



JIMMA UNIVERSITY

JIMMA INSTITUTE OF TECHNOLOGY

FACULTY OF CIVIL AND ENVIRONMENTAL ENGINEERING

ENVIRONMENTAL ENGINEERING CHAIR

**KINETICS AND ISOTHERM MODELING OF LIQUID PHASE ADSORPTION OF
FLUORIDE ONTO ACTIVATED *Lupinus albus***

BY CHALA WOJI

**A THESIS SUBMITTED TO ENVIRONMENTAL ENGINEERING CHAIR, FACULTY
OF CIVIL AND ENVIRONMENTAL ENGINEERING, JIMMA INSTITUTE OF
TECHNOLOGY, JIMMA UNIVERSITY; IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTERS OF SCIENCE IN
ENVIRONMENTAL ENGINEERING**

JANUARY,2020

JIMMA, ETHIOPIA

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ASSURANCE OF PRINCIPAL INVESTIGATOR

I, the undersigned, declare that this thesis is my original work, has not been presented for a degree in this or other university and that all sources of materials used for this have been fully acknowledged.

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Approval of the advisors:

This thesis has been submitted for examination with my approval as University Advisor.

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ABSTRACT

High concentration of fluoride (> 1.5 mg/L) in drinking water causes different health problems. Therefore, the aim of the study was fluoride removal capacity of activated L. albus under laboratory batch adsorption set up. The Physicochemical properties of the activated L. albus Moisture Content (%), Ash Content (%), pH and FTIR spectra of the adsorbent before and after adsorption were studied. The influence of parameters such as: pH of the solution, contact time, adsorbent doses, initial fluoride concentration, and the presence of co-existing anions was investigated. High fluoride removal efficiency (97.69%) was observed at PH 7 and equilibrium was achieved within 30 min of agitation time. The amount of fluoride adsorbed increase with increasing the dose of the adsorbent from 1 to 5 g/L. The equilibrium data tested with Langmuir, Freundlich, Sips and Redlich-Peterson Isotherm at room temperature and it was found that the Freundlich Isotherm ($R^2=0.9901$) best fitted the adsorption of fluoride. The equilibrium removal capacity was observed using 5 g/L of the adsorbent. The experimental Kinetics of the data was analyzed using pseudo-first-order, pseudo-second-order and Weber-Morris Intra-particle kinetics model. Kinetics data followed the non-linear pseudo-first-order model ($R^2 = 0.96$) for L. albus adsorbent. The adsorption capacity decrease from 68 to 56% with the increase of bicarbonate concentration from 10 to 200 mg/L. The results obtained from this study could provide important information for evaluating the application of L. albus for removal of fluoride from drinking water. Therefore, the result obtained uses for further investigation.

Key words: Adsorption, Adsorption isotherms, Adsorption kinetics, *L. albus*

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ACRONYMS

APHA	American Public Health Association
EPA	Environmental Protection Authority
FTIR	Fourier Transform Infrared Spectrum
IQ	Intelligence Quotient
<i>L.albus</i>	Lupinus albus
NLPFO	Nonlinear Pseudo First Order
NLPSO	Nonlinear Pseudo Second Order
USEPA	United State Environmental Protection Agency
UV-VIS	Ultra Violate Visible Spectrophotometer
WHO	World Health Organization

CHAPTER ONE: INTRODUCTION

1.1 Background

Fluoride is a naturally occurring compound in minerals, geochemical deposits and natural water systems (Chen *et al.*, 2010). Regarding the level of fluoride in drinking water, the WHO recommended guideline value is 1.5 mg/L (WHO,2008). Nevertheless, excessive exposure to fluoride can cause a number of adverse effects, which may range from mild dental fluorosis to crippling skeletal fluorosis (Tahir and Rasheed, 2013).

Fluorspar (found in sedimentary rocks), cryolite (found in igneous rocks) fluorapatite and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) are the main sources of fluoride in ground water (Veeraputhiran & Alagumuthu, 2010). Fluoride occurs mainly as sellaite (MgF_2), fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite [$3\text{Ca}_3(\text{PO}_4)_2\text{Ca}(\text{FCl}_2)$]. Fluorspar and cryolite minerals are nearly in-soluble in water. For this reason, fluorides are available in groundwater (the main source of drinking water) (Mohapatra *et al.*, 2009).

According to Tomar *et al.*, 2014 reports, the problem of high fluoride concentration in drinking water resources up to 30 mg/L in numerous countries like India, Pakistan, China, Sri Lanka, Spain, Holland, Poland, Italy, Iraq, Iran, Sudan, Uganda, Kenya, United Republic of Tanzania, Mexico, Thailand, Serbia, Eritrea, West Africa, Southern Africa, North and South American countries and Ethiopia. Today, different technologies have been used for the removal of fluoride from drinking water such as adsorption, coagulation, ion-exchange, membrane separation, electro dialysis (Wang *et al.*, 2013), reverse osmosis and nano-filtration (Chakraborty *et al.*, 2013).

The problem of fluoride removal from drinking water is an urgent duty for many regions of the world (Paudyal *et al.*, 2013). The interest of getting cheap and easily available materials for the removal of fluoride from drinking water by adsorption method has increased significantly in the current days which is especially very important for developing countries (Datsko *et al.*, 2011).

Fluorosis is a worldwide problem such as China, Italy, Holland, Ivory Coast, Sri Lanka, Spain, Ghana, Senegal, Algeria, Uganda, South Africa, Tanzania, Sudan, Nigeria, Kenya and Ethiopia are facing this problem (Yadav *et al.*, 2014). Most Ethiopian people those whom living in numerous areas of the main Ethiopian Rift Valley are suffering by consuming drinking water with up to 33

mg/l of fluoride concentration which is evaluated as a risk for a populations spread over different regional states such as; Afar, Amhara, Oromia and Southern Nations, Nationalities and Peoples Regional State (SNNPR) (Tikariha & Sahu, 2013). Consumption of this elevated fluoride concentration results dental fluorosis which has a significant socioeconomic impacts such as aesthetic problems and psychological impacts are hard to quantify yet should not be underestimated especially among young people. As a result of this, early retirement is the case of the Wonji/Shoa factory workers, who were the first with whom fluorosis was diagnosed in Ethiopia in the mid 1970's. But, at present there is no clear policy to address the fluorosis problem in Ethiopia (Steenbergen *et al.*, 2011).

To remove high fluoride concentration of above WHO guideline (1.5 mg/L) from drinking water, many research has focused on various types of inexpensive adsorption media such as red mud (Tor *et al.*, 2009), alum sludge, activated carbon (Hanumantharao & Kishore, 2011), bone char (Brunson & Sabatini, 2014), (Rojas *et al.*, 2013), bauxite (Sujana & Anand, 2011), activated rice husk (Mondal *et al.*, 2012), brick powder, pumice stone, charcoal, fly ash, seed extracts of *Moringaoleifera* (Ravikumar & Sheeja, 2014).

Adsorption using plant origins is an efficient, clean, cheap and user-friendly technique (Singha, *et al.*, 2011). In the present study, a low cost naturally available adsorbent has been investigated from *Lupinus albus* seed for the removal of fluoride from aqueous solution. This crop, locally known as “*gibto*” (*Lupinus albus*) grown in Ethiopia (mostly in the North-western part) for local alcoholic drink ‘Areki’ preparation (Tizazu and Emire, 2010).

L. albus is legume plant from the same family of Leguminosae. It has a green manure potential contributing to improve soil structure, can fix nitrogen, enhance availability of phosphorus and improve soil fertility, tolerant of infertile soils, disturbed sites, high tendency of growing on marginal lands and capable of remediating polluted (Nigussie, 2012). This adaptation allows lupine can grow without fertilizer (Engdawe, 2012).

1.2 Statement of the Problem

Recently, more than 200 million people consume fluoride concentration that exceeds the allowable limit of World Health Organization (WHO) guideline (Yadav *et al.*, 2014). Ethiopia is one of the twenty-three countries in the world where a significant number of its population suffers from the toxic effects of high levels of fluoride in drinking water (Tekle-haimanot *et al.*, 2006).

As a result of this, excess consumption of fluoride concentration is increased above standard limit which is a problematic due to the dental and skeletal fluorosis, mottling of teeth, crippling fluorosis (Cheng *et al.*, 2014) and various diseases such as osteoporosis, arthritis, brittle bones, cancer, infertility, brain damage, Alzheimer syndrome and thyroid disorder (Sandoval *et al.*, 2014); increased rates of hip fracture, increasing urinary fluoride in cattle (Tomar *et al.*, 2013), fetal cerebral function and neurotransmitters (Tikariha and Sahu, 2013) can attack human body on excessive intake of fluoride.

So, to overcome this serious problem, numerous technologies such as: adsorption, electro coagulation, ion exchange, coagulation, electro dialysis, reverse osmosis and membrane technology have been applied recently to remove fluoride from drinking water. Even though they are effective, most of them are expensive and produce large amount of sludge after treatment which is a detrimental effect on the environment (Roy and Dass, 2013).

Activated alumina coated silica gel, activated saw dust, activated coconut shell carbon, coffee Husk, bone charcoal, activated soil sorbent, etc. are some of the different materials investigated for adsorptive removal of fluoride from water. Activated carbon prepared from various raw materials exhibits good fluoride uptake capacity (McKee and Johnston, 2013).

A very good adsorbent such as activated alumina has been tested for the fluoride removal. But it is not cost effective. In contrast of this, there are several researches have been conducted on fluoride adsorption using different naturally available adsorbents so far.

Nevertheless, regardless of the unique combination of physical and chemical properties of *L. albus*, its importance is very cheap and available naturally. As an adsorbent for fluoride adsorption from drinking water in Ethiopia still has not been investigated. Therefore, the main aim of this research

is to investigate the efficiency of sorptive removal of fluoride from aqueous and natural water for drinking using *L. albus*.

1.3 Significance of the study

After this research has been accomplished, both developed and developing countries including Ethiopia will have supported from the high expenditures of budgets for the process of fluoride ion removal from natural water for drinking. In addition, this research can contribute in Ministry of Health, Ministry of Forestry and Environmental Protection and Environmental Policy Makers of our country (Ethiopia) in case of human health disturbed by excessive consumption of fluoride concentrations and environmental health deteriorated for the reason that of byproducts produced from different modified adsorbents in the country will be minimized by using a very cheap natural adsorbent *L. albus*.

1.4 Objective

1.4.1 General Objective

Kinetics and Isotherm Modeling of Liquid Phase Adsorption of Fluoride onto Activated *L. albus*

1.4.2 Specific Objectives

The specific of the study are:

- to characterize the composition of *L. albus*;
- to evaluate *L. albus* fluoride removal potential under different Kinetic and Isotherm Modeling and
- to determine fluoride adsorption optimum condition

1.5 Research Questions

- 1) What are the chemical composition of *L. albus*?
- 2) What factors affect the fluoride removal potential of *L. albus* under different Mathematical modeling?
- 3) Which optimum condition affects fluoride adsorption?

1.6 Scope of the Study

This research was investigated on efficiency of Activated *L. albus* removal fluoride from water. Focusing on the area that have above 1.5 mg/L fluoride concentration of water. With regard to the regression analysis the required correlation carried out by applying a single linear regression model and multiple linear regression models.

1.7 Limitation of the Study

This study entailed preparation of water remediation biomaterial for fluoride removal. The adsorption parameters including pH, contact time, adsorbent dose and co-existing ions were investigated to establish their effect on fluoride removal. Seasonal variations of the adsorbent growth were not considered. The data collection period was a sowing time. So, the adsorbent was not easily avail and waiting to harvesting time was obligatory.

CHAPTER TWO: LITERATURE REVIEW

2.1 Occurrence of Fluoride

Fluorine is entirely a common element that does not naturally occur in elemental form because of its high reactivity (Flanagan and Road, 2014). Thus they are also found in rocks, soil, plants, animals, humans and fresh water as well as ocean water and occur naturally in public water systems as a result of runoff from weathering of fluoride containing rocks and soils and leaching from soil into ground water and found in the form of fluorine, biotite, cryolite, fluoroapatite and villiaumite (NaF) (Chakraborty *et al.*, (2013)), (Tomar *et al.*, (2013)).

2.2 Characteristics of Fluoride

Chemically, both fluoride and hydroxide (OH⁻) ions are negatively charged and have almost similar ionic sizes. For this reason, during the chemical reaction, fluoride ion can easily replace OH⁻ ions present in rocks and enriched its concentration in rocks and minerals (Goswami and Purkait, 2014). Fluoride ion is categorized as a hard base with its high electro negativity, small ionic size and strong affinity towards multivalent metal ions including Al (III), Fe (III) Chai *et al.*, (2013).

2.3 Benefits of Fluoride

Fluoride is beneficial in human body for the calcification of dental enamel and maintenance of healthy bones when present within the allowable limit (Srivastav *et al.*, 2013). When the optimal amounts of fluoride in water and food are consumed and applied externally in fluoridated dentifrices (tooth cleaning compound), oral rinses, gels, foams and professionally applied office treatments, fluoride increases tooth mineralization, helps to reduce dental enamel demineralization, promote dental enamel re-mineralization and helps to reduce dental hypersensitivity (Academy, 2012).

2.4. Impact of Fluoride

2.4.1 Human Health

More than sixty percent of fluoride demand for human body is satisfied by the consumption of drinking water. India is one of the most nations where health problems occur due to the

consumption of fluoride contaminated water. Within India, most states have been identified as epidemic for fluorosis (Tripathi and Sharma, 2014). Groundwater with high fluoride concentrations associated with igneous and metamorphic rocks such as granites and gneisses have been reported from India, Pakistan, West Africa, Thailand, China, Sri Lanka and Southern Africa. Since rural populations depend mainly on groundwater and major drinking water sources are worst affected by consuming excess fluoride concentration in drinking water which has deleterious effects on human health. Consumption of high amount fluoride concentration in drinking water cause a dental disease called fluorosis which leads to mottled teeth, dental caries, stiffened brittle bones and joints, metabolic disorders and even paralysis in advanced stages. Also it causes molting of teeth and lesion of endocrine glands, thyroid, liver, lowers the IQ of children (Roy and Dass, 2013) and other organs when it is present in excess of 1.5 mg/L (Swarupa *et al.*, 2006). For this reason, the only remedy for the fluorosis is to remove excess fluoride from drinking water (Yadav *et al.*, 2014).

2.4.2 Ecological /Environmental/ Impact

Currently, quality of drinking water is a big challenge of worldwide due to excessive fluoride contamination of water bodies by different anthropogenic and natural activities. It has been reported that more than 200 million people consume fluoride concentration that exceeds the World Health Organization (WHO) guideline of 1.5 mg/L (Wang *et al.*, 2013). In Mexico, 5 million people (about 6% of the population) are affected by the excess consumption of fluoride in drinking water (Sánchez *et al.*, 2013). In China, the broad area with drinking water, endemic fluorosis covers about 2.2 million km², also 1.4 millions of people be sick with from skeletal fluorosis caused by drinking higher fluoride water (Chai *et al.*, 2013). Also, India was one of the worst fluorosis affected countries; with large number of people suffering because of a bulky number of Indians depend on groundwater (Srivastav *et al.*, 2013) for drinking purposes which is rich in fluoride at many places. In order that, 62 million people including 6 million children are estimated to have serious health problems due to consumption of fluoride contaminated drinking water (Veeraputhiran and Alagumuthu, 2010).

Fluoride contamination has been observed in various minerals and chemical processes and in some natural water systems over large areas in Asia, America, Europe, Africa, where the fluoride concentration can range from 0.01 to 3 mg/L in fresh water and 1–35 mg/L in ground water. As a result of high toxicity of fluoride to mankind, there is an urgent need to treat fluoride contaminated

drinking water to make it safe for human consumption (Swarupa *et al.*, 2006). Fluoride is one of the pollutants that threaten living organism particularly human beings (Wang *et al.*, 2013). It can enter aqueous environment by weathering of fluoride rich minerals and recently through different anthropogenic activities such as industrial drains (Koilaraj and Kannan, 2013).

2.5 Removal Methods of Fluoride

Today, different technologies have been available for the removal of fluoride from drinking water such as precipitation/coagulation/, ion-exchange, membrane separation, electro dialysis (Wang *et al.*, 2013), reverse osmosis, nanofiltration (Chakraborty *et al.*, 2013) and adsorption processes.

Even though these fluoride removal technologies are effective, they have their own limitations. For example, the precipitation/coagulation method creates large amount of sludge which can cause the adverse effect on environment such as leaching of undesirable elements; trace amounts of fluoride ions tend to remain in solution due to solubility restriction and the resulting high pH of the treated water (Roy and Dass, 2013), expensive, efficiency depends on pH and presence of competing ions in water, adjustment and readjustment of pH is required, elevated residual aluminum concentration, formation of sludge with high amount of toxic aluminum fluoride complex and high amount of retained water (sludge dewatering is required prior disposal) (Flanagan and Road, 2014).

Ion exchange is efficient but a boring and difficult process of preparation of resins and regeneration of resin, post treatment is required as a result of low pH as well as the high cost (Roy and Dass, 2013), (Srivastav *et al.*, 2013), (Razbe *et al.*, 2013), expensive, vulnerable to interfering ions (sulfate, phosphate, chloride and bicarbonate), replacement of media after multiple regenerations, used media present toxic solid waste, regeneration creates toxic liquid waste, efficiency highly pH dependent (Flanagan and Road, 2014), membrane processes are effective but it is expensive and fouling is an expected problem (Flanagan and Road, 2014), reverse osmosis have an ability to remove other ions but its cost is very high; needs skilled operation and can be interfered by turbidity (M and Metre, 2014), high running and maintenance costs, produce toxic waste water (Flanagan and Road, 2014).

Adsorption technology is an economical and efficient method which used to produces high quality water (Flanagan and Road, 2014). Theoretically, the adsorption of solute on to solid particles as a rule takes four essential steps: Firstly solutes diffuses through the fluid to an area near the solid particle surface; secondly solute diffuses to the external surface of the particle; thirdly solute diffuses to the pore wall and fourthly solute adsorbs to the internal surfaces of the pore wall(Mann and Mandal, 2014).

Adsorption of fluoride on to solid adsorbent usually occurs through three phases. Firstly diffusion or transport of fluoride ions to the external surface of the adsorbent from bulk solution across the boundary layer surrounding the adsorbent particle (external mass transfer), secondly adsorption of fluoride ions on to particle surfaces and thirdly the adsorbed fluoride ions are transferred to the internal surfaces for porous materials (intra particle diffusion) (Flanagan and Road, 2014).

Adsorption of fluoride which is studied by using different adsorbents like chitin, alginate, modified ferric oxide/hydroxide (Chai *et al.*, 2013); (Sánchez. *et al.*, 2013), hydroxyapatite, zirconium and cerium modified materials (Swain *et al.*, 2011), titanium-derived adsorbent, schwertmannite (Goswami and Purkait, 2014), modified cellulose (Yu *et al.*, 2013), zeolite (Wang and Peng, 2010) and magnesium-modified sorbent (Flanagan and Road, 2014).But they have some deficiencies with their use, such as: low adsorption capacity, narrow available pH range and poor selectivity and mixed metal oxides (Wang *et al.*, 2013).

Among various techniques of fluoride removal from drinking water, adsorption has an advantage such as: simplicity of design and operation (Wang *et al.*, 2013),cost effective and environmentally friendly (Srivastav *et al.*, 2013), (Miretzky and Cirelli, 2011) and minimize waste disposal (Koilaraj and Kannan, 2013). High fluoride concentrations in groundwater up to 30 mg/L occur extensively in many parts of the world including East African countries such as Sudan, Uganda, Kenya, United Republic of Tanzania, Mexico, Thailand, Serbia, West Africa, Eritrea and Ethiopia (Tomar *et al.*, 2013).

In the Ethiopian contexts attempts at defluoridation will not only be practical but too expensive and technically unattainable and sustainable for large populations (Tekle-haimanot *et al.*, 2006). To tackle this problem, there are low-cost adsorbents of fluoride such as: bone charcoal, calcite, clay charcoal, tree bark, saw dust, rice husk, ground nut husk (Sánchez *et al.*, 2013).

There are also natural adsorbents such as chitosan which is a plentiful natural biopolymer has currently been paid a standing for its economic, environmental and easy adjustment properties and fiery particle great interests in many fields such as pharmaceutical, cosmetics, health care and water treatment. However, the defluoridation capacity of natural chitosan is minimal (Ma *et al.*, 2014).

In addition to this, zeolites are a selective adsorbents (Bhatnagar and Sillanpää, 2010) that are a class of natural materials can be effectively used as adsorbents due to their cation exchange characteristics (Wang and Peng, 2010) and emphasized that the limited use of zeolites as fluoride adsorbents is probably due to the fact that zeolites usually have negative surface charges at all pH values, which causing a high adsorption capacities for cations, but low for anions because of electrostatic repulsions when anions approach the negatively charged zeolite surface (Teklehaimanot *et al.*, 2006). These many natural materials which have lower costs have sorption properties (Datsko *et al.*, 2011).

These many natural materials which have lower costs have sorption properties. But *L. albus* which is abundant in Northern Ethiopia has special interest among natural sorption materials.

2.6 *Lupinus albus*

2.6.1 Occurrence

Lupin is a traditional crop in Ethiopia which grows at 1500-3000 altitude. It is grown in North-western part of the country (Francis, 1999). Lupine has high above ground biomass (Engedaw, 2012) and deep taproots (often going down 2m) (Small, 2012) which make it highly useful in aerating soil, or supplying it with oxygen and water.

2.6.2 Formation

L. albus are highly valued as animal feed but have been underutilized as human food yet the seeds rich in source of protein and oil (William, 2000). There are also claims that the seeds are rich in dietary fiber and beneficial physiochemical. The use of *L. albus* as human food and livestock feed is limited due to its bitter taste attributed to its relatively high alkaloid (i.e. quinolizidine alkaloids) content in *L. albus* that hinders its consumption without processing to remove them (Yeheyis *et al.*, 2012). Its stem and leaves are dumped as waste product during cultivation.

2.6.3 Characteristics

The highlysine, low methionine content of lupin complements that of wheat flour proteins, which are poor in lysine and relatively high in the Sulphur containing amino acid (Bloksma and Bushuk, 1988). Chemical composition of the seed flour including moisture, crude fat, crude protein, total ash and crude fiber (AOAC, 2000). White lupine seeds are generally classified as sweet or bitter depending on the alkaloid content, which ranges from 0.01 to 4% (Bhardwaj and Hamama, 2012). The bitter seeds contain the quinolizidine alkaloids lupanine and sparteine. The presence of these alkaloids limits the use of lupine seed as food and feed.

2.6.4 Abundance

L. albus seed grown in Ethiopia and locally known as '*Gibto*' is used as roasted bean '*Kolo*' and to prepare local alcoholic drink '*Arekie*' and other food products especially the North Western part of the country. *L. albus* is legume plant from the same family of Leguminosae. It has a green manure potential contributing to improve soil structure, can fix nitrogen, enhance availability of phosphorus and improve soil fertility, tolerant of infertile soils, disturbed sites, high tendency of growing on marginal lands and capable of remediating polluted (Nigussie, 2012). This adaptation allows lupine can grow without fertilizer (Engdawe, 2012).

2.6.5 Benefits

Lupin plants can be used to remediate polluted soils by mechanisms of phytoremediation and phytoextraction including phytostabilization and revegetation (Vazquez, 2006). The local community in North-western Ethiopia used '*Gibto Areke*' as locally made antihypertensive medicinal preparation (Ranqunathan and Solomon, 2009).

CHAPTER THREE: MATERIALS AND METHODOLOGY

3.1 Study Design and Period

This research was investigated in a batch sequence adsorption experimental based and conducted at laboratory. Activation, carbonization, physicochemical characterization process of the adsorbent and effect of different parameters on the adsorption was studied at Addis Ababa Institute of Technology, Bioengineering Laboratory, Addis Ababa. FT-IR analysis of the adsorbents was carried out at Jimma Institute of Technology, Department of Material Science Laboratory in order to identify the surface functional groups, which can significantly enhance the adsorption efficiency of the activated sample by surface complexation October 2018-February 2019.

3.2 Study Variables

3.2.1 Dependent Variable

The dependent variable of the study is Fluoride ion adsorption.

3.2.2 Independent variables

The Independent variables of the studies are *L. albus* dose, pH of the solution, Contact time, Initial fluoride concentration, Co-existing ion.

3.3 Adsorbent Collection

The seed of *L. albus* was collected from local area of farm land around Debremarkos Town, which is 300 km North-West from Addis Ababa.

3.4 Adsorbent Preparation

Initially, the seed of *L. albus* was washed with distilled water to remove any surface impurities and dried with sun light for three days. After drying, kept in air tight plastic container for further preparation.

The dried sample was placed in an oven at 100° C for 24 h to accomplish carbonization (Bhaumik *et al.*,2014). The activated sample (seed of *L. albus*) was powdered by using grinding machine (Model: JP -1500B-8D) and then sieved with a 250-350 µm diameter sieve to get particle size of 250 - 350 µm adsorbents prior to being used for adsorption studies (Singha *et al.*,2011).

Finally, the resulting activated adsorbents prepared from *L. albus* seed were stored in an air tight plastic container.

3.5 Characterization of Adsorbent

Physicochemical analysis of moisture content, ash content, bulk density and pH of the adsorbent were performed. Fourier transform infrared (FT-IR) spectra of dried unloaded and fluoride loaded adsorbents were recorded at 4000–400 cm^{-1} to determine the surface functional groups.

➤ Moisture content

Oven drying method was used in the determination of moisture content of the sample. A clean empty crucible was oven dried at 105 °C, cooled in a desiccator and weighed accurately. Then, 1 g of the sample was weighed and placed in the cooled crucible. The sample was oven dried at 110 °C for 3hr Silgado *et al.*, (2014)) and the percentage of moisture content computed by applying the formula:

$$\text{Moisture content (\%)} = \left[\frac{\text{Weight Loss}}{\text{Samle Weight}} \right] \times 100 \text{-----(1)}$$

➤ Ash content

Ash content determination was done according to (Ektepe and Horsfall,2011)). A crucible was placed in a muffle furnace at 500 °C for 1 h, cooled down in a desiccator, and weighed in balance model (BP11OS). 1g of the activated sample was placed in the weighed crucible and placed into a preheated muffle furnace set at a temperature of 500 °C for 3 hours. The weight of the resulting ash was determined after it was cooled to room temperature and the percentage of ash content was calculated based on the initial and final weights using the equation:

$$\text{Ash content (\%)} = \left[\frac{\text{Weight of ash (g)}}{\text{Dry weight of sample befor ash (g)}} \right] \times 100 \text{-----(2)}$$

➤ Bulk density

In order to determine the bulk density, a 50 ml graduated cylinder was weighed accurately with a digital balance model (BP11OS) and filled with activated samples gently without compacting to 50 ml mark and weighed. The difference gave weight of powder. Then, the bulk density was calculated by taking the ratio of weight of powder to the volume of the cylinder (Singh, and Singh, 2012).

$$\text{Bulk density(\%)} = \left[\frac{\text{Weight of Powder (g)}}{\text{Apparatus Volume (ml)}} \right] \times 100 \text{ -----(3)}$$

➤ pH

In order to determine the pH of activated sample, 1 g of activated *Lupinus albus* were weighed and transferred into beaker. 100 ml of distilled water was added into beaker and stirred for one hour (Ektepe and Horsfall, 2011). The sample were allowed to stabilize before the pH was measured using a pH meter (PH 3505). The measurement was run in triplicate.

➤ Surface functional groups

In order to identify the surface functional groups in the adsorbent which can contribute to enhance adsorption efficiency of adsorbent by surface complexation, Fourier Transform Infrared Spectroscopy (FT-IR) study was carried out for both activated *L. albus* adsorbent before adsorption and the loaded adsorbent.

3.6 Preparation of Fluoride Solution

The fluoride ion obtained from 0.2210 g of anhydrous sodium fluoride to prepare stock fluoride solution (NaF) (Mondal et al., 2012) in distilled water and dilute to 1 L. Dissolve 958 mg SPANDS, [Sodium 2-(parasulphophenylazo)-1,8-dihydroxy-3,6-naphthalene disulphonate] in distilled water and diluted to 500 mL. Dissolve 133 mg zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) in about 25 mL of distilled water. Add 350 mL conc. HCl and dilute to 500 mL with distilled water. Dissolve 5.0 g NaAsO_2 and dilute to 1 L with distilled water used to remove residual chlorine. 0.1M HCl and 0.1M NaOH were used for pH adjustment.

3.7 Batch Kinetics and Equilibrium Adsorption Studies

Parameters greatly affects the adsorption process, like pH solution (4-10), initial fluoride concentration (2.5-25 mg/L), adsorbent dose (1-5 g/L) and Contact time (20-180 min) on the removal of fluoride. In each adsorption experiments were carried out at room temperature in plastic flasks with blank and control only with fluoride ion experiments. A 100 mL aqueous solution containing a known fluoride ion concentration and a desired adsorbent dose was agitated at 350 rpm on overhead stirrer for a predetermined contact time. Then after, the suspension was filtered through Whatman No.41 filter paper. Add 10 mL mix solution. Mix well. Then, fluoride

concentration of the supernatant in each sample was analyzed using UV-vis spectrophotometer UVD-3200 at wave length of 570 nm. Quantity adsorbent at a given time t was calculated using Eq. (4) and percentage removal was obtained using Eq. (5)

$$q_t = \frac{(C_0 - C_t)}{M} * V \text{-----} (4)$$

$$A = \frac{(C_0 - C_t)}{C_0} * 100 \text{-----} (5)$$

where, q_t (mg/g) is the amount of fluoride adsorbed at any time, t (min); A (%) is the percentage of fluoride adsorbed; C_0 (mg/L) is initial fluoride concentration; C_t (mg/L) is concentration of fluoride in the aqueous phase at any time t, V (L) is volume of the aqueous solution and M (g) is mass of the adsorbent media used in the experiment.

3.8 Mathematical Modeling

3.8.1 Isotherm Studies

To understand the adsorption performance and the adsorption mechanism, adsorption isotherm of fluoride adsorption on *L. albus* was investigated.

3.8.1.1 Langmuir Isotherm

The Langmuir isotherm model is used for monolayer sorption on a surface of adsorbent based on the assumption that the point of valance exists on the surface of the adsorbent and that each of these site is capable of adsorbing one molecule. It is assumed that the adsorption sites have equal affinities for molecules of adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The general equation of Langmuir isotherm is:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \text{-----} (6)$$

The experimental data obtained are plotted in a linear form of an equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} x C_e \text{-----} (7)$$

Where q_e is the equilibrium fluoride uptake per unit mass of sorbent, q_m is maximum amount of adsorbate uptake capacity (mg/g), K_L is the adsorption constant and C_e is equilibrium fluoride concentration in solution (mg/L) (Langmuir, 1916). The degree of isotherm model fittings was determined by using non-linear regression coefficient (R^2) value. The coefficient values were calculated by the equation:

$$R^2 = \frac{\sum (q_{cal} - \bar{q}_e)^2}{\sum (q_{cal} - \bar{q}_e)^2 + \sum (q_{cal} - q_e)^2} \text{-----} (8)$$

Where q_e is the amount of fluoride exchanged by an adsorbent obtained from the experiment (mg/g), q_{cal} is amount of fluoride obtained isotherm model and \bar{q}_e is the average of q_e (mg/g) (Koilaraj & Kannan, 2013). To examine the feasibility of the isotherm, the dimensionless equilibrium parameter R_L was determined by using the equation:

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

Where, C_0 (mg/L) and b (L/mg) are the initial fluoride concentration and Langmuir isotherm constant respectively. For favorable adsorption, R_L value should be less than 1 (Goswami & Purkait, 2014). There are four probabilities for the R_L value: (1) for favorable adsorption $0 < R_L < 1$ (2) for unfavorable adsorption $R_L > 1$ (3) for linear adsorption $R_L = 1$ and (4) for irreversible adsorption $R_L = 0$ (Malakootian *et al.*, 2011) and (Yu *et al.*, 2013).

3.8.1.2 Freundlich Isotherm

Freundlich isotherm provides the detailed idea about the effectiveness of the adsorbent and the maximum amount of adsorbate was get adsorbed by the adsorbent. The Freundlich equation is basically empirical but it is often useful as a means for data description. It describes the heterogeneous surface energies by multilayer adsorption.

The general equation is:

$$q_e = K_f C^n \text{-----} (10)$$

And the linear form of Freundlich equation is:

$$\log q_e = \log K_f + \frac{1}{n} C_e \text{-----} (11)$$

Where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of fluoride (mg/L) and, n is the Freundlich constant indicating the degree of favorability of adsorption and K_f is isotherm constant. K_f indicates adsorption capacity (mg/g) and $1/n$ an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. For values in the range $0.1 < 1/n < 1$, adsorption is favorable. The greater the values of K_f better is the favorability of adsorption. If $1/n > 1$ then bond energy decreases with surface density, if it is < 1 then bond energy increases with surface density and if $1/n = 1$ then all sites at the surface are equivalent (Freundlich, 1906).

3.8.1.3 Sips isotherm

The Sips isotherm is a combination of the Langmuir and Freundlich isotherms and can be derived using equilibrium approach.

$$q_e = \frac{q_m(K_{PR}C_e)^{n_S}}{1+(K_{PR}C_e)^{n_{RP}}} \text{-----} (12)$$

Where, K_S (L/mg) is the affinity constant and n_S describes the surface heterogeneity. When n_S equals unity, the Sips isotherm returns to the Langmuir isotherm and predicts homogeneous adsorption. On the other hand, deviation of n_S value from the unity indicates heterogeneous surface adsorbent.

3.8.1.4 Redlich–Peterson isotherm

The Redlich–Peterson isotherm combines the features of Langmuir and Freundlich isotherms. It can be represented as:

$$q_e = \frac{q_m(K_{PR}C_e)}{1+(K_{PR}C_e)^{n_{RP}}} \text{-----} (13)$$

where K_{RP} (L/mg) and n_{RP} are Redlich–Peterson constants. Redlich–Peterson isotherm parameters are similar to that of Sips isotherm parameters.

3.8.2 Kinetics Modeling

The Pseudo first-order and second-order kinetic models are the most popular models used to study the sorption kinetics of nonmetals and to quantify the extent of uptake in sorption kinetics. In order to evaluate the kinetics of fluoride adsorption and potential rate controlling steps, the pseudo first and pseudo second order models were checked. Kinetic studies are important in determining the optimal contact time required to reach equilibrium Paudyal *et al.*, (2013).

3.8.2.1 Pseudo First Order Kinetics

The nonlinear pseudo first-order rate expression is:

$$q_t = q_e(1 - \exp(-K_1 t)) \text{-----} (14)$$

Where q_e and q_t are the amounts of fluoride adsorbed (mg/g) at equilibrium and at any time, t (min), respectively. The adsorption rate constant k_1 will be determined from the slope of the nonlinear plots of q_e versus t which presents the fittings of this model (Srivastav *et al.*, 2013).

3.8.2.2 Pseudo Second Order Kinetics

The nonlinear pseudo second-order rate expression is:

$$q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \text{-----} (15)$$

Where q_e and q_t are the amounts of fluoride adsorbed (mg/g) at equilibrium and at any time t (min) respectively. The adsorption rate constant K_2 will be determined from the slope of the nonlinear plots of q_e versus t . The values of q_e and adsorption rate constant K_2 can be obtained by plotting q_e versus t (Srivastav *et al.*, 2013), (Koilaraj & Kannan, 2013).

3.8.2.3 Fractional Power kinetics model

The nonlinear and linear forms of Fractional power kinetic model equation are depicted by Eq(16) and Eq(17) respectively;

$$q_t = K * t^v \text{-----} (16)$$

$$\log q_t = \log K + v \log t \text{-----} (17)$$

where, q_t is the quantity of adsorbate adsorbed at time t (mg/g), $\log K$ and v are the intercept and slope of the plot of $\log q_t$ versus $\log t$ respectively thus anti log of intercept gives the value of constant k . v is also a constant that is usually less than unity if adsorption kinetic data fits well into power function model q_t is the quantity of adsorbate adsorbed at time t .

3.8.3 Validation of Adsorption Kinetics and Isotherm

Chi square and the normalized standard deviation given by the Eq. (18) and (19) were used to validate the kinetics model.

$$(X)^2 = \frac{\sum_{i=1}^n \frac{(q_{\text{exp}} - q_{\text{cal}})}{q_{\text{exp}}}}{N-1} \text{-----} (18)$$

$$\Delta q_e(\%) = \frac{100\sqrt{(q_{\text{exp}} - q_{\text{cal}})/q_{\text{exp}}}}{N-1} \text{-----}(19)$$

Where, N is the number of data points while q_{exp} and q_{cal} are experimentally determined quantity adsorbed at equilibrium and calculated quantity adsorbed at equilibrium respectively.

3.8.4 Adsorption Mechanism

Weber–Morris model was used to understand the possible contribution of intra-particle diffusion for the removal of fluoride on an adsorbent. The linear form of intra particle diffusion model given by Weber–Morris is:

$$q_t = k_{id} t^{0.5} \text{-----} (20)$$

Where q_t is the amount of fluoride adsorbed per unit mass of adsorbent (mg/g) at a given time t , k_{id} is the rate constant of intra-particle diffusion ($\text{min}^{-1/2}$) and t is contact time (min). The uptake is proportional to the square root of contact time during the course of adsorption:

$$q_t = k_p \sqrt{t} \text{-----} (21)$$

Where q_t is the amount adsorbed at equilibrium (mg/g), k_p is the rate constant of intra-particle transport ($\text{mg g}^{-1} \text{min}^{-1/2}$). The intra-particle diffusion rate constant (k_p) value estimated from the slope of plot of q_t versus square root of time (Weber, 1963).

The distribution coefficient (K_d) value for fluoride adsorption on the adsorbent was calculated by using equation:

$$K_d = \frac{q_t}{C_t} (L/g) \text{-----} (22)$$

Where, q_t is the concentration of fluoride in the solid particles (mg/g) and C_t is the concentration of fluoride in water (mg/L). If the surface is homogeneous, the K_d values at a given pH should not change with adsorbent dose (Beekam *et al.*, 2014).

3.9 Desorption of Fluoride from *L. albus*

Desorption study was examined for fluoride loaded adsorbent was prepared by agitated with optimum pH of the solution, equilibrium time, optimum dose of the adsorbents, initial fluoride of 10 mg/L and 300 rpm agitation speed. After adsorption, the residue of an adsorbent was separated from the supernatant solution by suction filtration. The fluoride loaded adsorbent was dried at 100 °C for 12 hours in an oven. Then, the desorption experiment was carried out by agitating the oven dried spent adsorbents at 300 rpm agitation speed for 30 minutes in 100mL of different concentration of NaOH solution (0.1- 0.5M) NaOH. The desorption percentage were calculated by using the following equation:

$$\% \text{Desorption} = \frac{C_0}{C_e} \times 100 \text{-----} (23)$$

3.10 Ground Water treatment with *L. albus*

Based on the optimum conditions that were determined by synthetic aqueous solution, it was tried the adsorption experiment of fluoride by *L. albus* using natural water samples.

3.11 Quality control

Sampling equipment was washed with tap water and rinsed by distilled water after each sampling occasions to avoid contamination of the samples. Laboratory measurement instruments were calibrated and standardized. Duplicate experiments were carried out to avoid any discrepancy in results with the reproducibility and the relative deviation of the orders. Blank samples without ions were used as control and average data was reported.

3.12 Dissemination plan

The finding will be submitted to Jimma Institute of Technology, and will be given to Oromia Water, Mineral and Energy Bureau. It will be published or an international peer Journal.

CHAPTER FOUR: RESULTS AND DISCUSSIONS

4.1 Adsorbent

4.1.1 Physicochemical Characteristics

The results obtained from physicochemical analysis of *L. albus* (adsorbent) are presented in Table 4.1. The adsorbents were characterized for moisture content, ash content, bulk density, and pH.

Moisture content can be said to be a measure of the amount of water (in any form) in a material, substance or adsorbent at any given time. Moisture content is observed to be 9%. The values of moisture content of *L. albus* are less than the moisture values of rice bran (10.68%) reported by Kumar *et al.* (2011) and moisture values of oil palm endocarp powder (25.81%) reported by Silgado *et al.* (2014). However still it was higher than the moisture values of some commercial activated carbons below 5% reported in literatures (Silgado *et al.*, 2014). This indicates that the carbons provided for this study needs appropriate packaging, transportation and storage conditions for moisture control. This might also be the effect of moisture uptake by the sample during the experiment even though the powder was dried properly after washing to remove the acidity.

The ash content value indicates the adsorption efficiency. Therefore, the value obtained from this study was 4.49%. Ash content of *L. albus* seed (4.49 %) was less than those of the reported results in the previous studies, ash content oil palm endocarp powder was 14.5 % (Silgado *et al.*, 2014), and ash content of bamboo waste was 21.66 % Dula *et al.*, (2014). The lower ash content attributed to lower inorganic content and higher fixed carbon which shows more adsorption efficiency and stability Thamilarasu *et al.*, (2011). Since its presence inhibits surface area development, high ash content value reduces adsorption efficiency. The lower the ash value therefore the better the activated carbon for use as adsorbent.

The bulk density of *L. albus* seed (0.41 g/cm^3) was less than that reported result in previous study, Carbons with bulk density of about 0.5 g/cm^3 are an acceptable adsorbent (Qureshi *et al.*, 2007). The lower the bulk density values indicates that the highly branched porous with more void space. This indicates that the lower the bulk density value satisfies the condition. So, the bulk density of this study fit the acceptable value.

The pH of adsorbents shown on Table 4.1. pH of adsorbent is an important parameter applied in adsorbents production. pH above or below the acceptable limit will have an effect on the material to be adsorbed (Itodo *et al.*, 2018). The pH value of activated carbon influences adsorption by affecting the surface properties of the adsorbents and ionization or dissociation of the adsorbate molecules. A carbon of pH 6-8 is acceptable for most application such as sugar decolorization and water treatment (Qureshi *et al.*, 2007). pH above or below the acceptable limit will have an effect on the material to be adsorbed. The acceptable limit for pH is 6.5 to 7.5. The pH values of the adsorbent in this study were found to be 6.75. So *L. albus* seed would be suitable carbon for environmental applications.

Table 4.1 Physicochemical properties of heat treated sample adsorbent

Characteristics	value
Moisture Content (%)	9.00
Ash content (%)	4.49
Bulk density(g/cm ₃)	0.41
pH	6.75

4.1.2 FTIR analysis for Fluoride adsorption

FT-IR spectra of pre-and post-fluoride loading activated *L. albus* adsorbents are shown in Figure 4.1. It is clearly shown that, after the adsorption of fluoride on *L. albus* adsorbents, there is a small shift in frequency values and some of the frequency regions were absent. This observation indicated the participation functional groups during the adsorption process. The FT-IR spectra of both fluorides loaded and unloaded were compared.

FTIR spectrum band assignments before adsorption was 2991 cm⁻¹ and these have been shifted to 3000 cm⁻¹ after treatment with fluoride solution. These belong to C-H stretching vibrations in methyl group. The peaks around 1500-1600 cm⁻¹ correspond to C=C stretching vibration in aromatics, around 1501 cm⁻¹ shifted to 1538 cm⁻¹ after adsorption belongs to C-H deformation vibration in alkane, 1318 cm⁻¹ shifts to 1324 cm⁻¹ belongs to C-O stretching vibration in alcohol. Adhikari *et al.* (1989) reported that due to making of new bonds like C-F, C-O stretching vibration alcohol may also result in the contribution of the peak in the region of 1400 to 1500 cm⁻¹.

Band of O-H stretching vibrations were observed around 3600-3200 cm^{-1} due to the existence of surface hydroxyl groups and chemisorbed water. As it can be seen from Table 4.2, a peak around 2800-3200 cm^{-1} shows the C-H stretching (CH_2 and CH_3 group) variations, the peak observed around 1600-1800 cm^{-1} was because of C=O stretch. The broad peak around 1500-1600 cm^{-1} alkenes(olefin) $-\text{C}=\text{C}-$. Generally, the spectra of activated *L. albus* adsorbent was closely identical to the spectra shown in bitter and sweet lupin (*L. albus*) seeds reported by Sbihit *et.al.*(2013). The shift in stretching frequency from 3623 to 3422 cm^{-1} is assigned to the FT-IR spectrum involvement of hydroxyl groups. The Stretching frequency of the Hydroxyl group shows the spectrum image at 3538 cm^{-1} . The adsorption bands in between 3600 to 3300 cm^{-1} show the characteristics of -OH group Diez *et, al* (2000). FT-IR spectrum revealed that the hydroxyl groups on the adsorbent surface were involved in the sorption of fluoride. Anion exchange and electrostatic interaction were suggested as the main mechanisms involved in the sorption of fluoride on the adsorbent. Table 4.2 represented the shift in the wavenumber of dominant peak associated with the fluoride loaded in the FT-IR plots by comparing between the fresh adsorbent and fluoride loaded adsorbent Figure 4.1. FT-IR spectrum also showed around 2229-2400 cm^{-1} no peak was observed. This indicates that P-H stretch are not participated in the process.



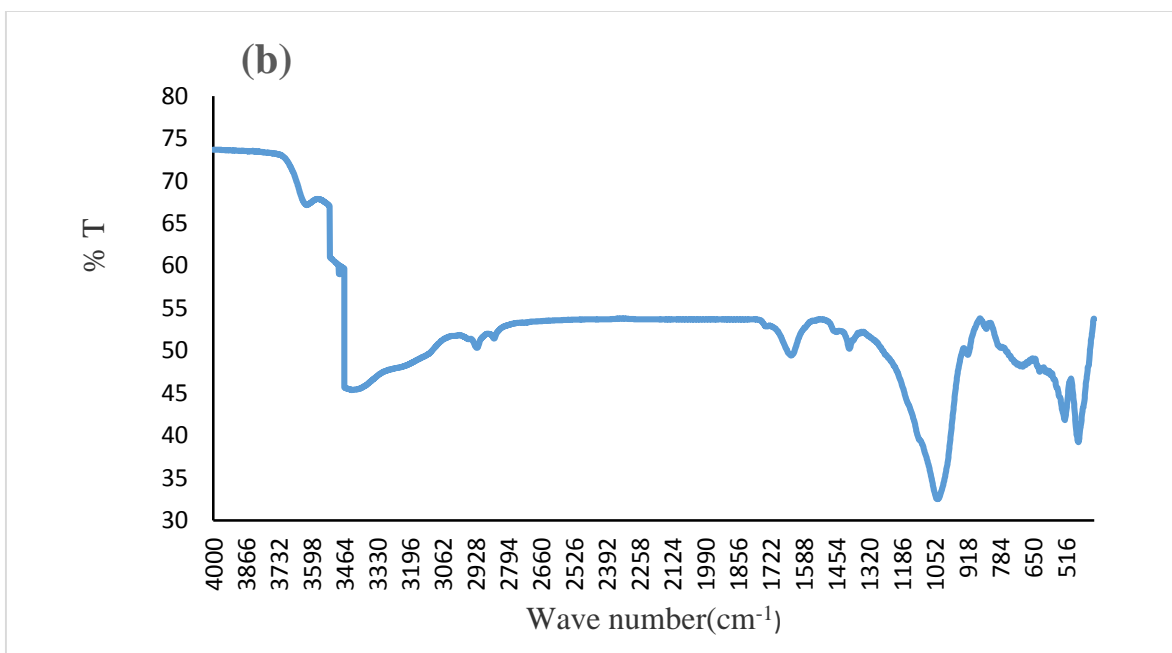


Figure 4.1.: FT-IR spectra before fluoride adsorption (a); and after fluoride loaded (b)

Table 4. 2: Frequencies and respective functional groups present on the surface before and after fluoride adsorption wavenumber.

Functional group	Wavenumber range (cm^{-1})	before adsorption (cm^{-1})	after adsorption (cm^{-1})
O-H and N-H stretches	3600-3200	3461-3401	3538-3384
C-H Stretch	3200-2800	2981-2741	2922-2768
P-H stretch	2400-2229	No peak	No change
C=O Stretch	1800-1600	1721-1600	1767-1613
Alkenes(olefin) –C=C-	1600-1500	1601-1301	1536-1382
Stretching Vibration of C-O ester group	1273-1100	1121-1001	1228-1074
–C=C– and aromatic ring C-H	<1000	761-521	612-458

4.2 Effect of pH of the Solution

The effect of pH on fluoride removal from aqueous solution by activated *L. albus* seed powder was studied at various pH values. The removal of fluoride by activated *L. albus* seed powder was noted to increase with increase in pH of the fluoride solution appreciably up to pH 7.0. The effect of pH on removal efficiency of fluoride of adsorbent dose 5 g/L. In this study the optimum pH was considered to be 7. The test solution is found to be neutral which was changed during the experiment from pH 4 to 10. It is observed that adsorption efficiency increases as the pH increases and gets the maximum at a pH of 7 and then starts decreasing. Figure 4.2 depicted that, high percentage removal of Fluoride was achieved at pH 7 for adsorbents 97.69%. The sharp decrease in the percentage removal of fluoride on *L. albus* from 83.6 to 80.7% was observed with pH of 8-10.

The pH range of maximum adsorption is found to be broader under lower surface loading conditions, and is narrower under higher surface loading conditions. Because protonated surface sites are normally responsible for anion adsorption, fluoride ion adsorption onto *L. albus* is favored under acidic pH conditions. However, according to fluoride speciation, hydrofluoride is predominant for pH condition less than 3.0 (Stumm *et al.*, 1996). Therefore, the decrease of fluoride adsorption, when the pH was less than 5, was caused by the formation of HF species, which is considered less adsorbable than F^- . Under alkaline pH conditions, deprotonation of *L. albus* surface sites occurs and it reduces the total amount of protonated surface sites, i.e., fluoride binding sites. Therefore, the adsorption of fluoride is decreased significantly in the alkaline pH range. However, the decrease in the adsorption capacity in the basic region (pH greater than 7) is due to the decrease in positive charges of the adsorbents and increase in competition of fluoride ion with the hydroxide ion (OH^-) since both have the same charge and ionic radii (Goswami & Purkait, 2014) and (Wang *et al.*, 2014). Therefore, lower values of adsorption were observed at higher pH because of repulsion between the fluoride and the adsorbent's negative charge surface which goes align with the findings of Sanghratna *et al.*, (2015) and Dangi *et al.*, (2015).

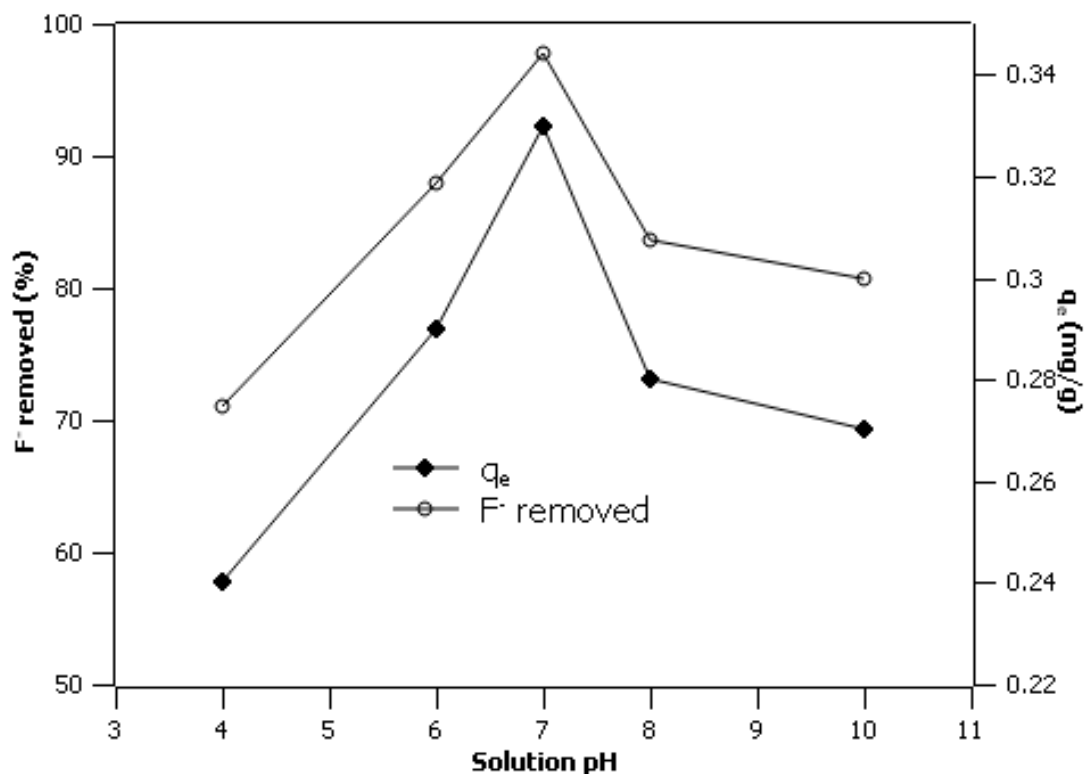


Figure 4. 2: Fluoride Removal Capacity Versus pH of *L. albus* (Dose 5 g, Time 30 min, Agitation speed 300 rpm, Initial Fluoride concentration 10 mg/L in 100 mL)

4.3 Effect of Adsorbent Dose

The removal capacity of fluoride adsorbed decreased from 0.76 to 0.18 mg/g as the adsorbent dose increased from 1 to 5 g/L and the removal efficiency increase from 75.7 to 88.1%. As Figure 4.3 revealed that the percentage removal of fluoride increased with increasing adsorbent dose while adsorption capacity decreased gradually with dosage. The maximum percentage removal for *L. albus* was noted to be 5 g/L of the adsorbent dose. Thereafter no significant increase in fluoride uptake was observed for additional increase in adsorbent dosage. This may be because active sites have less or on adsorbent atoms to interact with and hence are available to attract adsorbate. Also at higher dosage of adsorbent, there is the tendency of overlap or aggregation of the active site, which may result in active site interaction with adsorbent atoms rather than adsorbate and hence decreases the total adsorption area Annadurai *et al.*, (2002); Ameh *et al.*, (2012).

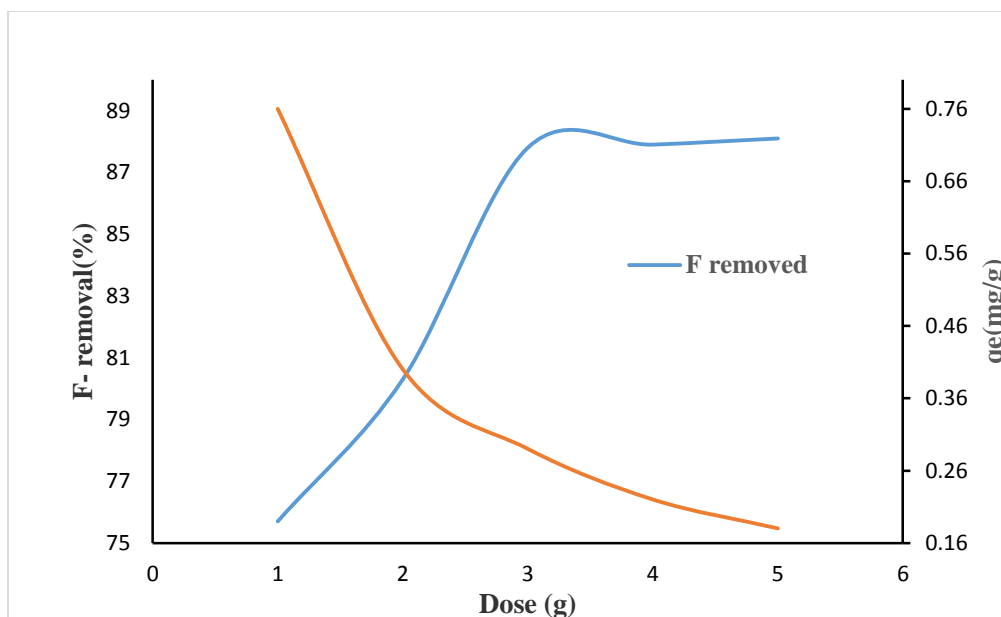


Figure 4.3: Fluoride Removal Capacity Versus Adsorbent Dose of *L. albus* (pH 7, Time 30 min, Agitation speed 300 rpm, Initial Fluoride concentration 10 mg/L in 100 mL)

4.4 Effect of Initial Concentration and Contact Time

The removal capacity of the adsorbent increases from 0.189 to 0.296 mg/g and the removal efficiency decreases from 99.9 to 76.75% as contact time increased from 20 to 180 min. The removal capacity of the adsorbent increases as percentage removal decreases. Figure 4.4 depict the effects of concentration and contact time on fluoride uptake onto *L. albus*. Quantity of fluoride adsorbed was observed to increase with increased time and concentration, fluoride uptake was rapid initially and gradually goes to equilibrium with increased time. Rapid initial adsorption may be attributed to contacts of fluoride molecules with available surface adsorption sites while subsequent gradual adsorption may be attributed to uptake of fluoride molecules into the pores of the adsorbents. Equilibrium was attained at 30 min.

As it is presented in Figure 4.4, the removal capacity of the adsorbent increase from 0.162 to 0.308 mg/g as the initial fluoride concentration increased from 2.5 to 25 mg/L and the removal efficiency decreases from 97.42 to 92.3%. The increase in the removal capacity with the increase in the initial fluoride concentration of the solution could be attributed to the availability of more fluoride for adsorption at higher concentration on poorly reachable sites with weak sorption energy.

Subsequently, the energetically less favorable sites become involved in the adsorption process with increasing fluoride concentration in the aqueous solution.

However, the percentage of fluoride removal decreased with the increase in the initial concentration of fluoride from 2.5 to 25 mg/L. As the initial concentration of fluoride increases, the number of available adsorption sites became fewer, thus resulting in a relatively lower percentage of fluoride removal. It was observed that with the increase of initial fluoride concentration, the percentage removal of fluoride decreases while the loading capacity increases. This suggests that there exists a reduction in immediate solute adsorption due to the lack of available active sites on the adsorbent surface compared with the relatively large number of active sites required for the higher initial concentration of fluoride which goes align with the finding of (Pali *et al.*, 2013).

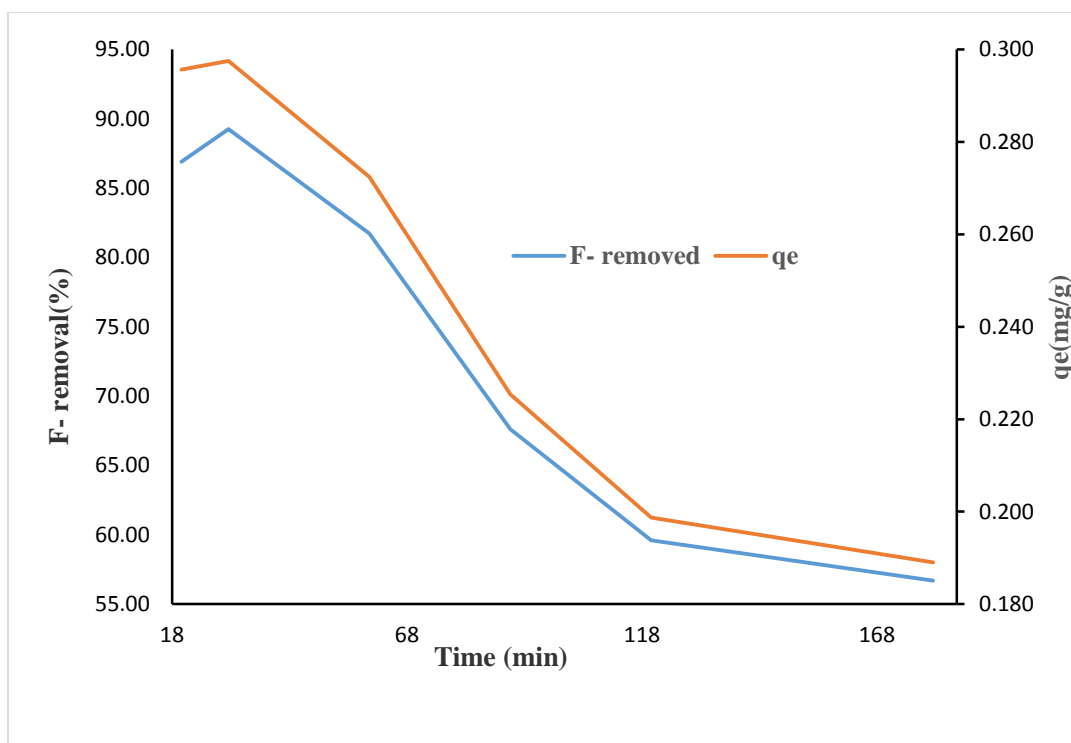


Figure 4.4. Effects of contact time and initial concentration on fluoride adsorption onto *L. albus* (Dosage 5 g, Agitation speed(300rpm), pH (7), Initial fluoride concentration in 100 mL).

4.5 Effect of Co-existing Anions

Along with the fluoride ion present in drinking water, the effect of different other co – anions such as HCO_3^- , SO_4^{2-} and Cl^- on the adsorption capacity of *L. albus* was also determined.

The effect of competing anions at different concentration levels on the removal efficiency was examined in such a way that each ion separately added to a container of 100 mL solution of a known concentration of fluoride at optimum pH of the solution and adsorbent doses. The synthetic mixtures of fluoride ion and one of the interfering ions was made the concentration of the interfering ions maintained at tenfold excess than the fluoride concentration. One hundred (100 mL) of these solutions were taken in stopped bottle and then correctly weighed optimum dose of the adsorbents was added.

The samples were agitated by overhead stirrer at equilibrium time. Then the samples were filtered and analyzed for fluoride. The percentage (%) of extraction was calculated from the data obtained.

The effects of co-existing anions such as Chloride, Sulphate and Bicarbonate on fluoride adsorption by the adsorbent were examined. Chloride and Sulphate did not perceptibly interfere with fluoride removal at a concentration of 100mg/L. However, bicarbonate showed great competitive adsorption with fluoride. The fluoride adsorption amount decreased quickly from 58.6 to 53% with the increase of bicarbonate concentration from 10 to 200 mg/L. This may be due to the competition of bicarbonate ions with the fluoride ions at the active site present on the surface of the sorbents. The order of interference for fluoride removal observed as in the following order, $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ for the adsorbent. The present results indicated that the addition of co-existing ions, in the concentration ranges investigated had no appreciable effect on the amount of fluoride ions removed by these adsorbents except for bicarbonates. Therefore, the result was goes aligned with result finding of (Sangratna *et al.*, 2015).

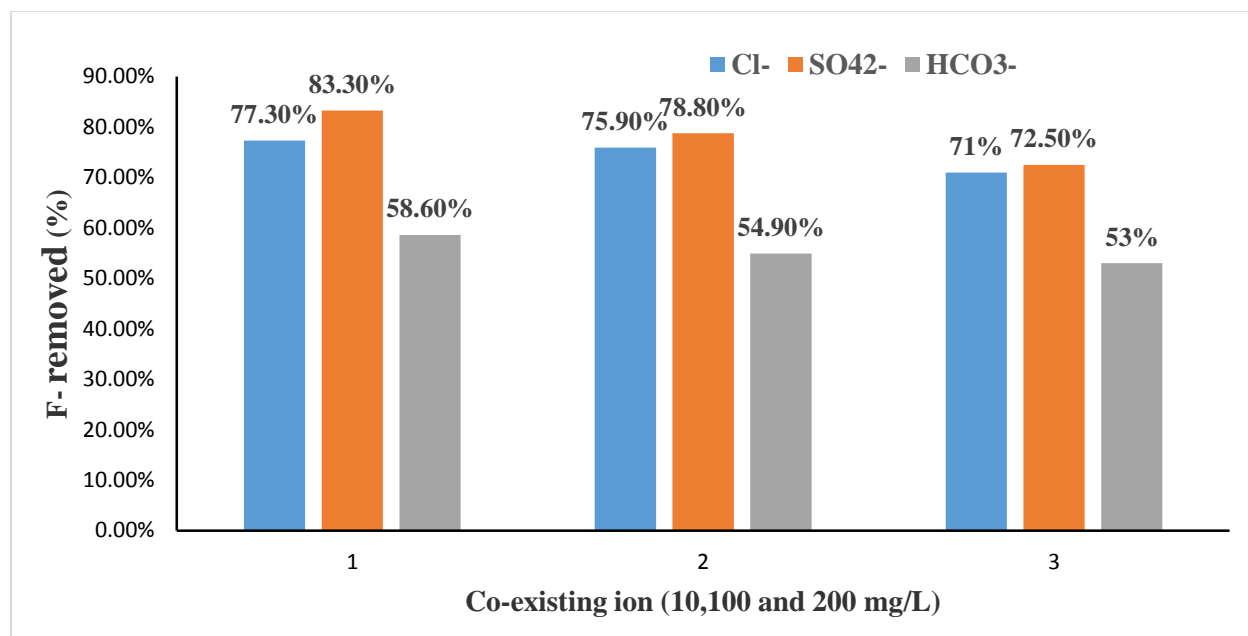


Figure 4.5. Fluoride percentage removal versus Co-existing ions, Dose (5 g), Contact Time (30 min), Agitation speed (300 rpm), pH (7), Initial Fluoride concentration (10 mg/L in 100 mL).

4.6 Adsorption Isotherm

The Freundlich and Langmuir isotherm parameters were obtained from the non-linear equation of these models as shown in Table 4.3. The values of the correlation coefficient, R^2 for the Freundlich and Langmuir isotherms were 0.9901 and 0.974 respectively.

Therefore, the finding of this study, fit better with Freundlich isotherms which leads the adsorption to the heterogeneous surface energies by multilayer adsorption. Freundlich isotherm best described the uptake of fluoride onto *L. albus* (R^2 value of 0.9901), this suggest that adsorption was not on to a uniform site rather a multilayer adsorption occurred. However, monolayer adsorption also played a very important role in the fluoride uptake onto *L. albus* (R^2 for Langmuir 0.974).

Figure 4.6 shows that the Freundlich isotherm is a better model than the Langmuir isotherm on the basis of correlation coefficients ($R^2=0.9901$ for Freundlich, $R^2= 0.974$ for Langmuir). The best fit Freundlich parameters are K_f 0.55, $n = 2.641$, $1/n= 0.379$. The $1/n$ value in the range of 0.1-1 indicates a favorable adsorption process. The Langmuir parameters fit are $Q_{max}=0.819$ mg/g, $b= 2.936$ L/mg.

The R_L value obtained was in range 0.0134-0.1199. The R_L value less than 1 shows the adsorption was favourable (Goswami & Purkait, 2014).

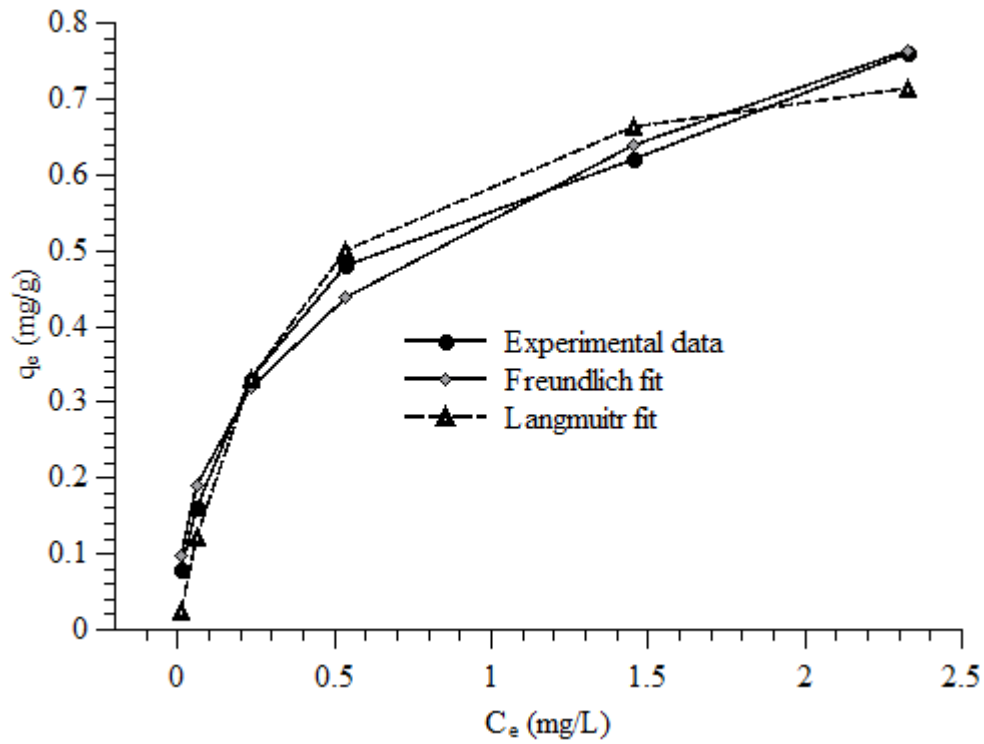


Figure 4.6: Langmuir and Freundlich isotherms for *L. albus* fluoride adsorption (pH: 7, agitation speeds: 300 rpm, equilibrium time: 30 minutes, adsorbent dose: 5 g/L and initial fluoride concentration: 10 mg/L in 100 mL solution).

Table 4.3: Langmuir and Freundlich Isotherm Parameters for fluoride Adsorption

Freundlich Isotherm			Langmuir Isotherm		
K_f (mg/L)	n	R^2	Q_{max}	B	R^2
0.55	2.641	0.9901	0.819	2.936	0.974

Sips isotherm is a combined form of Langmuir and Freundlich expressions deduced for predicting the heterogeneous adsorption systems and circumventing the limitation of the rising adsorbate concentration associated with Freundlich isotherm model. At low adsorbate concentrations, it reduces to Freundlich isotherm; while at high concentrations, it predicts a monolayer adsorption

capacity characteristic of the Langmuir isotherm. Therefore, from this scientific justification, the result obtained from this study best for Sips isotherm with the Value of R^2 0.995.

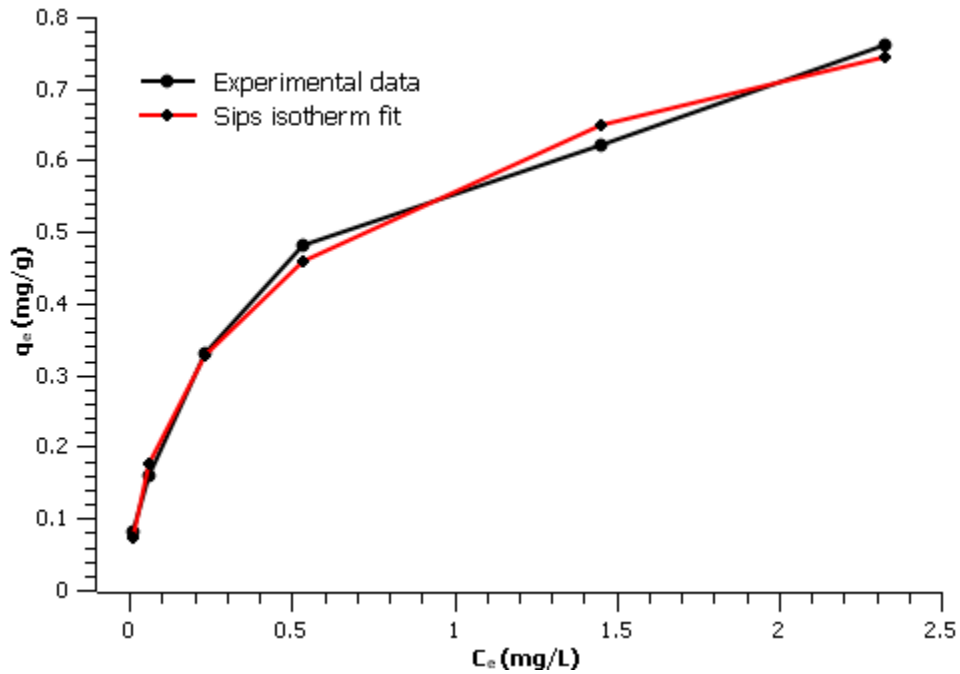


Figure 4.7: Sips isotherm for *L. albus* fluoride adsorption (pH: 7, agitation speeds: 300 rpm, equilibrium time: 30 minutes, adsorbent dose: 5 g/L and initial fluoride concentration: 10 mg/L in 100 mL solution).

Redlich–Peterson isotherm was also used to fit the equilibrium data of the adsorption of fluoride onto *L. albus*. Redlich–Peterson isotherm constants also varied in the same fashion as that of the Sips isotherm constants. Both these adsorption processes followed the Freundlich isotherm since the R^2 values were closer. Further Redlich–Peterson and Sips isotherm constants (n_{RP} and n_S) also confirmed that the surface of the prepared adsorbent was heterogeneous in nature. Therefore, from this scientific justification, the result obtained from this study best for Redlich-Peterson isotherm with the Value of R^2 0.993.

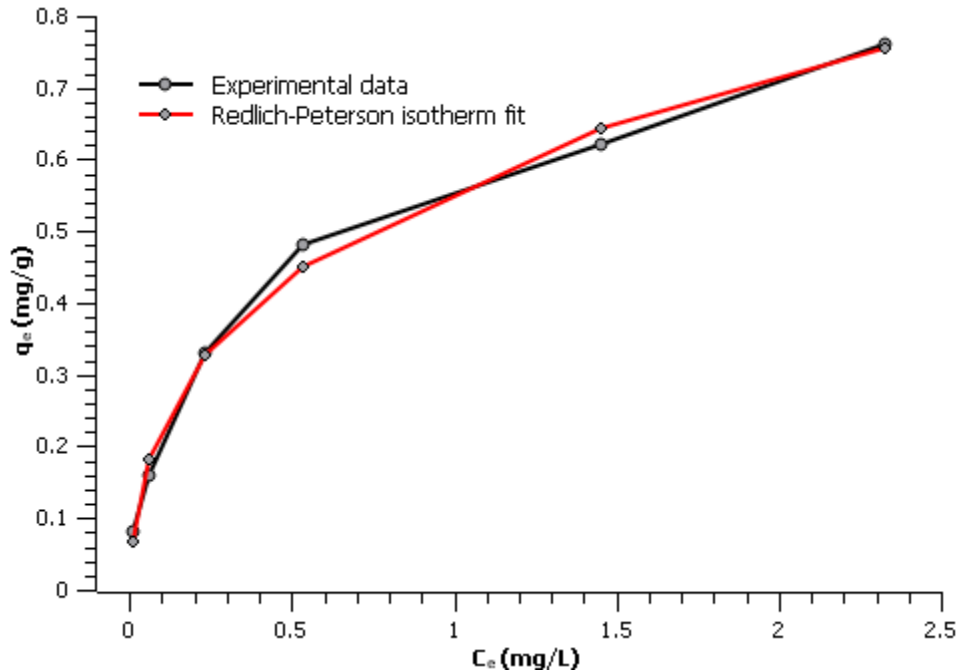


Figure 4.8: Redlich-Peterson isotherm for *L. albus* fluoride adsorption (pH: 7, agitation speeds: 300 rpm, equilibrium time: 30 minutes, adsorbent dose: 5 g/L and initial fluoride concentration: 10 mg/L in 100 mL solution).

4.7 Adsorption Kinetics

Adsorption kinetics, demonstrating the solute uptake rate, is one of the most important characters that represent the adsorption efficiency of the *L. albus*. Two possible models of kinetics were used to fit the experimental results Table 4.4: (1) pseudo-first-order model and (2) pseudo-second-order model Cheng *et al.*, (2013) and Zhao *et al.*, (2015). As shown in Figure 4.9, the pseudo-first-order model has a better fit with the experimental data with the higher squared correlation coefficients ($R^2 = 0.960$). The adsorption reaction is fast during the initial 20 min, and equilibrium was reached around 30 min. This result was in agreement with the equilibrium time found for alum sludge and quartz, which are reported in other studies Sujana *et al.*, (1998) and Nigussie *al et.*, (2007).

The nonlinear plot of pseudo-first order of fluoride adsorption on to *L. albus* with K_1 and the calculated equilibrium removal capacity were computed from the slope and intercept of the plot of q_e and t . The fluoride adsorption is nonlinear with the value of the correlation coefficient, $R^2 = 0.96$.

To distinguish kinetic equations based on adsorption capacity from solution concentration, Lagergren's first order rate equation has been called pseudo-first-order (Ho and McKay, 1998a).

In recent years, it has been widely used to describe the adsorption of pollutants from wastewater in different fields, such as the adsorption of methylene blue from aqueous solution by broad bean peels and the removal of malachite green from aqueous solutions using oil palm trunk fiber (Hameed and El-Khaiary, 2008a; 2008b; Tan *et al.*, 2008). Therefore, it can be concluded that the removal of fluoride on *L. albus* followed the pseudo-first order reaction.

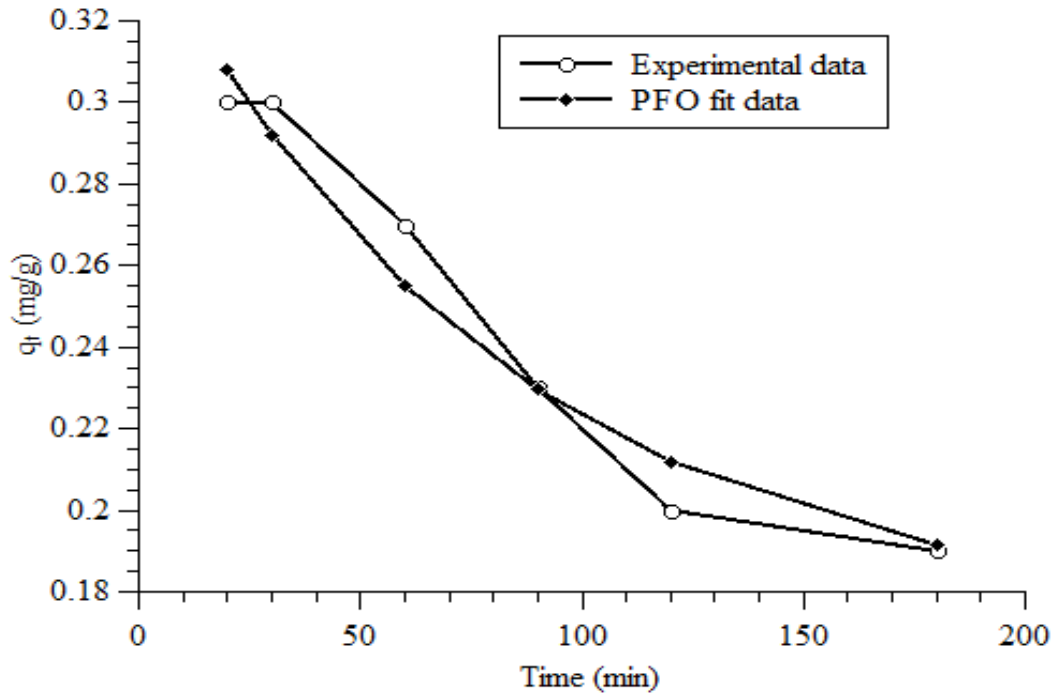


Figure 4.9: Plot of pseudo-first order kinetics of *L. albus* fluoride adsorption (pH: 7, agitation speeds: 300 rpm, equilibrium time: 30 minutes, adsorbent dose: 5 g/L and initial fluoride concentration: 10 mg/L in 100 mL solution)

Table 4.4: Pseudo first and second order kinetics parameters of fluoride adsorption on the *L. albus*

Parameters	Value	parameters	value
q_e, exp	0.173	q_e, exp	0.49
K_1	0.0124	K_2	$1.08 \cdot 10^8$
R^2	0.960	R^2	0.033

Besides adsorption at the outer surface of the adsorbent, the fluoride may also diffuse into the interior of the adsorbent. The intra-particle diffusion model based on the theory proposed by Weber and Morris (1963) was tested to determine if the particles' diffusion is the rate-limiting step for the fluoride adsorption onto *L. albus*. Intra-particle diffusion is a transport process involving movement of species from the bulk of the solution to the solid phase. In a well stirred batch adsorption system, the intra-particle diffusion model has been used to describe the adsorption process occurring on a porous adsorbent. A plot of the amount of sorbate adsorbed, q_t (mg/g) and the square root of the time, gives the rate constant (slope of the plot) in Figure 4.10.

As presented in Figure, the intra-particle diffusion rate constant (K_p) value estimated from the slope of plot of q_t versus square root of time. If intra-particle diffusion is a rate-controlling step, then the plots should be linear and pass through the origin (Weber and Morris, 1963). So, the plot is not a linear and does not pass through the origin. This indicates that the fluoride removal onto *L. albus* is a complex process and the intra-particle diffusion was not the only rate controlling step which is similar with the reports of Fufa *et al.*, (2013) and Beekam *et al.*, (2014).

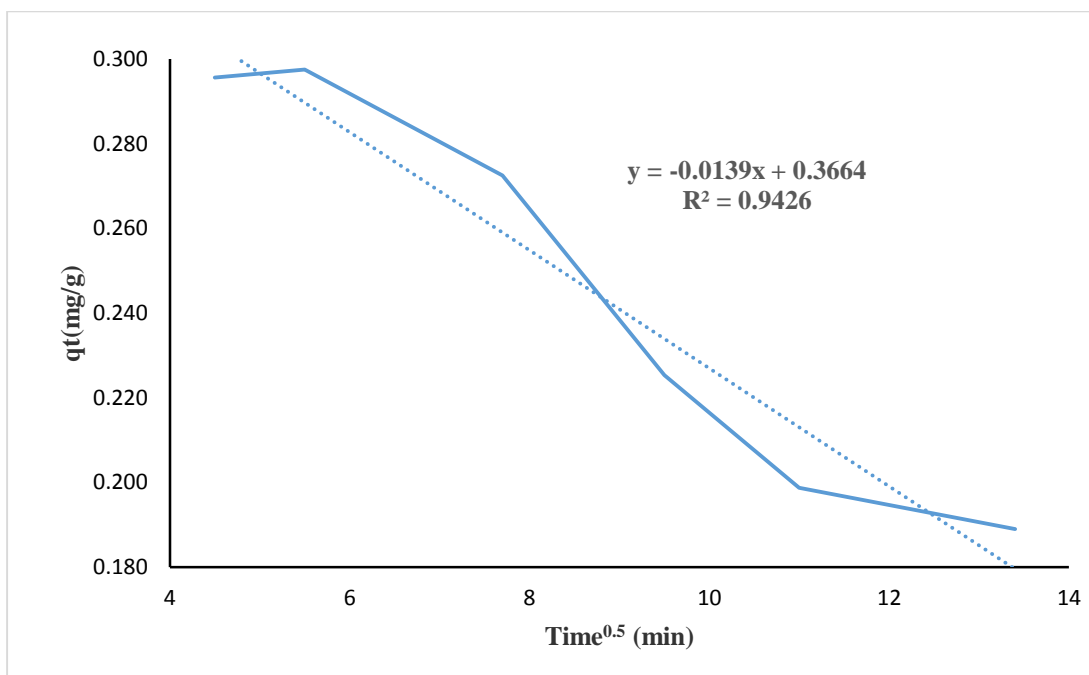


Figure 4.10: Plot of intra-particle diffusion of *L. albus* of fluoride adsorption (pH: 7, agitation speeds: 300 rpm, equilibrium time: 30 minutes, adsorbent dose: 5 g/L and initial fluoride concentration: 10 mg/L in 100 mL solution)

The Fractional Power kinetic is plotted between qt versus t for bio sorption of fluoride using *L. albus* at 10 mg/L of initial concentrations of fluoride at pH 7.0.

The time dependent experimental bio sorption data for the removal of fluoride using *L. albus* at initial concentrations are tested for kinetic modeling using Power function kinetic equation.

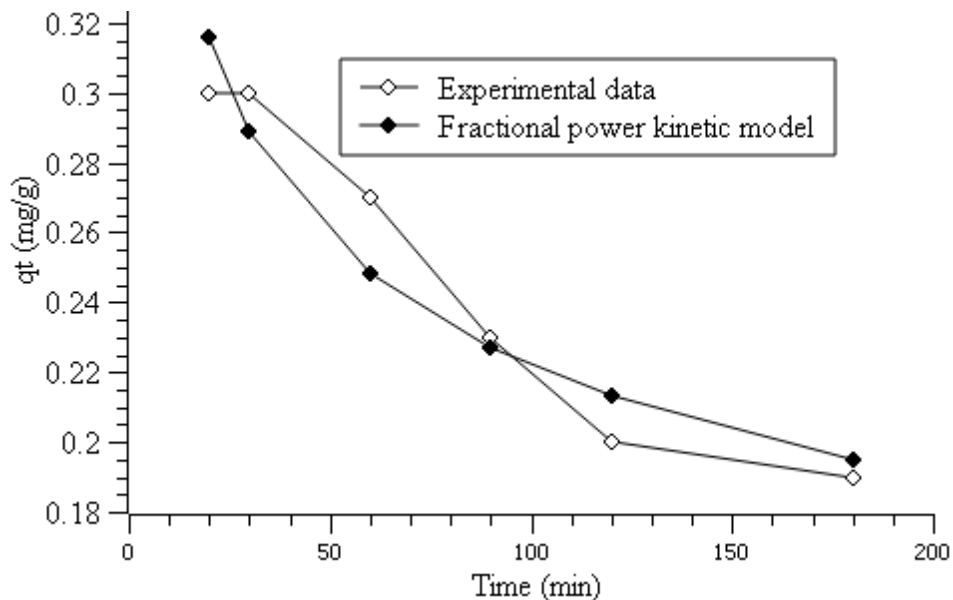


Figure 4.11: Plot of Fractional power kinetics of *L. albus* fluoride adsorption (pH: 7, agitation speeds: 300 rpm, equilibrium time: 30 minutes, adsorbent dose: 5 g/L and initial fluoride concentration: 10 mg/L in 100 mL solution)

4.8 Desorption of Fluoride

The percentage of fluoride desorbed increased from 46.7 to 73.3 % the concentration of NaOH increased from 0.1 to 0.5M in the solution.

As shown in Figure 4.2, the effect of pH of the solution on the fluoride adsorption efficiency and capacity by *L. albus* was very low at pH greater than 6. This suggests that, the possibility of desorbing adsorbed fluoride from the saturated *L. albus* using alkaline solution. Based on this, 0.1 and 0.5 M NaOH solution was used for desorption. The result showed that (Figure 4.12) the percentage of fluoride desorbed increased from 46.7 to 76.3 % as the concentration of NaOH increased from 0.1 to 0.5M in the solution *L. albus*. Consequently, fluoride *L. albus* could be regenerated using dilute NaOH solution.

This is due to at high pH of regeneration solution (NaOH) the abundance of hydroxide ions (OH^-) increases hindrance to diffusion of fluoride ions, thereby increasing detachment of the anion from the surface.

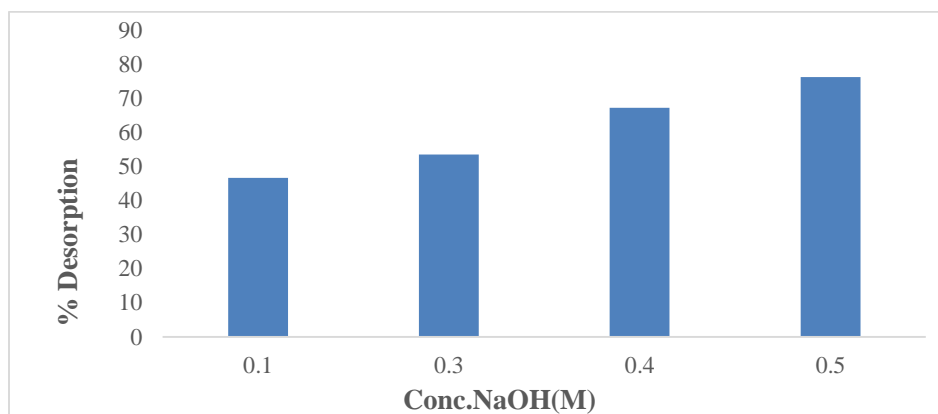


Figure 4.12: Percentage of fluoride desorbed of *L. albus*. (Dose 5, Time 30 min, Agitation speed 300 rpm, Initial fluoride 10 mg/L in 100 mL, pH 7, Concentration of NaOH 0.1-0.5 M).

4.9 Physicochemical Characteristics of Natural Water

Samples of natural water containing 18.65 mg/L fluoride were collected from one well which found in the Main Campus of Jimma University, Ethiopia. The physicochemical characteristics of the samples are given in Table 4.5.

Based on the optimum conditions that were determined by synthetic aqueous solution, it was tried the adsorption experiment of fluoride by *L. albus* using natural water sample. The results revealed that the fluoride removal efficiency from natural water with initial fluoride concentration of 18.65 mg/L and 5 g/L of *L. albus* with fine powder was ~ 98.8 %. Although it lowers the level of fluoride to the acceptable limit, it is in neutral media. Therefore, better to WHO permissible value for practical application of selected adsorbents for drinking water.

Table 4. 5: Physicochemical characteristics of natural water samples

Characteristic parameter	Value
Phosphate (mg/L, PO ₄ ⁻³)	0.084
Nitrate (mg/L, NO ₃ ⁻)	0.038
Bicarbonate (mg/L, HCO ₃ ⁻)	805.2
Carbonate (mg/L, CO ₃ ⁻²)	Bdl
Chloride (mg/L, Cl ⁻)	8.497
Fluoride (mg/L, F ⁻)	18.65
Total Alkalinity (mg/L, CaCO ₃)	660
Total hardness (mg/L)	60
Calcium hardness (mg/L, CaCO ₃)	40
Magnesium hardness (mg/L, MgCO ₃)	20
TDS (mg/L)	32
DO (mg/L)	0.82
Conductivity (μS/cm)	1281
Water Temperature (°C)	29.3
Turbidity (NTU)	1.26
Ambient Temperature (°C)	24
pH	6.4

Bdl: Below detection level

4.10 Cost Analysis

L.albus is an economically and agriculturally valuable plant (Sujak *et al.* 2006; Gulewicz *et al.*2008). Comparing the cost of *L. albus* with other like Rice, Moringa olifera and Palm oil has low cost than the other bioadsorbent in current Ethiopian market. Thus *L. albus* gives a good economic advantage over modified adsorbents and commercial activated carbon.

The relative cost of the material used in the present study is very much lower than that of commercial activated carbons.

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In conclusion, the present study was conducted to evaluate activated *L. albus* as a possible potential adsorbent for removal of Fluoride from aqueous solution in batch test. The higher removal, 97.69 % of Fluoride were achieved from aqueous solution by using 5 g/L. *albus* at pH 7. It is also important to remark that the *L. albus* is economic and easily available material and after treatment a very low amount of sludge is produced.

The higher removal also achieved at equilibrium time 30 min and the percentage removal of fluoride was decreased when the concentration of fluoride decreases.

Competing ions are ions that can interfere the adsorption process. In this study only chloride, Sulphate and bicarbonate ions was investigated. The bicarbonate shows high interference than the rest two ions.

Regarding to Adsorption kinetics, *L. albus* was pseudo first order kinetic than pseudo second order. The fitting of the fluoride removal to the pseudo-first order equation could suggest that fluoride should be adsorbed by chemisorption, which involves the sharing of electrons between fluoride and adsorbent.

L.albus adsorbent, obeying Freundlich model more appropriately than Langmuir Isotherm. However, the values of R^2 indicate that, Freundlich isotherm is better suited for *L. albus*. The adsorption of fluoride on *L. albus* adsorbent follow pseudo–first order kinetics and showed that the activated *L. albus* are very effective adsorbents which can remove sufficient amount of fluoride from aqueous solution in very short period of contact time (in this case 30 minutes). The rate of fluoride uptake by the sample adsorbent was fast, which is the required characteristics of an adsorbent because of lesser contact time requirements.

Desorption studies by using 0.5 M NaOH indicated that, only 76.3% of Fluoride could be desorbed from fluoride loaded *L. albus*. This shows presence of strong chemical bonding between *L. albus* and fluoride. Therefore, it can be concluded from the present studies *L. albus* can be used as an alternative adsorbent for the removal of fluoride from aqueous solution based on percentage recovery or reuse of the adsorbent without causing any harm to the environment.

5.2 Recommendations

Based on the finding of this study, the following recommendation is forwarded. Further study is required to investigate:

- The effect of other competing ions on the removal efficiency of Fluoride should also be studied
- The removal efficiency of *L. albus* is for removal Fluoride ion from water was good so, planting this plant in the area of high fluoride concentration existed.
- The removal efficiency of *L. albus* should be compared with other commercial bio adsorbent.

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ANNEX I

Apparatus

1. Spectrophotometer for use at 570 nm, providing a light path of at least 1 cm or longer or
2. a filter photometer equipped with a greenish yellow filter having maximum transmittance from 550 to 580nm
3. Nessler's tubes (100 mL)

Chemicals

- ✓ Sodium fluoride
- ✓ 2. Sodium arsenite
- ✓ Conc. HCl
- ✓ SPADNS
- ✓ Zirconyl chloride octahydrate

Reagents

1. **Stock Fluoride solution (0.221g/L)**: 221 mg anhydrous Sodium fluoride (NaF) was dissolved in distilled water and dilute to 1L. 1mL = 100 µg F or 0.1 mg F.
2. **Fluoride standards**: 10 mL of stock solution and diluted to 100 mL (1 mL=10 µg F or 0.01 mg F) was taken; A series of standard fluoride solutions in the range of 0.0 to 5.0 mg/L was prepared at intervals of 0.5 mg/L, by dilution of stock solution with distilled water.
3. **SPANDS solution**: 958 mg SPANDS, [Sodium 2-(parasulphophenylazo) - 1, 8- dihydroxide - 3, 6 naphthalene dilsulphonate] was dissolved in distilled water and dilute to 500mL. This solution is stable indefinitely if protected from sunlight.
4. **Zirconyl-acid reagent**: 133 mg zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) was dissolved in about 25 mL of distilled water. Add 350 mL conc. HCl and dilute to 500 mL with distilled water.
5. **(Acid zirconyl + SPANDS reagent)**: equal volume of SPANDS solution and zirconyl acid reagent was mixed. The combined reagent is stable for at least 2 years.
6. **Reference solution**: 10 mL of SPANDS solution to 100 mL distilled water was added. Dilute 7 mL conc. HCl to 10 mL and add to diluted SPANDS solution. The resulting solution, used for setting the reference point (zero) of the spectrophotometer. This solution is very stable and may be reused indefinitely.

7. **Sodium arsenite solution**: 5.0 g NaAsO₂ was dissolved and diluted to 1 L with distilled water.
(Caution: since sodium arsenite is toxic avoid ingestion).

Experimental Procedure

1. **Preparation of standard curve**: prepare fluoride standards in the range of 0 to 1.40 mg/L by diluting appropriate quantities of standard fluoride solution to 50 mL with distilled water.
2. In each 50 mL of Nessler tube, add 10 mL mix solution (or 5 mL of SPANDS and 5 mL zirconyl acid reagent). Was Mixed well. Take absorbance immediately of the bleached color at 570 nm using reference solution for setting zero absorbance.
3. Plot standard graph between concentration and absorbance (optical density)
4. F estimation in sample: Take 50 mL filtered sample and add 10 mL of mix solution, mix well and read the absorbance immediately of the bleached color at 570 nm using reference solution for setting zero absorbance. (Advice: After adding the mix solution take reading immediately)
5. If sample contain residual chlorine, remove it by adding NaAsO₂ solution; [1 drop (0.05mL) = 0.10 mg Cl)]. Note: Sodium arsenite concentration of 1300 mg/L produce an error of 0.1mg/L at 1 mg F/L).
6. If the transmission falls beyond the range of the standard curve, repeat the procedure using a smaller sample.

Calculation:

$$\text{mg/L F} = \mu\text{g F/ml of sample}$$

ANNEX II

Serial Dilutions

Serial dilution is the best method for the preparation of standards. Serial dilution means that an initial standard is diluted, using volumetric glassware, to prepare a second standard solution. The second standard is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.

1. **To prepare a 100 mg/L fluoride standard** – Pipette 10mL of the 1000 mg/L standard into a 100mL volumetric flask. Dilute to the mark with deionized water and mix well.
2. **To prepare a 10 mg/L standard** – Pipette 10mL of the 100 mg/L standard into a 100mL volumetric flask. Dilute to the mark with deionized water and mix well.
3. **To prepare a 1 mg/L standard** – Pipette 10mL of the 10 mg/L standard into a 100mL volumetric flask. Dilute to the mark with deionized water and mix well. To prepare standards with a different concentration use the following formula:

$$C1 * V1 = C2 * V2$$

C1 = concentration of original standard

V1 = volume of original standard

C2 = concentration of standard after dilution

V2 = volume of standard after dilution

ANNEX III

Results Tables

1. Standard Fluoride Solution

Standard Fluoride Solution (mL)	Fluoride Concentration (mg/L)	Absorbance
0.5	0.05	0.812
1	0.1	0.738
2	0.2	0.669
3	0.3	0.573
4	0.4	0.479
5	0.5	0.373

2. Effect of Dose on Fluoride Adsorption of *L. albus*

Dose (g)	C _o (mg/L)	C _e (mg/L)	q _e (mg/g)	% R
1	10	2.43	0.76	75.7
2	10	1.97	0.40	80.3
3	10	1.22	0.29	87.8
4	10	1.21	0.22	87.9
5	10	1.19	0.18	88.1

Experimental Condition, pH:6.5, Agitation speed:300 rpm, Contact time: 20 min, at Room temperature

3. Effect of pH on Fluoride adsorption of *L. albus*

pH	C _o (mg/L)	C _e (mg/L)	q _e (mg/g)	%R
4	10	2.9	0.24	71
6	10	1.21	0.29	87.9
7	10	0.23	0.33	97.7
8	10	1.64	0.28	83.6
10	10	1.93	0.27	80.7

Experimental Condition, Dose :5, Agitation speed :300 rpm, Contact time :20 min, at Room temperature.

4. Effect of Contact Time on Fluoride Adsorption of *L. albus*

Time (min)	C _o (mg/L)	C _e (mg/L)	q _e (mg/g)	%R
20	10	1.13	0.296	86.9
30	10	1.07	0.98	89.3
60	10	1.83	0.272	81.7
90	10	3.24	0.225	67.6
120	10	4.04	0.199	59.6
180	10	4.33	0.189	56.7

Experimental Condition, Dose:5 g, Agitation speed :300 rpm, pH:7, at Room temperature.

5. Effect of Initial Fluoride Concentration on Fluoride Adsorption of *L. albus*

C_o (mg/L)	C_e (mg/L)	q_e (mg/g)	%R
2.5	0.01	0.08	99.9
5	0.059	0.16	99.41
10	0.231	0.33	97.69
15	0.535	0.48	94.65
20	1.451	0.62	85.5
25	2.325	0.76	76.75

Experimental condition, Dose:5 g, Agitation speed 300 rpm, Contact time:30 min, pH:7, at Room temperature.

6. Co-existing Ion

Chloride

Cl ⁻ (mg/L)	C_o (mg/g)	C_e (mg/L)	q_e (mg/g)	%R
10	10	1.624	0.279	83.8
100	10	1.785	0.274	82.2
200	10	2.036	0.265	79.7

Sulphate

Sulphate (mg/L)	C_o (mg/L)	C_e (mg/L)	q_e (mg/g)	%R
10	10	1.381	0.287	86.2
100	10	1.535	0.282	84.6
200	10	2.472	0.251	75.3

Bicarbonate

Bicarbonate (mg/L)	C _o (mg/L)	C _e (mg/L)	q _e (mg/g)	%R
10	10	3.191	0.227	68.1
100	10	3.255	0.225	67.5
200	10	4.273	0.191	57.3

Experimental Condition: Dose:5 g, Agitation speed 300 rpm, Contact time :30 min, pH:7, at Room temperature.

7. Calculated values for determining adsorption isotherm

C _o (mg/L)	C _e (mg/g)	q _e (mg/g)	R _L
2.5	0.01	0.08	0.120
5	0.06	0.16	0.064
10	0.23	0.33	0.033
15	0.54	0.48	0.022
20	1.45	0.62	0.017
25	2.33	0.76	0.013

8. Calculated Values for determining Adsorption kinetics.

Time(min)	C _o (mg/L)	C _e (mg/L)	q _t (mg/g)	t ^{0.5} (min)
20	10	1.13	0.296	4.5
30	10	1.07	0.298	5.5
60	10	1.83	0.272	7.7
90	10	3.24	0.225	9.5
120	10	4.04	0.199	11
180	10	4.33	0.189	13.4