ADSORPTIVE REMOVAL OF FLUORIDE AND NITRATE FROM SYNTHETIC WATER USING SURFACE MODIFIED LATERITE SOIL

A DISSERTATION

Submitted in the partial fulfilment of the

requirements for the award of the degree

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MASTER OF TECHNOLOGY

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CHEMICAL ENGINEERING

(With Specialization in Industrial Pollution Abatement)

By

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JUNE, 2014

CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in this dissertation report entitled **"ADSORPTIVE REMOVAL OF FLUORIDE AND NITRATE FROM SYNTHETIC WATER USING SURFACE MODIFIED LATERITE SOIL"** in the partial fulfilment of the requirement for the award of the degree of Masters of Technology in Chemical Engineering with specialization in "Industrial Pollution Abatement" is an authentic record of my own work carried out during the period from June 2013 to June 2014 under the supervision of Dr. Prasenjit Mondal, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

The content in the report has not been submitted by me for the award of any other degree of this or any other Institute/University.

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

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ABSTRACT

Drinking water containing high amount of fluoride and nitrate can cause serious health hazards to the people across the globe. Fluoride concentrations between 0.5-1.5 mg/l are beneficial, for the prevention of dental caries or tooth decay, but concentrations above 1.5 mg/l can cause fluorosis (dental or skeletal) and neurological disorders in severe cases. For, nitrate concentrations above 45 mg/l can cause methemoglobinemia, also known as "blue baby syndrome" especially to infants. Hence it is required to keep the concentrations of fluoride and nitrate well in the limits prescribed by WHO. Techniques available for fluoride and nitrate removal include adsorption, chemical treatment, electrochemical methods, dialysis and ion exchange process. Among them, adsorption is found to be effective, environmental friendly and economical. Under the above backdrop, the present study has been undertaken to prepare efficient fluoride and nitrate adsorbent from raw laterite by acid followed by alkali treatment.

Batch experiments were performed to study the adsorption of fluoride and nitrate ions on Treated Laterite (TL) adsorbent with fixed size. Characterization of TL was carried out using various techniques such as BET Surface Area Analysis, FTIR, XRD, FE-SEM and EDAX. Effects of process parameters like pH, Adsorbent dose, contact time and initial ion concentration on the removal of fluoride and nitrate from synthetic water have been investigated using TL as adsorbent to determine optimum process conditions for maximum removal.

The fluoride concentration of 10 mg/l is removed upto 86% by TL effectively. Optimum adsorbent dose is found to be 12.5 g/l. The optimum time is determined to be 150 min at optimum pH of 6. Adsorption of fluoride ions on TL has been found to pseudo-second model among pseudo-first order, pseudo-second order and Webber-Morris model. Among the conventional isotherms, such as Langmuir, Freundlich and Temkin isotherms, the Temkin isotherm gave better prediction of specific uptake for fluoride ions at equilibrium.

For nitrate adsorption on TL, optimum adsorbent dose has been found to be 20 g/l for initial nitrate concentration of 100 mg/l at optimum pH of 5. TL could remove 80% nitrate ions effectively and the equilibrium was set in 120 min. Langmuir isotherm fitted well to the data than Freundlich and Temkin isotherm models and adsorption followed pseudo-second order kinetics.

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1. INTRODUCTION

1.1 GENERAL

Fluoride, highly reactive in nature, does not occur in elemental state. Fluoride is considered to be a micronutrient for health of humans, essential to prevent dental cavities, and to promote healthy bone growth. But too much fluoride can be detrimental. Therefore, it is vital to uphold the fluoride concentration in drinking water between 0.8 to 1.0 mg/L.

Long term ingestion of fluoride drinking water can cause fluorosis, teeth mottling, particularly in children [Mahramanlioglu et al. 2002]. When fluoride concentration in drinking water gets more than 5-10 ppm, severe forms above the above mentioned diseases develop. Though, symptoms may develop with consistent ingestion of drinking water having fluoride concentration of 1-2 ppm.

According to the standards set by World Health Organization (WHO) the permissible level is 1.5 mg/L for drinking water [Zhang et al. 2005], [Amini et al. 2008].

The excessive concentration of fluoride in drinking water and its injurious effect on health have increased the necessity for removal of fluoride.

One of the environmental problems that has become an increasingly important problem in developed and developing countries is nitrite and nitrate contamination of surface and ground water. To limit the risk to human health from nitrate and nitrite in drinking water, the World Health Organization (WHO) sat a maximum acceptable concentration to be 50 NO_3^- mg/L.

The proposed project aims at solving two problems (removing fluoride and nitrate from drinking water) with a sole pioneering solution which is efficient and cost-effective.

There are number of ways to remove fluoride and nitrate from water such as membrane processes, ion exchange, coagulation-precipitation, biological methods and adsorption processes.

The prevailing adsorbents are pretty costly and not easily available to rural areas. Thus a necessity arose to explore natural adsorbents having good adsorption capacities.

In the present study, natural occurring raw laterite (RL) soil's surface was modified by acid-base treatment and evaluated for the removal of fluoride and nitrate from aqueous solutions. Moreover, laterite soil may be highly apt for column adsorption for treatment of ground as well as wastewater.

1.2 SOURCES

1.2.1 The various sources of **fluoride** are:

Fluoride containing rocks

Fluoride is largely distributed in the geological environment in the form of minerals like eg. fluorite, biotites, topaz etc. Fluoride containing rocks are one of the major sources of fluoride ion. Fluoride ions present in these rocks gets dissolved in water and hence fluoride enters the ground water [Abe et al. 2004]. The Figure 1.1 below shows a comparison of the amount of fluoride released by different types of rocks.

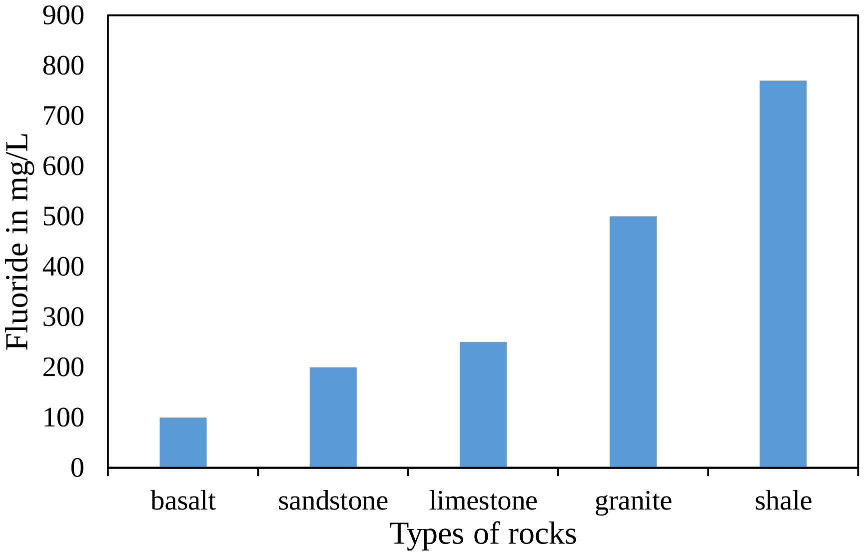


Figure 1.1 Comparison of amount of fluoride released by various types of rocks [Jacks et al. 2005]

Industries releasing fluoride

Fluoride ion is also released from a number of industries like glass, ceramic, electroplating, brick and iron work, etc which have a very high fluoride concentrations about ten to thousands of mg/l of fluoride [Bhatnagara et al. 2011].

1.2.2 Sources of nitrate are:

Nitrogen cycle

Nitrogen cycle is very important to the earth as it returns nitrogen to all the earth and all of the creatures around us, which in turn returns the nitrogen to our body.

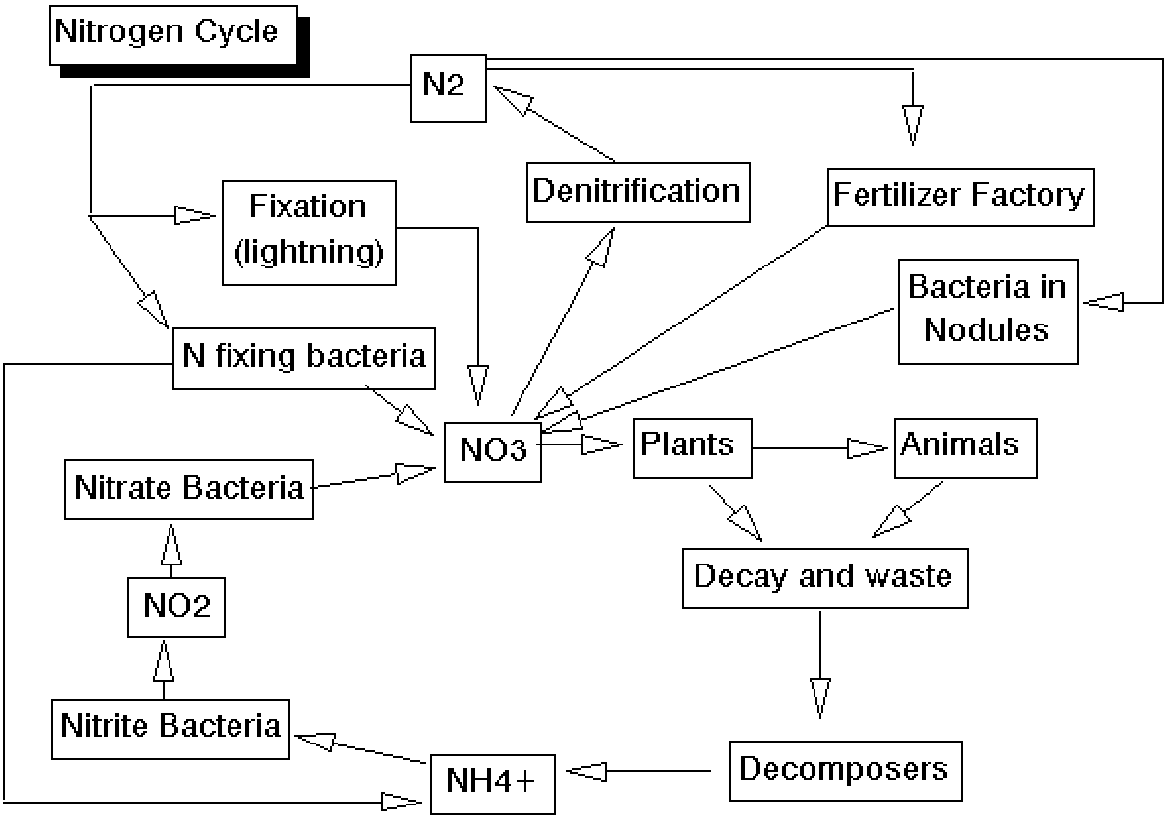


Figure 1.2 Biogeochemical Nitrogen Cycle

Natural occurrence:

These can be due to fixation of atmospheric N_2 by lightning or nitrogen fixing bacteria. Also is converted to NO_2^- by nitrite bacteria which is further oxidized to NO_3^- by nitrate bacteria.

Anthropogenic sources:

Most groundwater nitrates are because of anthropogenic sources. It includes on-site sanitation, application of fertilizers to land, tilling of the soil, irrigation and other activities.

1.3 PROPERTIES:

1.3.1 Fluoride:

Fluoride is a highly reactive and hence it does not occur in free state. The various properties of fluorine are listed in the Table 1.1.

Table 1.1 Properties of fluorine [web 1]

Property	Value
Physical state	Pale yellow green coloured gas
Melting point	-219 °C
Boiling point	-188 °C
Density	$1.8*10^{-3}$ g/cm^3 at 20 °C
Water solubility	42 g/litre at 10 °C
Atomic mass	18.99 g/mol

1.3.2 Nitrate:

Table 1.2 Properties of nitrate [web 2]

Property	Value
Atomic mass	62.0049g/mol
Density	$1.25*10^{-3}$ g/cm^3 at 20^{o}C
Melting point	-210 °C
Boiling point	-195.8 °C

1.4 HEALTH EFFECTS:

1.4.1 Fluoride:

The effect of fluoride on human health depends on the concentration and duration of its exposure. Fluoride in drinking water is beneficial to the health if the concentration is low and harmful if the concentration exceeds the permissible value.

On the other side, an excess of fluoride can cause:

1) Mottling of teeth (dental fluorosis).

2) Brain damage, brittle bones, and osteoporosis.

3) Bones embrittlement and neurological disorder in extreme cases.

Besides excess fluoride may also interfere with DNA synthesis and can cause structural and biochemical changes in muscles and nerves [Bhatnagara et al. 2011].

Table 1.3: Concentration of fluoride in drinking water and its impact on human health [Jacks et al. 2005]

Fluoride conc. (mg/l)	Effect on human health
0	Imperfect growth
<0.5	Dental caries
0.5-1.5	Promotes dental health and prevents tooth decay
1.5-4.0	Dental fluorosis
4.0-10.0	Dental fluorosis, skeletal fluorosis
>10.0	Crippling fluorosis

Table 1.4: Various forms of fluorosis [Jacks et al. 2005]

Type	Effect
Dental fluorosis	1. Affects teeth and it is common in children. 2. Teeth become yellow. 3. The disease has commonly cosmetic implication and has no cure.
Skeletal fluorosis	1. Bones and skeleton are affected. 2. Neck, hip, shoulder and knee joints are effected commonly. 3. Not easily detectable. 4. In severe cases complete rigidity of joints occurs.
Non-skeletal manifestations	1. Affects soft tissues.

1.4.2 Nitrate:

Specifications for potable water and stock watering

Table 1.5: The Specifications for Nitrate in Potable Water

NO_3^-N Specifications (mg/L)		
Potability Class	Ideal	< 6
	Acceptable	6-10
	Marginal	10-20
	Poor	20-40
	Unacceptable	>40
Livestock	Acceptable	<110

<u>Methemoglobinemia</u>

- Methemoglobinemia or blue-baby syndrome (name due to bluish or lavender skin color).
- Nitrite converts hemoglobin to methemoglobin (unable to transport oxygen from lungs to tissues).
- Methemoglobin levels > 50% can quickly lead to coma or death if not recognized and treated promptly.
- **Most at Risk**: Infants under six months of age because stomach pH levels are higher than adults that allows for proliferation of nitrate-reducing bacteria to grow in stomach, fetal hemoglobin in infants is more rapidly oxidized than adults and also because methemoglobin reductase enzyme is not completely developed in infants.

Apart from health effects, excess of nitrate in surface water can cause algal blooms.

1.5 PERMISSIBLE AMOUNT:

1.5.1 Fluoride:

The permissible for fluoride in drinking water is 1.5 mg/l as recommended by WHO [Zhang et al. 2005]. According to BIS (Bureau of Indian Standards), acceptable fluoride concentration is 1.0 mg/l and maximum allowable concentration is 1.5 mg/l in drinking water.

1.5.2 Nitrate:

WHO has recommended a nitrate concentration of 50 mg/l in drinking water.

1.6 CONTAMINATION IN INDIA:

1.6.1 Fluoride:

At least in 25 countries worldwide and about 62 million people are affected with fluorosis. India is one of the worst amongst affected ones. In India, almost 19 states have high fluoride concentrations in groundwater [Susheela et al. 1999] with Gujrat and Rajasthan having the highest upto 31 and 37 mg/l respectively.

1.6.2 Nitrate:

In India, many states are at risk where nitrate concentration in groundwater is more than 45 mg/l. Most of the districts of Andhra Pradesh, Chattisgarh, Gujrat, Haryana, Karnataka, Maharashtra, Madhya Pradesh, Orissa, Rajasthan, Tamil Nadu, Uttar Pradesh have nitrate levels more than described [Jain et al. 2008].

1.8 OBJECTIVES:

The aim of the present work is to develop a low cost adsorbent for the removal of fluoride and nitrate from water. Point wise objectives are as follows:

1. Preparation of adsorbents by surface modification of laterite soil and the selection of the best adsorbent.
2. To compare the characteristics of raw laterite (RL) and treated laterite (TL) soil.
3. Assessment of fluoride and nitrate removal capacity of naturally available laterite and treated laterite soil in batch reactor.
4. Kinetic and equilibrium modeling of the process.

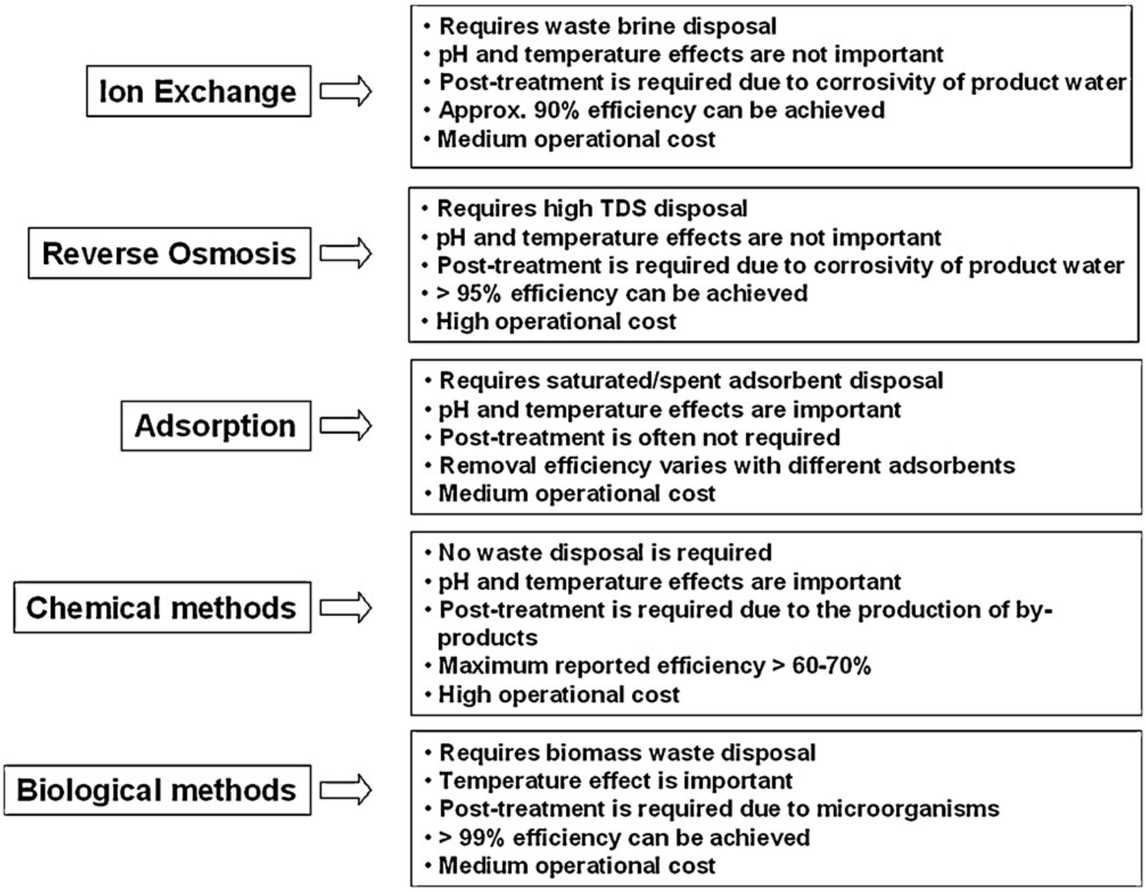
2. LITERATURE REVIEW

2.1 LATERITE SOIL

Laterite soils are rusty and red in colour and are found in various parts of the country. The word laterization means prolonged and intensive chemical weathering producing a variety in thickness, grade, chemistry and mineralogy. The common features of laterite are as follows:

1. It has high content of iron and aluminium oxides.
2. It is formed in hot and humid areas especially in the land areas between the tropics of Cancer and Capricorn.
3. Used in waste water treatment especially for removal of phosphorous and heavy metals like chromium, cadmium, lead, etc. It is also used for removal of arsenic and fluoride.

2.2 TECHNIQUES AVAILABLE FOR FLUORIDE AND NITRATE REMOVAL:



Ion Exchange ⇨
- Requires waste brine disposal
- pH and temperature effects are not important
- Post-treatment is required due to corrosivity of product water
- Approx. 90% efficiency can be achieved
- Medium operational cost

Reverse Osmosis ⇨
- Requires high TDS disposal
- pH and temperature effects are not important
- Post-treatment is required due to corrosivity of product water
- > 95% efficiency can be achieved
- High operational cost

Adsorption ⇨
- Requires saturated/spent adsorbent disposal
- pH and temperature effects are important
- Post-treatment is often not required
- Removal efficiency varies with different adsorbents
- Medium operational cost

Chemical methods ⇨
- No waste disposal is required
- pH and temperature effects are important
- Post-treatment is required due to the production of by-products
- Maximum reported efficiency > 60-70%
- High operational cost

Biological methods ⇨
- Requires biomass waste disposal
- Temperature effect is important
- Post-treatment is required due to microorganisms
- > 99% efficiency can be achieved
- Medium operational cost

Figure 2.1 Comparison of some removal technologies

Adsorption

Adsorption has been found to be better than other techniques for water purification in term of: ease of application, cost, simplicity of design and feasibility for in situ treatment of underground and surface water. Moreover adsorption does not need skilled maintenance and equipment intensive processes and can thus be applied in rural areas.

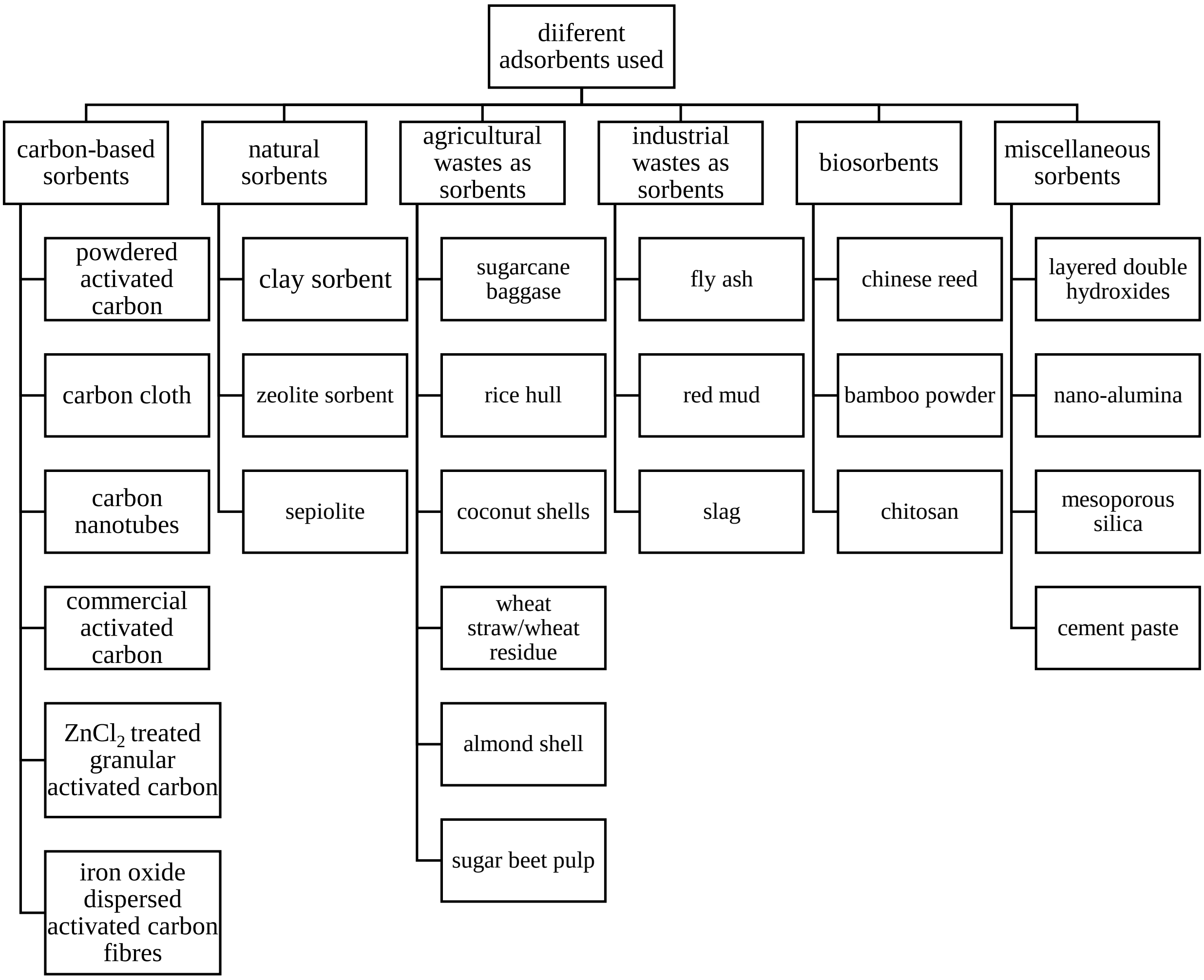


Figure 2.2 List of different adsorbents used for the removal of nitrate from water

2.3 WORK DONE BY DIFFERENT AUTHORS FOR FLUORIDE REMOVAL BY ADSORPTION:

1) Sollo et al. (1978), tested a no. of methods for fluoride removal with emphasis much laid upon coagulation methods. Most effective method was coagulation with alum at pH levels of 6.2 to 6.4 with water containing 5.0 mg/L of fluoride, adsorbent dose of 200 mg/L of alum reduced 60% fluoride content. By formation of fluorapatite, fluoride can also be removed, with 4.72 mg/L of fluoride in water, concentration was reduced to 63% by the application of 320 mg/L of phosphate, with the appropriate calcium addition and pH control. Also, adsorption on $Mg(OH)_2$ reduced the fluoride concentration by 57%, in water with 4.30 mg/L of fluoride and 73 mg/L of Mg ion, treatment with lime to precipitate 90% of this Mg also reduced the fluoride concentration by 57%.

2) Sujana et al. (1998), for the removal of fluoride from aqueous solution, treated alum sludge was used. The optimum pH and temperature were 6 and 303 K respectively. First order kinetics was followed. Langmuir adsorption isotherm model fits well to data. An increase in NO_3^- dose from 10 to 50 mg/l had least effect on fluoride removal as compared to SO_4^- and PO_4^-.

3) Tripathi et al. (2006), alum-impregnated activated alumina (AIAA) was used. Most of the fluoride was removed in the first 60 min and in 3 hours equilibrium was established and 92% fluoride was removed at optimum pH 6.5. The isotherm correlate to the Bradley equation. For 35 mg/l initial fluoride concentration, 8 g/l adsorbent dose was sufficient. Regeneration of AIAA was done by rinsing the spent AIAA with 0.1 M NaOH at pH 12 followed by 0.1 M HCl (for neutralization). Upto 99% of fluoride was removed for initial concentration of 20 mg/l.

4) Solangi et al. (2009), studied the modification of Amberlite XAD-4 resin to remove F^- from the groundwater of the Thar Desert (Pakistan). Amberlite XAD-4TM was modified by the treatment of beads of resin (10.0 g) with 20 mL of concentrated HNO_3 and 50 mL of concentrated H_2SO_4 for 30 min at 50°C with continuous stirring. The adsorption of fluoride increased as the dosage of immobilized resin was increased and the adsorption was nearly constant at dosage higher than 100 mg. The equilibrium was established within 40 min and showing a slight increase in percent sorption up to 60 min. The % adsorption increased with increasing pH of solution and reached a maximum value at pH 9.0. Using 10% HCl as eluent, desorption efficiency of the resin was studied and observed that 98.5%

desorption can effectively be done. The sorption capacity was found to be 5.04 $\times 10^{-3}$ mol/g. At a flow rate of 3 mL/min and more, there was a decrease in % adsorption.

5) Viswanathan et al. (2009), studied the defluoridation of fluoride by modification of Chitosan beads (CB). It was observed that Chitosan beads have very low defluoridation capacity (DC) but on modification by introduction of COOH and NH_3^+ groups via carboxylation and protonation the DC value increases for raw chitosan from 52 mgF^-/kg to 1800 mg F^-/kg for protonated cum carboxylated chitosan beads (PCCB). The suitability of PCCB was tested using water sample from fluoride endemic area .The sorbent lowered fluoride from 2.33 mg/l to the required level. About 0.5 g of PCCB was used for a 50 ml of sample, for 30 min at room temperature. It was also noticed that PCCB also removed other common ions but this did not affect the reduction of fluoride to the tolerance value. Equilibrium data was fitted to both Langmuir and Freundlich isotherm and the kinetics of the process was determined. Freundlich isotherm fitted better to the adsorption data. It followed the pseudo second order kinetics.

6) Chen et al. (2010), an adsorbent was developed using granular ceramic which is stable Al-Fe surface complex for removal of fluoride from water. Physical properties such as particle size , pore size, surface roughness of the granular ceramic were determined using BET, SEM and EDS. Batch experiments were performed and the effect of major parameters like pH , dose of adsorbent, rate of stirring, contact time and initial adsorbate concentration on fluoride removal efficiency were optimized. Equilibrium data was fitted to both Langmuir and Freundlich isotherm and the kinetics of the process was determined. Freundlich isotherm fitted better to the adsorption data. It followed the pseudo second order kinetics. Effect of anions, phosphate and sulfate and cation i.e. calcium and magnesium were studied. While the adsorption of fluoride increased with the concentration of cations, it decreased with an increase in the concentration of the anions. It was ensured that water quality was maintained and no aluminium or ferric ions were leached out.

7) Malakootian et al. (2011), pumice was used for fluoride removal from the synthetic water. Batch experiments were performed. It was noted that at neutral pH, time 3 hrs, 20 mg/l of pumice and with 2 mg/l of initial fluoride dose the adsorption process was 87.75% efficient. A case study was also performed on the Kuhbonan water keeping pH 7, time 3 hrs the adsorption process was 74.64 % efficient. Equilibrium data was fitted to both

Langmuir and Freundlich isotherm and the kinetics of the process was determined. Freundlich isotherm fitted better to the adsorption data. It followed the pseudo second order kinetics.

8) Ganvir and Das (2011), used surface modified RHA, coated with aluminum hydroxide and it was found that the adsorption capacity was increased with the amount of aluminum hydroxide coated. Adsorption capacity was found to be 9-10 mg/g for the RHA. For coated aluminum hydroxide adsorption RHA was 15.08 mg/g for the batch operation and 9.5 mg/g for the column mode. Method was found to be pH dependent, with 5 be the best pH. A filter unit has been developed to treat 1250 L of 5 mg/l of fluoride tap water at a flow rate of 5 L/h to the lower limit value of fluoride to prescribed limit.

Table 2.1 Various Types of sorbents used for adsorption of fluoride [Bhatnagara et al. 2011]

Adsorbent	**Example**	**Properties**
Aluminium-based sorbents	alumina	1) Inexpensive and highly efficient. 2) They require careful handling as aluminium is a neurotoxin.
Industrial based	Fly ash, alum	1) High defluoridation capacity in batch mode. 2) Inexpensive materials.
Carbon-based sorbents	Charcoal, activated carbon	1) Low defluoridation capacity in batch mode. 2) Surface modification is done to enhance defluoridation capacity.

Natural materials	bauxite, laterite, palygorskite, bentonite and kaolinite	1) Contain gibbsite or aluminium oxides 2) Laterite soil high defluoridation capacity in batch mode 3) Difficult regeneration 4) Low efficiency under high fluoride concentration
Nano sorbent	Carbon nano tubes	1) Latest technology 2) Operates in wide pH range 3) High defluoridation capacity
Agricultural-based sorbents	Calcium chloride, aluminium chloride , aluminium impregnated corn cobs etc	1) Inexpensive 2) Renewable 3) Eco-friendly 4) Lower defluoridation capacity in batch mode 5) Surface modification is done to enhance defluoridation capacity

2.4 WORK DONE BY DIFFERENT AUTHORS FOR NITRATE REMOVAL BY ADSORPTION:

Various researchers have reported use of zero-valent iron (ZVI) for nitrate reduction but this method has a major disadvantage of ammonium production and very cautious control of pH. And when ZVI is applied in-situ, these advantages become more critical. Biological denitrification is difficult to apply to inorganic wastewater as additional organic substrates are required to donate electrons. Other adsorbents used for nitrate removal are discussed below.

1) Ohe et al. 2003, activated carbon (AC) was made from coconut shell and charcoal from bamboo (CB) for removal of nitrate from aqueous solution. Maximum removal occurred at 2-4 pH, Langmuir model was well fitted and maximum adsorption capacity was found to be 0.104 mmol/g and 0.266 mmol/g for CB and AC respectively.

2) Afkhami et al. 2007, carbon cloth was used for adsorption of NO_3^- and NO_2^-. C-cloth was treated with 4 N H_2SO_4 prior to adsorption process carried out at neutral pH. Treatment with acid produced positive sites on carbon cloth and thus negatively charged anions were attached to it. The maximum adsorption capacities were found to be 2.03 and 1.01 mmol/g for nitrate and nitrite respectively which were higher than C-cloth treated with distilled water i.e. 0.38 and 0.05 mmol/g for nitrate and nitrite respectively.

3) Islam et al. 2007, co-precipitation method was used to develop Zn-Al-Cl layered double hydroxides (LDH). 85.5% of nitrate was removed from water using 3 g/l LDH at 10 mg/l initial nitrate concentration at neutral pH. Langmuir isotherm was followed with maximum langmuir adsorption capacity of 40.26 mg/g and first-order kinetics suited better. Increase in pH decreased NO_3^- removal and optimum pH was found to be 6. LDH had low desorption capacity and poor regeneration.

4) Khani et al. 2008, carbon nano-tubes (CNTs) and powdered activated carbon (PAC) were used for nitrate removal and had adsorption capacities of 25 and 10 mmol/g respectively. The equilibrium was established in 60 mins. Optimum pH was found to be 5.

5) Chatterjee and Woo, 2009, chitosan beads were used for nitrate removal from water and had adsorption capacity of 92.1 mg/g at 303 K and capacity decreased when temperature was raised to 323 K. Optimum pH was recorded to be 6.4. 87% desorption was attained at pH 12.

6) Arora et al, 2010, natural zeolite was coated with chitosan layer and was protonated either with H_2SO_4 or HCl acid and investigated for removal of nitrate from water at 293 K. Protonation with HCl resulted a higher NO_3^- exchange capacity when compared to H_2SO_4. Chitosan coated zeolite had an equivalent ion exchange capacity to other feeble anion exchangers with exchange capacity of 0.74 mmol nitrate per gram.

Among the different types of sorbents available laterite is inexpensive, abundantly available and has high defluoridation capacity. The Table 2.2 shows the work done on laterite as an adsorbent for fluoride removal.

Table 2.2 Work done on laterite soil

ADSORBENT	ADSORBENT CAPACITY	SPECIES TAKEN	INITIAL CONC. MG/L	pH	TEMP K	ISOTHERM	KINETICS FOLLOWED	REMARKS	REFERENCE
Natural laterite	78.2 % effifcient	Fluoride	10	6.8	303	Freundlich and Langmuir isotherm	pseudo-first-order rate	Process (batch) was efficient with 83.3-74.4% removal with laterite dose of 1.0 g/l. Particle size was 500 µm. The equilibrium time was found to be 195 min. Adsorption process was spontaneous and exothermic in nature.	Sarkar et al. 2006
Natural laterite	68 % efficient	Fluoride	20	7.5	303	Langmuir or a Freundlich isotherm	pseudo-first-order rate	The flow rate through the column was varied up to 10.0 cm^3/min for bed height of 20 cm. Upto flow rate of 6.5 cm^3/min, the column capacity was unchanged and decreased afterward.	Sarkar et al. 2007
Acid treated	37.9 mg/g.	Fluoride	10	3 to	305	Freundlich	shrinking	Batch process, Laterite was treated at pH 6.5 with	Maiti et al.

laterite				5.		and Langmuir	core model	6N HCl for 3 hours, the adsorbent dose was selected as 0.5 g/L of particle size 0.40 mm, HCO_3^- and PO_4^- only had noteworthy meddling effect on the adsorption.	2011
Natural laterite	-	Fluoride	25	5	-	Freundlich isotherms	-	Batch process, Studied the modelling and adsorption of F^- on laterite. Surface complexation modelling shows that both iron and aluminium ion account for adsorptive removal of fluoride.	Vithanage et al. 2012
Acid treated laterite	10.5 mg/g.	Fluoride	200-800	3.32	313	Freundlich and Langmuir isotherm.	-	Laterite soil with particle size less than 1000 microns was treated with 0.1 N HCl for 30 min. The effect of other ions like nitrate, chlorate, sulphate, chloride and phosphate was studied and result was that nitrate	Wambu et al. 2012

								ion has positive impact on fluoride removal. Also at high conc. and high temperature physisorption with intra- particle diffusion of Fluoride dominated whereas at low surface coverage ion exchange mechanism dominated.	
Thermally treated laterite	47 mmol/kg	Fluoride	20	-	673	Langmuir isotherm.	Two mechanism: an initial rapid adsorption followed by slower uptake	Experiment was conducted over 65 min. Studied the removal of fluoride using thermally treated laterite. RGS i.e red gullale soil from Adiss Ababa of particle size in the range170-320 microns and thermally treated at 400, 500, 550, 600 and 800 °C were used.	Gomoro et al. 2012
Laterite soil	68% efficient	Nitrate	10	6		Freundlich and Langmuir isotherms.	First order rate equation.	Laterite soil collected from Bidar urban having an average diameter of 150 µ. Kinetics study	Shivasharanappa et al. 2013

								showed that adsorption of NO_3^- is very rapid for initial 130 minutes and decreased towards approaching equilibrium. Optimum dosage was found to be 14 g/l.	

2.5 PROSPECT OF LATERITE AS FLUORIDE AND ARSENIC ADSORBENT:

Lateritic soils are described as product of highly weathered material, under tropical and subtropical condition, rich in secondary oxides of iron, aluminium or both. They are nearly void of bases and primary silicates, but may contain amounts of quartz or kaolinite. Also, the lateritic soils are either hard or capable of hardening on exposure to wetting and drying. Furthermore, the lateritic soils are composed of a wide variety of red, brown, and yellow fine-grained residual soils of light texture, as well as nodular gravels and cemented soils [Schellmann, 1994].

Laterite soil is red-coloured clay-rich in tropics and subtropics. It needs high temperatures and abundant rainfalls in the tropics of form. The water washes out the bases and silicic acid, and enriches it with aluminium, silicates, aluminium hydroslilicates, iron oxides and iron hydroxides [Maji et al. 2007]. Actually, it is the iron that makes laterite look red. Potential of laterite soil for adsorption of fluoride is due to the presence of Fe(III) and Al(III), as discussed in literature review. It is available in several parts of West Bengal, India, for eg. Purulia, Bankura, West Midnapore.

Therefore, we look to study the raw laterite and surface modified laterite as adsorbents for simultaneous adsorption fluoride and nitrate from their synthetic solution.

3. ADSORPTION MODELLING

To understand the adsorption process and to quantify the adsorption phenomenon both kinetic and adsorption models are applied.

3.1 KINETIC AND DIFFUSION MODELS

Adsorption kinetics is an important characteristic for evaluating efficiency of adsorption. It also predicts the rate at which adsorption takes place. Various kinetic models have been used to describe the reaction order but pseudo-first-order and pseudo-second-order kinetic models are well liked to study the adsorption kinetics. When adsorbent and adsorbate are in contact for sufficiently long time, equilibrium is established between amount of species adsorbed and amount remaining in the solution. For any system in equilibrium, the amount of material adsorbed on the surface of the adsorbent i.e. equilibrium uptake or adsorption capacity, q_e (mg/g) can be calculated using the Eq. (1)

$$\boldsymbol{q_e = (C_o - C_e)\frac{v}{m}} \qquad \textbf{(1)}$$

At any time, uptake q_t , can be calculated from Eq. (2)

$$\boldsymbol{q_t = (C_o - C_t)\frac{v}{m}} \qquad \textbf{(2)}$$

where,

- C_o is the initial nitrate concentration (mg/l)
- $C_e$equilibrium concentration (mg/l)
- v is the volume of sample (ml)
- m is the mass of the adsorbent (mg)
- q_t is the amount of adsorbate adsorbed at time t (mg/g)
- q_e is the adsorption capacity at equilibrium (mg/g)

3.1.1 Pseudo 1st Order Model

According to this model, the rate of adsorption is based on the residual adsorption capacity of the adsorbent at any point of time.

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad \textbf{(3)}$$

Where,

- K_1 is the pseudo first order rate constant
- t is the contact time

Upon integration of Eq. 3, with initial condition (q_t= 0), we get the following expression:

$$\ln(q_e - q_t) = lnq_e - k_1 t \qquad \textbf{(4)}$$

Eq. 4 is linearized form of pseudo-first-order kinetic model.

3.1.2 Pseudo 2nd Order Model

The pseudo-second order model is represented as

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad \textbf{(5)}$$

Where,

- K_2 is the pseudo second order rate(g/mg min).

Integrating above equation and noting that q_t =0 at t =0, the following equation is obtained:

$$q_t = \frac{q_e^2 k_2 t}{1+q_e k_2 t} \qquad \textbf{(6)}$$

The initial sorption rate, h (mg/g min), at t= 0 is defined as:

$$h = k_2 q_e^2 \qquad \textbf{(7)}$$

Eq. 7 can be linearized as:

$$t/_{q_t} = 1/_{k_2 q_e^2} + t/_{q_e} \qquad \textbf{(8)}$$

3.1.3 Inter particle diffusion study

The adsorbate transport process from the solution phase to the surface of the adsorbent occurs in several step. The overall adsorption process may be controlled by many factors such as pore diffusion, external or film diffusion, surface diffusion and adsorption on the pore surface, or a combination of one or more step.

According to Weber and Morris, the transient uptake of the solute varies almost proportionately with $t^{0.5}$ for most adsorption process. The intra particle diffusion model is given as

$$\boldsymbol{q_t = K_{id} t^{0.5} + C} \qquad \textbf{(9)}$$

Where $\boldsymbol{K_{id}}$ (mg/g $\text{min}^{0.5}$) is the rate constant for intra particle diffusion.

C (mg/g) is a constant that gives idea about the thickness of the boundary layer, i.e. the larger the value of C the greater is the boundary layer effect. If the plot of Eq. 9 yields a straight line, then the sorption process was controlled by intra-particle diffusion only and the slope gives the rate constant, $\boldsymbol{K_{id}}$. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process.

3.2 EQUILIBRIUM MODELLING

Adsorption Isotherms are the most significant tools to predict the adsorption capacity of the adsorbents and the mechanism of the adsorption. The different types of isotherms models used to explain equilibrium adsorption are as follows:

3.2.1 Langmuir adsorption isotherm

It assumes a mono-layer adsorption on homogeneous adsorbent surface with finite number of adsorption sites of equal energy [Jovanovic et al. 1991]. The linearized form of Langmuir isotherm equation is:

$$\boldsymbol{\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o}} \qquad \textbf{(10)}$$

Where,

- C_e is the equilibrium concentration of the adsorbate (mg/L),
- q_e is the amount of adsorbate per unit mass of adsorbent (mg/g),
- q_o and b are Langmuir constants related to adsorption capacity and rate of adsorption.

Also the essential characteristics of the Langmuir isotherm can be described by a separation factor R_L; which is defined by the following equation:

$$\boldsymbol{R_L = \frac{1}{1+bC_o}} \qquad \textbf{(11)}$$

Where,

- C_o is the initial concentration of adsorbate (in mg/L).

The value of separation factor R_L, indicates the isotherm's shape and the nature of the adsorption process, unfavourable for (R_L>1), linear for (R_L=1), favourable for (0 < R_L< 1) and irreversible (R_L= 0) [Hanumantharao et al. 2011].

3.2.2 Freundlich adsorption isotherm

It describes equilibrium on heterogeneous surfaces with a nonuniform distribution of heat of adsorption over the surface. The linear form of the Freundlich isotherm expression is:

$$\boldsymbol{lnq_e = lnK_F + {}^{1}\!/_{n}\, lnC_e} \qquad \textbf{(12)}$$

Where,

- K_F ((mg/g) (L/mg)$^{1/n}$) is related with adsorption capacity of the adsorbent
- n is Freundlich constant giving an indication of how favourable the adsorption process is.

The slope ($1/n$) ranging between 0 and 1 is a measure of surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for (n) below one indicates a normal Langmuir isotherm, while (n) above one is indicative of efficient adsorption [Mbadcam et al. 2009].

3.2.3 Temkin Isotherm

According to Temkin Isotherm,

- The interaction between the molecules already adsorbed and to be adsorbed is considered.
- Free energy of adsorption is a function of the surface coverage. Thus the rate of adsorption decreases as the adsorbed surface coverage increases.

Temkin isotherm is expressed as:

$$\boldsymbol{q_e = \frac{RT}{b_T}\ln(A_T C_e)} \qquad \textbf{(13)}$$

Or

$$\boldsymbol{q_e = B_1 lnA_T + B_1 lnC_e} \qquad \textbf{(14)}$$

$$\boldsymbol{B_1 = \frac{RT}{b_T}} \qquad \textbf{(15)}$$

Where,

A_T is equilibrium constant corresponding to maximum binding energy

b_T is Temkin isotherm constant

T is temperature (K)

R is ideal gas constant (8.314 J/mol K)

4. EXPERIMENTAL SET-UP AND INSTRUMENTATION

Present investigation was carried out to remove fluoride and nitrate from synthetic water samples with the objectives detailed in chapter 1. Removal of fluoride and nitrate from synthetic water using surface modified laterite soil was carried out in batch reactor. In this chapter, range of experimental parameters, analytical & auxiliary instruments used in the present study have been discussed.

4.1 BATCH STUDY

Batch study was undertaken to study the effect of individual process parameters on the removal of fluoride and nitrate for the optimization of process conditions and to extract design parameters like rate constants and isotherm constants. Considering the requirement of the sample for the analysis of fluoride and nitrate, 50 ml of the sample volume was taken for each experiment.

4.1.1 Set-up for Fluoride ions removal in batch reactor

All the experiments were conducted in batch reactor. For adsorptive removal of fluoride, the batch reactor was a sample volume of 50 ml air tight LDPE bottle. The agitation was performed in an orbital shaker incubator at 150 rpm. At a maximum, 12 batch reactors could be agitated. Range of operating parameters is given in Table 4.1.

Table 4.1 Range of operating parameters for fluoride removal

Type of experiment	Range of operating parameters					
	pH	Initial F^- conc. (mg/l)	Adsorbent dose (g/l)	Contact time (min)	Paricle size (mm)	Temp (K)
Effect of pH	3-10	10	10	180	1-1.7	303
Effect of adsorbent dose	6	10	7.5- 17.5	180	1-1.7	303
Effect of contact time	6	10	12.5	0-180	1-1.7	303
Effect of initial ion conc.	6	5-25	12.5	150	1-1.7	303

4.1.2 Set-up for Nitrate ions removal in batch reactor

All the experiments were conducted in batch reactor of sample volume of 50 ml in air tight LDPE bottles shaken at 150 rpm. Range of operating parameters is given in Table 4.2.

Table 4.2 Range of operating parameters for nitrate removal

Type of experiment	Range of operating parameters					
	pH	**Initial NO_3^- conc. (mg/l)**	**Adsorbent dose (g/l)**	**Contact time (min)**	**Paricle size (mm)**	**Temp (K)**
Effect of pH	3-10	100	20	180	1-1.7	303
Effect of adsorbent dose	5	100	5- 25	180	1-1.7	303
Effect of contact time	5	100	20	0- 180	1-1.7	303
Effect of initial ion conc.	5	100- 225	20	120	1-1.7	303

4.2 ANALYTICAL INSTRUMENTS USED IN THE PRESENT STUDY

1. Digital pH meter (CL 54+ pH meter, Toshniwal Instruments, Ajmer) with combined glass electrode was used for pH measurements, calibrated with buffer solutions.
2. Orbital shaker incubator was used for equilibration studies. (Metrex Scientific Instruments, New Delhi).
3. Hot air oven was used for heating purpose.
4. FE-SEM (FE-SEM QUANTA 200 FEG) study was conducted to observe the surface before and after the adsorption by laterite soil.
5. FT-IR Spectrophotometer (Nicolet 6700, USA) was used for spectrum analysis. Pellets of adsorbent were made with 1% KBr and 4000 to 400 cm^{-1} wavelenght was used.
6. BET (ASAP 2020 V3.05 H Micromeritics system) analysis of the soil samples was done to find out the surface area, pore size and pore volume of the sample.
7. XRD (BRUKER D8 ADVANCE) study was done to find out about the crystal

structure, chemical configuration and physical properties of the soil. It employed Cu-K_α radiation from 5^o - 90^o and data was analyzed using PANalytical X'Pert HighScore

8. ASTM test sieves were used.

5. EXPERIMENTAL PROCEDURE

In the present study laterite soil has been utilized for the adsorptive removal of fluoride and nitrate from their synthetic solutions. The preparation, activation and experimental procedure and data recording for adsorptive removal of fluoride and nitrate ions from synthetic water are discussed in this chapter. Experimental details of the study have been presented in this chapter.

5.1 ADSORBENTS AND CHEMICALS

Laterite soil was brought from the Burdwan district of West Bengal, India (GPS location: 23.5 ^{o}N, 87.5 ^{o}E). It was treated for surface modification and used as an adsorbent. All the chemicals that were used were of A.R grade and obtained from E. Merck India Limited, Mumbai, India.

5.2 PREPARATION OF ADSORBENTS

In this study surface modification of laterite soil was carried out to prepare seven types of adsorbents. The various adsorbent prepared were Thermal treated laterite (1), Acid treated (2), Base treated (3), Acid Base treated (4), $FeCl_3$ treated (5), Acid Base + $FeCl_3$ (6), Acid+$FeCl_3$ treated (7) in order to compare their fluoride and nitrate uptake ability with the raw laterite (RL).

5.2.1 Preparation of Raw laterite

Natural laterite was sun dried for two days to remove the moisture, it was then grinded and rinsed with tap water until the lightly attached fragments were removed and the wash water showed no color. After drying, the particles were sieved through various mesh sizes. Particle sizes in the range of 1-1.7 mm were selected. Screened material was then stored in a covered beaker. This was then used as an adsorbent. [Maji et al. 2007]

5.2.2 Preparation of treated laterite

1. Thermal treatment of laterite

100 gm of raw laterite was washed with distilled water and was kept in the furnace at 423 for overnight ie 12 hrs to evaporate all the water present.

2. Acid treatment

10 gm of thermal treated laterite was added to 40 ml of 6N HCl and the mixture was heated to 333 K for 3 hours with continuous stirring at 60 rpm. The mixture was filtered using Wattman filter paper and the filtrate was discarded and residue was kept in oven to dry at 110°C. [Maiti et al. 2010]

3. Base treatment

10 gm thermal treated laterite was added to 40 ml of distilled water and the final pH of the mixture was set to 12 by addition of 1 N NaOH. Mixture was heated to 333 K for 3 hours with continuous stirring at 60 rpm. The mixture was then filtered using Wattman filter paper and the filtrate was discarded and residue was kept in oven to dry at 110°C.

4. Acid base treatment

For the acid treatment, 50 grams of raw laterite (RL) was weighed and a 200 ml of 6N HCl solution (prepared from HCl 35.5 % w/v) was added to it. The mixture was heated at 343 K for 3 hours. The liquid part mostly containing Fe, Al and silicate ions was distilled under to recover 60% free acid as distillate. After that 200 ml distilled water was added to the solid portion remained and 4N NaOH solution (prepared using NaOH pellets of A.R grade) was added to it at room temperature under constant stirring and the final pH of the mixture was adjusted to 6.5. The mixture was kept undisturbed for 24 hours and the clear liquid was decanted from the top and the mixture was again washed with water and filtered by Wattman filter paper and the filtrate was discarded and the residue, i.e. solid mass was kept in oven to dry at 383 K. The dried mass was the acid base treated laterite **(TL)** [Maiti et al. 2010].

5. $FeCl_3$ impregnation

10 gm of thermal treated laterite was treated with 100 ml of ferric chloride solution which contains about 2.5% Fe^{+3} ions. The final pH set to 12 by addition of 1N NaOH. The solution was heated in water bath to evaporate all the water present in the solution. After that it was dried at 383 K for 24 hrs and then washed with distilled water. Washing was done to make liquid free from iron. [Mondal et al. 2008]

6. $FeCl_3$ impregnation of acid base treated laterite

10 gm on acid base treated laterite was treated with 100 ml of ferric chloride solution which contains about 2.5% Fe^{+3} ions. The final pH set to 12 by addition of 1N NaOH. The solution was heated in water bath to evaporate all the water present in the solution. After that it was dried at 383 K for 24 hrs and then washed with distilled water. Washing was done to make liquid free from iron.

7. $FeCl_3$ impregnation of acid treated laterite

10 gm on acid base laterite was treated with 100 ml of ferric chloride solution which contains about 2.5% Fe^{+3} ions. The final pH set to 12 by addition of 1N NaOH. The solution was heated in water bath to evaporate all the water present in the solution. After that it was dried at 110^{o}C for 24 hrs and then washed with distilled water. Washing was done to make liquid free from iron.

Fig. 4.1 to 4.7 show the different types of adsorbents prepared.

Fig. 5.1 Thermal treated laterite

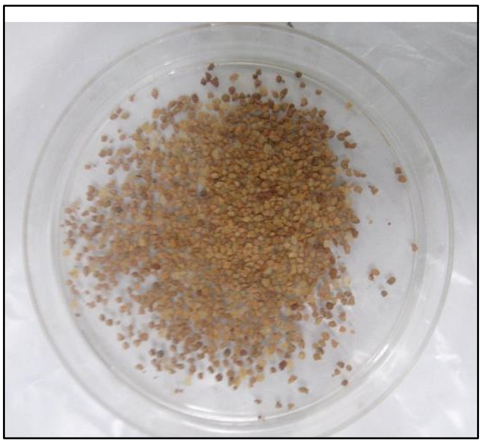


Fig. 5.2 acid treated laterite

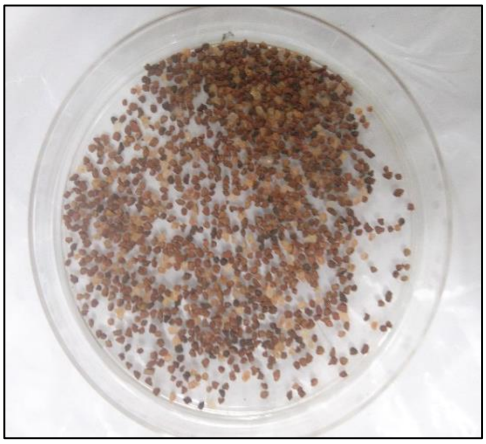


Fig. 5.3 Base treated laterite

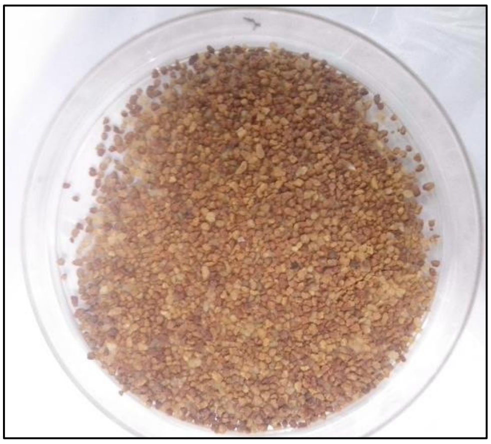


Fig. 5.4 Acid Base treated laterite

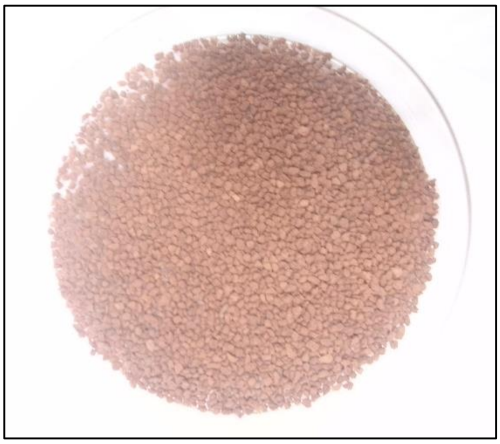


Fig. 5.5 $FeCl_3$ treated laterite

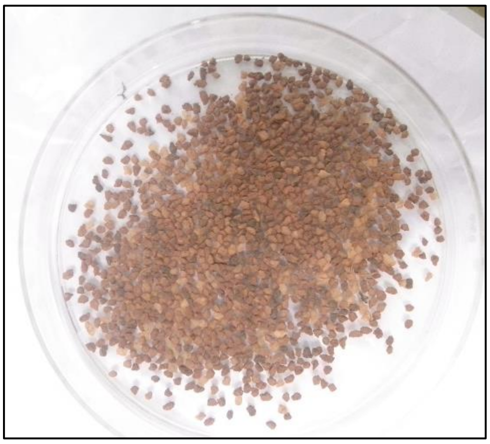


Fig. 5.6 Acid base $FeCl_3$ treated laterite

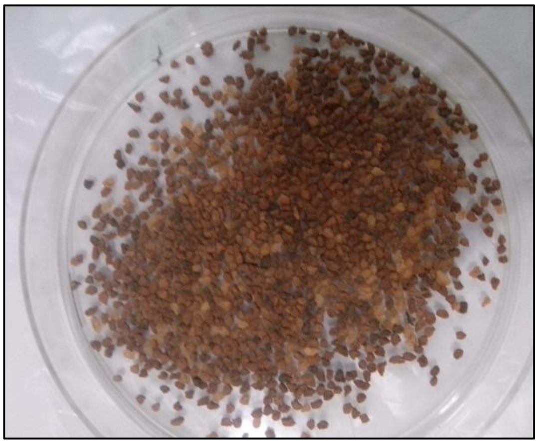


Fig. 5.7 Acid $FeCl_3$ treated laterite

5.3 PREPARATION OF THE SYNTHETIC SOLUTION

All reagents used in this study were of analytical grade (A.R.) and distilled water was used for dilution purposes.

1. **Synthetic fluoride solution** was prepared using Sodium Fluoride (molecular weight 41.99 g/mol). One liter of the NaF solution was prepared by adding 1 gram of NaF to 1000 ml distilled water and it was used as the stock solution and appropriate dilutions were done to prepare fluoride solutions of different concentration.
2. **Stock nitrate solution**: dissolve 163.08 mg anhydrous potassium nitrate and dilute to 1000ml with distilled water making a solution of 100 ppm and dilutions made thereafter for different nitrate concentrations.

5.4 ANALYTICAL METHODS

5.4.1 SPADNS method for fluoride determination:

The SPADNS calorimetric method was used for the analytical measurement of the fluoride sample .It utilizes the reaction between zirconium dye and the fluoride. Fluoride reacts with the dye and forms a colourless complex anion (ZrF_6^-). As the amount of fluoride increases the, the intensity of the colour so produced decreases.

1. **SPADNS solution:** About 958 mg of the SPADNS, sodium 2-(parasulfophenylazo)-1, 8- dihydroxy-3, 6-napthalene disulfonate, was dissolved in 500 ml of distilled water. Thi s solution is stable for one year if kept in shade i.e protected from direct sunlight.
2. **Zirconyl acid reagent:** About 133 mg of Zirconyl chloride octahydrate $ZrOCl_2.8H_2O$ was weighed. It was dissolved in 25 ml of distilled water, 350 ml of concentrated HCl (9.7 N) was added to the solution. The final mixture was diluted with distilled water and the volume was made upto 500 mL.
3. **Acid zirconyl-SPADNS reagent:** Equal volumes of SPADNS solution and Zirconyl-acid-reagent were taken and then mixed. The combined reagent so formed so formed is stable for at least 2 years.
4. **Reference solution:** The reference solution was made by adding 10 ml of SPADNS solution to 100 ml of distilled water .And the 7 ml of concentrated HCl (9.7 N) diluted to 10 ml was added to the diluted SPANS solution .The reference solution is stable for one year. It is used for setting the instrument reference point or zero point.

5. **Preparation of the standard curve:** Fluoride solutions of different concentration like 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 mg F^-/L were prepared by diluting suitable quantities of standard fluoride solution to 50 ml with distilled water. And then add 10 ml of mixed acid-zirconyl SPADNS reagent .The mixture was then added to each of the solution earlier prepared and mixed well. The reference solution was used to set the instrument i.e. UV Spectrophotometer to zero absorbance .The absorbance readings of the standards were used to plot a graph between the concentration of fluoride in milligrams and absorbance with λ_{max} as 575 nm .The calibration curve is shown in Figure 5.8

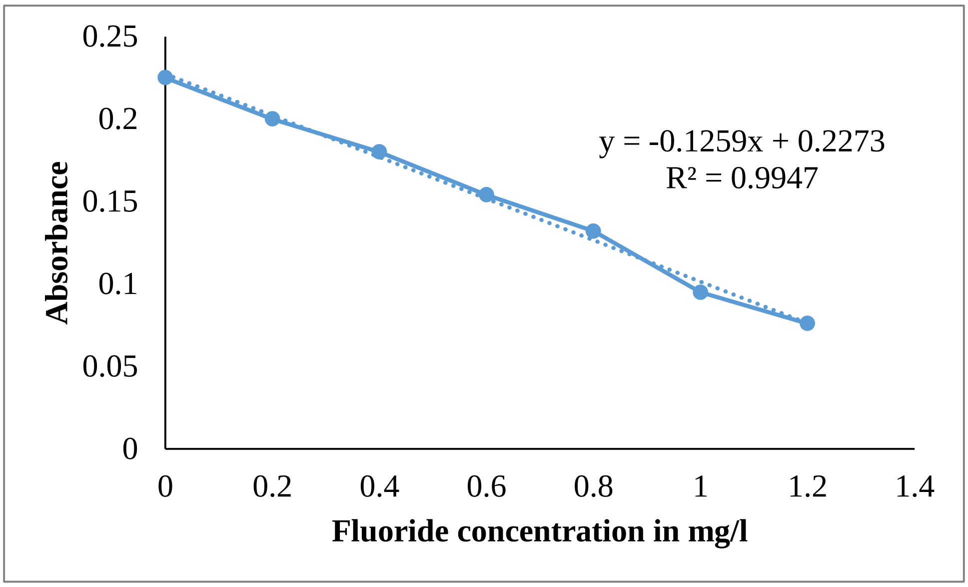


Fig. 5.8 Calibration curve between absorbance and concentration of fluoride

5.4.2 UV spectrophotometer method for Determination of nitrate (NO_3^-):

This method is beneficial for the water free from organic impurities. Ultraviolet absorption measurement at 220 nm allows determination of nitrate. The nitrate calibration curve follows Beer's law upto 44.3 mg/L NO_3^-.

1. **Calibration:** Prepare nitrate calibration standards of 0 to 25 ppm NO_3^- by diluting of the standard nitrate stock solution to 50 mL.

2. **Procedure:** Read the absorbance against redistilled water set at zero absorbance. At a wavelength of 220 nm, obtain the nitrate absorbance reading

and, if needed, at a wavelength of 275 nm to get interference because of dissolved organic matter.

3. **Calculation:** For correction for dissolved organic matter, subtract 2 times the absorbance reading at 275 nm from the reading at 220 nm to obtain the correct absorbance due to NO_3^-. Convert this absorbance value into equivalent concentration from standard calibration curve shown in Figure 5.2.

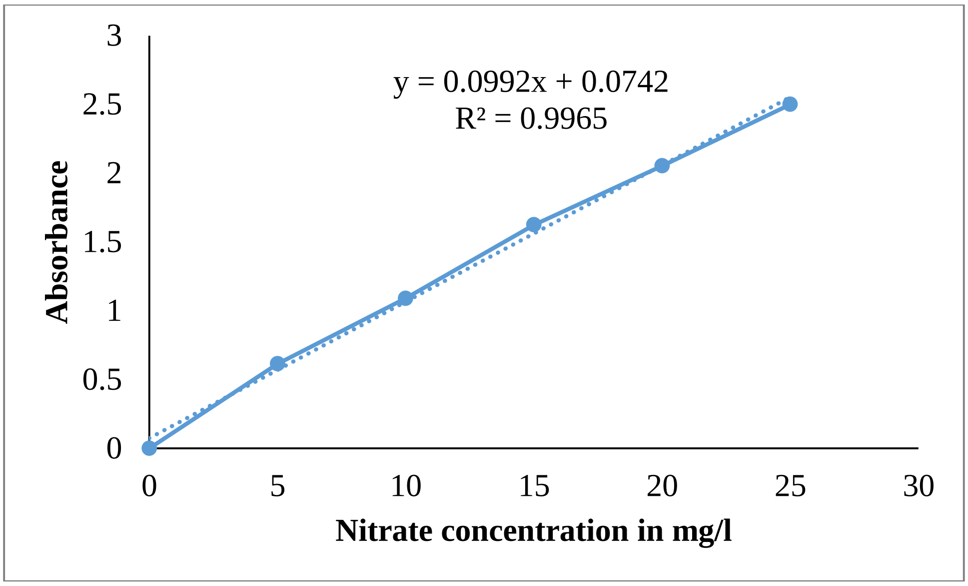


Fig 5.9 Calibration curve between absorbance and concentration of nitrate

5.5 Experimental procedure

For adsorption of fluoride:

Initially a preliminary adsorption run was carried out for all the seven adsorbents prepared; in a batch process under equilibrium conditions taken from literature to test which out of the seven adsorbents showed maximum removal capacity. The particle size was taken in the range of 1-1.7 mm and the adsorption was carried out using an adsorbent dose of 10 g/l; rpm of 150 and the temperature was set at 303 K and at pH 6. The contact time was set at 3 hr and the ions to be adsorbed were fluoride whose concentration was taken as 10 ppm. Fluoride solution was put in different LDPE bottles along with the adsorbent having a dose of 10 g/l. After the selection of best adsorbent, effects of process parameters were studied and data was generated for kinetic and equilibrium modelling.

For adsorption of nitrate:

Batch experiments were performed so as to study the effect of parameters like pH, adsorbent dose (m), initial nitrate concentration (C_o) and time (t). The adsorbent used was acid-base treated laterite (TL). The adsorption experiment was done by agitating known amount of adsorbent with 50 ml of nitrate solution of desired concentration and pH at 150 rpm, 303 K in an orbital shaker incubator. The pH of the solution was adjusted by adding either 0.1 N HCl or 0.1 N NaOH. Samples were tested at appropriate time intervals and analyzed for the residual nitrate concentration by UV spectrophotometer. The reaction was carried till nitrate-laterite system attained equilibrium. The equilibrium data so obtained was used for the generation of adsorption isotherms and for the determination of kinetics of the process.

6. RESULTS AND DISCUSSION

This chapter covers the discussion and interpretation of results of the present investigations. Studies embodied in this chapter have been divided into four sections as stated below:

Section 6.1 Adsorbents capacity comparisons

Section 6.2 Characterization of the adsorbents

Section 6.3 Adsorptive removal of fluoride from synthetic water

Section 6.4 Adsorptive removal of nitrate from synthetic water

6.1 COMPARISON OF ADSORBENTS FOR FLUORIDE REMOVAL CAPACITY

Raw Laterite soil (RL) is selected by conducting literature review for its low cost and high efficiency for adsorptive removal of fluoride from synthetic water. Afterwards it is activated by seven different methods. For an initial fluoride concentration of 10 mg/l at pH 6, the seven adsorbents prepared are investigated for their removal efficiency of fluoride in batch mode. At 10 g/l adsorbent dose, the reaction is carried out at 303 K with continuous stirring at 150 rpm for 180 min. Figure 6.1 shows the comparative study.

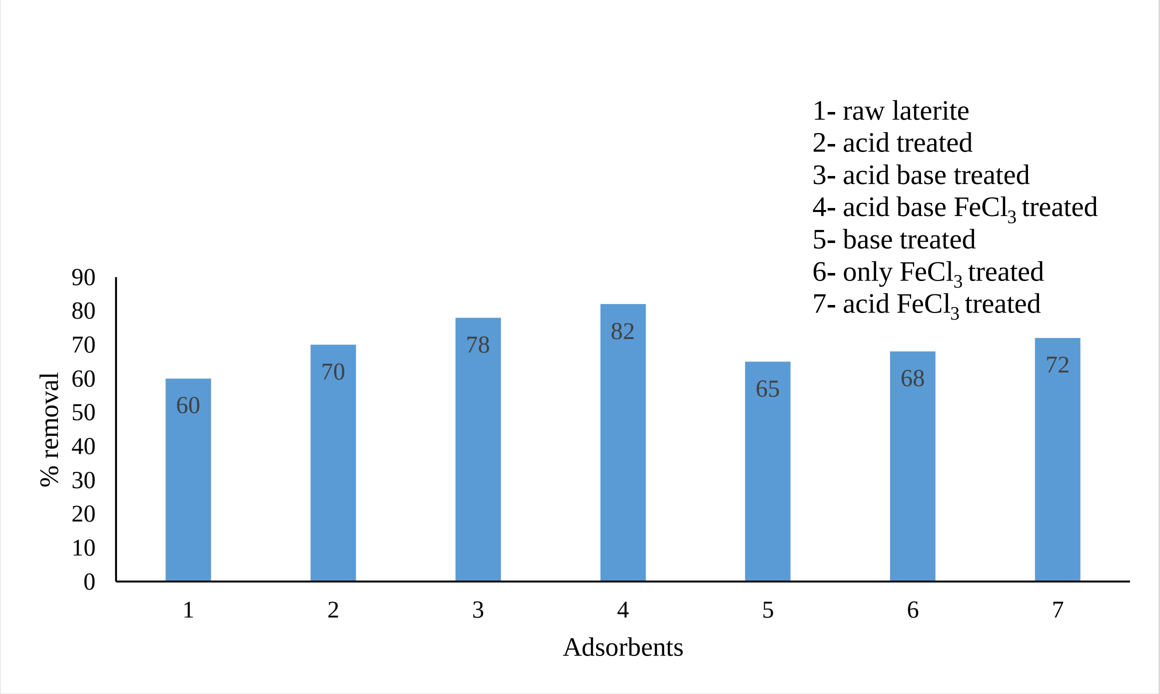


Figure 6.1 comparison of different adsorbents for the fluoride removal efficiency

The adsorbent that is good at adsorbing F^- is acid base $FeCl_3$ treated laterite with 82% removal of fluoride. And next is acid base treated laterite with 78% removal of fluoride. And therefore acid base treated laterite is chosen because its process is more feasible than acid base $FeCl_3$ treated laterite. After selecting acid base treated laterite as adsorbent, various optimization studies of adsorbent dose, contact time, pH, and initial concentration of F^- are studied.

6.2 CHARACTERIZATION OF THE ACID BASE TREATED LATERITE SOIL

Characterization includes bulk density, BET surface area, XRD, FTIR, FESEM, EDAX.

6.2.1 BULK DENSITY

The bulk density of the acid base treated laterite was found to be 1.352 kg/m^3

6.2.2 BET SURFACE AREA

The BET surface area of the raw laterite (RL) and acid-base treated laterite (TL) is given in the Table 6.1. It was observed that BET surface was 19.07 m^2/g for raw laterite and 36.70 m^2/g for acid base treated laterite. Increase in surface area indicates the loading of iron/aluminium oxyhroxide on the laterite surface. [Maiti et al. 2010]

Table 6.1 BET surface area values and pore volume values for raw and treated laterite

Parameter	RL	TL
Surface area (m^2/g)	19.07	36.70
Total pore volume (cm^3/g)	0.0096	0.047

6.2.3 XRD PATTERN

Figure 6.2 gives XRD data for TL before adsorption. The corresponding peaks of Fe_2O_3 are at $2\theta = 26, 67$. FeO is found to be at $2\theta = 36$, and FeO(OH) at $2\theta = 26, 63$. Al_2O_3 at $2\theta = 39, 61, 73$. Other peaks at $2\theta = 21, 49, 59, 73, 75, 79$ and 84 corresponds to SiO_2. Similar results were obtained by Maiti et al. 2010.

After adsorption XRD pattern in Figure 6.3 shows the decrease in intensity of peaks of oxides of Al, Fe and Si indicating the formation of aluminium nitride and iron nitride.

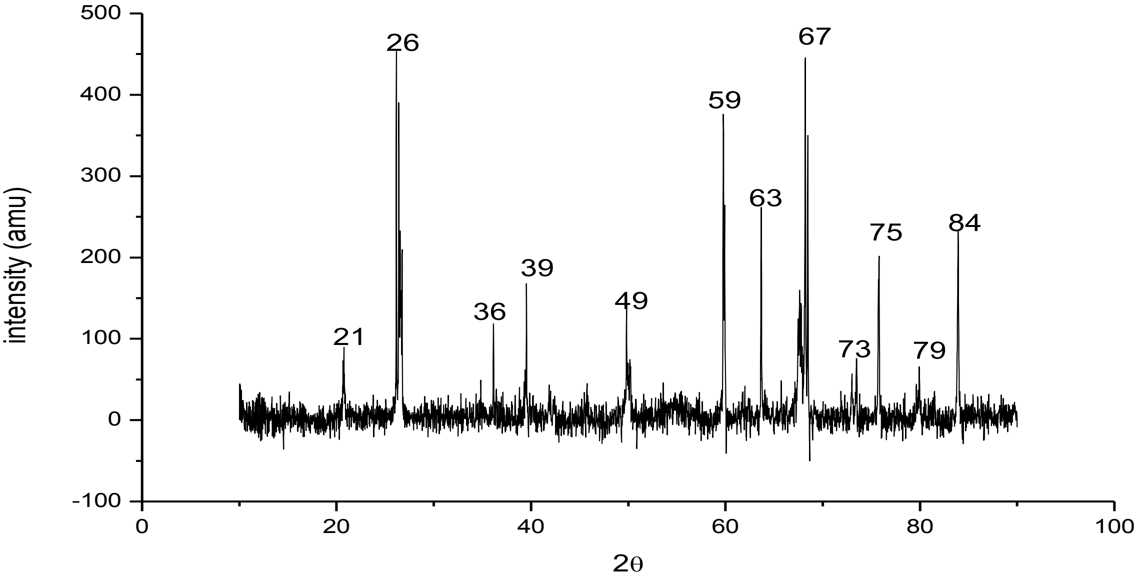


Figure 6.2 Powdered X-ray diffraction of TL before adsorption

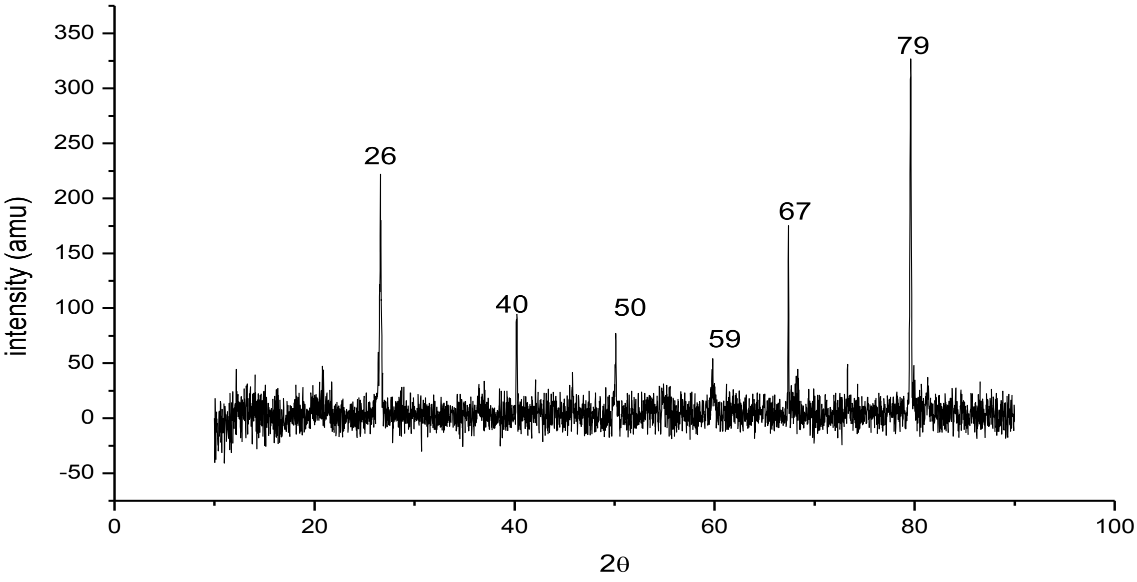


Figure 6.3 Powdered X-ray diffraction of TL after nitrate adsorption

6.2.4 FESEM

Figure 6.4 and Figure 6.5 show the FESEM (Field Emission Scanning Electron Microscopy) micrographs of RL and TL respectively, before adsorption. Figure 6.6 and Figure 6.7 show FESEM of TL after fluoride adsorption and after nitrate adsorption respectively. Surface morphology changes before and after the adsorption process confirming the sorption of fluoride and nitrate onto TL.

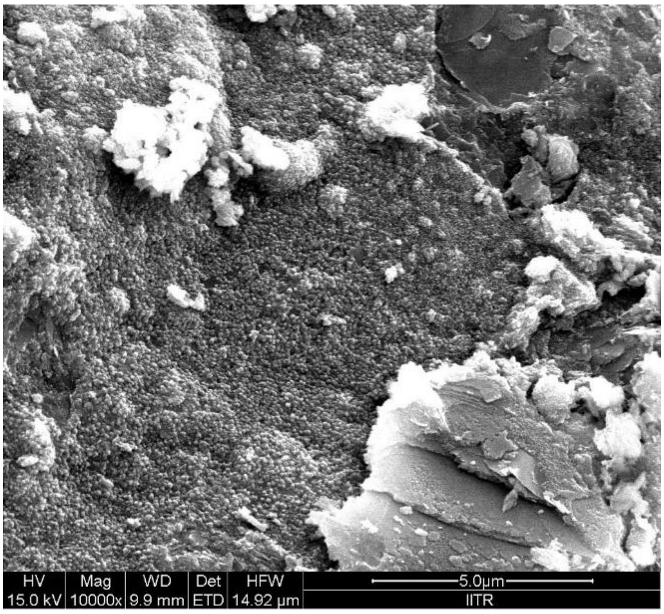


Figure 6.4 FESEM image of RL before adsorption

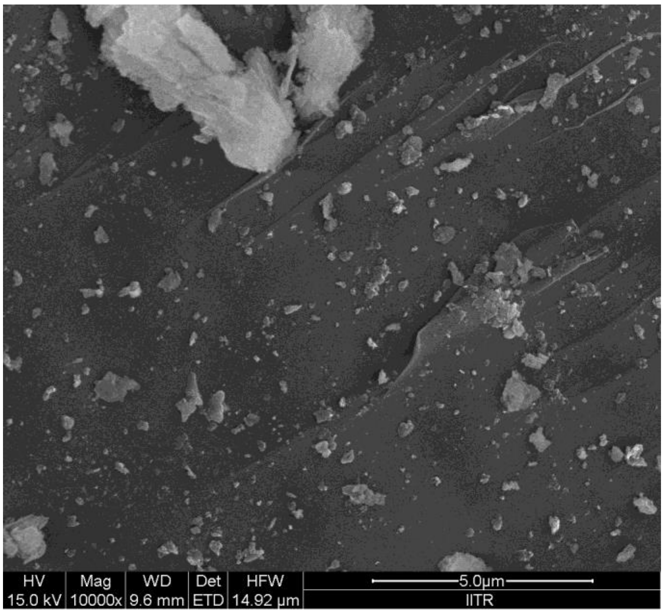


Figure 6.5 FESEM image of TL before adsorption

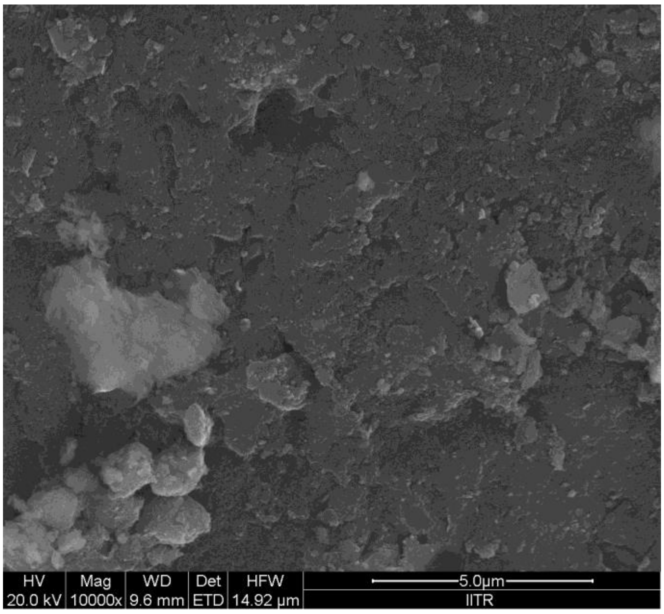


Figure 6.6 FESEM image of TL after fluoride adsorption

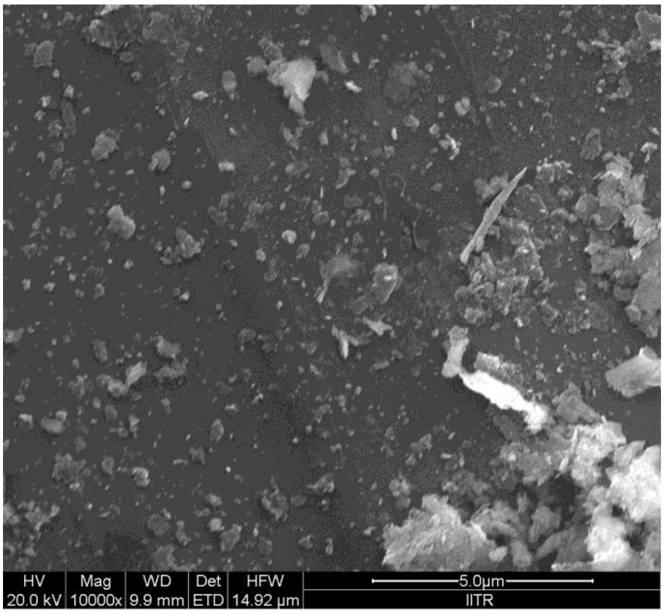


Figure 6.7 FESEM image of TL after nitrate adsorption

6.2.5 EDAX ANALYSIS

EDAX data of RL and TL (before and after adsorption) is shown in Table 6.2. It clearly shows that fluoride and nitrate has been adsorbed on the surface of TL. Also, the EDAX spectra confirms the presence of nitrogen and fluorine on the surface of TL after adsorption process.

Table 6.2 EDX data

Adsorbent	**Weight %**						
	C	**O**	**Al**	**Si**	**Fe**	**N**	**F**
RL	6.27	42.70	6.43	14.72	28.89	-	-
TL (before)	2.72	24.58	6.77	12.54	53.38	-	-
TL(after) fluoride adsorption	4.63	48.19	0.68	36.54	6.83	-	3.14
TL(after) nitrate adsorption	15.45	42.37	19.93	15.38	13.22	3.65	-

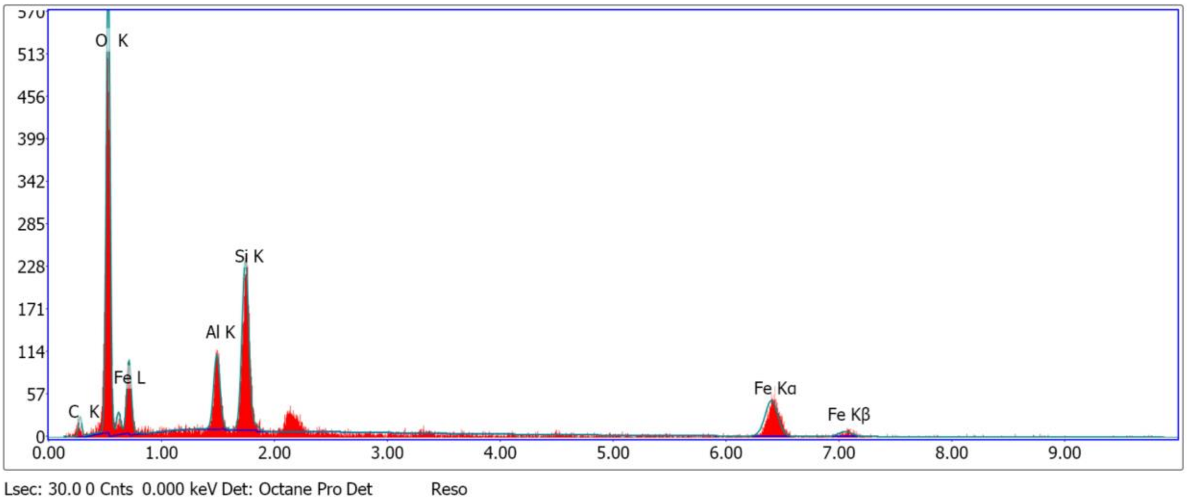


Figure 6.8 EDAX spectra for RL before adsorption

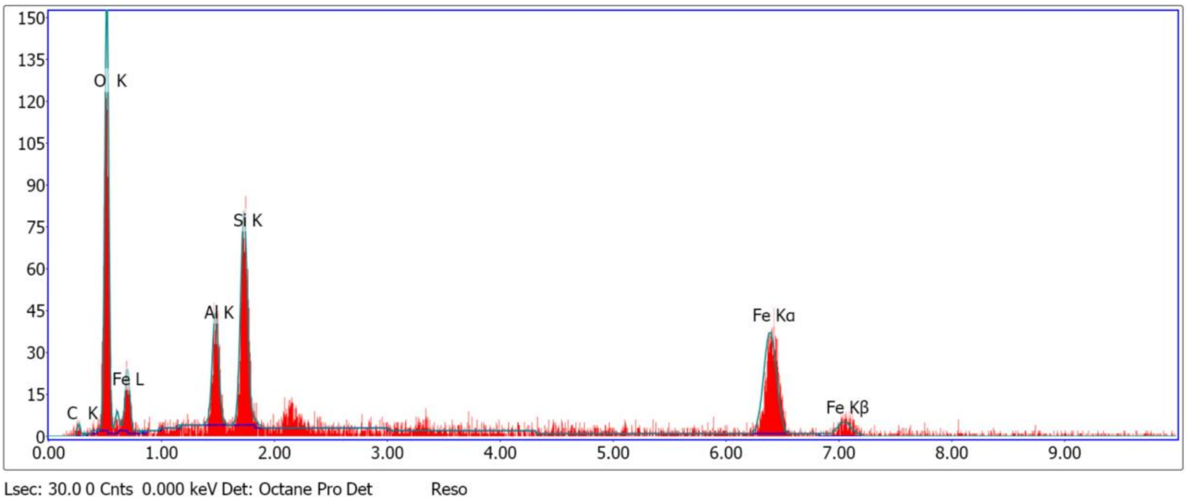


Figure 6.9 EDAX spectra for TL before adsorption

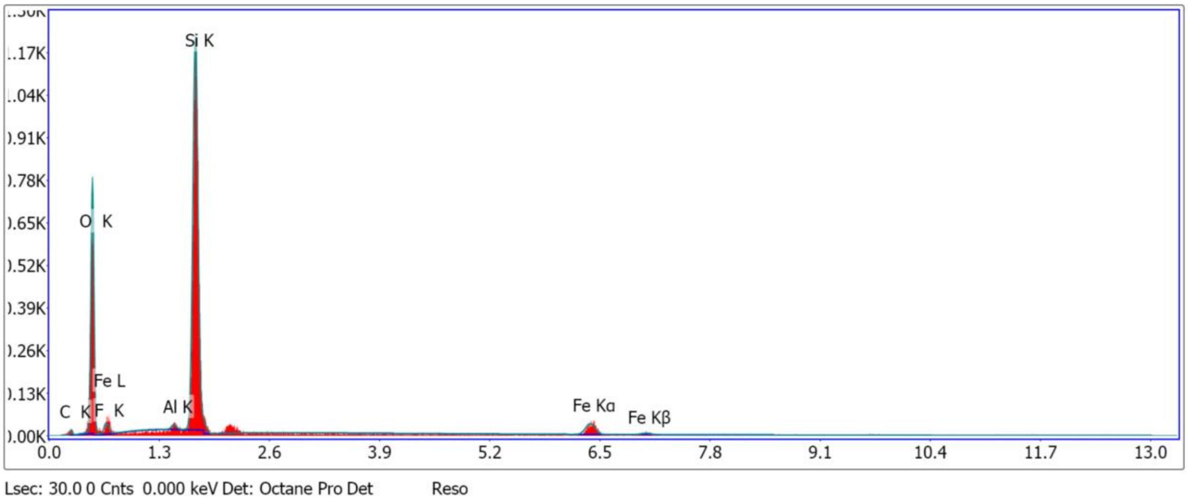


Figure 6.10 EDAX spectra for TL after fluoride adsorption

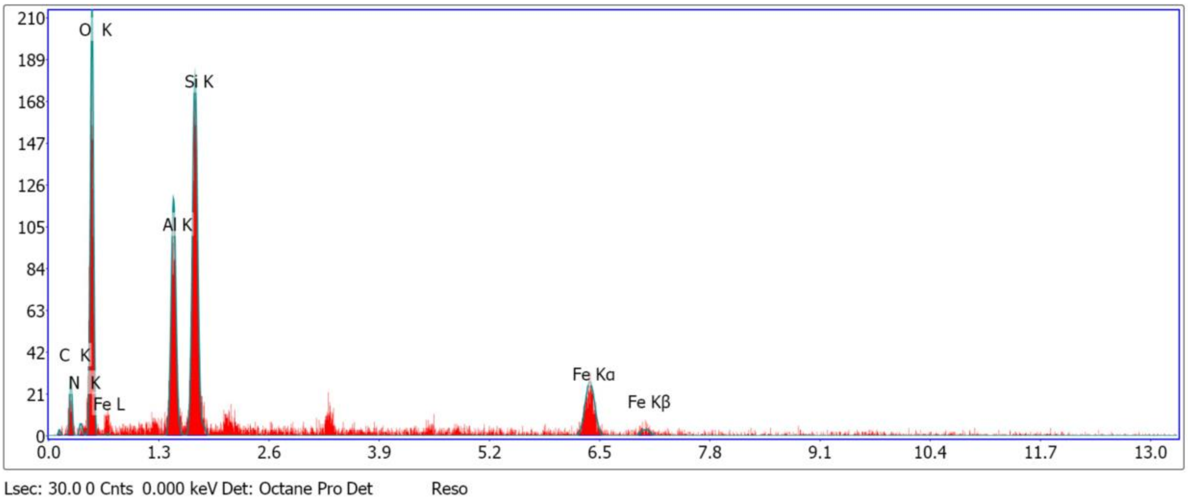


Figure 6.11 EDAX spectra for TL after nitrate adsorption

6.2.6 FTIR Study

Figure 6.12 represents FTIR spectra of TL before adsorption. The presence of iron, aluminium and silica oxides or hydroxides gets confirmed by studying these patterns. The adsorption within the range of 3696 to 3395 cm^{-1} attributes to OH group of Fe, Al, Si minerals. A peak at 1626 cm^{-1} is assigned to water molecules adsorbed on the surface of laterite. The Si-O bonds are strongly evident by very strong adsorption band at 1032 cm^{-1}. The Fe-O bond stretching at 534 and 466 cm^{-1} is highly intensified. The band at 790 cm^{-1} is attributed to cristobalite. At 914 cm^{-1}, band indicates Al-OH bond and 689 cm^{-1} Al-O bond. Similar result was reported by Maiti et al. 2010, Maiti et al. 2011, Wasse et al. 2014.

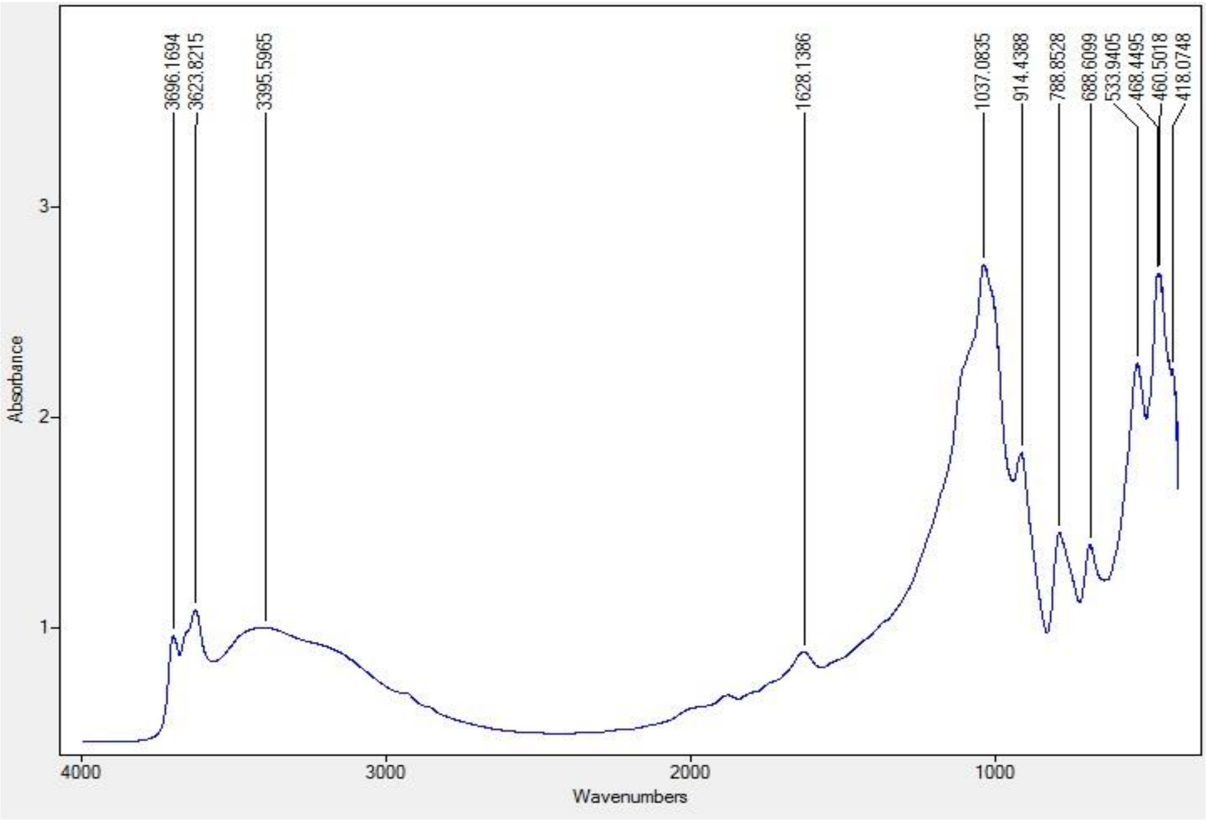


Figure 6.12 FTIR spectra of TL before adsorption

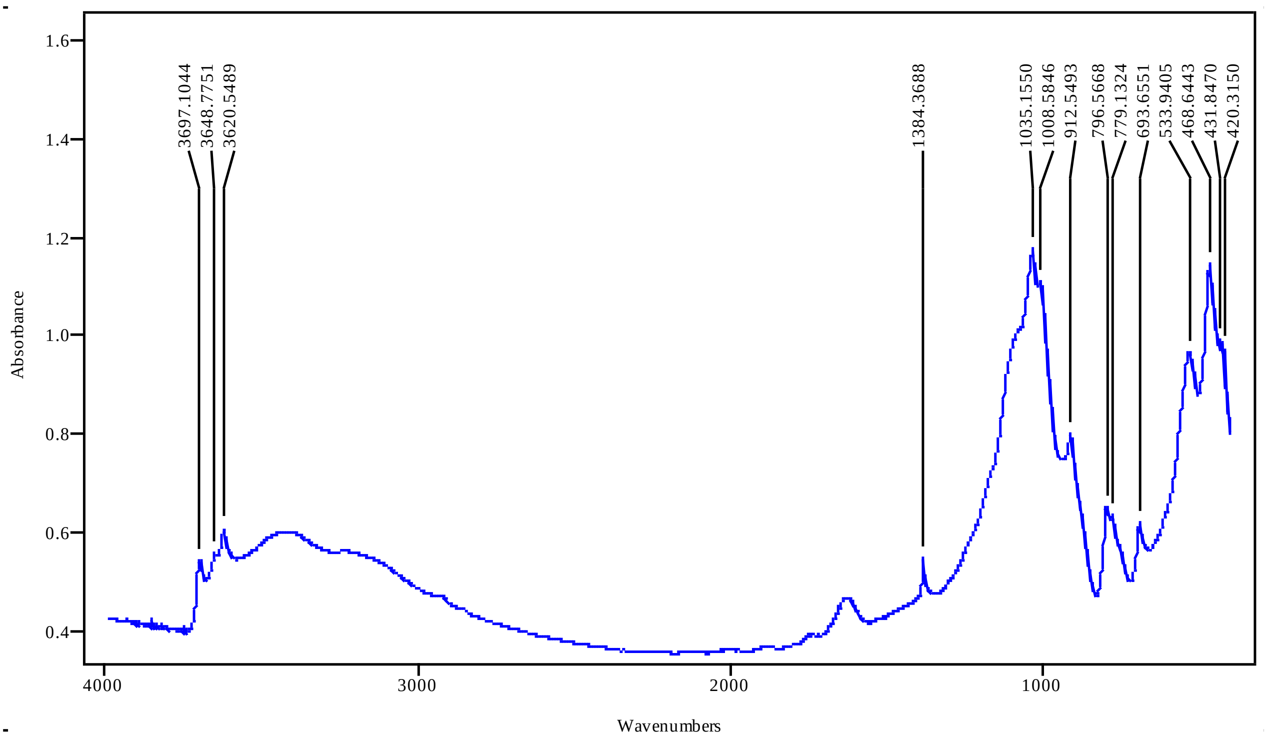


Figure 6.13 FTIR spectra of RL before adsorption

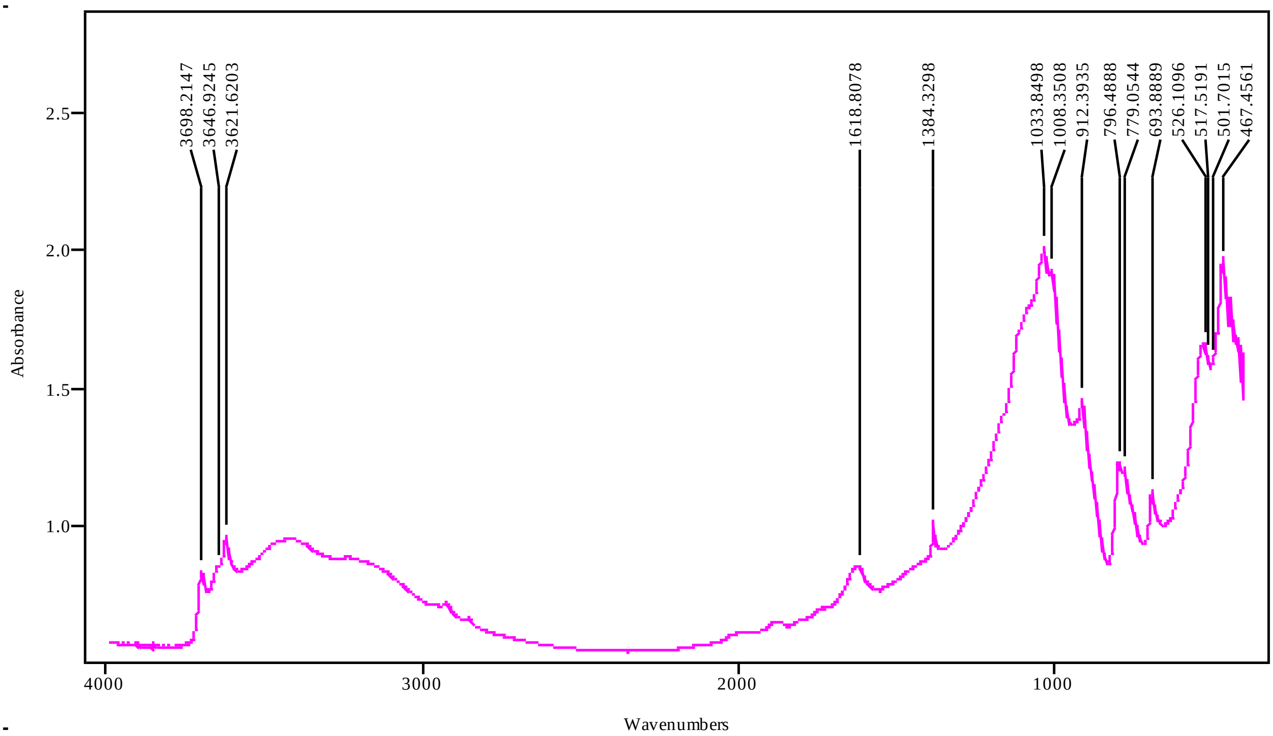


Figure 6.14 FTIR spectra of TL after fluoride adsorption

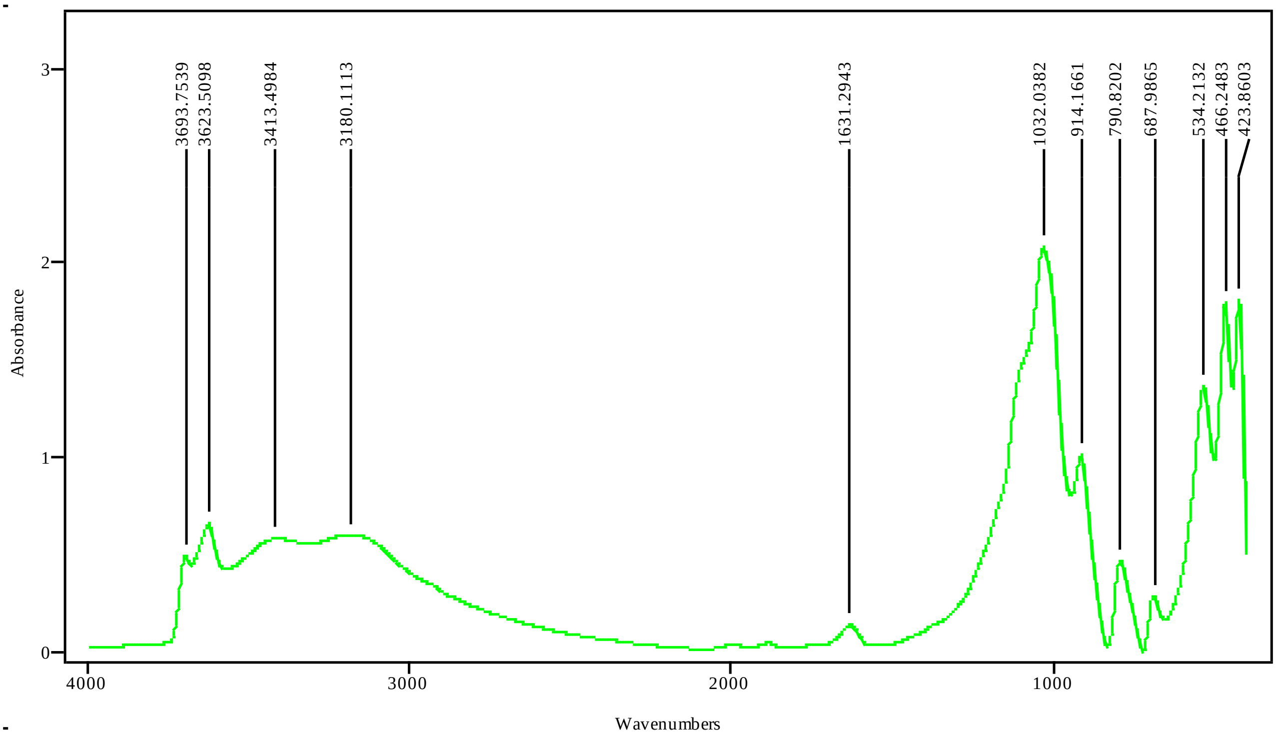


Figure 6.15 FTIR spectra of TL after nitrate adsorption

6.3 ADSORPTIVE REMOVAL OF FLUORIDE FROM SYNTHETIC WATER

Batch studies were performed to optimize various parameters for the removal of fluoride from aqueous solutions.

6.3.1 Effect of pH

Effect of pH on percentage removal of fluoride by TL is shown in Figure 6.16. Fluoride uptake increases with increase in pH upto 6, there being 78% removal and then decreases to 15% removal at pH 10. The decrease of fluoride uptake at pH greater than 7.0 is perhaps due to the electrostatic repulsion of F^- ion to the negative charge of surface and opposition for active sites by excessive amount of OH^- ions [Nigussie et al. 2007].

The specific adsorption of anion on metal oxyhydroxide surface sites occurs by following ligand-exchange reaction:

$$MOH \quad + \quad F^- \quad \leftrightarrow \quad SF^- + H_2O$$

$$MOH_2^+ \quad + \quad F^- \quad \leftrightarrow \quad MF^- + H_2O$$

Where, M stands for Fe, Al, Si.

Hence, an optimum pH of 6.0 was maintained for further studies.

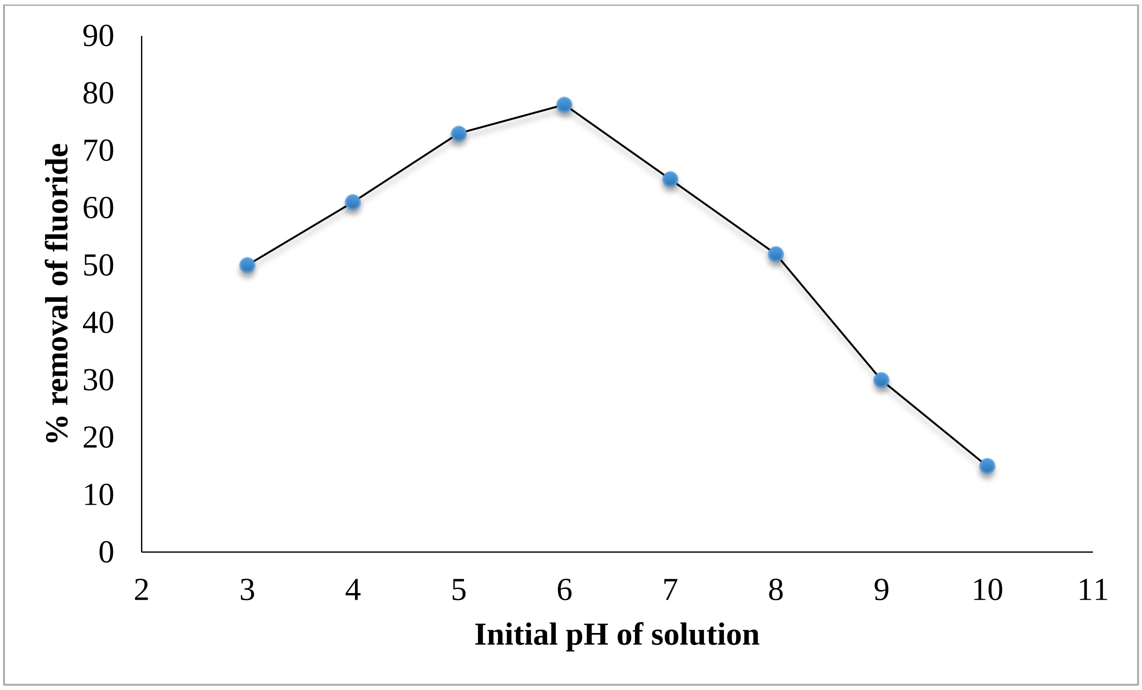


Figure 6.16 Effect of initial pH on adsorption of fluoride by TL

6.3.2 Effect of adsorbent dose

Effect of adsorbent dose on percentage removal of fluoride by TL is shown in Figure 6.17. The increase in sorption capacity with increase in adsorbent dose is apparent, because any adsorption process depends on number of active sites. Increasing the adsorbent dose increases the available binding sites. In the present study, percentage fluoride removal increases with increase in the adsorbent dose and for maximum removal of 86 % of fluoride the minimum adsorbent dose required was found to be 12.5 g/l. But no noteworthy change was observed beyond this dose.

Hence, sorbent dosage was optimized to be 12.5 g/l

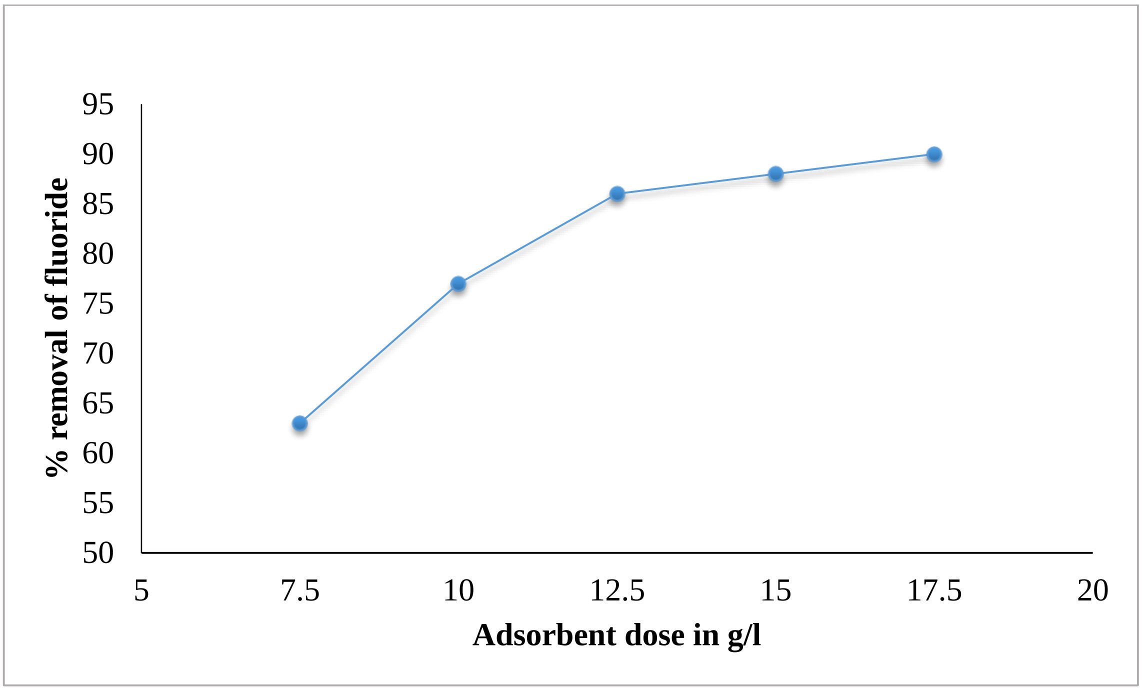


Figure 6.17 Effect of adsorbent dose on adsorption of fluoride by TL

6.3.3 Effect of contact time

Figure 6.18 shows the effect of contact time on percentage removal of fluoride. It is found that the removal of fluoride ion increases with increase in contact time. The rate of increment in percentage removal of fluoride is appreciably fast in the initial stage, i.e. from 0 to 30 min. at the beginning of the experiment the number of available sites of adsorbent as well as the concentration of fluoride in the solution is maximum. Thus the driving force for adsorption is maximum. Hence, at initial stage percentage removal increases very fast but after some time it slowly approaches a constant value (86% removal), representing accomplishment of equilibrium. Additional increase in contact time does not increase uptake owing to deposition of fluoride ions on the offered adsorption sites on adsorbent surface. As there is no significant increase in percentage of fluoride removal after 150 min, it is concluded that an equilibration time of 150 min is sufficient for batch experiments.

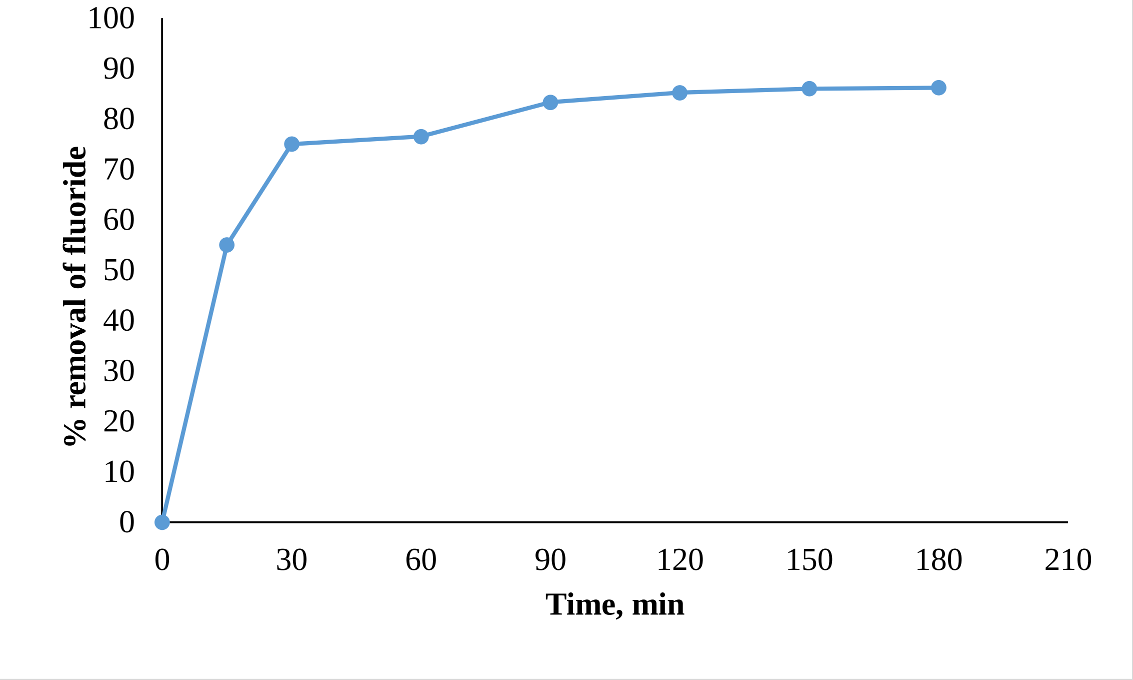


Figure 6.18 Effect of contact time on adsorption of fluoride by TL

6.3.4 Effect of initial fluoride concentration C_o

The figure 6.19 shows effect of initial fluoride concentration on percentage removal by TL. Percentage removal decreases gradually from 88% to 70% as the fluoride concentration is increased from 5 to 25 mg/l. As the fluoride concentration increases, the percentage removal decreases as less sorption sites are available for adsorption of fluoride on laterite and the already adsorbed fluoride ions also hinder the adsorption of new fluoride ions on the laterite surface.

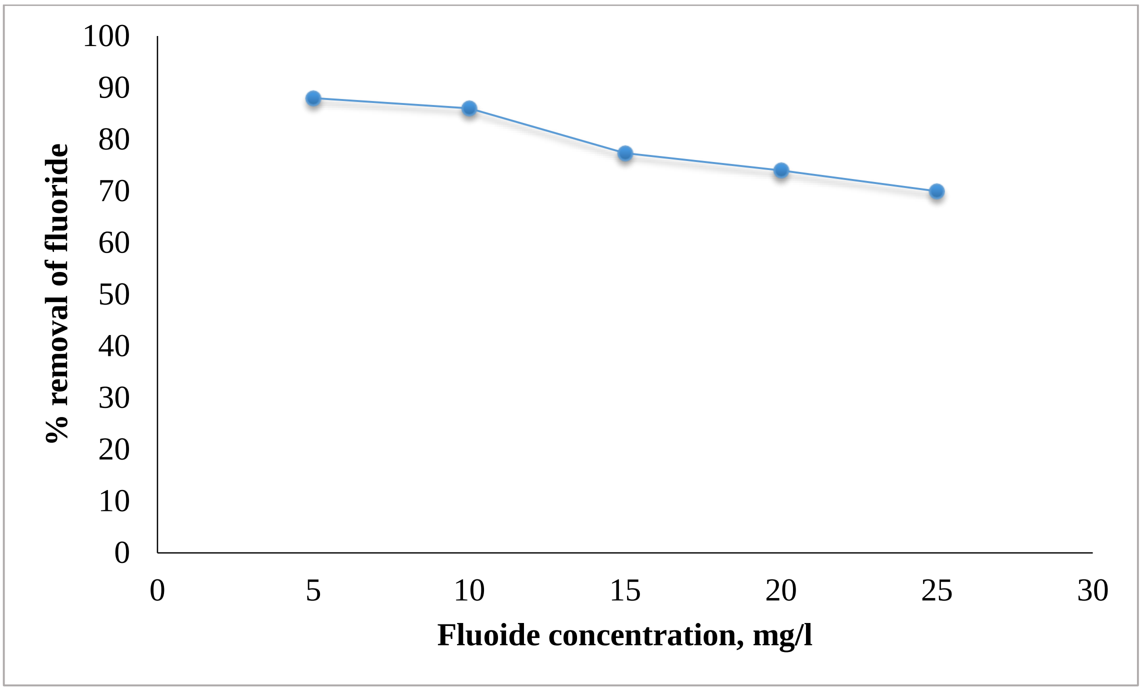


Figure 6.19 Effect of initial fluoride dose on adsorption of fluoride TL

6.3.5 Kinetic Modelling

Figure 6.20 and 6.21 show the plot for pseudo-first-order and pseudo-second-order kinetics respectively, for fluoride adsorption.

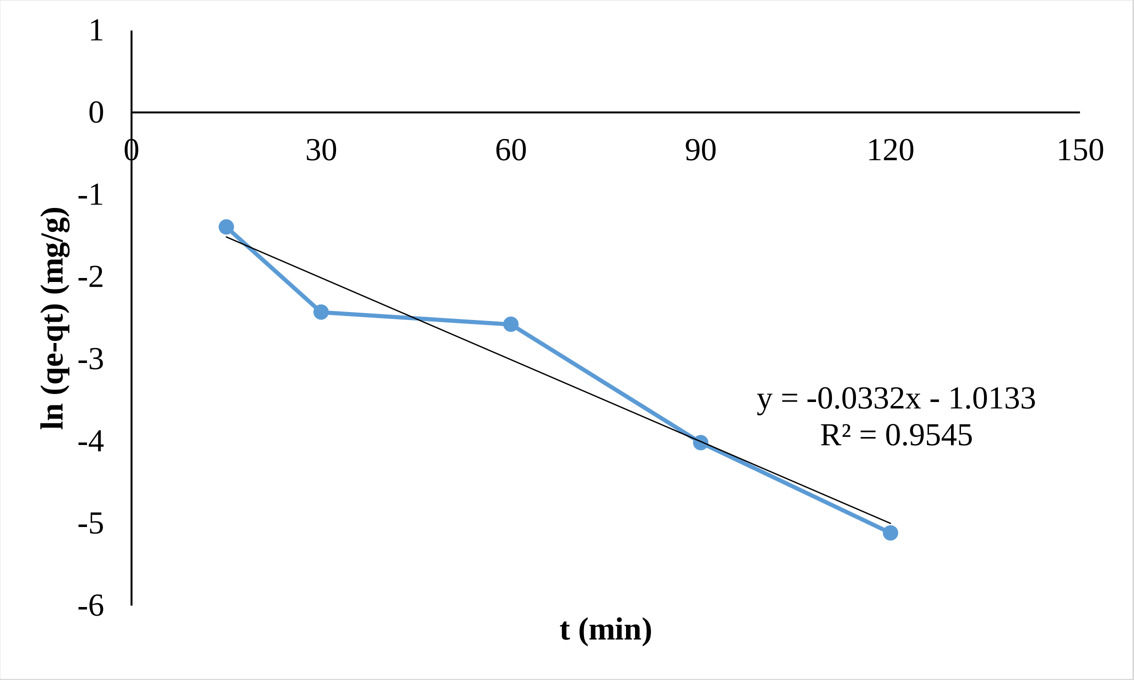


Figure 6.20 Plot for first order kinetics model for fluoride adsorption

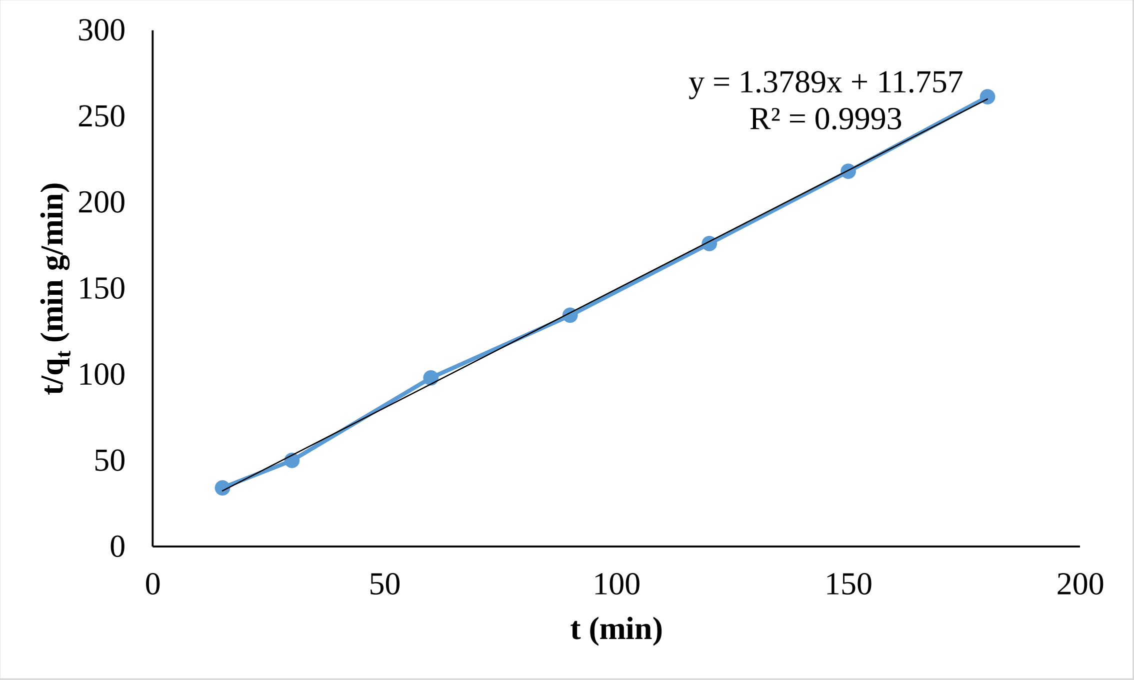


Figure 6.21 Plot for second order kinetics model for fluoride adsorption

The values of kinetics parameters are shown in Table 6.3. It was found that for first order plot, calculated q_e does not agree with experimental q_e showing an error of 47.4 %. This suggests that adsorption process does not follow first order kinetics [Aksu et al. 2000]. Whereas for second order plot, calculated q_e matches with experimental q_e with an error of 5.8 % and correlation coefficient, R^2 value for second order kinetic plot is more closer to unity. These results indicate that adsorption system belongs to second order kinetic model.

Table 6.3 Comparison of first and second order adsorption rate constants and experimental q_e and calculated values for fluoride adsorption

q_e (exp) (mg/g)	First order kinetics			Second order kinetics		
	k_1 (1/min)	q_e (cal) (mg/g)	R^2	k_2 (gm/mg/min)	q_e (cal) (mg/g)	R^2
0.69	0.332	0.363	0.954	0.162	0.73	0.9993

Figure 6.21 shows the Webber and Morris plot for fluoride adsorption on TL. It does not yield a straight line and exibit multi-linear points, that means intra-particle diffusion is not only the rate controlling step. Both the surface adsorption and intra-particle diffusion contribute to the rate determining step.

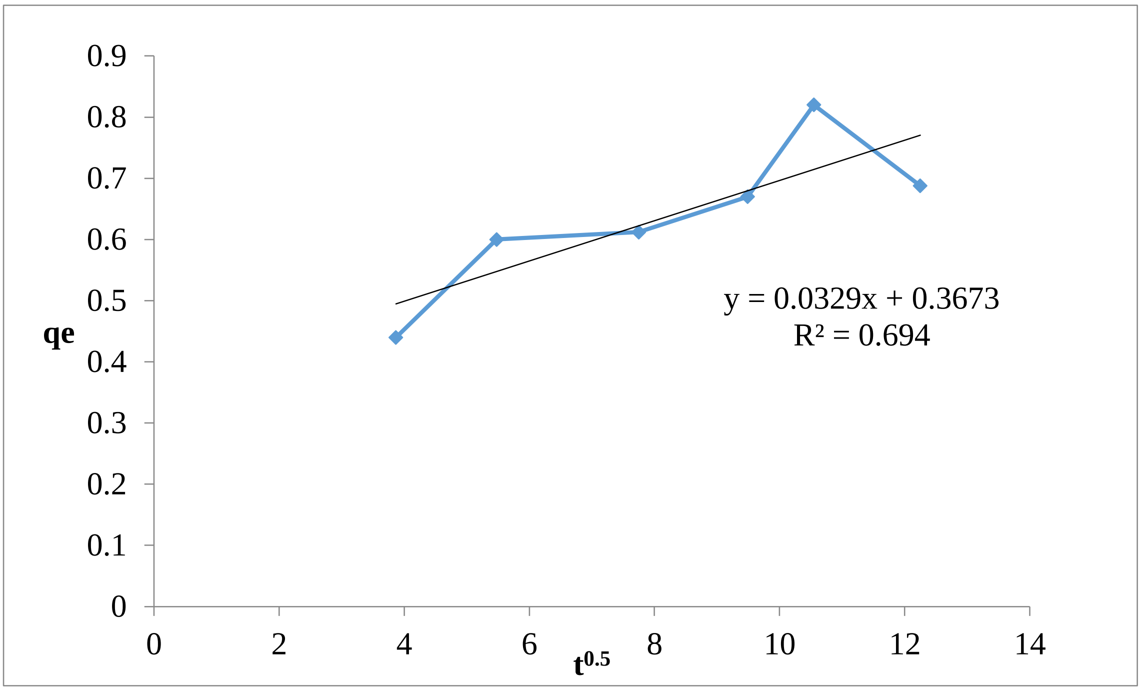


Figure 6.22 Webber & Morris plot for fluoride adsorption

Table 6.4 Webber & Morris Model parameters for adsorption of fluoride

K_{id} (mg/g min$^{0.5}$)	C (mg/g)	R^2
0.0329	0.3673	0.694

6.3.6 Adsorption Isotherms

Figure 6.23, 6.24 and 6.25 show the Langmuir, Freundlich and Temkin Isotherms plots for fluoride adsorption.

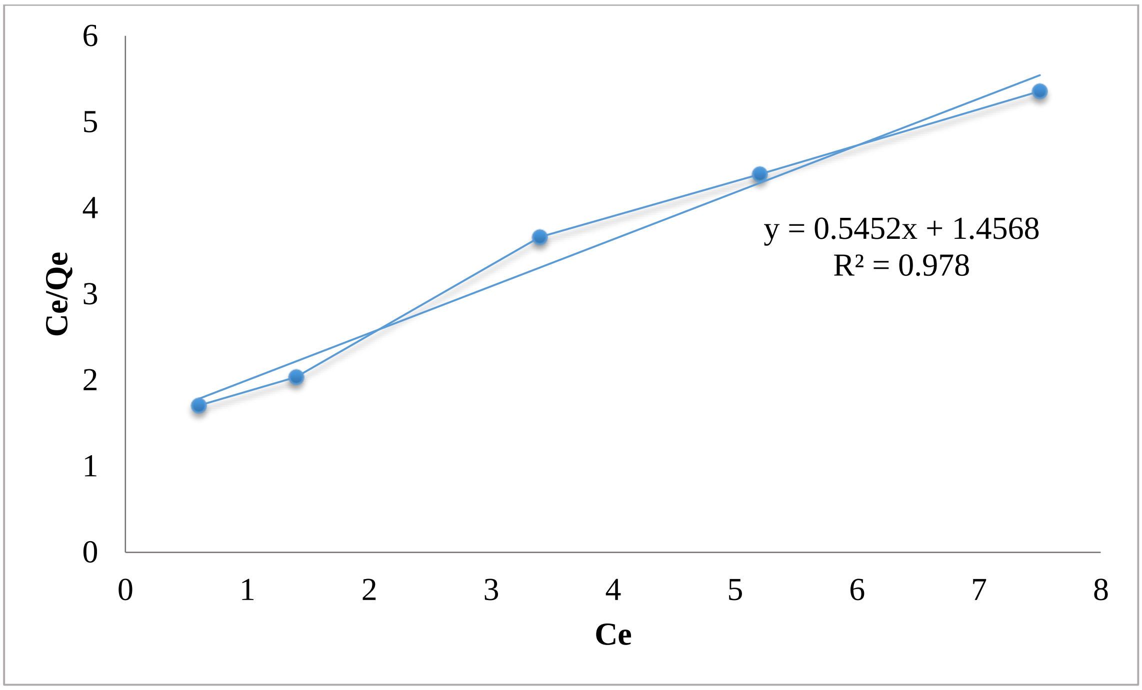


Figure 6.23 Langmuir plot for fluoride adsorption

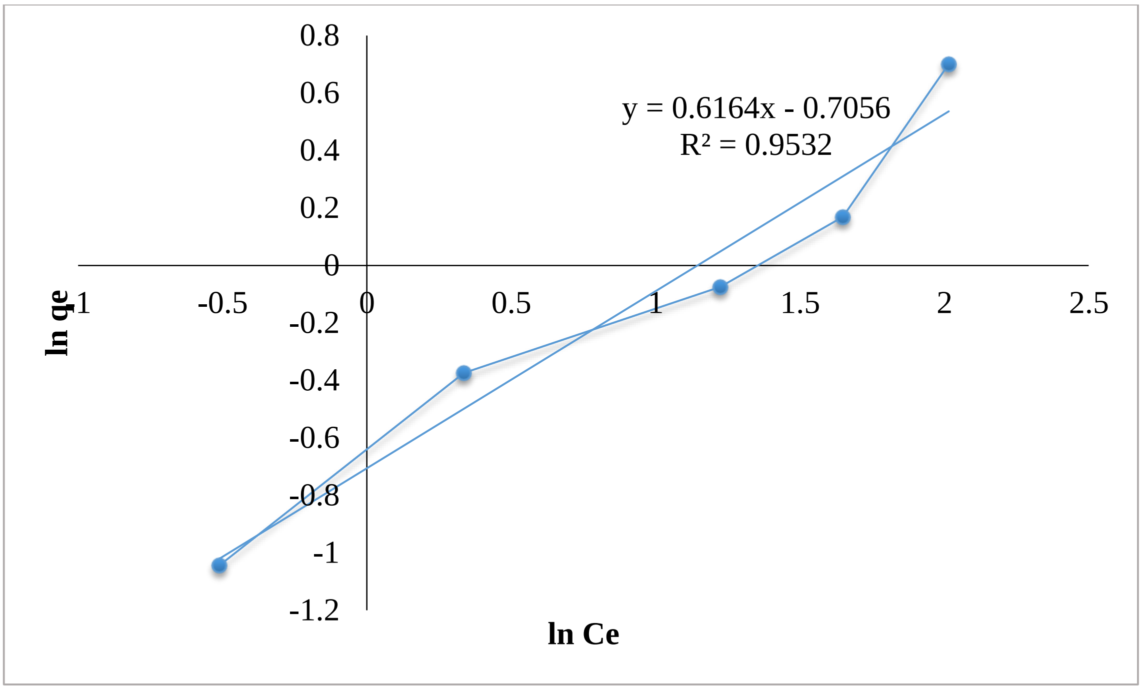


Figure 6.24 Freundlich plot for fluoride adsorption

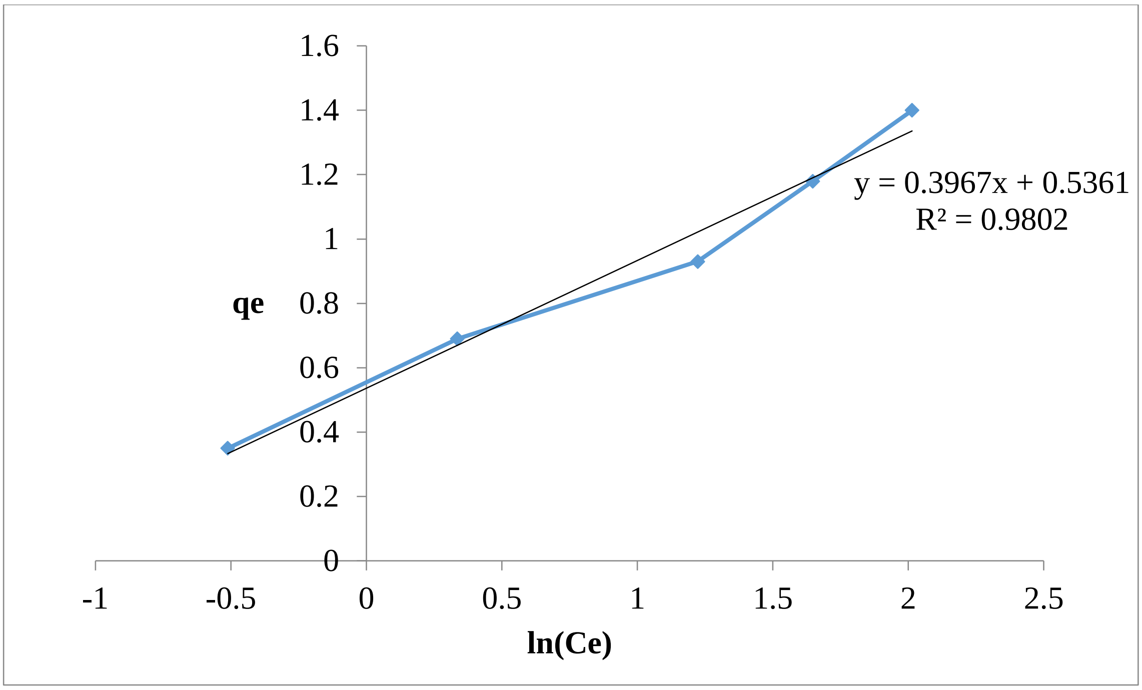


Figure 6.25 Temkin plot for fluoride adsorption

Table 6.5 Langmuir and Freundlich isotherm data for fluoride adsorption

Langmuir Isotherm				**Freundlich Isotherm**		
Parameters						
$\boldsymbol{R_L}$	$\boldsymbol{q_o}$**(mg/g)**	$\boldsymbol{b}$**(l/mg)**	**R^2**	$\boldsymbol{K_F}$ **((mg/g)(L/mg)$^{1/n}$)**	$\boldsymbol{n}$	**R^2**
0.35	1.83	0.37	0.978	0.5	1.89	0.975

Table 6.6 Temkin Isotherm Parameters for fluoride adsorption

B_1	**A_T (l/mg)**	**b_T (J/mol)**	**R^2**
0.3967	3.863	6350.24	0.9802

From Table 6.5, it can be seen that the value of n = 1.89, that it is in range set by Freundlich model which is between 1 and 10 showing favourable adsorption of fluoride on the TL prepared in this work. At the same time, the separation factor R_L= 0.35, is in the range $0<R_L<1$, which indicates a favourable adsorption process. In view of correlation coefficient, R^2 values, for Temkin it is closest to 1 than for Langmuir and Freundlich isotherms. Thus we can say Fluoride adsorption on TL at 303 K follows Temkin adsorption isotherm.

6.4 ADSORPTIVE REMOVAL OF NITRATE FROM SYNTHETIC WATER

6.4.1 Effect of adsorbent dose

Figure 6.26 shows the effect of adsorbent dose on the uptake of nitrate. Percentage removal increases with increase in dose of adsorbent due to availability of sorption sites or surface area. Also it is observed that as adsorbent dose increases, there was no change in percentage removal probably due to overlapping of active sites at higher dosage [Masukume et al. 2010]. So, for further experiments, adsorbent dose of 20 g/l showing 79% nitrate removal, was selected.

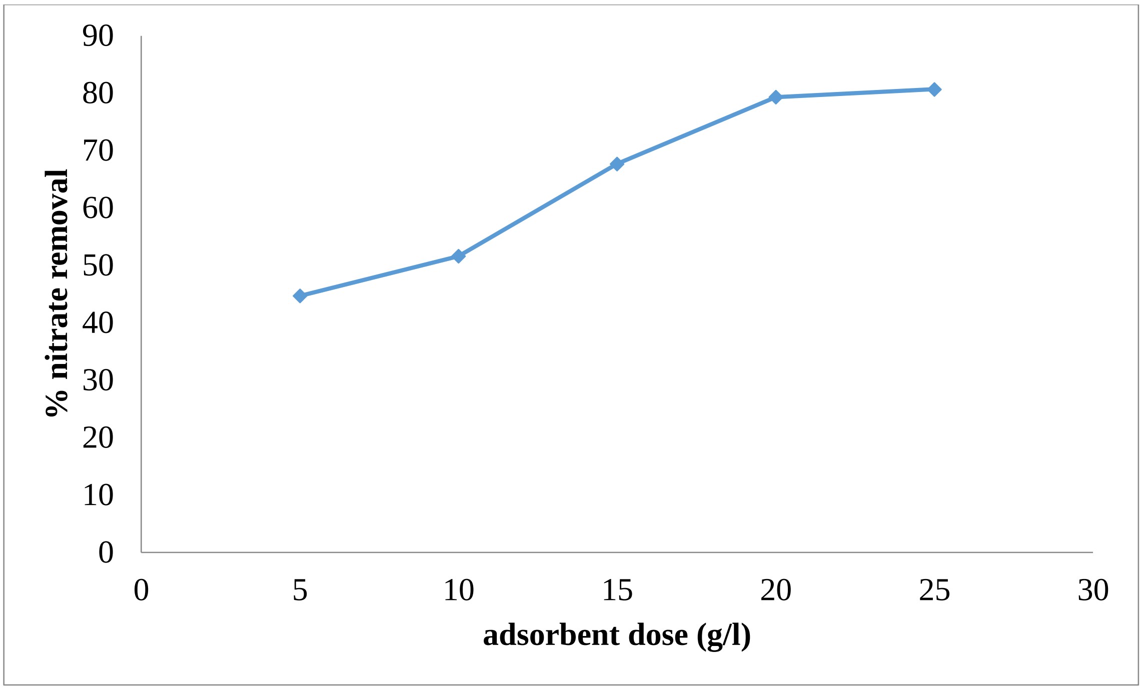


Figure 6.26 Effect of adsorbent dose on nitrate removal

6.4.2 Effect of pH

Anion adsorption is associated with OH^- ion release, so nitrate adsorption on TL is more feasible at lower pH but at very low pH, hindrance due to Cl^- (from HCl) is possible. The specific adsorption of anion on metal oxyhydroxide surface sites occurs by following ligand-exchange reaction [Tripathy et al. 2006].

$$MOH + H^+ \leftrightarrow MOH_2^+$$

$$MOH_2 + NO_3^- \leftrightarrow MOH\text{-}NO_3 \text{ (or } MNO_3 + H_2O)$$

Where M stands for metal ions (Al, Fe, Si). Figure 6.27 shows that higher adsorption is observed at lower pH values and decreases as pH is increased. Maximum removal (80%) was obtained at pH 5, and this value was selected for subsequent experiments.

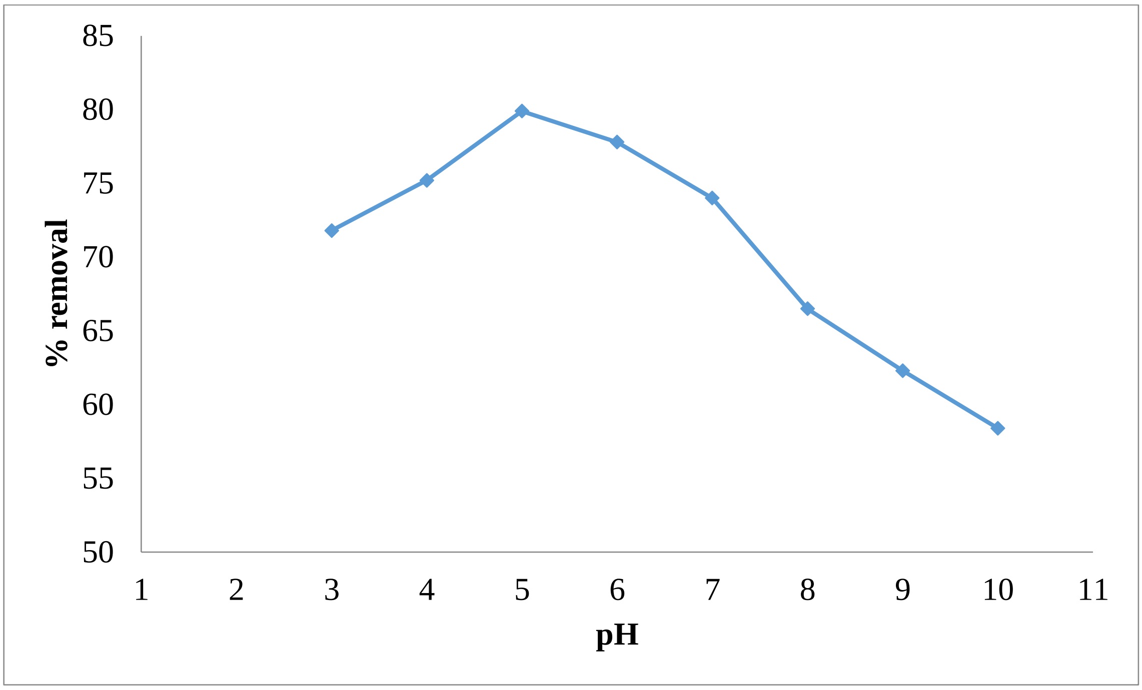


Figure 6.27 Effect of pH on nitrate removal

6.4.3 Effect of contact time

Figure 6.28 shows the effect of contact time on percentage removal of nitrate. The sorption increases from 0 to 120 min, and after that it remained constant. This trend attributes to the fact that between 0 to 120 min, there are a number of vacant sites on the surface of the adsorbent, but after 120 min, these sites are filled by the nitrate ions.

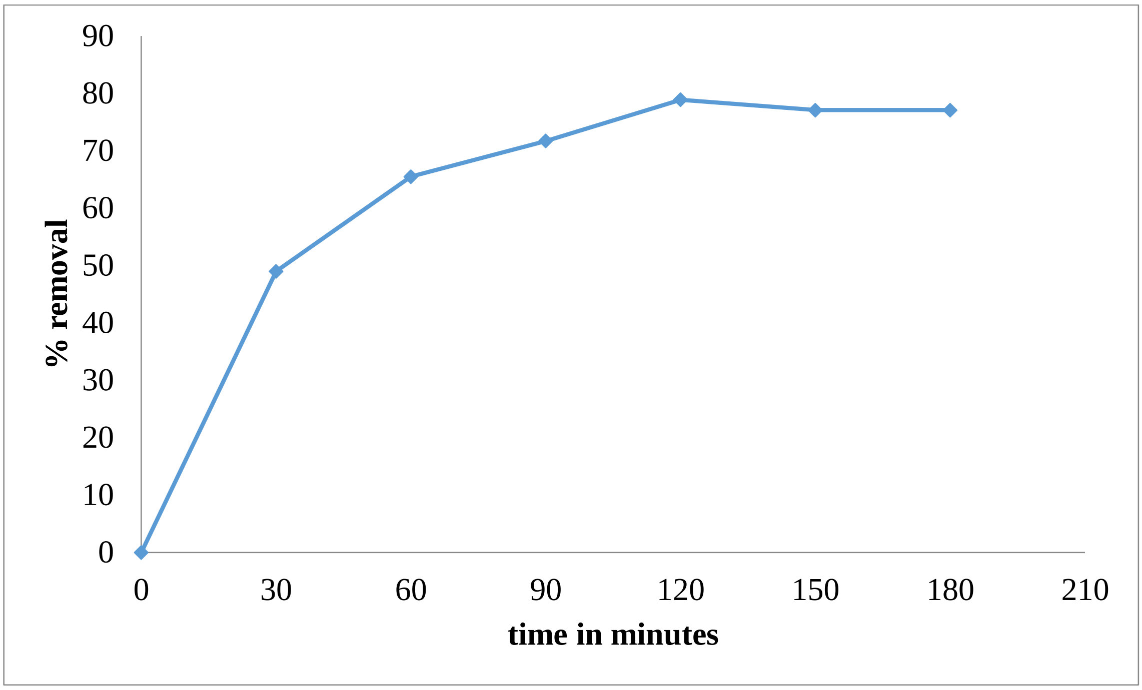


Figure 6.28 Effect of contact time on nitrate removal

6.4.4 Effect of initial nitrate concentration

As it can be seen from the result shown in figure 6.29, nitrate removal efficiency decreases from 78% to 56.5% with increasing initial nitrate concentration from 100 to 225 mg/l. This decrease is due to the saturation of the most active sites of the adsorbent due to increased diffusion rate of nitrate to adsorption sites, tending to saturate them, and in turn, the ulterior utilization of less accessible or less active sites of the adsorbent.

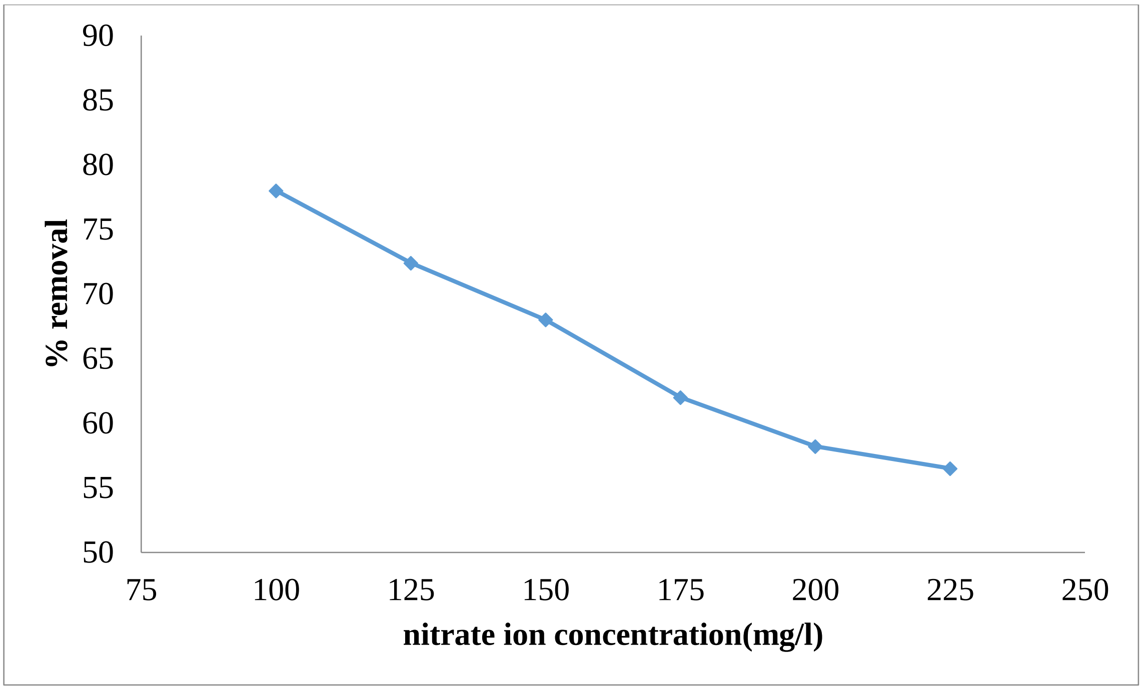


Figure 6.29 Effect of nitrate ion concentration on nitrate removal

6.4.5 Kinetic Modelling

Figure 6.30 and 6.31 show the plot for pseudo-first-order and pseudo-second-order kinetics respectively, for nitrate adsorption.

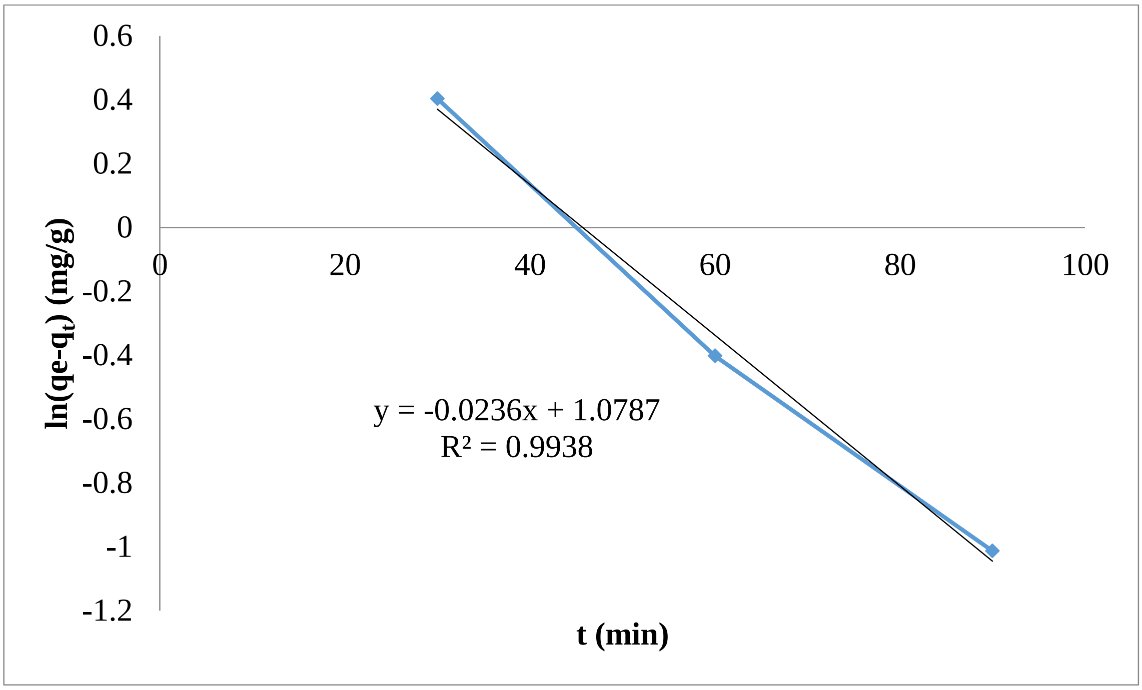


Figure 6.30 Plot for first order kinetics model for nitrate adsorption

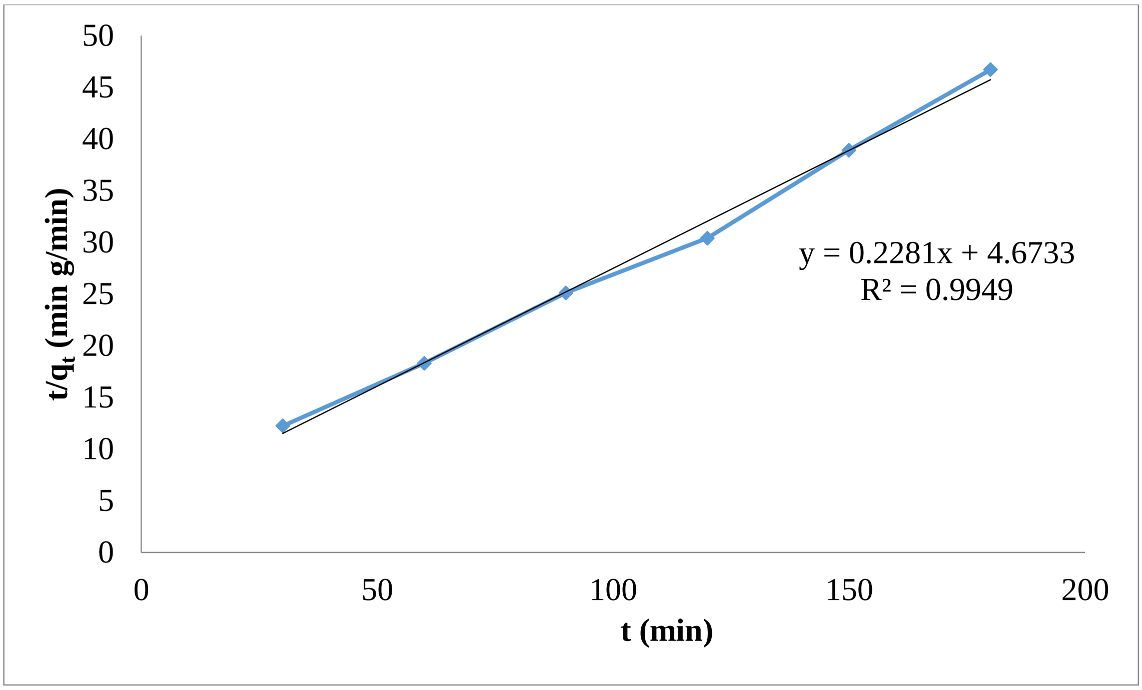


Figure 6.31 Plot for second order kinetics model for nitrate adsorption

The values of kinetics parameters are shown in Table 6.7. It was found that for first order plot, calculated q_e does not agree with experimental q_e showing an error of 26%. This suggests that adsorption process does not follow first order kinetics. Whereas for second order plot, calculated q_e matches with experimental q_e with an error of 10% and correlation coefficient, R^2 value for second order kinetic plot is more closer to unity. These results indicate that adsorption system belongs to second order kinetic model.

Table 6.7 Comparison of first and second order adsorption rate constants and experimental q_e and calculated values for nitrate adsorption

q_e (exp) (mg/g)	First order kinetics			Second order kinetics		
	k_1 (1/min)	q_e (cal) (mg/g)	R^2	k_2 (gm/mg/min)	q_e (cal) (mg/g)	R^2
3.95	0.023	2.94	0.993	0.0112	4.36	0.996

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Figure 6.32 shows the Webber and Morris plot for nitrate adsorption and it is almost linear which indicates the sorption process was controlled by intra-particle diffusion only

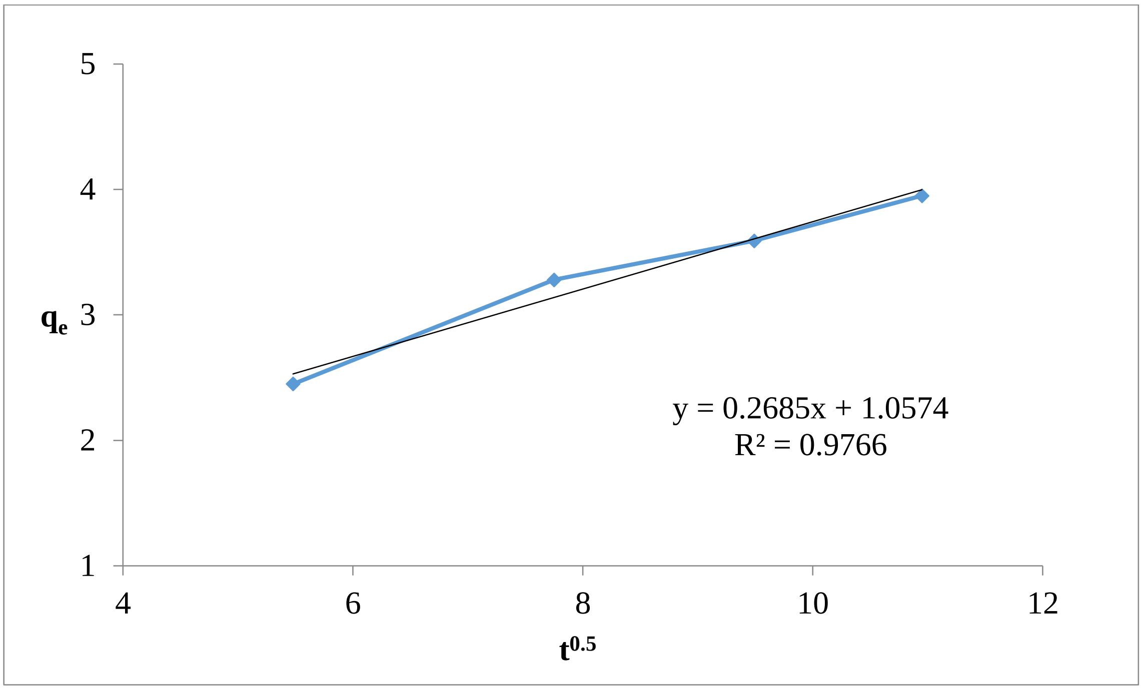

Figure 6.32 Webber & Morris plot for nitrate adsorption

Table 6.8 Webber & Morris Model parameters for adsorption of nitrate

K_{id} (mg/g min$^{0.5}$)	C (mg/g)	R^2
0.2685	1.0574	0.9766

6.4.6 Adsorption Isotherms

Figure 6.33, 6.34 and 6.35 show the Langmuir, Freundlich and Temkin Isotherms plots for nitrate adsorption.

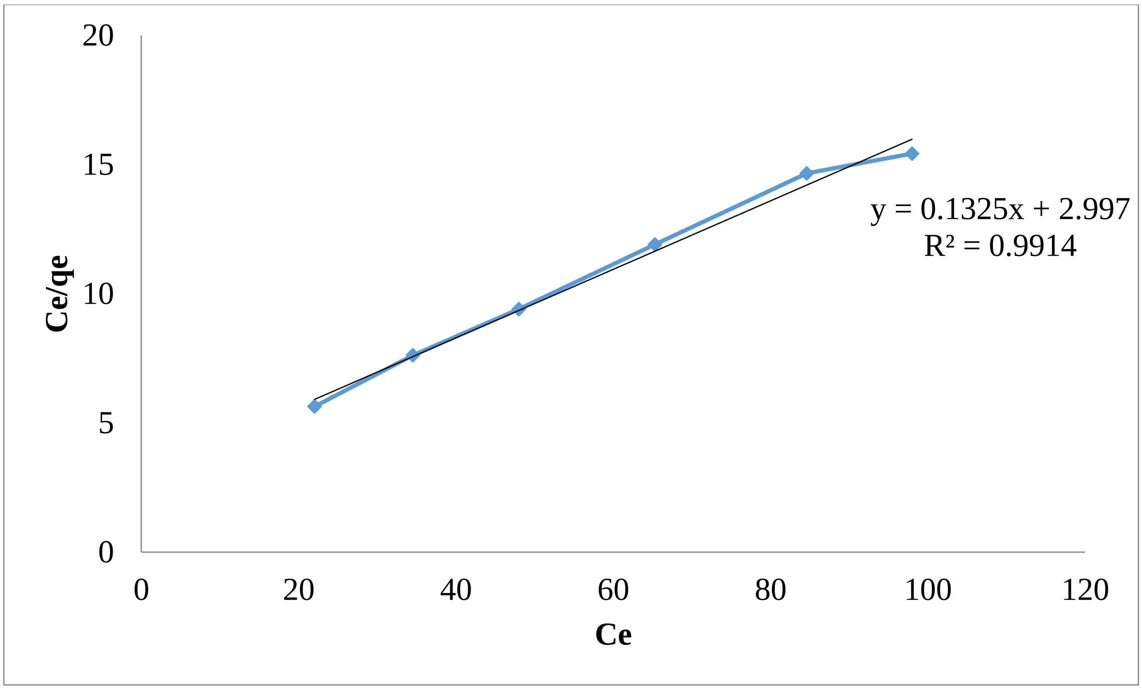

Figure 6.33 Langmuir plot for nitrate adsorption

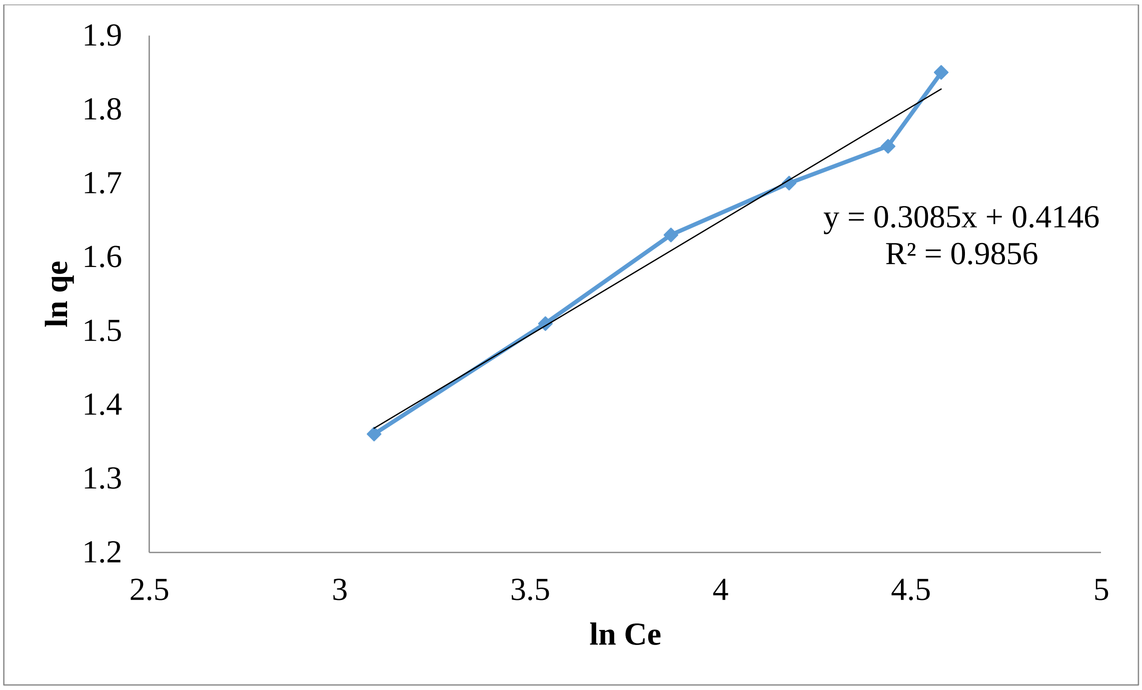

Figure 6.34 Freundlich plot for nitrate adsorption

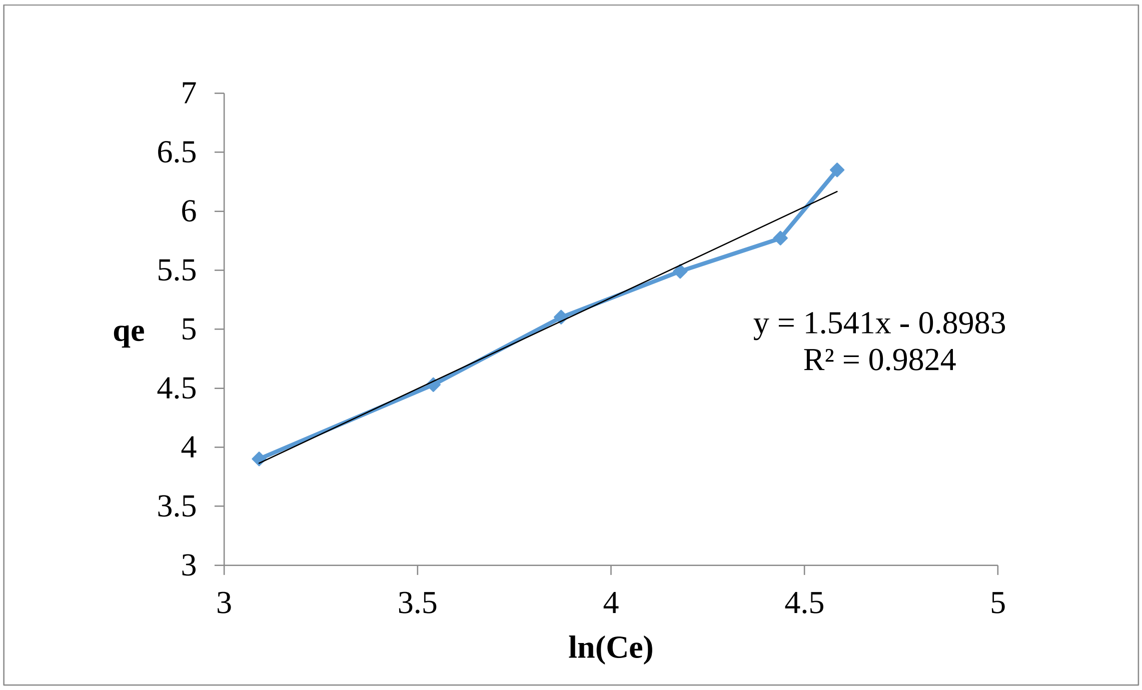

Figure 6.35 Temkin plot for nitrate adsorption

Table 6.9 Langmuir and Freundlich isotherm data for nitrate adsorption

Langmuir Isotherm				**Freundlich Isotherm**		
Parameters						
$\boldsymbol{R_L}$	$\boldsymbol{q_o}$**(mg/g)**	$\boldsymbol{b}$**(l/mg)**	**R^2**	$\boldsymbol{K_F}$ **((mg/g)(L/mg)$^{1/n}$)**	$\boldsymbol{n}$	**R^2**
0.18	7.576	0.044	0.991	1.513	3.25	0.985

Table 6.10 Temkin Isotherm Parameters for nitrate adsorption

B$_1$	**A$_T$ (l/mg)**	**b$_T$ (J/mol)**	**R^2**
1.541	0.558	1634.76	0.9824

From Table 6.9, it can be seen that the value of n = 3.25, that it is in range set by Freundlich model which is between 1 and 10 showing favourable adsorption of nitrate on the TL prepared in this work. At the same time, the separation factor R_L= 0.18, is in the range 0<R_L<1, which indicates a favourable adsorption process. In view of correlation coefficient, R^2 values, for Langmuir it is more close to 1 than for Freundlich model and Temkin model.

7. CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

In the present study, the adsorption batch study of fluoride and nitrate ions on the acid base treated laterite soil has been carried out. Following conclusions were drawn from this study:

1. TL served to be an inexpensive, and highly efficient adsorbent for fluoride and nitrate removal from synthetic water.
2. Fluoride and nitrate adsorption on TL is highly dependent on pH of the solution. The most suitable pH for fluoride and nitrate removal is 6 and 5 respectively.
3. Maximum removal of fluoride, i.e. 86% occurs at an adsorbent dose of 12.5 g/l for an initial fluoride concentration of 10 mg/l, while for nitrate removal, an adsorbent dose of 20 g/l is required to accomplish 80% removal for an initial nitrate concentration of 100 mg/l.
4. The adsorption capacity of TL for fluoride removal is found to be 0.69 mg/g and 3.95 mg/g for nitrate removal.
5. It is found that initially rapid defluoridation occurs but as the time increased further sorption sites get saturated with adsorbate and no further removal occurs. The equilibrium time for TL for fluoride removal is 150 min and for nitrate removal is 120 min.
6. Pseudo second order model explains the kinetics of adsorption better than intra particle diffusion models and pseudo first order model for both fluoride and nitrate removal.
7. For fluoride adsorption on TL, Temkin isotherm fitted better to data than Langmuir or Freundlich isotherms.
8. Langmuir adsorption isotherm fitted well to the data than Freundlich and Temkin isotherm models for nitrate adsorption.

7.2 RECOMMENDATIONS

Based on the results of the present study, the following recommendations are suggested for further investigations.

1. The effect of temperature can be studied.
2. The spent adsorbent could be used for useful purposes like brick manufacturing.
3. Simultaneous adsorption of fluoride and nitrate can also be studied.
4. The results of this batch study can be used to design column reactor and study various aspects of it using fluoride or nitrate as substrate or both simultaneously.
5. Study can also be performed on contaminated water directly taken from industrial waste.

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