** at 25 ^{0}C, 0.770** at 40 ^{0}C) and buffer power (0.512* at 25 ^{0}C, 0.531* at 40 ^{0}C).

Adsorption isotherms

Mo adsorption in soil is well explained by Freundlich adsorption isotherm followed by Tempkin and Langmuir adsorption isotherm.

Freundlich adsorption isotherm

All the soil samples at both temperatures followed Freundlich adsorption isotherm. More than 50 per cent of the adsorption data was explained by Freundlich adsorption isotherm for all the soils at both temperatures. Parameters of Freundlich adsorption isotherm for Mo adsorption are given in Table 63. Three samples at 25 ^{0}C and three samples at 40 ^{0}C were with 1/n value of >1. The highest value of 1/n at 25 ^{0}C (1.489) was in *Onattukara* sandy soil (Sample No. 12), whereas the highest value at 40 ^{0}C (1.085) was in the soil from Palakkad eastern plain (Sample No. 19). The lowest value of 1/n at 25 ^{0}C (0.110) was observed in the soil from Palakkad eastern plain (Sample No. 22), while at 40 ^{0}C (0.308) it was observed in the soil from *Kole* land (Sample No. 4). All the samples of *Kole* land at both temperatures were with 1/n value ranging from 0.308 to 0.393.

Highest value of constant related to strength of bonding (K_F) value at both temperatures (7373.95 at 25 ^{0}C, 2658.89 at 40 ^{0}C) was in *Kuttanad* soil (Sample No. 15). Lowest value of K_F at 25 ^{0}C (0.19) was noted in *Onattukara* sandy soil

(Sample No. 12) and the lowest value at 40 ^{0}C (0.61) in the soil from Palakkad eastern plain (Sample No. 20). Low land soils of *Pokkali, Kole* and *Kuttanad* were with high values of K_F. Soil from northern coastal plain, *Onattukara* sandy plain and Palakkad eastern plain were with low values of K_F.

Table 63. Parameters of Freundlich adsorption isotherm for Mo adsorption

Sample No.	Temp	Linear equation	1/n	K_F (mg kg^{-1}) (L kg^{-1})$^{1/n}$	R^2
1	25 ^{0}C	$\log q_e = 0.713 \log C_e + 2.81$	0.713	646.25	0.874
	40 ^{0}C	$\log q_e = 0.592 \log C_e + 2.83$	0.592	672.82	0.848
2	25 ^{0}C	$\log q_e = 0.76 \log C_e + 2.79$	0.760	608.98	0.913
	40 ^{0}C	$\log q_e = 0.666 \log C_e + 2.84$	0.666	693.75	0.956
3	25 ^{0}C	$\log q_e = 1.086 \log C_e + 2.94$	1.086	873.98	0.856
	40 ^{0}C	$\log q_e = 0.623 \log C_e + 2.76$	0.623	569.12	0.840
4	25 ^{0}C	$\log q_e = 0.375 \log C_e + 2.63$	0.375	429.24	0.988
	40 ^{0}C	$\log q_e = 0.308 \log C_e + 2.72$	0.308	525.53	0.826
5	25 ^{0}C	$\log q_e = 0.393 \log C_e + 2.66$	0.393	453.32	0.982
	40 ^{0}C	$\log q_e = 0.345 \log C_e + 2.63$	0.345	421.7	0.938
6	25 ^{0}C	$\log q_e = 0.355 \log C_e + 2.73$	0.355	536.54	0.982
	40 ^{0}C	$\log q_e = 0.367 \log C_e + 2.81$	0.367	649.08	0.960
7	25 ^{0}C	$\log q_e = 0.532 \log C_e + 0.97$	0.532	9.29	0.962
	40 ^{0}C	$\log q_e = 0.432 \log C_e + 1.14$	0.432	13.63	0.717
8	25 ^{0}C	$\log q_e = 0.535 \log C_e + 1.003$	0.535	10.06	0.920
	40 ^{0}C	$\log q_e = 0.51 \log C_e + 1.15$	0.510	14.15	0.854
9	25 ^{0}C	$\log q_e = 0.885 \log C_e + 0.25$	0.885	1.78	0.924
	40 ^{0}C	$\log q_e = 0.8941 \log C_e + 0.20$	0.894	1.60	0.731
10	25 ^{0}C	$\log q_e = 0.76 \log C_e + 0.25$	0.760	1.79	0.932
	40 ^{0}C	$\log q_e = 0.989 \log C_e - 0.044$	0.989	0.91	0.903
11	25 ^{0}C	$\log q_e = 0.64 \log C_e + 0.823$	0.640	6.64	0.978
	40 ^{0}C	$\log q_e = 0.680 \log C_e + 0.696$	0.680	4.96	0.927

Table 63. Continued

Sample No.	Temp	Linear equation	1/n	K_F (mg kg^{-1}) (L kg^{-1})$^{1/n}$	R^2
12	25 ^{0}C	log q_e = 1.489 log C_e - 0.726	1.489	0.19	0.939
	40 ^{0}C	log q_e = 0.838 log C_e + 0.445	0.838	2.77	0.631
13	25 ^{0}C	log q_e = 0.39 log C_e + 2.87	0.390	736.38	0.986
	40 ^{0}C	log q_e= 0.339 log C_e + 2.94	0.339	879.23	0.929
14	25 ^{0}C	log q_e= 0.549 log C_e + 3.09	0.549	1228.01	0.911
	40 ^{0}C	log q_e = 0.634 log C_e + 3.37	0.634	2351.8	0.889
15	25 ^{0}C	log q_e = 0.906 log C_e + 3.87	0.906	7373.95	0.971
	40 ^{0}C	log q_e = 0.377 log C_e + 3.43	0.377	2658.89	0.960
16	25 ^{0}C	log q_e = 0.355 log C_e + 1.66	0.355	46.03	0.775
	40 ^{0}C	log q_e = 0.539 log C_e + 1.38	0.539	23.77	0.776
17	25 ^{0}C	log q_e = 0.257 log C_e + 2.2	0.257	157.22	0.894
	40 ^{0}C	log q_e = 0.482 log C_e + 1.91	0.482	81.68	0.981
18	25 ^{0}C	log q_e = 0.542 log C_e + 1.40	0.542	25.26	0.864
	40 ^{0}C	log q_e = 0.564 log C_e + 1.31	0.564	20.58	0.980
19	25 ^{0}C	log q_e = 1.019 log C_e + 0.19	1.019	1.54	0.704
	40 ^{0}C	log q_e = 1.085 log C_e - 0.07	1.085	0.86	0.912
20	25 ^{0}C	log q_e = 0.716 log C_e+ 0.43	0.716	2.69	0.546
	40 ^{0}C	log q_e = 1.056 log C_e - 0.22	1.056	0.61	0.948
21	25 ^{0}C	log q_e = 0.739 log C_e + 0.33	0.739	2.15	0.711
	40 ^{0}C	log q_e = 1.018 log C_e - 0.21	1.018	0.61	0.812
22	25 ^{0}C	log q_e = 0.11 log C_e + 1.63	0.110	42.78	0.926
	40 ^{0}C	log q_e = 0.807 log C_e + 0.64	0.807	4.34	0.891

Correlation coefficients of parameters of Freudlich adsorption isotherm with soil properties are given in Table 64. pH had significant negative correlation with K_F (-0.427* at 25 ^{0}C, -0.539** at 40 ^{0}C), positive correlation with 1/n at 40 ^{0}C (0.771**). Organic carbon had significant negative correlation with 1/n at 40 ^{0}C (-0.509*), positive correlation with K_F (0.593** at 25 ^{0}C, 0.637** at 40 ^{0}C).

AEC also had the same trend, significant positive correlation with K_F (0.465* at 25 ^{0}C, 0.600** at 40 ^{0}C), negative correlation with 1/n at 40 ^{0}C (-0.473*).

Table 64. Correlation between parameters of Freundlich adsorption isotherm and soil properties for Mo adsorption

	1/n at 25 ^{0}C	**K_F at 25 ^{0}C**	**1/n at 40 ^{0}C**	**K_F at 40 ^{0}C**
1/n at 40 ^{0}C		-0.602**		
pH		-0.427*	0.771**	-0.539**
OC		0.593**	-0.509*	0.637**
Bd		-0.510*	0.508*	-0.740**
AEC		0.465*	-0.473*	0.600**
Sand		-0.445*	0.433*	-0.628**
silt				0.474*
clay		0.529*	-0.529*	0.567**
Av.N		0.642**	-0.613**	0.817**
Av.Ca			0.555**	
Av.Fe		0.608**	-0.586**	0.656**
Av.Si			0.687**	
Ex.Ca			0.600**	
Ex.Fe		0.550**		
Ex.Mn	-0.543**			
Ex.Cu			-0.456*	0.460*
WS+Ex.Al		0.533*		
CBD-Fe		0.583**	-0.527*	0.637**

**Correlation is significant at the 0.01 level (2-tailed)
*Correlation is significant at the 0.05 level (2-tailed)

Sand was significantly and negatively correlated with K_F (-0.445* at 25 ^{0}C, -0.628** at 40 ^{0}C). Significant positive correlation was found between sand and 1/n at 40 ^{0}C (0.433*). Clay had the opposite trend, significant positive correlation with K_F (0.529* at 25 ^{0}C, 0.567** at 40 ^{0}C), negative correlation with

1/n at 40 ^{0}C (-0.529*). Silt had significant positive correlation with K_F at 40 ^{0}C (0.474*).

Constant related to adsorption intensity (1/n) at 25 ^{0}C had significant negative correlation with Ex.Mn (-0.543**). K_F (constant related to strength of bonding) at 25 ^{0}C had significant positive correlation with Av.N (0.642**), Av.Fe (0.608**), Ex. Fe (0.550**), WS+Ex.Al (0.533*) and CBD-Fe (0.583**). 1/n at 40 ^{0}C showed significant negative correlation with Av.N (-0.613**), Av.Fe (-0.586**), Ex. Cu (-0.456*), CBD-Fe (-0.527*) and positive correlation with Av.Ca (0.555**), Av. Si (0.687**), Ex.Ca (0.600**). K_F at 25 ^{0}C had significant positive correlation with Av.N (0.817**), Av.Fe (0.656**), Ex.Cu (0.460*), and CBD-Fe (0.637**).

Langmuir adsorption isotherm

Langmuir adsorption isotherm was not followed by the Sample No. 3 and 22 at 25 ^{0}C, Sample No. 10 and 12 at 40 ^{0}C and Sample No. 19, 20, 21 at both temperatures. Other than these samples, samples with negative $K_L$values (Sample No. 12, at 25 ^{0}C, Sample No. 15 at 25 ^{0}C) were also avoided from comparing the parameters since it was giving erroneous information. Parameters of Langmuir adsorption isotherm is given in Table 65.

Highest value for adsorption maxima (q_m) at 40 ^{0}C (1405.68 mg kg^{-1}) was in *Kuttanad* soil (Sample No.14), whereas the highest value at 25 ^{0}C (1488.32 mg kg^{-1}) was in the soil from *Kole* land (Sample No. 2). Lowest value of q_m at 25 ^{0}C (98.97 mg kg^{-1}) was in the soil from *Onattukara* sandy plain (Sample No. 10) and the lowest at 40 ^{0}C (100.69 mg kg^{-1}) in coastal sandy soil (Sample No. 7). High values of q_m were recorded in low land soils of *Pokkali, Kole* and *Kuttanad* followed by laterite soil. Sandy soils of northern coastal plain and *Onattukara* sandy plain showed low values of q_m.

Table 65. Parameters of Langmuir adsorption isotherm for Mo adsorption

Sample No.	Temp	Linear equation	q_m (mg kg^{-1})	K_L (L mg^{-1})	R^2
1	25 ^{0}C	$C_e/q_e = 0.735C_e + 0.773$	1360.17	0.952	0.894
	40 ^{0}C	$C_e/q_e = 0.887C_e + 0.501$	1128.03	1.768	0.983
2	25 ^{0}C	$C_e/q_e = 0.672C_e + 0.924$	1488.32	0.727	0.878
	40 ^{0}C	$C_e/q_e = 0.753C_e + 0.63$	1327.32	1.2	0.944
3	40 ^{0}C	$C_e/q_e = 0.848C_e + 0.75$	1179.66	1.13	0.95
4	25 ^{0}C	$C_e/q_e = 1.105C_e + 0.735$	904.73	1.50	0.959
	40 ^{0}C	$C_e/q_e = 1.089C_e + 0.393$	918.27	2.78	0.972
5	25 ^{0}C	$C_e/q_e = 1.069C_e + 0.657$	935.63	1.63	0.986
	40 ^{0}C	$C_e/q_e = 1.238C_e + 0.544$	808.08	2.28	0.941
6	25 ^{0}C	$C_e/q_e = 1.147C_e + 0.323$	871.54	3.55	0.961
	40 ^{0}C	$C_e/q_e= 1.009C_e + 0.278$	991.28	3.63	0.972
7	25 ^{0}C	$C_e/q_e = 8.40C_e + 226.5$	119.03	0.037	0.981
	40 ^{0}C	$C_e/q_e = 9.93C_e + 167.74$	100.69	0.059	0.874
8	25 ^{0}C	$C_e/q_e= 6.19C_e + 269.22$	161.56	0.023	0.784
	40 ^{0}C	$C_e/q_e = 5.16C_e + 200.41$	193.86	0.026	0.61
10	25 ^{0}C	$C_e/q_e = 10.10C_e + 890.84$	98.97	0.011	0.635
11	25 ^{0}C	$C_e/q_e= 6.16C_e + 284.93$	162.26	0.022	0.942
	40 ^{0}C	$C_e/q_e = 3.83C_e + 471.56$	261.38	0.008	0.501
13	25 ^{0}C	$C_e/q_e= 0.99C_e + 0.228$	1008.57	4.35	0.95
	40 ^{0}C	$C_e/q_e = 0.919C_e + 0.135$	1087.43	6.81	0.951
14	25 ^{0}C	$C_e/q_e= 0.904C_e + 0.149$	1106.44	6.07	0.965
	40 ^{0}C	$C_e/q_e = 0.711C_e + 0.09$	1405.68	7.91	0.927
15	40 ^{0}C	$C_e/q_e = 0.949C_e + 0.01$	1053.52	97.86	0.861
16	25 ^{0}C	$C_e/q_e = 3.99C_e + 63.76$	250.48	0.063	0.653
	40 ^{0}C	$C_e/q_e = 4.32C_e + 57.94$	231.5	0.075	0.794
17	25 ^{0}C	$C_e/q_e= 1.85C_e + 13.79$	541.83	0.134	0.926
	40 ^{0}C	$C_e/q_e = 1.77C_e + 16.21$	565.96	0.109	0.997
18	25 ^{0}C	$C_e/q_e = 2.62C_e + 98.68$	381.65	0.027	0.544
	40 ^{0}C	$C_e/q_e = 3.264C_e + 97.15$	306.35	0.034	0.978
22	40 ^{0}C	$C_e/q_e = 2.177C_e + 364.02$	459.43	0.006	0.645

Exceptionally high value of K_L (97.86 L mg^{-1}) was noticed in *Kuttanad* soil (Sample No. 15) at 40 ^{0}C followed by Sample No. 14 of *Kuttanad* soil (7.91 L mg^{-1}). Highest value of K_L at 25 ^{0}C (6.07 L mg^{-1}) was also noted in *Kuttanad* soil (Sample No. 14), while the lowest value (0.011 L mg^{-1}) in the coastal sandy soil (Sample No. 10) and the lowest value at 40 ^{0}C (0.006 L mg^{-1}) was noted in (Palakkad eastern plain). Higher values of K_L were recorded in low land soils of *Pokkali, Kole* and *Kuttanad* at both temperatures.

Table 66. Correlation between parameters of Langmuir adsorption isotherm and soil parameters for Mo adsorption

	q_m at 25 ^{0}C	**K_L at 25 ^{0}C**	**q_m at 40 ^{0}C**	**K_L at 40 ^{0}C**
q_m at 40 ^{0}C		0.602*		
K_L at 40 ^{0}C	0.996**			
pH			-0.767**	
OC	0.516*		0.898**	0.541*
AEC			0.844**	
Sand		-0.606*	-0.769**	
Silt		0.556*	0.681**	
Clay			0.616*	
Av.N		0.587*	0.867**	0.549*
Av.Mg			0.625*	
Av.S			0.516*	
Av.Fe			0.897**	0.520*
Av.Cu			0.651**	
Ex.Al	0.955**			0.972**
WS+Ex.Al			0.652**	
CBD-Fe			0.759**	0.536*

**Correlation is significant at the 0.01 level (2-tailed)
*Correlation is significant at the 0.05 level (2-tailed)

Correlation coefficients of parameters of Langmuir adsorption isotherm with soil properties are given in Table 66. Adsorption maxima (q_m) at 25 ^{0}C was significantly and positively correlated with bonding energy constant (K_L) at 40 ^{0}C (0.996**), whereas q_m at 40 ^{0}C had significant positive correlation with K_L at 25 ^{0}C (0.602*). The pH had significant negative correlation with q_m at 40 ^{0}C (-0.767**). Organic carbon showed significant positive correlation with q_m (0.516* at 25 ^{0}C, 0.898** at 40 ^{0}C), K_L at 40 ^{0}C (0.541*). Anion exchange capacity had significant positive correlation with q_m at 40 ^{0}C (0.844**). Sand was negatively correlated with q_m at 40 ^{0}C (-0.769**), and with K_L at 25 ^{0}C (-0.606*). Silt was significantly and positively correlated with q_m at 40 ^{0}C (0.681**), and K_L at 25 ^{0}C (0.556*). Clay had significant positive correlation with q_m at 40 ^{0}C (0.616*).

Adsorption maxima (q_m) at 25 ^{0}C had significant positive correlation with Ex.Al (0.955**). Adsorption maxima (q_m) at 40 ^{0}C had significant positive correlation with Av.N (0.876**), Av.Mg (625*), Av.S (0.516*), Av.Fe (0.897**), Av.Cu (0.651**), WS+Ex. Al (0.652**) and CBD-Fe (0.759**). Bonding energy consatant (K_L) at 40 ^{0}C was significantly and positively correlated with Av.N (0.549*), Av.Fe (0.520*) and CBD-Fe (0.536*).

Tempkin adsorption isotherm

All the soils at both temperatures followed Tempkin adsorption isotherm. Parameters of Tempkin adsorption isotherm for Mo adsorption are given in Table 67. At 40 ^{0}C, exceptionally high value of constant related to strength of bonding (2160.6 L kg^{-1}) was noted in *Kuttanad* soil followed by 648.74 L kg^{-1} in the Sample No.13. Highest value of K_T (178.18 L kg^{-1}) at 25 ^{0}C was also noted in *Kuttanad* soil (Sample No. 13). Low land soils of *Pokkali, Kole* and *Kuttanad* were with high values of K_T. Sixteen samples showed decrease in K_T with increase in temperature. Highest value of b at 25 ^{0}C (137.09 J mol^{-1}) was noted in *Onattukara* sandy soil (Sample No. 10), whereas the highest value of b at 40 ^{0}C (133.05 J mol^{-1}) was recorded in the soil from Palakkad eastern plain (Sample

No.21). Lowest value of b at 25 ^{0}C (5.98 J mol^{-1}) was recorded in *Pokkali* soil (Sample No. 3). The lowest vale of b (constant realted to heat of adsorption) at 40 ^{0}C (9.49 J mol^{-1}) was recorded in *Kuttanad* soil (Sample No. 14).

Table 67. Parameters of Tempkin adsorption isotherm for Mo adsorption

Sample No.	Temp	Linear equation	K_T (L kg^{-1})	b (J mol^{-1})	R^2
1	25 ^{0}C	q_e= 266 lnC_e + 696.43	13.71	9.31	0.976
	40 ^{0}C	q_e = 236.9 lnC_e + 721.9	21.06	10.99	0.975
2	25 ^{0}C	q_e = 276.61 ln C_e + 669.34	11.24	8.96	0.971
	40 ^{0}C	q_e = 250.84 ln C_e + 719.9	17.64	10.37	0.956
3	25 ^{0}C	q_e = 414.18 ln C_e + 818.03	7.21	5.98	0.988
	40 ^{0}C	q_e = 247.78 ln C_e + 653.17	13.96	10.50	0.963
4	25 ^{0}C	q_e = 125.35 lnC_e + 528.26	67.65	19.77	0.935
	40 ^{0}C	q_e = 117.9 1n C_e + 611.1	178.18	22.07	0.904
5	25 ^{0}C	q_e = 130.84 lnC_e + 547.11	65.47	18.94	0.924
	40 ^{0}C	q_e = 123.04 lnC_e + 518.11	67.42	21.15	0.916
6	25 ^{0}C	q_e = 120.11 lnC_e + 608.7	158.83	20.63	0.915
	40 ^{0}C	q_e = 135.6lnC_e + 689.02	160.98	19.19	0.934
7	25 ^{0}C	q_e = 26.62lnC_e - 27.38	0.358	93.08	0.975
	40 ^{0}C	q_e = 24.41lnC_e - 16.82	0.502	106.59	0.567
8	25 ^{0}C	q_e = 31.74 lnC_e - 37.67	0.305	78.07	0.853
	40 ^{0}C	q_e = 42.16 lnC_e - 51.78	0.293	61.73	0.699
9	25 ^{0}C	q_e = 31.37 lnC_e - 59.71	0.149	78.99	0.833
	40 ^{0}C	q_e = 33.68 lnC_e - 68.04	0.133	77.26	0.801
10	25 ^{0}C	q_e = 18.07 lnC_e - 32.05	0.170	137.09	0.804
	40 ^{0}C	q_e = 30.58 lnC_e - 67.08	0.112	85.09	0.827
11	25 ^{0}C	q_e = 33.85lnC_e - 47.34	0.247	73.19	0.950
	40 ^{0}C	q_e = 37.87 lnC_e - 68.43	0.164	68.73	0.826
12	25 ^{0}C	q_e = 62.41 lnC_e - 156.5	0.081	39.7	0.775
	40^{0}C	q_e = 44.00 lnC_e - 81.69	0.156	59.14	0.557
13	25 ^{0}C	q_e= 141.09 lnC_e + 731.24	178.18	17.56	0.911
	40 ^{0}C	q_e = 127.17 lnC_e + 823.43	648.74	20.46	0.781

Table 67. Continued

Sample No.	Temp	Linear equation	K_T (L kg^{-1})	b (J mol^{-1})	R^2
14	25 ^{0}C	$q_e = 216.01 \ln C_e + 956.94$	83.94	11.47	0.978
	40 ^{0}C	$q_e = 274.27 \ln C_e + 1296.5$	112.97	9.49	0.988
15	25 ^{0}C	$q_e = 321.51 \ln C_e + 1547.5$	123.13	7.71	0.837
	40 ^{0}C	$q_e = 181.88 \ln C_e + 1396.5$	2160.6	14.31	0.842
16	25 ^{0}C	$q_e = 50.63 \ln C_e - 2.29$	0.956	48.93	0.578
	40 ^{0}C	$q_e = 65.32 \ln C_e - 52.49$	0.448	39.84	0.625
17	25 ^{0}C	$q_e = 59.19 \ln C_e + 186.77$	23.46	41.86	0.749
	40 ^{0}C	$q_e = 114.92 \ln C_e + 30.20$	1.301	22.64	0.990
18	25 ^{0}C	$q_e = 78.11 \ln C_e - 81.47$	0.352	31.72	0.646
	40 ^{0}C	$q_e = 65.85 \ln C_e - 67.84$	0.357	39.52	0.977
19	40 ^{0}C	$q_e = 51.62 \ln C_e - 123.79$	0.091	50.42	0.589
20	25 ^{0}C	$q_e = 27.86 \ln C_e - 52.35$	0.153	88.95	0.501
	40 ^{0}C	$q_e = 25.66 \ln C_e - 56.13$	0.112	101.41	0.912
21	25 ^{0}C	$q_e = 23.73 \ln C_e - 46.44$	0.141	104.40	0.718
	40 ^{0}C	$q_e = 19.56 \ln C_e - 37.85$	0.144	133.05	0.701
22	40 ^{0}C	$q_e = 56.27 \ln C_e - 107.68$	0.148	46.25	0.894

Correlation coefficients of parameters of Tempkin adsorption isotherm with soil properties is given in Table 68. Exceptionally high value of binding strength constant (K_T) at 40 ^{0}C in Sample No. 15 is not included in correlation study. K_T at 25 ^{0}C was significantly and negatively correlated with b at 25 ^{0}C (-0.527*), whereas K_T at 40 ^{0}C was significantly and positively correlated with constant related to heat of adsorption (b) at 40 ^{0}C (0.755**). pH had significant positive correlation with b (0.717** at 25 ^{0}C and 0.766** at 40 ^{0}C), and negative correlation with K_T (-0.511* at 25 ^{0}C). Significant negative correlation was found between EC and b at both temperatures. OC had significant positive correlation with K_T at 25 ^{0}C (0.480*), negative correlation with b (-0.791** at 25^{0}C, -0.737** at 40 ^{0}C). AEC was significantly and negatively correlated with b (-0.804** at 25 ^{0}C, -0.733** at 40 ^{0}C).

Table 68. Correlation between parameters of Tempkin adsorption isotherm and soil properties for Mo adsorption

	K_T at 25 ^{0}C	**b at 25 ^{0}C**	**K_T at 40 ^{0}C**	**b at 40 ^{0}C**
b at 25 ^{0}C	-0.527*			
b at 40 ^{0}C			0.755**	
pH	-0.511*	0.717**		0.766**
EC		-0.500*		-0.459*
OC	0.480*	-0.791**		-0.737**
AEC		-0.804**		-0.733**
Sand	-0.738**	0.712**	-0.581**	0.625**
Silt	0.476*	-0.556**		-0.490*
Clay	0.725**	-0.638**	0.543*	-0.575**
Av.S		-0.466*		-0.453*
Av.Fe	0.659**	-0.748**	0.529*	-0.685**
Av.Cu		-0.666**		0.681**
Av.Zn		-0.428*		-0.434*
Av.B	0.425*			
WS+Ex.Al		-0.599**		-0.539*
CBD-Fe	0.632**	-0.696**		-0.648**

**Correlation is significant at the 0.01 level (2-tailed)
*Correlation is significant at the 0.05 level (2-tailed)

Sand had significant negative correlation with K_T (-0.738** at 25 ^{0}C and -0.581** at 40 ^{0}C) and positive correlation with b (0.712** at 25 ^{0}C, 0.625** at 40 ^{0}C). Silt and clay had similar correlation which was opposite to sand. Silt was significantly and positively correlated with K_T (0.476* at 25 ^{0}C), negatively correlated with b (-0.556** at 25 ^{0}C and -0.490* at 40 ^{0}C). Clay content had significant positive correlation with K_T (0.725** at 25 ^{0}C and 0.543** at 40 ^{0}C) and negative correlation with b (-0.638** at 25 ^{0}C and -0.575** at 40 ^{0}C)

Constant related to strength of bonding (K_T) at 25 ^{0}C had significant positive correlation with Av.Fe (0.659**), Av.B (0.425*) and CBD-Fe (0.632**). Constant related to heat of adsorption (b) at 25 ^{0}C had significant negative correlation with Av.S (-0.466*), Av. Fe (-0.748**), Av.Cu (-0.666**), Av.Zn (-0.428*), WS+Ex.Al (-0.599**) and CBD-Fe (-0.696**). A significant positive correlation was found between K_T at 40 ^{0}C and Av.Fe (0.529*). Constant related to heat of adsorption (b) at 40 ^{0}C had significant negative correlation with Av.S (-0.453*), Av.Fe (-0.685**), Av.Cu (-0.681**), Av.Zn (-0.434*), WS+Ex.Al (-0.539*) and CBD-Fe (-0.648**).

Thermodynamics of Mo adsorption in soil

Thermodynamic parameters of Mo adsorption in soil are given in Table 69. Maximum value of thermodynamic equilibrium constant was recorded (13.30 at 25 ^{0}C and 13.04 at 40 ^{0}C) in *Kuttanad* soil (Sample No. 13 at 25 ^{0}C and Sample No. 15 at 40 ^{0}C respectively). Lowest value of K^0 (4.16 at 25 ^{0}C, 3.12 at 40 ^{0}C) was noted in the soil from Palakkad eastern plain (Sample No. 20).

Except Sample No. 15, all the samples had a decrease in thermodynamic equilibrium constant (K^0) with increase in temperature. Low land soils of *Pokkali, Kole* and *Kuttanad* were with high K^0 which was >10. Lower values of K^0 was recorded in the soils from Palakkad eastern plain (<5).

Free energy change of Mo adsorption in all the soils at both the temperatures were recorded negative. Highest negative value of ΔG^0 (-1.532 at 25 ^{0}C, -1.597 at 40 ^{0}C) was found in *Kuttanad* soil (Sample No. 13 and 15 respectively). ΔG^0 becomes less negative with increase in temperature for 19 samples. The remaining three samples showed an opposite trend. All soils, except one from *Kuttanad* (Sample No. 15) were recorded negative values for enthalpy change (ΔH^0). The highest value was recorded as 0.42 kcal mol^{-1}. The lowest value of -4.24 kcal mol^{-1} was in the soil from *Kole* land (Sample No. 5). Except three samples (Sample No. 12, 13 and 15), all others were with negative value for entropy change. Highest value of change in entropy (ΔS^0) was (6.44 cal mol^{-1}K^{-1}) in *Kuttanad* soil (Sample No. 15), whereas the lowest value of -15.34 cal mol^{-1} K^{-1} in laterite soil (Sample No. 17).

Table 69. Thermodynamic parameters of Mo adsorption

Sample No.	**surface area (m^{2}g^{-1})**	**K^0**		**ΔG^0 (kcal mol-1)**		**ΔH^0 (kcal mol^{-1})**	**ΔS (cal mol^{-1} K^{-1})**	
		25 ^{0}C	**40 ^{0}C**	**25 ^{0}C**	**40 ^{0}C**		**25 ^{0}C**	**40 ^{0}C**
1	62.24	11.21	9.48	-1.431	-1.399	-2.08	-2.16	-2.16
2	59.23	11.05	9.83	-1.423	-1.422	-1.44	-0.07	-0.07
3	67.45	10.52	9.30	-1.393	-1.387	-1.52	-0.43	-0.43
4	79.66	12.34	9.48	-1.488	-1.399	-3.26	-5.94	-5.94
5	112.44	11.93	8.46	-1.468	-1.328	-4.24	-9.31	-9.31
6	89.48	13.00	10.01	-1.519	-1.433	-3.23	-5.75	-5.75
7	6.34	8.02	6.05	-1.233	-1.12	-3.48	-7.54	-7.54
8	8.21	7.55	6.20	-1.197	-1.135	-2.44	-4.16	-4.16
9	6.11	6.59	5.40	-1.116	-1.049	-2.45	-4.48	-4.48
10	8.39	6.00	4.89	-1.061	-0.987	-2.54	-4.97	-4.97
11	15.66	6.75	5.10	-1.131	-1.013	-3.47	-7.86	-7.86
12	18.65	4.79	4.49	-0.927	-0.935	-0.78	0.49	0.49
13	84.32	13.30	11.29	-1.532	-1.507	-2.03	-1.67	-1.67
14	94.07	12.70	11.34	-1.505	-1.51	-1.40	0.35	0.35
15	124.78	12.61	13.04	-1.501	-1.597	0.42	6.44	6.44
16	38.92	7.21	5.13	-1.169	-1.017	-4.19	-10.15	-10.15
17	40.33	10.74	6.62	-1.406	-1.176	-5.98	-15.34	-15.34
18	53.56	6.40	4.80	-1.099	-0.976	-3.54	-8.19	-8.19
19	33.42	4.71	3.96	-0.918	-0.856	-2.15	-4.14	-4.14
20	40.73	4.16	3.12	-0.844	-0.709	-3.53	-9.00	-9.00
21	29.78	4.58	3.43	-0.901	-0.767	-3.55	-8.90	-8.90
22	39.69	4.708	4.353	-0.917	-0.915	-0.97	-0.17	-0.17

4.3.1.6. Adsorption study of silicon

All the collected soils showed desorption of Si at both the temperatures.

Quantity-intensity relationship

Adsorption study of Si in the soil was carried out following the procedure detailed in section 3.3.1.1.6. The quantity desorbed decreases after reaching a maximum value with the increasing concentration in equilibrium solution. The parameters of the quantity intensity curves are given in Table 70. All the soils were recorded with negative buffer power. The linear curve was fitted by excluding the final q_e and $C_e$value obtained from the experiment, since it was showing drastic reduction in desorption after reaching a maximum value. More than 80 per cent of the data were fitted into the linear form at both the temperatures except in one soil collected from Palakkad eastern plain (Sample No. 21).

Out of the 22 samples collected, 17 soils were reported with high values of maximum quantity desorbed at 40 ^{0}C than 25 ^{0}C, which means there was an increase in desorption with increase in temperature. At 25 ^{0}C, two soils from *Kole* land (Sample No. 4 & 5), all the laterite soils (Sample No. 16 - 18), and one soil from Palakkad eastern plain (Sample No. 19) showed adsorption behavior after reaching maximum desorption, whereas such an adsorption was not found in the same soils at 40 ^{0}C.

The highest value of maximum quantity desorbed (1501.6 mg kg^{-1} at 25 ^{0}C, 1758.4 mg kg^{-1} at 40 ^{0}C) at both temperatures was in the soil from *Onattukara* sandy plain (Sample No. 11). The lowest value of maximum quantity desorbed (250 mg kg^{-1} at 25 ^{0}C, 261.2 mg kg^{-1}at 40 ^{0}C) was noted in the soil from Palakkad eastern plain (Sample No. 21). Most of the soils were with negative intercept.

Correlation coefficients of parameters of Q-I curve with soil properties for Si desorption are given in Table 71. Buffer power at 25 ^{0}C was significantly and negatively correlated with maximum quantity desorbed (-0.976** at 25 ^{0}C,

-0.804** at 40 ^{0}C) and buffer power at 40 ^{0}C (0.716**). Maximum quantity desorbed at 25 ^{0}C was significantly and positively correlated with maximum quantity desorbed at 40 ^{0}C (0.835**), and buffer power (-0.743**) at 40 ^{0}C. Maximum quantity desorbed at 40 ^{0}C was significantly and negatively correlated with buffer power at 40 ^{0}C (-0.955**).

Table 70. Parameters of Q-I curve for Si desorption

Sample No.	Temp	Linear equation	Buffer power	Max. quantity desorbed (mg kg^{-1})	Intercept (mg kg^{-1})	R^2
1	25 ^{0}C	$q_e = -5.44C_e + 2.55$	-5.44	802	2.55	0.986
	40 ^{0}C	$q_e = -4.82C_e - 78.53$	-4.82	718	-78.53	0.99
2	25 ^{0}C	$q_e = -5.113C_e - 29.38$	-5.113	714	-29.38	0.986
	40 ^{0}C	$q_e = -5.107C_e - 77.33$	-5.107	776	-77.33	0.99
3	25 ^{0}C	$q_e = -5.27C_e - 15.91$	-5.27	732	-15.91	0.98
	40 ^{0}C	$q_e = -6.52C_e - 22.13$	-6.52	1064	-22.13	0.936
4	25 ^{0}C	$q_e = -4.49C_e + 2.46$	-4.49	576	2.46	0.989
	40 ^{0}C	$q_e = -6.96C_e + 15.79$	-6.96	1052	15.79	0.945
5	25 ^{0}C	$q_e = -7.37C_e + 53.54$	-7.37	1236	53.54	0.977
	40 ^{0}C	$q_e = -6.92C_e + 5.15$	-6.92	1060	5.15	0.997
6	25 ^{0}C	$q_e = -7.39C_e + 39.88$	-7.39	1132	39.88	0.991
	40 ^{0}C	$q_e = -5.22C_e - 28.79$	-5.22	700	-28.79	0.932
7	25 ^{0}C	$q_e = -5.76C_e - 33.01$	-5.76	822.2	-33.01	0.934
	40 ^{0}C	$q_e = -6.88C_e - 37.97$	-6.88	1013.4	-37.97	0.96
8	25 ^{0}C	$q_e = -5.61C_e - 39.82$	-5.61	818.8	-39.82	0.952
	40 ^{0}C	$q_e = -6.84C_e - 44.96$	-6.84	1187.4	-44.96	0.898
9	25 ^{0}C	$q_e = -4.46C_e - 37.45$	-4.46	564	-37.45	0.844
	40 ^{0}C	$q_e = -6.27C_e - 54.86$	-6.27	912	-54.86	0.889
10	25 ^{0}C	$q_e = -7.36C_e - 12.75$	-7.36	1113.6	-12.75	0.995
	40 ^{0}C	$q_e = -8.60C_e + 12.46$	-8.60	1506	12.46	0.999
11	25 ^{0}C	$q_e = -8.41C_e + 14.93$	-8.41	1501.6	14.93	0.972
	40 ^{0}C	$q_e = -10.24C_e - 25.21$	-10.24	1758.4	-25.21	0.942

Table 70. Continued

Sample No.	Temp	Linear equation	Buffer power	Max. quantity desorbed (mg kg^{-1})	Intercept (mg kg^{-1})	R^2
12	25 ^{0}C	$q_e = -9.38C_e + 27.13$	-9.38	1801	27.13	0.935
	40 ^{0}C	$q_e = -9.84C_e + 70.35$	-9.84	1958	70.35	0.957
13	25 ^{0}C	$q_e = -4.09C_e - 11.02$	-4.09	515.6	-11.02	0.986
	40 ^{0}C	$q_e = -3.35C_e - 31.09$	-3.35	440	-31.09	0.924
14	25 ^{0}C	$q_e = -3.04C_e - 23.52$	-3.04	398	-23.52	0.962
	40 ^{0}C	$q_e = -3.12C_e - 61.61$	-3.12	466.8	-61.61	0.657
15	25 ^{0}C	$q_e = -3.32C_e - 26.19$	-3.32	428	-26.19	0.989
	40 ^{0}C	$q_e = -4.12C_e - 36.83$	-4.12	610	-36.83	0.989
16	25 ^{0}C	$q_e = -7.1C_e + 23.78$	-7.10	1196	23.78	0.989
	40 ^{0}C	$q_e = -6.47C_e - 69.23$	-6.47	1080.8	-69.23	0.929
17	25 ^{0}C	$q_e = -4.19C_e + 19.47$	-4.19	725.8	19.47	0.715
	40 ^{0}C	$q_e = -10.69C_e + 105.45$	-10.69	1428.8	105.45	0.935
18	25 ^{0}C	$q_e = -6\ C_e + 41.42$	-6.00	745	41.42	0.947
	40 ^{0}C	$q_e = -6.54C_e - 4.7$	-6.54	998.6	-4.7	0.841
19	25 ^{0}C	$q_e = -8.06C_e + 0.23$	-8.06	1272	0.23	0.988
	40 ^{0}C	$q_e = -8.09C_e - 52.83$	-8.09	1408	-52.83	0.984
20	25 ^{0}C	$q_e = -7.33C_e - 39.41$	-7.33	1330.8	-39.41	0.948
	40 ^{0}C	$q_e = -7.81C_e - 79.86$	-7.81	1374	-79.86	0.989
21	25 ^{0}C	$q_e = -2.301C_e - 9.69$	-2.30	250	-9.69	0.859
	40 ^{0}C	$q_e = -1.58C_e - 40.84$	-1.58	261.2	-40.84	0.382
22	25 ^{0}C	$q_e = -8.43C_e - 6.99$	-8.43	1432.8	-6.99	0.988
	40 ^{0}C	$q_e = -9.39C_e - 31.64$	-9.39	1730	-31.64	0.994

Occluded Si fraction had significant negative correlation with maximum quantity desorbed (-0.470* 25 ^{0}C, -0.545** at 40 ^{0}C) and positive correlation with buffer power (0.473* at 25 ^{0}C, 0.493* at 40 ^{0}C). Organic carbon content of the soil also showed the same trend. Anion exchange capacity had significant negative correlation with maximum quantity desorbed (-0.498* at 25 ^{0}C and -0.500* at 40 ^{0}C), and positive correlation with buffer power at 25 ^{0}C (0.486*). A significant negative correlation was observed between clay content and maximum quantity desorbed at 40 ^{0}C (-0.461*). CBD-Fe had significant positive correlation with buffer power at 25 ^{0}C (0.440*) and negative correlation with maximum quantity desorbed at 40 ^{0}C (-0.499*).

Table 71. Correlation between parameters of Q-I curve and soil properties for Si desorption

	Max. quantity desorbed at 25 ^{0}C	**Buffer power at 25 ^{0}C**	**Max. quantity desorbed at 40 ^{0}C**	**Buffer power at 40 ^{0}C**
Buffer power at 25 ^{0}C	-0.976**			
Max. quantity desorbed at 40 ^{0}C	0.835**	-0.804**		
Buffer power at 40 ^{0}C	-0.743**	0.716**	-0.955**	
Occluded Si	-0.470*	0.473*	-.0545**	0.493*
OC	-0.478*	0.471*	-0.561**	0.525*
AEC	-0.498*	0.486*	-0.500*	
Clay			-0.461*	
CBD-Fe		0.440*	-0.499*	
Av.N	-0.495*	0.511*	-0.633**	0.581**
Av.Fe	-0.459*	0.444*	-0.604**	0.578**
Ex.Mg			-0.482*	0.557**
Ex.Na			-0.484*	0.484*

Maximum quantity desorbed at 25 ^{0}C had significant negative correlation with Av.N (-0.495*) and Av.Fe (-0.459*). Buffer power 25 ^{0}C had significant positive correlation with Av.N (0.511*) and Av.Fe (0.444*). Maximum quantity desorbed at 40 ^{0}C had significant negative correlation with Av.N (-0.633**), Av.Fe (-0.604**), Ex. Mg (-0.482*) and Ex.Na (-0.484*). Buffer power at 40 ^{0}C was significantly and positively correlated with Av.N (0.581**), Av.Fe (0.578**), Ex. Mg (0.557**) and Ex.Na (-0.484*).

Table 72. Thermodynamic parameters of Si desorption

Sample No.	surface area (m^{2}g^{-1})	K^0		ΔG^0 (kcal mol^{-1})		ΔH^0 (kcal mol^{-1})	ΔS^0 (cal mol^{-1} K^{-1})	
		25 ^{0}C	40 ^{0}C	25 ^{0}C	40 ^{0}C		25 ^{0}C	40 ^{0}C
1	62.24	6.08	6.57	-1.069	-1.171	0.959	6.81	6.81
2	59.23	6.35	6.61	-1.095	-1.175	0.493	5.33	5.33
3	67.45	6.10	6.19	-1.071	-1.134	0.167	4.16	4.16
4	79.66	5.46	5.73	-1.005	-1.086	0.596	5.37	5.37
5	112.44	5.23	5.54	-0.98	-1.065	0.716	5.69	5.69
6	89.48	5.56	5.79	-1.016	-1.092	0.501	5.09	5.09
7	6.34	8.47	8.53	-1.265	-1.333	0.087	4.54	4.54
8	8.21	8.36	8.41	-1.258	-1.324	0.068	4.45	4.45
9	6.11	8.40	8.66	-1.26	-1.343	0.377	5.50	5.50
10	8.39	8.39	8.06	-1.26	-1.298	-0.493	2.57	2.57
11	15.66	7.46	7.68	-1.19	-1.268	0.356	5.19	5.19
12	18.65	7.53	7.23	-1.195	-1.23	-0.503	2.33	2.33
13	84.32	5.72	5.77	-1.033	-1.09	0.104	3.81	3.81
14	94.07	5.33	5.76	-0.99	-1.088	0.958	6.54	6.54
15	124.78	5.45	5.58	-1.004	-1.069	0.285	4.33	4.33
16	38.92	6.57	7.01	-1.115	-1.212	0.802	6.43	6.43
17	40.33	5.57	6.02	-1.017	-1.116	0.949	6.60	6.60
18	53.56	5.63	5.83	-1.023	-1.096	0.43	4.88	4.88
19	33.42	6.93	7.12	-1.146	-1.221	0.342	5.00	5.00
20	40.73	6.92	6.99	-1.145	-1.21	0.135	4.30	4.30
21	29.78	5.80	4.53	-1.041	-0.94	-3.06	-6.77	-6.77
22	39.69	6.85	6.99	-1.139	-1.209	0.257	4.69	4.69

Thermodynamics of Si desorption in soil

The thermodynamic parameters of Si desorption in the soil are given in Table 72. The highest value of thermodynamic equilibrium constant (K^0) at 25 ^{0}C (8.47) was noted in coastal sandy soil (Sample No. 7) and the lowest (5.23) in the soil from *Kole* land (Sample No. 5). The highest value for K^0 at 40 ^{0}C (8.66) was in the coastal sandy soil (Sample No. 9), and the lowest value at 40 ^{0}C (4.53) was in the soil from Palakkad eastern plain (Sample No. 21). Out of the collected 22 samples, except two soils from *Onattukara* sandy plain and one from Palakkad eastern plain, all other soils showed an increase in thermodynamic equilibrium constant (K^0) value with increase in temperature.

Change in free energy for all the soils at both the temperatures was negative. Change in enthalpy was positive for all the soils except two soils from *Onattukara* sandy plain and one soil from Palakkad eastern plain. Change in entropy was positive for all the soils except the soil from Palakkad eastern plain (Sample No. 21).

Since none of the soils had adsorption of added concentration of Si, adsorption isotherms were not tried.

4.3.2. Adsorption study of P and B in binary system

Experiment on competitive adsorption of phosphorous and boron was carried out at 25 ^{0}C, following the procedure detailed in 3.3.1.2. Quantity-intensity curves were prepared for comparing the preferential adsorption of phosphorous and boron in soil. The parameters of Q-I curve of P or B adsorption at fixed concentration of the other anion is given in Table 73.

Solution containing different concentration of both P and B was used for adsorption study. A total of 132 adsorption studies were carried out using 36 combinations of B and P in each soil. More than 50 per cent variance was explained in 115 adsorption studies in the case of P adsorption and 113 adsorption studies in the case of B adsorption.

As a general trend it was observed that phosphorus was preferentially adsorbed over B on the adsorption sites in soil. Whether the solution contains high, low or equal concentration of B with that of P, preferential adsorption of P was found. B adsorption was decreasing with increasing concentration of added P. The trend was observed in all soils. Both buffer power and maximum quantity adsorbed was decreasing with increasing concentration of added P. In sandy soil, desorption of B was observed at higher concentration of added P.

Table 73. Parameters of quantity-intensity curve of P and B adsorption in binary mixture of P and B

S. No	**Adsorption of Pat fixed concentration of B**						**Adsorption of B at fixed concentration of P**				
	Added.Por B (mmol L^{-1})	**Linear equation**	**B (L kg^{-1})**	**K (mg kg^{-1})**	**M (mg kg^{-1})**	**R^2**	**Linear equation**	**B (Lkg^{-1})**	**K (mg kg^{-1})**	**M (mg kg^{-1})**	**R^2**
1	0	qe=42.14Ce+59.7	42.14	59.7	915	0.928	qe=0.47Ce-0.31	0.47	-0.31	20.2	0.984
	0.25	qe=37.23Ce+80.84	37.23	80.84	898	0.929	qe=0.344Ce-0.45	0.344	-0.45	15.24	0.907
	0.5	qe=42.24Ce+107.9	42.24	107.9	993.4	0.911	qe=0.31Ce-0.34	0.31	-0.34	13.22	0.998
	1	qe=37.57Ce+104.6	37.57	104.6	1000.9	0.899	qe=0.26Ce-0.08	0.26	-0.08	11.24	0.995
	2	qe=49.4Ce+95.69	49.4	95.69	992	0.923	qe=0.26Ce+0.032	0.26	0.03	11.29	0.956
	4	qe=45.85Ce+52.55	45.85	52.55	999.3	0.927	qe=0.23Ce+0.148	0.23	0.148	9.87	0.89
2	0	qe=26.41Ce+115.3	26.41	115.3	932.6	0.946	qe=0.41Ce-0.73	0.41	-0.73	17.25	0.945
	0.25	qe=C29.97e+108.2	29.97	108.2	981.3	0.951	qe=0.31Ce+0.81	0.31	0.81	13.75	0.961
	0.5	qe=26.16Ce+112.3	26.16	112.3	899.34	0.941	qe=0.24Ce+1.18	0.24	1.18	10.75	0.877
	1	qe=27.84Ce+109.4	27.84	109.4	942.74	0.948	qe=0.19Ce+1.29	0.19	1.29	9.32	0.809
	2	qe=28.59Ce+107.7	28.59	107.7	961.08	0.95	qe=0.16Ce+1.3	0.16	1.3	7.87	0.815
	4	qe=26.13Ce+118	26.13	118	898.6	0.923	qe=0.11Ce+1.39	0.11	1.39	5.43	0.723
3	0	qe=42.27Ce+102.9	42.27	102.9	996.4	0.942	qe=0.39Ce-1.23	0.39	-1.23	15.98	0.904
	0.25	qe=40.70Ce+167.2	40.7	167.2	981.4	0.806	qe=0.30Ce-0.65	0.30	-0.65	12.3	0.935
	0.5	qe=37.64Ce+189.1	37.64	189.1	969.4	0.692	qe=0.24Ce-0.16	0.24	-0.16	10.3	0.939
	1	qe=28.79Ce+190.9	28.79	190.9	991.08	0.734	qe=0.20Ce-0.29	0.20	-029	8.43	0.973
	2	qe=27.19Ce+177.3	27.19	177.3	1931.1	0.694	qe=0.13Ce+0.34	0.13	0.34	5.82	0.958
	4	qe=32.43Ce+181.6	32.43	181.6	1002	0.743	qe=0.14Ce+0.27	0.14	0.27	5.28	0.88

Table 73. Continued

S. No	Added. Por B (mmol L^{-1})	Adsorption of Pat fixed concentration of B					Adsorption of B at fixed concentration of P				
		Linear equation	B L kg^{-1}	K mg kg^{-1}	M (mg kg^{-1})	R^2	Linear equation	B L kg^{-1}	K mg kg^{-1}	M (mg kg^{-1})	R^2
4	0	qe= 55.18Ce+210.4	55.18	210.4	987.6	0.703	qe=0.26Ce+1.9	0.26	1.9	13.4	0.506
	0.25	qe=55.74Ce+190.1	55.74	190.1	999.8	0.765	qe=0.2Ce+2.1	0.2	2.1	8.3	0.582
	0.5	qe=61.89Ce+202.7	61.89	202.7	1017	0.74	qe=0.194Ce-0.65	0.194	-0.65	7.92	0.987
	1	qe=51.28Ce+190.8	51.28	190.8	1002	0.77	qe=0.199Ce-0.572	0.199	-0.572	7.71	0.942
	2	qe=34.92Ce+214.7	34.92	214.7	883	0.625	qe=0.066Ce+0.603	0.066	0.603	4.78	0.39
	4	qe=37.21Ce+215.4	37.21	215.4	865	0.607	qe=0.059Ce+1.01	0.059	1.01	3.28	0.439
5	0	qe=32.16Ce+217.3	32.16	217.3	933	0.68	qe=0.45Ce+0.93	0.45	0.93	15.22	0.8839
	0.25	qe=75.11Ce+211.7	75.11	211.7	991.1	0.71	qe=0.493Ce-3.13	0.493	-3.13	15.11	0.884
	0.5	qe=48.88Ce+187.2	48.88	187.2	980	0.803	qe=0.413Ce+0.199	0.413	0.199	16.1	0.623
	1	qe=43.19Ce+217.7	43.19	217.7	998.8	0.705	qe=0.274Ce-1.06	0.274	-1.06	10.89	0.686
	2	qe=44.13Ce+201.2	44.13	201.2	985.7	0.752	qe=0.257Ce-2.02	0.257	-2.02	9.42	0.633
	4	qe=65.1Ce+163.3	65.1	163.3	965.6	0.854	qe=0.214Ce+0.645	0.214	0.645	8.2	0.85
6	0	qe=14.13Ce+217.7	14.13	217.7	762.6	0.566	qe=0.293Ce+0.989	0.293	0.989	12.78	0.732
	0.25	qe=21.15Ce+191.5	21.15	191.5	792	0.713	qe=0.239Ce-0.668	0.239	-0.668	9.15	0.894
	0.5	qe=22.32Ce+134.6	22.32	134.6	832.6	0.901	qe=0.176Ce+0.423	0.176	0.423	6.32	0.813
	1	qe=19.12Ce+188.3	19.12	188.3	826.5	0.744	qe=0.092Ce+2.52	0.092	2.52	7.23	0.241
	2	qe=16.24Ce+196	16.24	196	784.6	0.675	qe=0.165Ce+0.354	0.165	0.354	6.91	0.974
	4	qe=19.23Ce+206.2	19.23	206.2	782.6	0.611	qe=0.09Ce+0.609	0.09	0.609	4.7	0.409

Table 73. Continued

S. No	Added. Por B (mmol L^{-1})	Adsorption of Pat fixed concentration of B					Adsorption of B at fixed concentration of P				
		Linear equation	B L kg^{-1}	K mg kg^{-1}	M (mg kg^{-1})	R^2	Linear equation	B L kg^{-1}	K mg kg^{-1}	M (mg kg^{-1})	R^2
7	0	qe=0.39Ce+24.69	0.39	24.69	45	0.222	qe=0.143Ce-0.6	0.143	-0.6	5.01	0.928
	0.25	qe=0.63Ce+20.71	0.63	20.71	73	0.725	qe=0.099Ce-0.024	0.099	-0.024	4.47	0.874
	0.5	qe=0.55Ce+22.86	0.55	22.86	49.4	0.346	qe=0.098Ce-0.417	0.098	-0.417	4.19	0.844
	1	qe=0.199Ce+28.3	0.199	28.3	79	0.109	qe=-0.059Ce+0.35	-0.059	0.35	1.24	0.352
	2	qe=0.236Ce+24.02	0.236	24.02	44.3	0.308	qe=-0.085Ce+0.16	-0.085	0.16	0.98	0.378
	4	qe=0.601Ce+21.71	0.601	21.71	70.6	0.726	qe=-0.027Ce-0.92	-0.027	-0.92	0.31	0.205
8	0	qe=0.354Ce+23.05	0.354	23.05	56	0.576	qe=0.215Ce-0.63	0.215	-0.63	8.83	0.994
	0.25	qe=0.524Ce+19.35	0.524	19.35	62.7	0.69	qe=0.094Ce-0.705	0.094	-0.705	2.76	0.963
	0.5	qe=0.29Ce+19.76	0.29	19.76	52.7	0.456	qe=0.085Ce-1.209	0.085	-1.209	2.37	0.954
	1	qe=0.589Ce+20.67	0.589	20.67	79	0.772	qe=0.076Ce-0.62	0.076	-0.62	2.62	0.959
	2	qe=0.26Ce+22.1	0.26	22.1	44	0.441	qe=0.064Ce-0.21	0.064	-0.21	2.79	0.874
	4	qe=0.732Ce+20.89	0.732	20.89	86.9	0.802	qe=0.057Ce-0.52	0.057	-0.52	1.78	0.932
9	0	qe=0.875Ce+4.93	0.875	4.93	97	0.973	qe=0.064Ce+0.162	0.064	0.162	2.76	0.737
	0.25	qe=0.282Ce+16.92	0.282	16.92	49.7	0.587	qe=0.056Ce-0.109	0.056	-0.109	2.44	0.97
	0.5	qe=0.148Ce+9.18	0.148	9.18	26.7	0.411	qe=-0.021Ce-0.206	-0.021	-0.206	Des	0.963
	1	qe=0.178Ce+10.8	0.178	10.8	34.3	0.416	qe=-0.07Ce+0.69	-0.07	0.69	Des	0.843
	2	qe=0.223Ce+5.69	0.223	5.69	27	0.484	qe=-0.092Ce-0.18	-0.092	-0.18	0.02	0.829
	4	qe=0.808Ce+4.36	0.808	4.36	91	0.87	qe=-0.11Ce+0.11	-0.11	0.11	0.11	0.895

Table73. Continued

S. No	Added. Por B (mmol L^{-1})	Adsorption of Pat fixed concentration of B					Adsorption of B at fixed concentration of P				
		Linear equation	B L kg^{-1}	K mg kg^{-1}	M (mg kg^{-1})	R^2	Linear equation	B L kg^{-1}	K mg kg^{-1}	M (mg kg^{-1})	R^2
10	0	qe=1.04Ce+29.49	1.04	29.49	130.9	0.684	qe=0.074Ce-0.354	0.074	-0.354	2.93	0.612
	0.25	qe=0.686Ce+32	0.686	32	92	0.521	qe=0.072Ce+0.159	0.072	0.159	2.86	0.804
	0.5	qe=1.06Ce+24.17	1.06	24.17	129	0.89	qe=0.009Ce+0.414	0.009	0.414	1.31	0.034
	1	qe=1.23Ce+25.44	1.23	25.44	147	0.906	qe=-0.082Ce+0.28	-0.082	0.28	0.8	0.789
	2	qe=0.525Ce+34.9	0.525	34.9	86.8	0.401	qe=-0.059Ce+0.36	-0.059	0.36	0.63	0.515
	4	qe=1.016Ce+28.2	1.016	28.2	103.9	0.65	qe=-0.244Ce+0.09	-0.244	0.09	0.71	0.749
11	0	qe=0.789Ce+36.7	0.789	36.7	121.3	0.558	qe=0.07Ce+0.036	0.07	0.036	2.86	0.911
	0.25	qe=1.03Ce+29.8	1.03	29.8	109.7	0.788	qe=0.067Ce-0.59	0.067	-0.59	2.37	0.879
	0.5	qe=0.782Ce+27.54	0.782	27.54	103.7	0.787	qe=-0.038Ce+0.12	-0.038	0.12	0.65	0.534
	1	qe=0.36Ce+33.15	0.36	33.15	74	0.356	qe=-0.026Ce-0.353	-0.026	-0.353	0.02	0.702
	2	qe=0.346Ce+36.8	0.346	36.8	76.5	0.252	qe=-0.042Ce-0.12	-0.042	-0.12	0.27	0.812
	4	qe=0.888Ce+35.2	0.888	35.2	103.6	0.87	qe=-0.051Ce-0.053	-0.051	-0.053	0.43	0.675
12	0	qe=0.656Ce+36.9	0.656	36.9	99	0.539	qe=0.043Ce+0.035	0.043	0.035	1.75	0.836
	0.25	qe=0.839Ce+33.4	0.839	33.4	97.5	0.659	qe=-0.005Ce+0.23	-0.005	0.23	0.84	0.028
	0.5	qe=0.529Ce+37.56	0.529	37.56	84	0.498	qe=0.004Ce+0.082	0.004	0.082	1.05	0.007
	1	qe=1.039Ce+33.1	1.039	33.1	129	0.823	qe=-0.031Ce-0.226	-0.031	-0.226	0.1	0.712
	2	qe=0.334Ce+36.9	0.334	36.9	74	0.273	qe=-0.052Ce+0.01	-0.052	0.01	Des	0.793
	4	qe=0.758Ce+38.84	0.758	38.84	95.1	0.558	qe=-0.188Ce+0.21	-0.188	0.21	0.11	0.958

Table 73. Continued

S. No	Added. Por B (mmol L^{-1})	Adsorption of Pat fixed concentration of B					Adsorption of B at fixed concentration of P				
		Linear equation	B L kg^{-1}	K mg kg^{-1}	M (mg kg^{-1})	R^2	Linear equation	B L kg^{-1}	K mg kg^{-1}	M (mg kg^{-1})	R^2
13	0	qe=47.94Ce+198.3	47.94	198.3	1029	0.762	qe=0.316Ce+0.72	0.316	0.72	11.94	0.515
	0.25	qe=47.92Ce+188.9	47.92	188.9	846.7	0.689	qe=0.251Ce-0.65	0.251	-0.65	10.16	0.974
	0.5	qe=51.53Ce+192.8	51.53	192.8	991.5	0.751	qe=0.224Ce+1.34	0.224	1.34	7.89	0.605
	1	qe=52.07Ce+197.2	55.07	197.2	1006	0.746	qe=0.117Ce+0.32	0.117	0.32	4.57	0.766
	2	qe=45.46Ce+181.4	45.46	181.44	908	0.739	qe=0.076Ce+1.33	0.076	1.33	4.82	0.371
	4	qe=42.8Ce+182.5	42.8	182.5	894.2	0.715	qe=0.078Ce+0.446	0.078	0.446	3.9	0.869
14	0	qe=174.7Ce+173.9	174.7	173.9	1150	0.799	qe=0.229Ce+2.65	0.229	2.65	11.2	0.774
	0.25	qe=174.5Ce+166.5	174.5	166.5	1050	0.76	qe=0.228Ce+2.24	0.228	2.24	10	0.681
	0.5	qe=67.42Ce+208.9	67.42	208.9	1028	0.729	qe=0.16Ce+0.58	0.16	0.58	6.28	0.814
	1	qe=49.02Ce+192.9	49.02	192.9	217.2	0.756	qe=0.124Ce+0.325	0.124	0.325	4.5	0.867
	2	qe=31.55Ce+217.2	31.55	217.2	868.1	0.612	qe=0.096Ce+0.237	0.096	0.237	4.5	0.883
	4	qe=58.77Ce+205.7	58.77	205.7	918.2	0.659	qe=0.079Ce+1.37	0.079	1.37	4.14	0.464
15	0	qe=68.05Ce+204.5	68.05	206.5	1192	0.797	qe=0.26Ce+1.9	0.26	1.9	13.4	0.506
	0.25	qe=47.7Ce+194.89	47.7	194.89	973.8	0.745	qe=0.2Ce+2.09	0.2	2.09	8.31	0.582
	0.5	qe=61.89Ce+202.7	61.89	202.7	1017	0.74	qe=0.199Ce-0.572	0.199	-0.572	7.71	0.942
	1	qe=51.28Ce+190.8	51.28	190.8	1002	0.765	qe=0.19Ce-0.65	0.19	-0.65	7.92	0.987
	2	qe=34.92Ce+214.7	34.92	214.7	883	0.625	qe=0.065Ce+0.603	0.065	0.603	4.75	0.339
	4	qe=37.21Ce+215.4	37.21	215.4	865	0.607	qe=0.058Ce+1.01	0.058	1.01	3.28	0.439

Table 73. Continued

S. No	Added. Por B (mmol L^{-1})	Adsorption of Pat fixed concentration of B					Adsorption of B at fixed concentration of P				
		Linear equation	B L kg^{-1}	K mg kg^{-1}	M (mg kg^{-1})	R^2	Linear equation	B L kg^{-1}	K mg kg^{-1}	M (mg kg^{-1})	R^2
16	0	qe=5.59Ce+120.98	5.59	120.98	485.1	0.793	qe=0.28Ce-0.087	0.28	-0.087	12.39	0.964
	0.25	qe=6.54Ce+104.72	6.54	104.72	428.6	0.801	qe=0.263Ce-0.42	0.263	-0.42	10.89	0.985
	0.5	qe=4.58Ce+124.33	4.58	124.33	403	0.68	qe=0.23Ce+0.037	0.23	0.037	10.23	0.958
	1	qe=5.3Ce+117.38	5.3	117.38	423.8	0.724	qe=0.17Ce+0.24	0.17	0.24	8.03	0.849
	2	qe=4.56Ce+116.35	4.56	116.35	373.2	0.651	qe=0.166Ce-0.25	0.166	-0.25	7.33	0.913
	4	qe=5.54Ce+102.56	5.54	102.56	421.5	0.823	qe=0.16Ce-0.49	0.16	-0.49	6.81	0.882
17	0	qe=19.9Ce+185.85	19.9	185.85	850.9	0.765	qe=0.243Ce-0.2	0.243	-0.2	10.68	0.937
	0.25	qe=21.29Ce+146.8	21.29	146.8	713.3	0.656	qe=0.24Ce+0.36	0.24	0.36	10.82	0.933
	0.5	qe=21.56Ce+131.6	21.56	131.6	793.4	0.906	qe=0.237Ce-0.14	0.237	-0.14	10.4	0.939
	1	qe=20.23Ce+183.1	20.23	183.1	783.5	0.717	qe=0.24Ce-0.16	0.24	-0.16	10.3	0.939
	2	qe=27.55Ce+131.1	27.55	131.1	800.8	0.906	qe=0.21Ce+0.005	0.21	0.005	9.42	0.847
	4	qe=25.69Ce+107.6	25.69	107.6	791.6	0.949	qe=0.16Ce-0.14	0.16	-0.14	8.1	0.739
18	0	qe=10.24Ce+139.1	10.24	139.1	661.4	0.845	qe=0.32Ce-0.202	0.32	-0.202	13.75	0.968
	0.25	qe=11.62Ce+113.3	11.62	113.3	564.8	0.869	qe=0.25Ce-0.03	0.25	-0.03	10.26	0.937
	0.5	qe=8.31Ce+141.49	8.31	141.49	565.9	0.745	qe=0.117Ce+0.89	0.117	0.89	5.58	0.621
	1	qe=8.87Ce+139.16	8.87	139.16	566.3	0.763	qe=0.109Ce+1.1	0.109	1.1	5.58	0.523
	2	qe=8.66Ce+146.65	8.66	146.65	538.5	0.711	qe=0.117Ce+0.54	0.117	0.54	4.4	0.649
	4	qe=13.28Ce+107	13.28	107	634.7	0.905	qe=0.097Ce+0.05	0.097	0.05	3.57	0.625

Table 73. Continued

S. No	Added. Por B (mmol L^{-1})	Adsorption of Pat fixed concentration of B					Adsorption of B at fixed concentration of P				
		Linear equation	B L kg^{-1}	K mg kg^{-1}	M (mg kg^{-1})	R^2	Linear equation	B L kg^{-1}	K mg kg^{-1}	M (mg kg^{-1})	R^2
19	0	qe=6.26Ce+62.13	6.26	62.13	505.8	0.933	qe=0.27Ce+0.078	0.27	0.078	12.01	0.971
	0.25	qe=3.45Ce+107.37	3.45	107.37	278.2	0.538	qe=0.188Ce+0.11	0.188	0.11	7.89	0.918
	0.5	qe=4.19Ce+92.27	4.19	92.27	384.5	0.797	qe=0.14Ce+0.47	0.14	0.47	3.18	0.869
	1	qe=5.08Ce+79.51	5.08	79.51	419.4	0.895	qe=0.14Ce+0.47	0.14	0.47	6.39	0.869
	2	qe=3.92Ce+79.83	3.92	79.83	320.4	0.824	qe=0.133Ce+0.376	0.133	0.376	5.86	0.919
	4	qe=5.04Ce+84.18	5.04	84.18	387.5	0.836	qe=0.127Ce+0.82	0.127	0.82	5.1	0.716
20	0	qe=3.28Ce+50.78	3.28	50.78	349.8	0.884	qe=0.19Ce+0.16	0.19	0.16	8.52	0.969
	0.25	qe=1.68Ce+67.9	1.68	67.9	161.8	0.562	qe=0.169Ce-0.044	0.169	-0.044	7.75	0.955
	0.5	qe=2.76Ce+62.22	2.76	62.22	288	0.879	qe=0.167Ce-0.71	0.167	-0.71	7.43	0.826
	1	qe=2.72Ce+58.41	2.72	58.41	279.4	0.893	qe=0.129Ce-0.199	0.129	-0.199	4.75	0.952
	2	qe=2.42Ce+82.56	2.42	82.56	295.7	0.485	qe=0.129Ce+0.29	0.129	0.29	4.68	0.906
	4	qe=2.94Ce+60.29	2.94	60.29	269.5	0.857	qe=0.065Ce+0.23	0.065	0.23	3.77	0.628
21	0	qe=3.46Ce+143.65	3.46	143.65	355.1	0.452	qe=0.25Ce+0.19	0.25	0.19	11.34	0.963
	0.25	qe=2.7Ce+127.84	2.7	127.84	249.8	0.339	qe=0.213Ce-0.091	0.213	-0.091	9.04	0.986
	0.5	qe=3.67Ce+138.69	3.67	138.69	381.7	0.534	qe=0.202Ce-0.469	0.202	-0.469	8.2	0.989
	1	qe=3.9Ce+131	3.9	131	373.3	0.514	qe=0.108Ce+0.457	0.108	0.457	4.82	0.939
	2	qe=4.26Ce+96.53	4.26	96.53	343.7	0.758	qe=0.114Ce+0.55	0.114	0.55	5.45	0.636
	4	qe=3.94Ce+96.27	3.94	96.27	341.9	0.756	qe=0.009Ce+1.28	0.009	1.28	3.32	0.023

Table 73. Continued

S. No	**Added. Por B (mmol L^{-1})**	**Adsorption of Pat fixed concentration of B**					**Adsorption of B at fixed concentration of P**				
		Linear equation	**B L kg^{-1}**	**K mg kg^{-1}**	**M (mg kg^{-1})**	**R^2**	**Linear equation**	**B L kg^{-1}**	**K mg kg^{-1}**	**M (mg kg^{-1})**	**R^2**
22	0	qe=3.98Ce+50.77	3.98	50.77	310.2	0.907	qe=0.151Ce+0.188	0.151	0.188	6.28	0.931
	0.25	qe=3.24Ce+55.95	3.24	55.95	264.5	0.865	qe=0.074Ce+1.1	0.074	1.1	4.85	0.401
	0.5	qe=1.13Ce+108.18	1.13	108.18	294.4	0.17	qe=0.053Ce+0.6	0.053	0.6	3.98	0.334
	1	qe=1.25Ce+108.27	358.3	1.25	108.3	0.122	qe=0.058Ce+0.705	0.058	0.705	2.55	0.646
	2	qe=2.32Ce+59.97	2.32	59.97	233.5	0.831	qe=0.069Ce+0.819	0.069	0.819	2.65	0.568
	4	qe=1.534Ce+73.54	1.534	73.54	205.9	0.508	qe=0.011Ce+1.06	0.011	1.06	2.790	0.034

B-Buffer power, K-intercept, M-Maximum quantity adsorbed

Highest value of maximum quantity of adsorbed B was found in *Pokkali* soil (Sample No. 1) at zero P concentration. All the low land soils from *Pokkali, Kole* and *Kuttanad* were recorded with comparatively high B adsorption. Maximum quantity of adsorbed B was very less in sandy soils from *Onattukara* sandy plain and northern coastal plain. Buffer power of B also showed the same trend of maximum quantity adsorbed. Negative buffer power was observed in sandy soils of northern coastal plain and *Onattukara* sandy plain.

High value of maximum quantity adsorbed and buffer power was observed in low land soils of *Pokkali, Kole* and *Kuttanad* in case of P adsorption. All the soils from northern coastal plain and *Onattukara* sandy plain were recorded with low value of buffer power and maximum quantity adsorbed in P adsorption. A general trend of increase or decrease in adsorption was not observed in case of P adsorption. The maximum quantity adsorbed and buffer power was found very high in the case of P adsorption than B adsorption from solution containing both P and B. Value of intercept also found very high in P adsorption compared to B adsorption. Even negative intercept value was found in case of B adsorption. Comparatively high intercept value was found in low land soils of *Pokkali, Kole* and *Kuttanad* in case of P adsorption. For P, none of the soils had negative intercept value. The higher values obtained in the case of intercepts of curves for boron was found much lesser than the lower values of intercepts for P.

4.4. STUDIES ON ANION EXCHANGE

Anion exchange capacity was estimated following P adsorption method as described in section 3.4.1. The adsorbed P was exchanged with high concentration of chloride. Details about AEC, amount of adsorbed P and P exchanged with Cl^- are given in Table 74. Highest value of AEC (34.49 cmol(-)kg^{-1}) was in *Pokkali* soil (Sample No. 3) and the lowest (3.91 cmol(-)kg^{-1}) recorded in Sample No. 12 from northern coastal plain (Table 74) . Higher values of AEC was recorded in all the three *Pokkali* soils (>30 cmol(-)kg^{-1}). Comparatively lower values of AEC were observed in soils from Palakkad eastern plain, sandy soils from northern coastal plain and *Onattukara* sandy soil.

Table 74. Comparison of adsorbed P and P exchanged with chloride ion

Sample No.	AEC (cmol(-) kg^{-1})	Contribution in determining AEC (%)		P adsorbed (mg kg^{-1})	P exchanged with Cl$^-$ (mg kg^{-1})	Percentage of P exchanged with Cl$^-$
		Adsorbed P	Bray-P			
1	30.96	94.90	5.10	1821.67	23.27	1.28
2	33.10	97.22	2.78	1994.83	23.47	1.18
3	34.49	96.83	3.17	2070.76	24.97	1.21
4	23.68	99.72	0.28	1464.16	34.70	2.37
5	17.39	99.42	0.58	1071.67	37.70	3.52
6	15.69	99.37	0.63	966.67	22.16	2.29
7	4.14	76.56	23.44	196.67	12.01	6.11
8	4.57	93.33	6.67	264.166	9.83	3.72
9	4.33	66.45	33.55	178.33	7.20	4.04
10	7.04	95.23	4.77	415.83	15.66	3.77
11	5.41	84.04	15.96	281.67	12.99	4.61
12	3.91	93.90	6.10	227.50	11.58	5.09
13	18.07	99.58	0.42	1115.83	2.35	0.21
14	26.38	99.80	0.20	1632.50	3.40	0.21
15	29.15	99.78	0.22	1803.50	3.34	0.19
16	12.54	97.95	2.05	761.67	31.58	4.15
17	20.56	99.71	0.29	1270.83	31.00	2.44
18	18.14	93.61	6.39	1052.50	33.50	3.18
19	10.56	90.15	9.85	590.00	21.18	3.59
20	7.45	96.88	3.12	447.50	24.92	5.57
21	8.88	98.37	1.63	541.67	6.93	1.28
22	5.80	90.09	9.91	324.17	31.35	9.67
Maximum	**34.49**	**99.80**	**33.55**	**2070.76**	**37.7**	**9.67**
Minimum	**3.91**	**66.45**	**0.20**	**178.33**	**2.35**	**0.19**

AEC was estimated as sum of adsorbed P and bray extractable P. Highest adsorbed P (2070.76 mg kg^{-1}) was noted in *Pokkali* soil (Sample No. 3) and the lowest (178.33 mg kg^{-1}) in the soil from northern coastal plain (Sample No. 9). Higher adsorbed P was noted in *Pokkali* soils and lower adsorbed P in sandy soils from northern coastal plain and *Onattukara* sandy plain. Contribution of adsorbed P in anion exchange capacity is 93.75 per cent and contribution of bray extractable P was the remaining 6.25 per cent. Percentage contribution of adsorbed P in anion exchange capacity was found very high than the contribution of bray extractable P in all the soils. Maximum percentage contribution of adsorbed P (99.8 per cent) in anion exchange capacity was recorded in *Kuttanad* soil (Sample No. 14) and the minimum value of 66.45 per cent was recorded in coastal sandy soil (Sample No. 9). Contribution of adsorbed P in anion exchange capacity was found very high (>99 per cent) in all the soils from *Kole* land and *Kuttanad.*

The adsorbed P was exchanged with higher concentration of chloride after leaching with water and drying at 40 ^{0}C. Maximum quantity of P exchanged with Cl $^-$ (37.7 mg kg^{-1}) was found in the soil from *Kole* land (Sample No. 5) and the lowest value (2.35 mg kg^{-1}) in *Kuttanad* soil (Sample No. 13). Highest percentage of adsorbed P exchanged with Cl$^-$ (9.67 per cent) was in the soil from Palakkad eastern plain (Sample No. 22) and the lowest value of 0.19 per cent in the soil from *Kuttanad* soil (Sample No. 15). All the *Kuttanad* soils were recorded with lower value of percentage adsorbed P exchanged with higher concentration of Cl$^-$ (<0.5 per cent).

Correlation coefficients of adsorbed P and exchanged P with physico-chemical properties are given in Table 75. AEC was significantly and positively correlated with adsorbed P (0.999**) and negatively correlated with percentage of adsorbed P exchanged with Cl$^-$ (-0.725**). The parameters which had significant positive correlation with AEC, showed positive correlation with adsorbed P and negative correlation with per cent of adsorbed P exchanged with Cl$^-$. The parameters which had significant negative correlation with AEC, showed negative correlation with adsorbed P and positive correlation with per cent of adsorbed P exchanged with Cl^-.

Table 75. Correlation coefficients of adsorbed and exchanged P with physico-chemical properties

	AEC	Adsorbed P	% of adsorbed P exchanged with Cl^-
AEC	1	-	-
Adsorbed P	0.999**	1	-
% of adsorbed P exchanged with Cl^-	-0.725**	-0.734**	1
CBD extractable Fe	0.765**	0.785**	-0.613**
pH	-0.754**	-0.756**	0.523*
EC	0.749**	0.731**	-0.435*
OC	0.944**	0.945**	-0.723**
Sand	-0.627**	-0.649**	0.539**
Silt	0.474*	0.482*	-0.337
Clay	0.576**	0.603**	-0.540**
Adsorption maxima at 25 ^{0}C (Langmuir isotherm)	0.892**	0.882**	-0.627**
Adsorption maxima at 40 ^{0}C (Langmuir isotherm)	0.843**	0.829**	-0.610**
Surface area	0.722**	0.741**	-0.566**

** Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

Table 76. Anions replaced by 250 mg L^{-1} of P

Sample No.	Silicate	Borate	Sulphate	Nitrate N
cmol(-)kg^{-1}				
1	2.60	0.012	138.21	3.15
2	2.21	0.017	134.99	1.62
3	2.45	0.015	155.57	3.31
4	2.38	0.008	9.23	0.33
5	2.07	0.006	5.70	0.37
6	2.09	0.006	7.20	0.45
7	1.48	0.004	1.02	0.12
8	0.95	0.007	1.30	0.15
9	0.99	0.007	1.49	0.11
10	2.53	0.009	1.22	Nd
11	1.42	0.005	1.46	Nd
12	2.19	0.006	2.16	0.55
13	4.06	0.016	11.43	0.28
14	4.84	0.022	8.71	0.23
15	2.49	0.039	24.94	0.26
16	4.16	0.041	15.26	0.15
17	2.91	0.038	4.03	0.40
18	3.87	0.039	12.25	0.65
19	5.70	0.044	20.58	0.27
20	5.69	0.038	7.93	0.44
21	2.71	0.045	6.65	0.36
22	5.39	0.046	4.19	0.33
Minimum	**0.95**	**0.004**	**1.02**	**0.11**
Maximum	**5.70**	**0.05**	**155.57**	**3.31**

Table 77. Exchangeable anions

Sample No.	Av. P-WS. P	Ex. Silicate	Ex. Borate	Ex. Sulphate	Ex. Nitrate	Total
	(meq/100g soil)					
1	1.33	2.37	0.001	15.83	3.15	22.69
2	0.73	1.97	0.002	11.59	1.62	15.91
3	0.87	2.19	0.002	13.53	3.31	19.90
4	0.02	1.53	0.001	6.29	0.33	8.16
5	0.05	1.37	0.001	3.05	0.37	4.85
6	0.06	0.41	0.001	4.93	0.45	5.85
7	0.87	0.67	0.001	0.51	0.12	2.17
8	0.26	0.26	0.003	0.83	0.15	1.49
9	1.36	0.52	0.004	0.64	0.11	2.64
10	0.22	1.14	0.001	1.02	Nd	2.38
11	0.78	0.57	0.001	0.99	Nd	2.34
12	0.14	1.49	0.001	1.28	0.55	3.46
13	0.03	1.88	0.010	8.79	0.28	11.00
14	0.01	2.59	0.014	6.33	0.23	9.17
15	0.01	2.30	0.029	12.92	0.26	15.51
16	0.08	1.36	0.011	14.34	0.15	15.94
17	0.01	0.71	0.028	2.43	0.40	3.58
18	1.06	0.75	0.027	11.06	0.65	13.55
19	0.79	0.81	0.002	9.64	0.27	11.50
20	0.12	0.97	0.026	7.73	0.44	9.29
21	0.07	0.76	0.035	5.09	0.36	6.32
22	0.36	0.73	0.035	3.41	0.33	4.86
Minimum	**0.01**	**0.26**	**0.001**	**0.51**	**Nd**	**1.49**
Maximum	**1.36**	**2.59**	**0.035**	**15.83**	**3.31**	**22.69**

AEC was significantly and positively correlated with adsorbed P (0.999**), CBD extractable Fe (0.765**), EC (0.749**), OC (0.944**), silt (0.474*), clay (0.576**), adsorption maxima of Langmuir P adsorption isotherm at 25 ^{0}C (0.892**) and 40 ^{0}C (0.843**), surface area (0.722**) and negatively correlated with per cent of adsorbed P exchanged with Cl^- (-0.725**), pH (-0.754**) and sand (-0.627**). Adsorbed P showed significant positive correlation with extractable Fe (0.785**), EC (0.731**), OC (0.945**), silt (0.482*), clay (0.603**), adsorption maxima of Langmuir P adsorption isotherm at 25 ^{0}C (0.882**) and 40 ^{0}C (0.829**), surface area (0.741**) and negatively correlated with per cent of adsorbed P exchanged with Cl^- (-0.734**), pH (-0.756**), sand (-0.649**). Percentage of adsorbed P exchanged with Cl^- had significant positive correlation with pH (0.523*), sand (-0.539**) and negatively correlated with CBD extractable Fe (-0.613**), EC (-0.435*), OC (-0.723**), clay (-0.540**), adsorption maxima of Langmuir P adsorption isotherm at 25 ^{0}C (-0.627**) and 40 ^{0}C (-0.610**), surface area (-0.566**).

Anions replaced by 250 mg L^{-1} of P is given in Table 76. Among the anions replaced, average value was in the following order: Sulphate> silicate> nitrare> borate. Highest value of Si replaced (5.7 cmol(-)kg^{-1}) was in the soil from Palakkad eastern plain (Sample No. 8) and lowest value (0.95 cmol(-)kg^{-1}) in sandy soil from northern coastal plain (Sample No. 8). Highest value of borate replaced (0.046 cmol(-)kg^{-1}) was in soil from Palakkad eastern plain (Sample No. 23) and the lowest (0.004 cmol(-)kg^{-1}) in the soil from northern coastal plain (Sample No. 7). All the soils from *Pokkali* soils were with more than 100 cmol(-)$kg^{-1}$of sulphate replaced. Highest value of sulphate replaced (155 cmol(-)kg^{-1}) was in *Pokkali* soil (Sample No. 3) and the lowest (1.02 cmol(-)kg^{-1}) in the soil from northen coastal plain (Sample No.7). Detectable limit of nitrate N replaced by P was not found in two soils (Sample No. 10 and 11) from *Onattukara* sandy plain and the highest value of 3.31 cmol(-)$kg^{-1}$was in *Pokkali* soil (Sample No. 3).

Amount of water soluble forms were deducted from the anions replaced by P. In case of P, amount of water soluble P was deducted from available P. Sum of all the exchangeable anions and P deducted from available P is given in Table 77. for comparison. Total was found less than the estimated AEC in most of the soils. Estimated AEC and the sum of exchangeable anions were significantly and positively correlated (0.773**). The highest value of sum of exchangeable anions (22.69 cmol(-)kg^{-1}) was noted in the *Pokkali* soil (Sample No. 1) and the lowest (1.49 cmol(-)kg^{-1}) was in the soil from northern coastal plain (Sample No. 8).

ZPC of soils could not be estimated following the procedure described in 3.4.2.

4.5. INTERFERENCE OF SILICON IN EXTRACTION AND ESTIMATION (COLORIMETRIC MOLYBDENUM BLUE) OF PHOSPHOROUS

4.5.1. P and Si extractability of different extractants

4.5.1.1. Content of P and Si extracted using different reagents

The content of P and Si extracted into solution using different extarctants are given in Table 78. When 0.5 M acetic acid was used as extractant, highest P content of 90.23 mg kg^{-1}was recorded in coastal sandy soil (Sample No. 9) and the lowest P content of 1.3 mg kg^{-1} was recorded in laterite soil (Sample No. 18). Using the same extractant, highest Si content of 226.23 mg kg^{-1} was recorded in the soil from Palakkad eastern plain (Sample No. 19), and the lowest content of 2.55 mg kg^{-1} in the coastsal sandy soil (Sample No. 8). Lower P content was observed in low lands of *Kole, Kuttanad,* laterite soils and in three soils from Palakkad eastern plains. All the soils from Palakkad eastern plain had higher content of Si and all the three soils from coastal sandy plain were with lower Si content. Si content was higher than P content in all the soils from *Kuttanad,* north central laterite and Palakkad eastern plain on extracting with 0.5M acetic acid, whereas all the soils from northern coastal plain showed lower Si content than P content.

On extracting the soil with 0.1 M HCl, highest content of P (208.8 mg kg^{-1}) was observed in *Pokkali* soil (Sample No. 1) and the lowest P (8.11 mg kg^{-1})

was observed in the soil from north central laterite (Sample No. 18). The highest Si content of 217.5 mg kg^{-1} was in the soil from Palakkad eastern plain (Sample No. 19) and the lowest (1.35 mg kg^{-1}) in the coastal sandy soil (Sample No. 9). All the soils from north central laterite were with lower P content. All the soils from Palakkad eastern plain showed higher Si content and all the coastal sandy soils showed lower Si content.

When the soils were treated with Citrate - Bicarbonate – Dithionite (CBD), highest content of P (246.54 mg kg^{-1}) was observed in *Pokkali* soil (Sample No. 1) and the lowest (35.12 mg kg^{-1}) in the soil from Palakkad eastern plain (Sample No. 21). Highest Si content of 343.34 mg kg^{-1} was recorded in *Pokkali* soil (Sample No. 2) and the lowest (15.02 mg kg^{-1}) in the coastal sandy soil (Sample No. 9). All the soils from *Pokkali, Kole* and *Kuttanad* had higher P content. All the soils from *Pokkali, Kole, Kuttanad* and Palakkad eastern plain showed higher content of Si.

When Bray I extractant was used, highest P content of 115.1 mg kg^{-1} was observed in *Pokkali* soil (Sample No.1) and the lowest content (8.35 mg kg^{-1}) in laterite soil (Sample No. 17). The highest Si content of 1681 mg kg^{-1} was recorded in soil from Palakkad eastern plain (Sample No. 20) and the lowest (1271 mg kg^{-1}) was in the *Pokkali* soil (Sample No. 2). All the soils showed high Si content.

Soil samples extracted with Bray reagent had very high content of Si than P. Extraction with CBD treatment showed relatively higher amount of P and Si. The pH of the acetic acid extract in different soils ranged from 2.75 to 4.05 of the HCl extract ranged from 1.6 to 1.93, of the CDB extract ranged from 6.28 to 8.17 and that of Bray extract ranged from 2.16 to 3.4.

Table 78. P and Si content extracted using different extractants in soil

	0.5 Macetic acid		0.1 M HCl		CBD		Bray I	
Sample No.	P	Si	P	Si	P	Si	P	Si
	(mg kg^{-1})							
1	38.68	14.16	208.8	9.41	246.54	318.59	115.1	1271
2	18.07	14.85	59.01	3.89	154.41	343.34	47	1234
3	28.15	32.78	110.6	8.97	184.8	293.56	77.7	1266
4	4.14	33.05	16.08	18.7	136.28	118.66	9.37	1474
5	2.7	14.12	14.96	8.79	126.18	106.15	11.33	1391
6	14.1	10.72	14.94	3.15	128.27	82.57	10.14	1431
7	14.04	5.01	43	1.53	128.27	40.49	42.11	1373
8	14.1	2.55	24.59	1.63	82.03	28.09	10.05	1332
9	90.23	5.6	72.14	1.35	38.61	15.02	59.34	1307
10	16.18	49.5	102.9	51.26	52.14	40.99	54.24	1490
11	8.83	5.21	35.49	2.31	46.9	16.09	37.18	1437
12	46.43	55.65	96.35	45.76	42.67	35.96	63.79	1535
13	3.28	15.04	20.75	10.34	145.75	112.12	13.86	1417
14	5.86	28.45	10.82	18.78	144.51	114.99	9.38	1436
15	4.22	17.56	15.01	9.17	130.12	124.26	10.43	1378
16	3.3	48.53	8.47	22.08	65.66	57.64	16.22	1478
17	2.94	19.95	13.56	8.3	54.63	57.49	8.35	1495
18	1.3	62.63	8.11	45.12	48.41	54.11	64.49	1572
19	29.93	226.23	169.9	217.5	99.01	132.34	15.46	1640
20	5.31	141.65	42.4	134.9	65.86	155.38	17.37	1681
21	3.87	104	52.31	130.2	35.12	178.89	8.36	1512
22	9.42	85.65	69.4	75.81	97.98	88.8	34.62	1473

4.5.1.2. Relationship between P and Si content extracted using different reagents

Correlation between P and Si content using different reagents are given in Table 79. P extracted by 0.5M acetic acid had significant positive correlation with P extracted by 0.1M HCl (0.548**) and P extracted Bray reagent (0.554**). Si extracted by 0.5M acetic acid was significantly and positively correlated with Si extracted by 0.1M HCl (0.984**) and Si extracted by Bray reagent (0.744**). P extracted by 0.1M HCl had significant positive correlation with P extracted by Bray reagent (0.676**) and Si extracted by CBD treatment (0.457*). Si extracted by 0.1M HCl and that extracted by Bray had significant positive correlation (0.731**). P extracted by CBD treatment showed significant positive correlation with Si extracted by CBD (0.709**) and negative correlation with Si extracted by Bray reagent (-0.577**).

Table 79. Correlation coefficients of P and Si extracted using different extractants

	P (0.5M acetic acid)	**Si (0.5M acetic acid)**	**P (0.1M HCl)**	**Si (0.1M HCl)**	**P (CBD)**
P (0.1M HCl)	0.548**				
Si(0.1M HCl)		0.984**			
Si (CBD)			0.457*		0.709**
P (Bray)	0.554**		0.676**		
Si (Bray)		0.744**		0.731**	0.577**

4.5.2. Interference of Si in colorimetric estimation of P (Moybdenum Blue method)

Standard procedure of molybdenum blue method for colorimetric estimation of P by Watanbe and Olsen (1965) was used for the estimation of different solutions containing P alone, Si alone and solution containing both P and Si. The absorbance by different concentrations of all the solutions was recorded (at 8 different wavelength) for estimation following the colorimetric estimation of P, irrespective of the element present in the solution. The absorbance by prepared P standards (0.1 to 2 mg L^{-1}) is given in Table 80. The absorbance of prepared Si standards (0.5 to 200 mg L^{-1}) is given in Table 81. The absorbance of solutions containing Si and P in specified ratios (keeping P concentration constant: 0.1 mg L^{-1}) is given in Table 82. The highest absorbance in all solutions was observed at the wavelength of 882 nm.

Since the wavelength of 660 nm is also commonly used for the colorimetric estimation of P, influence of Si in estimation of P at 660 nm and 882 nm was also compared (Table 83). The concentration of P calculated from calibration curve at 660 nm and 882 nm showed negative value up to 30 mg L^{-1} of Si. The solution containing 40 mg L^{-1} of Si showed 0 mg L^{-1} of P at 660 nm and 0.03 mg L^{-1} of P at 882 nm. From 50 mg L^{-1} of Si onwards, positive value was recorded as P concentration from calibration curve at both the wavelength. The value was increased with increasing concentration of Si. The estimated values were comparatively lower at 660 nm than 882 nm, in all solutions with greater than 40 mg L^{-1} of Si. Plate 2 shows the colour development of Si solutions following the procedure of colorimetric estimation of P.

The percentage of over estimation was calculated with respect to change in concentration of the known concentration of P (0.1 mg L^{-1}) from the calibration curve (absorbance at 882 nm) with the addition of increasing concentration of Si. Over estimation of 0.1 mg L^{-1} P was not recorded with the addition of Si up to Si:P ratio of 40:1. Above the Si:P ratio of 40:1, the percentage over estimation increased with increase in Si:P ratio. Greater than 1000 per cent over estimation was recorded when Si:P ratio was greater than 2500. At Si:P ratio of 5000:1, 1296.90 per cent over estimation was observed.

Plate 2. Colour development of Si following colorimetric estimation of P

Table 80. Absorbance by P standards in molybdenum blue color method at different wavelength

Sl. No	Conc. of P (mg L^{-1})	Wavelength (nm)							
		500	630	660	700	750	800	882	950
1	0.1	0.198	0.215	0.216	0.222	0.216	0.213	0.24	0.211
2	0.2	0.219	0.253	0.258	0.269	0.26	0.257	0.304	0.258
3	0.3	0.239	0.292	0.306	0.316	0.305	0.301	0.369	0.302
4	0.4	0.265	0.34	0.352	0.375	0.361	0.357	0.452	0.364
5	0.5	0.285	0.38	0.397	0.425	0.409	0.403	0.522	0.412
6	0.6	0.309	0.424	0.444	0.479	0.46	0.453	0.597	0.443
7	0.7	0.339	0.476	0.5	0.54	0.518	0.507	0.681	0.531
8	0.8	0.356	0.508	0.537	0.582	0.558	0.546	0.74	0.558
9	0.9	0.376	0.547	0.58	0.63	0.604	0.591	0.807	0.633
10	1	0.413	0.606	0.643	0.7	0.669	0.654	0.9	0.701
11	1.1	0.435	0.642	0.682	0.743	0.712	0.698	0.956	0.799
12	1.2	0.438	0.656	0.699	0.763	0.742	0.746	0.982	0.801
13	1.3	0.448	0.686	0.732	0.801	0.792	0.818	1.034	0.823
14	1.4	0.46	0.714	0.763	0.836	0.836	0.881	1.081	0.907
15	1.5	0.473	0.746	0.797	0.874	0.887	0.956	1.135	0.973
16	1.6	0.475	0.757	0.809	0.888	0.912	1.003	1.153	0.999
17	1.7	0.494	0.795	0.85	0.933	0.972	1.093	1.216	1.071
18	1.8	0.503	0.818	0.875	0.961	1.011	1.155	1.256	1.112
19	1.9	0.549	0.893	0.958	1.056	1.081	1.184	1.38	1.193
20	2	0.559	0.908	0.979	1.133	1.105	1.292	1.418	1.266

Table 81. Absorbance by Si standards estimated by blue color method of P estimation at different wavelength

Sl No.	Conc. of Si (mg L^{-1})	Wavelength (nm)							
		500	630	660	700	750	800	882	950
1	0.5	0.125	0.133	0.131	0.131	0.131	0.133	0.133	0.134
2	1	0.124	0.131	0.13	0.13	0.13	0.132	0.128	0.13
3	2.5	0.123	0.131	0.129	0.129	0.129	0.131	0.132	0.134
4	5	0.126	0.134	0.132	0.132	0.132	0.135	0.135	0.134
5	10	0.137	0.15	0.149	0.152	0.151	0.153	0.16	0.154
6	20	0.143	0.164	0.165	0.17	0.168	0.169	0.185	0.173
7	30	0.155	0.186	0.189	0.196	0.193	0.192	0.222	0.202
8	40	0.159	0.202	0.206	0.216	0.211	0.209	0.246	0.22
9	50	0.185	0.238	0.246	0.259	0.252	0.25	0.306	0.267
10	60	0.193	0.252	0.261	0.277	0.269	0.268	0.332	0.287
11	70	0.199	0.266	0.277	0.296	0.287	0.287	0.357	0.305
12	80	0.21	0.288	0.301	0.322	0.312	0.31	0.395	0.355
13	90	0.221	0.312	0.327	0.351	0.34	0.337	0.438	0.368
14	100	0.23	0.33	0.346	0.373	0.361	0.357	0.468	0.391
15	110	0.245	0.357	0.375	0.405	0.392	0.388	0.512	0.424
16	120	0.262	0.383	0.405	0.439	0.424	0.419	0.557	0.458
17	130	0.273	0.398	0.421	0.456	0.44	0.435	0.578	0.475
18	140	0.275	0.411	0.435	0.472	0.456	0.45	0.605	0.496
19	150	0.303	0.457	0.485	0.528	0.507	0.501	0.678	0.552
20	160	0.309	0.472	0.502	0.547	0.527	0.52	0.709	0.576
21	170	0.304	0.468	0.497	0.542	0.522	0.515	0.701	0.509
22	180	0.341	0.519	0.551	0.6	0.579	0.57	0.775	0.632
23	190	0.329	0.514	0.547	0.599	0.579	0.57	0.78	0.63
24	200	0.383	0.616	0.66	0.726	0.709	0.712	0.941	0.747

Table 82. Absorbance by solution containing P and Si estimated by blue color method of P estimation at different wavelength

Sl No.	Conc. (mg L^{-1})		Si:P	Wavelength (nm)							
	P	Si		500	630	660	700	750	800	882	950
1	0.1	0	P alone	0.148	0.18	0.183	0.191	0.187	0.187	0.293	0.196
2	0.1	0.1	1	0.151	0.186	0.19	0.198	0.194	0.194	0.288	0.202
3	0.1	1	10	0.194	0.194	0.221	0.202	0.194	0.194	0.293	0.202
4	0.1	2	20	0.15	0.182	0.186	0.193	0.19	0.19	0.299	0.198
5	0.1	4	40	0.157	0.193	0.19	0.207	0.203	0.203	0.295	0.211
6	0.1	8	80	0.166	0.205	0.209	0.219	0.215	0.214	0.301	0.225
7	0.1	10	100	0.159	0.2	0.205	0.215	0.21	0.208	0.301	0.221
8	0.1	12	120	0.163	0.207	0.212	0.223	0.218	0.217	0.308	0.23
9	0.1	16	160	0.168	0.214	0.221	0.233	0.227	0.225	0.319	0.26
10	0.1	20	20	0.172	0.223	0.231	0.244	0.237	0.236	0.328	0.252
11	0.1	25	250	0.178	0.235	0.243	0.25	0.251	0.249	0.336	0.268
12	0.1	50	500	0.204	0.289	0.302	0.324	0.313	0.309	0.4	0.34
13	0.1	100	1000	0.265	0.4	0.425	0.462	0.268	0.406	0.431	0.468
14	0.1	150	1500	0.32	0.504	0.537	0.587	0.564	0.555	0.768	0.621
15	0.1	200	2000	0.36	0.564	0.608	0.678	0.664	0.647	0.844	0.679
16	0.1	250	2500	0.391	0.644	0.698	0.733	0.775	0.869	0.987	0.745
17	0.1	300	3000	0.429	0.714	0.77	0.849	0.845	0.875	1.089	0.85
18	0.1	350	3500	0.437	0.722	0.781	0.867	0.878	0.951	1.092	0.881
19	0.1	400	4000	0.443	0.734	0.792	0.886	0.907	0.937	1.132	0.828
20	0.1	450	4500	0.455	0.744	0.815	0.903	0.923	0.976	1.152	0.874
21	0.1	500	5000	0.461	0.758	0.844	0.931	0.953	1.012	1.171	0.896

Table 83. Influence of Si in estimation of P at 660 nm and 882 nm

Sl. No.	Si content in test solution (mg L^{-1})	Absorbance at 660nm	Concentration calculated from calibration curve of P at 660nm	Absorbance at 882nm	Concentration calculated from calibration curve of P at 882nm
1	0.5	0.131	-0.19	0.133	-0.15
2	1	0.13	-0.19	0.128	-0.16
3	2.5	0.129	-0.19	0.132	-0.15
4	5	0.132	-0.19	0.135	-0.15
5	10	0.149	-0.14	0.16	-0.11
6	20	0.165	-0.10	0.185	-0.07
7	30	0.189	-0.04	0.222	-0.01
8	40	0.206	0.00	0.246	0.03
9	50	0.246	0.10	0.306	0.13
10	60	0.261	0.14	0.332	0.18
11	70	0.277	0.18	0.357	0.22
12	80	0.301	0.24	0.395	0.28
13	90	0.327	0.31	0.438	0.35
14	100	0.346	0.36	0.468	0.40
15	110	0.375	0.43	0.512	0.47
16	120	0.405	0.51	0.557	0.55
17	130	0.421	0.55	0.578	0.58
18	140	0.435	0.58	0.605	0.63
19	150	0.485	0.71	0.678	0.75
20	160	0.502	0.75	0.709	0.80
21	170	0.497	0.74	0.701	0.79
22	180	0.551	0.88	0.775	0.91
23	190	0.547	0.87	0.78	0.92
24	200	0.66	1.15	0.941	1.18

Table 84. Influence of Si:P in estimation of P at 882 nm

Sl. No.	Conc. of P added (mg L^{-1})	Conc. of Si added (mg L^{-1})	Si : P	Absorbance at 882nm	Conc. of P calculated from calibration curve	Percentage of over estimation
1	0.1	0	P alone	0.293	0.11	
2	0.1	0.1	1	0.292	0.11	0.00
3	0.1	1	10	0.293	0.11	0.00
4	0.1	2	20	0.291	0.11	0.00
5	0.1	4	40	0.295	0.12	2.95
6	0.1	8	80	0.301	0.13	11.82
7	0.1	10	100	0.301	0.13	11.82
8	0.1	12	120	0.308	0.14	22.16
9	0.1	16	160	0.319	0.15	38.40
10	0.1	20	200	0.328	0.17	51.70
11	0.1	25	250	0.336	0.18	63.52
12	0.1	50	500	0.4	0.29	158.05
13	0.1	100	1000	0.431	0.34	203.84
14	0.1	150	1500	0.768	0.90	701.62
15	0.1	200	2000	0.844	1.02	813.88
16	0.1	250	2500	0.987	1.26	1025.11
17	0.1	300	3000	1.089	1.43	1175.78
18	0.1	350	3500	1.092	1.43	1180.21
19	0.1	400	4000	1.132	1.50	1239.29
20	0.1	450	4500	1.152	1.53	1268.83
21	0.1	500	5000	1.171	1.56	1296.90

Discussion

5. DISCUSSION

Twenty two representative soil samples from seven different agro ecological units of Kerala with variation in pH, organic matter content and clay content were collected. Initial characterization of the samples was done to understand the soil properties and dominant minerals.

5.1. CHARACTERISATION OF SOIL SAMPLES

5.1.1 Physico-chemical properties

The data on the physico-chemical properties and available nutrient status of the 22 soil samples studied are presented in Table 3. The results derived from the data are discussed hereunder.

5.1.1.1. Soil pH

Most of the collected soils under study were acidic in nature (Fig. 6).The pH of the soils ranged from 3.17 to 7.52. The leaching of bases under tropical humid climate may be the reason for low pH in general. Out of 22 collected samples 10 samples were coming under extremely acid (3.5-4.5) to ultra-acid (<3.5) category, which mainly include *Pokkali, Kole* and *Kuttanad* soils. These soils are potential acid sulphate/saline soils. The presence of sulphide minerals and their oxidation on exposure to air along with high content of organic matter which might have accumulated organic acids lead to the extremely acidic condition in these soils (Bhindu, 2017). The near neutral pH (>6.5) of soils from Palakkad eastern plain is attributed by the presence of mixed layer lattice clays.

5.1.1.2. Electrical conductivity

Electrical conductivity of the soils ranged from 0.052 to 15.02 dS m^{-1}. Exceptionally high values of EC were recorded in *Pokkali* soils (7.85, 13.83 and 15.02 dS m^{-1}) because of inundation of sea water. Since the sea water inundation is controlled by barrages and weirs, EC of *Kuttanad* and *Kole* soils are comparatively less than that of *Pokkali soil.* The three soils of *Kole* land were reported with EC of 0.39, 0.54 and 0.67 dS m^{-1}, whereas the *Kuttanad* soils were reported with mild salinity (1.58, 1.13 and 3.91 dS m^{-1}). Bhindhu (2017) also reported EC of <1 dS m^{-1} for soils of *Kole* lands and mild salinity of *Kuttanad* soil. All other soils were reported with EC <1 dS m^{-1}.

5.1.1.3. Organic carbon

Organic carbon content of collected soils ranged from 0.32 to 6.74 per cent. Out of the collected soils 10 samples were reported with high organic carbon status, 6 were with medium and the remaining six were reported with low organic carbon status (Fig. 7). The high organic carbon status of *Pokkali, Kole* and *Kuttanad* soils (2.57 - 6.74 per cent) are due to the reduced decomposition rate of huge amounts of organic matter under submerged anaerobic condition. High organic carbon status of *Kuttanad, Pokkali* and *Kole* lands ranging from 1.72 to 10.72 per cent were also reported by Bhindhu (2107). All the soils from northern coastal plain and *Onattukara* sandy plain were low in organic carbon status. The same was reported by Santhosh (2013). All most all the soils from Palakkad eastern plain and north central laterite are medium in organic carbon status.

5.1.1.4. Bulk density

Bulk density of the soil ranged from 0.6 to 1.93 Mg m^3. All the samples collected from *Kuttanad* and *Pokkali were* recorded with low bulk densities which were in submerged condition (<1 Mg m^{-3}) and with high organic matter. The highest value recorded in soils collected from Palakkad eastern plain may be due to compaction.

5.1.1.5. Texture

A wide variety of texture was exhibited by the collected soils. Sand, silt and clay content of the collected soils are presented in Table 3. Sand content varied from 12.76 to 90.24 per cent, silt content varied from 5.76 to 42.5 per cent and the clay content ranged from 3.43 to 57.23 per cent. Kerala State behaves like a macro watershed with sloping terrain from east to west and hence the clay content will be more in low land areas of the State. *Kuttanad* soils exhibited high clay content (> 50 per cent) and less clay content was observed in northern coastal plain and *Onattukara* sandy plain. Among the low land soils, relatively higher content of sand was more in *Pokkali* soils due to the influence of sea tides.

5.1.1.6. Cation Exchange Capacity

Exchangeable cations viz. Ca, Mg, Na, K, Fe, Mn, Zn, Cu and Al extracted by 0.1M $BaCl_2$ and CEC are given in Table 5. Since the water soluble fraction of cations are high in low land soils, the amount of exchangeable cations are found out by deducting the water soluble fraction from 0.01M $BaCl_2$ extractable cations. Highest CEC of 27.38 cmol(+) kg^{-1} was noted in sample from Palakkad eastern plain, due to the dominance mixed inter layer clays and 2:1 layer lattice minerals as indicated by X-ray diffraction study. The lowest cation exchange capacity of 1.39 cmol(+)kg^{-1} was noted in soils of northern coastal plain. Sandy texture of the soils might be the reason for low CEC in these soils.

5.1.1.7. Anion exchange capacity

All the *Pokkali* soils were recorded with AEC >30 cmol(-) kg^{-1}. Low land soils of *Kole* and *Kuttanad* were also with high AEC, is mainly due to the high clay content with dominance of kaolinite mineral and high content of iron and aluminium oxides which can provide pH dependent positive charges under acidic condition. Low AEC recorded in northern coastal plain and *Onattukara* sandy plain are due to the dominance of sand content. Low AEC in soils from Palakkad eastern plain is due to the dominance of 2:1 phyllosilicate minerals with low ZPC. Bolan *et al.* (1999) reported high positive surface charges of 56 cmol(+) kg^{-1} for alumunium hydroxides and 72 cmol(+) kg^{-1} for iron hydroxide at pH 5.8.

5.1.2. Available nutrient status

5.1.2.1. Available nitrogen

The lowest available N status of 85.05 kg ha^{-1} was noted in soil of northern coastal plain. All the soils collected from northern coastal plain, *Onattukara* sandy plain, north central laterite and Palakkad eastern plain were deficient (< 280 kg ha^{-1}) in available N status. Out of the 22 collected samples, 13 were deficient in available N status and only two samples with high available N content (Fig. 8). All these soils contain relatively less organic matter content and the chance of leaching loss is also more. The available nitrogen status of low land soils of *Pokkali, Kole* and *Kuttanad* ranged from 327.60 to 730.80 kg ha^{-1} which comes under medium to high category. High clay and organic matter content might be the reason for this.

5.1.2.2. Available phosphorous

Available phosphorous of the soils under study ranged from 7.32 to 219.25 kg ha^{-1}. Out of the 22 samples only four samples were recorded with low phosphorous status and 14 samples with high phosphorous status (Fig. 9). High amount of available P in *Pokkali* soil may due to the presence of more soluble P and aluminium-P fraction in this soil. These two fractions have direct positive correlation with available phosphorous in the present study. Since the chance of fixation is very less in coastal sandy soil it showed high status for available phosphorous. Available phosphorous status in *Kole* and *Kuttanad* region ranged from 7.32 to 14.04 kg ha^{-1}. Low available P in *kole* and *Kuttanad* were reported by Bhindhu (2017). This may be due to the fixation of P by Fe, Al and Mn and by the precipitation of P with Fe and Al oxides and hydroxides. Beyond this, ligand exchange reactions may also leads to the unavailability of P in these soils. If the complex formed is mono-dendate, P can be plant available. The continuous use of P fertilizers may be the reason for high available P status of lateritic soils.

5.1.2.3. Available potassium

Available potassium content of the soil ranged from 17.92 to 855.62 kg ha^{-1}.Out of 22 samples collected six samples were low in fertility status, seven were medium and nine were recorded with high fertility status (Fig. 10). Lowest available K was found in northern coastal plain. Coarse texture of soils and low CEC results in low retention of K. Along with this condition, humid climate leads to leaching loss of K even if fertilizers are applied. The highest K content of 855.62 kg ha^{-1} was noted in the soil from Palakkad eastern plain where the prevalence of 2:1 type clay minerals is seen.

5.1.2.4. Available calcium

Available Ca content of the soil ranged from 74.45 to 4976.65 mg kg^{-1}. Sixteen samples collected were sufficient in fertility status of Ca, the remaining were deficient (Fig. 11). Available calcium status of more than 1000 mg kg^{-1} was recorded in soils from Palakkad eastern plain and *Pokkali.* Predominance of 2:1 clay minerals in the Palakkad eastern plain and the influence of sea water in *Pokkali* soils are the main reason for high Ca content in these soils. Coastal sandy soils are reported with deficient status of available Ca. Low CEC and conducive leaching environment are the reason for deficient status of Ca in soils from northern coastal plain.

5.1.2.5. Available magnesium

Available Mg content of the soils ranged from 29.11 to 2269.50 mg kg^{-1}. Ten samples were deficient and the remaining 12 samples sufficient in Mg (Fig. 12). *Pokkali* soils were reported with very high available Mg status (>1000 mg kg^{-1}). Inundation of salt water is the reason for high available Mg status of this soil. High CEC and predominance of 2:1 minerals are the reason for high Mg in Palakkad eastern plain. *Kuttanad* soils were also reported with high Mg status where EC was comparatively high due to the presence of soluble Mg salts. High Ca, Mg and S content of *Kuttanad* soil was also reported by Beena and Thampatti (2013).

5.1.2.6. Available sulphur

A wide variation was observed in available S content of collected soil ranging from 3.82 - 8291.67 mg kg^{-1}. Out of the 22 samples collected, only two samples were deficient in available S (Fig. 13). The influence of sea water may be the reason for very high available S content in low land soils of *Pokkali, Kole* and

Kuttanad. Even though the conditions to induce S deficiency are more prevalent in Kerala state, the application of fertilizers has alleviated the deficiency. Comparatively less S content was noted in northern coastal plain and *Onattukara* sandy plain because of the sandy texture and prevailing leaching environment.

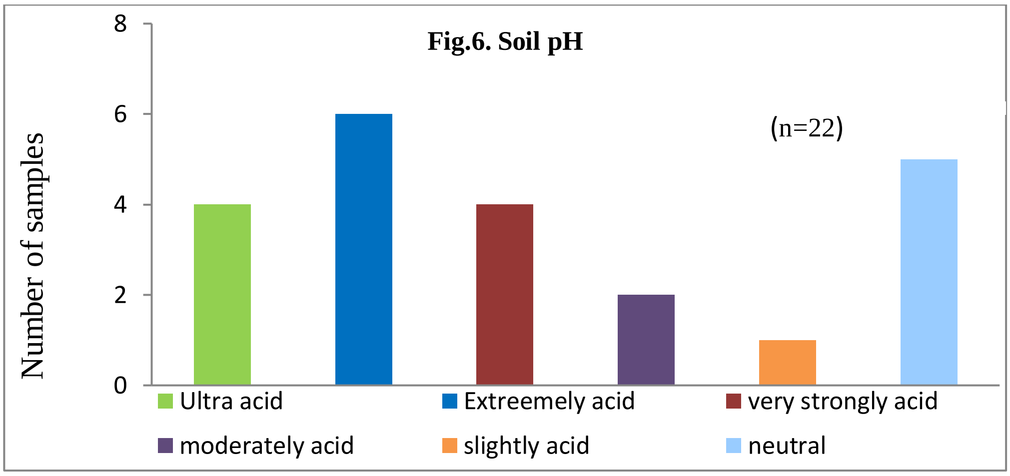


Fig.6. Soil pH

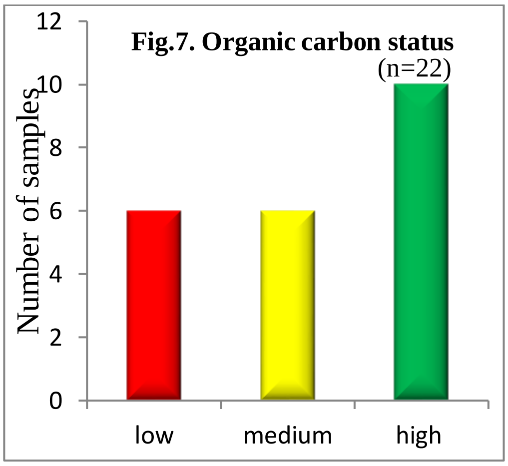


Fig.7. Organic carbon status

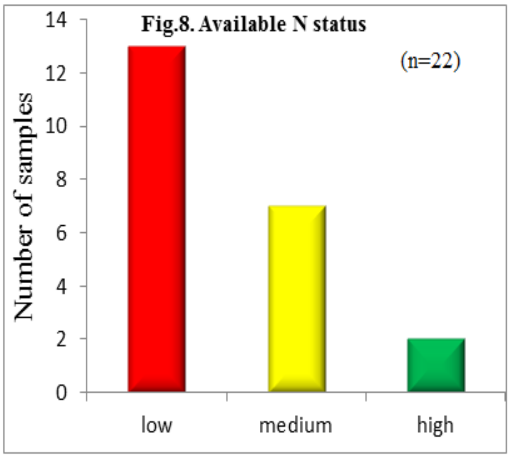


Fig.8. Available N status

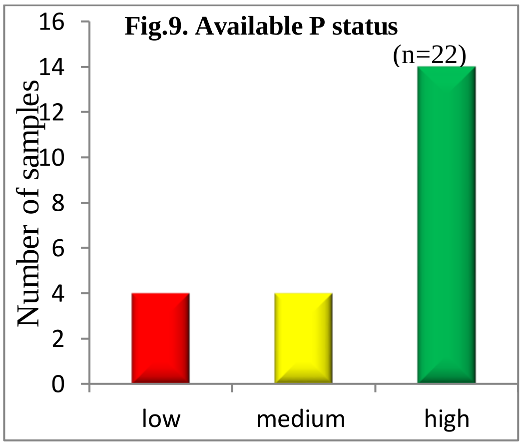


Fig.9. Available P status

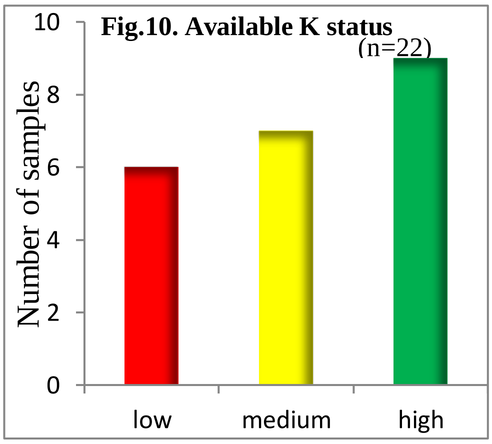


Fig.10. Available K status

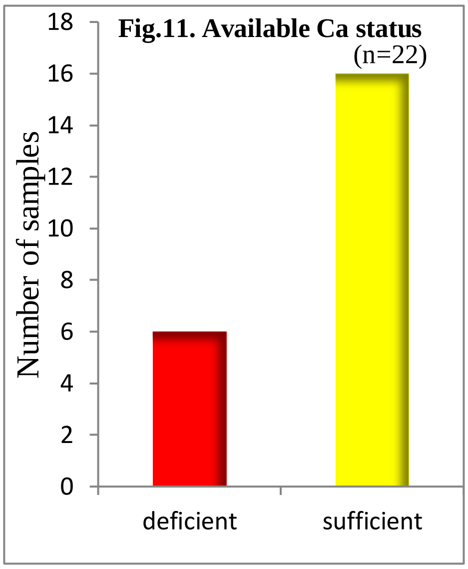


Fig.11. Available Ca status

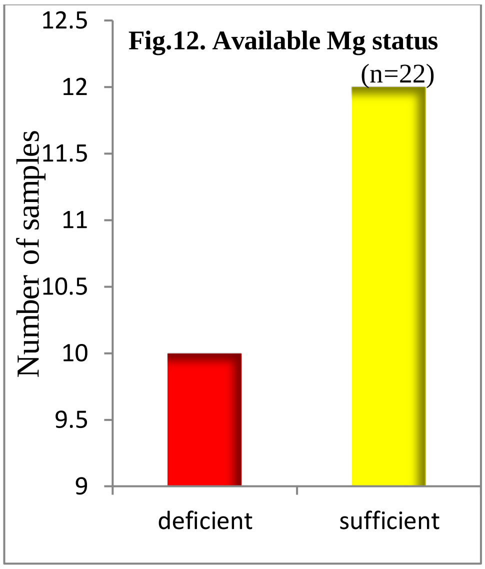


Fig.12. Available Mg status

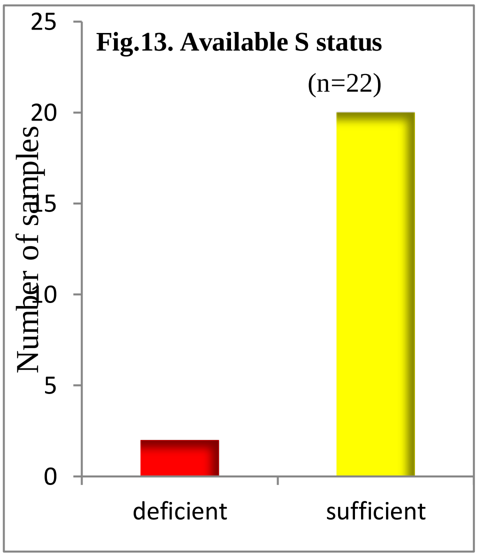


Fig.13. Available S status

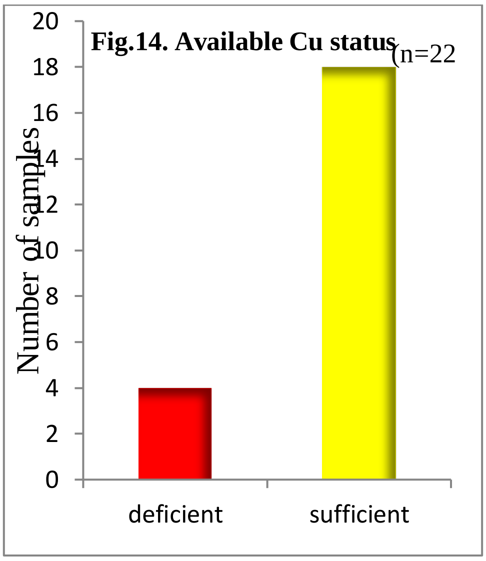


Fig.14. Available Cu status

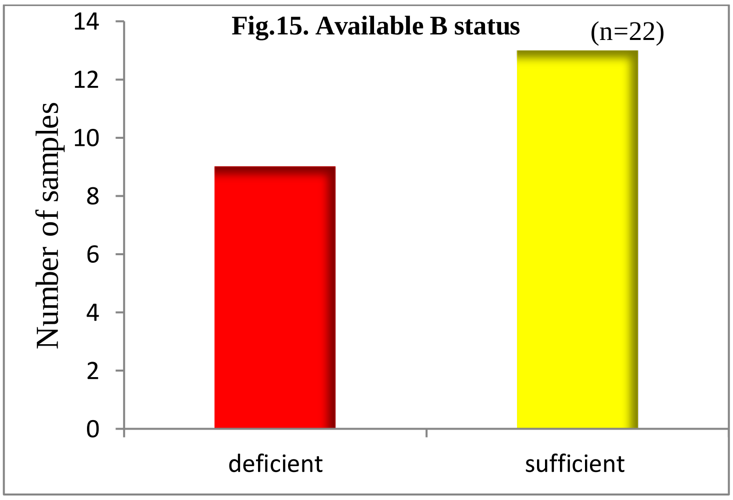


Fig.15. Available B status

5.1.2.7. Available iron

In *Pokkali* soils, all the micronutrients are exceptionally high. Other low land soils (*Kuttanad* and *Kole*) also exhibited relatively higher content of micronutrients. This may be due to dominance of reduced forms of micronutrients. *Onattukara* sandy soils and soils from northern coastal plain were with comparatively less micronutrients which might have resulted by low CEC of these soils. Available Fe content of the soil ranged from 22.2 to 1370 mg kg$^{-1.}$ Even iron toxicity was reported in *Pokkali, Kole* and *Kuttanad* soil (George, 2011). In this study the iron content of the low land soils ranged from 750.00 to 1370.00 mg kg^{-1}. None of the samples exhibited Fe deficiency.

5.1.2.8. Available manganese

Lowest Mn content of 2.72 mg kg^{-1} was recorded in soil of northern coastal plain and the highest (192.23 mg kg^{-1}) was observed in the soil of Palakkad eastern plain. None of the soils exhibited deficiency regarding Mn fertility.

5.1.2.9. Available copper

The content of available Cu in the collected soils ranged from 0.46 to 8.83 mg kg^{-1}. Out of the 22 collected samples four samples were deficient (<1 mg kg^{-1}) in available Cu (Fig. 14). Deficiency is mainly noted in the soils of northern coastal plain. Higher levels of Cu might have resulted from the use of Cu based fungicides.

5.1.2.10. Available zinc

Available Zn status of the soil ranged from1.2 to 246.8 mg kg^{-1}. None of the collected samples were deficient in available Zn. The highest value was recorded in *Pokkali* soil and the lowest in *Onattukara* sandy soil. Relatively higher content of exchangeable Zn was also noted in *Pokkali* soils.

5.1.2.11. Available boron

Available B content in the collected soils ranged from 0.04 to 5.42 mg kg^{-1}. Nine samples were deficient (<0.5 mg kg^{-1}) and the remaining soils recorded sufficient levels of B (Fig.15). Relatively higher B content was observed in *Pokkali, Kole* and *Kuttanad* soil. This might have resulted by the influence of sea water and presence of high organic matter content in these soils. Relatively low B content was observed in soils of northern coastal plain and *Onattukara* sandy soils is due to high leaching loss.

5.1.2.12. Available silicon

The available silicon content of soil ranged from 1 to 54.58 mg kg^{-1}. The process of desilication is prevalent in humid tropical climate of Kerala. It has resulted in the development of soil rich in iron and aluminium oxides and low in Si and nutrient bases. This could be one of the reasons for low available Si in major rice growing tracts of Kerala. Srivastava *et al.* (1994) reported that due to desilication in soils of humid tropical climates, silica is highly depleted. Friesen *et al.* (1994) reported that the soluble Si content in tropical soils of Ultisols and Alfisols is 5 to 10 times less than the temperate soils. Rice growing low land soils of *Pokkali, Kole* and *Kuttanad* were recorded with silicon content of less than 10 mg kg^{-1}. This might be due to the continuous monoculture of rice. Savant *et al.* (1997) reported that Si depletion can occur in traditional rice soils from continuous monoculture.

5.1.2.13. Available molybdenum

Detectable limit of Mo was not found in any of the collected soil samples. For strongly acidic (pH < 4.5) and acidic soils (pH 4.6–5.5), Mo concentration in the soil solution was lower than 0.02 μmol L^{-1} (Rutkowska *et al.*, 2017). Inner-sphere adsorption mechanism for Mo on kaolinite surfaces was reported by Xu *et al.* (2013). Highly acidic pH and specific adsorption mechanism of Mo with kaolinite, iron and aluminium are the reason for deficiency of Mo.

5.1.3. Citrate-Dithionite-Bicarbonate extractable iron

Low land soils of *Pokkali, Kole* and *Kuttanad* were recorded with high content of CBD-Fe indicating the presence of high amount of iron oxides in these low land soils. The north central laterite soil also reported with high CBD-Fe. The dominance of iron oxides in highly weathered tropical soils was reported by Fontes and Weed (1991).

5.1.4. Exchageable cations and water soluble plus exchangeable Al

Water soluble plus exchangeable Al was also considered under study since most of the soils are extremely acidic in pH where solubility of Al is high. The contribution of micronutrient cations was comparatively less in cation exchange capacity except in *Pokkali* and *Kuttand* soil. Contribution of copper to cation exchange capacity is negligible in all type of soil. Exchangeable aluminium has very less contribution in sandy soils, laterite and soils of Palakkad eastern plain

5.1.4.1. Exchangeable calcium (Ex.Ca)

The dominance of calcium was found in the exchange sites of all the soils as reported by Santhosh (2013) followed by sodium. All the four soils collected from Palakkad eastern plain showed higher amount of exchangeable calcium (>1000 mg kg^{-1}) due to the presence of 2:1 clay minerals.

5.1.4.2. Exchangeable magnesium (Ex.Mg)

Low content of exchangeable Mg content was noted in the soils from northern coastal plain and *Onattukara* sandy plain due to high sand content. High exchangeable Mg content recorded in low land soils of *Pokkali, Kole* and *Kuttanad* was due to the salt deposition by sea water entry.High exchangeable Mg content in soils of Palakkad eastern plain was due to the presence of 2:1 minerals.

5.1.4.3. Exchangeable sodium (Ex.Na)

Exchangeable Na content of the soils under study ranged from 100.17 mg kg^{-1} to 662.5 mg kg^{-1}. The lowest value was recorded in the soil of *Onattukara* sandy plain, mainly due to the prevalent leaching environment and low clay content. The highest value was recorded in *Pokkali* soil due to the uncontrolled sea water entry.

5.1.4.4. Exchangeable K (Ex.K)

Soil from northern coastal plain (Sample No. 7) had the lowest value (2.66 mg kg^{-1}) for exchangeable K content, due to the sandy nature of soil and low clay content. Soils from Palakkad eastern plain showed the high exchangeable K content due to the dominance of 2:1 type clay minerals.

5.1.4.5. Exchangeable iron (Ex.Fe)

The highest content of exchangeable Fe was recorded from *Pokkali* soil (Sample No. 1) and the lowest in the soil from northern coastal plain (Sample No. 10). Exceptionally very high exchangeable Fe was found in *Pokkali* soils due to the ultra-acidic pH of soil.

5.1.4.6. Exchangeable manganese (Ex.Mn)

Lowest content of exchangeable manganese (1.43 mg kg^{-1}) was noted in the soil from northern coastal plain (Sample No. 9) due to the sandy nature of soil. The soil from *Kole* land (Sample No. 4) had the highest exchangeable Mn content of 106.58 mg kg^{-1}.

5.1.4.7. Exchangeable copper (Ex.Cu)

Exchangeable copper content in the soils varied from 0.14 to 0.67 mg kg^{-1}. The highest content of exchangeable Cu was noted in *Pokkali* soil (Sample No. 1) due to high organic matter content.

5.1.4.8. Exchangeable zinc (Ex.Zn)

Exchangeable Zn was found very high in *Pokkali* soil. Most of the soil were with <10 mg kg^{-1} exchangeable Zn content.

5.1.4.8. Exchangeable Al and exchangeable plus water soluble aluminium (Ex.Al and Ex.+WS Al)

Exchangeable aluminium and water soluble plus exchangeable Al content was found not in a detectable limit in three soils (Sample No. 9 and 10 from northern coastal plain and Sample No. 12 from *Onattukara* sandy plain). Highest value of water soluble plus exchangeable Al (874.9 mg kg^{-1}) was found in *Pokkali* soil (Sample No. 3) due to the ultra-acidic pH of soil where solubility of Al is high.

5.1.5. N pools (Exchangeable ammoniacal N, nitrate and total N)

Low land soils of *Pokkali*, *Kole* and *Kuttanad* were recorded with high value of ammonical nitrogen, due to the reduced condition prevalent in low land areas. Hence oxidation of ammonical form to nitrate form is not possible. All the soils from coastal sandy plain were with low value of both ammoniacal and nitrate N, where clay content was very less which is the site for both cation and anion exchange. Total N content (4800 mg kg^{-1}) was very high in low land soils, where high organic matter content was also recorded. Total N content was low in sandy soils from northern coastal plain and *Onattukara* sandy plain, because these soils contain low organic matter.

5.1.6. Mineralogy

X-ray diffraction pattern of clay, silt and sand fractions of representative soil samples from seven agro-ecological units are given in Figure 16-22. The dominant mineral in clay fractions of all soils except the soil from Palakkad eastern plain was kaolinite. Mixed layer minerals were the dominant mineral present in clay fraction of soil from Palakkad eastern plain. Quartz and kaolinite were the common minerals present in silt fraction. Hematite was the common mineral present in all the fractions in laterite soil. Calcite was present in clay, silt and sand fractions of soil from Palakkad eastern plain. Gibbsite was common mineral present in all soils.

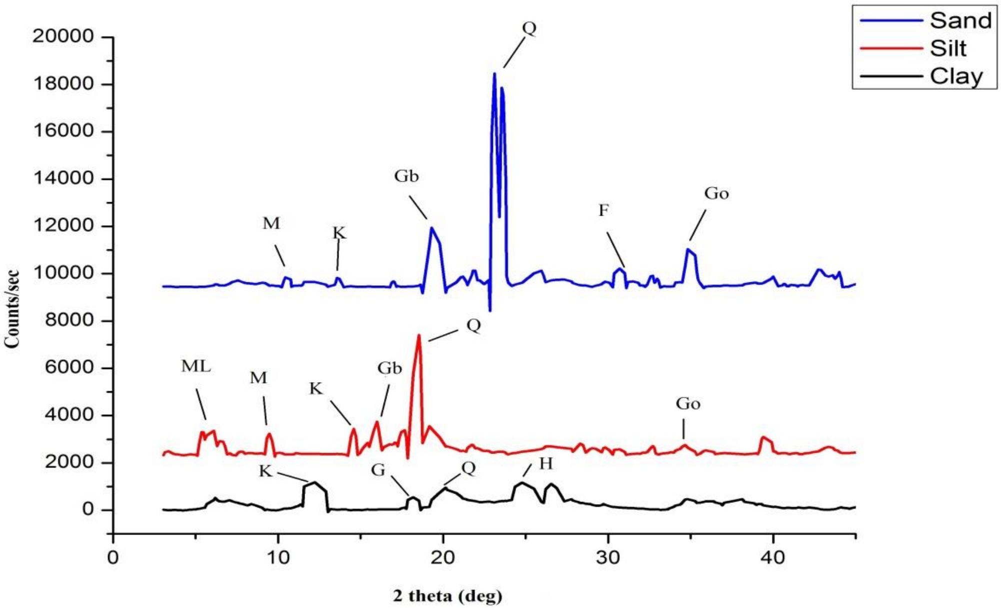


Fig.16. X-ray diffraction pattern of *Pokkali* soil

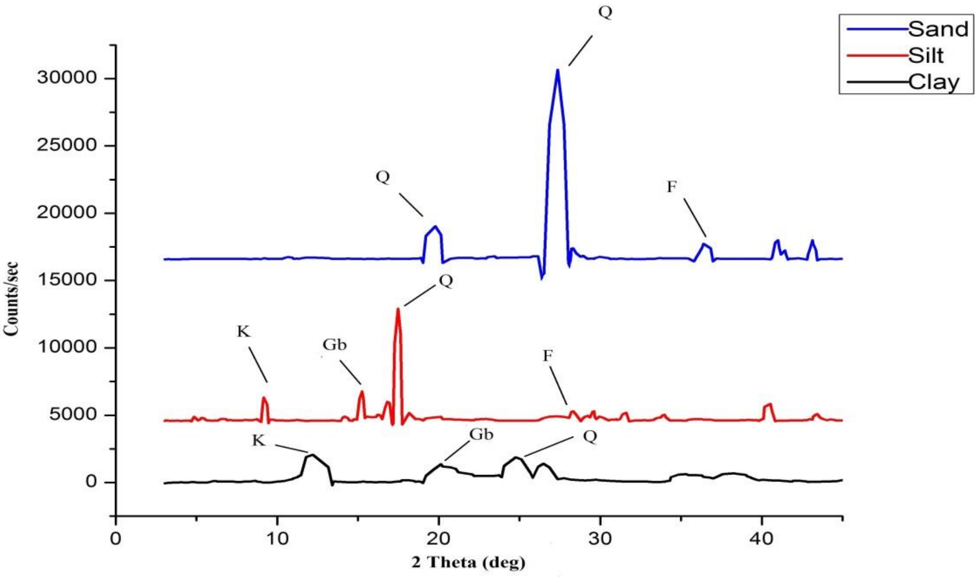


Fig.17. X-ray diffraction pattern of *Kole* soil

K-kaolinite, Gb-gibbsite, Q-quartz, H-hematite, ML-mixed layer minerals, M-mica, Go-goethite, F-Feldspar

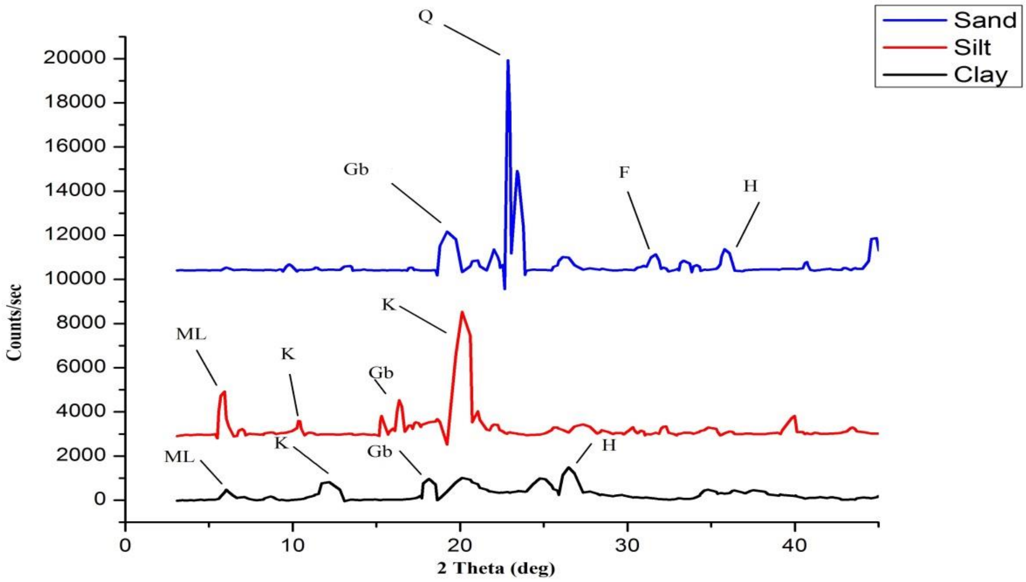


Fig.18. X-ray diffraction pattern of *Kuttanad* soil

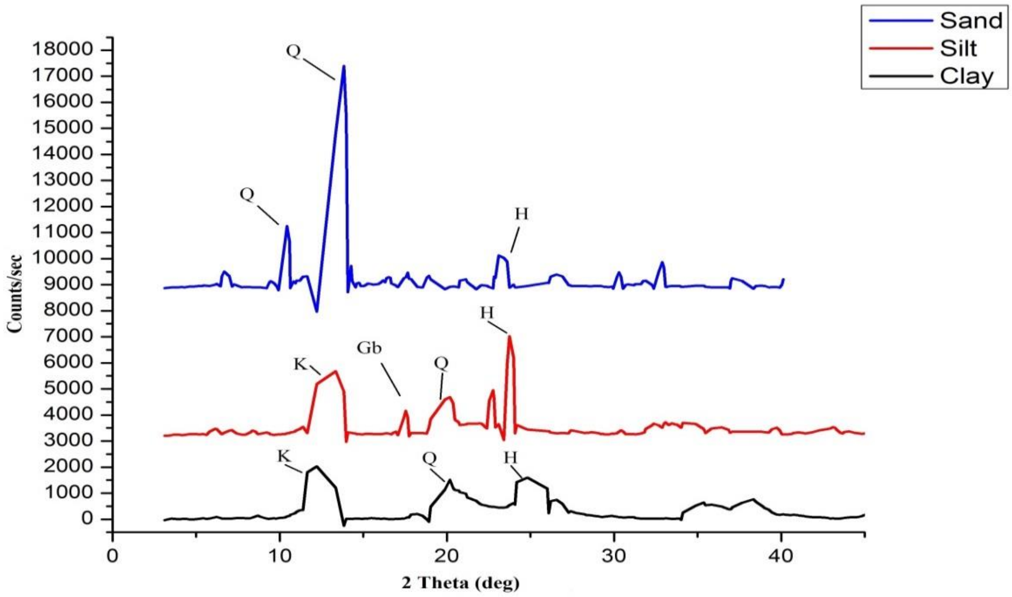


Fig.19. X-ray diffraction pattern of Laterite soil

K-kaolinite, Gb-gibbsite, Q-quartz, H-hematite, ML-mixed layer minerals, F-Feldspar

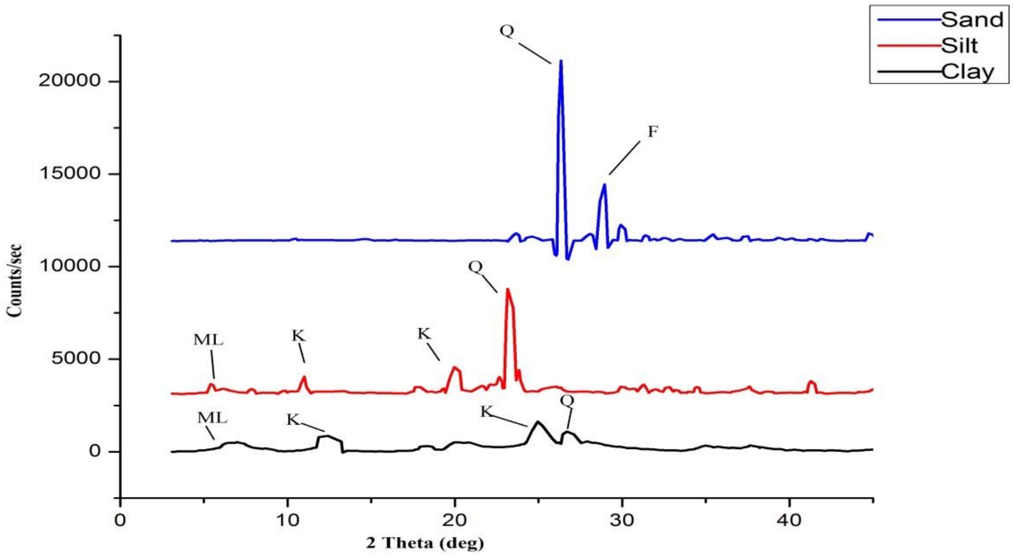


Fig.20. X-ray diffraction pattern of coastal sandy soil

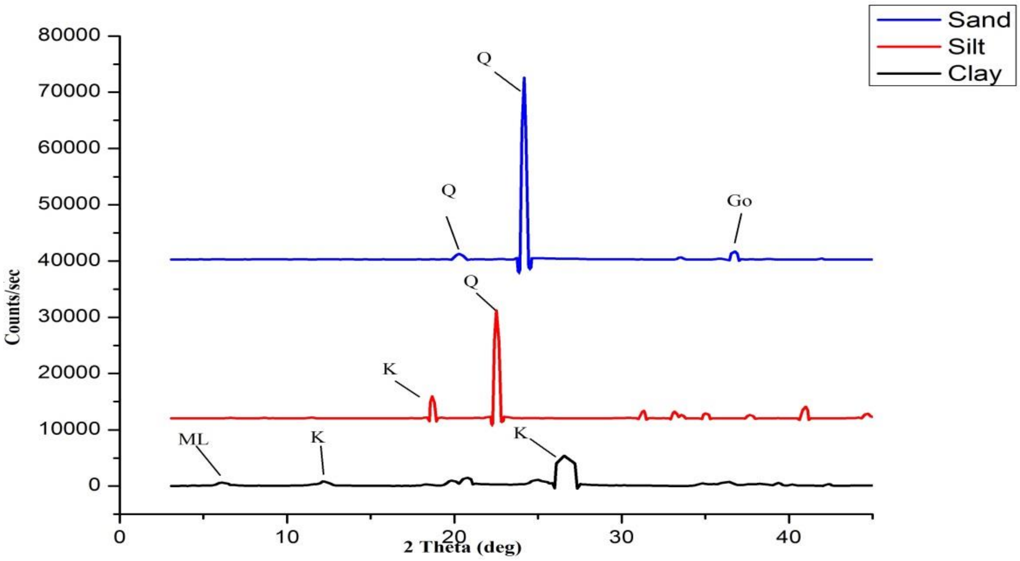


Fig.21. X-ray diffraction pattern of *Onattukara* sandy soil

K-kaolinite, Gb-gibbsite, Q-quartz, H-hematite, ML-mixed layer minerals, Go-goethite, F-Feldspar

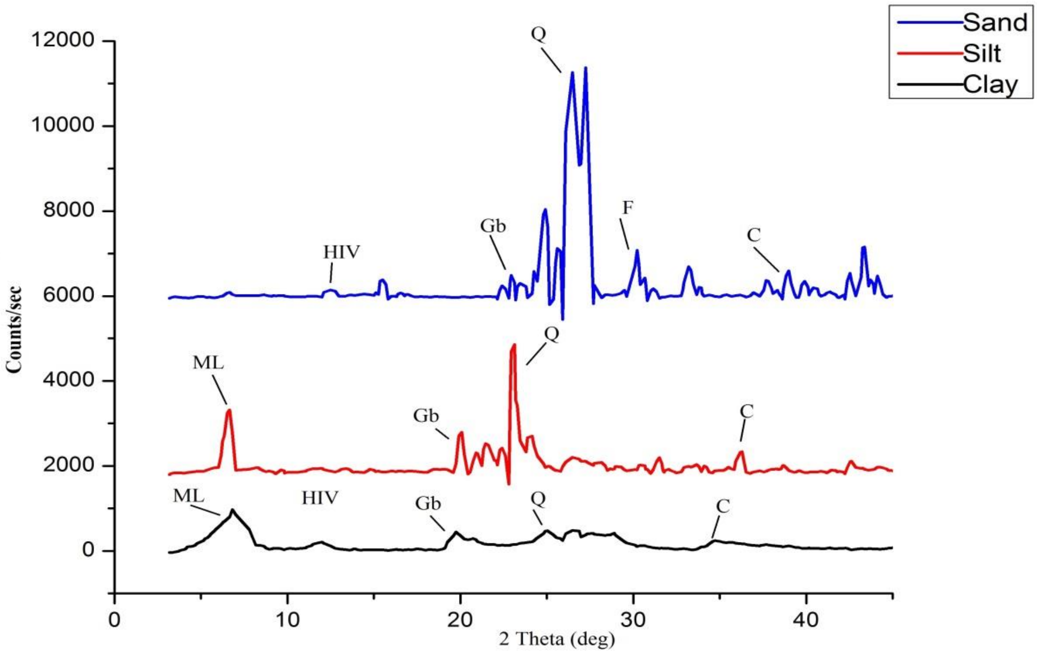


Fig.22. X-ray diffraction pattern of soil from Palakkad eastern plain

HIV-hydroxy interlayered vermiculite, Gb-gibbsite, Q-quartz, C-calcite, ML-mixed layer minerals, F-Feldspar

5.1.7. Correlation study

5.1.7.1. Relattionship between soil physico-chemical properties and available nutrient

pH had significant positive correlation with CEC and negative correlation with AEC. Increase in pH increases the negative charge and decreases the positive charge on surface and hence CEC increased and AEC decreased with increase in pH (Shamshuddin and Ismail, 1995). Most of the available nutrients had negative correlation with pH, indicating the possibility of deficiency at higher soil pH. EC showed significant positive correlation with available sulphur and magnesium content due to the presence of these salts in low land soils of Kerala by sea water entry. Organic matter content can contribute to the available nutrients on mineralization, releaving significant positive correlation with most of the available nutrients. Significant positive correlation of available N and organic matter was already reported by John (2019).

AEC had significant positive correlation with anionic nutrients like available S and B. Iron oxides can provide pH dependent positive charges in acidic soil pH and hence the presence of iron oxides increases the AEC of soil. This is supported by the positive correlation of CBD-Fe content and AEC. Clay and silt content showed positive correlation with AEC, because of the dominance of kaolinite mineral in the clay and silt fraction of soil. Content of sand had negative correlation because silica can contribute to pH dependent positive charge and AEC only when the soil pH is less than 2, which is practically not possible. CEC was significantly and positively correlated with available Ca and Mg because of the contribution of exchangeable fraction of Ca and K in the exchange site. Sand fraction showed negative correlation with available nutrients, whereas clay and silt content showed positive correlation. Exchangeable sites are more in clay and silt content.

5.1.7.2. Relationship between physico-chemical properties, available nutrients contents and exchangeable cations

Correlation between exchangeable cations, soil properties and available nutrient status indicated that exchangeable fractions of micronutrient cations are major contributor to their available pool. Available Ca and K were also correlated positively to their respective available pools. Exchangeable Ca, Mg and K showed significant positive correlation with CEC indicating the dominance of these cations in the exchange sites. pH showed significant positive correlation with exchangeable Ca and negative correlation with other cationic micronutrients.

5.2. FRACTIONATION

5.2.1. Fractionation of phosphorous

5.2.1.1. Different fractions of phosphorous in soil

Different fractions of P in soil are given in Figure 23. Saloid bound (soluble and loosely bound) P of the collected soil ranged from 0.50 to 38.58 mg kg^{-1}. It has been observed that the SB-P is the fraction in least quantity which has also been previously observed by many authors (Lungmuana *et al.,* 2012; Dutta and Mukhopadhyay, 2007). The highest quantity of saloid bound P was in sandy soil, mainly due to relatively near neutral pH and less fixation.

High Al-P content was observed in *Pokkali* soils where the soils are ultra-acidic. Chng *et al.* (2014) also reported the dominance of Al-P in acid soils. The range of Fe-P in the soils under study varied from 21.40 to 405.35 mg kg^{-1}. The dominance of Fe-P was observed in north central laterite. Similarly dominance of Fe-P has been recorded in Alfisols of Bangalore (Patle *et al.,* 2019) and acid soils of north western Indian Himalayas (Shah *et al.,* 2019).

The lowest value of reductant soluble phosphate (29.97 mg kg^{-1}) was noted in *Onattukara* sandy soil and the highest (101.75 mg kg^{-1}) in the north central laterite soil. Singh *et al.* (2013) reported the high content of sesquioxides in laterite soils. This might be the reason for high RS-P in north central laterite soil. Lungmuana *et al.* (2012) observed the dominance of RS-P and Fe-P among the inorganic P fractions of laterite soils of West Bengal. The similar results were obtained here for the north central laterite soils.

The range of Ca-P in the soils was from 5.95 to 100.60 mg kg^{-1}. Comparatively lower values of Ca-P (other than SB-P) were reported in soils of northern central laterite, which is in accordance with the findings of Lungmuana *et al.* (2012). Low land soils of *Pokkali, Kole* and *Kuttanad* also had comparatively low Ca-P than other soils.

Content of Org-P in soils ranged from 12.25 to 527.50 mg kg^{-1}. Northern coastal plain and *Onattukara* sandy plain (with low OC content) had comparatively less organic phosphate content than other soils. High content of Org-P was observed in low lands of *Pokkali, Kole* and *Kuttanad,* where a corresponding high value of organic carbon content was observed.

Residual phosphate content in the soils showed a wide range. *Pokkali* soil had the lowest value (8.47 mg kg^{-1}) and the highest value (433.21 mg kg^{-1}) was observed in the soil of Palakkad eastern plain. Total phosphate content ranged from 199.75 to 1032.25 mg kg^{-1}. Northern coastal sandy soils and *Onattukara* sandy soils exhibited relatively less total phosphate content where all the different fractions of phosphorous were at lower levels. Presence of more sand, less organic matter and iron and aluminum oxides are the reason for low content of total P and other P fractions in sandy soils from northern coastal plain and *Onattukara* sandy plain.

5.2.1.2. Percentage distribution of fractions of P in soil

Percentage distribution of fractions of P in soil is presented in Table 11. The contribution of SB-P was the least due the fixation of P in Kerala soils. *Onattukara* sandy soil had the highest per cent of SB-P due to near neutral pH, and less fixation in sandy soils. The contribution of Al-P ranged from 1.58 to 34.42 per cent. Iron bound phosphate contributed to the total P in the tune of 6.10 to 44.22 per cent. The content of RS-P ranged from 4.19 to 22.08 per cent with a mean value of 11.30 per cent.

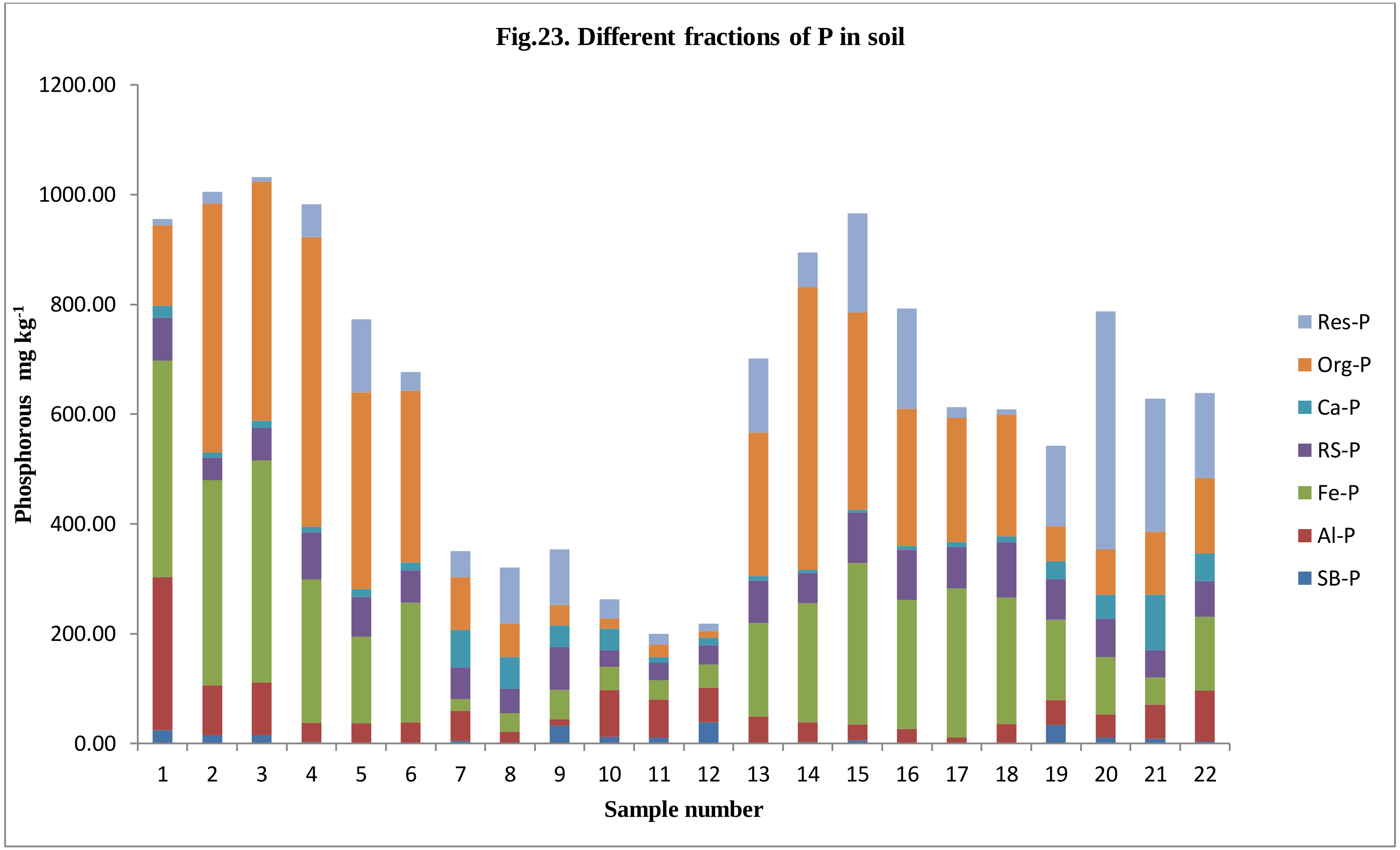


Fig.23. Different fractions of P in soil
Phosphorous mg kg^{-1}
1200.00
1000.00
800.00
600.00
400.00
200.00
0.00
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22
Sample number
Res-P
Org-P
Ca-P
RS-P
Fe-P
Al-P
SB-P

5.2.1.3. Contribution of different P fractions to the available pool

The available pool of phosphorous was significantly and positively correlated with SB-P and Al-P, negatively correlated with Org-P and Res-P. Path analysis showing the direct and indirect effect of these fractions on available pool through path coefficients depicts clearer picture that the direct effect of SB-P and Al-P to available pool is positive and high. Saloid – bound P includes easily soluble and loosely bound phosphorus which is readily available to plants. Saloid-bound P showed significant positive correlation with Av.P (0.529**).

Out of the 22 samples collected, ten samples showed pH value less than 4.5. As a result of increasing solubility of Al at this pH, P in Al-P becomes plant available. So there is every possibility of increasing the contribution to available P from Al-P. In this study Al-P showed significant positive correlation with Av.P (0.512**). Path coefficient (0.330) showed the direct effect of Al-P on available P which is positive and high. The findings of Li and Johnson (2016) corroborate with this result. They reported that Al solubility increases with soil depth when pH is less than 4.5. As pH decreases, inorganic and organic Al complexes tend to dissociate to offset the drop in pH, which in turn increases the mobilization of inorganic monomeric Al (Johnson, 2002). The dominance of Al-P in contributing towards the available P has been reported by many authors (Dongale, 1993; Laxminarayana, 2007). The available P was influenced by the forms of Al (Amorphous Al > Exchangeable Al > Extractable Al) and also by the free Fe_2O_3 (Dutta and Mukhopadhyay, 2007). This might suggest the higher sorption capacity of the soils for P to the binding sites of Al and free Fe_2O_3.

Organic P compounds are classified into orthophosphate esters, phosphonates and anhydrides based on the nature of the P bond. Among which orthophosphate monoesters are the dominant form of organic P in most soils (Condron *et al.,* 2005) Orthophosphate monoesters adsorb by ligand exchange to the same sites as orthophosphate (Ognala *et al.,* 1994; Celi *et al.,* 1999), and forms a binuclear inner-sphere complex (Goldberg and Sposito, 1985). This may lead to the unavailability of Org-P into the available pool. The predominance of inositol phosphates in soil may be partly attributed to its association with the structural components (alkyl-C) of senescent plant material, which limits its susceptibility to mineralization (Stewart and Tiessen, 1987; Gressel *et al*., 1996).The above two factors may be the reason for significant negative correlation between Av.P and Org-P (-0.278*). Moreover the submerged condition of *Pokkali, Kole* and *Kuttanad* soil limits the decomposition of organic matter and mineralization. Hence the contribution to Av.P is also limited. Residual P also had significant negative correlation with Av.P. Availability of P in soil mainly depends on dissolution of inorganic P and mineralization of organic P.

5.2.1.4. Relationship between different fractions of P and soil properties

Correlation coefficients of different fractions of P with physico-chemical properties, nutrient availability and exchangeable cations are shown in Table 14, 15 and 16 respectively**.** Saloid-bound P had significant negative correlation with clay (-0.430*) which is in accordance with the findings of Dutta and Mukhopadhyay (2007). Significant positive correlation of SB-P and Al-P with Av.P is detailed in 5.2.1.3. Dutta and Mukhopadhyay (2007) also reported the positive correlation of extractable Al with Al-P. In this study also 0.1M $BaCl_2$ extractable (WS+Ex.Al) Al showed significant positive correlation with Al-P (0.512*) which indicates the availability of Al to form Al-P. Exchangeable Al in intensely weathered and sesquioxide rich acidic (pH < 5.5) soils enters the solution causing P deficiency through precipitation as Al-P (Melese *et al.,* 2015).

The content of Fe-P had significant positive correlation with Av. Fe and Ex. Fe which shows the abundance of Fe to form Fe-P especially in soils of *Pokkali, Kole, Kuttanad* and northern central laterite. Reduced forms of micronutrients are high in low lands of *Pokkali, Kole* and *Kuttanad.* This could be the reason for significant positive correlation of Fe-P with Av.Zn and Av.Cu. Since availability of micronutrients like Fe, Zn, and Cu mainly depends on the exchangeable fraction, Ex.Zn and Ex.Cu also showed positive correlation with Fe-P. Fixation of P in acid soils is mainly by Fe-P and Al-P.

A significant positive correlation of Av. Mn was noted only with RS-P fraction. Dutta and Mukhopadhyay (2007) reported a positive relation between free Fe_2O_3 and RS-P, because reductant soluble phosphate fraction is the phosphate occluded in Fe and Al oxides. Calcium P fraction was significantly and positively correlated with pH, Av.Ca and Ex.Ca. The possibility of forming Ca- P is high in soils containing Av.Ca. The major contribution to the available Ca is exchangeable form. And the availability of Ca increases with increases with Ca-P occurs in slightly alkaline pH (Ferguson *et al.,* 1973).

Organic P fraction of soil is seen in organic matter content which is defined as P bonded in some way with C. So Org-P showed positive correlation with OC. Kaila (1956) expressed organic P as a percentage of the organic dry matter which ranged from 0.01 to 0.25 per cent in peat soils. Low lands of *Pokkali, Kole* and *Kuttand* contains high amount of organic matter. Since organic matter has positive correlation with Av.N, Av.Cu, and Ex.Cu, all these parameters showed positive correlation with Org-P. Organic P showed negative correlation with pH and Av.P due to the unavailability of Org-P.

Residual P had significant positive correlation with CEC, Av.Ca, Ex.Ca, Av.Si and negative correlation with Av.P and Ex.Cu. Total P has significant positive correlation with OC and available and exchangeable micronutrients are due to the presence of high amount OC and micronutrients in lowlands of *Pokkali, Kole* and *Kuttanad.* The correlation coefficients of different fractions of an element with available and exchangeable cations are different based on the extractability of extractants used.

5.2.2. Fractionation of sulphur

5.2.2.1. Different fractions of S in soil

The fractionation procedure followed here is not sequential fractionation. All the sulphur fractions were high in *Pokkali* soils. This is due to the inundation of sea water in *Pokkali* lands. Young *et al.* (1959) reported the chemical composition of Atlantic provinces of Canada and reported sulphate content in the sea water as 2.36 g kg^{-1}.The reason for the high content of all the S fractions in *Kuttanad* and *Kole* soils are also the same. Since the sea water entry is controlled in *Kole* and *Kuttanad,* it is showing less S fraction values than *Pokkali* soils where inundation of sea water is not controlled. Average S content of 298.77 mg L^{-1}was found in source water in *Pokkali* soil where paddy-shrimp land use pattern is being followed (Silpa, 2020).

Less sulphur fraction contents were reported in northern coastal sandy soil and *Onattukara* sandy soils. The possibility of extensive leaching in sandy textured soil is the reason for this. Ensminger (1954) reported that light textured soils had only low capacity to adsorb sulphate. Dominance of different fractions of S in soil was as follows; total organic S >sulphate soluble after ignition > heat soluble S > total water soluble S >sulphate S. The same trend was observed by Williams and Steinbergs (1959). Srinivasarao *et al.,* (2004) also reported the dominance of organic S fraction in surface soil.

Williams and Steinbergs (1962) reported that the amount of soluble sulphate, as indicated by calcium chloride extraction, was low in the surface horizon of most well-drained soils, whether of acid or alkaline reaction, and generally comprised only a small fraction of total S. Total water soluble sulphates in soil include free sulphates and some of the organic sulphur present in soil. That is why content of total water soluble fraction was found higher than sulphate sulphur. More organic S is released by gentle hydrolysis. This fraction is also coming under heat-soluble S. Williams and Steinbergs (1959) reported that heat is the main factor leading to the release of additional sulphur in soil. The content of sulphate soluble after ignition was found next to these fractions since much more organic S might have solubilized in this fraction.

The presence of high organic matter content in *Pokkali*, *Kole* and *Kuttanad* soils are also the reason for high content of all S fractions in these soils, whereas the soils from *Onattukara* sandy plain and northern coastal plain with very low organic matter were reported with less content of all S fractions.

5.2.2.2. Contribution of different S fractions to the available pool

The direct effect of total water soluble S and indirect effects of other fractions through water soluble S on available S was positive and moderate. The direct and indirect effects through other fractions (except sulphate soluble after ignition) were positive and moderate. Any changes in the organic matter as a whole are likely to be reflected in the sulfur fractions. This is the reason for common trend in all fractions. Anderson (1975) studied about the sulphur in organic matter. The breakdown of some organic sulfur compounds in soils is very rapid and hence its contribution to available pool is very important. The aerobic decomposition of cysteine or cystine usually ends in the formation of sulfate. Comparison of the amounts of sulfate produced during decomposition of different sulfur to the conclusion that the rate of decomposition could not be related to the type of sulfur linkage (Frederick *et al.,* 1957).

5.2.2.3. Relation between different fractions of S in soil and soil properties

All the S fractions had significant negative correlation with pH and positive correlation with EC, OC and AEC. Williams and Steinbergs (1962) reported significant negative correlation between sulphate adsorption and pH. Srinivasarao *et al.* (2004) also reported significant negative correlation of available S with pH (-0.63**) in the surface soil layer. Sulphate is adsorbed to the positive site of soil. The number of positive sites increases (AEC increases) with decrease in soil pH. That is why sulphate fractions under this study showed significant positive correlation with AEC and negative correlation with pH. The other reason for negative correlation of available S with pH and positive correlation with EC is the influence of acid saline/sulphate soils under study. The very high positive correlation of all the sulphur fractions with organic carbon is in accordance with the results of Sharma *et al.* (2014).

5.2.3. Fractionation of boron

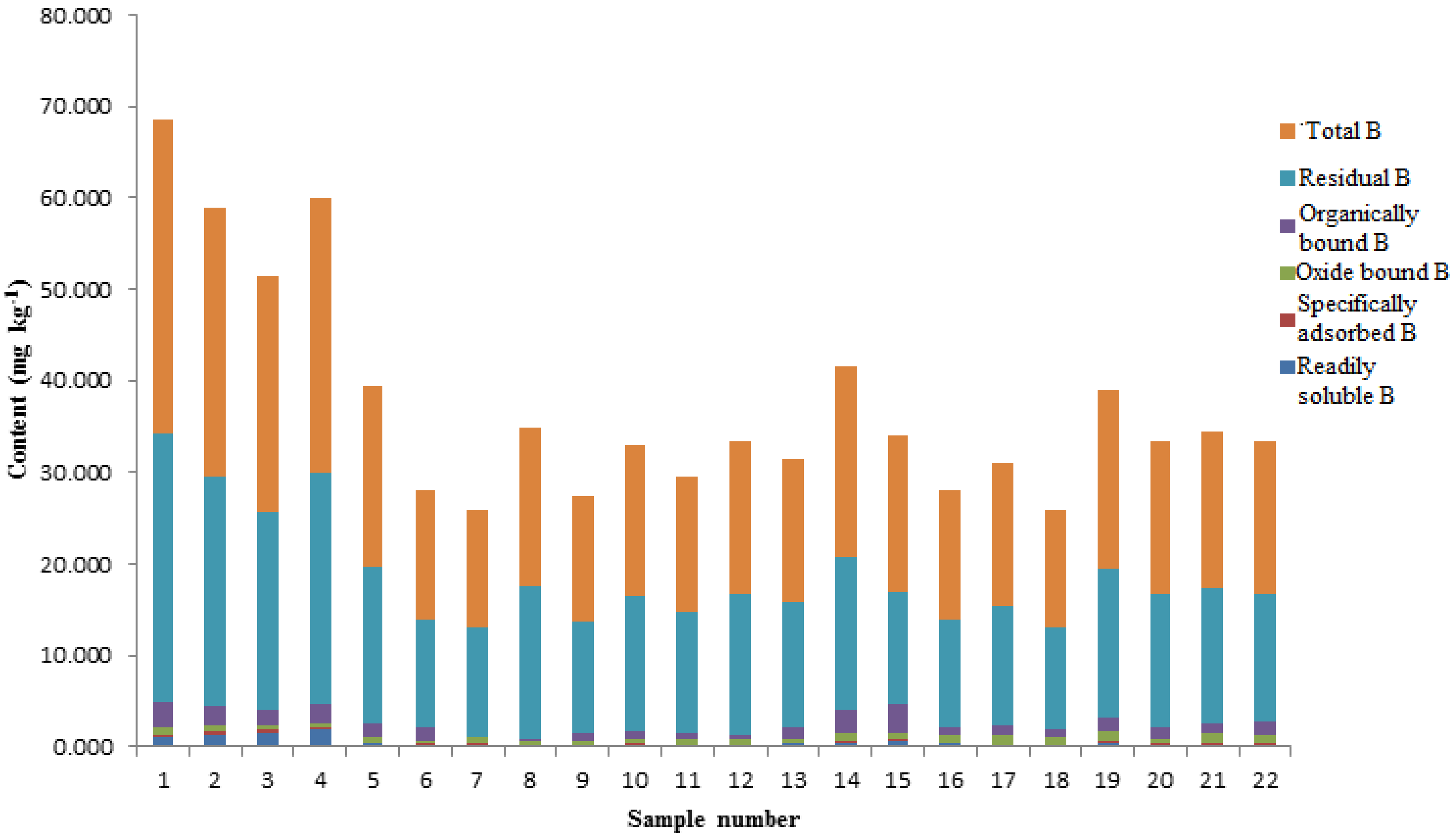
5.2.3.1. Different fractions of B in soil

Different fractions of B and total B in the collected soils are presented in Figure 24. Readily soluble boron in the soil ranged from 0.180 to 1.980 mg kg^{-1}. Lowest value recorded in coastal sandy soil is due to leaching losses and low anion exchange capacity. Similar range of readily soluble B was reported by Santhosh (2013) in different soils from Kerala and Datta *et al.* (2002) in soils of different locations in India. This pool of B in soil, which includes dissolved plus B adsorbed non-specifically on edges of clays and other variable charged surfaces. B in weakly binding sites of both organic and inorganic constituents especially that is adsorbed to specific sites in soil such as Fe and Al oxyhydroxides are specifically adsorbed B fraction (Hou *et al.,* 1994). All the *Pokkali* soils showed comparatively higher values of specifically adsorbed B due to the presence of oxides and hydroxides of Fe and Al. Oxide bound boron content in soil ranged from 0.322 to 1.059 mg kg^{-1}.

Low lands soils of *Pokkali, Kole* and *Kuttanad* were with higher values of organically bound boron content due to the presence of higher content of organic matter and low content of organically bound B was recorded in sandy soils due to low organic matter content. Compared to mineral constituents organic constituents adsorb more amount of B on a weight basis (Santhosh, 2013).

Residual B content in the soil ranged from 10.992 to 29.343 mg kg^{-1}. *Pokkali* soils had high values of residual B and total B. Lowest total boron was noted in coastal sandy soil. The dominance of different fractions of B in soil was in the order, Residual B>> organically bound B> oxide bound B≈ readily soluble B> specifically adsorbed B.

Fig.24. Different fractions of B in soil



5.2.3.2. Contribution of different fractions of B to the available pool

Available B was significantly and positively correlated with readily soluble B, organically bound B, residual B and total B. Readily soluble B fraction includes dissolved B and non-specifically adsorbed B on edges of clays and other variable charged surfaces and hence this fraction showed positive correlation with available B. The available B status of the major soil groups of Madhya Pradesh showed a positive correlation with organic matter content (Saha *et al.,* 1998). Similar results were also reported by Ghosh and Sarkar (1994). Organic matter form complexes with B and remove it from the soil solution when the levels are high after B fertilization. It then replenishes the soil solution B on depletion by crop removal or leaching. Significant positive correlation of residual and total B indicates the slow solubility of these fractions which are in dynamic equilibrium.

5.2.3.3. Relationship between different fractions of B and soil properties

Significant positive correlation among different fractions of B indicates these fractions are in dynamic equilibrium. Significant positive correlation of the readily soluble B with specifically adsorbed B, organically bound B, residual B and total B indicates the contribution of these fractions to readily soluble pool of B in soil. As the readily soluble B is depleted, it will be replenished immediately by these fractions. Significant correlation was not observed in case of oxide bound B with readily soluble B indicating the negligible contribution made by this fraction to readily soluble B.

The significant negative correlation of readily soluble B with pH indicates that this pool of B increases with decrease in pH. This is due to solubilisation of different forms of B and the formation of boric acid which is water soluble (Santhosh, 2013). Significant positive correlation of readily soluble B with pH and AEC is due to the presence of more pH dependent positive charges for B adsorption at acidic soil pH. Significant positive correlation of readily soluble B, residual B and total B with silt indicates the presence of B in the finer fractions of soil. Organically bound B had significant positive correlation with organic matter.

Significant positive correlation of EC and exchangeable Na with readily soluble B is due to direct effect of highly soluble salts of B such as Na and potassium borate, on the total soluble salt content in soil which is prevalent in soils of *Pokkali, Kole* and *Kuttanad.*

5.2.4. Fractionation of silicon

Silicon in the soils most commonly occurs in quartz followed by that Si in primary silicates and clay minerals. In general, Si released during weathering of primary silicates can be leached or consumed in the formation of secondary silicates, or it may precipitate as pedogenic silica from the soil solution (McKeague and Cline, 1963b)

5.2.4.1. Different fractions of silicon in soil

Percentage contribution of different fractions of Si to the total Si content excluding the residual Si is shown in Figure 25. It was found that compared to other fractions, mobile Si was very low in the collected soils and its contribution to total Si content was to the tune of only 0.001 to 0.053 per cent. Lekshmi (2016) also reported less content of mobile silicon fraction in major rice growing soils of Kerala when compared to other fractions. *Onattukara* sandy soil and northern coastal sandy soil were reported with comparatively low mobile silicon content than other soils. This may be due to the leaching of uncharged monomeric silicic acid in these soils.

Adsorbed Si in the collected soils ranged from 23.51 to 196.40 mg kg^{-1}. Silicic acid can be adsorbed to the surface of various soil components and the adsorption depends on soil reaction, soil composition and specific surface area of the soil particles. It can be adsorbed to the surface of pedogenic oxides and hydroxides also. Immobilization of silicic acid in soils by adsorption to Al and Fe oxides were also reported by Haynes (2014). Physical adsorption may also happen on organic matter in soil. This type of adsorption is possible in soils of Kerala. The low adsorbed Si content of coastal sandy soil might be due to unavailability of surfaces like pedogenic oxides, hydroxides and organic matter for adsorption.

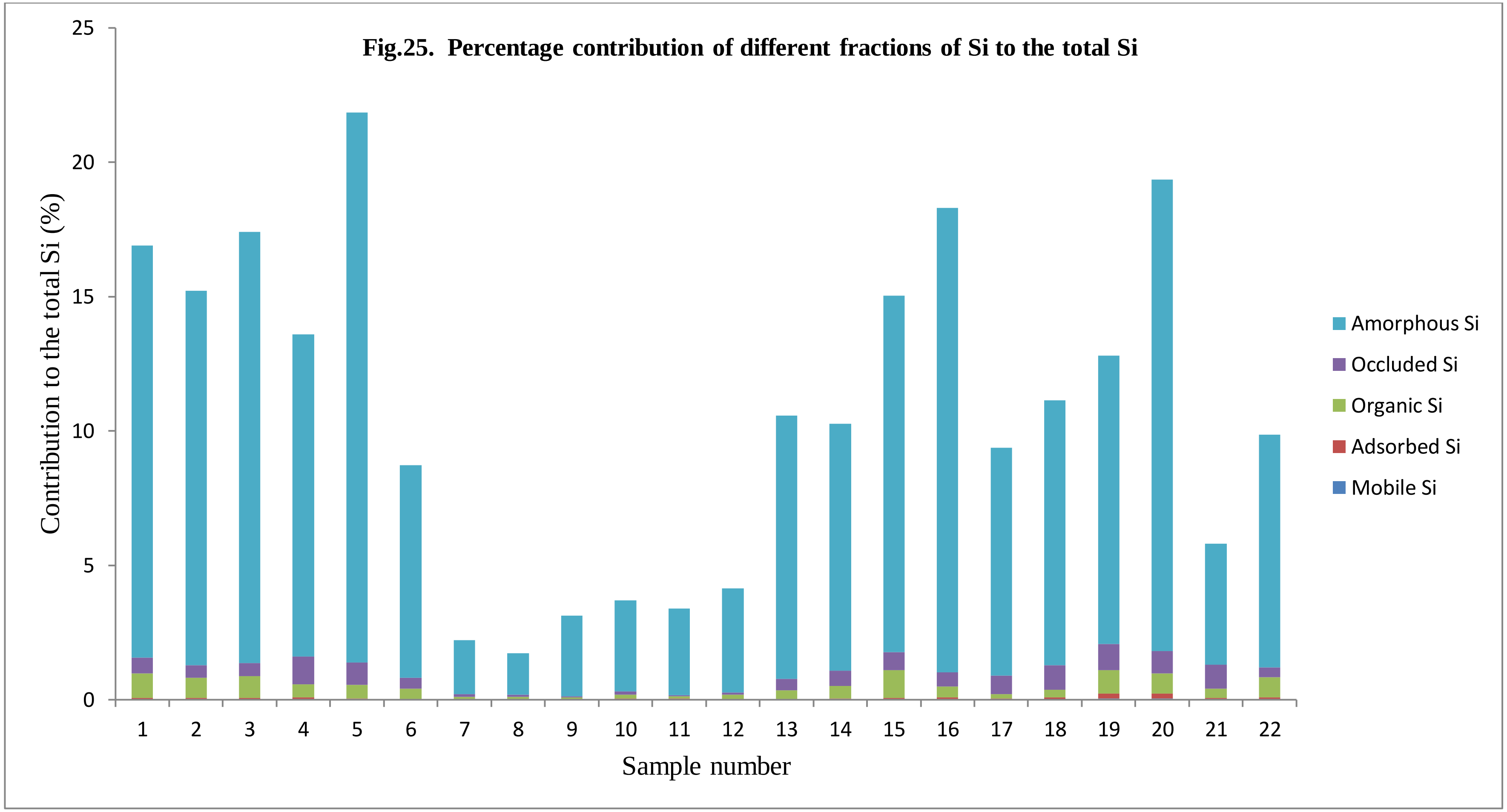


Fig.25. Percentage contribution of different fractions of Si to the total Si

Georgiadis *et al.* (2013) reported that adsorption of silicon was more in smectite than goethite, gibbsite and kaolinite. High values of adsorbed silicon noted in the soils from Palakkad eastern plain might be due to the dominance of 2:1 clay minerals.

Silicon in soil organic matter could be obtained through destruction of soil organic matter. Organic silicon content in the soils ranged from 116.13 to 1746.90 mg kg^{-1}. *Onattukara* sandy soils and northern coastal soils showed less organic Si where the organic matter content is very less. The highest organic Si content was recorded in Pokkali soils could explain itself the clear role of organic matter in the retention of Si.

Silicon could be occluded in the oxides and hydroxides during pedogenic process. Hence the presence of aluminium and iron oxides and hydroxides decrease the amount of silicon in soil solution (Jones and Hendreck, 1967). Pedogenic oxides and hydroxides could be completely dissolved in order for getting the occluded Si released. The content of occluded silicon in the soils ranged from 71.64 to 1134.40 mg kg^{-1}. Very less content of occluded Si was noted in *Onattuakara* sandy soils and coastal sandy soils, because these soils contain less oxides and hydroxides. The highest value of occluded Si was found in *Kole* which is in accordance with the result of Lekshmi (2016).

The amorphous silica pool includes minerogenic and biogenic silica. Biogenic silica produced by plants as phytoliths, microorganism remains *viz.*, diatoms and sponge spicules (Sauer *et al.*, 2006; Sommer *et al.*, 2006). Minerogenic amorphous silica is a non-crystalline inorganic fraction such as Si included in iron oxides/hydroxides and Si in inorganic alumino-silica coatings. Low amorphous silicon content was observed in soils from northern coastal plain and *Onattukara* sandy plain. Amorphous Si was the second largest fraction in soil. This result is supported by the findings of Danilova *et al.* (2010) who reported that Si extracted by NaOH (amorphous silicon) constituted the largest fraction of extractable Si in almost all soil samples of SW Germany. The high pH of the

NaOH extractant ensures that all amorphous silicon is extracted from soil sample (Saccone *et al.*, 2007). Deposition of diatoms through the inundation of sea water, litter deposition and presence of humus layer is the reason for high amorphous Si content in *Pokkali, Kole* and *Kuttanad* soil.

Residual Si content of the soils varied from 77058.48 to 190401.70 mg kg^{-1}. The highest total Si content of 212.9 g kg^{-1} was noted in *Kuttanad* soil. The lowest value of 97.6 g kg^{-1} was recorded in laterite soil, which may be due to process of laterisation. The percentage distributions of the different fractions of Si were in the order; residual Si > amorphous Si > occluded Si ≃oragnic Si > adsorbed Si> mobile Si.

5.2.4.2. Contribution of different Si fractions to the available pool

The available Si content was significantly and positively correlated with mobile Si (0.504*) and adsorbed Si (0.798**); negatively correlated with residual Si (-0.513*) and total Si (-0.526*). Path analysis showing the direct and indirect effect of these fractions on available pool through path coefficients depicts the following conclusion.

The direct effect of mobile Si on available Si is very high and positive (0.414), because it is the readily soluble fraction and the indirect effect through adsorbed Si is also positive and high, which indicated that the contribution of residual silicon is via solubilisation, which in turn may be influenced by the physical and chemical factors. The direct effect of adsorbed Si on available Si is also very high and positive (0.665). The contribution of adsorbed Si is more than mobile Si to the available pool. It is suggested that silicic acid get adsorbed to the surface of Fe oxides and to the edge sites of kaolinite. Silicic acid adsorbs onto Fe oxides via ligand exchange to form inner-sphere complexes (Taylor, 1995). Ma (2011) reported the weak electrostatic bonding of sodium silicate with kaolinite. The residual and total Si in soil had significant negative correlation with available Si.

5.2.4.3. Relationship between different fractions of Si and soil properties.

The soluble silicon compounds contain monosilicic acid, polysilicic acid and organic silicon compounds. Matichenkov and Bocharnikoa (2001) observed that monosilicic acid regulates chemical properties of the soil solution and polysilicic acid have an effect on soil physical properties.

Mobile Si had significant positive correlation with clay (0.538**). Georgisdis *et al.,* (2013) found that the horizons with >20 per cent clay content were with more mobile Si content and they suggested that clay mineral surfaces were the major source of mobile Si in soil. Mobile Si had significant positive correlation with OC, CEC, AEC, silt, Av.N,Av.K,Av.Fe, Av.Cu, Av.B, Ex.Ca, Ex.Mg and Ex.K; and negative correlation with sand. Adsorbed Si had significant positive correlation with CEC, Av.Ca and Ex.Ca which indicated the chance of adsorption of Si through cation bridging and a shift in equilibrium between adsorbed and mobile silicon, which was mainly due to the monosilicate mobile fraction being adsorbed or desorbed. The sand fraction having only coarser particle is not expected to contain silicon in either mobile or adsorbed form. Organic Si showed significant positive correlation with organic carbon which indicates the binding of silicon to organic compounds as sorbed physically. It showed significant positive correlation with EC and negative correlation with pH which indicated that the soils with high organic matter naturally contained higher Si. Such soils included in the present study are acid saline and acid sulphate and hence it got a relation with EC. Significant positive correlation with Av.N, Av.Cu and Ex.Cu was due to the effect of organic matter.

Occluded Si showed significant positive correlation with OC, AEC, CEC, silt content, clay content, Av.N, Av.K, Av.Mg, Av.Fe, Av.Mn, Av.Cu, Av.B, Ex.Mg, Ex.Na, Ex.K, Ex.Fe, and WS+Ex.Al; and negative correlation with sand content. There was significant and negative correlation of amorphous Si with pH; positive correlation with EC, OC, Av.N, Av.Cu, Ex.Cu ,Av.S and Ex.Na, may be the effect of *Pokkali, Kole* and *Kuttanad* soil where there is high chance for the occurrence of biogenic silica. The significant positive correlation with WS+Ex.Al indicates the chance of formation Al-silica coating on mineral surfaces.

Residual Si fraction is the dominant Si fraction and the significant correlations it showed with physicochemical properties of soil are negative. Total Si content in the soil had significant positive correlation with EC, Av.Mg, Av.S, Av.Zn, Ex.Na, Ex.Cu, and WS+Ex.Al; negative correlation with pH, Av.Ca, Ex.Ca, Av.Mn, Ex.Mn and Ex.K.

5.3. ADSORPTION STUDY

5.3.1. Adsorption study of single anions

In general adsorption of anions in the collected soils was well explained by Freundlich adsorption isotherm followed by Tempkin and Langmuir adsorption isotherm. Linear fit of the models were tried. Isotherm parameters for linear and non-linear Freundlich and Temkin models were almost same, whereas Langmuir parameters were found quite different in linear and non-linear models (Khandelwal *et al.,* 2020). Linear fit of Langmuir adsorption isotherm was not observed in most of the adsorption data. Desorption was dominant in case of Si and S with added concentration of the element. Adsorption of P and Mo followed typical L shaped curve in low land soils of *Pokkali, Kole* and *Kuttanad.*

5.3.1.1. Adsorption study of nitrate

Quantity-intensity relationship

Q-I plot of representative soil samples from each agro-ecological unit at 25 ^{0}C and 40 ^{0}C is given in figure 26. All the soils could give best fit curves explaining more than 50 per cent variance at both 25 ^{0}C and 40 ^{0}C with the exception of soil from Palakkad eastern plain at 40 ^{0}C. This would mean that there exists a linear relationship between the solid phase - solution phase equilibrium of nitrate though the balanced equilibrium of adsorption- desorption.

In most of the soil, after reaching a maximum adsorption a decrease in adsorption was observed with added concentration of nitrate which is due to the saturation of adsorption sites in soil. High buffer power and maximum value of nitrate adsorbed by low land soils of *Pokkali, Kole* and *Kuttanad* is resulted by the presence of more anion exchange sites. These soils have got a greater power to retain nitrate on solid phase and replenish its level in solution as and when it is depleted by the plant uptake or leaching losses. Y Intercept of the Q-I curves indicates the amount of nitrate adsorbed per unit weight of soil only beyond which it can contribute to intensity factor upon depletion of nitrate in soil. All the soils from low lands were with positive Y-intercept. All the sandy soils and most of the laterite soils and soils from Palakkad eastern plain were with negative Y intercept, indicating that, this nitrate will be the labile pool and when this level of labile pool exceeds a particular value, only then soil matrix starts adsorbing nitrate. Maximum quantity adsorbed and buffer power was found decreasing with increase in temperature, which is indication of physical nature of adsorption.

Buffer power was significantly and positively correlated with maximum quantity adsorbed. When the amount adsorbed per unit weight of soil increases, the capacity of soil to supply the nutrient into soil solution upon depletion also increases. Nitrate in soil could be adsorbed to positive sites in the minerals. Kaolinite is the dominant mineral present in clay and silt fractions of most of the soils under study, which provides pH dependent positive charge at low pH values. Fe and Al oxides present in the soil also lead to the development of positive charges in soil under acidic pH. That is why Kerala soils showed significant positive correlation of buffer power and maximum quantity adsorbed with clay content, silt content, CBD extractable Fe content and negative correlation with sand content, for nitrate adsorption. The significant negative correlation of buffer power and maximum quantity adsorbed with pH and positive correlation with AEC would be resulted from the development of more positive sites for the adsorption of nitrate with decrease in pH. Klucakova (2010) reported that nitrates are adsorbed to solid humic particles and a small amount is bonded to dissolved humic macromolecules or aggregates. The binding sites of nitrate in humic materials and adsorption mechanism is yet to be confirmed. High positive correlation of buffer power and maximum quantity adsorbed corroborate with the result of Klucakoa (2010). The influence of organic matter lead to the positive correlation of buffer power and maximum quantity adsorbed with Av.S, Av.N, and Av.Cu.

Adsorption isotherms and thermodynamics of adsorption

Adsorption isotherms were fitted for soils with minimum four points with positive slopes in Q-I curve. All the soils collected from northern coastal plain and one sample from *Onattukara* sandy plain (Sample No. 10) showed dominance of desorption at 40 ^{0}C. Hence isotherms were not fitted for those soils (Sample No. 7, 8, 9 and 10).

Nitrate adsorption was well explained by Freundlich isotherm. This assumes that the affinity for adsorption decreases exponentially with the increase in surface coverage which is more logical in real situation. Mohsenipour *et al.* (2015) reported that Freundlich adsorption isotherm model was more accurate than Langmuir adsorption model in predicting of nitrate adsorption in kaolin clay. Freundlich adsorption isotherm for nitrate adsorption at 25 ^{0}C and 40 ^{0}C in representative soils from each agro-ecological unit is given in figure 27. The constant K_F in Freundlich equation represents the amount adsorbed at unit solution concentration (Sureshkumar, 1993). It is an indication of adsorption capacity (Santhosh, 2103; Inam *et al.,* 2017). Most of the soils were reported with a decrease in K_F and 1/n with increase in temperature. Temperature decreases the adsorption capacity and adsorption intensity since nitrate adsorption in soil is physical in nature. Soils with maximum adsorption capacity were with less adsorption intensity and hence 1/n was negatively correlated with K_F.

Only four soils (*Onattukara* sandy soils and one coastal sandy soil) followed Langmuir adsorption isotherm for nitrate adsorption. Langmuir adsorption isotherms of representative soils are given in Figure 28. Adsorption maxima (q_m) was very less (<30 mg kg^{-1}) since AEC of these soils are less. K_L is the constant related to binding strength. Soils followed Langmuir adsorption isotherm were reported with very low value of K_L (<0.05 L mg^{-1}). Since binding strength of nitrate to the adsorption site is very less it can be easily desorbed with increase in temperature.

Nineteen soil samples followed Tempkin adsorption isotherm. Tempkin adsorption of representative soil samples are given in Figure 29. K_T is the constant related to strength of binding, indicating the adsorbate-adsorbent interaction. b is the constant related to heat of adsorption. All the soil samples except *Onattukara* sandy soil (Sample No. 12 at 25 ^{0}C) were with K_T value less than 1, indicating nitrate adsorption in soil occur with less binding energy. The Temkin isotherm model assumes that the heat of adsorption of all molecules decreases linearly with the increase in coverage of the adsorbent surface, and that adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy.

Fig. 26. Quantity-intensity curve for nitrate adsorption at 25 ^{0}C and 40 ^{0}C

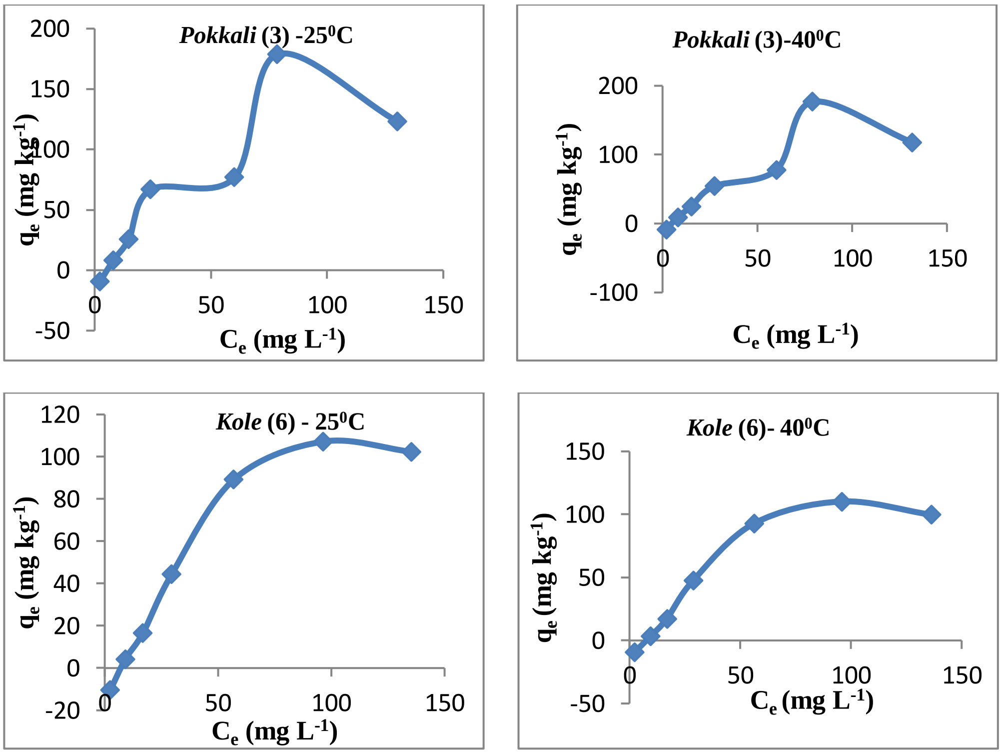


Fig.26. Continued

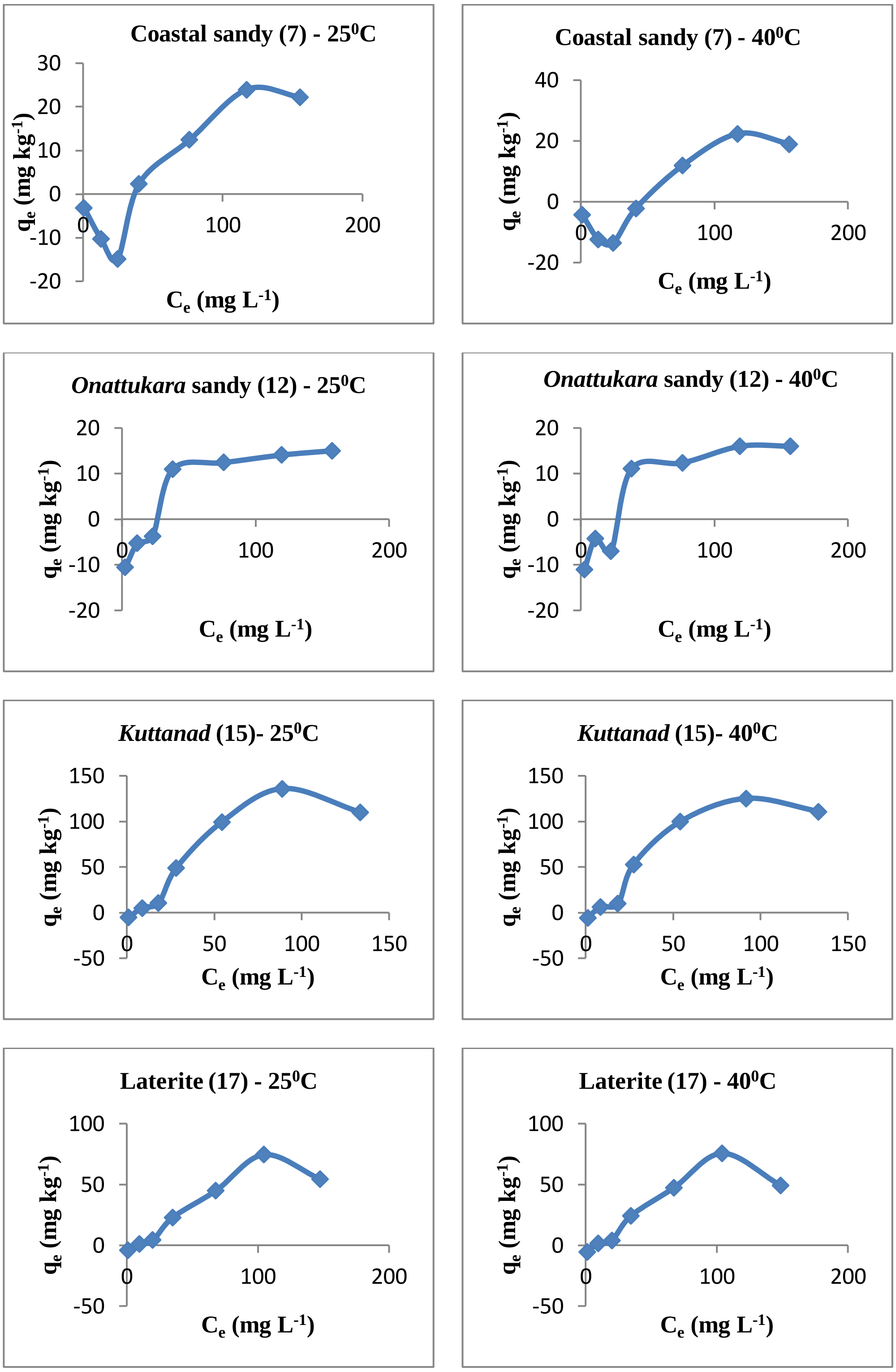


Fig.26. Continued

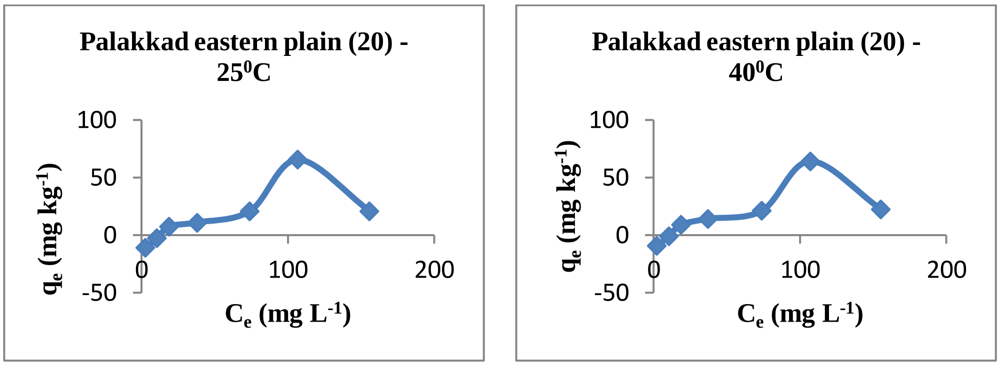


Fig. 27. Freundlich adsorption isotherm for nitrate adsorption at 25 ^{0}C and 40 ^{0}C

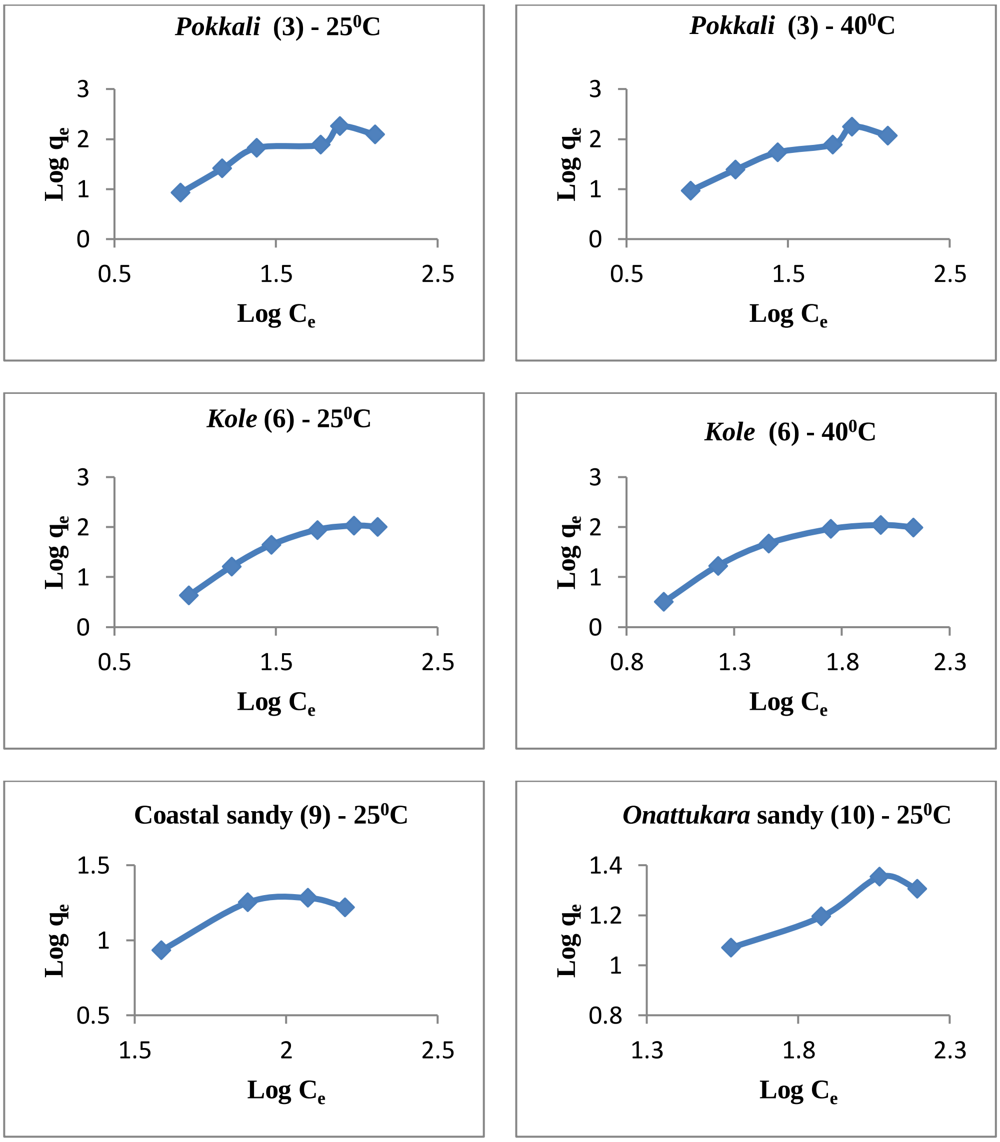


Fig. 27. Continued

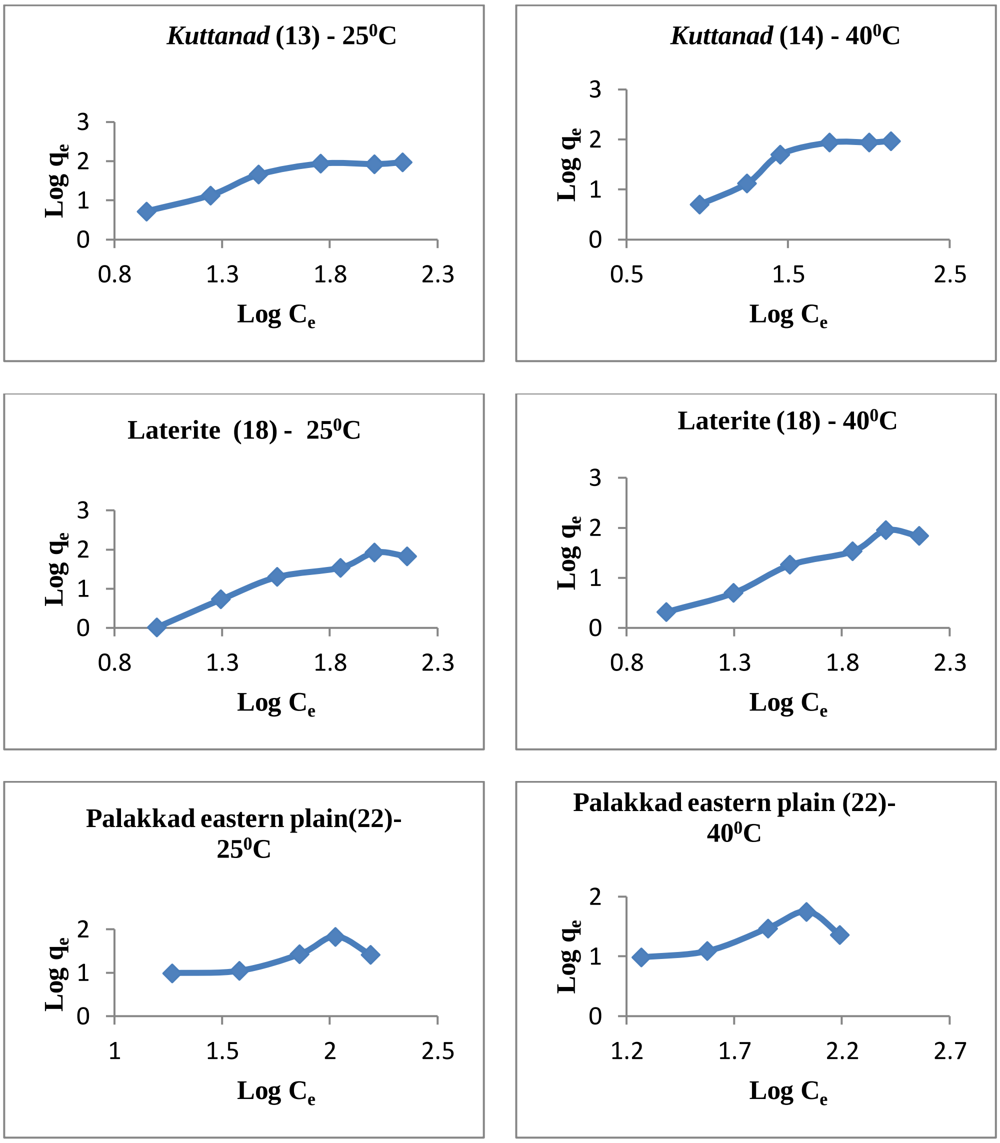


Fig.28. Langmuir adsorption isotherm for nitrate adsorption at 25 ^{0}C

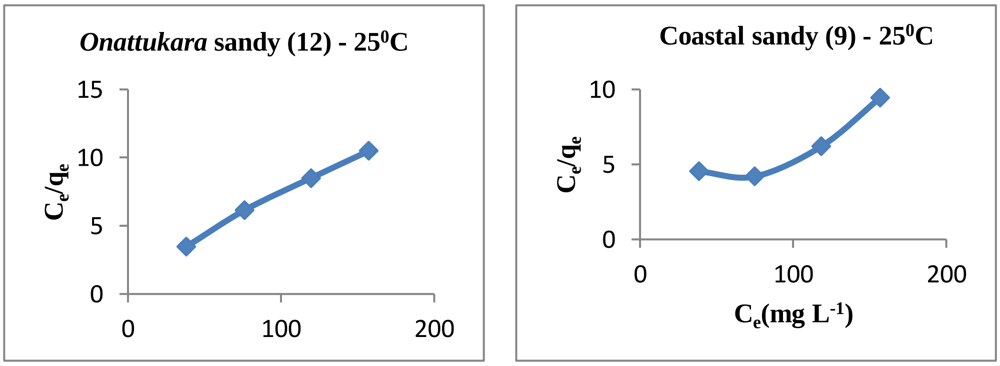
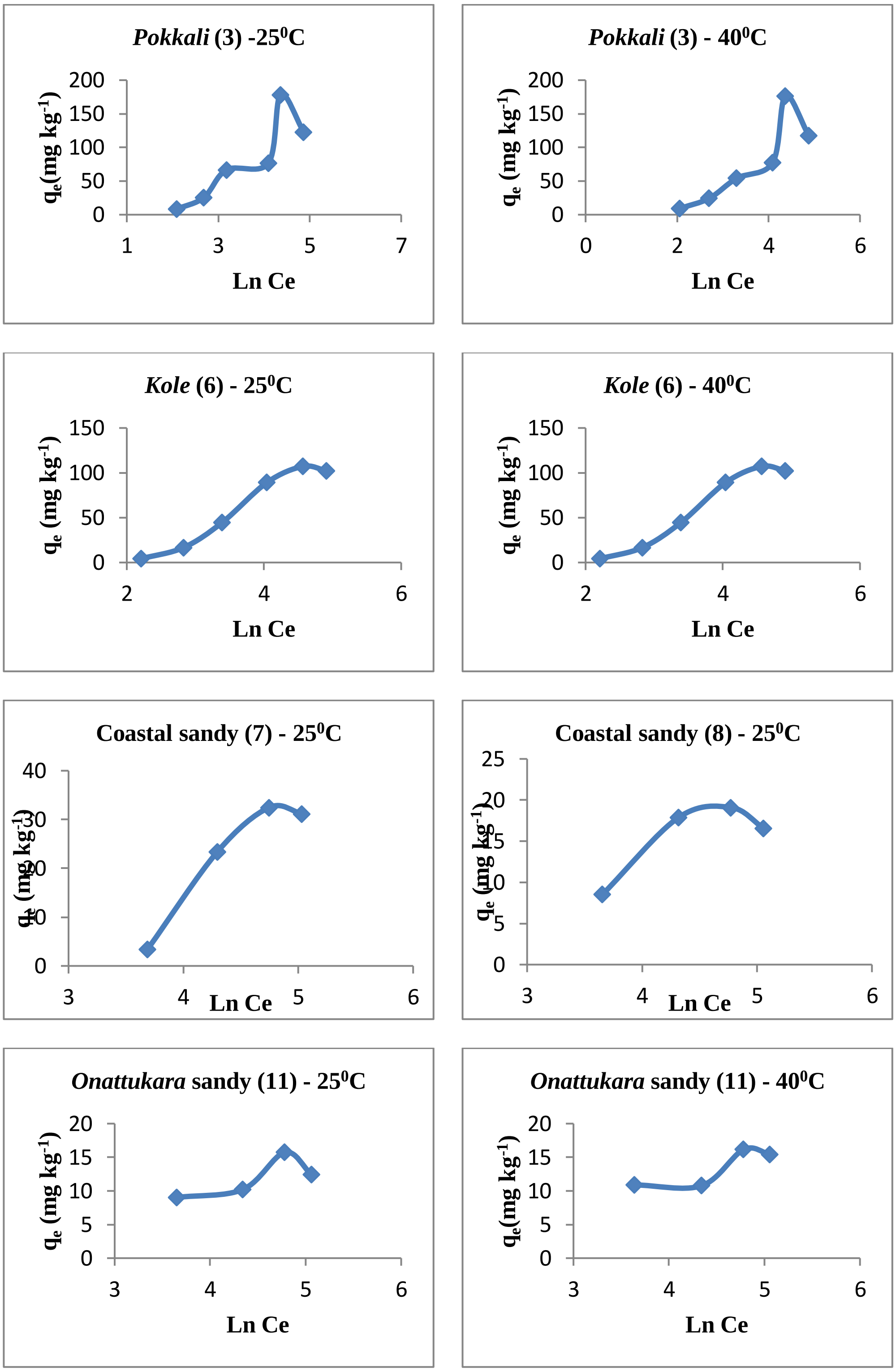


Fig. 29.Tempkin adsorption isotherm for nitrate adsorption at 25^{0}C and 40^{0}C



Pokkali (3) -25^{0}C

Pokkali (3) - 40^{0}C

Kole (6) - 25^{0}C

Kole (6) - 40^{0}C

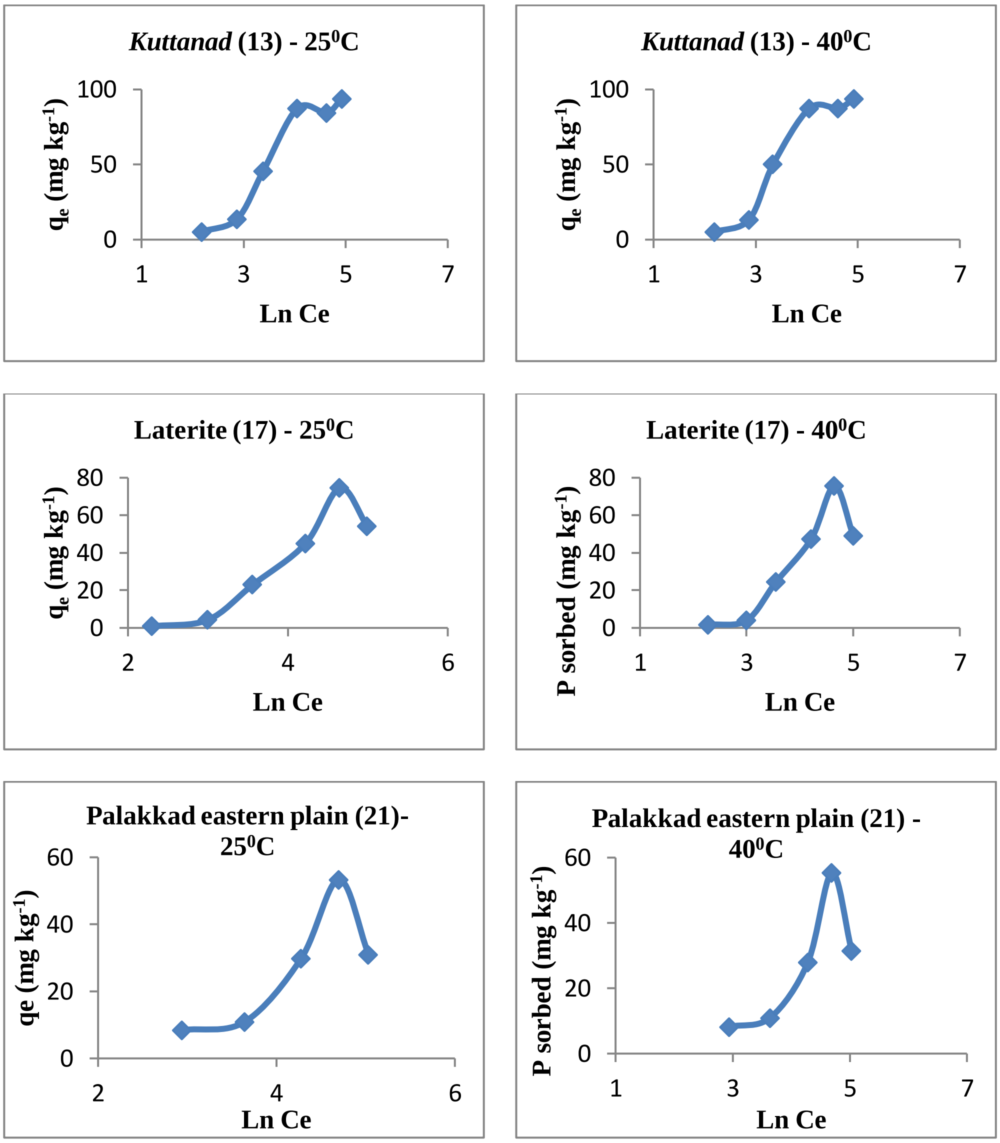
Coastal sandy (7) - 25^{0}C

Coastal sandy (8) - 25^{0}C

Onattukara sandy (11) - 25^{0}C

Onattukara sandy (11) - 40^{0}C

Fig. 29. Continued



The change in free energy of adsorption/desorption (ΔG^0) was negative at both the temperatures indicating the spontaneous nature of adsorption/desorption of nitrate in soil. Negative value of change in enthalpy (ΔH^0) indicates the exothermic reaction. Nitrate adsorption in all the soils collected from *Kole* land is spontaneous and exothermic. A simultaneous decrease in the equilibrium constant (K^0) with increase in temperature was also observed indicating decrease in adsorption with increase in temperature.

Toner *et al.* (1989) revealed that nitrate adsorption in soil is rapid and reversible as a result of van der Waals type interactions or outer-sphere complexation mechanism and they found that adsorbed and desorbed quantity is equal. In the outer sphere complex, the ion retains its hydration sphere and attaches to the surface via electrostatic forces, whereas the inner sphere complex is partially dehydrated and directly bound to the surface. Nitrate adsorption study conducted in the collected soil samples also suggested the weak binding of nitrate in the adsorption sites.

5.3.1.2. Adsorption study of phosphorous

Quantity-intensity relationship

Measurement of phosphate potential (White and Beckett, 1964) is widely used to study the quantity-intensity relation of phosphorous in soil. This method can be used in soils where phosphate adsorption follows Schofields ratio law. This method cannot be used in Kerala soil because of specific adsorption nature of P with kaolinite and oxides and hydroxides of Fe and Al. Concentration of P in equilibrium solution after equilibration period was considered as intensity factor and the amount adsorbed per unit weight of the soil was considered as quantity factor like the way it was used in case of other elements in the present study.

Q-I curve of representative soil samples from each agro-ecological unit is given in figure 30. L-shaped curve was obtained for low land soils of *Pokkali, Kole* and *Kuttanad*. Such adsorption behavior could be explained by the high affinity of the adsorbent for the adsorbate at low concentrations, which then decreases as concentration increases (Sparks, 2003). Q-I curve of all soils except low land soils showed a maximum adsorption beyond which an increase in equilibrium concentration showed a decrease in adsorption. The S shaped adsorption isotherm, where the slope initially increases with adsorbate concentration, but eventually decreases and becomes zero as vacant adsorbent sites are filled.

Highest buffer power and highest value of maximum quantity adsorbed was noted in *Kuttanad* soil. Lower buffer power and lower value of maximum quantity adsorbed was noted in sandy soils of *Onattukara* sandy plain and northern coastal plain and soils from Palakkad eastern plain. High amount of Fe oxides are present in *Kuttanad* soil. Specific adsorption of P occurs in the surface of Fe and Al oxides (Weil and Brady, 2017). The dominance of kaolinite minerals also enhanced phosphate adsorption in soil. Q-I curve of all the soils except coastal sandy soil (Sample No. 9) at 40^0C showed positive intercept values. Positive intercepts of Q-I curves indicate the requirement of a minimum amount of phosphorous at the solid phase below which there will not be any P desorption.

Almost all the low land soils of *Pokkali*, *Kole* and *Kuttanad* showed an increase in maximum quantity adsorbed with increase in temperature is an indication of chemical nature of bonding. Both buffer power and maximum quantity adsorbed was decreased with increase in temperature in all the soils from Palakkad eastern plain where dominance of 2:1 clay minerals are seen. Hence the chance of specific adsorption is less in the soils from Palakkad eastern plain.

Buffer power was significantly and positively correlated with maximum quantity of P adsorbed per unit weight of soil indicating the capacity of those soils to replenish the soil solution on uptake by plants. Buffer power and maximum quantity adsorbed was significantly and positively correlated with clay content, AEC, CBD-Fe and negatively correlated with pH and sand content indicates that pH dependent positive charges in clay minerals and iron oxides are the sites of P adsorption in soil. Silt also showed significant positive correlation with maximum quantity adsorbed which is due to the presence of kaolinite minerals in silt fraction.

High P adsorption of aluminium-peat complex was due to the adsorption of complex Al-phosphate cations by the peat and by the precipitation of amorphous Al-hydroxy-phosphate, likely $AlH_2P0_4(OH)_2$ (Bloom, 1981). That is why buffer power and maximum quantity of adsorbed P showed positive correlation with WS+Ex.Al and OC. Yang *et al.* (2019) reported he maximum adsorption capacity of P with the increase of soil organic matter. Fe-P, org-P and total P showed significant positive correlation with buffer power and maximum quantity adsorbed, whereas Ca-P showed significant negative correlation with maximum quantity adsorbed. It indicates the possible compounds that can be formed by the adsorption process in the collected soils.

Adsorption isotherms and thermodynamics of adsorption

Adsorption of P in all soils were observed with added concentration of P. Freundlich adsorption isotherm was found best to explain P adsorption followed by Tempkin and Langmuir adsorption isotherm.

Freundlich adsorption isotherms of representative soil sample from each agro-ecological unit are given in figure 31. All the soils were recorded with 1/n value less than 1, which indicates the increase in bonding energy with surface density (Salahi and Ghorbani, 2014). It is a measure of adsorption intensity also. High K_F (constant related to strength of adsorption) was recorded in low land soils of *Kole, Kuttanad,* laterite soils followed by *Pokkali* soils were high amount of CBD-Fe was also reported. Sandy soils of *Onattukara* sandy plain and coastal sandy plain showed very low K_F indicating the adsorption capacity and strength of adsorption is low in these soils.

Adsorption of P in one coastal sandy (Sample No. 9) soil and one *Onattukara* sandy soil were not fitted into Langmuir adsorption isotherm. Langmuir adsorption isotherms of representative soil samples from each agro-ecological unit are given in figure 32. Very high value of adsorption maxima (q_m) was recorded in *Pokkali* and *Kuttanad* soils followed by soil from *Kole* land. Adsorption maxima was recorded low in sandy soils of northern coastal plain and *Onattukara* sandy plain. The trend of q_m was same as that of AEC. K_L indicates the binding energy or strength of binding. Comparatively high K_L was recorded in soils from *Kole* land and *Kuttanad* where CBD-extractable Fe content was also high.

P adsorption in all the soils at both temperatures was fitted into Tempkin adsorption isotherm. Tempkin adsorption isotherms of representative soil samples from each agro-ecological unit are given in Figure 33. High values of constant related to bonding strength (K_T) were recorded in soils of *Kole* land, *Kuttanad* and laterite soils which is an indication of strength of binding. Fifteen samples showed an increase in K_T with increase in temperature which is indication of chemical nature of bonding.

Correlation study of parameters of different adsorption isotherm with soil properties reveals the important points regarding P adsorption. The isotherm constants related to strength of binding in all the three isotherms ($K_{F,}$ K_L and K_T) showed significant positive correlation with clay content, silt content and CBD extractable Fe content and negatively correlated with sand content at least at one of the two temperatures. Hence it is clear that Fe oxides, kaolinite mineral present in clay and silt fractions are the major sites of P adsorption where it was adsorbed with high binding energy.

Among the different fractions of P, Freundlich adsorption isotherm constant related to strength of bonding (K_F) showed significant positive correlation with Fe-P, RS-P, org-P, total-P and negative correlation with SB-P and Ca-P. K_L(bonding energy constant of Langmuir isotherm) and K_T (constant related to strength of bonding in Tempkin isotherm) also showed significant positive correlation with Org-P and negative correlation with SB-P. Saloid-bound (SB) P is soluble and loosely bound P, and hence it showed negative correlation with the constants related to binding energy, whereas the Fe-P, RS-P, org-P are not easily available. It is strongly bonded. Negative correlation of pH with constants of Freundlich isotherm (1/n, K_F) and adsorption maxima of Langmuir isotherm (q_m) indicates that, adsorption of P and binding strength decreases with increase in pH due to the reduction in pH dependent positive charges. AEC was significantly and positively correlated with 1/n, $K_{F,}$ $q_{m,}$ which indicated that the presence of pH dependent positive sites in soil are important for maximum quantity that can be adsorbed.

Fig.30. Quantity-intensity curve for P adsorption at 25 ^{0}C and 40 ^{0}C

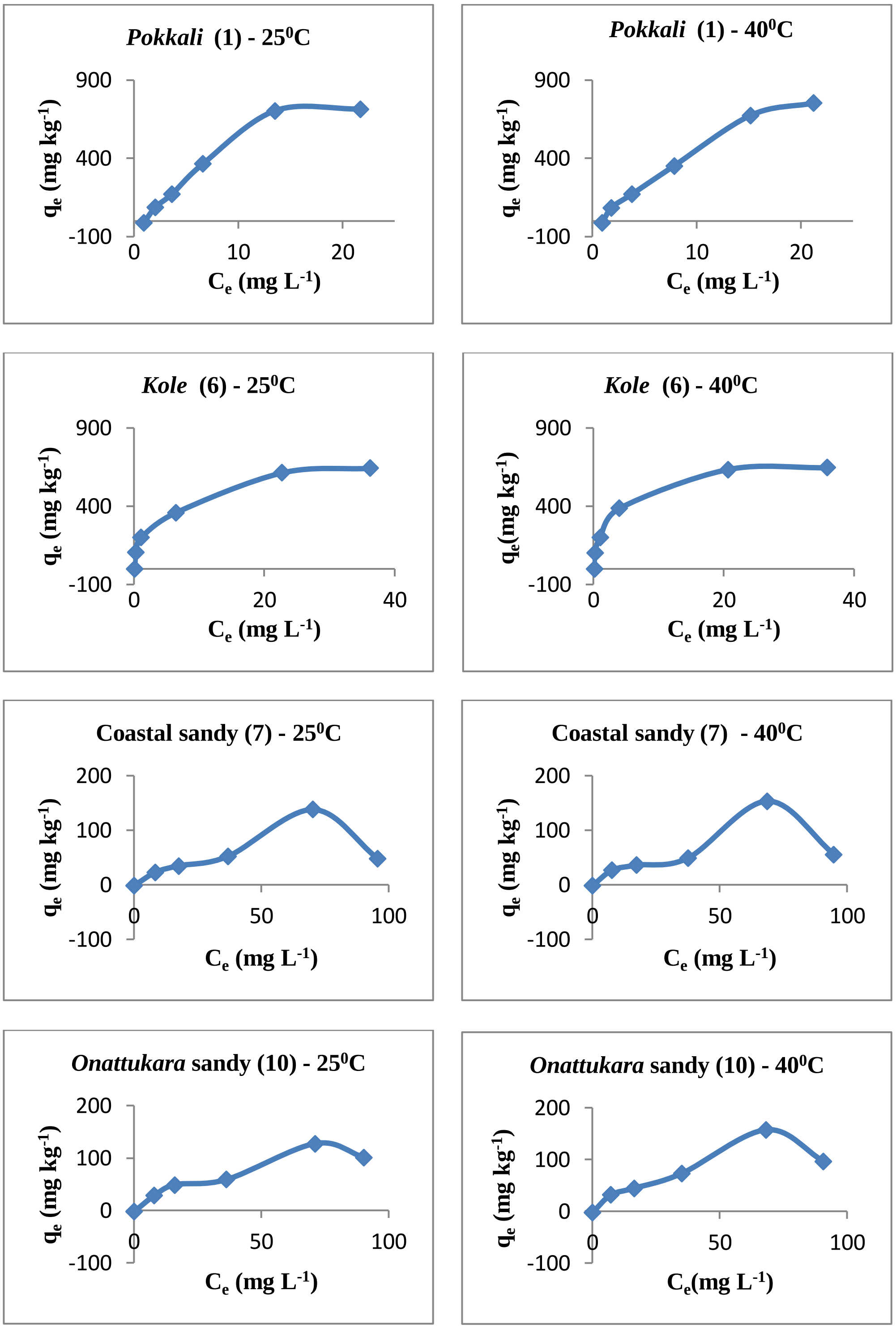


Fig.30. Continued

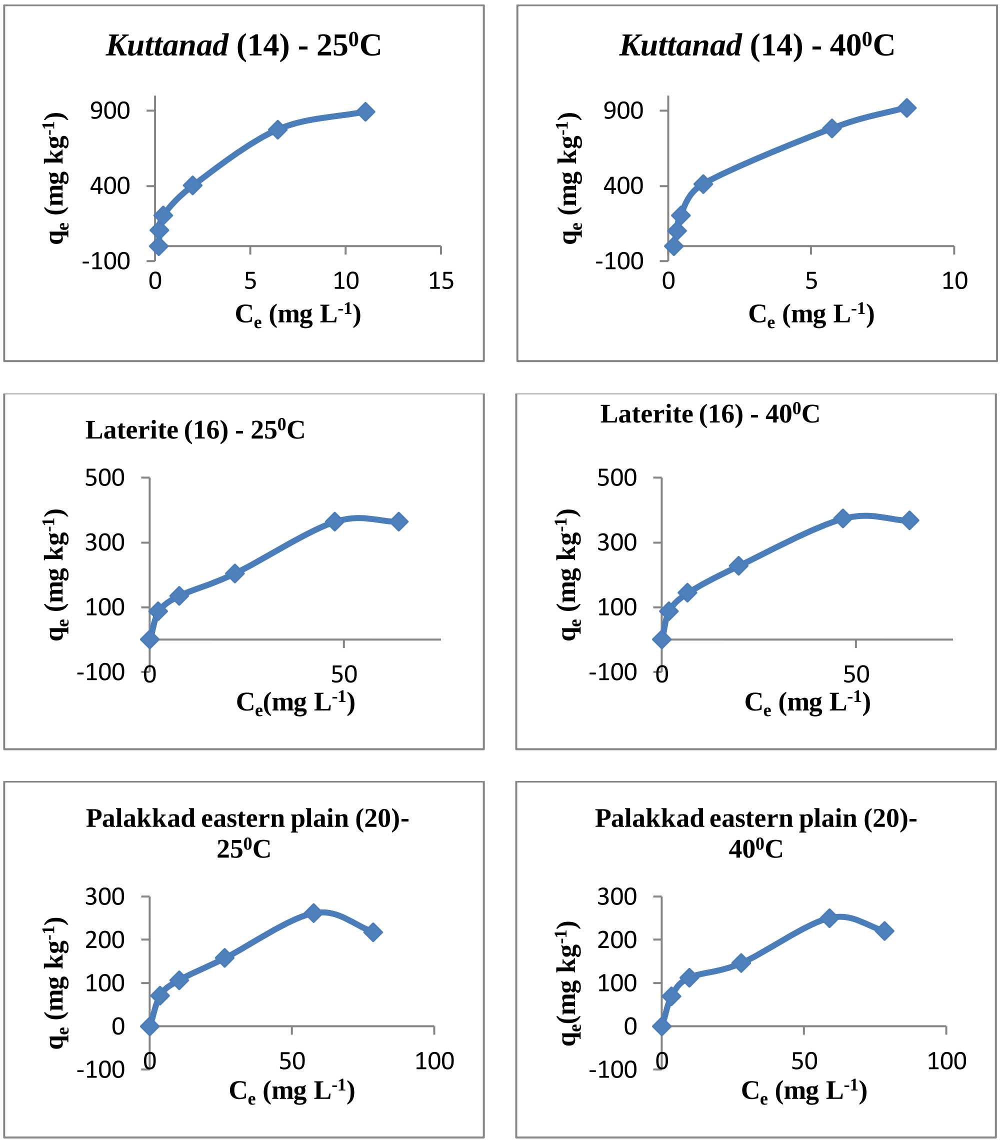


Fig.31. Freundlich adsorption isotherm for P adsorption at 25 ^{0}C and 40 ^{0}C

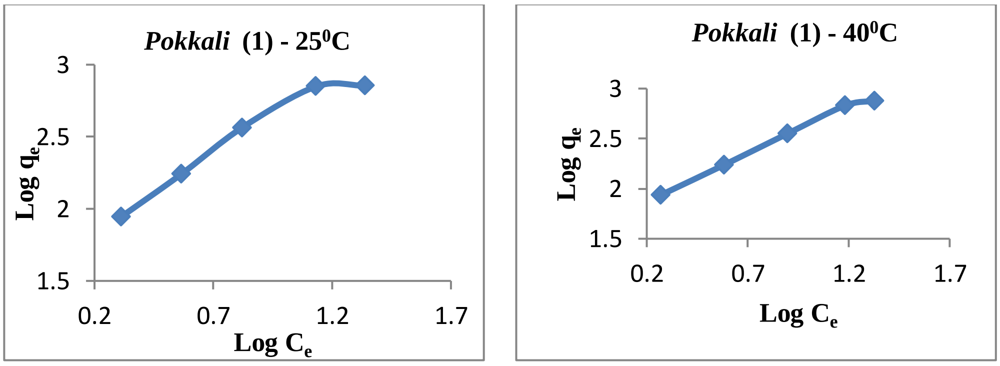


Fig.31. Continued

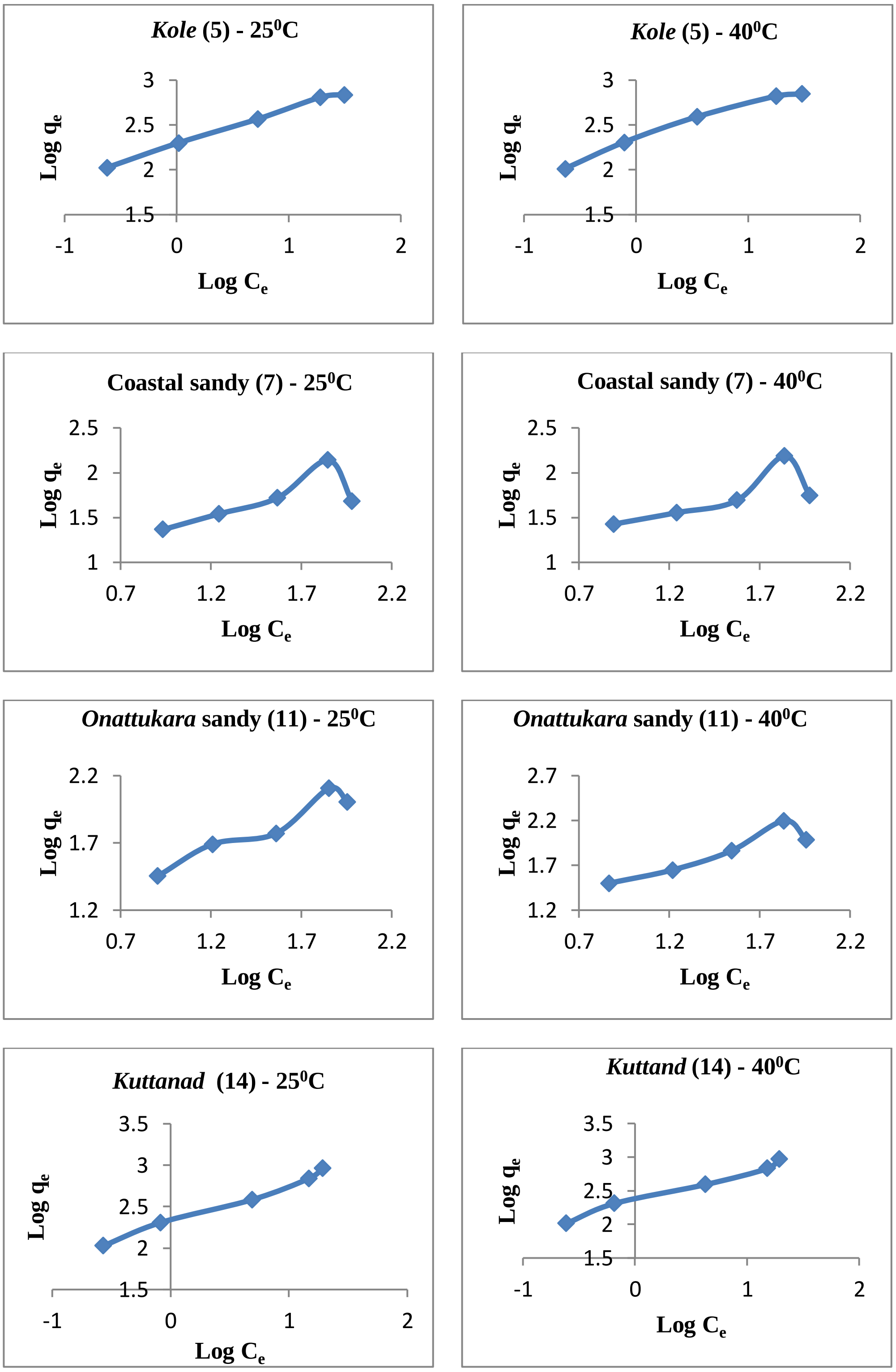


Fig.31. Continued

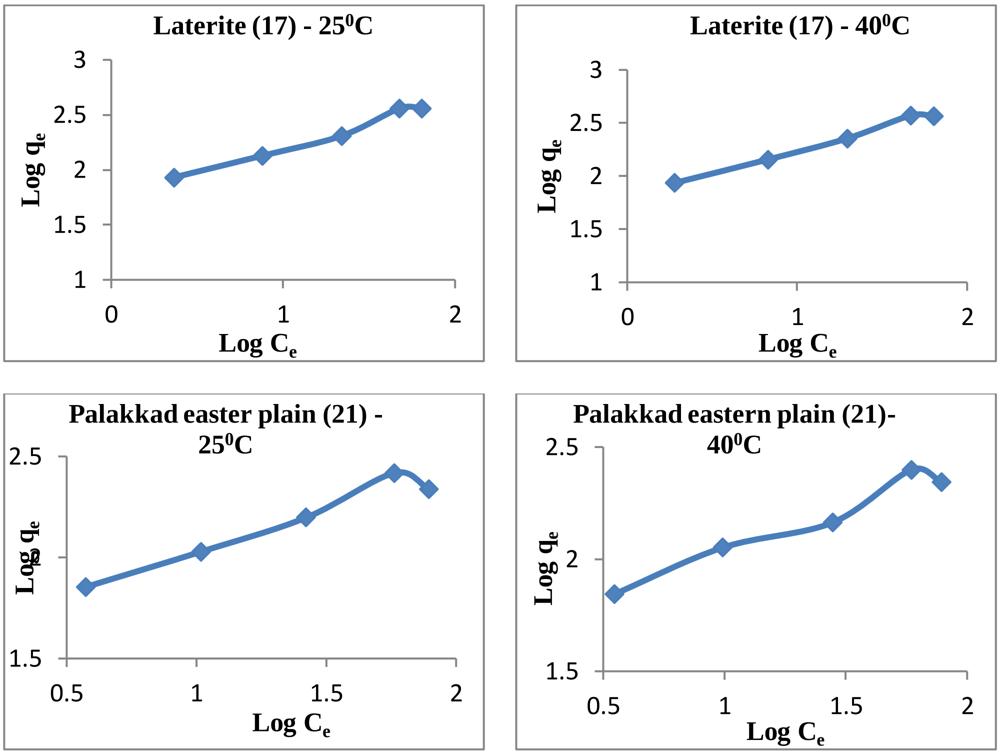


Fig.32. Langmuir adsorption isotherm for P adsorption at 25 ⁰C and 40 ⁰C

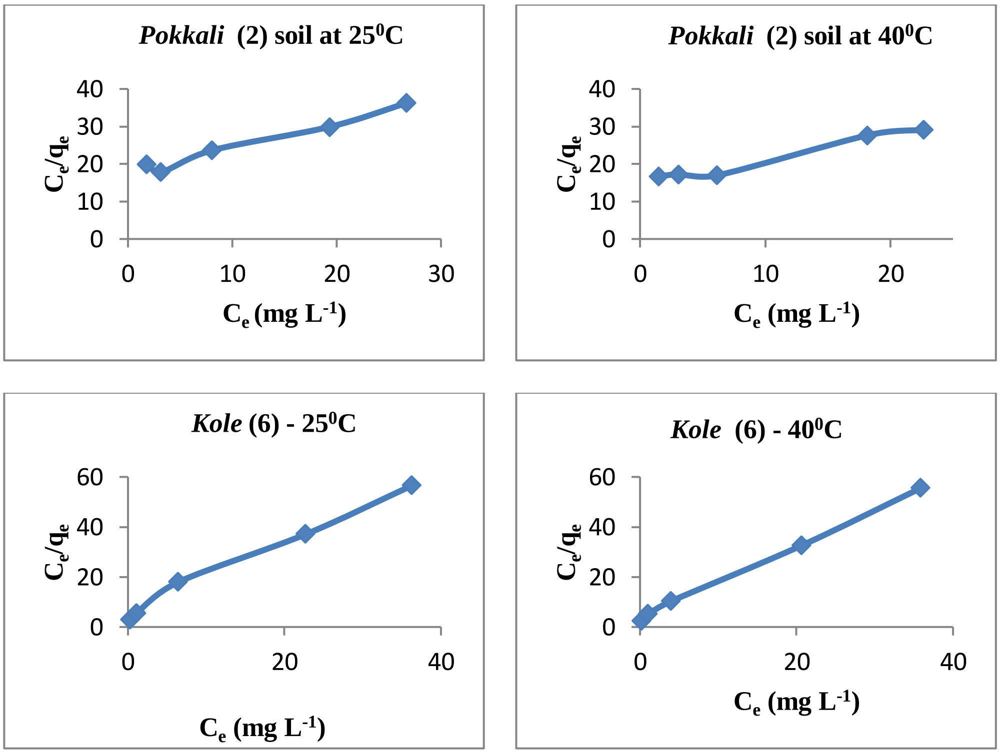
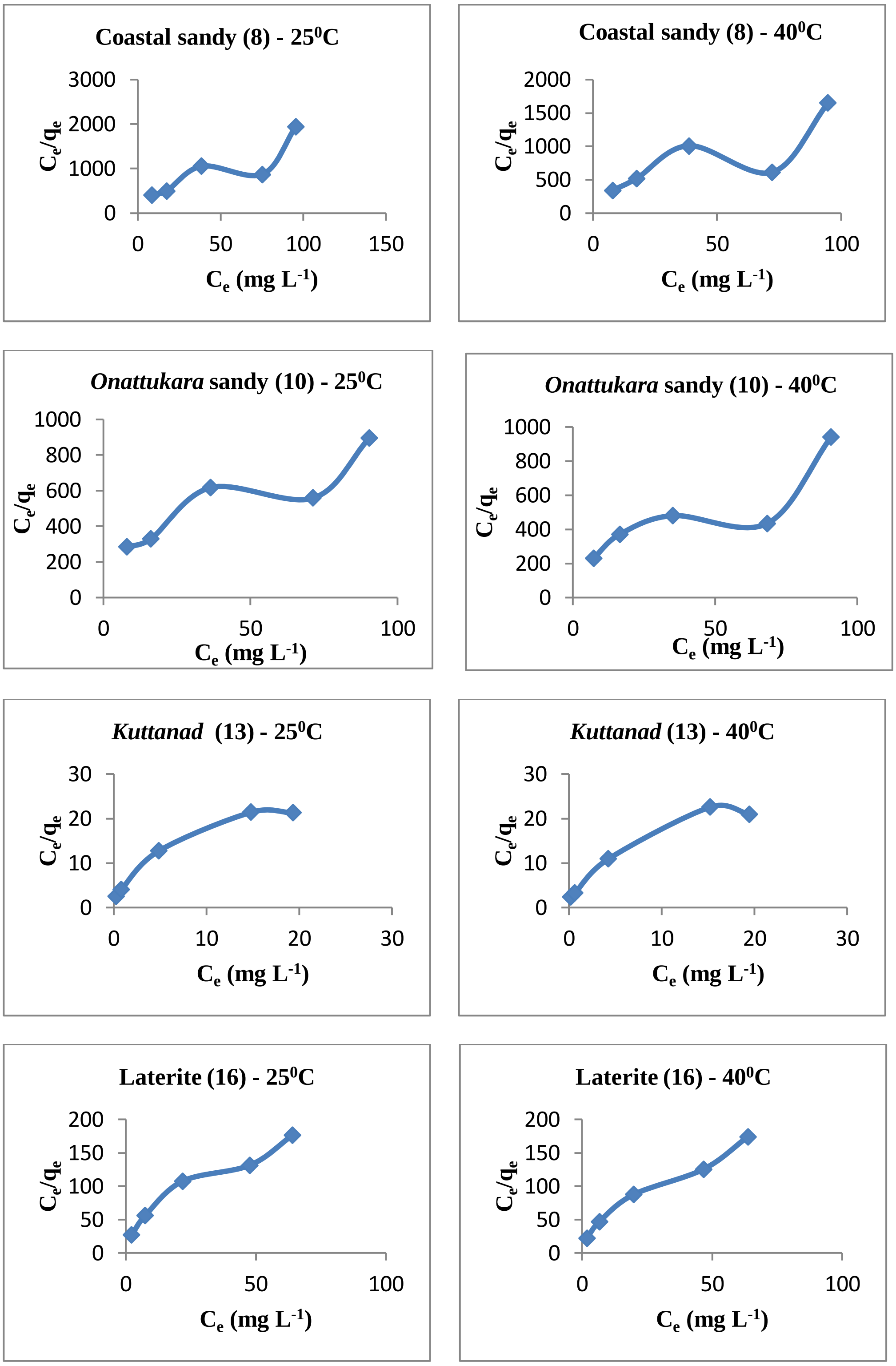


Fig.32. Continued



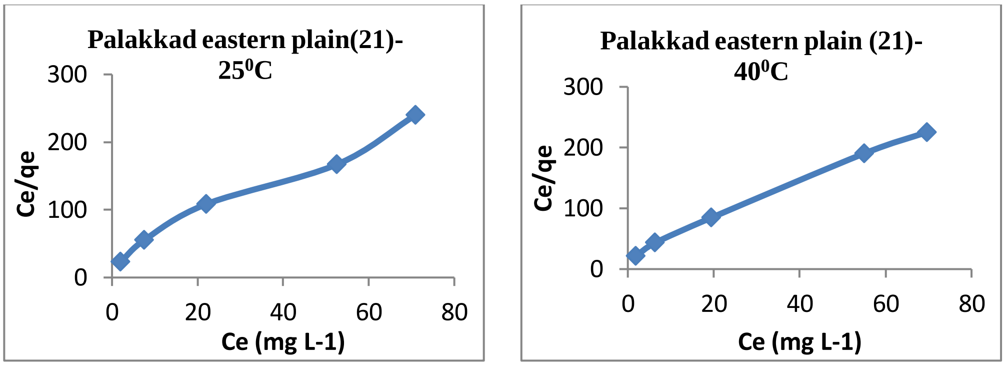


Fig.33. Tempkin adsorption isotherm for P adsorption at 25 ^{0}C and 40 ^{0}C

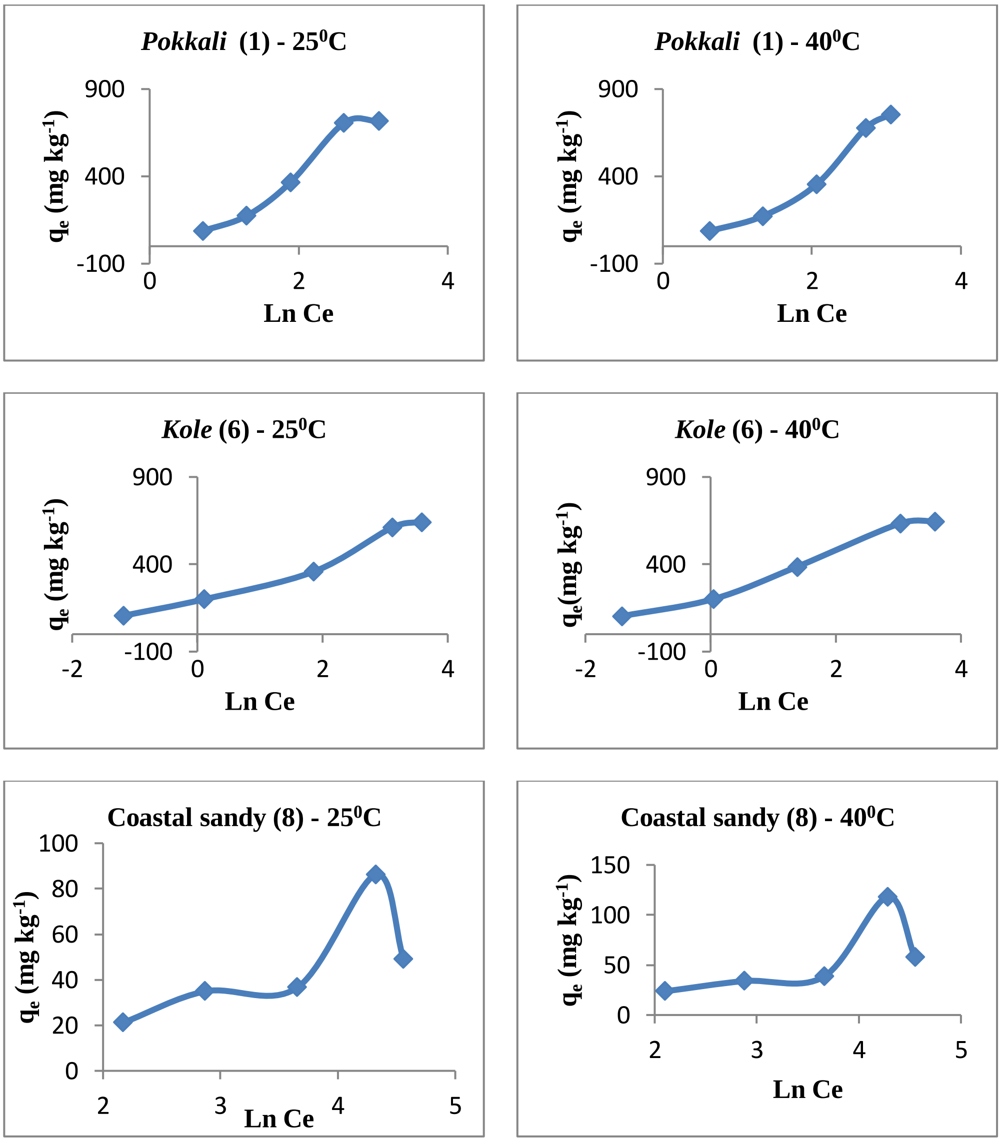
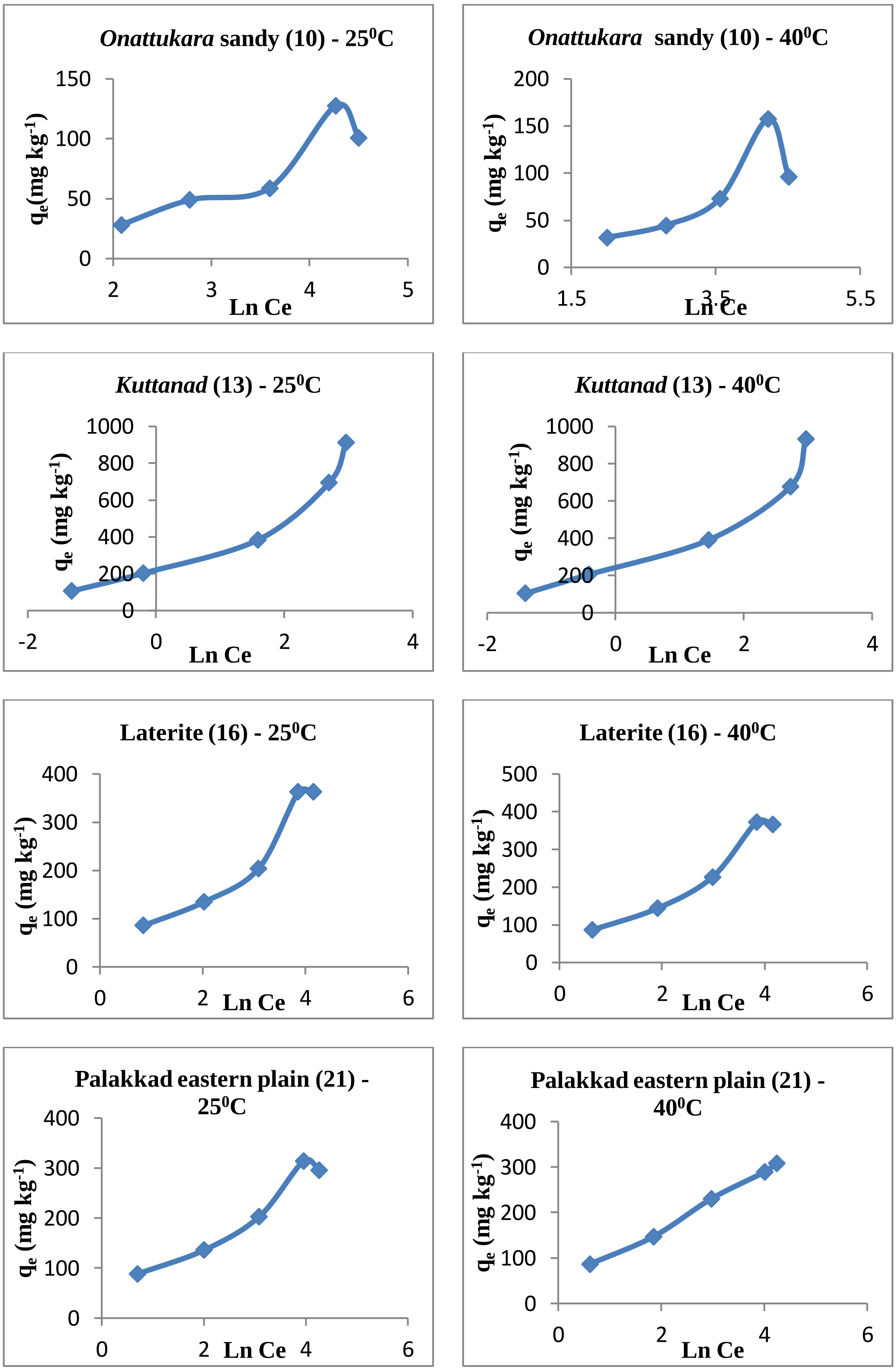


Fig.33. Continued



Increase in thermodynamic equilibrium constant with increase in temperature was observed in all soils. Change in free energy (ΔG^0) was negative and change in entropy (ΔS^0) was positive for P adsorption in all soil indicating the spontaneous nature of P adsorption. Change in enthalpy was positive in most of the soils which means adsoption was endothermic in nature. Wang *et al*. (2017) also reported the spontaneous nature of P adsorption in soil.

P adsorption was found very high in low land soils of *Kole, Kuttanad* and *Pokkali.* In laterite soils, even though the maximum quantity adsorbed is not as higher as low land soils, constants related to binding strength was found high, especially greater than *Pokkali* soil. At higher temperature P adsorption was increased indicating that P is strongly held on the surface (Mehadi and Taylor, 1988). The content of amorphous and free iron in soil showed significant positive correlation with isotherm constants of Freundlich, Langmuir, Tempkin and Van Huay adsorption isotherms (Tamungang *et al.,* 2016) which are in accordance with the results of present study. Inner-sphere surface complex formation of P with goethite (Persson *et al.,* 1996), ferrihydrite (Arai and Sparks, 2001), oxides and hydroxide of Fe and Al (Weil and Brady, 2017) were already reported. Specific adsorption is the reason for high adsorption of P in tropical soils of Kerala.

5.3.1.3. Adsorption study of sulphur

Quantity-intensity relationship

All the collected samples except laterite soil (Sample No. 17) at 40 ^{0}C showed dominance of desorption at both temperatures. Q-I curves of representative soil samples from each agro-ecological unit are given in figure 34. *Pokkali* soil remains an exception because it contain very high amount of sulphate S due to the uncontrolled entry of sea water into the field. Even available S was reported >5000 mg kg^{-1}. Adsorption of added S was not practically possible in case of *Pokkali* soil at both temperatures. Hence high values of maximum quantity desorbed and negative buffer power was recorded in all the soils of *Pokkali* at both the temperatures. Q-I curves clearly tell that adsorption is possible in all other soils, but in the concentration of added sulphate dominance of desorption was observed. Further addition of higher concentration may lead to adsorption of S. Gokila *et al.*, (2017) observed adsorption of S at very high concentration range (100 -1600 mg kg^{-1}) of added S.

Positive buffer power was observed in all the soils from *Kole, Kuttanad,* northern coastal plain and *Onattukara* sandy plain at both temperatures and laterite and Palakkad eastern plain at 40^{0}C. Negative buffer power was observed in laterite and Palakkad eastern plain at 25^{0}C. Most of the soils showed an increase in buffer power with increase in temperature. Quantity factor is increased with increase in temperature. Formation of both outer-sphere complexes and inner-sphere mono-dentate complexes with S were reported (Wijnja and Schulthess, 2000). In most of the soils desorption was found decreasing with increase in temperature indicating the possibility of inner-sphere complexes.

Increase in buffer power with temperature indicates the ability of soil to adsorb element and contribute to the quantity factor. Hence maximum quantity desorbed showed significant negative correlation with buffer power at 25^{0}C. All the sulphur fractions were negatively correlated with buffer power and positively correlated with maximum quantity desorbed at both temperatures indicating the source of desorption of S in soil are different fractions of S in soil; especially the solubilisation of organic S. Organic S is the major contributor to the total S.

Fig.34. Quantity-intensity curve for S adsorption at 25 ^{0}C and 40 ^{0}C

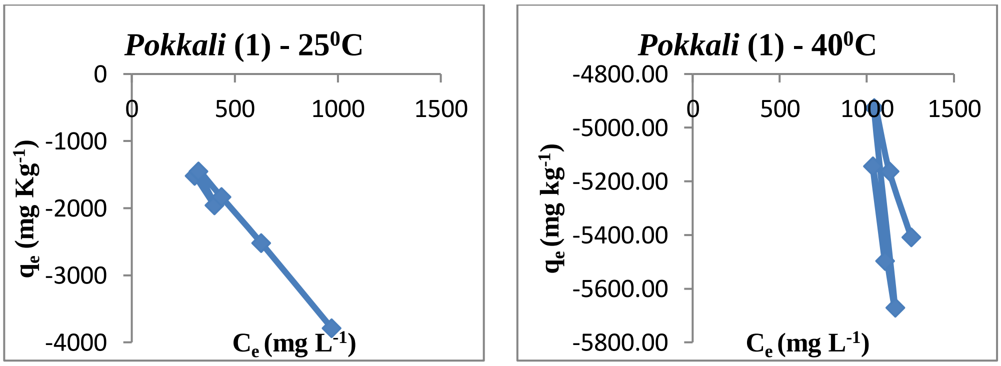


Fig.34. Continued

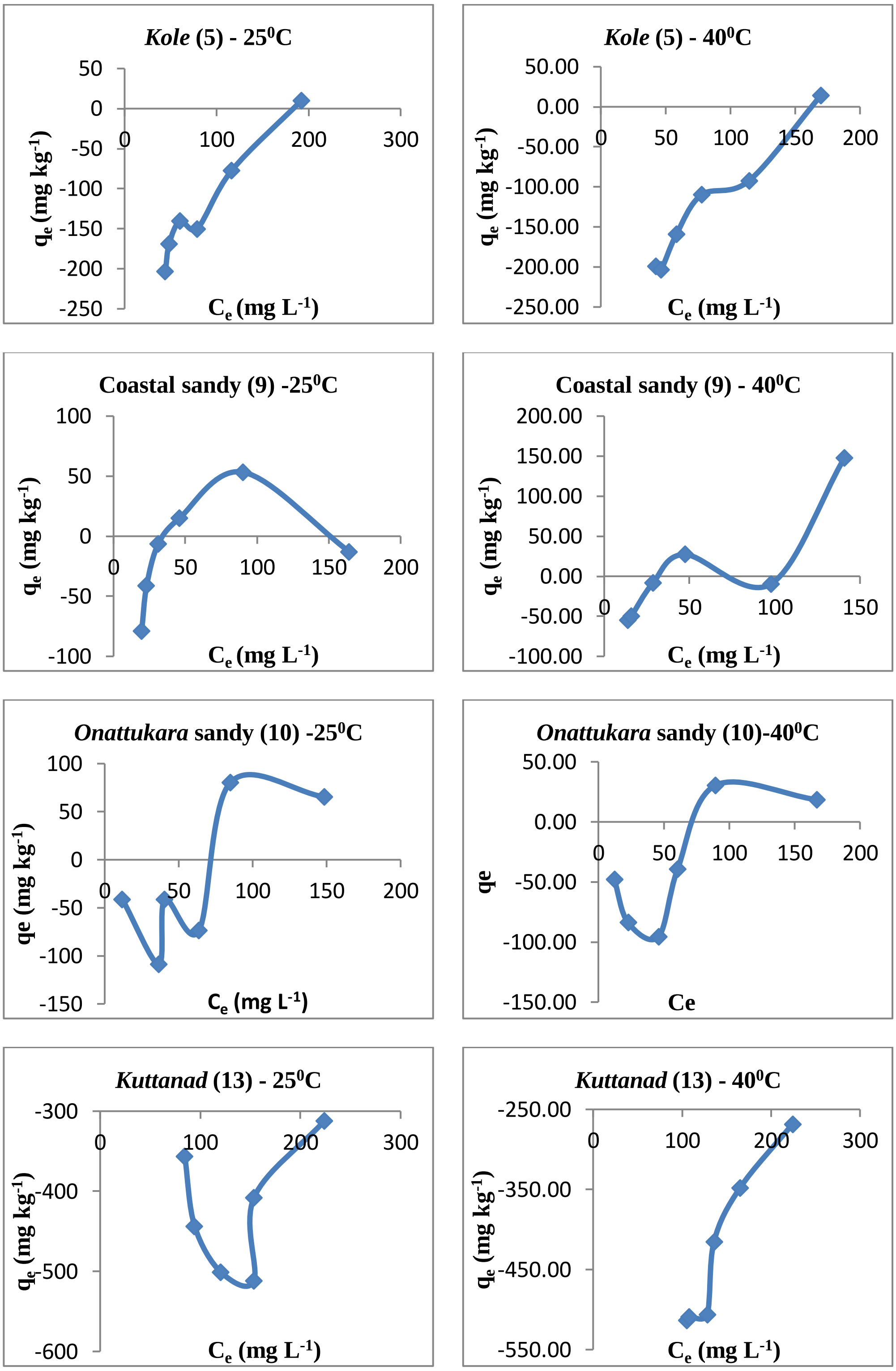


Fig.34. Continued

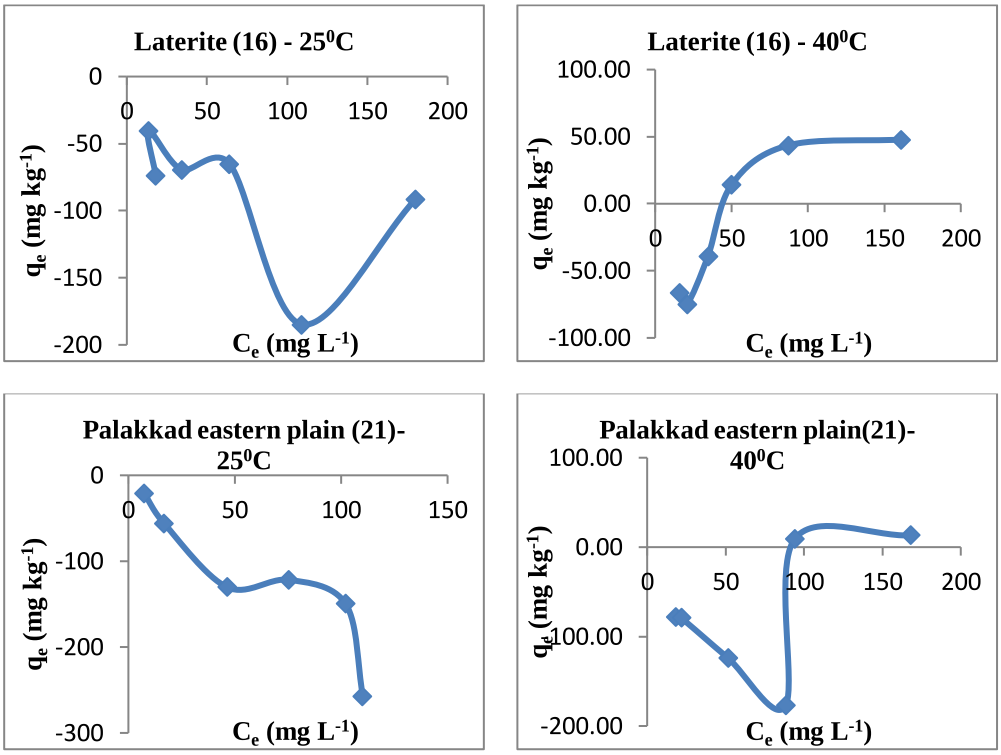


Fig. 35. Freundlich adsorption isotherm for S adsorption in laterite soil (17) at 40 ^{0}C

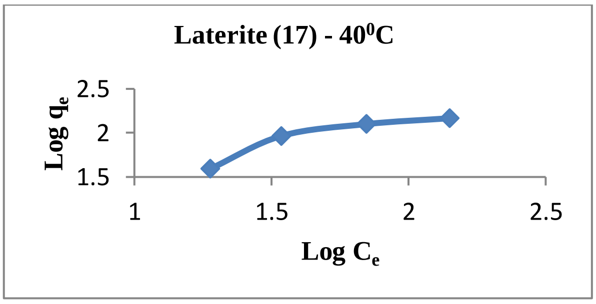


Fig. 36. Langmuir adsorption isotherm for S adsorption in laterite soil (17) at 40 ^{0}C

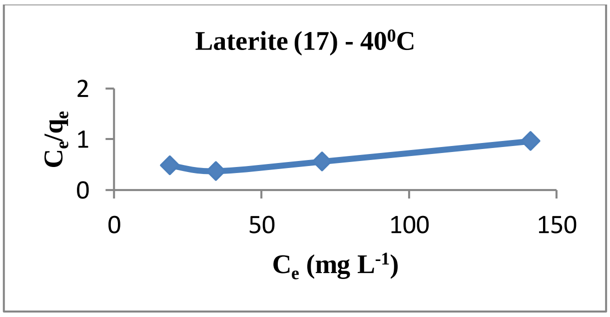
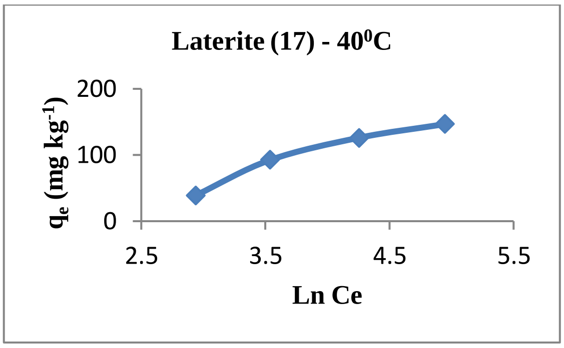


Fig. 37. Tempkin adsorption isotherm for S adsorption in laterite soil (17) at 40^0C



Adsorption isotherms and thermodynamics of adsorption/desorption

Soils with minimum four points with positive slopes in Q-I curves were tried to fit into different adsorption isotherms. So only laterite soil (Sample No. 17) at 40 ^{0}C was fitted into different adsorption isotherms (figure.35, 36 and 37). R^2 value of all the three adsorption isotherm was >0.8.

Whether it is adsorption or desorption, the process is spontaneous in nature. Change in enthalpy was reported negative for all soils indicating exothermic nature of S desorption. Thermodynamic equilibrium constant of desorption of S in *Pokkali* soils was found increased with increase in temperature. The reaction is exothermic in eleven soils and endothermic in remaining soils. Change in entropy was reported positive in most of the soils.

5.3.1.4. Adsorption study of B

Quantity-intensity relationship

Q-I curve of B adsorption in representative soil samples are given in figure 38. Complete desorption was observed in coastal sandy soil (Sample No. 9) at 40^0C. Highest buffer power was noted in soil from *Kole* land indicating that these soils have got a greater power to retain boron on solid phase and replenish its level in solution as and when it is depleted by the plant uptake or leaching losses.

This is in accordance with findings of Santhosh (2013). The lowest buffer power was observed in sandy soils due to the coarse texured nature and low AEC. Negative buffer power value of coastal sandy soil at 40^0C indicates practically no capacity for the soil to replenish the solution B. Positive intercepts of Q-I curves indicate the requirement of a minimum amount of boron at the solid phase below which there will not be any desorption. Most of the soils showed negative intercept. This much amount of B will be the labile pool and when this level of labile pool exceeds a particular value, only then soil matrix starts absorbing B. Decrease in buffer power with increase in temperature was observed in all the soils from *Kuttanad,* became more negative indicating desorption from the solid phase below equilibrium concentration indicating practically no retension. The highest value of maximum quantity adsorbed was recorded in *Kole* land and the lowest was recorded in sandy soils. A decrease in maximum quantity adsorbed with increase in temperature was observed in seventeen soil samples. It is due to the physical nature of adsorption.

Boric acid is a very weak acid with a pKa value of 9.2. At a lower pH than 7, boron is present in its non-dissociated form (boric acid) and at a pH greater than 10.5, it is present in the dissociated borate form. The exact percentage of boric acid and borate in any aqueous system is basically dependent on pH. The borate monovalent anion dominates at higher pH while non-ionized boric acid $B(OH)_3$ is prevalent at lower pH. pH of the equilibrium solution ranged from 2.81 to 6.5 in all the soils except soils from Palakkad eastern plain. So the existence of borate anion was very less which lead to low adsorption of B in those soils. Between pH 6 and 11 and at high concentration, polyborate ions such as $B_5O_6(OH)_4^{-4}$ and $B_3O_3(OH)_4^-$ are formed. At high boron concentration, the formation of tetra borates and pentaborates can appear (Kabay and Bryjak, 2015). This polymerization reaction can be wrongly interpreted as adsorption. That is why soils of Palakkad eastern plain were recorded with high maximum quantity adsorbed. The pH of equilibrium solutions of Palakkad eastern plain ranged from 6.1 to 8.58.

Buffer power at 25^0C and 40^0C showed significant positive correlation with maximum quantity adsorbed at their respective temperature shows that soils with more buffer power can adsorb more B per unit weight of soil. All the fractions of B showed positive correlation with buffer power or maximum quantity adsorbed. Significant positive correlation of buffer power and maximum quantity adsorbed with AEC, CBD-Fe, Ex.Fe, WS+Ex. Al indicates the possibility of B adsorption in different sites. Maximum quantity adsorbed at 40^0C showed significant positive correlation with clay content. The primary B adsorbing surfaces in soils are: aluminum and iron oxides, clay minerals, calcium carbonate, and organic matter (Goldberg, 1997).

Adsorption isotherms and Thermodynamics of adsorption/desorption

Dominance of desorption was observed in all the samples from *Onattukara* sandy plain (Sample No. 10, 11 and 12), coastal sandy plain (Sample No. 7 and 8), two samples from *Pokkali* (Sample No. 2 and 3), one sample from Palakkad eastern plain (Sample No. 22) at 40^0C and Sample No. 9 at both 25^0C and 40^0C. Hence adsorption data of these soils were not used for isotherm fitting. Freundlich adsorption was best to explain adsorption of B in soil followed by Tempkin adsorption isotherm. None of the adsorption data fitted into Langmuir adsorption isotherm. Freundlich and Tempkin adsorption isotherms of representative soil samples are given in figure 39 and 40 respectively. Particular trend was not found in the parameters of Freundlich and Tempkin isotherms and the parameters didn’t show correlation with soil properties. This may be due to the effect of non-ionised boric acid in low pH equilibrium solutions and polymeric borate formation in high pH equilibrium solution (soils of Palakkad eastern plain).

Adsorption and desorption of B in soil showed negative value for change in free energy indicating the spontaneous nature of reaction. Adsorption of B in *Kole* land was endothermic where change in enthalpy was positive. For all other soil the adsorption process was exothermic.

Fig. 38. Quantity-intensity curve of B adsorption at 25 ^{0}C and 40 ^{0}C

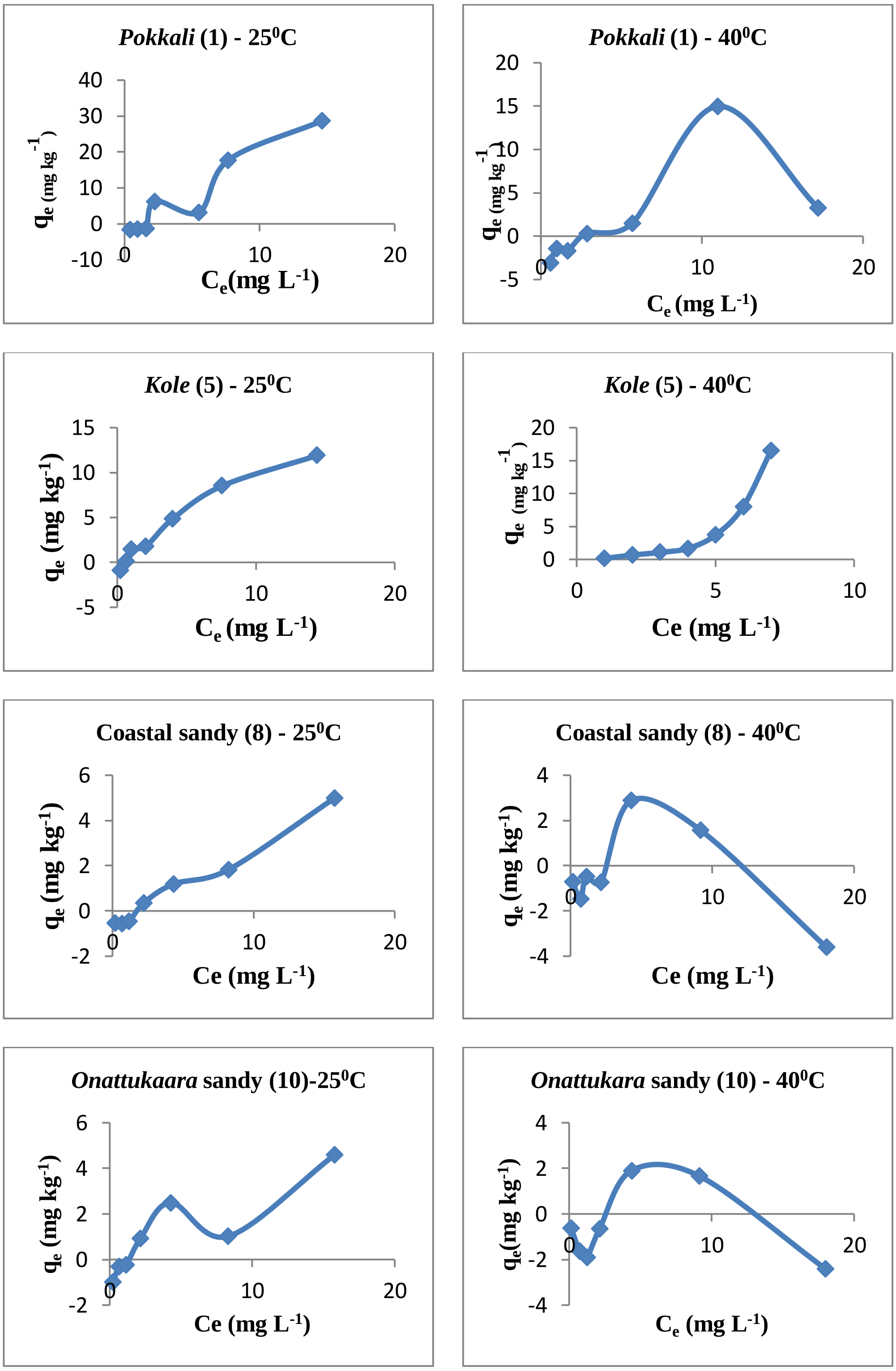


Fig. 38. Continued

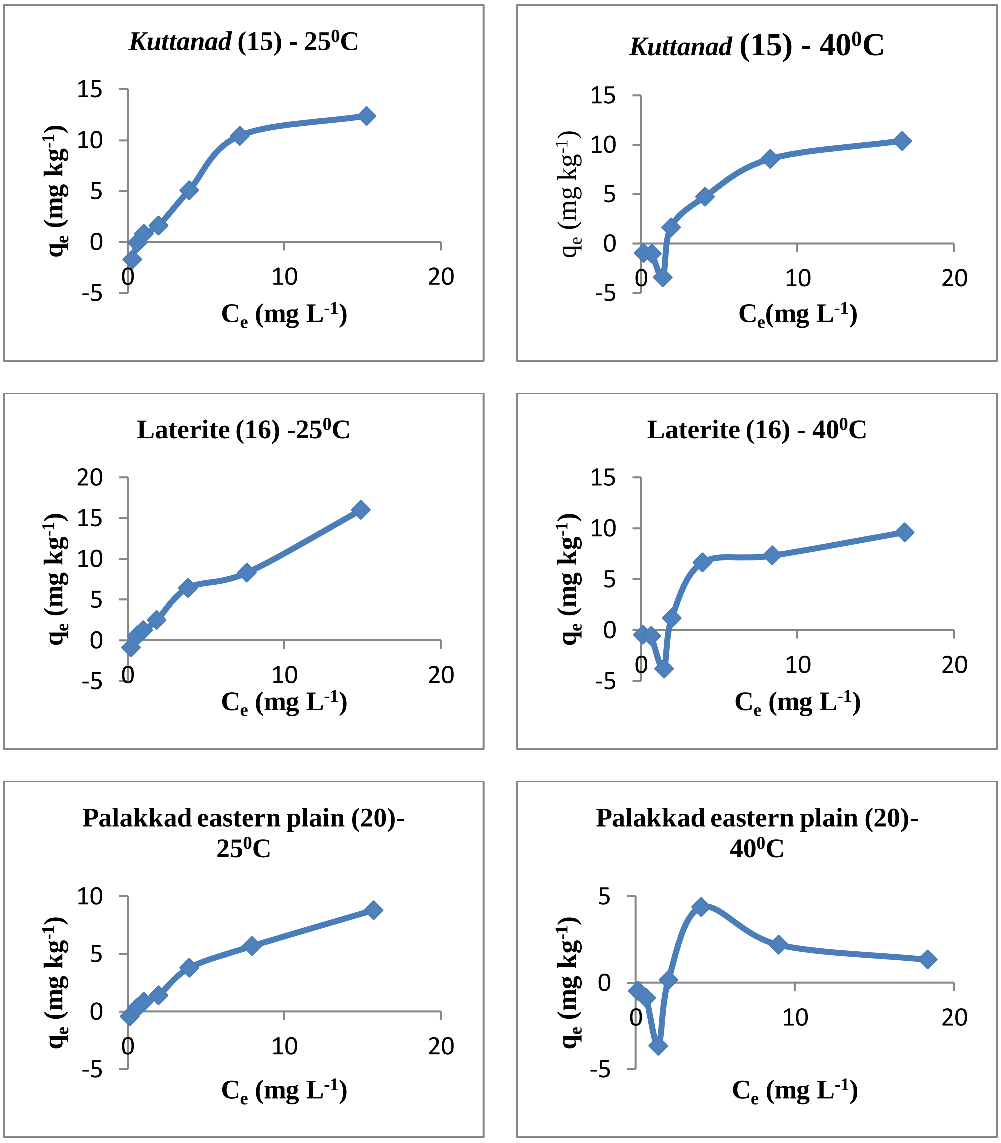


Fig. 39. Freundlich adsorption isotherm for B adsorption at 25 ⁰C and 40 ⁰C

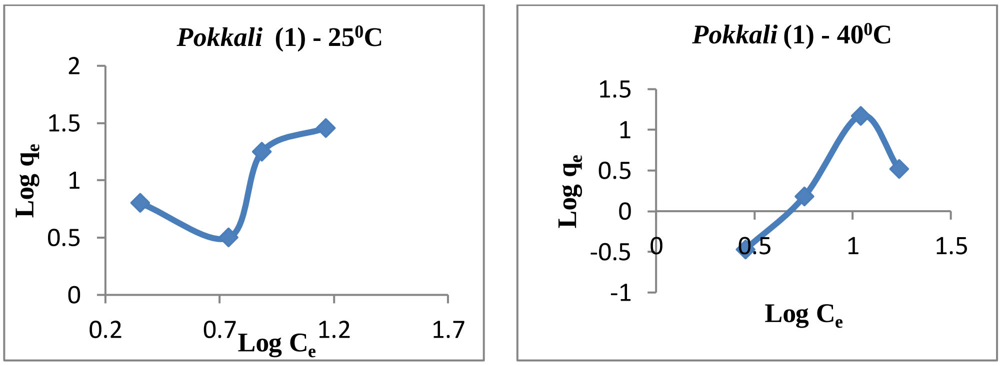


Fig. 39. Continued

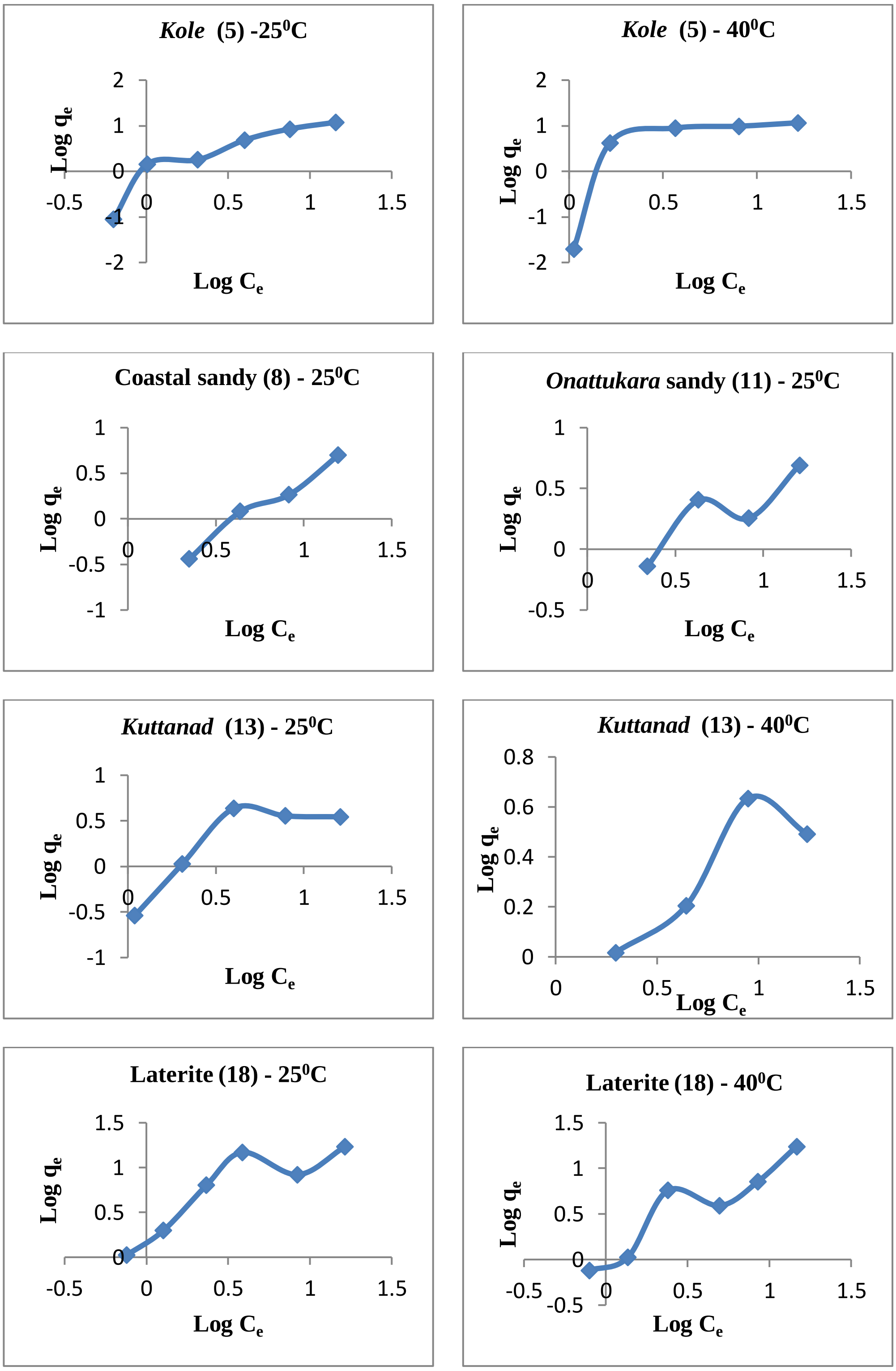


Fig. 39. Continued

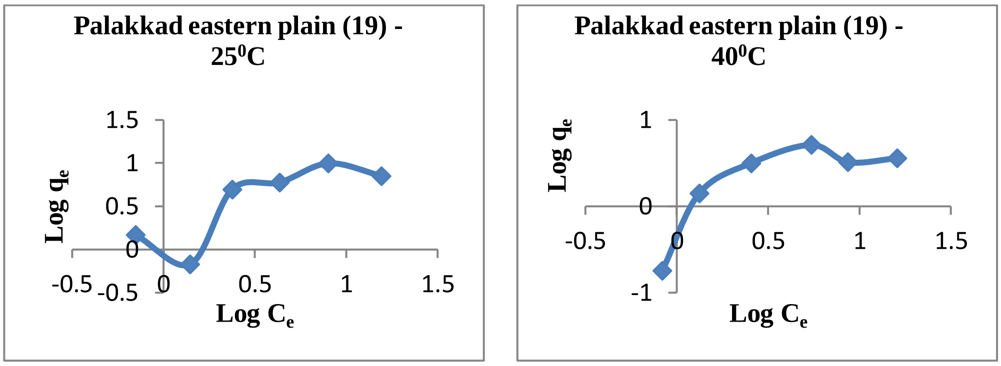


Fig. 40. Tempkin adsorption isotherm for B adsorption at 25^{0}C and 40^{0}C

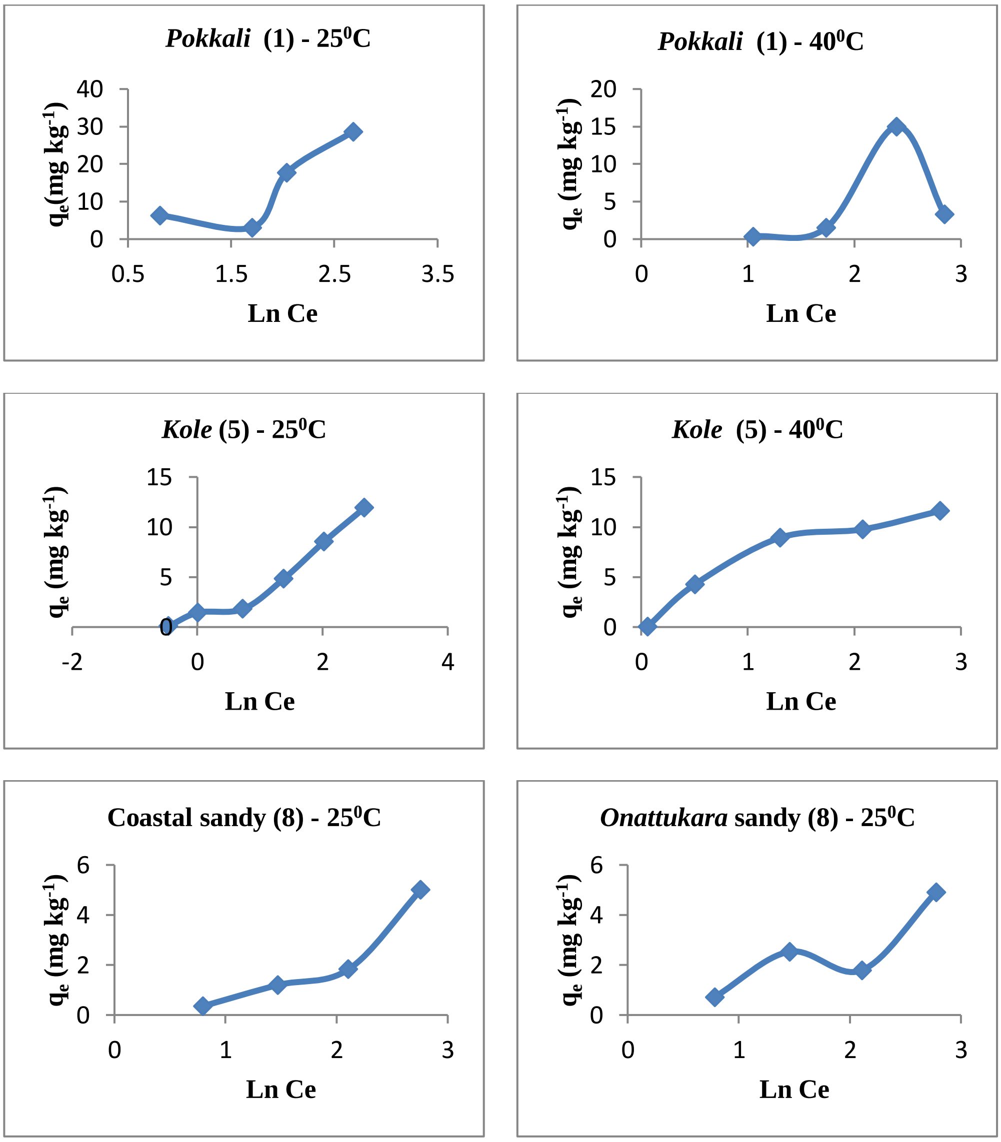
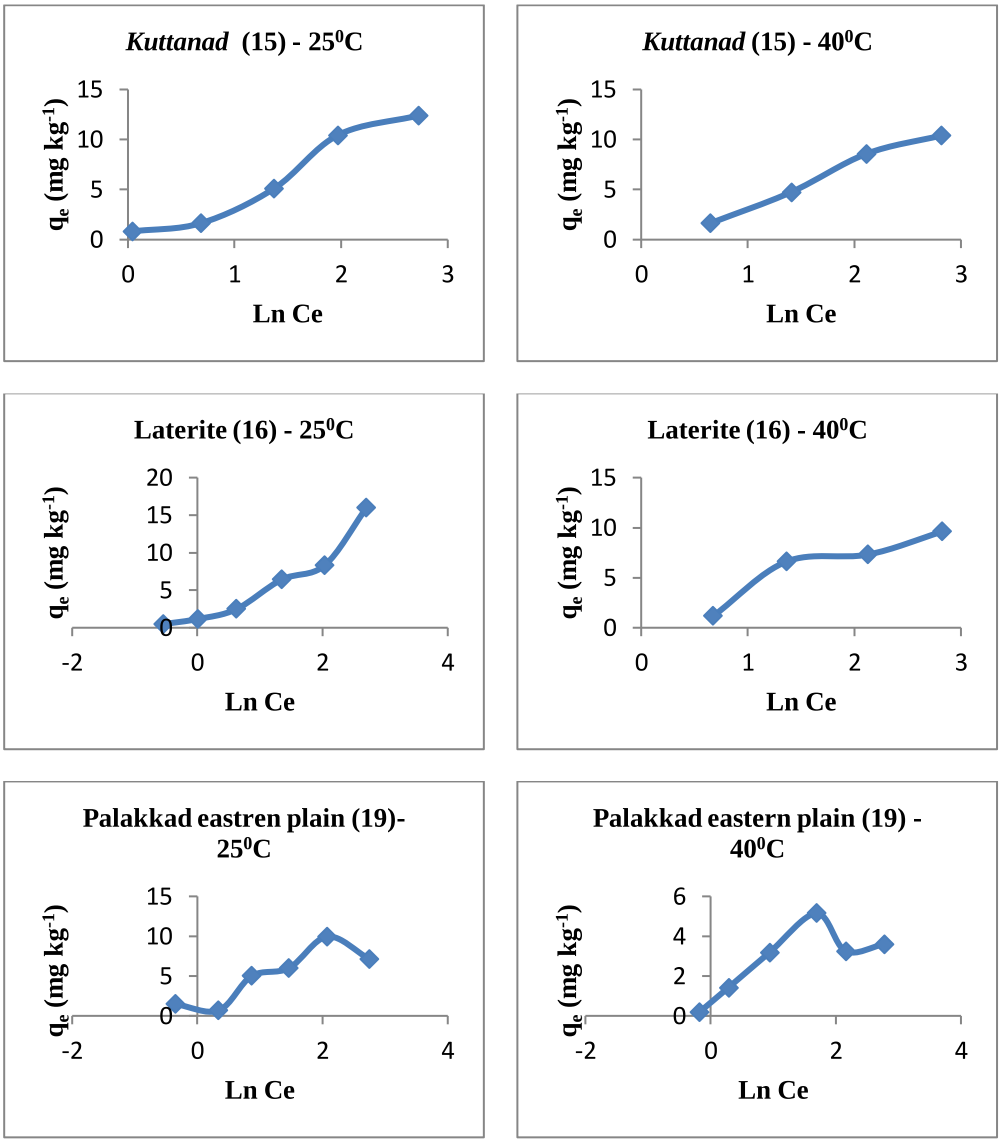


Fig. 40. Continued



5.3.1.2. Adsorption study of molybdenum

Quantity-intensity relationship

Q-I curve of Mo adsorption in representative soil samples from each agro ecological unit is given in figure 41. L-shaped curve was obtained for low land soils of *Pokkali*, *Kole* and *Kuttanad* due to the high affinity of the adsorbent for the adsorbate at low concentrations, which then decreases as concentration increases (Sparks, 2003). In these soils a decrease in adsorption after reaching a maximum was not found. Q-I curves of Mo adsorption was similar to Q-I curve of P adsorption.

Maximum quantity adsorbed with added concentration of Mo was very high in low land soils of *Pokkali, Kole* and *Kuttanad* soil. Mo adsorption was found very high in low pH values (Goldberg *et al.,* 2008). Lower values were recorded in sandy soils of northern coastal plain and *Onattukara* sandy plain due to the sandy nature and less AEC of those soils. Most of the soils exhibited an increase in maximum quantity adsorbed with increase in temperature indicating that the nature of adsorption is not physical. Inner-sphere adsorption mechanism for Mo on kaolinite surfaces was reported by Xu *et al.* (2013). Kaolinite is the dominant clay mineral in collected soils except in soils from Palakkad eastern plain where peak of kaolinite was not obtained in XRD analysis. That is why the trend was reverse in soils from Palakkad eastern plain with high pH values in case of maximum quantity adsorbed.

Very high buffer power was recorded in *Kuttanad* soil followed by *Pokkali* and *Kole*. Low buffer power was recorded in sandy soil and soils from Palakkad eastern plain. The sites for Mo adsorption in soil is high in low land soils of *Pokkali, Kole* and *Kuttanad* and low in soils from Palakkad eastern plain and sandy soils. Q-I curves of all the soils were with positive intercept with 2 exceptions (*Onattukara* sandy soil at 25^0C and soil from Palakkad eastern plain at 40^0C). Intercept value is very high in low land soils of *Pokkali, Kole* and *Kuttanad,* indicating that below which no desorption happens that is why none of the samples showed any detectable level of available Mo in soil.

Maximum quantity adsorbed was significantly and positively correlated with clay content, AEC and negatively correlated with pH, sand content and Av. Si. Both buffer power and maximum quantity adsorbed at both temperatures showed significant positive correlation with CBD-Fe. These results indicate that pH dependent positive charges in clay minerals and iron oxides are the sites of Mo adsorption in soil. Kaolinite is the dominant mineral present in the collected soils except in Palakkad eastern plain. The fact that Mo can be adsorbed by organic matter was reported by King *et al.* (2017). That is why maximum quantity adsorbed and buffer power showed positive correlation with OC and Av.N.

Adsorption isotherms and Thermodynamics of adsorption

Adsorption of Mo was observed in all the soils at both temperatures with all the added concentration of Mo. Mo adsorption in soil was well explained by Freundlich adsorption isotherm followed by Tempkin and Langmuir adsorption isotherm.

Frendlich adsorption isotherms of representative soil samples from each agro-ecological unit are given in figure 42. Highest value of Freundlich constant related to strength of binding (K_F) value at both temperatures was recorded *Kuttanad* soil. Low value of K_F was recorded in *Onattukara* sandy soils and soils from Palakkad eastern plain (Except Sample No. 21). K_F value indicates the strength of bonding. Mo is strongly bonded to the adsorption sites in low land soils of *Kuttanad, Pokkali, Kole,* whereas adsorption strength is very less in sandy soils. Most of the soils were recorded with 1/n value <1, indicating the adsorption intensity was less. The possibility of more adsorption still exists.

Langmuir adsorption isotherms of representative soil samples from each agro-ecological unit are given in figure 43. High value of adsorption maxima (q_m) was recorded in low land soils of *Pokkali, Kole and Kuttanad* followed by laterite soil. Sandy soils were recorded with low $q_{m.}$ Possibility of specific adsorption is very high in low land soils of *Pokkali, Kole and Kuttanad* because of high clay content dominated by kaolinite mineral and presence of oxides and hydroxides of Fe and Al. Exceptionally very high value of K_L was found in *Kuttanad* soil (Sample No. 15 at 40^0C), where highest value of K_F was also recorded. Comparatively high values of K_L were observed in all the *Kuttanad* soil followed by soils from *Kole* and *Pokkali* indicating the high bonding energy between Mo and adsorption sites in these soils. Very low K_L was recorded in sandy soils and laterite soils indicating less bonding energy in the adsorption process.

All the soils at both temperatures followed Tempkin adsorption isotherm. Tempkin adsorption isotherms of representative soil samples from each agro ecological units are given in figure 44. Exceptionally high value of Tempkin isotherm constant related to strength of binding (K_T) value was observed in *Kuttanad* soil (Sample No. 15 at 40^0C), where exceptionally high K_F value was also recorded. All other low land soils of *Pokkali, Kole and Kuttanad* showed high values of K_T. Value of K_T was increased with increase in temperature in all the low land soils. That means the strength of bonding increased with increase in temperature in these soils indicating the chemical nature of bonding. Low K_T value was recorded in sandy soils and soils from Palakkad eastern plain, where comparatively high constant related to heat of adsorption (b) values were recorded.

The constants of different adsorption isotherm indicating the strength of binding (K_F, K_L and K_T) showed positive correlation with CBD-Fe and silt or/and clay content and negative correlation with sand content at 25^0C or 40^0C indicating that iron oxides and kaolinite mineral dominant in clay and silt fraction are the site which has more binding strength towards Mo. Since some of the soils didn't fit into Langmuir adsorption isotherm, significant correlations were less in case of constant related to bonding energy (K_L). K_L showed significant positive correlation with Ex. Al. K_T and K_F showed significant negative correlation with pH. Goldberg *et al.* (2008) reported that adsorption of Mo decreases with increase in pH above 5. Adsorption maxima was significantly and positively correlated with OC, AEC, clay content, silt content, CBD-Fe and Ex. Al at 40^0C,which clearly indicate the sites of Mo adsorption. Adsorption maxima showed negative correlation with pH. Number of positive charge decreases with increase in pH and hence the adsorption of anions also decreases. Constant related to heat of adsorption (b) showed reverse trend of constants related to binding strength.

Fig. 41. Quantity- intensity curve of Mo adsorption in soil at 25 ^{0}C and 40 ^{0}C

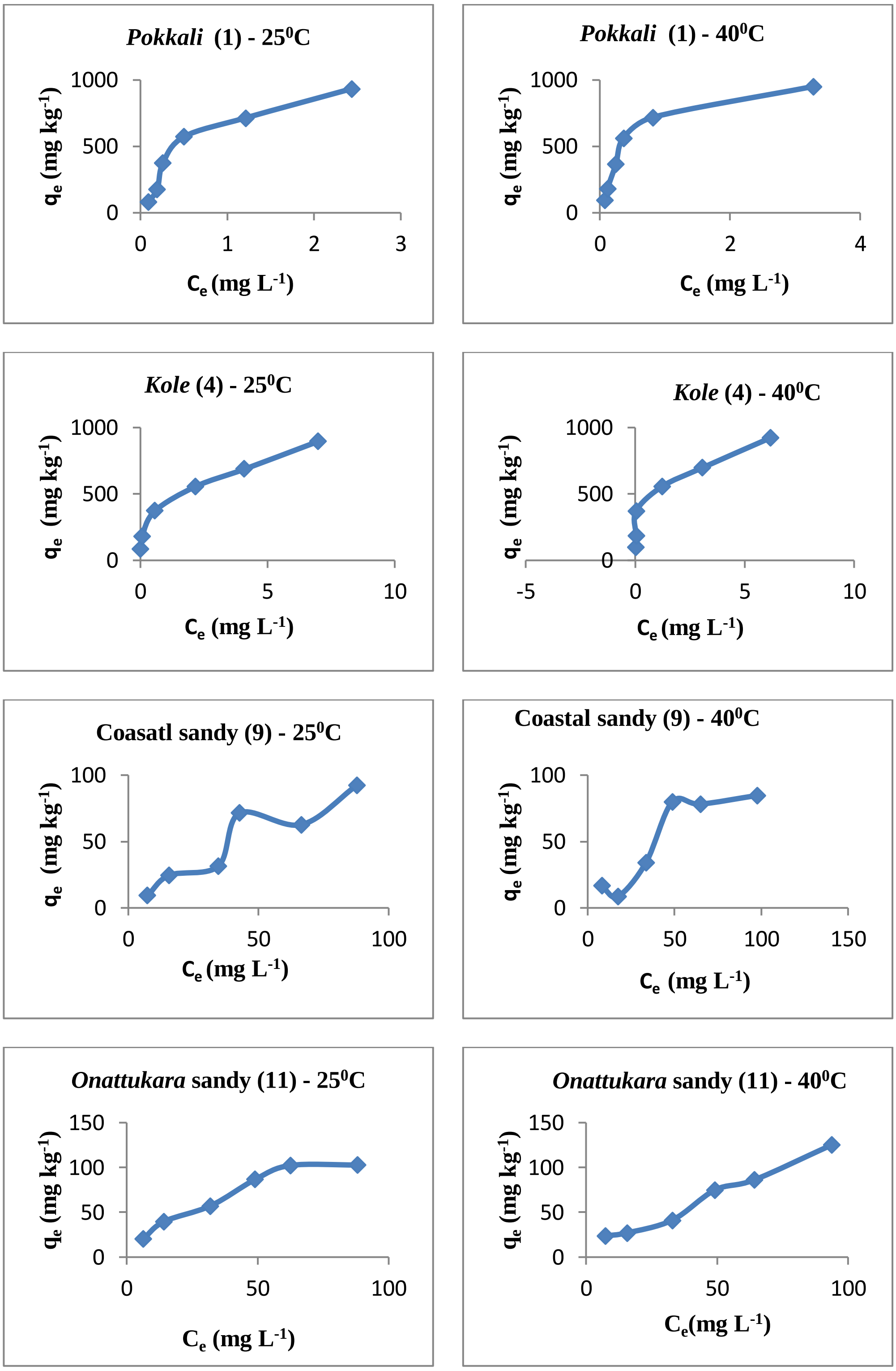
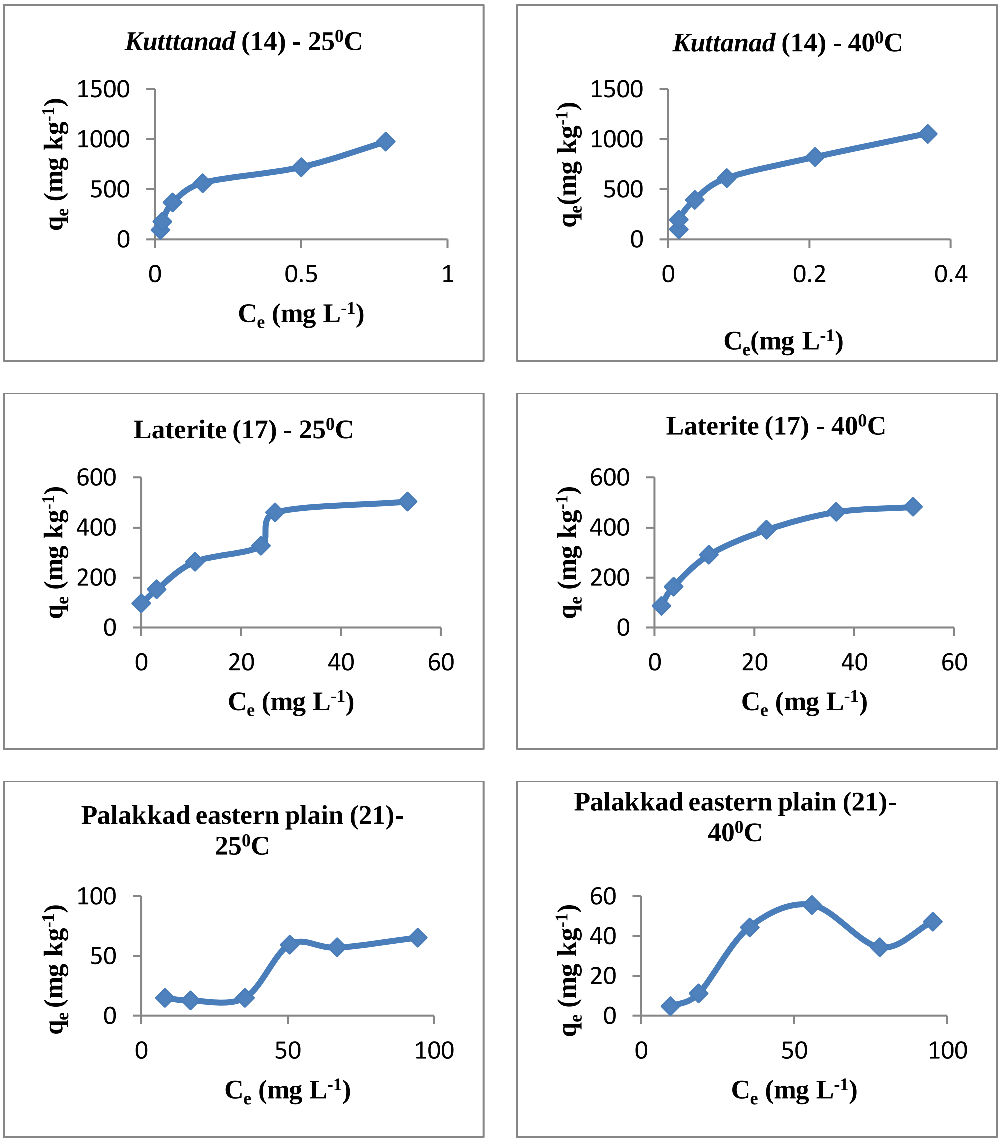


Fig. 41. Continued


Kutttanad (14) - 25^0C

Kuttanad (14) - 40^0C

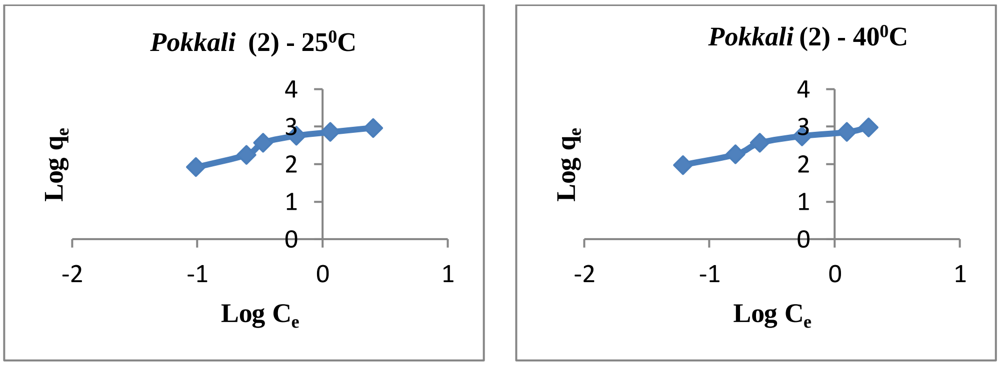
Laterite (17) - 25^0C

Laterite (17) - 40^0C

Palakkad eastern plain (21)- 25^0C

Palakkad eastern plain (21)- 40^0C

Fig 42. Freundlich adsorption isotherm for Mo adsorption at 25 ^{0}C and 40 ^{0}C


Pokkali (2) - 25^0C

Pokkali (2) - 40^0C

Fig 42. Continued

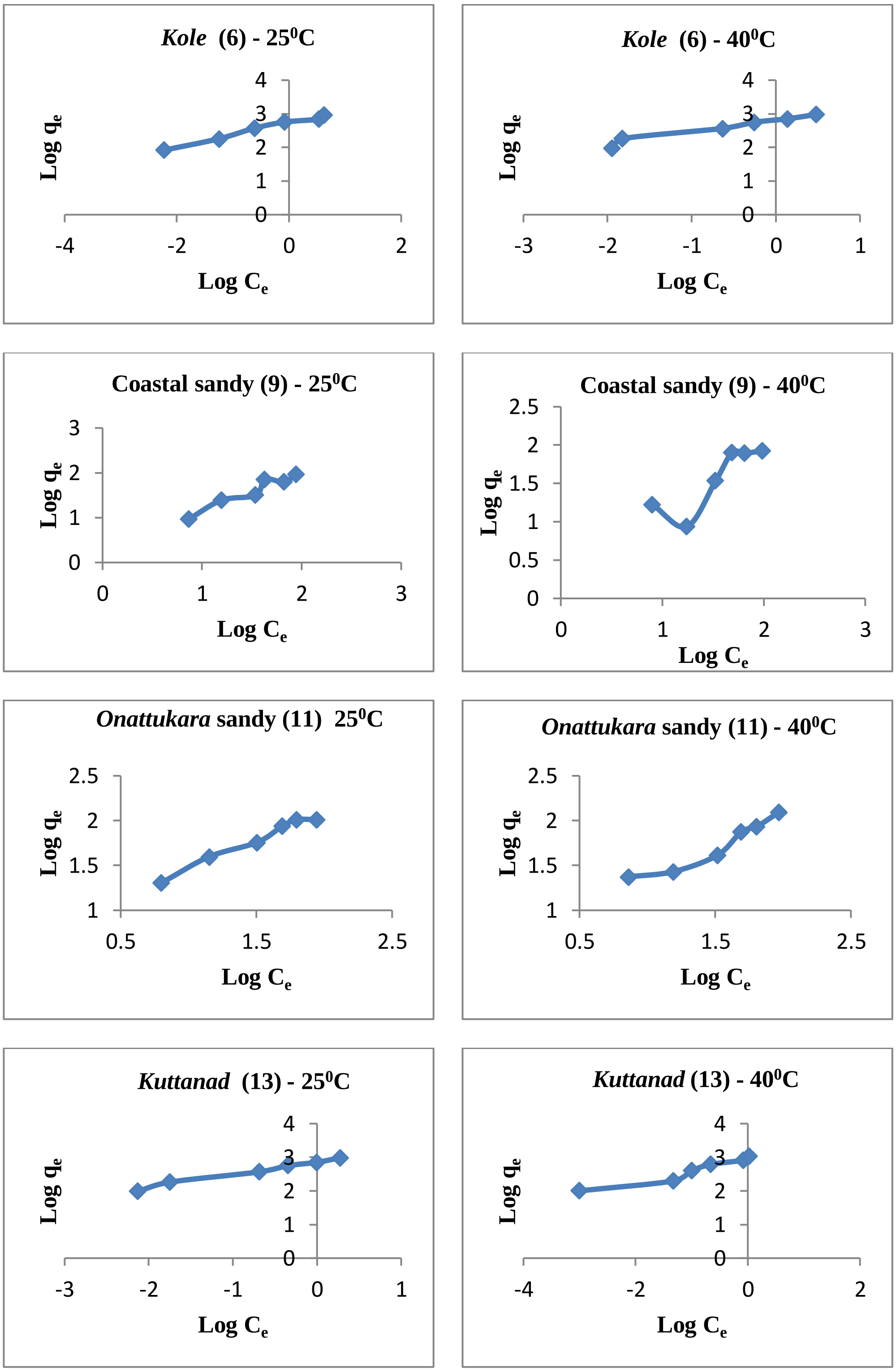


Fig 42. Continued

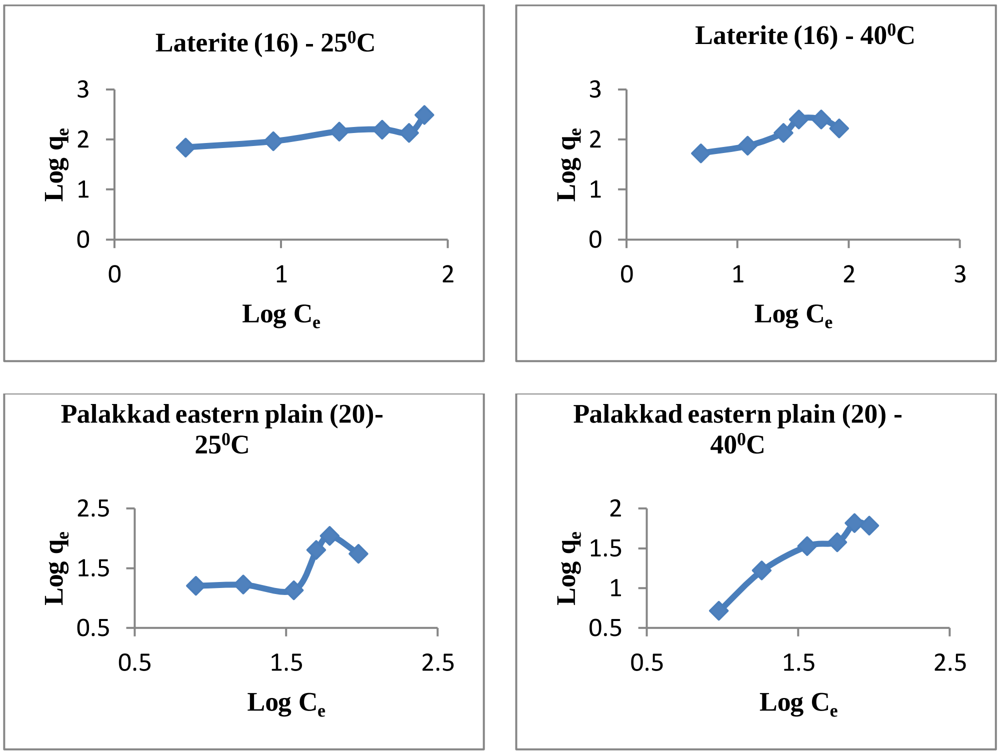


Fig 43. Langmuir adsorption isotherm for Mo at 25 ^{0}C and 40 ^{0}C

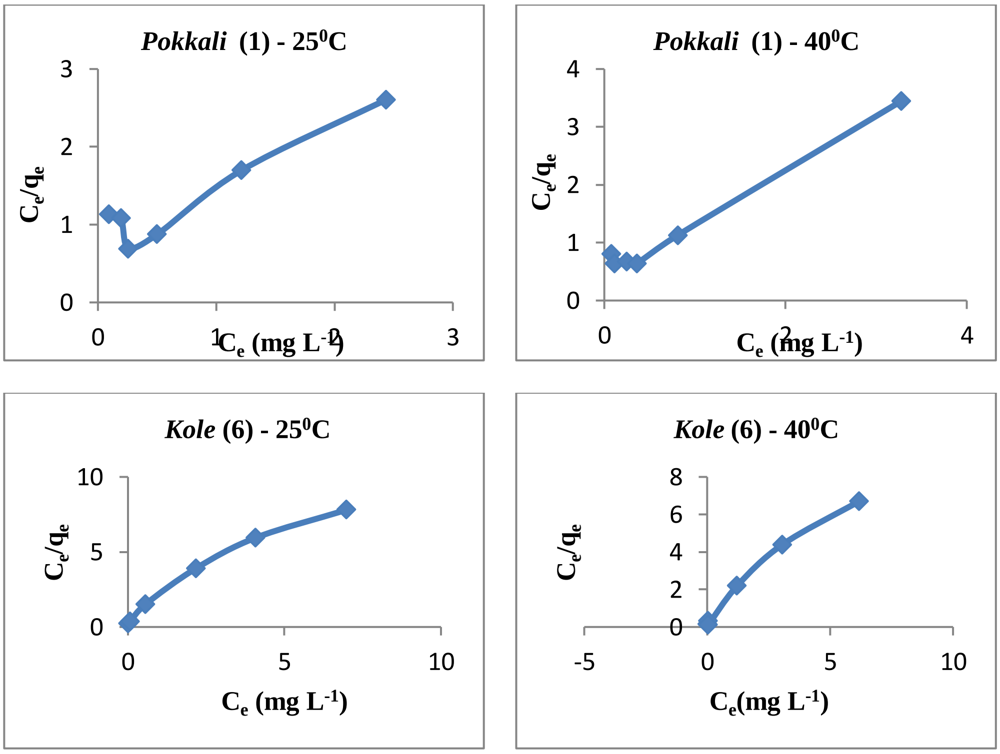


Fig 43. Continued

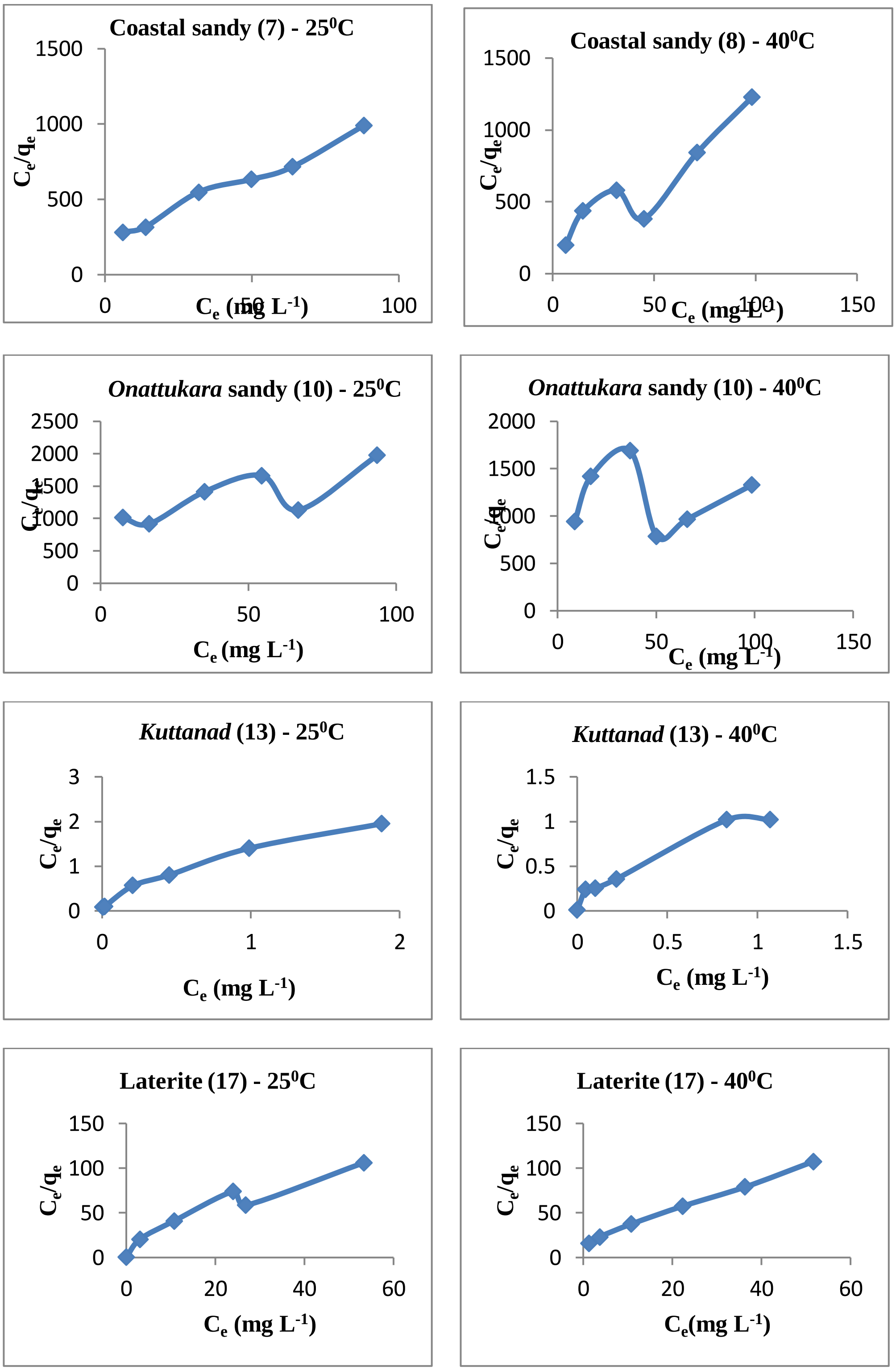


Fig. 43. Continued

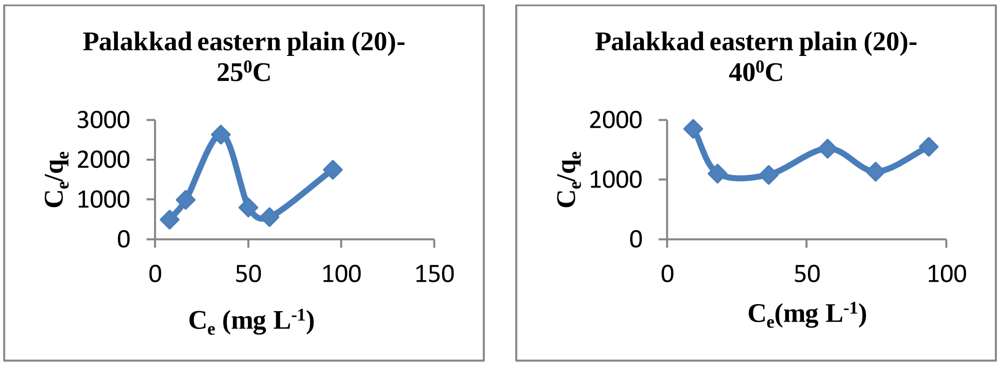


Fig. 44. Tempkin adsorption isotherm for Mo adsorption at 25 ^{0}C and 40 ^{0}C

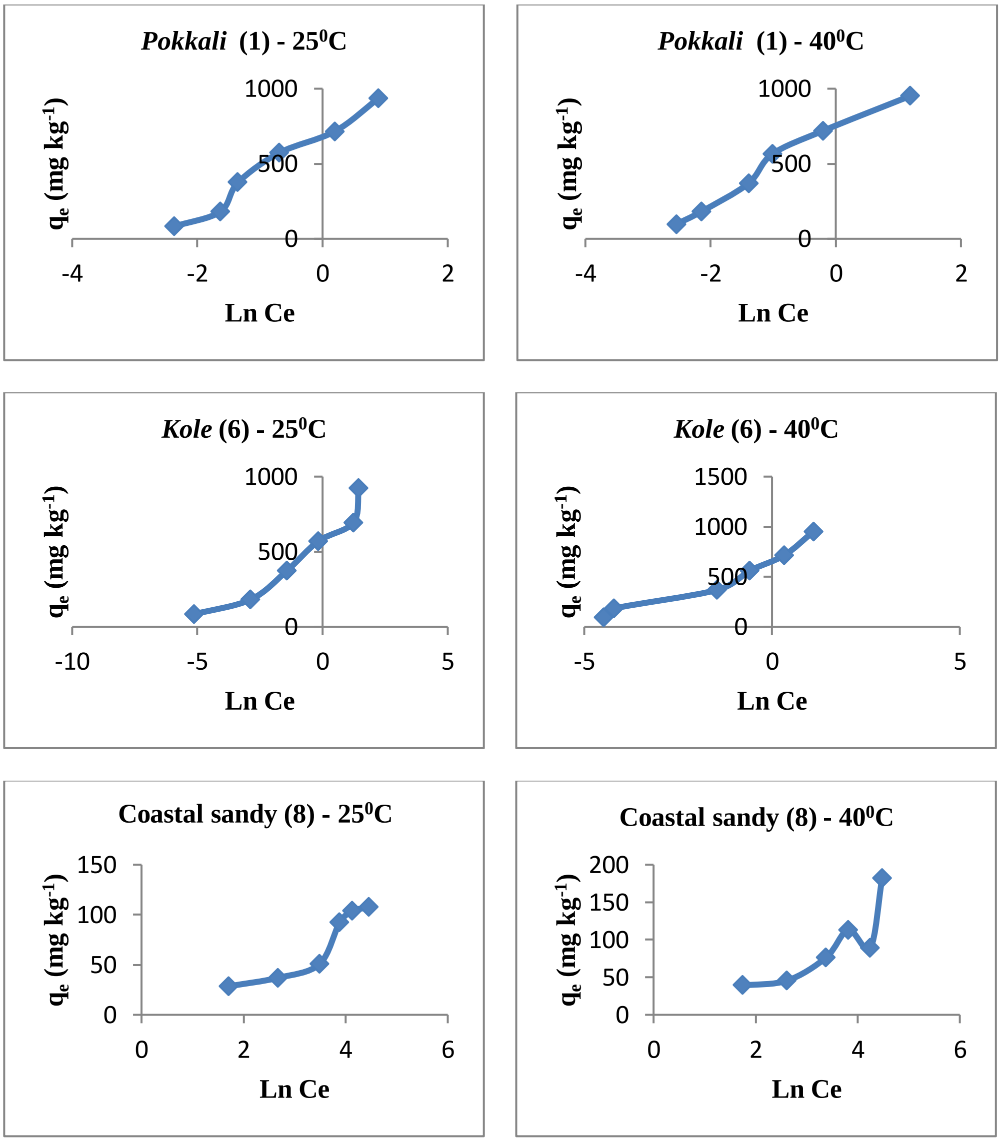
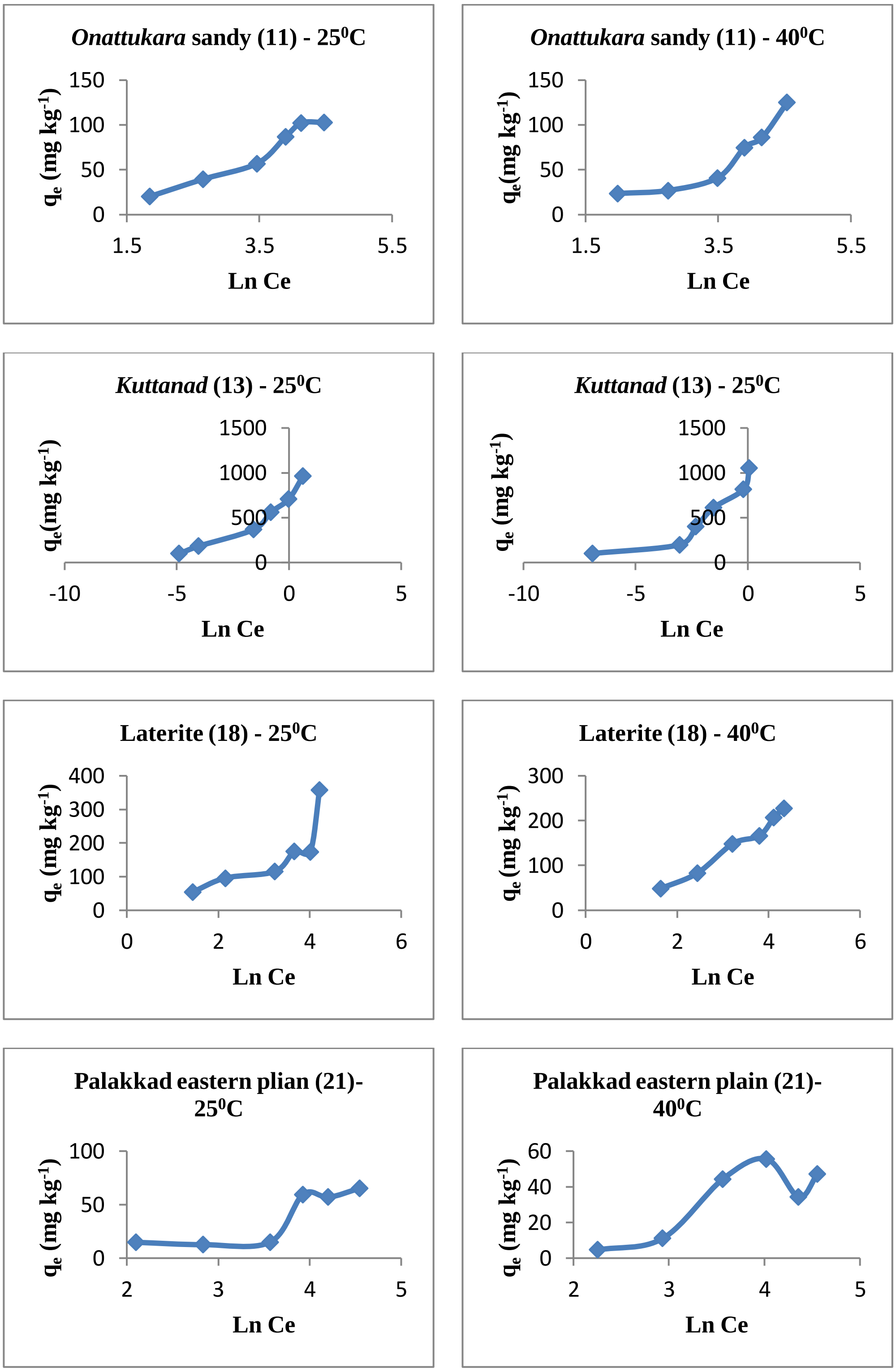


Fig. 44. Continued



All the soils showed a negative value for change in free energy indicating the spontaneous nature of adsorption. Change in enthalpy was positive for one *Kuttanad* soil (Sample No. 15). The adsorption was endothermic in nature for this soil where exceptionally high adsorption isotherm constants related to binding energy were reported. For all the remaining soils adsorption process was exothermic spontaneous reaction.

5.3.1.6. Adsorption study of silicon

All the collected soils showed desorption of Si at both temperatures. Hence adsorption iostherms were not tried.

Quantity-intensity relationship and thermodynamics of desorption

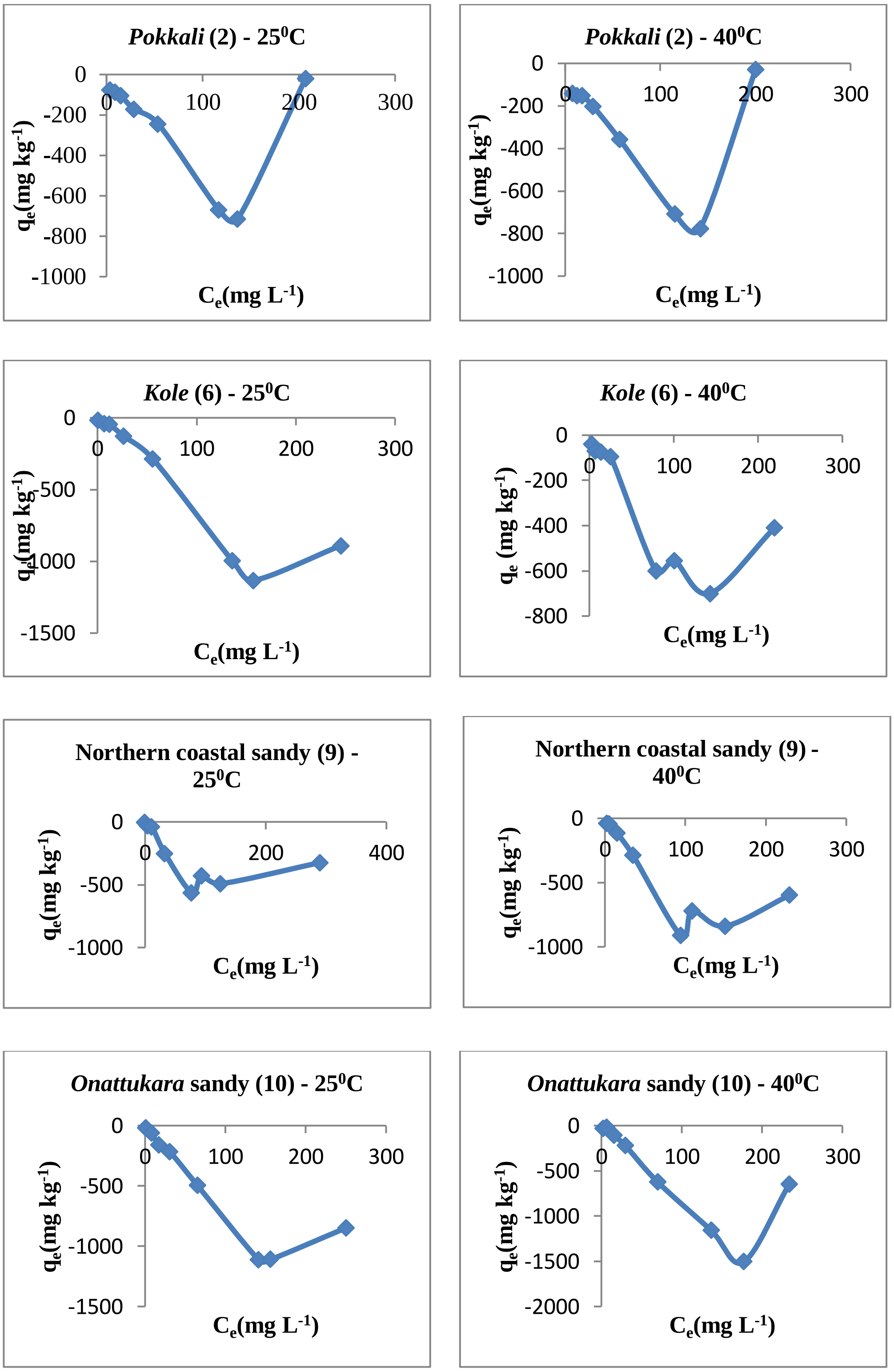
The Q-I curve of representative soil samples are given in figure 45. After reaching a maximum desorption a drastic reduction was observed in all soils at both temperatures. Si in soil solution (intensity factor) is largely influenced by its dissolution kinetics, which in turn is influenced by various soil factors such as Al, Fe oxides, organic matter, redox potential and moisture (Lekshmi, 2016) Most of the soils exhibited negative intercept indicating desorption of Si from the solid phase below equilibrium concentration. Seventeen samples showed an increase in desorption with temperature which may be due to increase in dissolution of silica at high temperature.

Adsorption is favored most strongly near the pKa values of the silicic acid because the proportion of negatively charged ions increases rapidly near the pKa values. pKa for silicic acid (H_4SiO_4) is at pH 9.8. At typical soil pH values (5–7), Si is present in soil solution predominantly as uncharged silicic acid. Si is preferentially adsorbed as the oxyanion $H_3SiO_4^-$ (Hingston *et al.*, 1972) and since the proportion of Si present as $H_3SiO_4^-$ in the solution increases with increasing pH up to about 9.8, Si adsorption also increases. Above that pH, electrostatic repulsion between silicate and the negatively charged surfaces, plus competitive effects of OH^-, results in a decrease in adsorption (Haynes and Zhou, 2018). The pH of equilibrium solution was ranged from 3.34 to 6.62. So the proportion of silicate anion present in soil solution at the equilibrium pH is less. This also lead to lack of adsorption of Si in the collected soils. Dissolution of silica from different fractions of Si also plays an important role in adsorption/desorption of Si in soil. A study conducted by Herbillion and Vinhan (1969) reveals the polymerization nature of Si. Belton *et al.* (2012) repoted the autopolycondensation of orthosilicic acid above the solubility limit of amorphous phase (100 ppm). After reaching a maximum desorption, desorption was decreased in large amount indicate the chances of polymerization with further addition of Si. Baumann (1959) provided the first systematic study of the polymerization and depolymerization at 30 ° C within pH 5.8-9, and several initial dissolved silica concentrations. He observed that the polymerization rate increased with increasing pH (above 3), dissolved silica and salt concentrations.

Highest value of maximum quantity desorbed at both temperatures was noted in sandy soil from *Onattukara* region. Lowest value was noted in soil from Palakkad eastern plain where the pH was near neutral. Buffer power showed significant positive correlation with occluded Si, OC, AEC, CBD-Fe and Av. Fe, indicating that pH decpendednt positive charges on clay minerals abd iron oxides are the sites where Si adsorption can occur. Maximum quantity desorbed showed significant negative correlation with all these parameters. Buffer power showed significant negative correlation with maximum quantity desorbed. When supplying power of a soil is more, the more will be its capacity to adsorb that particular nutrient.

Most of the soils showed an increase in thermodynamic equilibrium constant with increase in temperature and change in free energy was recorded negative for Si desorption in all the collected soils, indicating the spontaneous nature of Si desorption in soil. Change in entropy was also recorded positive for 21 soils. Desorption reaction was endothermic for all the soils except Sample No, 10, 12 and 21.

Fig 45. Quantity - intensity curve of Si in different soils at 25 ^{0}C and 40 ^{0}C



Pokkali (2) - 25^{0}C

Pokkali (2) - 40^{0}C

Kole (6) - 25^{0}C

Kole (6) - 40^{0}C

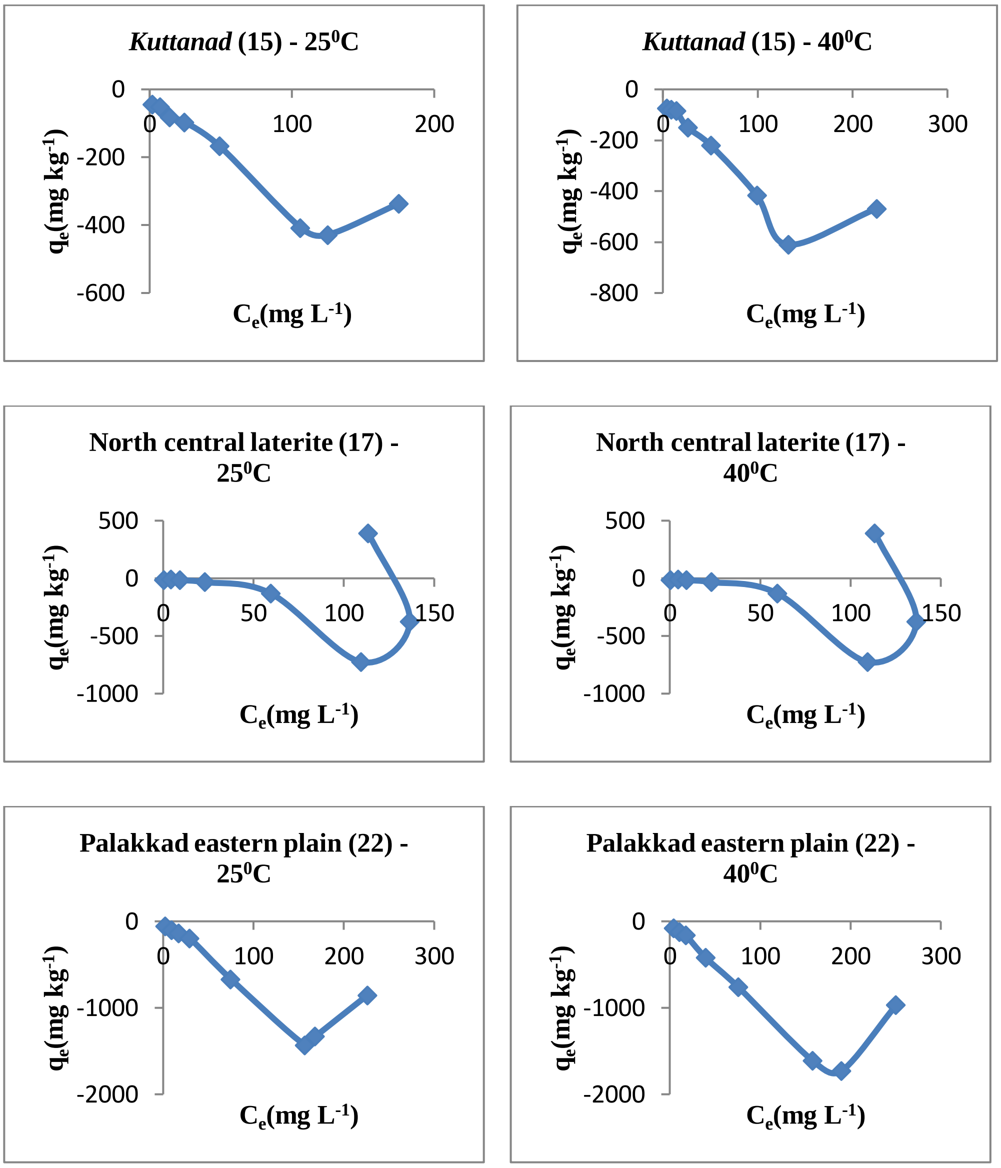
Northern coastal sandy (9) - 25^{0}C

Northern coastal sandy (9) - 40^{0}C

Onattukara sandy (10) - 25^{0}C

Onattukara sandy (10) - 40^{0}C

Fig. 45. Continued



Considering the adsorption of all these anions in together, dominance of desorption was observed in case of Si and S. Q-I curve of these elements showed reduction in desorption after reaching a maximum desorption, indicating the possibility of adsorption on further addition of higher concentration of these elements. It may be polymerization in case of Si. Adsorption of B was less because only lower concentration of B was used in adsorption study and the existence of non-ionised forms of B at the equilibrium solution pH. Due to these reasons adsorption of B, S and Si was found less than nitrate adsorption; even though nitrate is last in the lyotropic series. P and Mo showed very high similarity in adsorption behavior. Typical L-shaped adsorption curve was obtained in low land soils of *Pokkali, Kole* and *Kuttanad,* indicating the high affinity of these elements to the adsorption sites, which is due to the inner-sphere bi-dentate complex formation by these elements.

Freundlich adsorption isotherm was the best to explain adsorption of anions in soil followed by Tempkin and Langmuir adsorption, which implies that the bonding energy of the adsorbate anion on the soil surface decreases with the fractional coverage of the adsorbent surface. This is closer to reality for a heterogenous surface like soil, than the constant bonding energy concept of Langmuir isotherm. The failure of Langmuir adsorption isotherm may be due to the linear fitting of isotherm and the assumptions of Langmuir adsorption isotherm in not full filled in the normal soil conditions. Bonding energy constants of different adsorption isotherms for P and Mo adsorption was found very high in *Kuttanad* soils followed by soils from *Kole* land, where high CBD-Fe content and clay content also followed the same order. Among P and Mo, the constants related to strength of adsorption were high for Mo adsorption than P adsorption. It may be due to the native concentration of these elements in soil, Mo was not found in detectable limit in any of the collected soil samples and hence the chance of Mo adsorption with added concentration of Mo is very high. P deficiency was very rare in *Kerala* soil. Detectable level of available Mo was not found in any of the collected soils. Adsorption maxima were recorded high in *Pokkali* soils, in case of P than Mo, which is due to the possibility of Al-P complex formation where high amount of water soluble and exchangeable Al was present.

Correlation study indicates that pH, AEC, clay or silt content, iron oxides and organic matter are the major factors affecting the adsorption of anions in soil. Some opposite correlations were obtained in case of S due to the high S content in *Pokkali* soils by the uncontrolled sea water entry. More research has to be done in finding out the role of organic matter in anion adsorption. Still some controversial opinions exist in this aspect. XRD data revealed the dominance of kaolinite mineral present in all the representative soils from the collected samples, except in soil from Palakkad eastern plain where black cotton soils prevail. Beyond that, the presence of gibbsite and hematite was also observed. Relatively high ZPC of these minerals than the acidic soil pH in Kerala soils lead to the development of pH dependent positive charges. Hence AEC also increases. So the adsorption of anions increases. Moreover, iron oxides, Al oxides and kaolinite clay mineral can form inner-sphere complexes (ligand exchange) especially with P and Mo. If the complex formed is mono-dentate it can be somewhat labile and if it is bi-dentate it will not be available. If the outer-sphere complexes are formed, adsorption will be reversible and adsorption decreases with increase in temperature.

5.3.2. Adsorption study of P and B in binary system

Preferential adsorption of P over B was observed in all the binary adsorption studies conducted in all the collected soils. Change in adsorption of P and B with increasing concentration of added B and P in two representative soils are shown in figure 46 (a, b) and 47 (a, b). Bolt (1976) reported a decreasing order of preferential adsorption among anions as $SiO_4^{4-} > PO_4^{3-} >> SO_4^{2-} > NO_3^{-} = Cl^{-}$. Young (2000) also suggested this lyotropic series, and that adsorption process was physical in nature. So it is evident that, even in case of physical adsorption, P has high ability to get adsorbed on soil. Moreover P forms mono-dentate and bi-dentate inner-sphere complexes with soil components (Pansu and Gautheyrou, 2007). XRD data revealed the dominance of kaolinite mineral in the collected soils, except in soil from Palakkad eastern plain and the dominance of iron oxides is revealed by the high content of CBD extractable-Fe. So there is every chance of specific adsorption in soils of Kerala for P. These two reasons lead to the preferential adsorption of P over B in the collected soils.

Figure 2 and 4 clearly indicates that the soils with high clay content and CBD-Fe didn’t show any deviation in P adsorption (*Kuttanad* soil) at different concentration of added B. Whereas the soil with more sand content and less CBD-Fe showed some deviation in P adsorption at different concentration of added B (coastal sandy soil). But a trend of increasing or decreasing adsorption with added B concentration was not found.

Kuttanad soil (Sample No. 13)

Fig. 46 a. B adsorption at different concentration of P

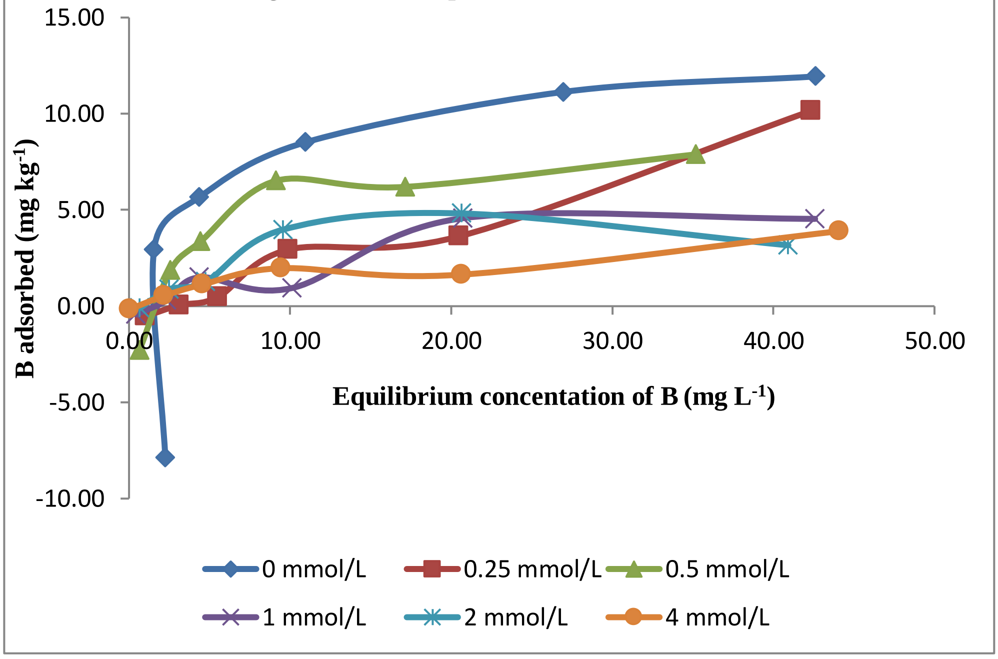
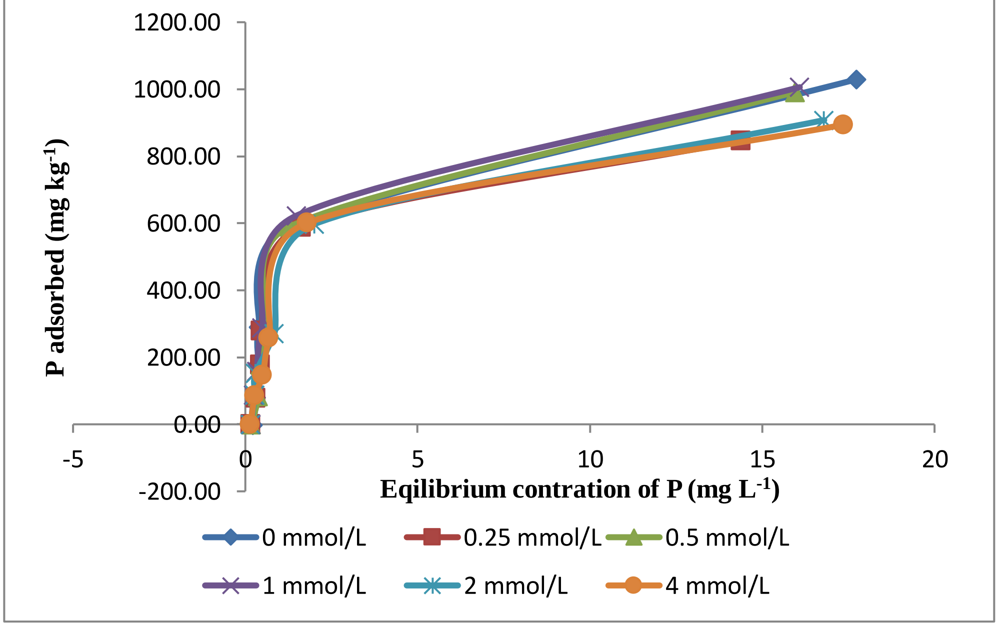


Fig. 46 b. P adorption at different conentation of B



Coastal sandy soil (Sample No.7)

Fig. 47 a. B adsorption at different concentration of P

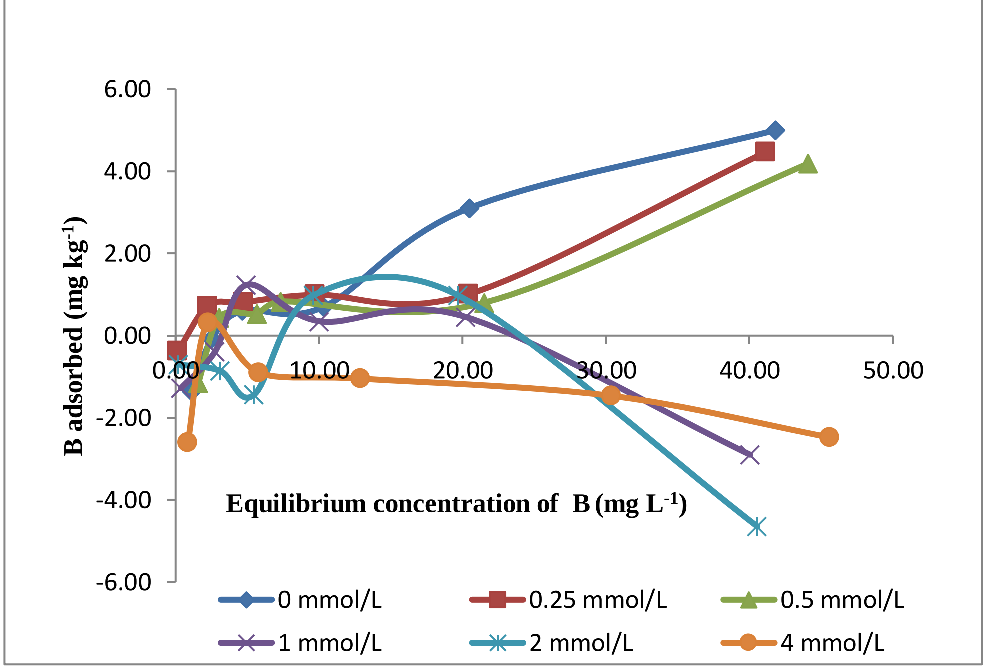
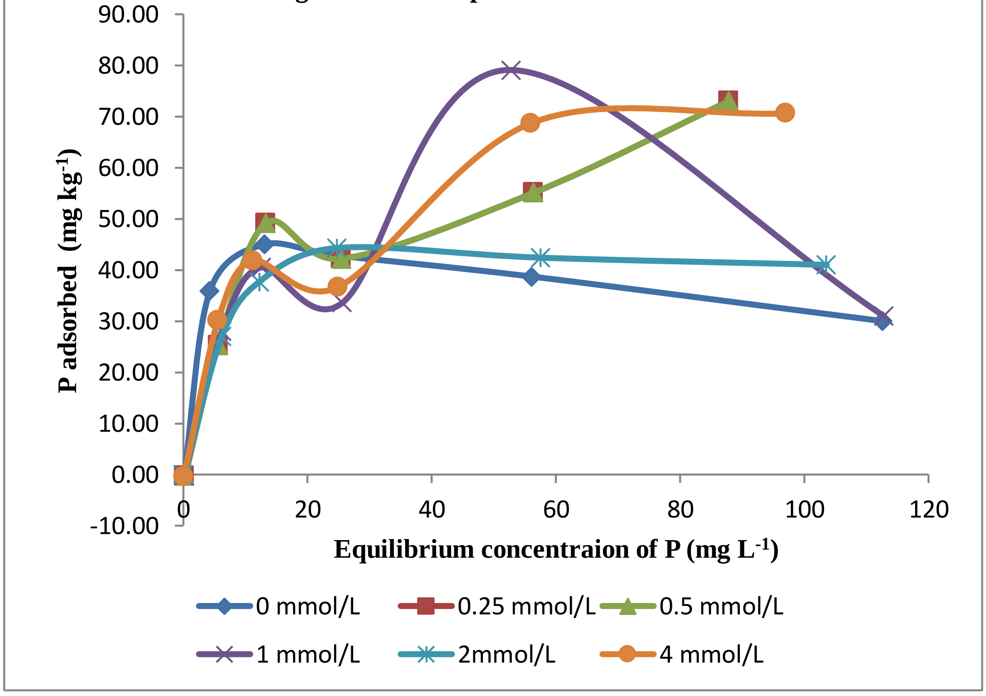


Fig. 47 b. P adsorptio n at different concentration of B



Choudhary *et al.* (n.d.) used multicomponent Freundlich type, i.e. Sheindorf - Rebhun - Sheintuch (SRS) equation (Sheindorf *et al.,* 1981) to examine the interaction of binary-anion mixture containing phosphorus and boron in two different soils. They found that B has negligible effect on the adsorption of P in acidic Andretta silt loam soil due to the decreased affinity of B anion for the adsorption sites under acidic conditions.Competing ions such as silicate, sulfate, phosphate, and oxalate decreased the magnitude of B adsorption on oxides (Bloesch *et al.,* 1987; Choi and Chen, 1979).

The ability of competing anions to leach adsorbed B from oxides increased in the order: chloride < sulfate = arsenate < phosphate (Metwally *et al.,* 1974). Bloesch *et al.* (1987) and Metwally *et al.* (1974) reported that the effect of sulphate on B adsorption can be slight and substantial in the case of phosphate. A decrease of B content in soils under increasing P doses was reported by Muhlbachova *et al.* (2017). The results of the present study also suggest the same. The decrease in both buffer power and maximum quantity adsorbed with increasing concentration of added P leads to the inefficiency of soil to replenish the B in soil solution on depletion, which results in P induced B deficiency in unfertilized situation. The chances of leaching loss of B also increases with decrease in adsorption and buffer power with high concentration of P in soil solution due to failure in retension.

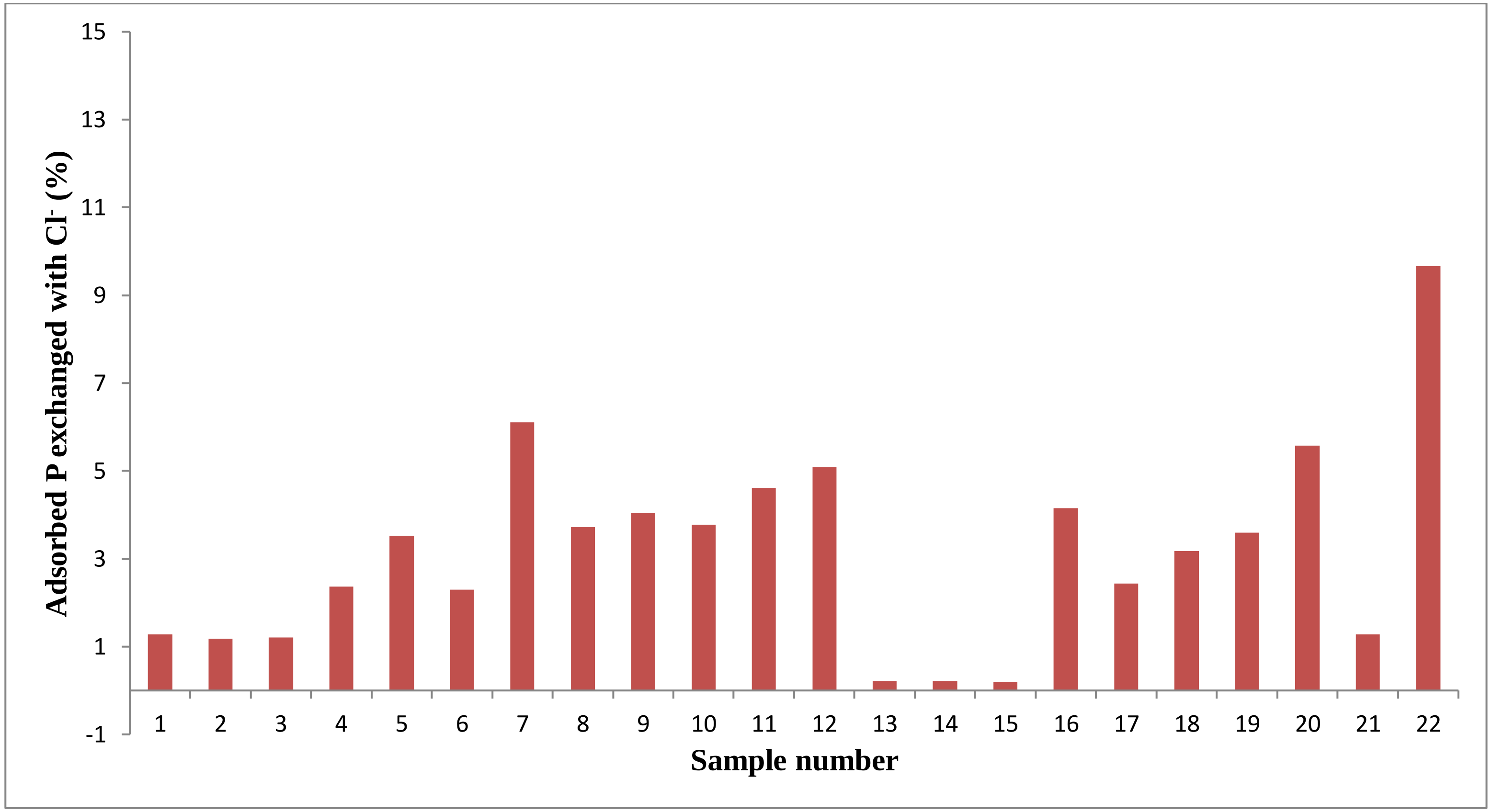
5.4. Studies on anion exchange

Anion exchange capacity was found greater than cation exchange capacity in some highly weathered tropical soils (Weil and Brady, 2017). The tropical soils in hot and humid conditions are generally thought to be deep, red, highly weathered and dominated by kaolinite and oxide minerals (Bhattacharyya and Pal, 2015). AEC of the collected soils ranged from 3.91 to 34.49 cmol(-)kg^{-1}. Among the samples, *Pokkali* soils were recorded with higher AEC; sandy soils and soils from Palakkad eastern plain were recorded with lower AEC. Higher AEC in *Pokkali* soils were due to the dominance of kaolinite and iron and aluminium oxides. Lower AEC recorded in soils from Palakkad eastern plain is due to the dominance of 2:1 minerals (Soil Survey Organisation and Agriculture Department, 2007). Clay minerals provide positive charge when pH is lesser than ZPC (Spark, 2003). Since the ZPC of 2:1 minerals like montmorillonite is 2.5, it cannot provide pH dependent positive charges at the near neutral pH value of soil from Palakkad eastern plain. XRD data showed the dominance of mixed layer minerals and absence of kaolinite peak in soil from Palakkad eastern plain. Exchange will be more in clay particles, that is why both cation and anion exchange capacity was found lesser in sandy soils from northern coastal plain and *Onattukara* sandy plain.

The procedure followed here for the estimation of AEC uses the element phosphorous (Hesse, 1971). Sum of adsorbed P and bray exctractable P was considered as anion exchange capacity. The percentage contribution of adsorbed P in anion exchange capacity ranged from 66.45 to 99.8 per cent. The tropical soils of Kerala are dominant in high amount of oxides and hydroxides of Fe and Al. Many scientists reported the specific adsorption behavior of P (Sparks, 2003; Pansu and Gautheyrou, 2007). Mono and bidentate complexes can be formed as a result of specific adsorption. Only a part of this phosphorous is recovered by desorption analysis. Monodentate complex is somewhat labile, whereas bidentate complex is irreversible (Hingston *et al.,* 1974). Possibility of formation of these type of complexes are more in tropical soils of Kerala which may not be a part of anion exchange complex, which indicates the possibility of over estimation of anion exchange capacity.

The soil with adsorbed P in the determination of AEC, after leaching and drying, the soil was treated with higher concentration of Cl^- in order to exchange P from exchange site. Percentage of adsorbed P exchanged with Cl^- is shown in figure 48. The percentage of adsorbed P exchanged with Cl^- ranged from 0.19 to 9.67 only.

Fig. 48. Percentage of adsorbed P exchanged with Cl^-



Amount of water soluble forms were deducted from the anions replaced by 250 mg L^{-1}P. In case of P, amount of water soluble P was deducted from available P. Sum of all the exchangeable anions and P deducted from available P were calculated. Estimated AEC and the sum of exchangeable anions were significantly and positively correlated but the sum of exchangeable anions were found less than estimated AEC in most of the soils. This also ensures the possibility of over estimation.

Very high and significant positive correlation among AEC adsorbed P indicated that AEC determination in this method is purely based on adsorption of P. The percentage of adsorbed P exchanged with Cl^- showed significant negative correlation with AEC and adsorbed P, which indicated that the soils with more adsorbed P exchanged less P with Cl^-. This was due to the presence of difference in bonding of P with the components in soil where high P adsorption happened, which is not merely electrostatic. Significant positive correlation of CBD extractable Fe with AEC, adsorbed P and negative correlation with percentage of adsorbed P exchanged with Cl^-, ensures the role of oxides and hydroxides of Fe and Al in specific adsorption of P.

AEC determination is dependent on the pH dependent positive charge, so care should be taken to avoid the change in pH during estimation of AEC. The use of anions with behavior of specific adsorption should be avoided from determination of AEC.

ZPC of the soils could not be found out. An intersecting point was not found in the graph. All lines were parallel. Different components in soil possess different ZPC. ZPC of organic matter (Gu and Schulz, 1991) and silica (Spark, 2003) is 2. The lower ZPC of these components provides pH dependent negative charges in existing soil pH, whereas relatively high ZPC of kaolinite, oxides and hydroxides provide pH dependent positive charges on these minerals. Interaction of different soil components with wide variation in ZPC, in balancing the charges makes difficulty in the determination of ZPC. Numerous functional groups present in organic matter and incumbent acid nuetarlising capacity of soil are also reason for difficulty in determination of ZPC.

5.5. INTERFERENCE OF SILICON IN EXTRACTION AND ESTIMATION (COLORIMETRIC MOLYBDENUM BLUE) OF PHOSPHOROUS

5.5.1. Phosphorous and Silicon extractability of different extractants

5.5.1.1. Content of P and Si extracted using different reagents

P and Si extracted from soil using different extractants are represented graphically in table 78. A general trend in silicon extractability was in the order; Bray reagent > CBD > 0.5M acetic acid > 0.1M HCl. A general trend was not visible in P content as in case of Si extraction. Since crystalline and amorphous Fe and Al oxides are prominent in low lands of *Pokkali, Kole* and *Kuttanad,* these soils exhibited high P and Si extraction in CBD treatment.

Bray No. 1 reagent consists of 0.03 N NH_4F and 0.025 N HCl which extracts both adsorbed and acid soluble form of P (Bray and Kurtz, 1945). The reaction of HF with SiO_X was successfully replaced by ammonium fluoride indicating its etching effect on silica (Gonchar *et al.,* 2019). Formation of $(NH_4)_2SiF_6$, or SiF_6^{2-} ions was the dominant reaction pathway in the NH_4F etching of Si crystals (Niwano *et al.,* 1993). Thus it is evident that high content of Si in the Bray extract of all the collected soils indicated the extraction of Si from mineral structure.

5.5.1.2. Relationship between P and Si content extracted using different reagents

P extracted by Bray reagent showed significant positive correlation with P extracted by 0.5M acetic acid and 0.1M HCl, indicating the possibility of extraction from same pool from those acid soluble forms. P extracted by CBD treatment did not show any correlation with P extracted by other extarctants, indicating different pools of extraction. Similarly Si extracted by Bray reagent showed significant positive correlation with Si extracted by 0.5M acetic acid and

0.1M HCl and didn’t show any correlation with Si extracted by CBD treatment. Significant positive correlation between CBD extracted P and Si showed that amount of occluded forms of these elements with Fe and Al oxide was high. Negative correlation of Si extracted by Bray reagent with P extracted from CBD treatment showed that Bray could extract high Si from soils with lower content of Fe and Al oxide, probably where high amount of phyllosilicate minerals were present.

5.5.2. Interference of Si in colorimetric estimation of P (Moybdenum Blue method)

Absorbance by all the solutions with different concentration of P and Si at different wavelength, following the colorimetric (molybdenum blue) estimation of P is given in Fig. 49 and 50. Maximum absorbance was measured at 882 nm for solutions containing different concentarions of P (Murphy and Riley, 1962; Ciavatta *et al.*, 1990) and solutions containing different concentration of Si.

SiO_4^{4-} has long been considered one of the main interferents in phosphate molybdenum blue methods as it also forms heteropoly acids (α and β-12-Molybdo Silicic Acid) reducible to molybdenum blues (Nagul *et al.*, 2015). This study also corroborates with the same result and the interference was found only at very high concentration. Silicate interference was found very high when the reaction acidity is too low (Boltz and Mellon, 1947). In Murphy and Riley method the reaction acidity is too high, because of the use of concentrated H_2SO_4. Comparison of estimated P from calibration curve, using solution containing various concentration of Si showed that the values are less at 660 nm than values at 882nm, at all the concentration. That means the interference of Si in molybdenum blue colorimetric estimation of P was found comparatively less at 660nm than at 882 nm. For lower concentration of P (0.1 mg L^{-1}), more accurate estimation was recorded in 882 nm. So the study on Si:P ratio was concentrated on absorbance at 882nm.

Ciavatta *et al.* (1990) suggested the possibility of overestimates of the P concentration up to 400 per cent in P determinations of soil extracts and natural waters. In this study greater than 10 per cent over estimation was observed if Si:P ratio is greater than 80, and it reached to above 1000 if the ratio was greater than 2500.

Fig. 49. Absorbance of different concentration of P at different wavelength

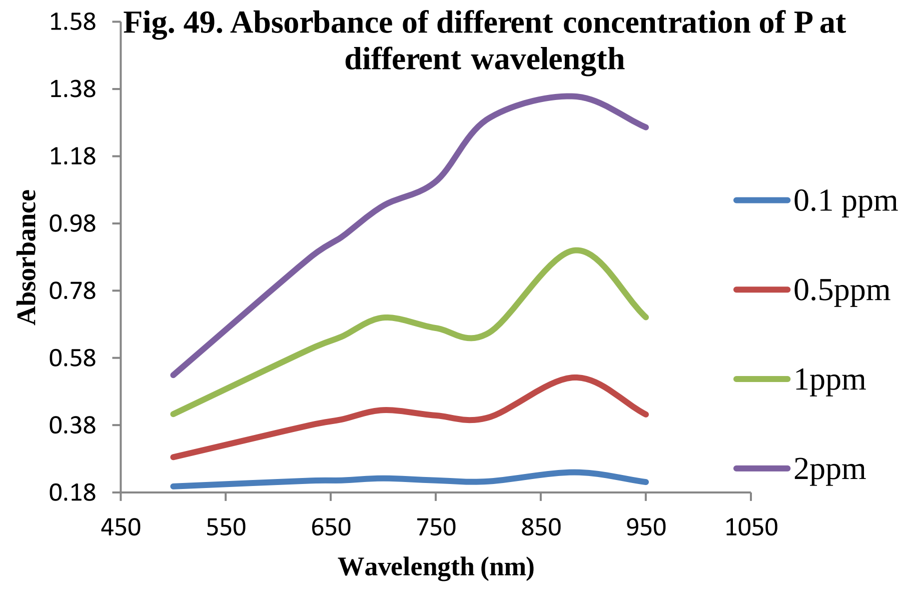
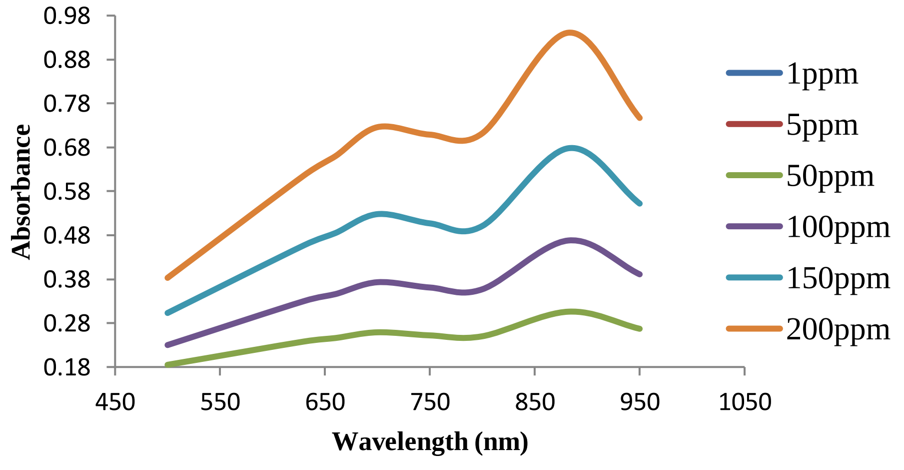


Fig. 50. Absorbance of different concentration of Si estimated by standard procedure of P



Summary

6. SUMMARY

Representative soil samples (22 Nos) from seven agro-ecological units under five agro ecological zones in Kerala with wide variation in clay content, organic matter and pH were collected and characterized for the study on "Anionic equilibria in major soil types of Kerala". Samples were characterized with respect to pH, EC, OC, AEC, CEC, texture, available nutrients (N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu, B, Mo and Si), CBD-Fe, exchangeable ammonical N, nitrate N and total N. Clay, silt and fine sand fractions were separated from one representative soil from each agro-ecological unit to have an idea about dominant minerals present in theses fractions by XRD analysis.

All the soil samples were subjected to fractionation to quantify the different forms of each of the anionic nutrinets contributing to total content. Sequential fractionation was carried out for inorganic P, B and Si. Non-sequential fractionation method was carried out in case of S. Total P, B and S was determined by complete digestion and total S by dry combustion method. Different fractions of P studied were saloid-bound P, aluminium phosphate, iron phosphate, reductant soluble phosphate, calcium phosphate, organic P and residual P. Sulphate S, total water soluble S, heat-soluble S, sulphate soluble after ignition and total organic S were different S fractions under study. Different fractions of B studied were readily soluble B, specifically adsorbed B, oxide bound B, organically bound B and residual B. Different fractions of Si studied were mobile Si, adsorbed Si, silicon in organic matter, Si occluded in pedogenic oxides and hydroxides, amorphous Si and residual Si.

Single anion adsorption study of nitrate N, P, S, B, Mo and Si were carried out at 25^0C and 40^0C. The quantity-intensity relationships were charaterized to understand buffer power and intercept from quantity-intensity curve. The data obtained from these experiments were fitted to Langmuir, Freundlich and Tempkin adsorption isotherms. The thermodynamic parameters i e. change in free energy of adsorption (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) were also calculated. Binary adsorption of P and B were carried out to understand the preferential adsorption of these anions in soil. The quantity-intensity relationships were determined from quantity-intensity curve to understand change in buffer power of these anions in the presence of other.

Studies on anion exchange were carried out to find out whether there is any over estimation of anion exchange capacity if P is used to determine the AEC. Experiment was conducted to determine ZPC of the soils under study.

Extractability of different extarctants for P and Si were determined following standard procedure to compare it with extractability of Si in Bary I reagent. Known standards of P and Si were estimated by molybdenum blue colorimetric method to ensure the possibility of over estimation of P by Si interference.

The salient results of the study are summarised and listed below:

- Ten samples were coming under extremely acid (3.5-4.5) to ultra acid (<3.5) category, which mainly include *Pokkali, Kole* and *Kuttanad* soils. Near neutral pH was recorded in soils from Palakkad eastern plain.
- Electrical conductivity of the soils ranged from 0.052 to 15.02 dS m^{-1}. Exceptionally high values of EC were recorded in *Pokkali* soils followed by *Kuttanad* soil.
- The high organic carbon status was reported in *Pokkali, Kole* and *Kuttanad* soils (2.57 - 6.74 per cent). All the soils from northern coastal plain and *Onattukara* sandy plain were low in organic carbon status.
- Soil from Palakkad eastern plain was recorded with highest bulk density (1.93 Mg m^{-3}).
- *Kuttanad* soils exhibited high clay content (> 50 per cent) and less clay content was observed in soils from northern coastal plain and *Onattukara* sandy plain.
- All the soils collected from northern coastal plain and *Onattukara* sandy plain were recorded with more than 50 per cent sand content. The soils collected from *Kuttanad* showed <20 per cent sand content.

- Among the collected soil samples, all soils from Palakkad eastern plain were recorded with high CEC (>10 cmol(+) kg^{-1}). All the three samples collected from northern coastal plain were recorded with CEC less than 2 cmol(+) kg^{-1}.
- High AEC was recorded in *Pokkali* soils (>30 cmol(-) kg^{-1}). Low AEC was recorded in sandy soils and soils from Palakkad eastern plain.
- Thirteen soils showed low available nitrogen (<280 kg ha^{-1}) and only 2 samples of *Kuttanad* were recorded with high status of available N.
- Fourteen samples were recorded with high (>24 kg ha^{-1}) available phosphorous status and low (<10 kg ha^{-1}) available phosphorous status was found only in 4 samples.
- Soil from northern coastal plain showed lowest available K and soil from Palakkad eastern plain showed highest value of K (855.62 kg ha^{-1}). 17.92 kg ha^{-1} to 855.62 kg ha^{-1}. Soil from northern coastal plain was lowest value of available K (17.92 kg ha^{-1}).
- Eight samples were recorded with greater than 1000 mg kg^{-1} available Ca which includes all the samples collected from Palakkad eastern plain and *Pokkali* soils.
- Ten samples were deficient in available magnesium (<120 mg kg^{-1}) which includes all the samples from northern coastal plain, *Onattukara* sandy plain, northern central laterite and the two soils from *Kole* lands. All the three *Pokkali* soils were with very high Mg (>1000 mg Kg^{-1}).
- All the three *Pokkali* soils were very high in available sulphur (>5000 mg kg^{-1}). Two samples of northern coastal plain was under deficient category (<5 mg kg^{-1}).
- All the soils were sufficient in available Fe status (>5 mg kg^{-1}). All the soils from *Pokkali*, *Kole* and *Kuttanad* region showed very high status of available Fe (>500 mg kg^{-1}).
- All the collected soil samples exhibited sufficient status of available Mn (>1 mg kg^{-1})

- A total of four samples from northern coastal plain and *Onattukara* sandy plain were coming under deficient status of available Cu.
- All the collected soil samples exhibited sufficient status of available Zn. All the three *Pokkal i*soils showed comparatively very high available Zn status (>150 mg kg^{-1}).
- Lowest available B (0.04 mg kg^{-1}) was found in the soil from northern coastal plain, and the highest (5.42 mg kg^{-1}) was in the soil from *Kole* land.
- Detectable amount of available Mo was not found in any of the collected soil samples.
- Available silicon content of the soil ranged from 1 to 54.58 mg kg^{-1}.
- Low nitrate and ammoniacal nitrogen was recorded in coastal sandy soils. High content of nitrate N, ammonical N and total N was found in *Pokkali* and *Kuttanad* soil.
- Sandy soils from *Onattukara* sandy plain and northern coastal plain were with low fertility.
- Low land soils were high in fertility.
- pH showed significant positive correlation with CEC and negative correlation with most of the available nutrients and AEC. Available nutrient was significantly and positively correlated with clay and negatively correlated with sand.
- All the available micronutrient cations were significantly and positively correlated with exchangeable micronutrient cations indicating exchangeable fraction is contributing to the available pool.
- The dominant mineral present in clay and silt fraction is kaolinite except in soil from Palakkad eastern plain, where the dominance of mixed layer mineral is seen and the peak of kaolinite was not observed in X-ray diffraction pattern.
- Quartz is the dominant minerals present in sand fraction.
- The significant correlations among the fractions explain the existence of dynamic equilibrium between different fractions of each anion.

- Saloid-bound P was the fraction in least quantity among different P fractions.
- The direct effect of saliod-bound P and aluminium phosphate to the available pool is high.
- Total Si content in the soil was very high (97.6-212.9 g kg^{-1}). The contribution of residual Si to the total Si was more than 80 per cent.
- Mobile and adsorbed Si had significant positive correlation with available Si, whereas residual and total Si showed significant and negative correlation with available Si.
- All the S fractions were very high in *Pokkali* soils.
- All the fractions of S had very high significant and positive correlation among themselves.
- The dominance of different fractions of B in soil was in the order, residual B>> organically bound B> oxide bound B≈ readily soluble B>specifically adsorbed B.
- Available B was significantly and positively correlated with readily soluble B, organically bound B, residual B and total B.
- Freundlich adsorption isotherm was the best to explain adsorption of anions in soil followed by Tempkin and Langmuir adsorption isotehrm.
- Among the anion adsorption studied, only P and Mo adsorption was explained by Langmuir isotherm.
- Dominance of desorption was observed in case of Si and S. Q-I curve of these elements showed reduction in desorption after reaching a maximum desorption.
- Dominance of desorption was observed in case of B and nitrate in sandy soils at 40 ^{0}C.
- Whether it is adsorption or desorption, the process was spontaneous in most of the soil for all anions under study.
- Adsorption of B, S and Si was less than nitrate adsorption with the added concentration of respective elements.

- Phosphorous and molybdenum showed very high similarity in adsorption behavior.
- Typical L-shaped adsorption curve was obtained in low land soils of *Pokkali, Kole* and *Kuttanad* in case of P and Mo adsorption.
- Bonding energy constants of different adsorption isotherms for P and Mo adsorption was found very high in *Kuttanad* soils followed by soils from *Kole* land.
- Among P and Mo, the constants related to strength of adsorption were high for Mo adsorption than P adsorption.
- Increase in buffer power and maximum quantity adsorbed with added concentration of P and Mo was observed especially in low land soils of *Pokkali, Kole* and *Kuttanad.*
- Adsorption of anions was high in soils with high clay content and CBD extractable Fe content and low in soils with less acidic pH and more sand content.
- Adsorption of anions was found less in sandy soils from northern coastal plain and *Onattukara* sandy plain and soils from Palakkad eastern plain
- High buffer power and maximum quantity adsorbed with added concentration of nitrate was found in *Pokkali* soils.
- Preferential adsorption of phosphorous over boron was observed in binary adsorption of anions.
- Buffer power and maximum quantity adsorbed was found decreased with increasing concentration of added P in binary adsorption of P and B.
- Desorption of B was found with increasing concentration of P in sandy soils in binary adsorption study.
- A general trend in silicon extractability of different extractants was in the order; Bray I reagent > CBD > 0.5M acetic acid > 0.1M HCl.
- Very high Si content was extracted by bray reagent, regardless of soil type.

- In molybdenum-blue colorimetric estimation of P, maximum absorbance was measured at 882 nm for solutions containing different concentrations of P and solutions containing different concentration of Si.
- The possibility of over estimation of P in molybdenum blue colorimetric estimation was observed at high concentration of Si.
- The components of soils under study were with wide variation of ZPC. Constant interaction of these components in balancing the charge makes difficulty in determining ZPC and hence ZPC of the soils could not be estimated.
- Estimation of AEC using anions like P which can form inner-sphere complexes in soil lead to the over estimation of AEC of soil.

References

REFERENCES

Akosman, C. and Ozdemir, T. 2010. Adsorption dynamics and equilibrium studies of nitrate onto various soils. *Fresenius Environ. Bull.* 19(10): 2246-2252.

Anderson G. 1975. Sulfur in soil organic substances. In: Gieseking J E. (ed). *Soil Components*. Springer, Berlin, Heidelberg. pp. 333-341.

Arai, Y. 2010. X-ray absorption spectroscopic investigation of molybdenum multinuclear sorption mechanism at the goethite-water interface. *Environ. Sci. Technol.* 44(22): 8491-8496.

Arai, Y., and Sparks, D. L. 2001. ATR-FTIR Spectroscopic investigation on phosphate adsorption mechanisms at the ferrihydrite-water interface. *J. Colloid Interface Sci.* 241(2): 317-326.

Arnon, D. I. and Stout, P. R. 1939. Molybdenum as an essential element for higher plants. *Plant Physiol.* 14(3): 599-602.

Barrow, N. J. 1989. Testing a mechanistic model. X. The effect of pH and electrolyte concentration on borate sorption by soil. *J. Soil Sci*. 40: 427-435.

Barrow, N. J., Bowden, J. W., Posner, A. M., and Quirk, J. P. 1980. Describing the effects of electrolyte on adsorption of phosphate by a variable charge surface. *Aust. J. Soil Res*.18: 395-404.

Baruah, B. K., Das, B., Haque, A., Medhi, C., and Misra, A. K. 2011. Sequential extraction of common metals (Na, K, Ca and Mg) from surface soil. *J. Chem. Pharm. Res*. 3(5): 565-573.

Baumann, H. 1959. Polymerization and depolymerization of silicic acid under different conditions. *Kolloid Zeitschrift* 162: 28-35.

Beena, V. I. and Thampatti, K. C. M. 2013. Characterization of acidity in acid sulphate soils of Kerala. *J. Life Sci. 7*(8): 907-912.

Belton, D. J., Deschaume, O., and Perry, C. C. 2012. An overview of the fundamentals of the chemistry of silica with relevance to biosilicification and technological advances. *FEBS J.* 279(10): 1710-1720.

Berger, K. C. and Truog, E. 1939. Boron determination in soils and plants. *Indian Eng. Chem. Anal. Ed*. 11: 540-542.

Berger, K. C. and Truog, E. 1946. Boron availability in relation to soil reaction and organic matter content. *Soil Sci. Soc. Am. J.* 10: 113-116.

Bhattacharyya, T. and Pal, D. K. 2015. State of Indian soils. In: Pathak, H., Sanyal, S. K., and Takkar, P. N. (eds), *State of Indian Agriculture*. National Academy of Agricultural Sciences, New Delhi, pp. 6-35.

Bhindhu, P. S. 2017. Chemistry and transformations of calcium and magnesium in tropical acid soils of Kerala. PhD(Ag) Thesis, Kerala Agricultural University, 277p.

Biggar, J. W. and Cheung, M. W. 1973. Adsorption of Picloram (4-amino 3, 5, 6-trichloropicolinic acid) on Panoche, Ephrata, and Palouse soils: A thermodynamic approach to the adsorption mechanism. *Soil Sci. Soc. Am. Proc.* 77: 863-868.

Biggar, J. W. and Fireman, M. 1960. Boron adsorption and release by soils. *Soil Sci. Soc. Am. J.* 24(2): 115-120.

Bigham, J. M., Golden, D. C., Bowen, L. H., Buol, S. W., and Weed, S. W. 1978. Iron oxide mineralogy of well-drained Ultisols and Oxisols: I. Characterization of iron oxides in soil clays by Mossbauer spectroscopy, X-ray diffractometry, and selected chemical techniques. *Soil Sci. Soc. Am. J.* 42: 816-825.

Bingham, F. T., Page, A. L., Coleman, N. T., and Flach, K. 1971. Boron adsorption characteristics of selected soils from Mexico and Hawaii. *Soil Sci. Soc. Am. J.* 35: 546-550.

Biswas, H., Rattan, R. K., Datta, S. P., and Singh, A. K. 2003. Adsorption and translocation of sulfur in some tropical acid soils. *J. Plant Nutr. Soil Sci.* 166(4): 519-524.

Bleam, W. F., Pfeffer, P. E., Goldberg, S., Taylor, R. W., and Dudley, R. 1991. ^{31}P solid-state nuclear magnetic resonance spectroscopy of aluminum phosphate minerals. *Langmuir* 7: 1702-1712.

Bloesch, P. M., Bell, L. C., and Hughes, J. D. 1987. Adsorption and desorption of boron by goethite. *Aust. J. Soil Res*. 25: 377-390.

Bloom, P. R. 1981. Phosphorus adsorption by an aluminum-peat complex. *Soil Sci. Soc. Am. J.* 45(2): 267-272.

Bolan, N. S., Naidu, R., Syer, J. K., and Tillman, R. W. 1999. Surface charge and solute interactions in soils. *Adv. Agron*. 67: 87-140.

Bolan, N. S., Syers, J. K., and Tillman, R. W. 1986. Ionic strength effects on surface charge and adsorption of phosphate and sulphate by soils. *J. Soil Sci*. 37: 379-388.

Bolland, M. D. A., Posner, A, M., and Quirk, J. P. 1976. Surface charge on kaolinites in aqueous suspension. *Aust. J. Soil Res*. 14: 197-216.

Bolt, G. H. 1976. Adsorption of anions by soil. In: Bolt, G. H. and Bruggenwert, M. G. M. (eds.). *Soil Chemistry: A. Basic Elements*. Elsevier Science, Amsterdam, Newyork. pp. 91-95.

Boltz, D. F. and Mellon, M. G. 1947. Determination of phosphorus, germanium, siliconand arsenic by the heteropoly blue method. *Anal. Chem*. 19: 873-877.

Bray, R. H. and Kurtz, L. T. 1945. Determining total, organic and available forms of phosphate in soils. *Soil Sci*. 59: 39-45.

Broyer, T. C., Carlton, A. B., Johnson, C. M., and Stout, P. R. 1954. Chlorine-a micronutrient element for higher plants. Plant physiology. 29(6): 526-532.

Carter, D. L., Heilman, M. D., and Gonzalez, C. L. 1965. Ethylene glycol monoethyl ether for determining surface area of silicate minerals. *Soil Sci.* 100: 356-360.

Carter, M. R. and Gregorich, E. G. 2007. Soil sampling and methods of soil analysis (2nd Ed.). CRC Press Taylor and Francis Group 6000 Broken Sound Parkway NW. 1224p.

Cataldo, A., Haroon, M., Schrader, L. E., and Youngs, V. L. 1975. Rapid colorimetric determination of nitrate in plant tissue by nitrate in plant-tissue by nitration of salicylic-acid. *Commun. Soil Sci. Plant Anal.* 6(1): 71-80.

Celi, L., Lamacchia, S., Marsan, T. A., and Barberis, E. 1999. Interaction of inositol phosphate on clays: adsorption and charging phenomena. *Soil Sci.* 164: 574-585.

Cerozi, B. S. and Fitzsimmons, K. 2019. The effect of pH on phosphorus availability and speciation in an aquaponics nutrient solution. *Bioresour. Technol.* 219: 778-781.

Chander, G., Verma, T. S., and Sharma, S. 2007. influence of boron and farmyard manure on available boron and exchangeable calcium and their removal by cauliflower in the boron- deficient soils of Himachal Pradesh. *J. Indian Soc. Soil Sci.* 55(1): 62-66.

Chao, T. T., Harward, M. E., and Fang, S. C. 1962. Adsorption and desorption phenomenon of sulphate ions in soils. *Soil Sci. Soc. Am. Proc.* 26: 234-237.

Chng, H. Y., Ahmed, H. O., and Majid, N. M. 2014. Improving phosphorus availability in an acid soil using organic amendments produced from agro-industrial wastes. *Sci. World J.* 2014: 1-7.

Choi, W. W. and Chen, K. Y. 1979. Evaluation of boron removal by adsorption on solids. *Environ. Sci. Technol.* 13: 189-196.

Chorover, J., Amistadi, M. K., and Chadwick, O. A. 2004. Surface charge evolution of mineral-organic complexes during pedogenesis in Hawaiian basalt. *Geochimica et Cosmochimica Acta* 68:4859-4876.

Choudhary, O. P., Hundal, H. S., and Kumar, S. n. d. Competitive Adsorption of Phosphate, Molybdate, Borate and Silicate in Binary-anion mixture with soils. Available: http://natres.psu.ac.th/link/SoilCongress/bdd/symp6/728-r.pdf [21 june 2019].

Ciavatta, C. Antisari, L.V., and Sequi, P. 1990. Interference of soluble silica in the determination of orthophosphate-phosphorus. *J. Environ. Qual.* 19: 761-764.

Condron, L. M., Turner, B. L., and Cade-Menun, B. J. 2005. Chemistry and dynamics of soil organic phosphorus. In Sims, I. T. and Sharpley, A. N. (eds), *Phosphorus:Agriculture and the Environment*. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, Madison,Wiscousin, pp. 87-121.

Cruywagen, J. J., Draaijer, A. G., Heyns, J. B. B., and Rohwer, E. A. 2002. Molybdenum(VI) equilibria in different ionic media: Formation constants and thermodynamic quantities, *Inorg. Chim. Acta* 331: 322-329.

Danilova, A. A., Sauer, A. D., Breuer, B. J., Herrmann, A. L., Zarei, A. M., and Stahr, K. 2010. Development of a method for sequential extraction of Si-pools from soils. 19th World Congress of Soil Science, Soil Solutions for a Changing World, 1-6 August 2010, Brisbane, Australia.

Datta, S. P., Rattan, R. K., Suribabu, K., and Datta, S. C. 2002. Fractionation and colorimetric determination of boron in soils. *J. Plant Nutr. Soil. Sci.* 165: 179-184.

Deepa, K. P. 1995. Fertility investigations and taxonomy of the Regional Agricultural Research Station, Pattambi, MSc(Ag) thesis, Kerala Agricultural University, Thrissur. 114p.

Dey, A., Dwivedi, B. S., Meena, M. C., and Datta, S. P. 2013. adsorption-desorption of boron in major soils of India. *J. Indian Soc. Soil Sci.* 61(3): 179-187.

Doddamani, V. S. and Rao, T. S. 1996. Phosphorus forms and fixation in acidic soils. *Mysore J. agric. Sci.* 23, 18-25.

Dolui, A. K. and Nandi, S. 1989. Adsorption and desorption of sulphate in some soils of West Bengal. *Proc. Indian Natl. Sci. Acad.* 5- 6: 483-488.

Dongale, J. H. 1993. Depth wise distribution of different forms of phosphorus in lateritic soils of coastal region. *J. Indian Soc. Soil Sci.* 41: 62-66.

Dutta, S. and Mukhopadhyay. D. 2007. Fractionation of inorganic phosphorus in some acid soils of West Bengal (India). *Asian J. Soil Sci.* 2(1): 18-23.

El-Baruni, B. and Olsen, S. R. 1979. Effect of manure on solubility of phosphorus in calcareous soils. *Soil Sci.* 128(4): 219-225.

Elgawhary, S. M. and Lindsay, W. L. 1972. Solubility of silica in soils. *Soil Sci. Soc. Am. J.* 36(3): 439-442.

Elkins, D. M. and Ensminger, L. E. 1971. Effect of soil pH on the availability of adsorbed sulfate. *Soil Sci. Soc. Am. J.* 35(6): 931-934.

Elrashidi, M. A. and O'Connor, G. A. 1982. Influence of solution composition on sorption of zinc by soils. *Soil Sci. Soc. Am. J.* 46(6): 1153-1158.

Ensminger, L. E. 1954. Some factors affecting the adsorption of sulfate by Alabama soils. *Soil Sci. Soc. Am. J.* 18(3): 259-264.

Ferguson, J. F., Jenkins, D., and Eastman, J. 1973. Calcium phosphate precipitation at slightly alkaline pH values. *Water Pollut. Control Fed.* 45(4): 620-631.

Fontes, M. P. F. and Weed S. B. 1991. Iron oxides in selected Brazilian Oxisols: I. Mineralogy. *Soil Sci. Soc. Am. J.* 55(4):1143-1149.

Frederick, L. R., S tar key, R. L., and Segal, W. 1957. Decomposability of some organic sulphur compounds in soils. *Soil Sci. Soc. Am. Proc*. 21, 287-292.

Friesen, D. K., Sanz, J. I., Correa, F. J., Winslow, M. D., Okada, K., Dantoff, L. E., and Snyder, G. H. 1994. Silicon deficiency of upland rice on highly weathered Savanna soils in Colombia.I. Evidence of major rice yield. IX *Conferencia Internaciaonal America Latina*, Marco. Brazil. 21-25.

Fu, Y., Hamsen, R. S., and Barlette, F. E. 1948. Thermodynamics of adsorption from solutions. I. The mobility and activity coefficients of adsorbed layers. *J. Phy. Chem.* 52: 374-386.

Geetha P. 2008. Quantity - Intensity relations of phosphorus with reference to its bioavailability in lateritic soils. MSc(Ag) Thesis. Kerala Agricultural University, Thrisuur. 111p.

George, A. 2011. Availability indices of boron in major soil groups of Kerala. M.Sc.(Ag.) thesis, Kerala Agricultural University, Thrissur, 89p.

Georgiadis, A., Sauer, D., Herrmann, L., Breuer, J., Zarei, M., and Stahr, K. 2013. Development of a method for sequential Si extraction from soils. *Geoderma* 209-210: 251-261.

Ghosh, G. K. and Sarkar, A. K. 1994. Availability of sulphur and some micronutrients in acid sedentary soils of Chotonagpur region. *J. Indian Soc. Soil Sci.* 42(3): 464-466.

Gokila, B., Sivagnanam, S., Saravanapandian, P., and Baskar, K. 2017. Sorption and desorption behavior of sulphur in soils of Tamil Nadu, India. *Int. J. Chem. Stud*. 5(4): 1118-1123.

Goldberg, S. 1997. Reactions of B in soil. *Plant Soil* 193(2): 35-48.

Goldberg, S. and Forster, H. S. 1998. Factors affecting molybdenum adsorption by soils and minerals. *Soil Sci.* 163: 109-114.

Goldberg, S. and Glaubig, R. A. 1986. Boron adsorption on California soils. *Soil Sci. Soc. Am. J*. 50: 1173-1176.

Goldberg, S., and Sposito, G. 1985. On the mechanism of specific phosphate adsorption of hydroxylated mineral surfaces: A review. *Commun. Soil Sci. Plant. Anal.* 16: 801-821.

Goldberg, S., Forster, H. S., and Godfrey, C. L. 1996. Molybdenum adsorption on oxides, clay minerals and soils. *Soil Sci. Soc. Am. J.* 60: 425-432.

Goldberg, S., Forster, H. S., and Heick, E. L. 1993. Temperature effects on boron adsorption by reference minerals and soils. Soil Sci. 156(5): 316-321.

Goldberg, S., Scalera, E., and Adamo, P. 2008. Molybdenum adsorption by volcanic Italian soils. *Commun. Soil Sci. Plant Anal*. 39: 693-706.

Gonchar, K. A., Kitaeva, V. Y., Zharik, G. A., Eliseev, A. A., and Osminkina, L. A. 2019. Structural and optical properties of silicon nanowire arrays fabricated by metal assisted chemical etching with ammonium fluoride. *Frontiers Chem.* 6: 653.

Gonzales-Batista, A., Hernandez-Moreno, J. M., Fernandez-Caldas, E and Herbillon, A. J. 1982. Influence of silica content on the surface charge characteristics of allophanic clays. *Clays Clay Miner.* 30(2): 103-110.

Gressel, N., McColl, J. G., Preston, C. M., Newman, R. H., and Powers, R. F. 1996. Linkages between phosphorus transformations and carbon decomposition in a forest soil. *Biogeochemistry* 33: 97-123.

Gu, B. and Schulz, R. K. 1991. Anion retention in soil: possible application to reduce migration of buried technetium and iodine (No. NUREG/CR--5464). Nuclear Regulatory Commission. 32p.

Gu, B. H., Schmitt, J. Chen, Z. Liang, L. Y., and McCarthy, J. F. 1995. Adsorption and desorption of different organic-matter fractions on iron oxide. *Geochimica et Cosmochimica Acta* 59: 219-229.

Gunary, D. 1970. A new adsorption isotherm for phosphate in soil. J. *Soil Sci.* 21(1): 72-77.

Hamdi, W., Gamaoun, F., Pelster, D. E., and Seffen, M. 2013. Nitrate Sorption in an Agricultural profile. *Appl. Environ. Soil Sci.* 2013: 1-7.

Haque, I. and Walmsley, D. 1973. Adsorption and desorption of sulphate in some soils of the West Indies. *Geoderma* 9(4): 269-278.

Harrison, R. B., Johnson, D. W., and Todd, D. E. 1989. Sulfate adsorption and desorption reversibility in a variety of forest soils. *J. Environ. Qual.* 18: 419-426.

Haynes, R. J. 2014. A contemporary overview of silicon availability in agricultural soils. *J. Plant Nutr. Soil Sci.* 177(6): 831-844.

Haynes, R. J., and Zhou, Y.-F. 2018. Competitive and noncompetitive adsorption of silicate and phosphate by two acid Si-deficient soils and their effects on P and Si extractability. *Soil Sci. Plant Nutr.* 64(4): 535-541.

Hendershot, W. H. and Duquette, M. 1986. A simplified barium chloride method for determining cation exchange capacity and exchangeable cations. *Soil Sci. Soc. Am. J.* 50: 605-608.

Hendershot, W. H. and Lavkulich, L. M. 1983. Effect of sesquioxide coatings on surface charge of standard mineral and soil samples. *Soil Sci Soc. Am. J.* 47: 1252-1260.

Herbillion, A. J. and Vinhan, J. T. 1969. Heterogeneity in silicon-iron mixed hydroxides. *J. Soil Sci.* 20: 223-235.

Hesse P R. 1971. *A Textbook of Soil Chemical Analysis* (Indian reprint, 1994). CSB Publishers & Distributors Private Ltd. New Delhi, 520p.

Hingston, F. J., Posner, A. M., and Quirk, J. P. 1972. Anion adsoption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. *Eur. J. Soil Sci.* 23(2): 177-192.

Hingston, F. J., Posner, A. M., and Quirk, J. P. 1974. Anion adsorption by goethite and gibbsite. II. Desorption of anions from hydrous oxide surfaces. *J. Soil Sci.* 25(1): 16-26.

Hou, J., Evans, L. J., and Spiers, G. A. 1994. Boron fractionation in soils. *Commn. Soil Sci. Plant Anal.* 25(9): 1841-1853.

Hou, J., Evans, L. J., and Spiers, G. A. 1996. Chemical fractionation of soil boron. I. Method development. *Can. J. Soil Sci.* 76: 485-491.

Hug, S. J. 1997. In Situ Fourier Transform Infrared measurements of sulfate adsorption on hematite in aqueous solutions. *J. Colloid Interface Sci*. 188(2): 415-422.

Inam, E., Etim, U. J., Akpabio, E. G., and Umoren, S. A. 2017. Process optimization for the application of carbon from plantain peels in dye abstraction. *J Taibah Univ. Sci.* 11(1): 173-185.

Jackson, M. L. 1958. *Soil Chemical Analysis*. Prentice Hall , Inc. Englewood Cliffs, New Jersey. 498p.

Jackson, M. L. 1979. Soil Chemical Analysis – Advanced Course (2nd Ed.): A Manual of Methods Useful for Instruction and Research in Soil Chemistry, Physical Chemistry of Soils, Soil Fertility, and Soil Genesis, University of Wisconsin, Madison, WI, USA, p. 895.

John, I. E. 2019. Carbon: Nitrogen dynamics in acid sulphate and acid saline rice soils of Kerala. PhD(Ag) Thesis, Kerala Agricultural university, 163p.

Johnson, C.E., 2002. Cation exchange properties of acid forest soils of the northeastern USA. *Eur. J. Soil Sci*. 53: 271-282.

Jones, L. H. P. and Handreck, K. A. 1967. Silica in soils, plants, and animals, *Adv. Agron*. 19: 107-149.

Kabay, N. and Bryjak, M. 2015. Boron removal from seawater using reverse osmosis integrated processes. *Boron Separation Processes*. Elsevier, 412p.

Kaila, A. 1956. Phosphorus in virgin peat soils. 1959. *Agric. Food Sci.* 28(1):142-167.

Karak, T., Das, D. K., Singh, U. K., and Maiti, D. 2005. Influence of pH on soil charge characteristics and cadmium sorption in some non-contaminated soils of Indian subtropics. *Sci. World J.* 5: 183-194.

Karimian, N. and Cox, F. R. 1978. Adsorption and extractability of molybdenum in relation to some chemical properties of soil. *Soil Sci. Soc. Am. J.* 42: 757-761.

Karltun, E. and Gustafsson, J. P. 1993. Interference by organic complexation of Fe and Al on the $SO_4{}^{2-}$ adsorption in spodic B horizons in Sweden. *J. Soil Sci.* 44: 625-632.

Keeney, D. R. and Nelson, D. W. 1982. Nitrogen in organic forms. In. Page, A. L. (eds), *Methods of Soil Analysis*, American Society of Agronomy, Madison, 643-698.

Khandelwal, A., Narayanan, N., and Varghese, E. 2020. Linear and nonlinear isotherm models and error analysis for the sorption of Kresoxim-Methyl in agricultural soils of India. *Bull. Environ. Contam. Toxicol.* 104: 503-510.

Khawmee, K., Suddhiprakarn, A., Kheoruenromne, I., and Singh, B. 2013. Surface charge properties of kaolinite from Thai soils. *Geoderma* 192: 120-131.

King, E. K., Perakis, S. S., and Pett-Ridge, J. C. 2017. Molybdenum isotope fractionation during adsorption to organic matter. *Geochimica et Cosmochimica Acta* 222: 584-598.

Klucakova, M. 2010. Adsorption of nitrate on humic acids studied by flow-through coulometry. *Environ. Chem. Lett.* 8: 145-148.

Koch, C. B., Bentzon, M. D., Larsen, E. W., and Borggaard, O. K. 1992. Clay mineralogy of two Ultisols from Central Kalimantan, Indonesia. *Soil Sci.* 154(2): 158-167.

Kodera, K., and Onishi, Y. 1959. Molecular cross sectional areas for the determination of specific surface areas of solids: carbon block. *Chem. Japan Bull.* 32: 356-361.

Korndorfer, G. H., Snyder, G. H., Ulloa, M., and Datnoff. L. E. 2001. Calibration of soil and plant silicon for rice production. *J. Plant Nutri.* 24: 1071-1084.

Krishnakumar, P. G. 1991. Taxonomy and fertility capability assessment of the soils in the command area of Edamalayar project. MSc(Ag) thesis, Kerala Agricultural University, Thrissur, 117p.

KSHIS [Kerala Soil Health Information System]. 2020. KSHIS home page [online]. Available: http://www.keralasoilfertility.net/en/fertility_status_kerala.jsp [10 April 2020].

Lang, F. and Kaupenjohann, M. 1999. Molybdenum fractions and mobilization kinetics in acid forest soils. *J. Plant Nutr. Soil Sci.* 162: 309-314.

Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc*. 40: 1361-1403.

Laxminarayana, K. 2007. Distribution of inorganic p fractions and critical limits of available p in rice soils of Mizoram. *J. Indian Soc. Soil Sci.* 55(4): 481-487.

Lekshmi, A. V. 2016. Silicon availability of tropical soils with respect to rice nutrition. PhD(Ag) Thesis, Kerala Agricultural University. 235p.

Li, W. and Johnson, C. E. 2016. Relationships among pH, aluminum solubility and aluminum complexation with organic matter in acid forest soils of the Northeastern United States. *Geoderma* 271: 234-242.

Lindsay, W. L. 1979. *Chemical Equilibria in Soils*. New York, John Wiley and Sons, 450p.

Lindsay, W. L. and Norvell, W. A. 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper. *Soil Sci. Soc. Am. J.* 42: 421-428.

Lungmuana, Ghosh, S. K., and Patra, P. K. 2012. Distribution of different forms of phosphorus in surface soils of rice growing areas of red and laterite zone of West Bengal. *J. Indian Soc. Soil Sci.* 60(3): 204-207.

Ma, M. 2011. The dispersive effect of sodium silicate on kaolinite particles in process water: Implications for iron-ore processing. *Clays Clay Miner.* 59(3): 233-239.

Majidi, A., Rahnemaie, R., Hassani, A., and Malakouti, M. J. 2010. Adsorption and desorption processes of boron in calcareous soils. *Chemosphere* 80(7): 733-739.

Massoumi, J. and Cornfield, A. H. 1963. A rapid method for determination sulphate in water extracts of soils. *Analyst* 88: 321-322.

Matichenkov, V. V. and Bocharnikova, E. A. 2001. Chapter 13 The relationship between silicon and soil physical and chemical properties. *Studies in Plant Science.* Elsevier, pp. 209-219.

McKeague, J. A. and Cline, M. G. 1963a. Silica in soils, *Adv. Agron.*, 15: 339–396.

McKeague, J. A. and Cline, M. G. 1963b. The form and concentration of dissolved silica in aqueous extracts of some soils. *Can. J. Soil. Sci.* 43: 70-82.

McVay, K. A., Radcliffe, D. E., West, L. T., and Cabrera, M. L., Tisdale, S. L., Nelson, W. L. 2004. Anion exchange in saprolite. *Vadose Zone J.* 3: 668-675.

Mehadi, A. A. and Taylor, R. W. 1988. Phosphate adsorption by two highly-weathered soils. *Soil Sci. Soc. Am. J.* 52(3): 627-632.

Mehra, O. P. and Jackson, M. L. 2013. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays Clay Miner.* 7(1): 317-327.

Melese, A., Gebrekidan, H., Yli-Halla, M., and Yitaferu, B. 2015. Phosphorus status, inorganic phosphorus forms, and other physicochemical properties of acid soils of Farta District, Northwestern Highlands of Ethiopia. *Appl. Environ. Soil Sci.* 2015: 1-11.

Metwally, A. I., El-Damaty, A.H., and Yousry, M. 1974. Anion adsorption as a possible mechanism of boron retention by soils. *Egypt J. Soil Sci.* 14: 23-31.

Mise, S. R. and Bashetty, R. 2013. Study of nitrate adsorption characteristics on red soil. *Int. J. Res. Eng. Technol.* IC-RICE Conference Issue: 334-337.

Moghimi, A. H., Hamdan, J., Shamshuddin, J. Samsuri, A. W., and Abtahi, A. 2013. Physicochemical properties and surface charge characteristics of arid soils in southeastern Iran. *Appl. Environ. soil sci.* 2013: 1-11.

Mohsenipour, M., Shahid, S., and Ebrahimi, K. 2015. Nitrate adsorption on clay kaolin. *J. Chem.* 2015: 1-6.

Mott, C. J. B. 1981. Anion and ligand exchange. In. Greenland, D. J. and Hayes, M. H. B. (eds) ,*The Chemistry of Soil Processes*. John Wiley and Sons. pp 179-219.

Motta, M. M. and Miranda, C. F. 1989. Molybdate adsorption on kaolinite, montmorillonite and illite: Constant capacitance modeling. *Soil Sci. Soc. Am. J.* 53: 380-385.

Muhlbachova, G., Cermak, P., Vavera, R. Kasi, M., Pechova, M., Markova, K., Kusa, H., Ruzek, P., Hlusek, J., and Losak, T. 2017. Boron availability and uptake under increasing phosphorus rates in a pot experiment. *Soil Environ.* 63(11): 483-490.

Murata, K. and Ikeda, S. 1983. Studies on yellow and colourless molybdophosphate complexes in the aqueous solution by laser Raman spectroscopy. *Polyhedron* 2: 1005-1008.

Murphy, J. and Riley, J. P. 1962. A modified single solution method for the determrnation of phosphate in natural waters. *Anal. Chim. Acta* 27: 31-36.

Nagul, E. A., McKelvie, I. D., Worsfold, P., and Kolev, S. D. 2015. The molybdenum blue reaction for the determination of orthophosphate revisited: Opening the black box. *Analytica Chimica Acta* 890: 60-82.

Nair, K. M., Sureshkumar, P. and Narayanankutty, M. C. 2013. Soils of Kerala. In: Rajasekharan, P., Nair, K. M., Rajasree, G., Sureshkumar, P., Narayanankutty, M. C. (eds.), *Soil Fertility Assessment and Information Management for Enhancing Crop Productivity in Kerala.* Kerala State Planning Board, Thiruvananthapuram, pp. 72-92.

Niwano, M., Kurita, K., Takeda, Y., and Miyamoto, N. 1993. Formation of hexafluorosilicate on Si surface treated in NH_4F investigated by photoemission and surface infrared spectroscopy. *Appl. Phys. Lett.* 62(9): 1003-1005.

Nor, Y. M. 1981. Sulphur mineralization and adsorption in soils. *Plant Soil* 60(3): 451-459.

Oberg G. 1998. Chloride and organic chlorine in soil. *Acta Hydrochimica et Hydrobiologica* 26(3): 137-144.

Ognala, M., Frossard, E. and Thomas, F. 1994. Glucose-1-phosphate and myo-inositol hexaphosphate adsorption mechanisms on goethite. *Soil Sci. Soc. Am. J.* 58: 332-337.

Okamura, Y. and K. Wada. 1983. Electric charge characteristics of horizons of ando(B) and red-yellow B soils and weathered pumices. *J. Soil Sci*. 34: 287-295.

Olsen, S. R., and Watanabe, F. S. 1957. A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir isotherm. *Soil Sci. Soc. Am. J.* 21(2): 144-149.

Olsen, S. R., Cole, C. V., Watanabe, I., and Dean, L. A. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. *USDA Circ. 939*. USDA, Washington DC. 19p.

Pansu, M. and Gautheyrou, J. 2007. *Handbook of Soil Analysis Mineralogical, Organic and Inorganic Methods.* Springer-Verlag, Berlin Heidelberg New York, 993p.

Parfitt, R. L. and Smart, R. S. C. 1978. Mechanism of sulfate adsorption on iron oxides. *Soil Sci. Society of Am. J.* 42: 48-50.

Patle, T., Khaddar, V. K., Tiwari, R., and Para, P. 2019. Phosphorus fractions in different soil orders in India and their relationship with soil properties. *Int. J. Curr. Microbiol. App. Sci.* 8(5): 1609-1620.

Pendias, K. A., and Pendias, H. 2001. *Trace Elements in Soils and Plants*, (3rd ed), CRC Press, New York, 260–267.

Persson P., Nilsson N., and Sjrberg S. 1996. Structure and bonding of orthophosphate ions at the iron oxide-aqueous interface. *J. Colloid Interface Sci*. 177, 263-275.

Peterson, G. W. and Corey, R. R. 1966. A modified Chang and Jackson procedure for routine fractionation of inorganic soil phosphorus. *Soil Sci. Soc. Am. Proc.* 30: 563-564.

Peterson, L. A., and Newman, R. C. 1976. Influence of Soil pH on the Availability of Added Boron1. *Soil Sci. Soc. Am. J.* 40(2): 280.

Qafoku, N. P., Ranst, E. V., Noble, A., and Baert, G. 2004. Variable charge soils: their mineralogy, chemistry and management. *Adv. Agron.* 84: 159-215.

Qafoku, N. P., Sumner, M. E. and Radcliffe, D. E. 2000. Anion transport in columns of variable charge subsoils: nitrate and chloride. *J. Environ. Qual.* 29(2): 484-493.

Qiu, L. P., Zhang, X. C., Cheng, J. M. and Han, X. N. 2010. Isotherms and kinetics of Si adsorption in soils, *Soil. Plant Sci.* 60(2): 157-165.

Randhawa, P. S., Condron, L. M., Di1, H. J., Sinaj, S., and McLenaghen, R. D. 2005. Effect of green manure addition on soil organic phosphorus mineralization. *Nutrient Cycling in Agroecosystems* 73:181-189.

Righi, D. and De-Coninck, F. 1977. Mineralogic evolution in hydromorphic sandy soils and Podzols in “Landes du Medoc”, France. *Geoderma* 19: 339-359.

Robinson, G. W. 1922. A new method for the mechanical analysis of soils and other dispersions. *J. Agri. Sci*. 12: 306-321.

Roy, W. R., Hassett, J. J., and Griffin, R. A. 1986. Competitive coefficients for the adsorption of arsenate, molybdate, and phosphate mixtures by soils. *Soil Sci. Soc. Am. J.* 50: 1176-1182.

Rutkowska, B., Szulc, W., Spychaj-Fabisiak, E., and Pior, N. 2017. Prediction of molybdenum availability to plants in differentiated soil conditions. *Plant Soil Environ.* 63(11): 491-497.

Saccone, L., Conley, D. J., Koning, E., Sauer, D., Sommer, M., Kaczorek, D., and Kelly, E. F. 2007. Assessing the extraction and quantification of amorphous silica in soils of forest and grassland ecosystems. *Eur. J. Soil Sci.* 58(6): 1446-1459.

Saha, J. K., Singh, M. V., and Sharma, B. L. 1998, Available status of boron in major soils groups of Madhya Pradesh. *J. Indian Soc. Soil Sci.* 46(3): 478-479.

Sakurai, K., Teshima, A., and Kyuma, K. 1990. Changes in Zero Point of Charge (ZPC), Specific Surface Area (SSA), and Cation Exchange Capacity (CEC) of kaolinite and montmorillonite, and strongly weathered soils caused by Fe and Al coatings. *Soil Sci. Plant Nutr.* 36(1): 73-81.

Salahi, S. and Ghorbani, M. 2014. Adsorption parameters studies for the removal of mercury from aqueous solutions using hybrid sorbent. *Adv. Polym. Tech.* 33(4): 1-6.

Santhosh, C. 2013. Chemistry and transformation of boron in soils of Kerala. PhD(Ag) thesis, Kerala Agricultural University, Thrissur, 257p.

Saren, S., Barman, S., Mishra, A., and Saha, D. 2016. Effect of added organic matter and sulphur on transformation of different fractions of sulphur in soil. *The bioscan.* 11(4): 2399-2403.

Sauer, D., Saccone, L., Conley, D.J., Herrmann, L., and Sommer, M., 2006. Review of methodologies for extracting plant-available and amorphous Si from soils and aquatic sediments. *Biogeochemistry* 80 (1): 89-108.

Saunders, W. M. H and Williams, E. G. 1955. Observations on the determination of total organic phosphorous in soils. *Eur. J. Soil Sci.* 6(2): 254-267.

Savant, N. K., Snyder, G. H., and Datnoff, L. E. 1997. Silicon management and sustainable rice production. *Adv. Agron*. 58: 151-199.

Schlesinger, W. H., and Bernhardt, E. S. 2013. *Biogeochemistry: An Analysis of Global Change.* Academic press. 668p.

Shafiq, M., Ranjha, A. M., Yaseen, M., Mehdi, S. M., and Hannam, A. 2008. Comparison of Freundlich and Langmuir adsorption equations for boron adsorption on calcareous soils. *J. Agric. Res*. 46(2): 141-148.

Shah, T. I., Rai, A. P., and Aziz, M. 2019. Relationship of phosphorus fractions with soil properties in mothbean growing acid soils of North Western Indian Himalayas. *Commun. Soil Sci. Plant Anal.* 50(9): 1192-1198.

Shamshuddin, J. and Ismail, H. 1995. Reactions of ground magnesium limestone and gypsum in soils with variable-charged minerals. *Soil Sci. Soc. Am. J.* 59: 106-112.

Sharma, U., Subehia, S. K., Rana, S. S., Sharma, S. K., and Negi, S. C. 2014. Soil sulphur fractions and their relationship with soil properties and rice (*Oryza sativa* L) yield under long-term integrated nutrient management in an acid Alfisol. *Res.Crops* 15(4) : 738-745.

Sheindorf, C. H., Rebhun, M., and Sheintuch, M. 1981. A Freundlich-type multicomponent isotherm. *J. Colloid Interface Sci.* 79(1): 136-142.

Sheoran, O. P., Tonk, D. S., Kaushik, L. S., Hasija, R. C., and Pannu, R. S. 1998. *Statistical Software Package for Agricultural Research Workers*. Recent advances in information theory, statistics & computer applications, Department of Mathematics Statistics, CCS HAU, Hisar, 139-143.

Shivasharanappa, Srinivas, P., and Kushtagi, S. 2013. Adsorption studies of nitrate by geo-physical environment (Laterite soil) of the study area Bidar Urban and its industrial area, Karnataka state, India. *Int. Lett. Chem. Phys. Astronom.* 6: 66-76.

Shuman, L. M. 1975. The effect of soil properties on zinc adsorption by soils. *Soil Sci. Soc. Am. Proc*. 39: 455-458.

Siever, R. and Woodford, N. 1973. Sorption of silica by clay minerals, *Geochim. Cosmochim. Ac*. 37: 1851-1880.

Silpa P. 2020. [Spatial and temporal variations in nutrient dynamics in *Pokkali* soils of Kerala]. Unpublished raw data.

Silva E. C., Muraoka, T., Franzini, V. I., Villanueva, F. C. A., Buzetti, S., and Moreti, D. 2012. Phosphorus utilization by corn as affected by green manure, nitrogen and phosphorus fertilizers. *Pesq. agropec. Bras.* 47(8): 1150-1157.

Sims, J. R. and Johnson, G. V. 1991. Micronutrient soil tests. In: Mortvedt, J. J., Cox, F. R., Shuman, L. M. and Welch, R. M. (eds), *Micronutrient in Agriculture* (2nd Ed.). Soil Science Society of America, Madison, USA, pp. 427-476.

Singh, M. 1971. Equilibrium adsorption of boron in soils and clays. *Geoderma* 5(3): 209-217.

Singh, T. B., Patra, S. K., and Devi, K. N. 2013. Study on sesquioxide content and lime requirement of lateritic soils. *Int. J. Bio-resour. Stress Manag.* 4(4): 518-522.

Skjemstardand, J. O. and Koppi, A. J. 1983. Chemical and charge characteristics of kaolinite soils of South-east Queensland. *Aust. J. Soil Res*. 21:271-283.

Smedley, P. L. and Kinniburgh, D. G. 2017. Molybdenum in natural waters: A review of occurrence, distributions and controls. *Appl. Geochem*, 84: 387-432.

Soil Survey Organisation and Agriculture (S.C. unit) Department. 2007. *Bench mark soils of Kerala.* Govt. of Kerala

Sokolova, T. A. 2013. The destruction of quartz, amorphous silica minerals, and feldspars in model experiments and in soils: Possible mechanisms, rates, and diagnostics (the analysis of literature). *Eurasian soil sci.* 46(1): 91-105.

Sommer, M., Kaczorek, D., Kuzyakov, Y., and Breuer, J. 2006. Silicon pools and fluxes in soils and landscapes-a review. *J. Plant Nutr. Soil Sci*. 169: 310-329.

Sparks, D. L. 2003. *Environmental Soil Chemistry* (2nd Ed.). *Elsevier,* Academic Press, London, 352p.

Sposito, G. 1982. On the use of the Langmuir equation in the interpretation of “adsorption” phenomena: ii. the “two-surface” Langmuir equation. *Soil Sci. Soc. Am. J.* 46(6): 1147-1152.

Sposito, G. 1984. *The Surface Chemistry of Soils*. Oxford University Press, NewYork, 245p.

Srinivasarao, C., Ganeshamurthy, A. N., Ali, M., Singh, R. N. and Singh, K. K. 2004. Sulphur fractions distribution and their relationships with soil properties in different soil types of major pulse-growing regions of India. *Commun. Soil Sci.Plant Anal.* 35(19-20): 2757-2769.

Srivastava, P., Prakash, B. Sehgal, J. L., and Kumar, S. 1994. Role of neotectonics and climate in development of Holocene geomorphology and soils of the Gangetic Plains between the Ramganga and Rapti rivers. *Sedimen. Geology*. 94: 129-151.

Stewart, J. W. B. and Tiessen, H. 1987. Dynamics of soil organic phosphorus. *Biogeochemistry* 4(1): 41-60.

Strahm, B. D. and Harrison, R. B. 2006. Nitrate sorption in a variable-charge forest soil of the Pacific Northwest. *Soil Sci.* 171: 313-321.

Stumm, W. 1992. *Chemistry of the Solid-Water Interface*. Wiley, New York, 432p.

Stumm, W. and Morgan, J. J. 1981. *Aquatic Chemistry.* Wiley, New York, 1042p.

Su, C. and Suarez, D. L. 1995. Coordination of adsorbed boron: A FTIR spectroscopic study. *Environ. Sci. Technol.* 29(2): 302-311.

Subbiah, B. and G. L. Asija. 1956. Alkaline permanganate method of available nitrogen determination. *Curr. Sci.* 25: 259.

Sun, W. and Selim, H. M. 2018. Kinetics of molybdenum adsorption and desorption in soils. *J. Environ. Qual.* 47(3): 504-512.

Sureshkumar, P. 1993. Variability in zinc availability in soils and cultivars of rice and wheat. PhD(Ag) thesis, Indian Agricultural Research Institute, New Delhi, 160p.

Syers, J. K., Browman, M. G., Smillie, G. W., and Corey, R. B. 1973. Phosphate sorption by soils evaluated by the Langmuir adsorption equation. *Soil Sci. Soc. Am. J.* 37(3): 358-363.

Tabatabai, M. A. 1982. Sulfur. In: Page, A. L. Keeney, D. R., Baker, D. E., Miller, R. H., Roscoe Ellis Jr., and Rhoades, J. D. (eds), *Methods of Soil Analysis Part 2. Chemical and Microbiological Properties* (2nd Ed.). American Society of Agronomy, Madison, Wisconsin, USA, pp. 501-538.

Tamungang, N, E, B., David, M. A., Alakeh M. N., and Adalbert, O. A. 2016. Phosphorus adsorption isotherms in relation to soil characteristics of some selected volcanic affected soils of Foumbot in the West Region of Cameroon. *Int. J. Soil Sci*. 11 (2): 19-28.

Tan, K. H. 2011. *Principles of soil chemistry*. CRC press. 362p.

Tan, K. T. 2000. *Soil Sampling, Preparation and Analysis*. Taylor and Francis. 245p.

Taylor, P. 1995. Interactions of silica with iron oxides: Effects on oxide transformations and sorption properties. Available: https://inis.iaea.org/collection/NCLCollectionStore/_Public/27/012/27012842.pdf [30 Nov 2019].

Tejedor-Tejedor, M. I. and Anderson, M. A. 1990. The protonation of phosphate on the surface of goethite as studied by CIR-FTIR and electrophoretic mobility. *Langmuir* 6(3): 602-611.

Theng, B. K. G., Russell, M. Churchmanand, G, J., and Parfitt, R. L. 1982. Surface properties of allophane, halloysite, and imogolite. *Clays Clay Miner.* 30:143-149.

Tisdale, S. L., Nelson, W. L., and Beaton, J. D. 1985. *Soil Fertility and Fertilizers* Macmillan Publishers. New York, pp. 107-510.

Toner, C. V., Sparks, D. L., and Carski, T. H. 1989. Anion exchange chemistry of Middle Atlantic soils: Charge properties and nitrate retention kinetics. *Soil Sci. Soc. Am. J.* 53(4): 1061-1067.

Truesdale, V. W. and Smith, C. J. 1975. The Formation of molybdosilicic acids from mixed solutions of molybdate and silicate. *Analyst* 100: 203-212.

Walkley, A. J. and Black, I. A. 1934. Estimation of soil organic carbon by chromic acid titration method. *Soil Sci*. 31: 29-38.

Wang, B., Sun, J. S., Liu, H., and Ma, Y. B. 2017. The characteristics of phosphorus adsorption and desorption in gray desert soil of Xinjiang, China. IOP Conf. Ser.: *Earth Environ. Sci.* 77:1-10.

Wang, Y., Jiang, J., Xu, R. K., and Tiwari, D. 2009. Phosphate adsorption at variable charge soil/water interfaces as influenced by ionic strength. *Aust. J. Soil Res.* 47: 529-536

Wang, Y., Xiao, X. and Chen, B. 2018. Biochar impacts on soil silicon dissolution kinetics and their interaction mechanisms. *Sci Rep*. 8(1): 1-11.

Warington, K. 1923. The effect of boric acid and borax on the broad bean and certain other plants. *Annals Bot.* 37(148): 629-672.

Watanabe, F. S. and Olsen, S. R. 1965. Test of an ascorbic acid method for determining phosphorus in water and sodium bicarbonate extracts from soil. *Soil Sci. Soc. Am. Proc*. 29: 39-45.

Weil, R. R. and Brady, N. C. 2017. *The nature and properties of soils* (15th Ed.). Pearson Education Limited, Harlow, England. 1104p.

Weitz, E. 1950. Silicic acid and silicates. *Chem. Ztg*. 74: 256-257.

White, R. E. and Beckett, P. H. T. 1964. Studies on the phosphate potentials of soils - Part I - The measurement of phosphate potential. *Plant Soil* 20(1):1-16.

Wijnja, H. and Schulthess, C. P. 2000. Vibrational spectroscopy study of selenate and sulfate adsorption mechanisms on Fe and Al (Hydr)oxide Surfaces. *J. Colloid Interface Sci.* 229(1): 286-297.

Williams, C. H. and Steinbergs, A. 1959. Soil sulphur fractions as chemical indices of available sulphur in some Australian soils. *Aust. J. Agric. Res.* 10(3): 340-352.

Williams, C. H. and Steinbergs, A. 1962. The evaluation of plant-available sulphur in soils. II. The availability of adsorbed and insoluble sulphates. *Plant Soil* 21: 50-62.

Williams, L. A. and Crerar, D. A. 1985. Silica diagenesis, II. General mechanisms. *J. Sed. Pet.* 55: 312-321.

Wu, C. H., Lo, S. L., and Lin, C. F. 2000. Competitive adsorption of molybdate, chromate, sulfate, selenate, and selenite on γ -Al_2O_3. *Colloids Surfaces : Physicochem. Eng. Asp.* 166 (1-3): 251-259.

Wu, C. H., Lo, S. L., Lin, C. F., and Kuo, C. Y. 2001. Modeling competitive adsorption of molybdate, sulfate, and selenate on γ -Al_2O_3 by the Triple-Layer model. *J. Colloid Inter. Sci.* 233: 259-264.

Xiao-quan, S., Bin, C., Long-zhu, J., Yan, Z., Xiao-ping, H., and Shi-fen, M. 1992. Determination of sulfur fractions in soils by sequential extraction, inductively coupled plasma-optical emission spectroscopy and ion chromatography. *Chem. Speciat. Bioavailab.* 4(3): 97-103.

Xu, N., Braida, W., Christodoulatos, C., and Chen, J. 2013. A Review of molybdenum adsorption in soils/bed sediments: Speciation, mechanism, and model applications. *Soil Sediment Contam*: *Int. J.* 22(8): 912-929.

Xu, N., Christodoulatos, C., and Braida, W. 2006. Adsorption of molybdate and tetrathiomolybdate onto pyrite and goethite: Effect of pH and competitive anions. *Chemosphere* 62: 1726-1735.

Xu, R. K., Xiao, S. C., Zhang, H., Jiang, J., and Ji, G. L. 2007. Adsorption of phthalic acid and salicylic acid by two variable charge soils as influenced by sulphate and phosphate. *Eur. J. Soil Sci.* 58: 335-342.

Xu, R., Jiang, J., and Cheng, C. 2010. Effect of Ionic strength on specific adsorption of ions by variable charge soils: experimental testification on the adsorption model. *Molecul. Environ. Soil Sci.* 78-80.

Yang, X., Chen, X., and Yang, X. 2019. Effect of organic matter on phosphorus adsorption and desorption in a black soil from Northeast China. *Soil Tillage Res.* 187:85-91.

Young, E. G., Smith, D. G., and Langille, W. M. 1959. The chemical composition of sea water in the vicinity of the Atlantic provinces of Canada. *J. Fisheries Res. Board Can.* 16(1): 7-12.

Young, J. L. and Aldag, R. W. 1982. Inorganic Forms of Nitrogen in Soil. *Agron. Monogr.* 22: 43-66.

Young, R. N. 2000. *Geoenvironmental Engineering: Contaminated soils, pollutant fate, and mitigation*. Taylor & Francis/CRC Press, Boca Raton, FL.

Zhang, J-Z., Fischer, C. J. and Ortner, P.B. 1999. Optimization of performance and minimization of silicate interference in continuous flow phosphate analysis. *Talanta* 49: 293-304.

Zhang, Z. Y., Huang, L., Liu, F., Wang, M. K., Fu, Q. L., and Zhu, J. 2016. Characteristics of clay minerals in soil particles of two Alfisols in China. *Appl. Clay Sci.* 120: 51-60.

ANIONIC EQUILIBRIA IN MAJOR SOIL TYPES OF KERALA

By

RESHMA M. R.

(2015- 21-032)

ABSTRACT

Submitted in partial fulfilment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY IN AGRICULTURE

Faculty of Agriculture

Kerala Agricultural University

DEPARTMENT OF SOIL SCIENCE AND AGRICULTURAL CHEMISTRY
COLLEGE OF HORTICULTURE
VELLANIKKARA, THRISSUR - 680 656
KERALA, INDIA
2020

ABSTRACT

Soils formed under tropical humid climate of Kerala are one of the best to study about chemistry of anions. Twenty two representative soil samples were collected from 7 different agro-ecological units of Kerala with wide variation in organic matter content and texture. The study aimed to understand the relative adsorption of selected anions on soil solid phase and to know the competitive interaction of fractions of these anions with respect to their adsorption behavior and bio-availability and the relative intensities of each of these anions. Out of the 22 samples collected, 5 samples were in near neutral pH, all others were acidic. Low lands of *Pokkali*, *Kole* and *Kuttanad* showed high organic carbon status. In general, sandy soils from northern coastal plain and *Onattukara* sandy plain were low in fertility and low land soils of *Pokkali, Kole* and *Kuttanad* were high in fertility. XRD data revealed the dominance of kaolinite mineral in all the representative soils except the soil from Palakkad eastern plain.

Fractionation of phosphorous, sulphur, boron and silicon was carried out to know the major fractions and its contribution to the available pool. Dominance of P fractions was different in different types of soil. Saloid - bound phosphorous is contributing least to the total P content. All the S fractions were high in *Pokkali* soil. The percentage contribution of different fractions of Si to the total Si were in the order; residual Si > amorphous Si > occluded Si ≈ organic Si > adsorbed Si> mobile Si. The percentage contribution of different fractions of B to the total B were in the order; residual B > organically bound B > oxide bound B> readily soluble B > specifically adsorbed B. Among all the fractions, readily soluble and mobile fractions are the major contributor to the available pool.

Single anion adsorption experiments were conducted for nitrate, P, S, B, Mo and Si at 25^0C and 40^0C. Quantity - intensity relations and thermodynamic parameters were worked out based on the adsorption data. Freundlich, Langmuir and Tempkin isotherms were fitted using the adsorption data. Dominance of desorption was observed in case of Si and S, with added concentration of these elements. Whether it is adsorption or desorption, the process was spontaneous in

most of the soil for all anions under study. Q-I curve of these elements showed reduction in desorption after reaching a maximum desorption, indicating the possibility of adsorption on further addition of higher concentration of these elements. Adsorption of B was less because only lower concentration of B was used in adsorption study and the existence of non-ionised forms of B at the acidic equilibrium solution pH. Due to these reasons adsorption of B, S and Si was found less than nitrate adsorption. P and Mo showed very high similarity in adsorption behavior with high affinity of these elements to the adsorption sites, which is due to the inner-sphere complex formation by these elements. Increase in buffer power and maximum quantity adsorbed with added concentration of P and Mo was observed especially in low land soils of *Pokkali*, *Kole* and *Kuttanad* indicating the chemical nature of adsorption.

Freundlich adsorption isotherm was the best to explain adsorption of anions in soil followed by Tempkin and Langmuir adsorption isotherm, which implies that the bonding energy of the adsorbate anion on the soil surface decreases with the fractional coverage of the adsorbent surface. Among P and Mo, the constants related to strength of adsorption were high for Mo adsorption than P adsorption. Kaolinite, hematite, goethite, other oxides and hydrous oxides of Fe and Al are the major sites for anion adsorption. Preferential adsorption of phosphorous over boron was observed in all soils in adsorption study conducted with binary system of P and B. Using P, for estimation of AEC can lead to the overestimation due to the specific adsorption behavior of P. A general trend in silicon extractability of different extractants was in the order; Bray I reagent > CBD > 0.5M acetic acid > 0.1M HCl. The possibility of over estimation of P due to the interference of Si in molybdenum blue colorimetric estimation was observed at high concentration of Si. Greater than 10 per cent over estimation was observed if Si:P ratio is greater than 80.

കേരളത്തിലെ പ്രധാനപ്പെട്ട മണ്ണിനങ്ങളിലുള്ള ഋണ അയോണുകളുടെ സന്തുലിതാവസ്ഥ

കേരളത്തിലെ ഈർപ്പമുള്ള ഉഷ്ണമേഖല കാലാവസ്ഥയിൽ രൂപപ്പെടുന്ന മണ്ണിനങ്ങൾ ഋണ അയോണുകളുടെ രസതന്ത്ര പഠനത്തിന് അനുയോജ്യമാണ്. ഏഴ് വ്യത്യസ്ത കാർഷിക പരിസ്ഥിതി യൂണിറ്റുകളിൽ നിന്നായി, രചനയിലും ജൈവാംശത്തിന്റെ അളവിലും വ്യത്യസ്തത പുലർത്തുന്ന 22 സാമ്പിളുകൾ പഠനത്തിനായി ശേഖരിച്ചു. ഋണ അയോണുകളുടെ മണ്ണിന്റെ ഖര ഭാഗത്തേയ്ക്കുള്ള അധിശോഷണം, മൂലകങ്ങളുടെ വ്യത്യസ്ത ഘടകങ്ങൾ തമ്മിലുള്ള പരസ്പര പ്രവർത്തനങ്ങൾ, അധിശോഷണത്തിൽ അവയ്ക്കുള്ള പങ്ക്, സസ്യലഭ്യതയിലേക്ക് മൂലകങ്ങളുടെ വ്യത്യസ്ത ഘടകങ്ങൾക്കുള്ള പങ്ക് എന്നിവ മനസ്സിലാക്കുക എന്നതാണ് ഗവേഷണത്തിന്റെ ഉദ്ദേശ ലക്ഷ്യങ്ങൾ. ശേഖരിച്ച 22 സാമ്പിളുകളിൽ അഞ്ച് എണ്ണം നിർവീര്യാവസ്ഥയോട് ചേർന്നു നിൽക്കുന്നവയും ബാക്കിയുള്ളത് അമ്ലസ്വഭാവത്തോട് കൂടിയതുമായിരുന്നു. സമുദ്ര നിരപ്പിൽ നിന്നും താഴ്ന്ന് കിടക്കുന്ന പൊക്കാളി, കോൾ, കുട്ടനാട് എന്നിവിടങ്ങളിലെ വയലേലകളിൽ നിന്നും ശേഖരിച്ച മണ്ണ് ഫലഭൂയിഷ്ഠമായതും ജൈവകാർബണിന്റെ ആധിക്യം ഉള്ളതുമായിരുന്നു. എന്നാൽ ഉത്തരമേഖല തീരദേശ സമതലങ്ങളിൽ നിന്നും ഓണാട്ടുകരയിൽ നിന്നും ശേഖരിച്ച മണലിന്റെ അളവ് കൂടുതലുള്ള സാമ്പിളുകൾ താരതമ്യേന ഫലഭൂയിഷ്ഠത കുറവുള്ളവയായിരുന്നു. പാലക്കാട് കിഴക്കൻ സമതലങ്ങളിൽ നിന്നും ശേഖരിച്ച മണ്ണിൽ ഒഴികെ ബാക്കി എല്ലാ സാമ്പിളുകളിലും കയോലിനൈറ്റ് എന്ന ധാതുവിന്റെ ആധിക്യം എക്സ്. ആർ.ഡി. പരിശോധനയിൽ വ്യക്തമായി.

ഓരോ മൂലകങ്ങൾക്കും എത്ര വിധം ഘടകങ്ങൾ ഉണ്ട് എന്നും, സസ്യലഭ്യതയ്ക്ക് ഉതകുന്ന ഘടകം ഏത് ആണ് എന്നും മനസ്സിലാക്കുന്നതിനുവേണ്ടി ഭാവഹം, ഗന്ധകം, ബോറോൺ,സിലിക്കൺ എന്നീ മൂലകങ്ങളുടെ വിവിധ ഘടകങ്ങളെ വേർതിരിയ്ക്കുന്ന പരീക്ഷണം നടത്തുകയുണ്ടായി. വ്യത്യസ്ത ഇനം മണ്ണിനങ്ങളിൽ ഭാവഹത്തിന്റെ വ്യത്യസ്ത ഘടകങ്ങളുടെ ആധിക്യമാണ് കാണാൻ സാധിച്ചത്. വേഗത്തിൽ വെള്ളത്തിൽ ലയിക്കുന്നതും അയഞ്ഞ രീതിയിൽ മണ്ണിലെ ഖര ഭാഗത്തോട് ചേർന്നിരിക്കുന്നതുമായ ഭാവഹത്തിന്റെ ഘടകം, ആകെ ഭാവഹത്തിന്റെ അളവിലേക്ക് തുച്ഛമായ രീതിയിൽ ആണ് പങ്ക് നൽകുന്നത്. പൊക്കാളിയിലെ വയലേലകളിലെ മണ്ണിൽ ഗന്ധകത്തിന്റെ എല്ലാ ഘടകങ്ങളുടെ അളവും വളരെ കൂടുതലായി കാണപ്പെടുന്നു. ആകെയുള്ള സിലിക്കണിന്റെ അളവിലേയ്ക്കുള്ള വിവിധ ഘടകങ്ങളുടെ പങ്ക് ഇപ്രകാരമാണ്: അവശേഷിക്കുന്ന സിലിക്കൺ> അരൂപസ്ഥിതിയിലുള്ള സിലിക്കൺ> ഓക്സൈഡുകളും ഹൈഡ്രോക്സൈഡുകളുമായി ബന്ധപ്പെട്ട സിലിക്കൺ ≈ ജൈവ കാർബണുമായി ബന്ധപ്പെട്ടിട്ടുള്ള സിലിക്കൺ> അധിശോഷണം ചെയ്യപ്പെട്ട സിലിക്കൺ> ചലന സ്വാതന്ത്ര്യമുള്ള സിലിക്കൺ. ആകെയുള്ള ബോറോണിന്റെ അളവിലേയ്ക്കുള്ള വിവിധ ഘടകങ്ങളുടെ പങ്ക് ഇപ്രകാരമാണ്: അവശേഷിക്കുന്ന ബോറോൺ> ജൈവകാർബണുമായി ബന്ധപ്പെട്ട ബോറോൺ> ഓക്സൈഡുകളുമായി ബന്ധപ്പെട്ട ബോറോൺ> വേഗത്തിൽ ലയിക്കുന്ന ബോറോൺ> പ്രത്യേക തരത്തിൽ അധിശോഷണം ചെയ്യപ്പെട്ട ബോറോൺ. വേഗത്തിൽ ലയിക്കുന്നതും ചലന സ്വാതന്ത്ര്യമുള്ളതുമായ ഘടകങ്ങളാണ് സസ്യലഭ്യതയ്ക്ക് ഉതകുന്ന തരത്തിലുള്ളത്.

നൈട്രേറ്റ്, ഭാവഹം, ഗന്ധകം, ബോറോൺ, മോളിബ്ഡിനം, സിലിക്കൺ എന്നീ മൂലകങ്ങളുടെ മണ്ണിലേയ്ക്കുള്ള അധിശോഷണ പ്രക്രിയയെ പറ്റി മനസ്സിലാക്കുന്നതിന് രണ്ട് താപനിലയിൽ ($25^{o}C$, $40^{o}C$) പരീക്ഷണം നടത്തി. മണ്ണിന്റെ ഖര ഭാഗത്തേക്ക് അധിശോഷണം ചെയ്യപ്പെടുന്ന അളവിനേയും, ദ്രാവകഭാഗത്ത് സസ്യലഭ്യതയ്ക്ക് ഉതകുന്ന തരത്തിലുള്ള മൂലകത്തിന്റെ അളവിനേയും പറ്റിയുള്ള താരതമ്യ പഠനവും ഘർമപ്രവർത്തനപരമായ മറ്റ് സ്വഭാവങ്ങൾ മനസ്സിലാക്കുന്നതിനും ഈ പരീക്ഷണത്തിലൂടെ സാധിച്ചു. ഫ്രണ്ടലിച്ച്, ലാംഗ്മിയർ, ടെംകിൻ എന്നീ മോഡലുകളിൽ അധിശോഷണ പരീക്ഷണത്തിന്റെ വിവരങ്ങൾ ബന്ധിപ്പിച്ചു നോക്കി. ഗന്ധകത്തിന്റെയും സിലിക്കണിന്റെയും പരീക്ഷണത്തിൽ മൂലകങ്ങൾ മണ്ണിലേക്ക് ചേർക്കുന്നതിനനുസരിച്ച് ഖര ഭാഗത്തു നിന്നും മണ്ണിന്റെ ദ്രാവക ഭാഗത്തേക്ക് എത്തിചേരുന്നതായി കാണപ്പെട്ടു. ഖര ഭാഗത്തുനിന്നും ദ്രാവക ഭാഗത്തേയ്ക്ക് വരുന്ന പ്രക്രിയ അതിന്റെ പാരമ്യത്തിൽ എത്തിയതിനുശേഷം കുറയുന്നതായി കണ്ടു. പ്രസ്തുത മൂലകങ്ങൾ മണ്ണിലേക്ക് ഇനിയും കൂടുതലായി ചേർക്കപ്പെട്ടാൽ അധിശോഷണം സംഭവിക്കാനുള്ള സാധ്യത ഇതിൽ നിന്നും മനസ്സിലാക്കി. ബോറോണിന്റെ ഗാഢത കുറവായതിനാലും അമ്ല സ്വഭാവമു

ള്ള സന്തുലിതാവസ്ഥയിലുള്ള ലായിനിയിൽ അയോണീകരിക്കപ്പെടാത്ത ബോറോൺ ആണ് കാണപ്പെടുന്നത് എന്നതിനാലും ബോറോണിന്റെ അധിശോഷണപ്രക്രിയ താരതമ്യേന കുറവായിരുന്നു. ഈ കാരണങ്ങളാൽ നൈട്രേറ്റിന്റെ അധിശോഷണ പ്രക്രിയ, ഗന്ധകത്തിന്റെയും ബോറോണിന്റെയും സിലിക്കണിന്റെയും അധിശോഷണപ്രക്രിയയേക്കാൾ കൂടുതലായി കാണപ്പെട്ടു. ഭാവഹത്തിന്റെയും മോളിബ്ഡിനത്തിന്റെയും അധിശോഷണ പ്രക്രിയ ഒരേ സ്വഭാവം ഉള്ളതായിരുന്നു. ഈ മൂലകങ്ങളുടെ അധിശോഷണം മണ്ണിൽ താരതമ്യേന കൂടുതലായി കാണപ്പെട്ടു. അധിശോഷണ പ്രക്രിയയിൽ വേഗത്തിൽ വിഘടിച്ചു പോരാത്ത തരത്തിലുള്ള സങ്കീർണ്ണമായ മിശ്രിതം ഉണ്ടാക്കുന്നതിനുള്ള കഴിവ് ഈ മൂലകങ്ങൾക്ക് ഉള്ളതായി മനസ്സിലാക്കാൻ സാധിച്ചു. പൊക്കാളി, കോൾ, കുട്ടനാട് എന്നിവിടങ്ങളിലെ വയലേലകളിൽ നിന്നും ശേഖരിച്ച മണ്ണിലെ അധിശോഷണ പരീക്ഷണങ്ങളിൽ ഈ വസ്തുത വളരെയധികം പ്രകടമായിരുന്നു. മണ്ണിലെ ഖര ഭാഗത്ത് അധിശോഷണം ചെയ്യപ്പെടുന്ന മൂലകങ്ങൾ, ദ്രാവക ഭാഗത്തെ അതേമൂലകങ്ങളുടെ ഗാഢത കുറയുന്നതിനനുസരിച്ച്, ഖര ഭാഗത്തുനിന്നും ദ്രാവക ഭാഗത്തേക്ക് എത്തുന്നതിനുള്ള കഴിവുള്ളതായും കാണപ്പെട്ടു.

ഫ്രണ്ട്ലിച്ച് മോഡലിന്, ടെംകിൻ മോഡലിനേക്കാളും ലാംഗ്മിയർ മോഡലിനേക്കാളും കൂടുതൽ കൃത്യതയോടും വ്യക്തതയോടും കൂടെ അധിശോഷണ പ്രക്രിയ അവതരിപ്പിക്കാൻ കഴിഞ്ഞു. അധിശോഷണത്തിന് കാരണമാകുന്ന മണ്ണിലെ ഖരഭാഗത്തുള്ള സ്ഥലങ്ങൾ പൂരിതമാകുന്നതിനനുസരിച്ച്, അധിശോഷണ പ്രക്രിയയിലെ ഊർജ്ജം കുറഞ്ഞുവരുന്നു എന്നതാണ് ഈ വസ്തുത സൂചിപ്പിക്കുന്നത്. അധിശോഷണ പ്രക്രിയയിൽ ഉണ്ടാകുന്ന ബന്ധത്തിന്റെ ദൃഢത സൂചിപ്പിക്കുന്ന സംഖ്യ, മോളിബ്ഡിനം അധിശോഷണത്തിൽ കൂടുതലാണ്. മണ്ണിൽ ലവണ അയോണുകളുടെ അധിശോഷണ പ്രക്രിയ നടക്കുന്ന പ്രധാനപ്പെട്ട സ്ഥലങ്ങൾ കയോലിനൈറ്റ്, ഹേമറ്റൈറ്റ്, ജിയോതൈറ്റ് എന്നീ ധാതുക്കളും, ഇരുമ്പിന്റെയും അലുമിനിയത്തിന്റെയും ഓക്സൈഡുകളും ഹൈഡ്രോക്സൈഡുകളുമാണ്. ഭാവഹത്തിന്റെയും ബോറോണിന്റെയും സമ്മിശ്ര അധിശോഷണ പ്രക്രിയയിൽ, ഭാവഹത്തിന്റെ അധിശോഷണത്തിന് മുൻതൂക്കം ഉള്ളതായി കാണപ്പെട്ടു. പ്രത്യേക തരത്തിലുള്ള അധിശോഷണ പ്രക്രിയ ഭാവഹത്തിന് ഉള്ളതിനാൽ, മണ്ണിലെ ലവണായന വിനിമയ ശേഷി കണ്ടെത്തുന്നതിന് ഈ മൂലകം ഉപയോഗിക്കുന്നത് തെറ്റായ ഫലം ലഭിക്കുന്നതിന് കാരണമാകും. മണ്ണിലുള്ള സിലിക്കണിനെ പുറത്തെടുക്കുന്നതിന് പല ലായനികൾക്കും ഉള്ള കഴിവ് വ്യത്യസ്തമാണ്: ബ്രെ । > സിട്രേറ്റ് ബൈകാർബണേറ്റ് ഡൈതയോണേറ്റ് > 0.5 M അസറ്റിക് ആസിഡ് > 0.1 M ഹൈഡ്രോക്ലോറിക്ക് ആസിഡ്. മോളിബ്ഡിനം ഉപയോഗിച്ചുള്ള നിരോക്സീകരണ പ്രക്രിയ പ്രകാരം ഭാവഹത്തിന്റെ അളവ് കണ്ടുപിടിക്കുമ്പോൾ, സിലിക്കണിന്റെ ഗാഢത കൂടുതലാണെങ്കിൽ തെറ്റായ ഫലം ലഭിക്കുന്നു. സിലിക്കണിന്റേയും ഭാവഹത്തിന്റേയും അനുപാതം എൺപതിൽ അധികമായപ്പോൾ, യഥാർത്ഥ അളവിനേക്കാളും പത്തുശതമാനം അധികം ഭാവഹം ഉണ്ടെന്ന ഫലം ലഭിച്ചു.