

JIMMA UNIVERSITY
JIMMA INSTITUTE OF TECHNOLOGY
SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING
ENVIRONMENTAL ENGINEERING CHAIR



Experimental Evaluation of Sorptive Removal of Boron Using Laterite Soil

By: DEREJE KITABA

A THESIS SUBMITTED TO THE SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING, ENVIRONMENTAL ENGINEERING CHAIR, JIMMA INSTITUTE OF TECHNOLOGY, AND JIMMA UNIVERSITY FOR PARTIAL FULFILMENT OF THE REQUIREMENTS OF THE MASTER OF SCIENCE IN ENVIRONMENTAL ENGINEERING.

March, 2016
JIMMA ETHIOPIA

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ASSURANCE OF PRINCIPAL INVESTIGATOR

The undersigned to accept responsibility for the scientific ethical and technical conduct of the research project and for provision of required progress reports as per terms and conditions of the Jimma Institute of Technology (JIT) in effect at the time of grant is forwarded as the result of this application.

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Abstract

Ground water is essential resource that requires protection can continue to sustain the human life and the various ecosystems that depend on it. Many pollutants that occur naturally in soil, sediments and rocks for example boron can also degrade quality of groundwater. Boron exists abundantly in the surrounding the form of boric acid or borate salts. In industry, boron minerals are used for manufacturing glass, fertilizers, food preservatives and detergents. The main objective of this study is to investigate the sorption of Boron using LS under batch experimental setup. The chemical characterization of the LS used was determined by Ethiopian Geological Survey Laboratory and the Adsorption Procedure Effect of Contact Time, pH, initial Concentration, adsorbent Dose, co-existing ions, Adsorption Kinetics and Isotherm were assessed. The result of this study was the optimum contact time occurred at 60 min, it was considered as equilibrium with removal efficiency of 90.500% and adsorption capacity of 0.302 mg/g. The optimum adsorbent dose is 2 g/L, at this dose percentage of boron adsorbed 92.200% and amount of boron adsorbed 0.307 mg/g. The equilibrium pH ~ 8, in this pH the removal efficiency is 94.500% and adsorption capacity is 0.315 mg/g, at shaking speed 200 rpm and grain size between 0.075 – 0.425 mm in all adsorption procedure. The boron adsorption kinetics data followed the pseudo-second order equation with the correlation coefficient, $R^2 = 0.99$ and this implies that the adsorption process is chemical adsorption. The Langmuir and Redlich - Peterson isotherms are better fitted model with the correlation coefficient, $R^2 = 0.99$ described the boron adsorption giving an adsorption capacity of 2.07 mg/g and 2.13 mg/g respectively. The presences of competing anions (bicarbonate) slightly influence boron adsorption efficiency while chloride and fluoride were not significantly interfering. The adsorption/desorption of adsorbent was tested using NaOH solution on two concentration so; the efficiency was increased from 67.72% to 83.28%. The adsorbent was reduced 5 mg/L boron spiked ground water in to 0.55 mg/L which is within the permissible range of WHO guidelines. From the results of this study we concluded that LS can be used in water treatment for removal boron is highly efficient adsorbent.

Keywords: Boron, Laterite Soil, Sorption Kinetics and Equiliberem

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Abbreviation

ASTM	According to Standard Methods
EPA	Environmental Protection Authority
EGSL	Ethiopian Geological Survey Laboratory
LS	Laterite soil
MER	Main Ethiopian Rift valley
OWWDSEL	Oromia water works design and supervision enterprise laboratory
USGS	U.S. Geological Survey
USEPA	U.S Environmental Protection Authority
WHO	World Health Organization

CHAPTER ONE

Introduction

1.1 Background

Most of the Earth's liquid fresh water is found to store underground in the aquifers. Ground water is essential resource that requires protection can continue to sustain the human life and the various ecosystems that depend on it. The contribution from groundwater is two billion people depend directly upon aquifers for drinking water. In the future, aquifer development will continue to be fundamental to economic development and reliable water supplies will be needed for domestic and irrigation purposes (Belay et al., 2015).

Even though groundwater may be plentiful in a particular area, if the quality of the groundwater has been degraded by the entry of contaminants, the aquifer may not be usable as water supply. Many pollutants that occur naturally in soil, sediments and rocks for example boron can also degrade quality of groundwater (Saracino and Phipps, 2002).

Population explosion, expansion of urban areas increased adverse impacts on water resources. Currently, water use and reuse has become a major concern. Population growth leads to significant increases in default volumes of waste water, which makes it an urgent imperative to develop effective and affordable technologies for water treatment (Segneanu et al., 2013). The emissions of waste materials from these manufacturing factory result in the prefunds problem of boron pollution (Halim et al., 2013; Paez et al., 2014). It became highly toxic if boron is mingled with heavy metals rather than boron and heavy metals (Korkmaz et al., 2014). For this reason, the World Health Organization (WHO) has given a recommendation of below 1.5 mg/L boron for the quality of drinking water (WHO, 2011).

Boron exists abundantly in the surrounding the form of boric acid or borate salts (Halim et al., 2013). As a result of its range for deficiency and toxicity boron suits naturally for plants, It's vital use for human and plants in carbohydrate metabolism, sugar translocation, pollen germination, hormone action, normal growth and functioning, nucleic acid synthesis, and membrane structure and function and It uses for manufacturing of glass, fertilizers, food preservations and detergents (Demirçivi and Saygili, 2008).

A number of passive and active technologies have been developed and implemented for decontamination of boron-rich water and they include: ion exchange (Demirçivi and Saygili, 2008), desalination (Masindi et al., 2015), liquid-liquid extraction and chemical precipitation (Y and JQ, 2008), electro coagulation (Y. et al., 2009), reverse osmosis (Arias et al., 2011), and adsorption (Maji et al., 2008). Among them, the adsorption process is an attractive approach for water treatment, particularly if the adsorbent is cheap and does not require a pretreatment step before its application. For many applications, this process has been proven to be superior to other techniques for a variety of reasons including the simplicity of design, low cost, high removal efficiency, ease of operation, and availability (Paez et al., 2014).

Red colored clay rich soil especially the iron rich called laterite is found in semi dry and dry land. It needs high temperature of the dry land and the abundant rainfall to form. The bases and silica acids are removed by water and it fills with aluminum silicates, aluminum hydro silicates, iron oxides and iron hydroxides (Maji et al., 2008). The laterite soil (LS) occurs widely in several districts in Ethiopia (e.g.: Borona, Jimma, Wollega and Benishangul Gumuz). However, little or no information is available about the adsorptive interactions between boron and LS in the aqueous system. Thus, an attempt was made to study their feasibility as an adsorbent for removal of boron from aqueous solution.

1.2. Statement of the problem

Boron compounds are toxic to all species tested at high doses, but they are not mutagenic or carcinogenic. The major chronic toxicities on developmental and reproductive systems (Bakirdere et al., 2010)

Boron is involved in calcium and bone metabolism. Experiments with boron supplementation or deprivation show that its effects are more marked when magnesium is deficient. Boron may be involved in cerebral function due to its effects on the transport across membranes. Boron is involved in the synthesis of extracellular matrix and is helpful in wound healing (Bakirdere et al., 2010).

Although boron is essential for plant growth, in excess of 2.0 mg/L in irrigation water, it is deleterious to certain plants species. Boron deficiencies cause growth problems and difficulties in sugar mobilization (D.Eaton et al., 2005). Globally boron concentrations are found in sea water (4.7 mg/L), domestic waste water (0.5-2 mg/L) and reach to 8 mg/L in ground water in Italy, Cyprus and Greece (Bekta and Oztiirk, 2004; N. et al., 2008). The Assessment of U.S. Geological Survey (USGS) in ground water from the Sacramento Valley aquifer, boron was detected in all thirty-one samples; concentrations ranged from 12 to 1100 µg/L. Two of the thirty-one samples had concentrations in excess (U.S.EPA, 2008) and, in Ethiopian conditions groundwater in MER often show the average concentration of boron is 17.27 µg/L in rivers, 2516.67 µg/L in hot springs, 2070.5 µg/L in geothermal wells, 430.45 µg/L in groundwater wells, 28.25 µg/L cold springs and 3309.4 µg/L in lakes, with maximum values of 114 , 4975, 2888, 5408, 42.2 and 14,770 µg/L respectively, (Rango et al., 2010). It has to be noted that 35% of the MER groundwater wells are the main source of potable water, contain more than the safe limit 1500 µg/L of boron (WHO, 2011).

1.3 SIGNIFICANCE OF THE STUDY

There are concerns at all levels that fresh water resources particularly in the developing world could keep on getting polluted from the excessive domestics, agricultural and industrial discharges they receive and lead to serious health and ecological problems. Water treatment plants which draw water from such water bodies are facing growing problems in delivering desired water quality. In developing countries, such as in sub-Sahara African countries including Ethiopia this problem is compounded by their financial resources. The lack of knowledge of the mechanisms of boron removal and the relatively high cost and complexity of providing the necessary treatment has led to either inadequate or no treatment. Thus, in many cases, the polluted water is often used for the domestic as well as irrigation purpose.

Therefore, this study may give some guideline information about adsorption technology to stakeholders for developing low cost adsorption water treatment technology. And the data will also be used as a baseline to apply the finding for pilot- and full-scale treatment plant systems.

CHAPTER TWO

LITREATURE REVIW

2.1 Boron occurrence and nature

Elemental boron does not exist in nature, but is always found combined with oxygen in the form of inorganic borates or boric acid. Boron is a non-metallic, electron deficient element that forms compounds by reacting with electronegative elements such as oxygen (Frey et al., 2004). The environmental abundance of ^{11}B is about 80.1 percent and that of ^{10}B is about 19.9 percent. Boron is mixed with elements such as borate salts boron, silicate, it became unstable in nature. Boron is group 3 (IIIA) in the predict table and is the only non metal of this groups. Boron appears predominantly in the form of boric acid in aquatic environment. Boric acid is a solid substance soluble in the water with solubility of 55 g/L at 25 °C. Boric acid acts as a weak acid. Its pKa value can be determined at relatively low concentrations, particularly below 22 mg/L, when mononuclear species $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ present only. In the fraction of boric acid and borate as a function of pH is presented. When pH is increased above pKa value, most borate anions can be found. Polyborates appear at higher than 1000 mg/L concentration of boron (Wolska and Bryjak, 2013).

The stable-isotope ratio of boron in leachate from fly ash can differ greatly from that in natural ground water (Davidson and Bassett, 1993). Boron isotopes have been used to distinguish water affected by detergent residues, treated municipal wastewater, and saline ground water. Several of those investigators (Verstraeten et al., 2005) used water samples with known or suspected contaminant sources to define typical concentrations of boron and boron stable isotopes for each representative source of boron. Hypothetical mixtures between those potential sources were used to identify the possible sources of boron in other samples from areas with unknown sources of boron (Seiler, 2005; Verstraeten et al., 2005).

A geochemically-based classification of the source of boron in ground water could potentially identify the similarity of boron in a water sample to potential sources or mixtures between potential sources or whether the relative age of ground water predated the potential sources of contamination. A geochemical classification of boron source would have the advantage of limiting the need to remove and reinstall well plumbing and pumps for direct, camera-based

observations of well depth and screen interval. No previous analyses of boron isotope ratios in CCP-affected ground water, domestic-wastewater-affected ground water, and potential natural ground-water sources (surficial and basal sand aquifers) had been reported for the study area before this investigation. To evaluate the application of boron isotopes and tritium data in indicating potential sources of boron in ground water, it was necessary to collect and analyze samples of those representative ground-water sources. Data were also needed from the immediate area of study to validate the use of tritium as a characteristic to distinguish relatively younger ground water from shallow aquifers and relatively older ground water from confined aquifers (Buszka et al., 2007).

Boron occurs as a trace element in most soil and is estimated to constitute approximately 0.001% of the earth's crust. Even though boron is widespread, large deposits are uncommon and confined to a few locations. The boron concentration in the world's oceans ranges between 1 – 10 mg/ L, with an average of 5 mg /L. Boron's presence in water is often a result of weathering of Boron-containing minerals and soils (Parks and Edwards, 2005). Another significant source of boron is boric acid, which is released through volcanic eruptions. Boron is also released into water from anthropogenic sources such as mining of boron oxide (Rahman et al., 2009).

2.3 Effects of Boron on Health and Agriculture

Boron is a micronutrient essential for plant growth. Plant requirements for boron are critical, but only small amounts are needed to provide adequate growth, hence, it is categorized as a soil micronutrient. Many crops have had yield reductions due to deficiencies of boron. Boron regulates the transport of sugars through plant cell membranes, the rate of cell development, cell division, and the synthesis of proteins. Plants are unable to mobilize boron from the old to new plant tissues. Deficiency symptoms of the plant are first noticed at the terminal growing points: new leaves, flower buds, stem tips (Sasaki et al., 2011). Boric acid normally used for preservation of food products. It can cause to health problem if the food containing boric acid was ingested by human as boric acid and borates are toxic to cell. The common symptoms from several incidents of boric acid poisoning included coughing, eye irritation, vomiting and oral irritation. For cancer effect studies, boric acid was classified as a group E carcinogen by the US EPA. However, boric acid is not considered a potent human carcinogen based on laboratory

animals test which showed that boric acid is no carcinogenicity in humans, excess boron manifests as nervous system disorders and infertility (See et al., 2010).

2.4 Factors affecting B adsorption

2.4.1 Effect on Initial B concentration

A study on Removal of boron from Waste Waters by Ion Exchange in a Batch System show that boron removal decreased with increasing boron concentration. Maximum boron removal was obtained with minimum solution concentration (20 mg/L) with 98.86% yield. The other removal yields for initial solution concentrations 40 and 60 mg/L are 97.46% and 96.89%, respectively (Demirçivi and Saygili, 2008).

Boron adsorption by magnesium oxide and aluminum oxide was researched by Konstantinou, Kasseta and Pashalidis (2006). A periodically mixed batch technique was used for all their adsorption experiments under atmospheric conditions at 25°C with the ionic strength maintained at 0.1 M. For 25 g/L magnesium oxide, a maximum boron removal of 90% was achieved from a solution containing an initial concentration of 2.2 mg/L boron. In contrast, aluminum oxide removed just over 50% of boron from the same solution using the same concentration of adsorbent (Rahman et al., 2009).

2.4.2 Effect on Contact time

A study on Evaluation of boron removal from water by hydrotalcite-like compounds showed that Mg–Fe (HTFe) and Mg–Al (HTAl) hydrotalcite-like compounds can be used as adsorbents for boron [$B(OH)_4^-$] removal from aqueous media. It was found that 120 min is enough for the equilibrium state to be reached in the adsorption experiments (Ferreira et al., 2006). Boron removal by Cur-AC is optimal at pH~5.5 and at 120 min of contact time. The adsorption of boron onto Cur-AC and bare AC can be described better by Freundlich isotherm. The maximum adsorption capacity of boron for Cur-AC was significantly higher than that for bare AC (Halim et al., 2013).

A study on removal of boron from aqueous solution using magnesite and bentonite clay composite showed that the effect of contact time on the equilibrium of boron adsorption onto the composite. The percentage removal of boron was observed to increase with an increase in contact time in the first 20 min. Thereafter, the adsorption equilibrium curve leveled off

throughout the investigation period. At 30 min, the system managed to remove 100% of boron from the solution (Masindi et al., 2015).

A study on Arsenic removal from real-life groundwater by adsorption on laterite soil a shaking time of 30-min is arsenic removal reached at 98% Thus adopted as the equilibrium time (Maji et al., 2008).

2.4.3 Effect on pH

Artificial and natural cause the pollution of water bodies by boron of the natural environment. Boron's adsorption in the environment is PH dependent. The species of boron are boric acid $[B(OH)_3]$ at low pH and borate $[B(OH)_4^-]$ at alkaline pH conditions (Masindi et al., 2015).

Boron adsorption on crystalline and amorphous Al and Fe oxides increased with increase in pH. Number of studies indicates that boron adsorption was maxima up to pH 6 to 8 for Al oxides; whereas maximum adsorption was at pH 7 to 9 for Fe oxides The adsorption capacity of LDH-550 toward boron increased when the pH was raised to 8, reached a maximum at pH = 8 and then decreased considerably by raising the pH to 11. This behavior can be illustrated by calculating the mass of boron adsorbed at different pH values and considering a concentration of boron at equilibrium of 50 mg/L. The masses of boron adsorbed were 6.4, 10.3, 16.2 and 5.9 mg/g at pH values of 4, 6, 8 and 10, respectively. Thus, the mass of boron adsorbed was almost doubled and halved when the solution pH was increased from 4 to 8 and from 8 to 10, respectively (Paez et al., 2014). Boric acid is a very weak Lewis acid that reacts with water, accepting a hydroxyl ion and releasing a proton to form the borate anion as indicated by the following reaction:

In aqueous environments, boron is mainly present as boric acid and partially as borate ions according to the dissociation reaction ($K_a = 6 \times 10^{-10}$, pK_a 9.1) (Demirçivi and Saygili, 2008; Geffen et al., 2006) shown in the following equation: $B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$

The result is that maximum removal ability for magnesium oxide to remove boron occurs at pH 9.5, while for aluminum and iron oxide was at pH~8. That maximum boron removal was achieved at pH value between (9.5-10.5) for adsorption onto magnesium oxide and pH (8-8.5) for adsorption onto aluminum and pH 8 for adsorption onto iron oxide. Magnesium oxide is more favorable to remove boron; it has a more removal ability than aluminum and iron oxide (Abbas et al., 2013).

The dissociation curve of boric acid is shown in (Fig.1.). Boric acid is principally present at pH below 9.24, whereas at higher pH borate ions are dominantly present. Boric acid is poorly hydrated and so possesses a small molecular size, whose Stokes radius is estimated to be about 0.00155nm (which is only double that of the water molecule). Having three hydroxyl groups, boric acid can form up to six hydrogen bonds with water leading to strong association with water (Tu, 2014).

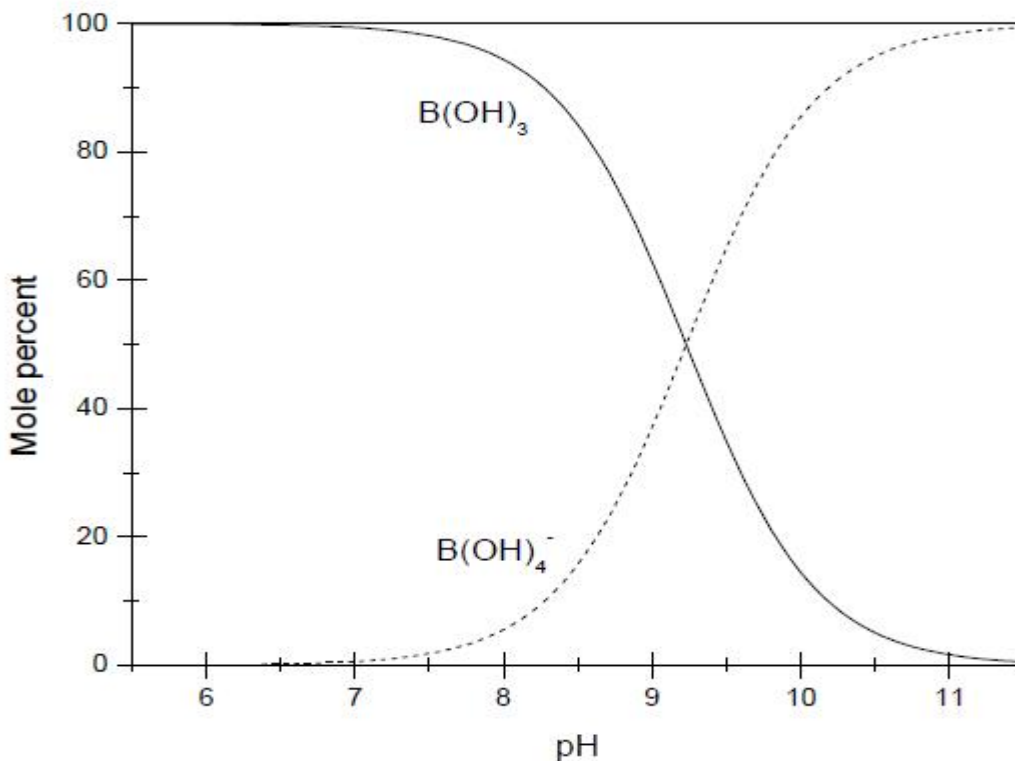


Fig. 1. The dissociation of boric acid in diluted solution.

A study on removal of boron from aqueous solution by 2, 3 Dihydroxybenzaldehyde modified silica gel showed that the effect of pH value influenced boron uptake behavior considerably. The uptake of boron on the surface of SGDHB increased greatly from pH 5.7 up to 7, increased slightly between pH values of approximately 7 and 8.6 and then gradually decreased. It was therefore concluded that the highest removal of boron occurred over the pH range 7.0– 8.6. Subsequent experiments were therefore conducted at pH~8.3 (Kara, 2015). And the other study on treatment of boron-containing optoelectronic wastewater by precipitation process. It was found that for both wastewater boron removal efficiency increased with increasing pH, it has

been pointed out that 90% boron can be removed at pH~13, probably due to the increase of borate concentration in the solution (Irawan et al., 2011).

2.4.4 Effect on Dose

A study on Evaluation of boron removal from water by hydrotalcites-like compounds showed that, when HTAl was used as adsorbent, a maximum adsorption was found at 2.5 g/L (92%). After this point, the increase in adsorbent dose (increase in the number of adsorption sites) did not result in the increase of the boron removal capacity. However, when HTFe was used as adsorbent, the boron removal increased linearly with increasing adsorbent dose, but the maximum removal capacity of removal was only 33% (Ferreira et al., 2006). And the other study on boron removal by adsorption onto different oxides showed that the effect of adsorbent dose on the removal of boron is about 82%, 42.5%, and 37% for magnesium, aluminum and iron oxide respectively at adsorbent dose of 10 g/L, stirring time of 1h and initial concentration of 5mg/L (Abbas et al., 2013).

A study on treatment of boron-containing optoelectronic wastewater by precipitation process the dose of $\text{Ca}(\text{OH})_2$ was varied from 2 to 20 g/L, when at $\text{Ca}(\text{OH})_2$ dose of 4 g/L; boron removal was only 50%, indicating that the super saturation level was insufficient to drive calcium borate precipitation. Increasing the $\text{Ca}(\text{OH})_2$ dose also increased the surface area of lime; therefore calcium borate precipitation was enhanced. Beyond 10 g/L of $\text{Ca}(\text{OH})_2$ dose, no significant increase in boron removal was observed, and approximately 90% boron was removed (Irawan et al., 2011).

Studies showed that the arsenic removal efficiency was increased with increase of adsorbent dose and 20 g/L of that adsorbent could remove 98% of arsenic. Thus the adsorbent dose 20 g/L was used for the optimum dose (Maji et al., 2008).

2.4.5 Effect on competing ions

Competing ions such as silicate, sulfate, phosphate, and oxalate decreased the magnitude of boron adsorption on oxides. The effect of competing ions on boron adsorption can be slight, in the case of sulfate, or substantial in the case of phosphate. The ability of competing anions to leach adsorbed boron from oxides increased in the order: chloride < sulfate arsenate < phosphate.

Significant silicate adsorption produced only a slight decrease in boron adsorption by aluminum oxide suggesting that some boron sorption sites show boron preference (Parks and Edwards, 2005).

2.5 Boron sorption capacity under batch setup

A study in Brazil shows boron removal was independent of the initial pH of the solutions because of the high buffering capacity of the LDHs. On the other hand, the adsorption capacity increases with increasing the adsorbent quantity (Paez et al., 2014). After treatment of a solution containing 5.2 mg/L boron with Mg–Al hydrotalcites the final boron concentration reached the recommended limit by WHO for drinking water (1.5 mg/L). A study of India Adsorption of boron by foothill soils was found to be higher in soil I and soil-II and this may be attributed to the high amount of clay content and CEC of the soils. Soil-III had the lowest adsorption capacity for boron which is likely due to its sandy loam texture and low CEC (Arora and Chala, 2007).

Other study on removal of boron from aqueous solution using magnesite and bentonite clay composite in South Africa shows an increase in adsorption capacity of boron with an increase in dosage was attributed to more adsorption sites becoming available. One gram of composite dosage has provided enough surfaces for adsorption of boron from aqueous solution. This was shown by stabilization in percentage removal hence showing that the composite scavenged all the chemical species that were in aqueous solution. As such, the composite showed optimum removal efficiency at 30 min of equilibration and 1 g of composite dosage hence denoting that those conditions should be used in the subsequent experiments (Masindi et al., 2015).

Study in Poland also shows that maximum adsorption capacity of amorphous zirconium dioxide on boron adsorption is 2.759 mg/g. The maximum adsorption capacity was comparable to the adsorption capacities of other boron removal adsorbents type oxides of metals (Kluczka, 2015).

2.6. Boron desorption in soil

The percentage of desorbed boron was higher at higher level of added boron in all the soils. The coarse textured soils tended to desorb higher amount of boron as compared to fine textured soils. The soils which have higher affinity for boron adsorption, like soil-I, tended to desorb less amount of boron (34.5%), whereas soil-III desorbed 57.8% of the adsorbed boron. Desorption of boron was found to be maximum in soil III which indicated that this soil was more likely to

release the applied boron which may be attributed to the lower clay and CEC values of the soil, whereas, the soils I and II showed less desorption of boron as these soils have high amount of clay and organic matter and thus higher adsorption sites (Arora and Chala, 2007).

2.7. Laterite soils

The term laterite is derived from the Latin word later, meaning brick. It was first used in 1807 by Buchanan to describe a red iron-rich material found in the southern parts of India. Laterite are widely distributed throughout the world in the regions with high rainfall, but especially in the inter-tropical regions of Africa, Australia, India, South-East Asia and South America, where they generally occur just below the surface of grasslands or forest clearings. Their extension indicates that conditions were favorable for their formation at some point in time in the history of the world, but not necessarily simultaneously in all regions (Maignien, 1966). Laterites contribute to the general economy of the regions where they are found. Their scope is very wide and includes civil engineering, agronomic, mining research (iron, aluminum and manganese) deposits. There is no need to emphasize the importance of laterite for various building purposes.

2.7.1. Adsorption Capacity of soil

Among Soil texture separates, clay is a major sink for boron adsorption on its exchange sites, that vermiculite adsorbs more boron than any other minerals. Similarly, reported significant positive correlation between boron and clay contents. Boron follows the following order for adsorption on clay minerals: kaolinite < montmorillonite < illite. Fine textured soils retain more boron compared with coarse textured soils. Fleming (1980) reported leaching of boron in sandy soil resulting into boron deficiency. Boron adsorption increased with increasing clay content and soils having higher clay contents adsorbed more boron. In the same way boron adsorption on clay minerals increased with increasing solution pH 8 to 10. An increase in soil pH from 7 to 10 results in a rapid increase in the concentration of the $B(OH_4)^-$ and an increase in boron adsorption due to the relatively strong affinity towards the clay. Generally, boron adsorption increases with increasing soil temperature. Variation in temperature may alter the interaction between boron adsorption and soil solid components (Billong et al., 2009).

2.7.2. Physical Properties of Lateritic Soils

The physical properties of LS vary according to the mineralogical composition and particle size distribution of the soil. The granulometry can vary from very fine to gravel according to its origin, thus influencing geotechnical properties such as plasticity and compressive strength. One of the main advantages of lateritic material is that it does not readily swell with water. This makes it an excellent packing material particularly when it is not too sandy (Maignien, 1966).

A study in Taiwan shows Nature and Properties of LS shows the physical properties in five different towns. Munsell soil color notation of these soils appears in 2.5 to 5 year, indicating that the color of these soils is red or reddish brown. Loupi, Soka, and Tungwei contain high amounts of clay fraction, while Tamshui and Pingchen consist mostly of silt fraction. They belong to clay and silt clay in texture classification, respectively. Except for Pingchen, all the soils possess moderate structure. Tamshui and Tungwei appear moderate and very fine granular in structure; the others appear sub angular blocky and angular blocky (Ko, 2014).

2.7.2. Chemical Properties of Lateritic Soils

A study in nature and Properties of LS derived from different parent materials in Taiwan shows the chemical properties of the soils. The $\text{pH}_{(\text{H}_2\text{O})}$ values of the soils are 4.85, 4.06, 4.02, 4.46, and 8.13 for Tamshui, Pingchen, Loupi, Soka, and Tungwei, respectively. Obviously, all soils are acidic in nature except Tungwei. The difference in pH ($\text{pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}}$) shows a negative value for all soils, suggesting that the dominative charge on the surface of all soils is negative. On the other hand, this also indicates that a portion of the exchange sites have hydrogen ions. This provides anion exchange capacity and lessens the value for cation exchange capacity. At $\text{pH} \sim 7$, the hydrogen ions are gone, and thus the cation exchange capacity is an inflated value. In the case of Tungwei, its pH value belongs to alkaline region. This is due to the fact that this site contains large amounts of calcium carbonate and shell nodules. Therefore, the exchangeable cations of Ca^{2+} and Mg^{2+} for Tungwei are 9.28 and 8.73 (c mol /kg), respectively. The value is significantly higher than that of other lateritic soils, indicating that the high pH value for Tungwei resulted from great amounts of Ca^{2+} and Mg^{2+} (Ko, 2014).

Laterites vary in color, but are usually brightly colored. The shades most frequently encountered are pink, ochre, red and brown; however, some occurrences are mottled and streaked with violet, and others exhibit green marbling. A single sample may exhibit a whole range of colors merging more or less perceptibly into one another in a variety of patterns and forms. Laterite owe their color to iron oxides in various states of hydration and sometimes also to manganese (Maignien, 1966). Their mineralogy generally involves quartz, kaolinite, hematite, goethite and sometime (Billong et al., 2009).

CHAPTER THREE

Objective

3.1 General objective

- The main objective of this study is to investigate the sorption of Boron using LS under batch experimental setup.

3.2 Specific objectives

- to assess the boron adsorption pattern with respect to varying contact time, solution pH, adsorbent dose, initial boron concentration, and concentration of competing anions;
- to examine the boron sorption capacity of LS;
- to determine the sorption efficiency of LS when using spiked groundwater;
- to investigate the reusability of the boron loaded adsorbent.

CHAPTER FOUR

MATERIALS AND METHODS

4.1. Apparatus and instruments

All the apparatus used were soaked in 10% 0.1 M HNO₃ for 12 h and afterwards washed initially with distilled water. Then the apparatus were dried in hot air oven. A digital pH meter (pH 196, WTW, Germany) was used for measuring pH of solution. A high precision analytical balance (BP 110S, Sartorius) was used for weighing. All absorbance measurements were carried out with spectrophotometer (6400 JENWAY) equipped with 1cm quartz cells. A horizontal shaker (SM 30C, Edmund Buhler) was used for shaking purpose.

4.2. Characterization of adsorbent

Adsorbent media: All the four LS samples used were representative samples, collected from four different sites by using auger in depth of from 0 to 15 cm in Qarsa District, Jimma Zone, Oromia Regional State, Ethiopia according to standard soil sampling procedures, soil textural classification system (Liu and Evett, 2003). At the beginning, the four samples were mixed thoroughly on an equal proportion to make a composite sample, and dried afterwards at room temperature in a laboratory for remove moisture. The dried composite sample of the adsorbent media was crushed by hand in a mortar, and sieved to obtain different particle sizes and used (0.075 – 0.425 mm) of particle size and sand size in diameter using the American Society for Testing and Materials (ASTM D 422). Finally, the sieved samples were kept in airtight plastic container at room temperature until beginning of the adsorption experiments.

Adsorbent Characterization: - The chemical characterization of the LS used was determined by complete silicate analysis in the Ethiopian Geological Survey Laboratory. The pH of the adsorbent was measured using a Microprocessor pH meter (Model of the pH meter) at a 1:2.5 LS/water ratio according to the standard method.

4.3. Adsorbate solution

A standard boron solution was prepared and used in the laboratory. The stock solution was prepared by adding 5.72 g of boric acid, H_3BO_3 analytical reagent-grade to a 1 L plastic volumetric flask and dissolving the solution with distilled water. Subsequently, the boron solution was stored in a plastic container to prevent any reaction between the glass walls and boron in the solution. Working solution for adsorption experiments was prepared by diluting the stock solution immediately prior to their use.

4.4. Experimental studies

A series of duplicate batch adsorption experiments was conducted at room temperature in acid washed polyethylene plastic bottles with blank (only with LS) and control (only with boron) experiments. In all sets of the experiments, a 5 mg/L of initial boron concentration and a desired amount of LS independently were mixed in 100 mL aqueous solution. Then, it was shaken on a horizontal shaker at 200 rpm to homogenize & facilitate the reaction. After this process, 50 mL of prepared solution was centrifuged in Table top centrifuge (PL 002, Taiwan) at 3000 rpm for 15 min, and the solid was separated afterwards using 0.45 μ m watters man filter paper. Then, boron concentration in the filtrate was analyzed on Oromia water works design and supervision enterprise laboratory (OWWDSEL) by curcumin method on spectrophotometer at 540 nm. The average of the duplicate measurements was reported.

4.5. Adsorption Procedure

4.5.1. Effect of Contact Time

In order to determine the equilibrium contact time at which the adsorption completed, the time-dependent adsorption of boron on LS was carried out with 1.5 g of the adsorbent and 5 mg/L boron solution. The mixtures were stirred at speed of 200 rpm for different time intervals (5 - 60 min), centrifuged at pH ~ 7 and the amount of boron adsorbed per unit mass of LS, and the percentage of boron adsorbed was computed respectively using (Eqs. 1 and 2) given below:

$$qt = \frac{C_o - C_t}{M} \times V \quad (1)$$

$$A\% = \frac{C_o - C_t}{C_o} \times 100 \quad (2)$$

Where, q_t (mg/g) is the amount of boron adsorbed at any time, t (min); A (%) is the percentage of Boron adsorbed; C_o (mg/L) is initial boron concentration; C_t (mg/L) is concentration of boron in the aqueous phase at any time, t ; V (L) is volume of the aqueous solution; and M (g) is mass of LS used in the experiment.

4.5.2. Sorption Kinetics

To examine the controlling mechanisms of the adsorption process, three kinetic models were tested to fit the experimental data points: pseudo-first order, pseudo-second order and intra-particle diffusion. Mathematical expressions of these models are given in 3 – 5, respectively (Kumar et al., 2010). The pseudo-first-order kinetic equation is,

$$\log(q_e - q_t) = (\log q_e) - \frac{k_1 t}{2.303} \quad (3)$$

Where k_1 is the rate constant (1/min) of pseudo-first-order model, q_e and q_t are adsorption capacity (mg/g) at equilibrium and at time t respectively. The values of K_1 and q_e , are the plot of $\log(q_e - q_t)$ versus t .

Pseudo-second-order kinetic model was also applied to analyze kinetic adsorption for liquid solution kinetic adsorption in the following linear form (HO, 2004).

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} (t) \quad (4)$$

Where K_2 is the rate constant of pseudo-second-order model [g/ (min mg)] and q_t and q_e are the amount of Adsorbate adsorbed at time t and at equilibrium (mg/g), respectively.

The intra-particle diffusion kinetic model explains about the nature of the adsorption process. If a plot of the linearized form of the intra-particle diffusion model passes through the origin, the process is affected by only intra-particle diffusion; otherwise, adsorptive processes other than intra-particle diffusion might occur (Halim et al., 2013).

Determination of rate parameter for intra-particle diffusion uses the following equation

$$q_t = K_i t^{0.5} + C \quad (5)$$

Where, C is the intercept and K_i is the intra-particle diffusion rate constant (mg/g min^{-1/2}).

4.5.3. Effect of adsorbent Dose

The effect of the adsorbent was determine the optimum dose required for the reduction of boron to a desired level, with increasing amounts of LS from 1 to 3 g/L. The mixtures were stirred at speed of 200 rpm for 60 min, with initial concentration of boron 5 mg/L then the pH ~ 7, and after shaken on shaker 50 mL was centrifuged and the supernatant solutions were collected for boron determination.

4.5.4. Effect of pH

A series of volumetric flasks were taken with 100 mL of 5 mg/L boron solution to determine the optimum pH. Optimum dosage of LS 2 g/L was added .The pH of the flasks was adjusted ranging from 4.0 to 10.0. The flasks were shaken on a horizontal shaker at 200 rpm for optimum contact time 60 min. After stirring the samples were centrifuged, filtered and analyzed for the residual boron concentration.

4.5.5. Effect of initial Concentration

The effect of initial concentration was examined varying the concentration of boron from 2 to 150 mg/L while maintaining the solution pH ~ 8, adsorbent dose 2 g/L, shaking speed 200 rpm and contact time 60 min at equilibrium and 50 mL of supernatant was taken for centrifuge and amount of boron concentration was determined.

4.5.6. Adsorption Isotherm

In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH. Adsorption equilibrium (the ratio between the adsorbed amount with the remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration (Limousin et al., 2007). There are several isotherm models with two or more than two parameters available for analyzing the experimental parameters. The parameters of each model often provide insights into the sorption mechanism, the surface properties and the affinity of the sorbent. In this study, three different isotherm models were tested (Foo and Hameed,

2010). These models are: Langmuir, Freundlich and Redlich– Peterson isotherm models expressed in Eqs.(6) and (8), respectively, All models were used for the evaluation of experimental results (Halim et al., 2013; Fufa et al., 2014). The non-linear regression analysis using mathematical program, was used for direct determination of each model parameters.

The Langmuir adsorption isotherm has been successfully applied to many pollutants adsorption processes and has been the most widely used sorption isotherm for the sorption of a solute from a liquid solution (Han et al., 2009). The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent, and it has been used successfully for many adsorption processes of monolayer adsorption (Fufa et al., 2014; Han et al., 2009)

$$q_e = \frac{Q_{\max} b C_e}{1 + b C_e} \quad (6)$$

Where C_e (mg/L) is the concentration of boron in the aqueous phase at equilibrium; q_e (mg/g) is the amount of boron adsorbed at equilibrium per unit mass of LS; Q_{\max} (mg/g) is the adsorption capacity based on the Langmuir equation; b (L/mg) is the Langmuir constant;

Freundlich isotherm is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. The slope ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Whereas, a value below unity implies chemisorptions process where $1/n$ above one is an indicative of cooperative adsorption (Foo and Hameed, 2010).

$$q_e = K_F C_e^{1/n} \quad (7)$$

Where C_e (mg/L) is the concentration of boron in the aqueous phase at equilibrium; q_e (mg/g) is the amount of boron adsorbed at equilibrium per unit mass of LS ; K_F ($\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$) is the adsorption coefficient based on the Freundlich equation; $1/n$ is the adsorption intensity based on the Freundlich equation.

Redlich and Peterson incorporate three parameters into an empirical isotherm. The R-P isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. It approaches the Freundlich model (heterogeneous systems) at high concentration and is in accordance with the low concentration limit of the Langmuir (homogeneous systems) equation. Typically, a minimization procedure is adopted in solving the equations by maximizing the correlation coefficient between the experimental data points and theoretical model predictions with solver add-in function of the Microsoft excel. In the limit, it approaches Freundlich isotherm model at high concentration (as the exponent g tends to zero) and is in accordance with the low concentration limit of the ideal Langmuir condition (as the g values are all close to one) (Foo and Hameed, 2010). Furthermore, the R-P equation incorporates three parameters into an empirical isotherm, and therefore, can be applied either in homogenous or heterogeneous systems due to the high versatility of the equation (Mall et al., 2006). It can be described as follows:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \quad (8)$$

Where: K_R is the R–P isotherm constant (l/g), a_R the R–P isotherm constant (l/mg) and g the exponent which between 0 and 1, C_e the equilibrium liquid phase concentration (mg/L).

Weber and Chakarborti expressed the essential characteristics and the feasibility of the Langmuir isotherm in terms of a dimensionless constant separation factor R_L , which is defined as:

$$R_L = \frac{1}{(1 + bC_0)} \quad (9)$$

Where b is the Langmuir constant and C_0 is the initial concentration of boron. According to (Fufa et al., 2014; Pandey et al., 2009) R_L values between 0 and 1 indicate favorable adsorption, $R_L > 1$ unfavorable adsorption, $R_L = 1$ Linear and $R_L = 0$ Irreversible.

The sum of the squares of the errors (SSE) function has a major drawback in that it provides isotherm parameters showing a better fit at the higher end of the adsorbate concentration. To identify a suitable these isotherm models for the sorption of boron on LS, the sum of the squares of the errors (SSE) analysis was carried out (Mane et al., 2007; Fetene et al., 2015). It can be described as follows:

$$SSE = \sum (q_{e,cal} - q_{e,exp})^2 \quad (10)$$

Where: $q_{e, cal}$ (mg/g) is the equilibrium capacity obtained by calculation from the model, and $q_{e, exp}$ (mg/g) is the experimental data on the equilibrium capacity.

4.5.7. Effect of interference

The influence of co-existing ions at different concentration levels ranging from 10 to 300 mg/L (Zhang et al., 1987) was examined in such a way that each Chloride, Fluoride, and Bicarbonate ion was prepared from their respective potassium salts separately and in a mixture added to a container of 100 mL solution of 5 mg/L boron at pH ~ 8 with 2 g/L LS and shaken at 200 rpm for 60 min. Then supernatant was taken to determine the effect of interference.

4.5.8. Desorption

To evaluate the regenerability property of the boron loaded LS, 5 mg/L boron in aqueous solution was initially allowed to adsorb on 2 g/L LS at pH ~ 8 shaking at 200 rpm for 60 min. After adsorption, the solid was separated by filtration and dried at 105⁰C for 24 h in an oven. Then desorption was conducted by shaking the dried boron loaded LS at 200 rpm for 60 min in 100 mL solution of 0.1 and 0.2 M NaOH (Fufa et al., 2014). The amount of boron ion desorbed from the spent adsorbent into the solution was determined by quantifying the concentration of boron in the supernatant solution. Afterward, the amount of desorbed boron was measured and desorption ratio of boron was calculated using Eq. (11).

$$\text{Desorption ratio (\%)} = \frac{\text{Amount desorbed}}{\text{Amount adsorbed}} \times 100 \quad (11)$$

4.5.9. Groundwater

A sample of groundwater was collected from a hand pump well in the Jimma University, Jimma town, Oromia Regional, Western Ethiopia. Then physicochemical characteristics of the sample were analyzed following standard methods water and wastewater (APHA, 1999) Temperature (Multi-parameter), pH (Multi-parameter), EC (Multi-parameter), carbonate, bicarbonate, chloride (Argentometric), alkalinity (Titrimetric method), fluoride (Ion electrode) and hardness (EDTA Titrimetric method). The water sample was spiked with 5 mg/L boron and treated afterwards

with 2 g/L LS to evaluate the boron adsorption efficiency of the adsorbent under natural ground water conditions.

4.6. Data Analysis

The data from the experiments was entered and analyzed using OriginPro 8 SRO v8.0724 (OriginLab Corporation, Northampton, USA). The findings were presented using tables, charts and graphs.

4.7. Quality Assurance

The quality of the data was assured through reanalysis of samples or replicates the samples by using standard operating procedures. Calibration, precision and accuracy were used and the samples were duplicate and the average was reported.

4.8. Dissemination plan

The final result of this study will be submitted to Environmental Chair, Jimma Institute of Technology, Jimma University and it will be published on a peer reviewed international journal.

CHAPTER FIVE

RESULT AND DISCUSSION

5.1. Adsorbent Characterization

The analyzed chemical compositions of the adsorbent presented in the Table 1, showed that LS contains high concentration of SiO₂ (63.52%), Al₂O₃ (13%), Fe₂O₃ (9.78%), TiO₂ (1.79%), and other < 1% respectively, which makes its removal efficiency high which is similar with other finding (Maji et al., 2008). Physicochemical properties of adsorbent are highly affected both negatively and positively in the removal efficiency of LS due to the high contents of clay, Al³⁺, Fe³⁺ and low organic content (Ackerman et al., 2007; Dowuona et al., 2012).

Table 1 Chemical composition of LS

Oxide	Weight (%)	Oxide	Weight (%)
SiO ₂	63.52	K ₂ O	<0.01
Al ₂ O ₃	13	MnO	0.38
Fe ₂ O ₃	9.78	P ₂ O ₅	0.18
CaO	0.78	TiO ₂	1.79
MgO	<0.01	H ₂ O	1.25
Na ₂ O	0.82	LoI*	8.25

*LoI: Loss on ignition

5.2. Batch Study

5.2.1. Effect of Contact Time and Adsorption kinetics

Contact time has great influence on the adsorption process. The effect of contact time on boron adsorption was investigated at initial boron concentration 5 mg/L, dose of LS 1.5 g/L, particle size 0.075 - 0.425 mm, agitation rate 200 rpm and pH~7. As show in Fig.2, the removal of boron by LS at varying contact time (0-60 min) had high adsorption capacity of boron concentration in the first 10 min agitation time (Fig. 2.). This might be due to the presence of competent active adsorbing sites on the surface of the adsorbent at the initial stage of the contact time (Fufa et al., 2014). However, optimum time was occurred at 40 min with removal efficiency of 90.10% and

maximum adsorption capacity of 0.30 mg/g. In the previous study (Halim et al., 2013) of boron adsorption on curcumin-impregnated activated carbon, it was found that the equilibrium time needed for it was longer (120 min) than is shown by current study. These results indicate that LS has higher affinity toward the adsorbate than activated carbon. For further investigation, 60 min was considered as an optimum contact time.

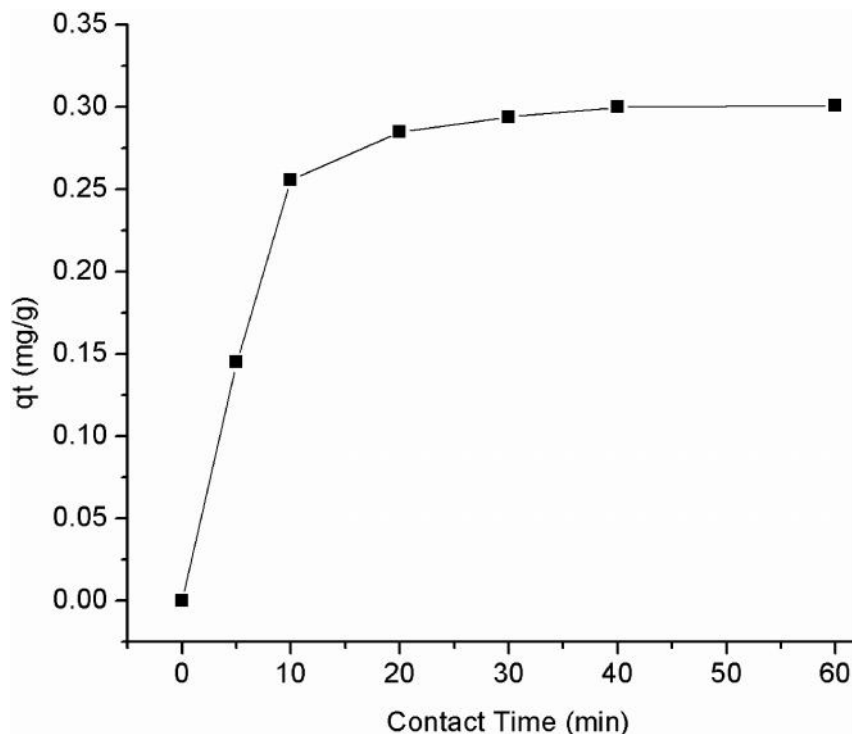


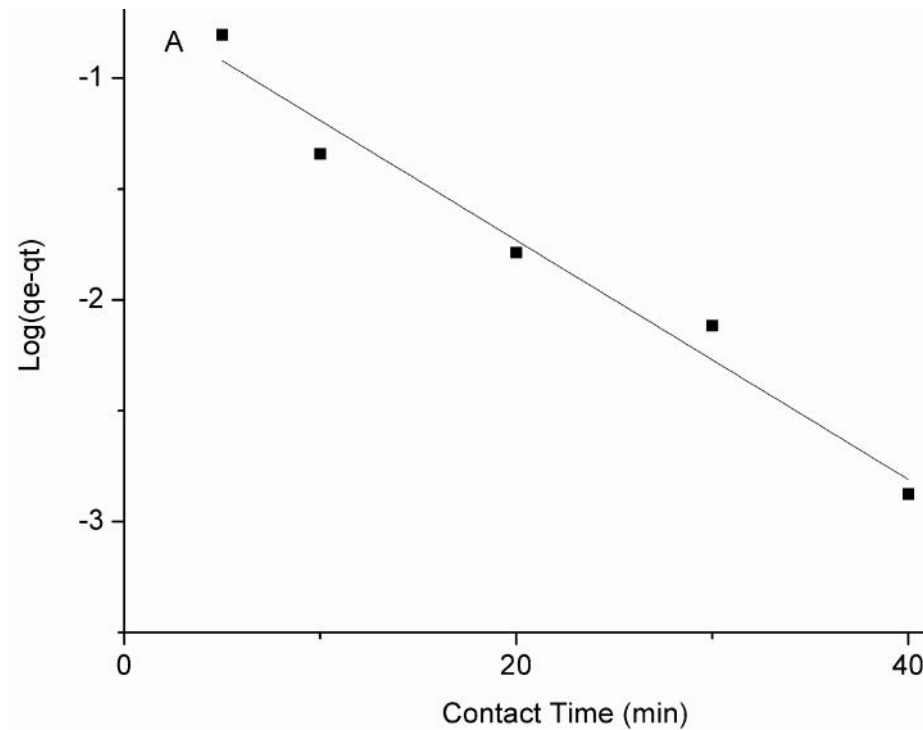
Fig. 2. Effect of contact time (pH: 7, Initial concentration: 5 mg/L, adsorbent dose: 1.5 mg/L, shaking speed: 200 rpm).

The kinetics of the adsorption process was investigated to describe the rate of boron adsorption on LS and the effect of the equilibrium time constructing the kinetic sorption curves. The coefficient of determination (R^2) for the pseudo- second - order kinetic model was greater than that of the pseudo- first- order kinetic models ($0.995 > 0.972$). The linearity of this plot indicates the applicability of the pseudo-second-order kinetic equation for adsorption of boron onto LS under experimental conditions. In addition, the values of the calculated equilibrium capacities, $q_{e,cal}$, were comparable to the experimental equilibrium capacities, $q_{e,exp}$. Thus, the kinetic of boron adsorption on LS could be well described by the pseudo-second order model implying that the adsorption process is chemical adsorption. Overall, these results indicate that the kinetics of

the adsorption process was dominated by chemisorption which involves a chemical reaction between the surface and the adsorbate forming new chemical bonds at the sorbent surface (Kara, 2015).

Table 2 The kinetics parameters for adsorption of B onto LS

Pseudo-first-order		Pseudo-second-order		Intra-particle diffusion	
Parameters	Value	Parameters	Value	Parameters	Value
$q_{e,exp}$ (mg/g)	0.302	$q_{e,exp}$ (mg/g)	0.302	K_i [g/(mg.min ^{0.5})]	0.038
$q_{e,calc}$ (mg/g)	0.223	$q_{e,calc}$ (mg/g)	0.326	C (mg/g)	0.062
K_1 [g/(mg.min)]	0.124	K_2 [g/(mg.min)]	0.784	R^2	0.800
R^2	0.972	R^2	0.995		



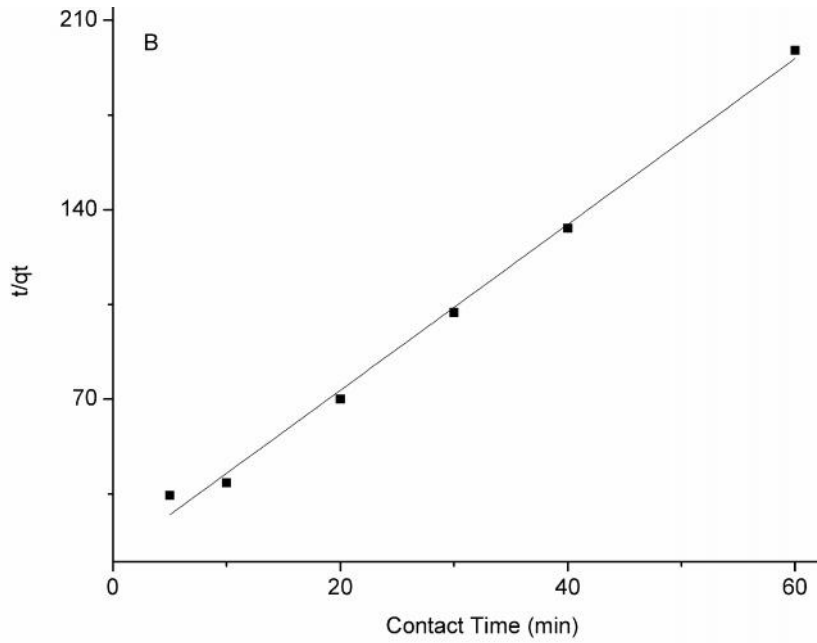


Fig. 3. Plot of pseudo-First-order model (A) and pseudo-second-order model (B)

Intra-particle diffusion model

The intra-particle diffusion kinetic model explains about the rate limiting step in the adsorption process. The plot of the intraparticle diffusion model for the adsorption of boron on LS is given in Fig. 4. The plot of the intraparticle diffusion model for the adsorption of boron on LS was not passes through the origin indicate that the intraparticle diffusion was not the only rate limiting diffusion mechanism (Fufa et al., 2014). Therefore, the adsorption of boron and its kinetics could be the cumulative result of the external diffusion transport of boron, the intraparticle diffusion of the ions and the adsorption of boron ions by the active sites on LS, the result is similar to previous observations (Maiti et al., 2011).

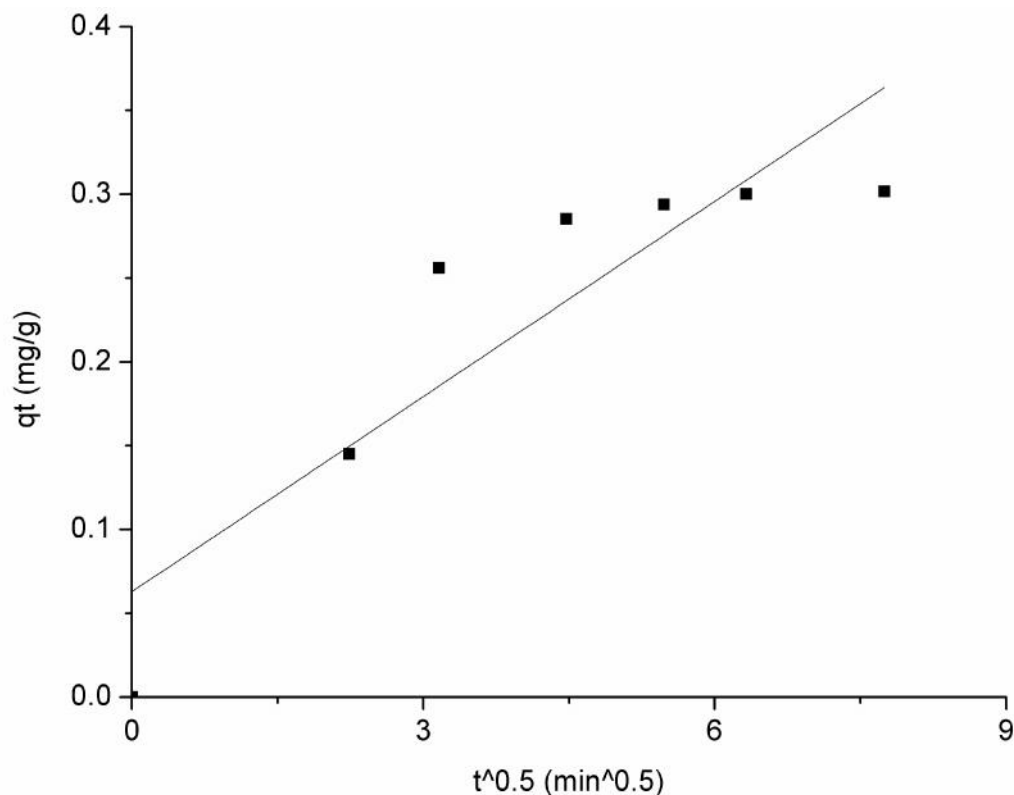


Fig. 4. Plot of intraparticle diffusion model for B absorption onto LS

5.2.4. Effect of Adsorbent Dose

Effect of adsorbent dose on boron adsorption was investigated at initial boron concentration 5 mg/L, contact time values were fixed at the optimum values obtained from the first set of experiments, particle size 0.075 - 0.425 mm, agitation rate 200 rpm and pH ~ 7. The results are presented in Fig. 5. According to the result of this study the percent of boron removal increase with increasing adsorbent dose, as a result of the increases in the total available surface area of the adsorbent particles which is similar with (Maji et al., 2008). When the adsorbent concentration was increased from 1 to 3 g/L, the percentage of boron ions adsorption increased from 89.900% to 92.600% and the amount of mass loaded on to the solid was increased from 0.299 to 0.308 mg/g. It was observed that the adsorption capacity reaches an equilibrium value, beyond which, there was a negligible change in the residual boron concentration, because saturation level attained during an adsorption process. This finding also agrees with (Wambu et al., 2012). High percentage removal of boron may also be attributed to the presence of SiO₂, Al₂O₃, Fe₂O₃, TiO₂ on the composite matrices. It was also observed that 2 g/L LS for further

studies. In general for low adsorbent dose the boron uptake capacity is high, because of the better utilization of the available active sites and at high adsorbent dose, too many sites are available for a fixed boron ion in the solution according to (Abbas et al., 2013).

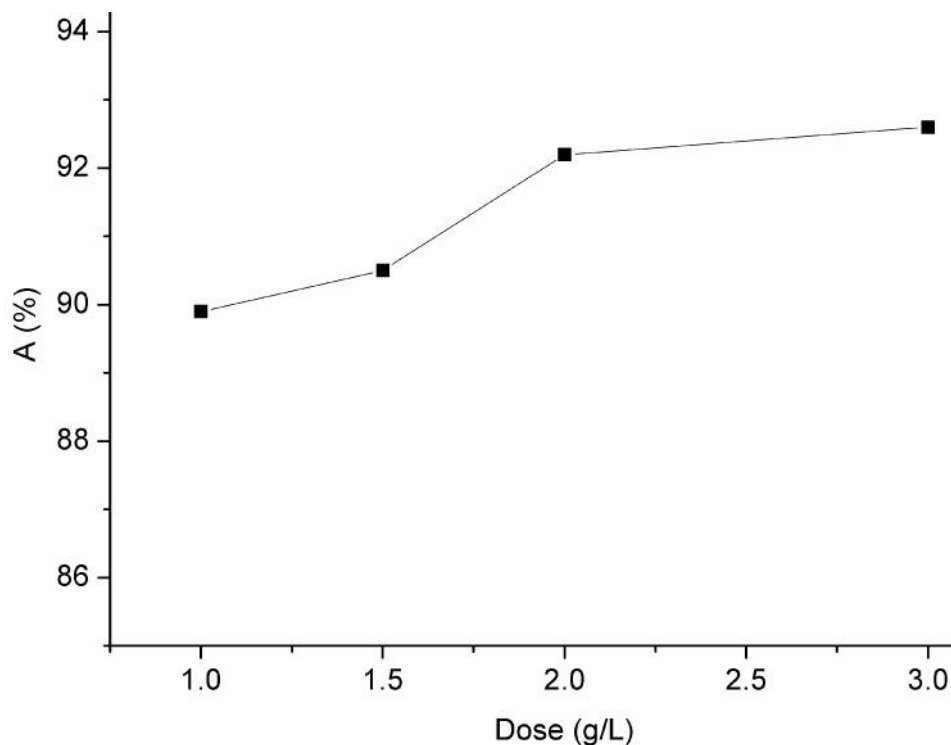


Fig. 5. Effect of adsorbent dose (pH: 7, Initial concentration: 5 mg/g, contact time: 60 min, shaking speed: 200 rpm).

5.2.5. Effect of pH

The adsorption data obtained for the effect of different pH values from 4 to 10 on boron sorption were shown in Fig.6. The maximum adsorption capacity of 0.3153 mg/g was observed at pH value of 8, however the pH (fig.6.) indicted that the uptake of boron on the surface of LS increased greatly from pH of 4 up to 8, and gradually decreased from pH 8 up to 10, A similar result was also observed by other researchers investigating adsorption on aluminum and iron oxide (Abbas et al., 2013) and calcined AlMg layered double hydroxide (Paez et al., 2014). This pH value indicates that the best conditions for boron removal are given when the surface has no charge and boric acid is the predominant specie in solution as discussed by (Abbas et al., 2013). In addition to this pH increase the adsorption efficiency showed be decreased whereas at higher

pH borate ions are dominantly present and increase in the negative charge due to this repeat each other according to reported by (Tu, 2014) and less than pH~7 the surface sites becomes protonated, dissociation of the boric acid at the surface is unlikely to occur and thus the efficiency of boron removal is decreasing (Abbas et al., 2013). The result is shows that the Equilibrem removal ability for LS to remove boron occurs at pH~8. Other important thing was compared to the initial or before shaking and final or after shaking pH was recorded. The initial pH of the solution is 8.02 and the final pH recorded after shacking was 7.34. The pH indicates near to neutral pH because of this used to know save disposal of final waste.

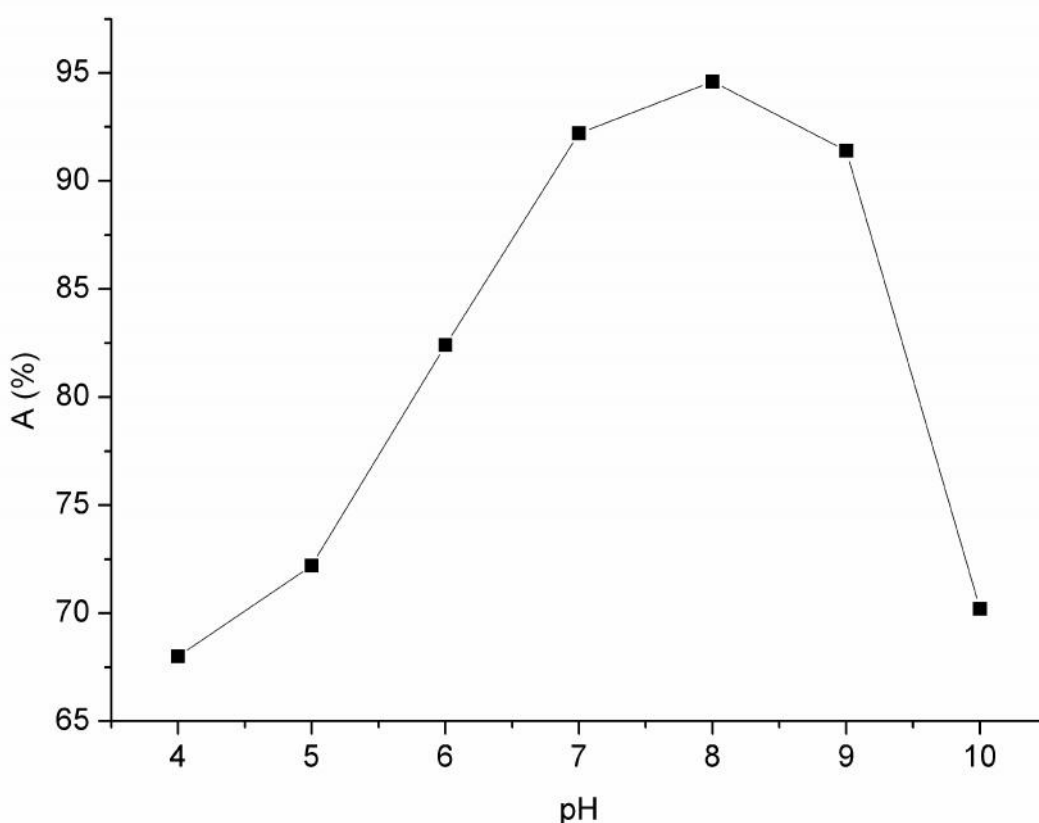


Fig. 6. Effect of pH (adsorbent dose: 2 g/L, Initial concentration: 5 mg/L, contact time: 60 min, shaking speed: 200 rpm).

5.2.6. Effect of initial concentration

Effect of initial boron concentration on boron adsorption was investigated at a dose of LS 2 g/L, particle size between 0.075 to 0.425 mm, agitation speed 200 rpm, contact time 60 min and

pH~8. The results are presented in fig.7. It was at lower concentration the amount of boron loaded in to adsorbent decrease and the efficiency was increased. These mines with increasing the concentration of boron from 2 to 150 mg/L, the amount of boron ions per unit of adsorbent increased from 0.0974 to 2.0715 mg/g. The increase in the adsorption capacity with the increase in the initial concentration of the solute could be attributed to the availability of more boron ions for adsorption at higher concentration on poorly reachable sites with weak sorption energy and the increase of boron in the solution occupied more active sites of the adsorbent that decreases percent removal efficiency (Fufa et al., 2014; Kebede et al., 2014). However, the percentage of boron removal decreased from 97.43 to 27.83% within the increase in the initial concentration of boron. This effect is due to the increase of boron in the solution occupied more active sites of the adsorbent that decreases percent removal efficiency. This is in agreement with the findings from various studies that suggest the more concentrated solution is the better adsorption (Masindi et al., 2015).

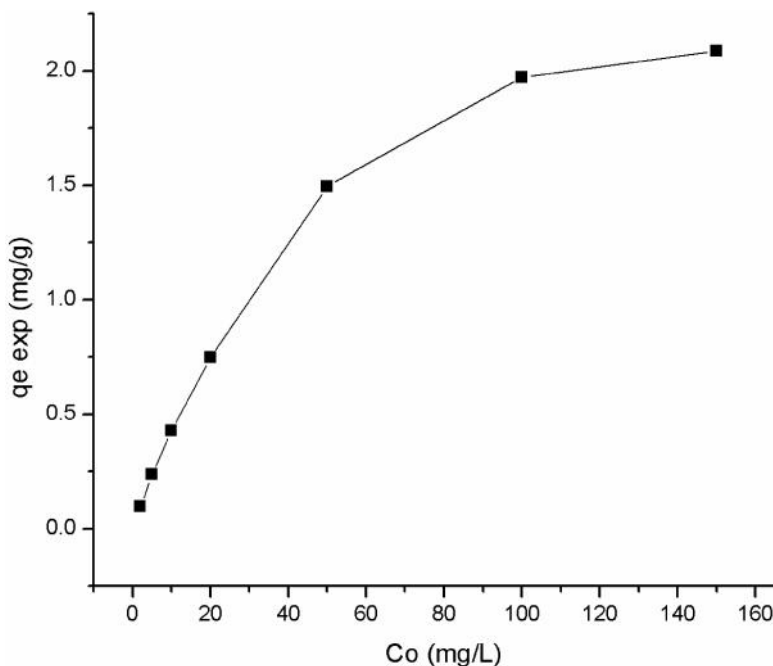


Fig. 7. Effect of initial concentration (adsorbent dose: 2 g/L, PH: 8, contact time: 60 min, shaking speed: 200 rpm).

5.2.7. Adsorption Isotherm

The isotherm plots of the equilibrium adsorption of boron on LS are given in fig. 8. Values of the equilibrium constants computed from nonlinear equations of the isotherms are presented in Table

3. In this study, the Langmuir, Freundlich and Redlich-Peterson isotherms are applied in order to determine the efficiency of LS used as a boron adsorbent. Langmuir, Freundlich and Redlich-Peterson adsorption constants and correlation coefficients (R^2) are checked and to find the most appropriate model for the boron adsorption; Results showed that Langmuir and the Redlich-Peterson isotherm are the higher correlation coefficients ($R^2 > 0.99$) value and the lowest SSE value was found. The fitting of the equilibrium data to the Langmuir isotherm indicated that the monolayer adsorption of boron on the homogeneous surface sites of LS with similar with (Paez et al., 2014; Kara, 2015) and the Redlich-Peterson the exponent value are all close to one (0.869) indicated that the low concentration limit of the ideal Langmuir condition according to (Foo and Hameed, 2010). The nature of adsorption isotherm can be predicted by evaluating the essential characteristic of the Langmuir isotherm expressed in terms of a dimensionless constant separation factor, R_L . The separation factor was computed by equ. 5. The values of R_L computed for boron adsorption on LS were from 0.057 to 0.820 with decreasing in value at high level of initial concentration. The obtained values of R_L (0.364 ± 0.290) this indicated that the favorable adsorption of boron on LS.

Table 3. Isotherm equilibrium parameter

Models	Parameters	Value
Langmuir	Q_{\max} (mg/g)	2.246
	b (L/mg)	0.109
	R_L	0.364 ± 0.29
	R^2	0.993
	SSE	0.0083 ± 0.0108
Freundlich	K_F ($\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$)	0.468
	1/n	0.335
	R^2	0.975
	SSE	0.0157 ± 0.0155
Redlich-Peterson	K_R (1/g)	0.385
	a_R (1/mg)	0.316
	g	0.869
	R^2	0.993
	SSE	0.0064 ± 0.0068

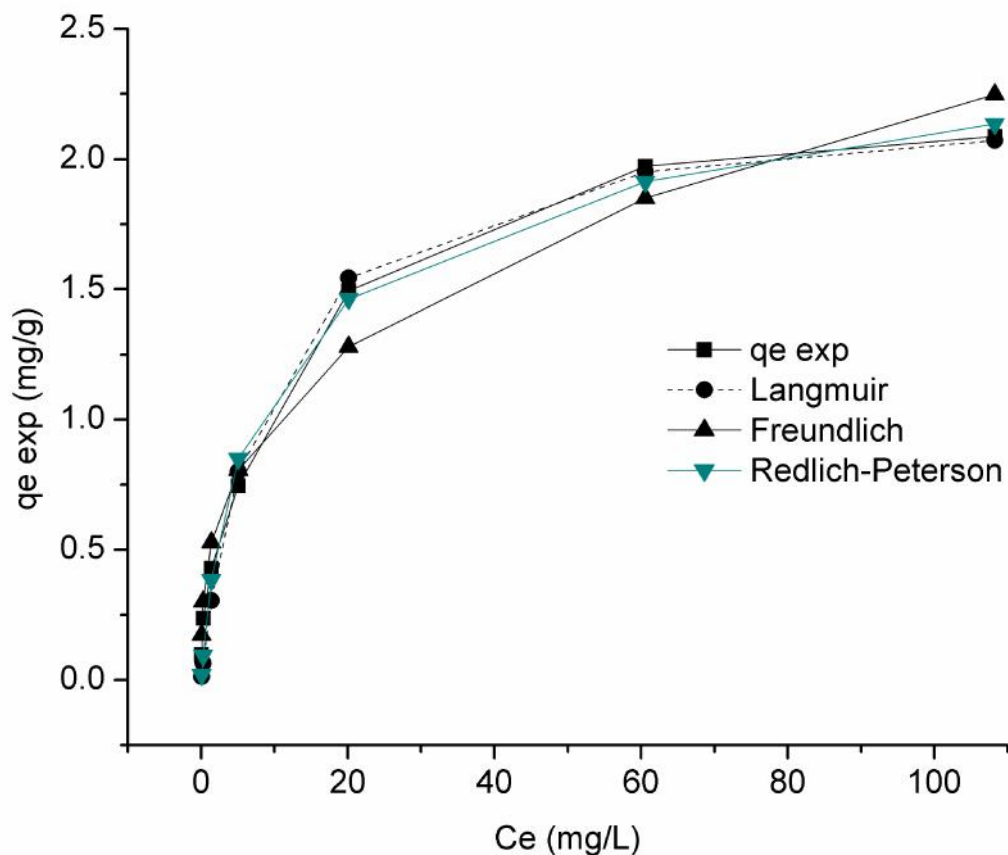


Fig. 8. Isotherm parameters of the equilibrium adsorption of B on LS

5.2.8. Effect of coexisting ion

The effect of competing anions such as chloride, fluoride and bicarbonate those commonly found in ground water. In order to assess the potential applicability of LS as an adsorbent for boron removal from natural water, adsorption efficiency was evaluated as a function of various concentrations of chloride, fluoride, bicarbonate, and their mixture anions, it's the plots of the effect of the presence of competing anions on the boron removal are given in Fig. 9. The result was observed that boron adsorption efficiency was slightly interfering by bicarbonate and their mixture within the concentration range tested (100 and 300 mg/L) and at 10 mg/L all are not significantly affect. However, the presence of fluoride, and chloride did not significantly affect boron adsorption efficiency within the concentration range tested (10–300 mg/L).

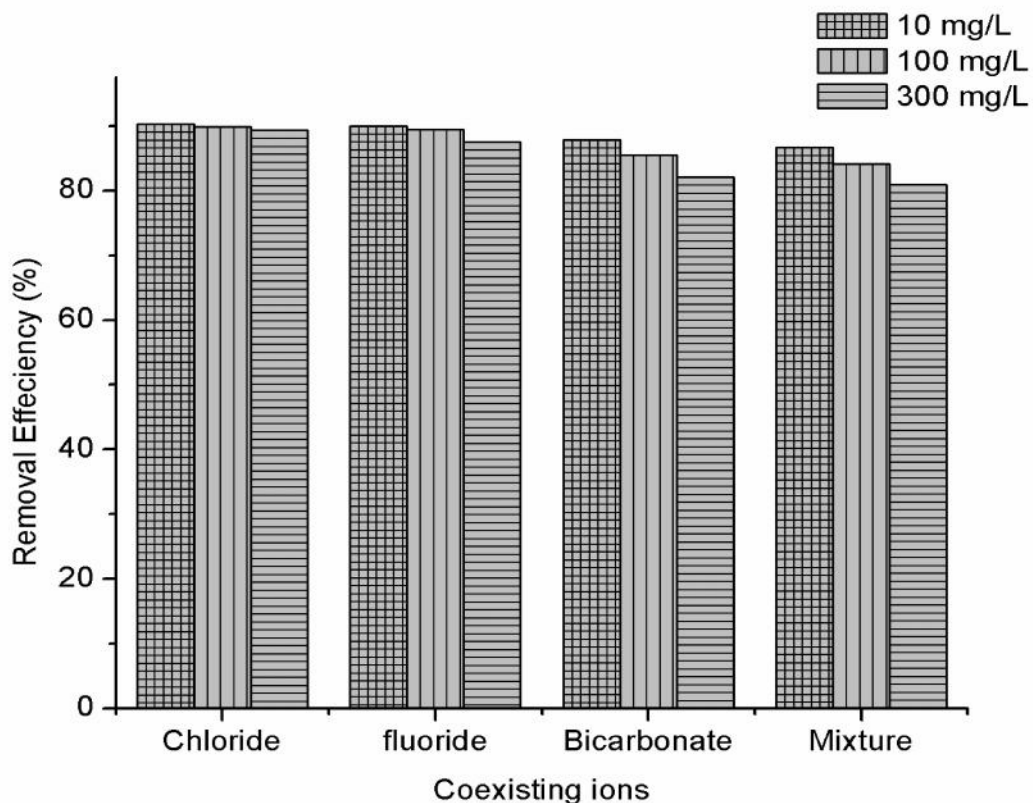


Fig. 9. Effect of coexisting ion (initial concentration: 5 mg/L, adsorbent dose: 2 g/L, PH: 8, contact time: 60 min, shaking speed: 200 rpm)

5.2.9. Desorption study

The reusability of adsorbent was investigated using NaOH solution at two concentration. The result showed that the percentage of boron desorbed increased from 67.72% to 83.28% as the concentration of NaOH increased from 0.1 to 0.2 M NaOH in the solution respectively, the result is similar to previous studies (Maji et al., 2008). According to Maji et al., study the regenerated adsorbent showed even better performance compared to the original soil. This is possibly due to the fact that on NaOH treatment the surface becomes fresh and the numbers of active sites are increased. In general, adsorption/ desorption process can be minimize the waste disposal problems and maximize the resources. So a detail regeneration experiment should be conducted to determine the reusability of the LS.

5.2.10. Removal of Boron from ground water

Based on the optimum conditions (except pH) that were determined by LS under natural groundwater conditions was evaluated using 5 mg/L boron spiked groundwater sample. The results revealed that the boron removal efficiency from spiked ground water with initial boron concentration of 5 mg/L was 88.9 %. This removal efficiency reduced the initial boron in spiked ground water to a level of 0.55 mg/L which is within the permissible range of WHO guidelines. In general the adsorbent was effective to reduce boron from spiked ground water to the level of permissible range.

Table 4 Physicochemical properties of groundwater

Parameter	Value
Cl ⁻ (mg/L)	17
HCO ₃ ⁻ (mg/L)	585.6
CO ₃ ²⁻ (mg/L)	Null
F ⁻ (mg/L)	14.17
Total Alkalinity (mg/L)	480
Conductivity (µs/cm)	1309
pH	7.82
Total Hardens (mg/L)	16
Ca Hardens (mg/L)	12
Mg Hardens (mg/L)	4

CHAPTER SIX

Conclusion and Recommendation

6.1 Conclusion

The present study investigated the boron adsorption behavior of LS under various batch adsorption experimental parameters. The equilibrium time was found to be at 60 min within (90.5%) of removal efficiency and adsorption capacity is (0.302 mg/g) and the optimum dose was 2 mg/L (92.2%) removal efficiency and adsorption capacity is (0.307 mg/g). The adsorption capacity of LS toward boron was highly dependent on the solution pH and Maximum amount of boron was achieved at pH~8 (0.32 mg/g). The adsorption kinetics was follows the pseudo-second-order reaction kinetics with the correlation coefficient, $R^2 = 0.99$. The fitting of the pseudo-second order equation may suggest that the mechanism of boron adsorption on the adsorbent should be chemisorptions and the intra-particle diffusion is not the only rate-limiting step. The amount of boron uptake increases with increasing the initial boron concentration. The equilibrium boron adsorption data followed the non-linear Langmuir and Redlich - Peterson isotherms with the correlation coefficient, $R^2 = 0.99$. The Langmuir and Redlich -Peterson isotherm provided a better fitting with the maximum adsorption capacity of 2.07 mg/g and 2.13mg/g respectively, the Langmuir isotherm indicating the homogeneous surface of the LS. Desorption was tested using NaOH solution in different concentrations. The concentrations were increased from 0.1 to 0.2 M NaOH as the percentage of boron desorbed increased from 67.72% to 83.28%. The presences of bicarbonate and Mixture significantly influence boron adsorption efficiency while chloride and fluoride were interfering slightly. The adsorbent was reduced boron concentration of spiked ground water from 5 mg/l to 0.55 mg/l which is within the permissible range of WHO guidelines.

6.2 Recommendation

Based on experimental study, and entire research process, the following recommendations were made for concerned bodies just under here.

- Recommend LS could be useful for removing the impacts of boron in ground water.
- To investigation other factors which were not considered under this work like particle size of the adsorbent, agitation Speed and temperature.
- For Practical applicability of Ls for boron removal requires for large-scale application, further fixed bed column adsorption investigation.

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ANNEX I Laboratory procedures for determination of Boron by curcumin Method

1. General Discussion

A. Principle: when a sample of water containing boron is acidified and evaporated in the presence of curcumin, a red-colored product called rosocyanine is found. The rosocyanine is taken up in a suitable solvent and the red color is compared with standards visually or photometrically.

B. Interference: NO_3^- -N concentration above 20 mg/L interferes. Significantly high results are possible when the total of calcium and magnesium hardness exceeds 100mg/L as calcium carbonate (CaCO_3). Moderate hardness levels also can cause a considerable percentage error in the low boron range. This interference springs from the insolubility of the hardness salts in 95% ethanols and consequent turbidity in the final solution. Filter the final solution or pass the original sample thoroughly a column of strongly acidic cation-exchange resin in the hydrogen form to remove interfering cations. The latter procedure permits application of the method on samples of high hardness or solids content. Phosphate does not interfere.

C. Minimum detectable quantity: 0.2 μg B.

2. Apparatus

A. Spectrophotometer, for use at 540 nm, with a minimum light path of 1 cm.

B. Evaporating dishes, 100 to 150 mL capacity, of high-silica glass, platinum, or other suitable material.

C. Water bath set at $55 \pm 2^\circ\text{C}$.

D. Glass-stoppered, volumetric flasks, 25 and 50 mL capacity.

E. Ion-exchange column, 50 cm long by 1.3 cm in diameter.

3. Reagents

Store all reagents in polyethylene or boron-free containers.

A. Stock boron solution: Dissolve 571.6 mg anhydrous boric acid, H_3BO_3 , in distilled water and dilute to 1000 mL; 1.00 mL = 100 μg B. Because H_3BO_3 loses weight on drying at 105°C , use a

reagent meeting ACS specifications and keep the bottle tightly stoppered to prevent entrance of atmospheric moisture.

B. Standard boron solution: Dilute 10.00 mL stock boron solution to 1000 mL with distilled water; 1.00 mL = 1.00 μg B.

C. Curcumin reagent: Dissolve 40 mg finely ground curcumin and 5.0 g oxalic acid in 80 mL 95% ethyl alcohol. Add 4.2 mL conc. HCl, make up to 100 mL with ethyl alcohol in a 100 mL volumetric flask, and filter if reagent is turbid (isopropyl alcohol, 95%, may be used in place of ethyl alcohol). This reagent is stable for several days if stored in a refrigerator.

D. Ethyl or isopropyl alcohol, 95%.

E. Reagents for removal of high hardness and cation interference:

1) Strongly acidic cation-exchange resin.

2) Hydrochloric acid, HCl, 1 + 5.

4. Procedure

A. Precautions: Closely control such variables as volumes and concentrations of reagents, as well as time and temperature of drying. Use evaporating dishes identical in shape, size, and composition to insure equal evaporation time because increasing the time increases intensity of the resulting color.

B. Preparation of calibration curve: Pipet 0 (blank), 0.25, 0.50, 0.75, and 1.00 μg boron into evaporating dishes of the same type, shape, and size. Add distilled water to each standard to bring total volume to 1.0 mL. Add 4.0 mL curcumin reagent to each and swirl gently to mix contents thoroughly. Float dishes on a water bath set at $55 \pm 2^\circ\text{C}$ and let them remain for 80 min, which is usually sufficient for complete drying and removal of HCl. Keep drying time constant for standards and samples. After dishes cool to room temperature, add 10 mL 95% ethyl alcohol to each dish and stir gently with a polyethylene rod to insure complete dissolution of the red-colored product.

Wash contents of dish into a 25 mL volumetric flask, using 95% ethyl alcohol. Make up to mark with 95% ethyl alcohol and mix thoroughly by inverting. Read absorbance of standards and samples at a wavelength of 540 nm after setting reagent blank at zero absorbance. The calibration curve is linear from 0 to 1.00 μg boron. Make photometric readings within 1 h of drying samples.

C. Sample treatment: For waters containing 0.10 to 1.00 mg B/L, use 1.00 mL sample. For waters containing more than 1.00 mg B/L, make an appropriate dilution with boron-free distilled water, so that a 1.00 mL portion contains approximately 0.50 μg boron.

Pipet 1.00 mL sample or dilution into an evaporating dish. Unless the calibration curve is being determined at the same time, prepare a blank and a standard containing 0.50 μg boron and run in conjunction with the sample. Proceed as in '4b', beginning with "Add 4.0 mL curcumin reagent" If the final solution is turbid, filter through filter paper before reading absorbance. Calculate boron content from calibration curve.

D. Visual comparison: The photometric method may be adapted to visual estimation of low boron concentrations, from 50 to 200 $\mu\text{g/L}$, as follows: Dilute the standard boron solution 1 + 3 with distilled water; 1.00 mL = 0.20 μg B. Pipet 0, 0.05, 0.10, 0.15, and 0.20 μg boron into evaporating dishes as indicated in '4b'. At the same time add an appropriate volume of sample (1.00 mL or portion diluted to 1.00 mL) to an identical evaporating dish. The total boron should be between 0.05 and 0.20 μg . Proceed as in '4b', beginning with "Add 4.0 mL curcumin reagent" Compare color of samples with standards within 1 h of drying samples.

e. Removal of high hardness and cation interference: Prepare an ion-exchange column of approximately 20 cm \times 1.3 cm diam. Charge column with a strongly acidic cation-exchange resin. Backwash column with distilled water to remove entrained air bubbles. Keep the resin covered with liquid at all times. Pass 50 mL 1 + 5 HCl through column at a rate of 0.2 mL acid/mL resin in column/min and wash column free of acid with distilled water. Pipet 25 mL sample or a smaller sample of known high boron content diluted to 25 mL, onto the resin column. Adjust rate of flow to about 2 drops/s and collect effluent in a 50-mL volumetric flask. Wash column with small portions of distilled water until flask is filled to mark. Mix and transfer 2.00 mL into evaporating dish. Add 4.0 mL curcumin reagent and complete the analysis as described in '4b' preceding.

5. Calculation

Use the following equation to calculate boron concentration from absorbance readings

$$\text{mg B/L} = \frac{A_2 \times C}{A_1 \times S}$$

Where:

A_1 = absorbance of standard,

A_2 = absorbance of sample,

C = $\mu\text{g B}$ in standard taken, and

S = mL sample.

6. Precision and Bias

A synthetic sample containing 240 $\mu\text{g B/L}$, 40 $\mu\text{g As/L}$, 250 $\mu\text{g Be/L}$, 20 $\mu\text{g Se/L}$, and 6 $\mu\text{g V/L}$ in distilled water was analyzed in 30 laboratories by the curcumin method with a relative standard deviation of 22.8% and a relative error of 0% (APHA et al., 1999).

ANNEX II Effect of contact time on B adsorption

Time	Co (mg/L)	Ce (mg/L)			A (%)	qe (mg/g)
		Trail 1	Trail 2	Average		
0.00	5.00	5.00	5.00	5.00	0.00	0.00
5.00	5.00	2.81	2.84	2.83	43.50	0.15
10.00	5.00	1.19	1.13	1.16	76.80	0.26
20.00	5.00	0.70	0.74	0.72	85.60	0.29
30.00	5.00	0.52	0.66	0.59	88.20	0.29
40.00	5.00	0.48	0.51	0.50	90.10	0.30
60.00	5.00	0.50	0.45	0.48	90.50	0.30

ANNEX III Effect of dose on B adsorption

pH in 1	pH in 2	Dose	Co (mg/L)	Ce (mg/L)			A (%)	qe (mg/g)	pH fi1	pH fi2
				Trail 1	Trail 2	Average				
7.01	7.05	1.00	5.00	0.49	0.52	0.51	89.90	0.30	6.45	6.57
7.09	7.02	1.50	5.00	0.50	0.45	0.48	90.50	0.30	6.46	6.48
7.06	6.97	2.00	5.00	0.34	0.44	0.39	92.20	0.31	6.64	6.57
6.99	7.03	3.00	5.00	0.40	0.34	0.37	92.60	0.31	6.42	6.48

ANNEX IV Effect of pH on B adsorption

pH in1	pH in2	Co (mg/L)	Ce (mg/L)			A (%)	qe (mg/g)	pH fi1	pH fi2
			Trail 1	Trail 2	Average				
4.07	3.98	5.00	1.30	1.90	1.60	68.00	0.23	4.54	4.50
5.02	5.01	5.00	1.41	1.37	1.39	72.20	0.24	5.55	5.52
6.00	6.02	5.00	0.92	0.84	0.88	82.40	0.27	6.35	6.22
7.09	7.02	5.00	0.34	0.44	0.39	92.20	0.31	6.46	6.48
8.09	7.94	5.00	0.24	0.30	0.27	94.60	0.32	7.28	7.39
9.00	8.99	5.00	0.46	0.40	0.43	91.40	0.30	8.40	8.27
10.05	10.05	5.00	1.47	1.51	1.49	70.20	0.23	9.33	9.27

ANNEX V Effect of initial concentration on B adsorption

pH in1	pH in2	Co (mg/L)	Ce (mg/L)			A (%)	qe (mg/g)	pH fi1	pH fi2
			Trail 1	Trail 2	Average				
8.08	8.03	2.00	0.06	0.05	0.05	97.43	0.10	6.94	7.06
8.09	7.94	5.00	0.24	0.30	0.27	94.60	0.32	7.28	7.39
8.02	8.05	10.00	1.45	1.41	1.43	85.70	0.43	7.17	7.32
7.94	8.07	20.00	5.02	5.10	5.06	74.70	0.75	7.26	7.51
8.05	8.09	50.00	20.13	20.10	20.12	59.77	1.49	7.68	7.71
8.09	7.94	100.00	60.54	60.59	60.57	39.44	1.97	7.86	7.71
7.92	7.90	150.00	108.24	108.27	108.26	27.83	2.09	7.79	7.75

ANNEX VI Effect of LS on B adsorption isotherm

Co (mg/L)	Ce (mg/L)	qe (mg/g)	Freundlich isotherm		Langmuir isotherm			Redlich-Peterson		A (%)
			qe, calc	SSE	qe, calc	SSE	RL	qe, calc	SSE	
2.0	0.05	0.0974	0.1733	0.0058	0.0126	0.0072	0.8204	0.0193	0.0061	97.43
5.0	0.27	0.2365	0.3019	0.0043	0.0645	0.0296	0.6462	0.0943	0.0202	94.60
10.0	1.43	0.4285	0.5278	0.0099	0.3041	0.0155	0.4773	0.3845	0.0019	85.70
20.0	5.06	0.7470	0.8060	0.0035	0.8008	0.0029	0.3135	0.8493	0.0105	74.70
50.0	20.12	1.4943	1.2798	0.0460	1.5449	0.0026	0.1544	1.4636	0.0009	59.77
100.0	60.57	1.9718	1.8515	0.0145	1.9519	0.0004	0.0837	1.9138	0.0034	39.44
150.0	108.26	2.0873	2.2492	0.0262	2.0715	0.0002	0.0574	2.1344	0.0022	27.83
			sum	0.1101	sum	0.0584		sum	0.0452	

ANNEX VII Effect of co-existing ions on B adsorption

concentration mg/L	Chloride A (%)	Fluoride A (%)	Bicarbonate A (%)	Mixture A (%)
0	94.6	94.6	94.6	94.6
10	90.3	90	87.9	86.7
100	89.9	89.5	85.5	84.1
300	89.3	87.5	82.1	80.9

ANNEX VIII Adsorption/Desorption using 0.1 and 0.2 M NaOH

Adsorption (%)		Desorption (%)	
LS			
0.1 M	0.2 M	0.1 M	0.2 M
94.8	94.5	67.72	83.28