Chapter 1

INTRODUCTION

1.1 Background

Throughout history, the quality of drinking water has been a factor in determining human welfare. It is clear that water pollution should be a concern of every citizen. Water polluted by natural sources has caused great hardship for people forced to drinking it or use it for irrigation. Currently, waterborne chemicals pose the greatest threat to the safety of water supplies, particularly of ground water in some parts of the world [1]. Contamination of drinking water by fluoride, due to its natural presence from dissolution of fluoride containing rocks, or discharge by agricultural and industrial activities, such as steel, aluminium, glass, electroplating, [2-4] is one that affects human health and wellbeing.

Fluoride has dual significance; if its content is less then it may result in problems like dental caries. World Health Organization (WHO) recommends it in the range of 0.1– 0.5 ppm. The standard of the United States is between 0.6 and 0.9 ppm, and of India 1 and 1.5 ppm. Fluoride is an essential mineral that in permissible guideline level (WHO, 2006) is beneficial to mankind in dental protection and excessive intake led to various disorders and diseases such as crippling skeletal fluorosis, brittle bones, cancer (lung and bladder), infertility in women, brain and hepatit damage and Alzheimer syndrome.

Almost all parts of the world have reported high concentration of fluoride in drinking water. North America, Africa and Asia are the mostly affected continents of the world. Countries like India, Srilanka and China have reported high concentrations of fluoride. Rift valley countries in Africa have reported high concentrations of fluoride due to the weathering of alkaline volcanic rocks.

In India, some of the groundwater sources reveal enhanced concentration of fluoride over a passage of time. This may be due to depletion of water tables and/or over withdrawal of water and/or inadequate re-charging of underground aquifer. In India 17 out of the 28 states have reported fluoride toxication results.

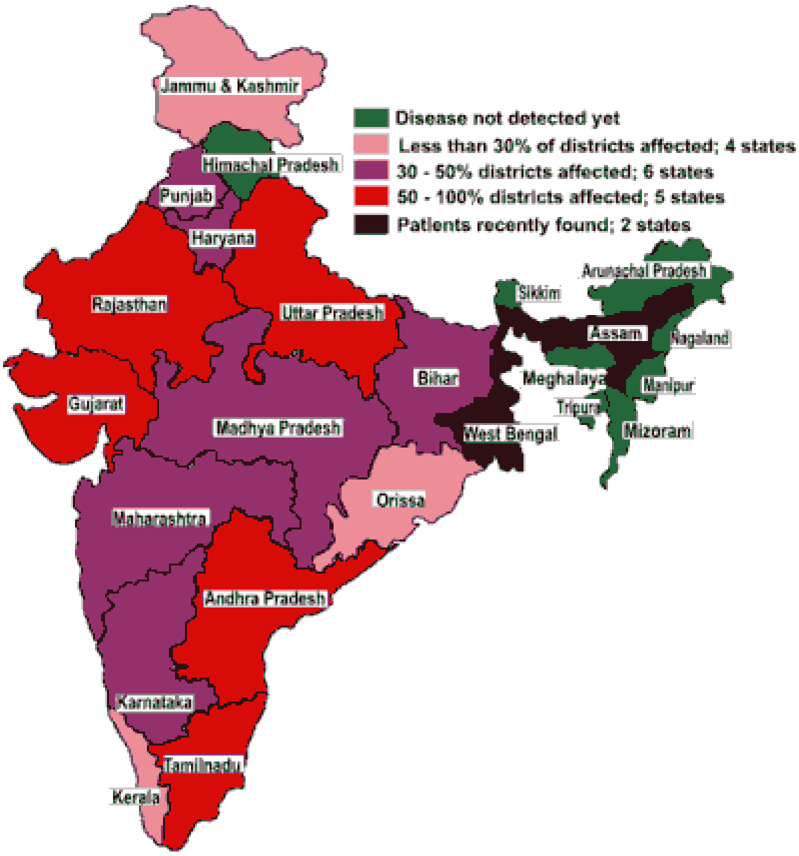


Figure 1.1: Map of India showing endemic states for fluorosis

Fluoride is an essential constituent for both humans and animals depending on the total amount ingested or its concentration in drinking water. It is purposely added to drinking water in small quantities to prevent dental caries. The presence of fluoride in drinking water, within the permissible limits of 0.5-1.0 mg L^{-1}, is beneficial for the production and maintenance of healthy bones and teeth, while excessive intake of fluoride causes dental or skeletal fluorosis which is a chronic disease manifested by mottling of teeth in mild cases, softening of bones and neurological damage are severe cases [5-9].

Surface waters seldom contain fluoride beyond this level, whereas excess fluoride may be present in ground waters depending on the presence of fluoride rich minerals as well as hydro-geological conditions. It should be known, however, that the WHO guidelines are not universal as many countries have established their own standards and hence in setting national standards for fluoride in drinking water, it is important to consider the local condition. For countries in tropical regions, the recommended fluoride concentration is even lower (about 0.8 mg L^{-1}) because of the relatively higher water consumption [10].

For a community that is supplied with water containing excessive fluoride, there are two possible control options. The first approach is to seek an alternative water source either for direct consumption or for diluting fluoride containing water, the use of bottled water is an extreme example of the first approach and the second one is to eliminate fluoride by physical or chemical treatment of the water. In areas where alternative sources are not available and the provision of bottled water is not economical, as in the case of most tropical regions of developing countries, the second option is probably the most reasonable approach.

At present, there are few treatment options that are used for controlling excessive levels of fluoride in drinking water. Based on the mechanism of fluoride removal, the methods can be categorized into chemical precipitation (by alum, lime, lime and alum and calcium chloride), adsorption (activated alumina, clay and flay ash), ion exchange (by synthetic resins and bone char) and membrane technologies (reverse osmosis and electro dialysis). The methods used by industrialized countries such reverse osmosis, electro-dialysis and ion exchange require more technical support for operation and maintenance and the capital investment cost is very high. Among the various available techniques for removal of fluoride, adsorption method is relatively simple, economical and suitable for small communities.

1.2 Fluoride and health effects

High fluorine levels in the drinking water adversely affect the health of consumers and have been recognised as a cause of fluorosis. The three degrees of fluorosis are:

Dental fluorosis which "refers to developmental defects of enamel, induced by fluoride. Clinically, it is characterised by a pattern of white opacities affecting homologous teeth. The opacities may vary from minor white striations to small or extensive areas of opaque enamel.The severity and the distribution of fluorosis depend on the fluoride concentration, duration of exposure to fluoride, and individual variations in susceptibility"(Wondwossen, 2004). Pictures showing the effects of dental fluorosis are given in Figure 1.1.

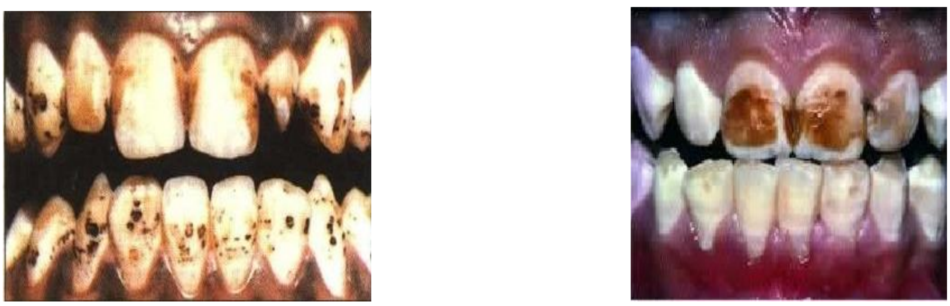


Figure 1.2: Effect of dental fluorosis

Skeletal fluorosis which is characterised by the inhibition of joint movement due, for example, to the presence of nodules of excess bone or to the calcification of the ligaments surrounding joints (Teckle-Haimanot, 2006b). Pictures showing the effects of skeletal fluorosis are given in Figure 1.3.

Figure 1.3: Disabilities caused by skeletal fluorosis

Crippling fluorosis which is the most advanced state of skeletal fluorosis and can also cause neurological defects. It is characterised by osteosclerosis or extreme bone deformity (Fawell et al., 2006).

The correlation between the concentration of fluorine in drinking water and the level of fluorosis is shown in Table1.1.

Table-1.1 Different fluoride doses(long term ingestion through water)and their effect on human body.

Fluoride(mg/l)	**Effects on human body**
Below 0.5	Dental caries
0.5 to 1.0	Protection against dental caries. Take care of bone and teeth
1.5 to 3.0	Dental fluorosis
3.0 to 10	Skeletal fluorosis(adverse change in bone structure)
Above 10	Crippling skeletal fluorosis and severe osteoclerosis

The WHO Standard for fluorine concentration in drinking water is 1.5 mg/l (WHO, 2004). However, this value must be adapted from location to location due to the effect of the ambient temperature of the environment which will influence the volume of drinking water consumed. This is why the WHO (1996) recommends lower standards for countries with hot average temperatures. As such, for Ethiopia, which has a mean maximum daily temperature between 26 and 32°C, the WHO Standard is 0.8mg/l.

1.3 Problem Statement

Due to the nature of some water bodies with high fluoride content whether it is because of industrial effect or natural occurrence and the effect fluoride have on human body, it is becoming important to remove this constituent of water to safe level before consumed by people. At present, there are few treatment options that are used for controlling excessive levels of fluoride in drinking water. Based on the mechanism of fluoride removal, the methods can be categorized into chemical precipitation (by alum, lime, lime and alum and calcium chloride), adsorption (activated alumina, clay and flay ash), ion exchange (by synthetic resins and bone char) and membrane technologies (reverse osmosis and electro dialysis). The methods used by industrialized countries such reverse osmosis, electro-dialysis and ion exchange require more technical support for operation and maintenance and the capital investment cost is very high.

Sawdust and Banana peel powder are some example of waste materials that can remove fluoride from water effectively. Putting it aside, these materials are easily found and needs simple processing before being able to be used for defluoridation process. However, more investigation regarding the capabilities of this material is still need to be done.

1.4 The objectives of the study

Water is one of the most important natural resources upon which all life process depends. Indiscriminate use and misuse of water is making it unfit for human consumption. A recent survey reveals that, 90% of water available contains many pollutants which cause number of health problems. The purification of water is a major challenge in future years to come.

The objective of the research is to study on effective and cheap adsorbents for the removal of fluoride from the water.

The objectives are as follows:

- To investigate the removal of fluoride from aqueous solutions in batch process at different operating conditions (contact time, initial concentration,pH, adsorbent dose etc) using low cost materials like saw dust and Banana peel powder.

- To compare the fluoride removal efficiencies of the materials selected above.

- The experimental adsorption data will be fitted with Langmuir , Freundlich and Tempkin adsorption isotherm.

- To study the kinetics of adsorption using four models, pseudo first order model, pseudo second order model, Intraparticle diffusion model and Elovich model.

- To interpret the data to know the feasibility of the above study

Chapter 2

LITERATURE REVIEW

This chapter gives an overview of previous investigations described in publications where a variety of low cost adsorbents have been used to remove fluoride ions in aqueous solution.

Pali Shahjee, B.J.Godboley, A.M.Sudame (2013) investigated or checked efficiency of low cost adsorbent (Bleaching Powder) for the removal of excess fluoride from aqueous solution.The studies were conducted under batch adsorption. The investigators concluded that the bleaching powder is a good adsorbent for flouride removal from aqueous solution. The optimal conditions for the effective removal of fluoride by bleaching powder were found to be at pH 10, contact time 8 hours and optimum dose of adsorbent was found 7.3gm/100ml for removal of fluoride of 5ppm concentration[11].

Naba Kumar Mondal*,Ria Bhaumik, Tanmoy Baur,Biswajit Das, Palas Roy and Jayanta Kumar Datta(2012) studied the removal of fluoride using Tea ash as adsorbent through batch studies. The authors reported that the adsorbent was efficient for the uptake of fluoride at pH 6 and contact time 180 minutes. Tea ash was found to me more efficient at an initial concentration of 5mg/l and temperature 303 k. The authors also reported that the data nicely fitted with Langmuir adsorption isotherm indicating monolayer adsorption and adsorption of fluoride decreased with increase in temperature in the range of 303-333 K. Again the adsorption process was observed to follow a pseudo-second-order kinetic model[12].

G. Alagumuthu, V. Veeraputhiran and R. Venkataraman (2010) investigated the removal of flouride from the water using *cynodon dactylon* as adsorbent. By conducting batch adsorption studies at constant temperature (25-32°C), the maximum removal of fluoride was 83.77 % while keeping 3.0 mg/L fluoride concentration and 1.25 g dosage of adsorbent at neutral pH., contact time 105 minutes. Various adsorption isotherm models were applied to evaluate the adsorption data. The adsorption of flouride ions followed Redlich-Peterson isotherm as well as Langmuir isotherms. The authors concluded that the adsorbent used in this work shows superior adsorptive efficiency than previously studied defluoridation works using natural adsorbents was most effective[13].

Bhagyashree M Mamilwar, A.G.Bhole, A.M.Sudame(2012) investigated the adsorption of Fluoride using bark of babool as adsorbent.The investigators conducted batch studies and used Freundlich and Langmuir isotherms to understand the adsorption mechanism. Optimum dose of bark of babool was found 5g/L for removal of fluoride concentration of 5 mg/L. Adsorption capacity was more in the pH range of 6-8.Optimum time of contact was found 8 hrs. The removal increased with time and adsorbent dose, but with higher initial concentration decreased with time and adsorbent dose. The present study on defluoridation using bark of babool shows that the equilibrium data fits better to Langmuir isotherm as compared with Freundlich isotherm.The pseudo-second-order kinetic model fitted well as compared to pseudo first-order model [14]**.**

N. Gandhi, D. Sirisha, K.B. Chandra Shekar and Smita Asthana(2012) carried out their study on effective and cheap adsorbents for the removal of fluoride from the water. Batch adsorption studies were carried out. The experiments were carried out in laboratory on certain low cost adsorbents like concrete, ragi seed powder, Red soil, horse gram seed powder, orange peel powder, chalk powder, pineapple peel powder and multhani matti. Results indiacate 86% fluoride removal for chalk powder and pineapple peal powder. Orange peel powder and horse gram seed powder showed the removal of 79% and 75%. Percentage removal for ragi seed and red mud was found to be 65% and 71%. Removal efficiency was recorded less for multani mitti and concrete which was 56 % and 53%[15].

Patil Satish, Renukdas Sameer, Patel Naseema(2012) conducted tests to investigate the efficacy of various treated natural adsorbents such as Mangrove plant leaf powder (MPLP), Almond tree bark powder (ATBP), Pineapple peel powder (PPP), Chiku leaf powder (CLP), Toor plant leaf powder (TPLP) and Coconut coir pith (CCP). Observed the effect of pH, contact time, adsorbent dose and initial metal ion concentration to remove fluoride ions from the aqueous solutions using batch studies. Uptake of fluoride ions by adsorbents at equilibrium is found to be in the order of MPLP > CCP > TPLP > CLP > PPP > ATBP. The optimum contact time for all the adsorbents was 60 minute with a adsorbent dose of 10g/l for initial fluoride concentration of 5ppm. Percentage removal at pH 2 was found to be high[16].

R. Bhaumik, N. K. Mondal, B. Das , P. Roy, K. C. Pal, C. Das, A. Banerjee, and J. K. Datta (2011) Studied the role of eggshell powder as an adsorbent for removal of fluoride from aqueous solution using batch technique. The maximum adsorption was acheived at pH

2.0-6.0. The investigators achieved around 94% removal of fluoride at initial metal ions concentration of 5 mg/l at optimum dose of 2.4 g/100ml and optimum time of 120minutes. Experimental data provided best fit with the Langmuir isotherm model, indicating monolayer sorption on a homogenous sur. The adsorption kinetics followed pseudo-second-order kinetic model indicating towards chemisorption. Intra-particle diffusion was not the sole rate controlling factor[17].

Naba Kr Mondal, Ria Bhaumik, Arnab Banerjee, Jayanta Kr Datta, Tanmoy Baur(2012) done a comparative study for removal of fluoride using activated silica gel (ASiG) and activated rice husk ash (ARHA) as adsorbents through batch studies. The authors reported that both adsorbents were efficient for the uptake of fluoride at pH2.0 and contact time 100 minutes. ASiG was found to be more efficient than ARHA with an initial fluoride concentration of 5mg/l,percentage of removal was 88.30 and 96.7 for ARHA and ASiG respectively.. The study on equilibrium sorption revealed that Langmuir isotherm model give best fit to experimental data. The nature of adsorption of fluoride on ARHA and ASiG was physical adsorption as inferred from the Dubinin-Radishkevich (D-R) isotherm model[18].

C.M.Vivek Vardhan and J.Karthikeyan(2011) carried out investigations for removal of Fluoride from water employing physico-chemical processes of adsorption and coagulation employing abundantly available and low-cost materials like Rice Husk, seed extracts of Moringa Oleifera (Drum stick), and chemicals like Manganese Sulphate and Manganese Chloride. Rice husk of 6g/l accomplished a removal of 83% of Fluoride from a 5mg/l of Fluoride solution requiring an equilibrium time of 3 hours. Equilibrium Isothermal data fitted well into rearranged linearised Langmuir adsorption model. Moringa oleifera seed extracts,Manganese Sulphate and Manganese Chloride accomplished removal percentages of 92, 94 and 91 of Fluoride from a 5mg/l test solution at a dosage of 1000 mg/l. A slightly acidic pH of 6.0 was found favorable for Fluoride removal by Manganese sulphate,Manganese Chloride and MOE[19].

S. T. Ramesh, R. Gandhimathi, P. V. Nidheesh and M. Taywade(2012) investigated the adsorption potential of bottom ash for defluoridation of drinking water using batch and continuous fixed bed column studies. The optimum contact time for fluoride was found to be 105 minutes with the maximum efficiency of 73.5 % at 70mg/100ml bottom ash dosage. The optimum pH was found to be pH 6 with the maximum efficiency of 83.2 %.During the column studies, increase in fluoride ion uptake with an increase in the bed height was due to an increase in the contact time.A high degree of linearity of the BDST plot indicates the validity of the BDST Model when applied to continuous column studies[20].

S. Kagne, S. Jagtap, P. Dhawade, S.P. Kamble, S. Devotta, S.S. Rayalu(2007) investigate the potential of cement hydrated at various time intervals for the removal of excess F^- from aqueous solution by using batch adsorption studies.It was found that the HC shows significant F^- removal over a wide range of pH (3–10). the maximum removal of fluoride was 92.37% with 10gm/l of hydrated cement, contact time 24 hours and initial fluoride concentration 5.9 mg/l.The experimental data generated from batch adsorption experiments fitted well into the linearly transformed Freundlich and Langmuir isotherms[21].

Das Kumar Malay and Attar J. Salim(2011) conducted comparative study of batch adsorption of fluoride using commercial and natural adsorbent. Different activated adsorbent samples like activated alumina, activated bauxite, Activated rice husk were taken and equilibrium studies were conducted to find a suitable adsorbent. Equilibrium adsorption study was carried out by the author and by Freundlich isotherm it was observed that activated alumina was the best as it gave minimum value of slope (0.152) and equilibrium constant (0.601) ,which shows that it is having maximum adsorption capacity. Activated bauxite was with slope of 0.965 and equilibrium constant 0.593 which was followed by activated rice husk with slope of 0.659 and equilibrium constant 0.155. So authors concluded activated alumina as best adsorbent and activated rice husk as inferior adsorbent.

According to Langmuir isotherm the value of RL was maximum for activated alumina (0.448) than activated bauxite (0.246) and minimum for activated rice husk is (0.152) and also the value of R^2 0.986, 0.982, 0.814 shows the same result. So activated alumina is more favorable for this adsorption with respect to activated bauxite and activated rice husk[22].

Veeraputhiran V. and Alagumuthu G (2011) studied flouride removal from aqueous solution using Phyllanthus emblica adsorbent. The highest adsorption capacity was obtained at neutral pH with adsorbent dose 0.75g and initial metal ions concentration of 3 ppm. The percentage removal of fluoride from the solution was observed 82.1%. The adsorption of fluoride by Phyllanthus emblica was heterogeneous in nature[23].

S. A. Valencia-Leal, R. Cortés-Martínez, R. Alfaro-Cuevas-Villanueva(2012) Evaluated the Guava Seeds (Psidium Guajava) as Low-Cost Biosorbent for the Removal of Fluoride from Aqueous Solutions. Maximum adsorption occurred between pH5.0 to 8.0..The adsorption of fluoride was found endothermic in nature Langmuir and Freundlich adsorption isotherm models were applied to evaluate the adsorption data. The pseudo-second order model describes the fluoride sorption kinetics using guava seed at different temperature. The Langmuir model best describes the isotherm's experimental data, which may indicate that the sorption mechanism of fluoride ions on guava seed is chemisorption on a homogeneous material[24].

A. V. Jamode, V. S. Sapkal and V. S. Jamode (2004) assessed the suitability of inexpensive leaf adsorbents to effectively remediate fluoride-contaminated water. The leafs of neem (*Azadirachta indica*), pipal (*Ficus religiosa*) and khair (*Acacia catechu willd*) trees were used in this study.the study concludes that at the highest flouride ion concentration (15 mg/l), the fluoride ion level in the effluent gradually decreased to 0 mg/l within 180 min at 29 ± 0.5°C when the dose of adsorbent is 10 g/l. The process adsorption by treated biosorbents follows Langmuir isotherm, which comprises statistical and empirical data estimated from Isotherm equation[25].

Mohammad Mehdi Mehrabani Ardekani, Roshanak Rezaei Kalantary, Sahand Jorfi, Mohammad Nurisepehr (2013) Compared the efficiency of Bagas, Modified Bagas and Chitosan for fluoride removal from water by adsorption. The pH value of 7, contact time of 60 min and adsorbent dose of 2 g/L were determined as optimum conditions for all three adsorbents. Chitozan and bagas did not show good capability for fluoride removal, but modified bagas showed more than 90% removal at optimized conditions, including the pH value of 7, contact time of 60 min and adsorbent dosage of 2 g/L. Both Langmuir and Freundlich isotherms show good correlation for description of results, but the Langmuir model with the correlation value of 0/99 is superior[26].

Kaushik Bandyopadhyay , Chandrima Goswami , Devaleena Chaudhuri , Arunabha Majumdar , Amal. K. Misra (2009) studied removal of fluoride from groundwater using broken concrete cubes as the adsorbing media. In batch adsorption study broken cube was found to remove about 80% fluoride at 120 mins of contact time with adsorbent dose of 6mg/100ml at pH 7.0. In column experiment with an influent fluoride concentration of

8mg/L, pH of 7, the effluent fluoride concentration was reached 1.5mg/L at 26L cumulative flow which has been considered as cut off point of the curve[27].

Dwivedi Shubha, Mondal Prasenjit and Balomajumder Chandrajit (2014) investigated the removal of fluoride using *Citrus limetta* in batch reactor. The Freundlich isotherm gives well prediction of the equilibrium adsorption (R2 = 0.996). The specific uptake increases from 0.089 mg/g to 1.35mg/g with the increase in initial fluoride concentration from 1 mg/L to 20 mg/L.Maximum specific uptake obtained from Langmuir isotherm is found to be 1.82 mg/g. When the initial fluoride concentration is 5mg/L, the removal efficiency of mosambi peel is 82.5%. Adsorption kinetics is presented well by pseudo second order rate equation and the estimated equilibrium concentration falls within ~ 6 % error limit [28].

Chapter 3

MATERIALS AND METHODS

3.1 Materials

In this study an attempt will be made to suggest and compare certain low cost materials for effective removal of fluoride.

The adsorbent primarily selected are sawdust and Banana peel powder.

3.2 Adsorbent collection and preparation

Adsorbent	Sampling Site
Sawdust	Sawdust of kail wood is collected from the workshop of Kasturba Polytechnic for Women, pitampura, Delhi and washed with distilled water followed by drying in a hot air oven at 150^0C for 24 hrs. The dried sawdust was grinded and sieved well in fraction of 90, 150, 300µm mesh size particles that were preserved in different air tight containers for subsequent use as adsorbent
Banana peel powder	Banana peels are collected from houses and then sun dried, after sun drying the peels the peels are dried in oven for 24 hrs at 150^0c then grinded to a fine powder and sieved well in fraction of 90, 150, 300µm mesh size particles that were preserved in different air tight containers for subsequent use as adsorbent

Figure3.1:Image of sawdust

Figure3.2: Image of Banana peel powder

3.3 Preparation of adsorbate solution

Stock solution of fluoride was prepared by dissolving 0.22g sodium fluoride (MERCK, Germany) in 1L double distilled water. The required concentration of fluoride solution was prepared by serial dilution of 100 mg/L fluoride stock solution.

3.4 Apparatus Required:

Orion ion selective electrode was used to measure the pH and Orion 720 A+ ion analyzer was used to measure the fluoride concentration. Calibration was made in the range 0.1-10 ppm of Flouride by using known concentration of sodium fluoride standard.

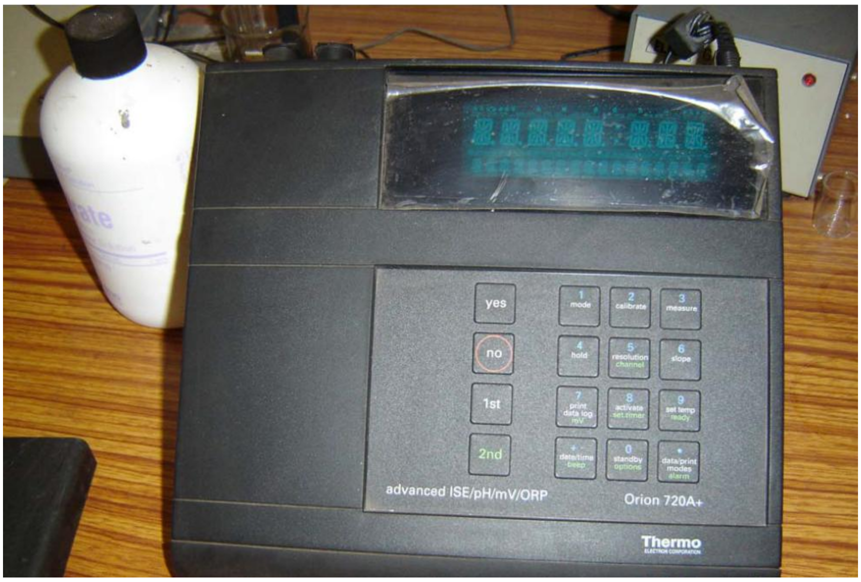
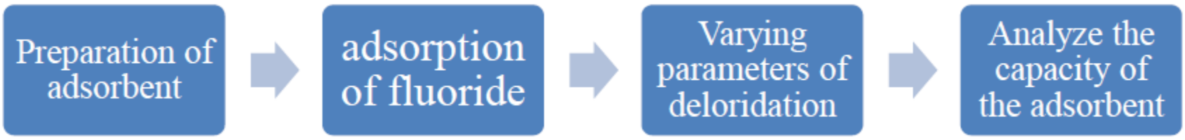


Figure-3.3: Orion 720 A+ ion analyzer with ion selective electrode

3.5 Experimental procedure

The figure below will show the experimental procedure that is implemented in this study.



Batch sorption studies were conducted to study the effect of controlling parameters like contact time, adsorbent dosage, solution pH, particle size, initial concentration etc. All the experiments were conducted at room temperature (29±2$_0$C).

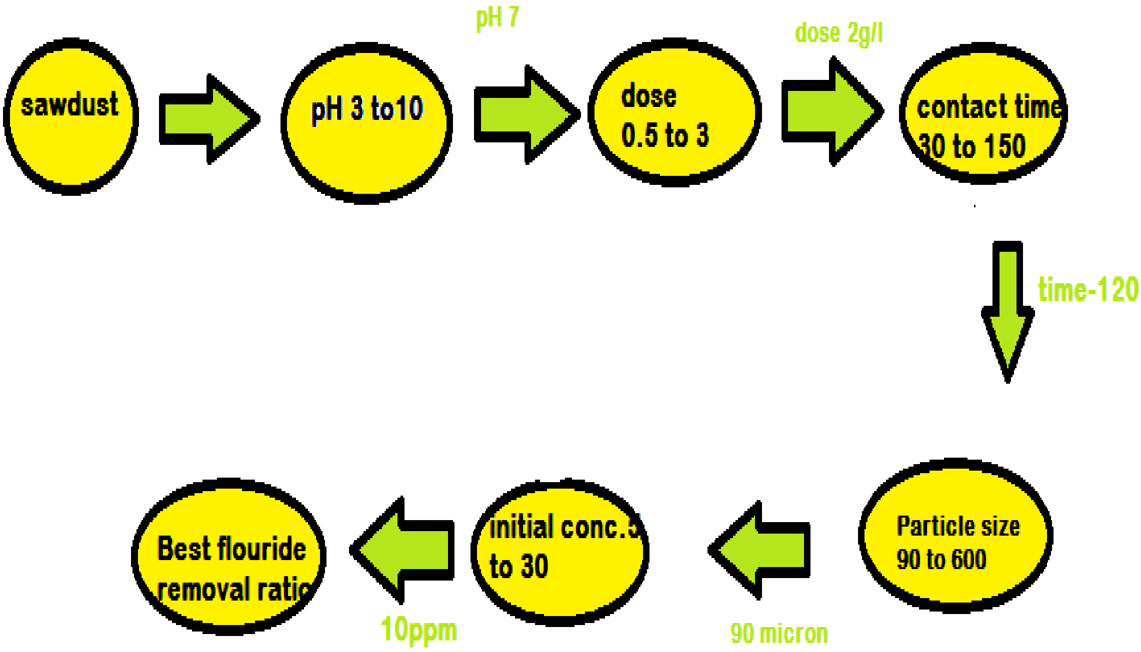


Figure 3.4: Experimental programme for sawdust

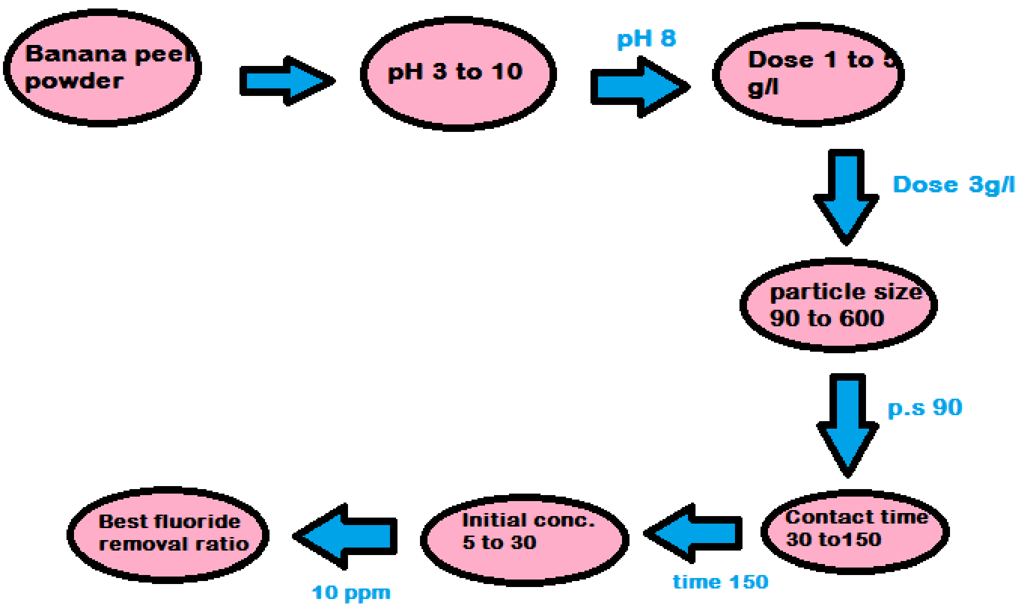


Figure 3.5: Experimental programme for Banana peel powder

3.6. Methodology(Batch adsorption)

Adsorption experiments were carried out for the determination of pH, adsorbent dose variation, equilibrium time and kinetics, selection of an isotherm, effect of temperature and evaluation of thermodynamic parameters. The influence of pH , adsorbent concentration and particle size ,contact time , initial fluoride concentration were evaluated during the present study. Experiments were carried out by adding desired amount of adsorbent to 500ml of the test solution in a jar and then kept in jar test apparatus for continuous agitation at 150 rpm and fixed time. Initial fluoride concentration was kept at 10mg/L in all cases except in those, where the effect of initial fluoride concentration was to be studied. After the fixed time the solids were separated through filtration. The solutions were collected for analysis and fluoride concentration in the solution was determined by using ion selective meter. Control experiments, performed without addition of adsorbent, confirmed that the sorption of fluoride on the walls of jar was negligible. The amount of fluoride adsorbed per unit adsorbent (qe) (mg g-1) was calculated according to a mass balance on the fluoride concentration using equation

q_e= (C0-Ce)V/m

Where, V = Volume (L) of the equilibrated solution,

m = Mass of the adsorbent (g),

Ci = Initial concentration of metal ion (mg L-1),

Ce = Equilibrium concentration of Fe+2 (mg L-1).

The percent removal (%) of fluoride was calculated using the following equation:

Removal(%) =(C0-Ce/C0) x 100

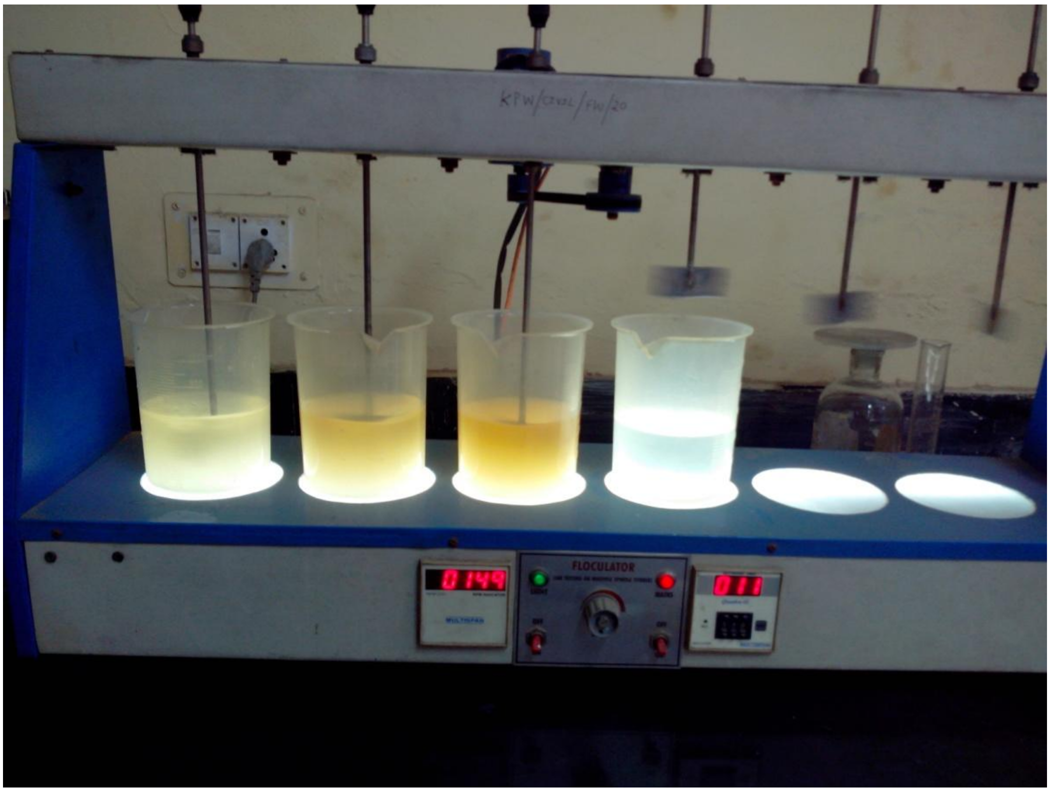


Figure 3.6: Image of jar test apparatus used in the study

Chapter-4

RESULTS AND DISCUSSIONS

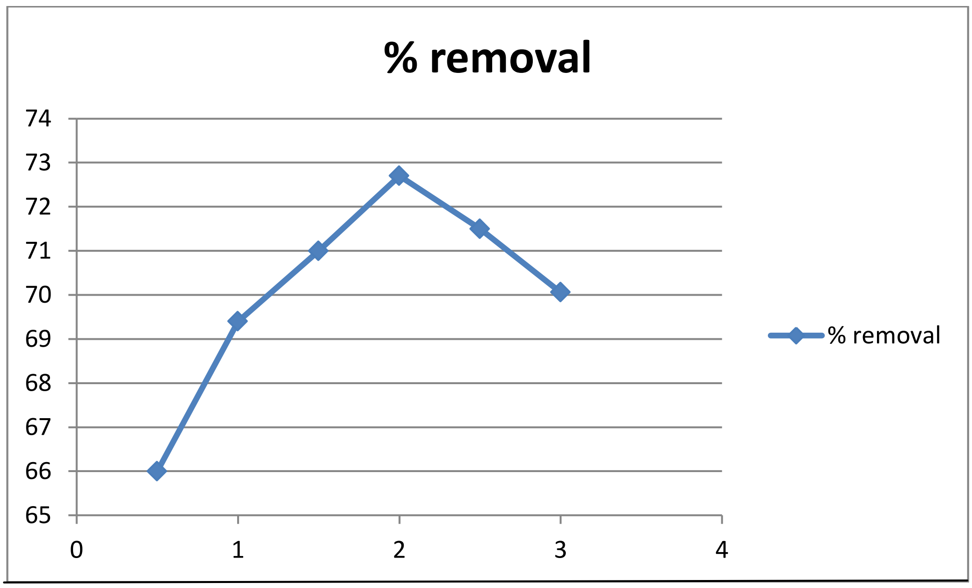
4.1Effect of adsorbent dose:

Adsorbent dose is an important parameter owing to its effect on efficiency (% removal) and on the amount of fluoride adsorbed per unit weight of biomass (qe). The influence of adsorbent dose on fluoride removal is checked at a fixed initial fluoride concentration of 10 mg/L, pH 6-7 at temperature 27±3°C, agitation speed: 150 rpm, Contact time: 150 minutes, particle size 150µm.

Table4.1: Effect of Adsorbent dose on the adsorption of fluoride using sawdust and Banana peel powder.

Sawdust			Banana peel powder		
Dose	**% removal**	**qe(mg/g)**	**Dose**	**% removal**	**qe(mg/g)**
0.5	66	13.2	1	57	5.7
1	69.4	6.94	2	60	5.2
1.5	71	4.73	3	65.7	2.19
2	72.7	3.635	4	73	1.82
2.5	71.5	2.86	5	76.4	1.52
3	70.06	2.35			

From the table it is clear that the percentage removal increased with increase in the adsorbent dose while loading capacity qe(amount of fluoride adsorbed per g of the adsorbent) is decreasing with increase in adsorbent dose



Adsorbent dose in gm/l →

Figure 4.1: Effect of Adsorbent dose on the adsorption of fluoride using sawdust

It was noticed that percentage removal of fluoride increased from 66% to 72.7% with a change in adsorbent dose from 0.5 g/L to 3 g/L respectively for sawdust. From Fig.4.1 result shows that the optimum dose of adsorbent was found 2 g/L for sawdust as adsorbent for fluoride concentration of 10mg/L, which gives 72.7% fluoride ion removal efficiency. An adsorbent dose of 2 g/L of sawdust is used for further study.

From the graph it can be seen that removal percentage for fluoride increases with increase in adsorbent dose of sawdust upto 2g/l after that the percentage removal starts decreasing maybe because of desorption of fluoride ion from sawdust.

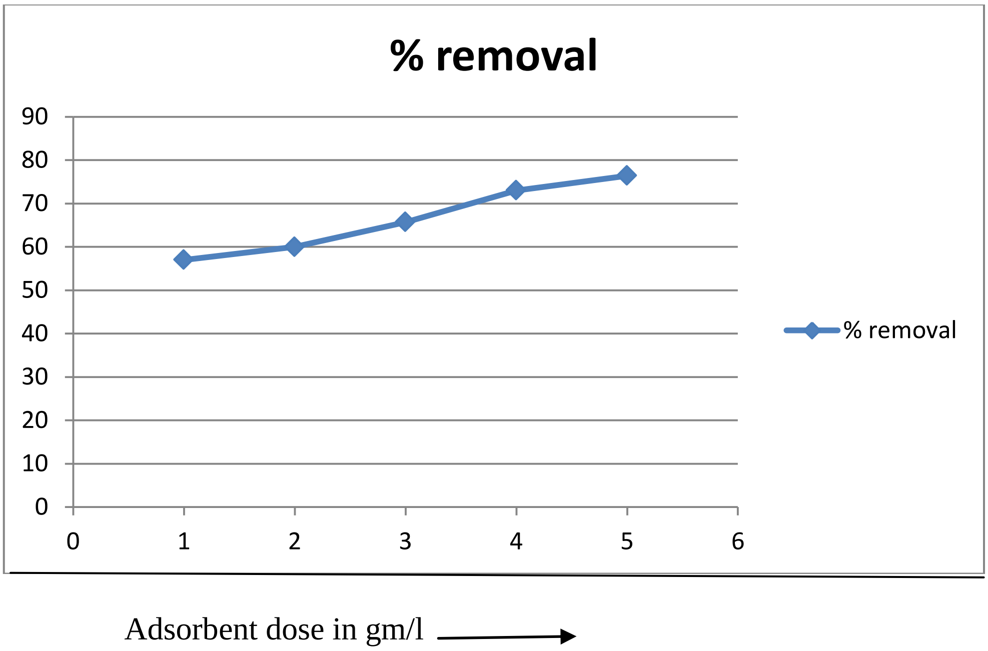


Figure 4.2: Effect of Adsorbent dose on the adsorption of fluoride using Banana peel powder

For banana peel powder adsorbent percentage removal increased from 57% to 76.4% with a change in adsorbent dose from 1g/l to 5g/l. From figure 4.2 result shows that the optimum dose of adsorbent was found 5g/l for banana peel powder used as adsorbent for fluoride concentration of 10mg/L, which gives 76.4% fluoride ion removal efficiency. An adsorbent 5g/l was used for further study.

For Banana peel powder the percentage removal of fluoride increased with increase in the adsorbent dose while loading capacity qe (amount of fluoride adsorbed per g of the adsorbent) gradually decreased with decreasing the number of interaction site between the adsorbent and adsorbate. This is probably due to increase of adsorption sites [29-30]. From the graph it is clear that a maximum level of fluoride adsorption occurs with increase in adsorbent dose of Banana peel powder.

4.2 Effect of pH

The pH of the solution affects the extent of adsorption because the distribution of surface charge of the adsorbent can change (because of the composition of raw materials and the technique of activation) thus varying the extent of adsorption according to the adsorbate functional groups [31-34].To find the effect of pH on adsorption by sawdust and Banana peel powder, study was conducted from pH 3 to10 in acidic and alkaline conditions respectively.

Table 4.2: Effect of pH on the adsorption of fluoride using sawdust

pH	% removal	qe(mg/g)
3	24.7	1.23
4	34.3	1.71
5	40.7	2.03
6	57	2.85
7	72.7	3.63
8	69.1	3.45
9	64	3.2
10	59.6	2.98

The percentage removal and adsorbent capacity of sawdust is calculated in the above table with experimental conditions: Initial fluoride concentration: 10.0 mg/L, Dose 2g/l, agitation speed: 150 rpm, Contact time: 150 minutes, Temperature: 303 K, particle size 150µm

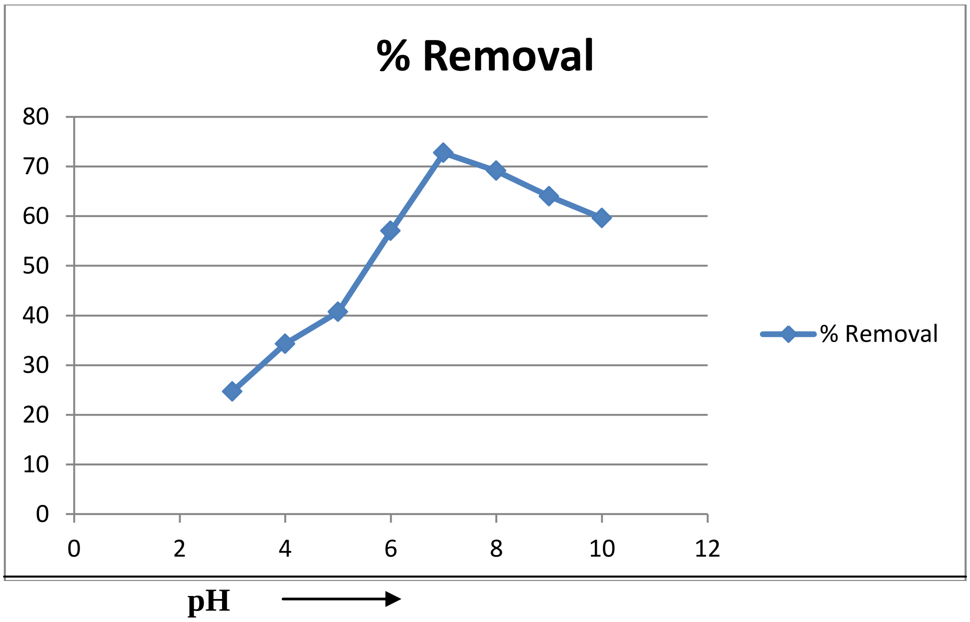


Figure 4.3: Effect of pH on the adsorption of fluoride using sawdust

The graphical representation of effect of pH on adsorption onto sawdust is shown in Figure 4.3 and found that the removal of fluoride was increased up to pH 7 and then decreases for sawdust. Highest adsorption of fluoride was found to be between 70.6% to 75.6 % in the pH range 6.0 and 8.0. It is seen that the adsorption of fluoride is good in the pH range 6.0-8.0.This may be due to neutralization of the negative charge at the surface of adsorbent material by greater hydrogen concentration at lower pH values.

Table 4.3: Effect of pH on the adsorption of fluoride using Banana peel powder

pH	% removal	qe(mg/g)
3	49.8	0.99
4	54.8	1.096
5	59.9	1.198
6	65.9	1.318
7	68	1.36
8	73.4	1.468
9	78	1.56
10	74.4	1.488

The percentage removal and adsorbent capacity of Banana peel powder is calculated in the above table with experimental conditions: Initial fluoride concentration: 10.0 mg/L, Dose 5g/l, agitation speed: 150 rpm, Contact time: 150 minutes, Temperature: 303 K, particle size 150µm

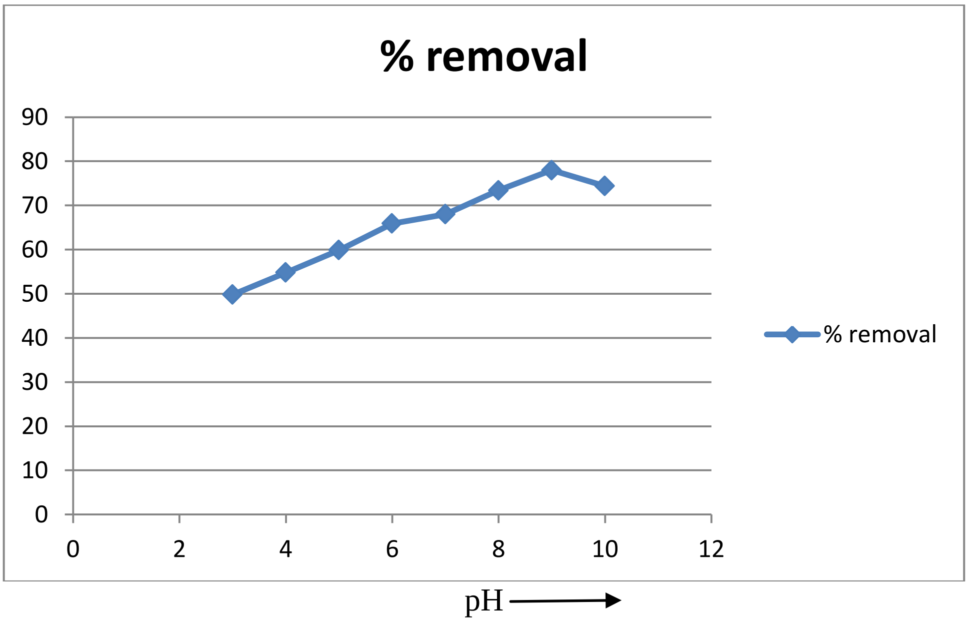


Figure 4.4: Effect of pH on the adsorption of fluoride using Banana peel powder

The removal of fluoride by Banana peel powder was noted to increase with increase in pH of the fluoride solution appreciably up to pH 9.0 as shown in Figure 4.4. Highest percentage removal of fluoride with Banana peel powder is measured as 78 % at pH 9.0.

For both the adsorbent (Sawdust and banana peel powder) in the acidic pH range, the amount of fluoride adsorbed slightly decreased and this can be due to the formation of weak hydrofluoric acid. In the alkaline condition pH range there was sharply drop in adsorption which may be due to the competition of the hydroxyl ions with the fluoride for adsorption.

4.3 Effect of particle size

Since adsorption is a surface phenomenon, the extent of adsorption is proportional to the specific surface area which is defined as that portion of the total surface area that is available for adsorption [35,36]. Thus more finely divided and more porous is the solid greater is the amount of adsorption accomplished per unit weight of a solid adsorbent [37]. The major contribution to surface area is located in the pores of molecular dimensions.

Experiments were conducted to find the influence of adsorbent particle size for a constant weight on the removal of fluoride ions, the defluoridation experiments were conducted using *sawdust and Banana peel powder* with three different particle sizes viz. 90–150, 150–300, and 300-600µm and experimental conditions: Initial fluoride concentration: 10.0 mg/L, pH: 7.0 for sawdust and 9.0 for Banana peel powder, agitation speed: 150 rpm, Contact time: 150 minutes, Temperature: 303 K, Dose: 2g/l for sawdust and 5g/l for banana peel powder.

Adsorption process will also depend on pore size and number of micro-, meso-, and macropores in the structure(Streat et al. 1995).

Table4.4: Effect of particle size on the adsorption of fluoride using sawdust and Banana peel powder

Particle size	Sawdust		Banana peel powder	
	% Removal	qe(mg/g)	% Removal	qe(mg/g)
90-150	71	3.55	76.4	1.52
150-300	69.6	3.48	64.5	1.29
300-600	69	3.45	57	1.14

As the adsorption process is a surface phenomenon, it is clear from table that the defluoridation efficiency of both(sawdust and banana peel powder) the sample with size

90µm registered high defluoridation efficiency, this is mainly true since the surface area and the number of active pores of the adsorbent increase with the decrease in particle size.

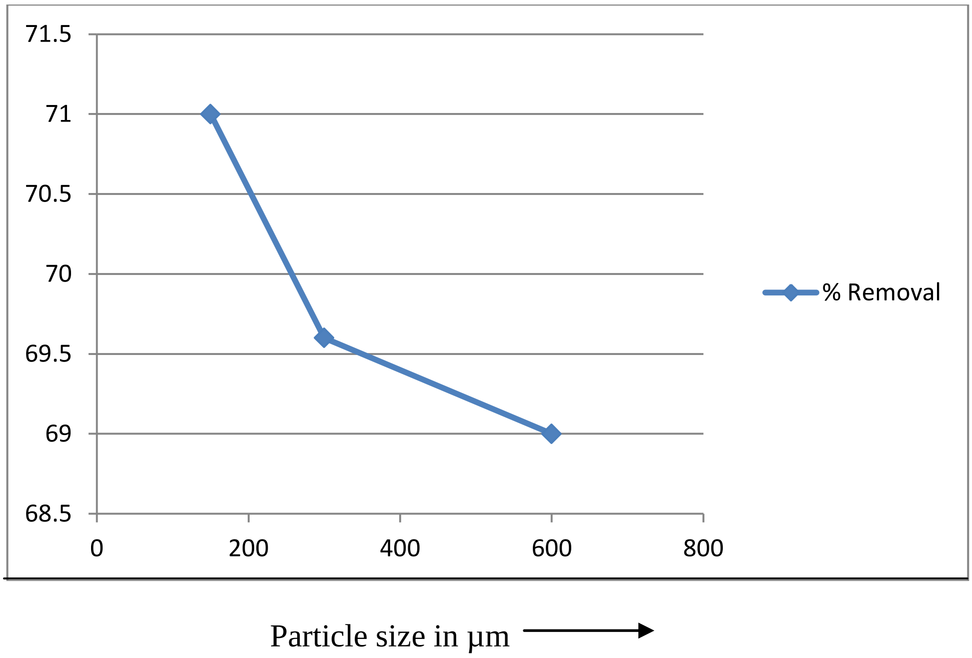


Figure 4.5: Effect of particle size on the adsorption of fluoride using sawdust

The percentages of fluoride removal by the sample with different particle sizes are seen in figure 4.5 with maximum percentage removal at 90µm size. Hence, the material with particle size of 90µm has been chosen for further experiments of sawdust as the adsorbents.

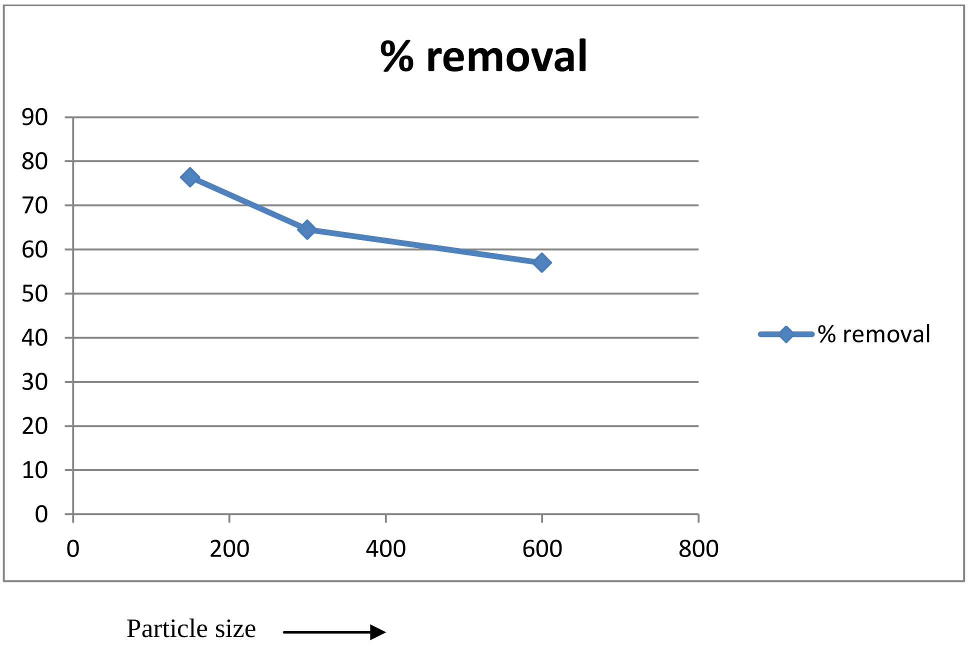


Figure 4.6: Effect of particle size on the adsorption of fluoride using Banana peel powder

The defluoridation efficiency of the sample with 90µm registered high defluoridation efficiency of 76.4 % due to larger surface area as shown in figure 4.6. Hence, the material with particle size of 90µm has been chosen for further experiments with Banana peel powder. Higher percentage of adsorption by both the adsorbents(sawdust and Banana peel powder) with smaller particle size is due to the availability of more specific surface area on the adsorbent surface.

4.4 Effect of contact time

It is very necessary to determine the effect of contact time required to reach equilibrium for designing batch adsorption experiments. The fluoride removal capacity qe (mg/g) on sawdust and Banana peel powder was determined by varying contact time (30-150 minutes) for the given experimental conditions: Initial fluoride concentration: 10.0 mg/L, pH: 7.0 for sawdust and 9.0 for Banana peel powder, agitation speed: 150 rpm, particle size: 90µm, Temperature: 303 K, Dose: 2g/l for sawdust and 5g/l for Banana peel powder.

Table 4.5: Effect of contact time on the adsorption of fluoride using sawdust

Contact time	Sawdust		Banana peel powder	
	%Removal	qe(mg/g)	%Removal	qe(mg/g)
30	65.2	3.26	76.4	1.52
60	71	3.55	79	1.58
90	72.6	3.63	80	1.6
120	73	3.65	81	1.62
150	72.7	3.635	81.3	1.62

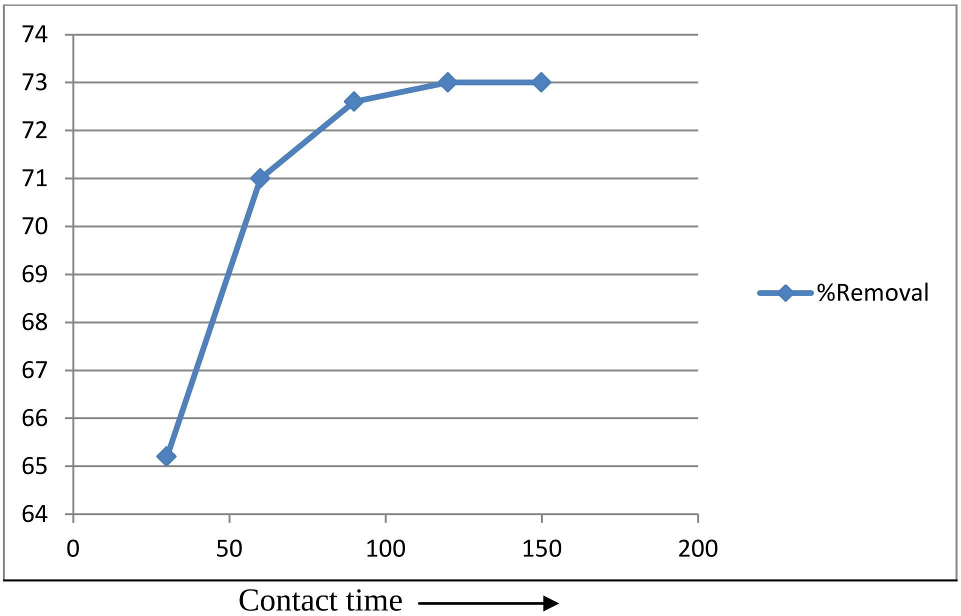


Figure 4.7: Effect of contact time on the adsorption of fluoride using sawdust

As illustrated in Figure 4.7, the adsorption of fluoride increased with rise in contact time up to 120 min and further increase in contact time did not enhance the fluoride adsorption process of sawdust. The adsorption process attained equilibrium after 120 min for sawdust. The fast adsorption rate at the initial stage may be explained by an increased availability in the number of active binding sites on the adsorbent. Similar pattern was observed for adsorption of fluoride from aqueous solution onto tamarind seed, an unconventional biosorbent[38].

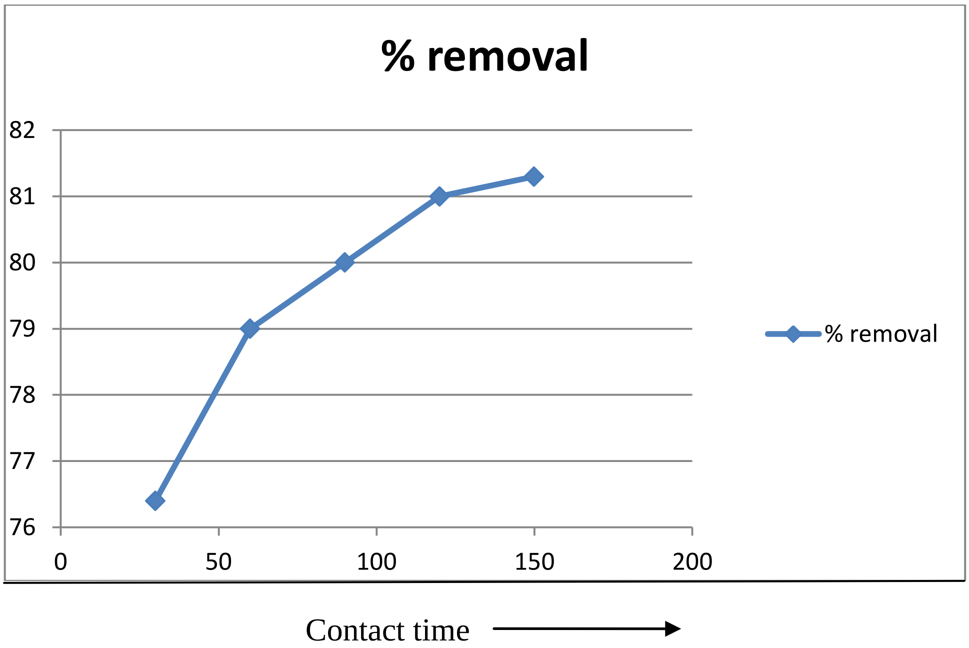


Figure 4.8: Effect of contact time on the adsorption of fluoride using Banana peel powder

For banana peel powder removal of fluoride as a function of contact time is shown in Figure 4.8. It was observed that with fixed amount of adsorbent the removal of fluoride increased with time and then attained equilibrium after 120 min. After reaching maximum point of removal the adsorbent reached in saturated condition (see Figure 4.8).

This experimental adsorption data of both adsorbents are analyzed for application of the pseudo-first-order, pseudo-second-order kinetic models, intraparticle diffusion and Elovich model.

4.5 Effect of initial concentration

The efficiency of fluoride adsorption for different initial F- concentrations ranging from 5 to 30.0 mg/L was investigated by carrying out adsorption experiments at optimum adsorbent dose (2.0 g /l for sawdust and 5g/l for banana peel powder) with 90 µm particle size, pH 7.0 for sawdust and 9.0 for banana peel powder, agitation speed 150 rpm at temperature 30 ^{0}C for a contact time of 120 min.

Table4.6: Effect of initial concentration on the adsorption of fluoride using sawdust

C_0	C_e	q_e
5	2.3	1.35
10	2.72	3.64
15	2.82	6.09
20	2.85	8.57
25	2.91	11.04
30	3.05	13.4

Table4.7: Effect of initial concentration on the adsorption of fluoride using banana peel powder

C_0	C_e	q_e
5	2	0.6
10	2.36	1.52
15	7.4	1.52
20	8.12	2.37
25	9.5	3.1

It follows from the tables 4.6 and 4.7 that the amount of fluoride uptake, and qe i.e. uptake per unit weight of sorbent increased with increase in initial fluoride concentrations for both the adsorbents.

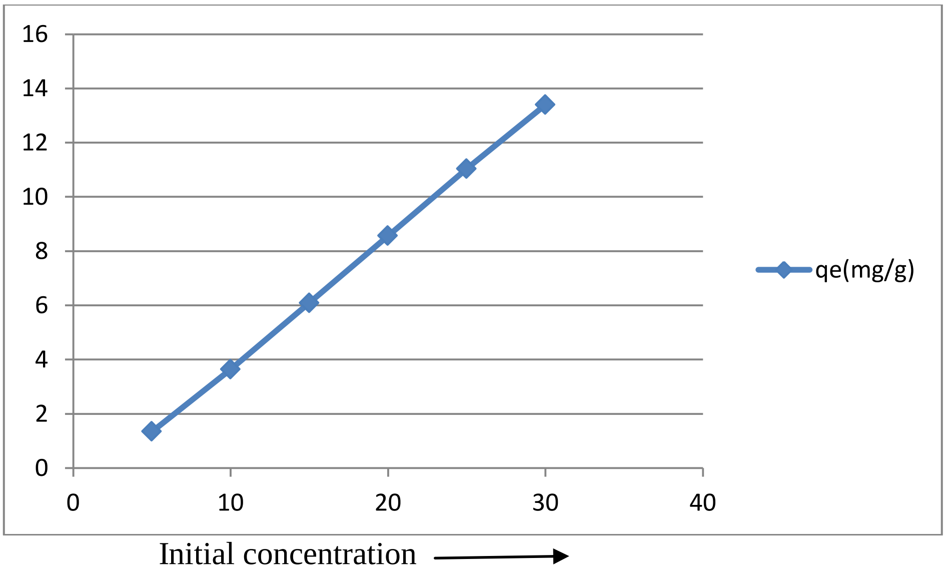


Figure4.9: Effect of initial concentration on the adsorption of fluoride using sawdust

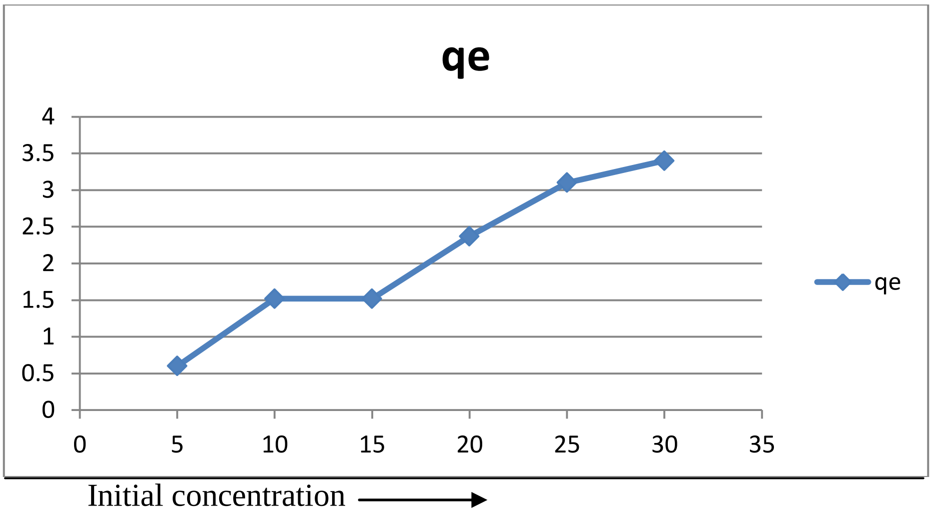


Figure4.10: Effect of initial concentration on the adsorption of fluoride using banana peel powder

Similar observations have been reported elsewhere (Choi and Chen, 1979, Muthukumaran, 1995). The increase in amounts of fluoride uptake by unit weight of sorbent with increase in initial fluoride concentrations is perhaps due to sorbate concentration gradient, which is the driving force for intraparticle transport which facilitates diffusion of sorbate molecule to the surface sites for ultimate attachment (Karthikeyan, 1982).

This experimental adsorption data is analyzed for application of the equilibrium study using Langmuir model, freundlich model and Tempkin model

4.6 Equilibrium of Sorption study

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the homogeneity/ heterogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms, such as Langmuir and Freundlich isotherms. These isotherms relate fluoride uptake per unit mass of adsorbent, qe, to the equilibrium adsorbate concentration in the bulk fluid phase Ce

Isothermal equilibrium studies were conducted employing different initial fluoride concentrations of 5, 10, 15, 20, 25, and 30 mg.L-1 of adsorbate. Experimental results along with experimental conditions are presented in Table 4.8 and 4.9.

Table 4.8: Experimental results for sawdust

Dose (mg/l)	Initial concentration Co	final concentration Ce	(C0-Ce) mg/l	qe (mg/g)
2g/l	5	2.3	2.7	1.35
2g/l	10	2.72	7.28	3.64
2g/l	15	2.82	12.18	6.09
2g/l	20	2.85	17.15	8.57
2g/l	25	2.91	22.09	11.04
2g/l	30	3.05	26.95	13.4

Experimental conditions employed for the results in above table are pH: 7.0, agitation speed: 150 rpm, particle size:90µm, Temperature: 303 K, Dose: 2g/l, time: 120 min.

Table 4.9: Experimental results for Banana peel powder

Dose (mg/l)	Initial concentration Co	final concentration Ce	(C0-Ce) mg/l	qe (mg/g)
5g/l	5	2	3	0.6
5g/l	10	2.36	7.64	1.52
5g/l	15	7.4	7.6	1.52
5g/l	20	8.12	11.8	2.37
5g/l	25	9.5	15.5	3.1
5g/l	30	13	17	3.4

Experimental conditions maintained for the results in above tables are pH: 9.0, agitation speed: 150 rpm, particle size:90µm, Temperature: 303 K, Dose: 5g/l, time: 120 min.

4.6.1. The Langmuir isotherm

The Langmuir model is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane.

The Langmuir adsorption isotherm equation is represented in Eq. (1):

$$q = a\frac{bCe}{1+bCe} \qquad (1)$$

And the linearized form can be represented as:

$$\frac{1}{q} = \frac{1}{a} + \frac{1}{ab}\left(\frac{1}{Ce}\right) \qquad (2)$$

Where, q is the amount of solute adsorbed per unit weight of material, a is the maximum adsorption capacity, b is the Langmuir constant, and C_e is the equilibrium solute concentration.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, RL which is defined by Hall and Vermeylem (1966) as

RL = 1 / (1+bC0)

The values of *R*L indicate the type of isotherm to be irreversible (RL = 0), favorable (0 < RL < 1), linear (RL = 1) or unfavorable (RL > 1) (Ouazene et al., 2010).

The plot between 1/qe and 1/Ce is as shown in the figure 4.11 and 412

Table 4.10 Calculations for qe Langmuir using sawdust

Dose	Initial concentration Co	final concentration Ce	(C0-Ce) mg/l	qe (mg/g)	1/Ce	1/qe	qe langmuir
2g/l	5	2.3	2.7	1.35	0.434	0.74	0.195
2g/l	10	2.72	7.28	3.64	0.367	0.274	3.57
2g/l	15	2.82	12.18	6.09	0.354	0.164	5.204
2g/l	20	2.85	17.15	8.57	0.35	0.116	5.98
2g/l	25	2.91	22.09	11.04	0.343	0.09	8.43
2g/l	30	3.05	26.95	13.4	0.327	0.074	-2.12

qe Langmuir for Sawdust as adsorbent is calculated in the table 4.10 using the values of a and b measured from the slope and intercepts of figure 4.11

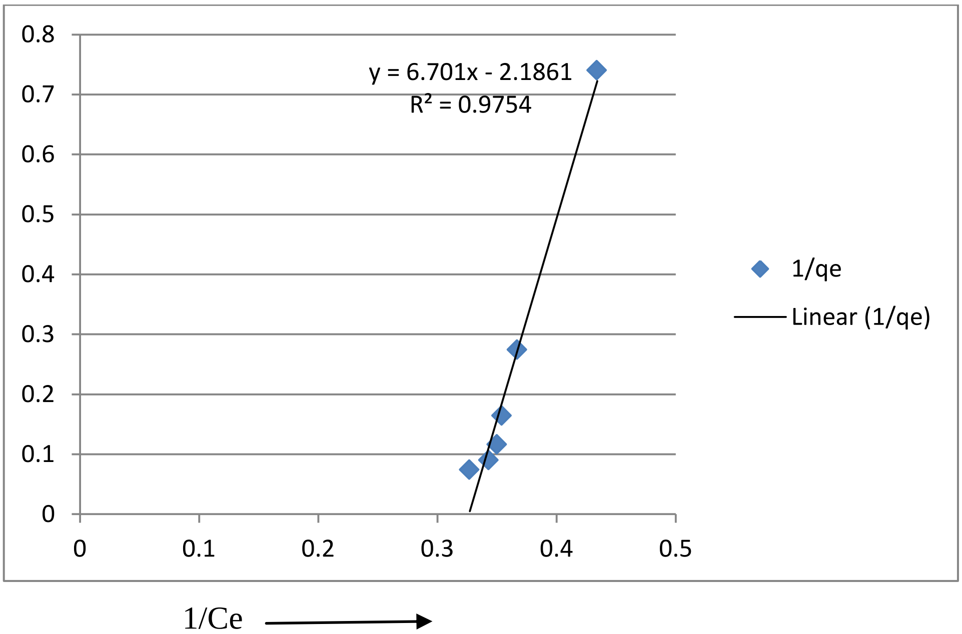


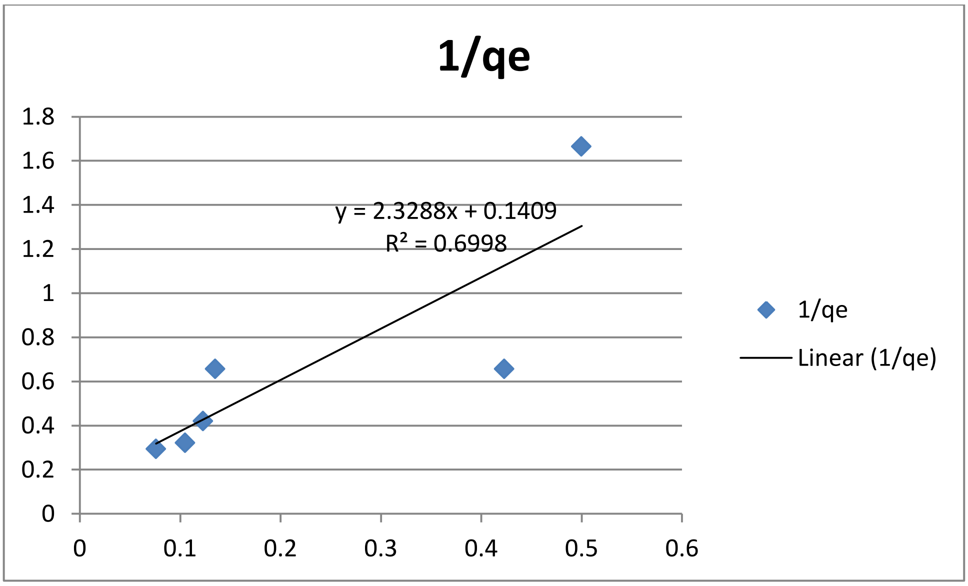
Figure 4.11 Langmuir isotherm for fluoride adsorption using sawdust

From the figure 4.11 values of a is 0.457 and b is 0.326 are determined from slopes and intercepts of the plot. The value of coefficient of correlation was found to be 0.9754 indicating Langmuir isotherm model showed excellent fit to the experimental data with high correlation coefficients. The values of *R*L =0.234 indicate the favourable adsorption isotherm.

Table 4.11 Calculations for qe Langmuir using Banana peel powder

Dose	Initial concentration Co	final concentration Ce	(C0-Ce) mg/l	qe (mg/g)	1/Ce	1/qe	qe langmuir
5g/l	5	2	3	0.6	0.5	1.666	0.759
5g/l	10	2.36	7.64	1.52	0.423	0.657	0.8794
5g/l	15	7.4	7.6	1.52	0.135	0.657	2.213
5g/l	20	8.12	11.8	2.37	0.123	0.421	2.322
5g/l	25	9.5	15.5	3.1	0.105	0.322	2.574
5g/l	30	13	17	3.4	0.076	0.294	3.106

qe Langmuir for Banana peel powder as adsorbent is calculated in the table 4.11 using the values of a and b measured from the slope and intercepts of figure 4.12



1/Ce →

Figure 4.12: Langmuir isotherm for adsorption of fluoride using Banana peel powder

From the figure 4.12 values of a is 7.097 and b is 0.0605 are determined from slopes and intercepts of the plot. The value of coefficient of correlation was found to be 0.6998 indicating Langmuir isotherm model does not fit well to the experimental data with low correlation coefficients.

4.6.2. The Freundlich isotherm

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amounts of flouride adsorbed per unit mass of adsorbent, qe, and the concentration of the flouride at equilibrium, Ce.

$$q = KfCe^{1/n} \quad (3)$$

The logarithmic form of the equation becomes

$$logq = log(Kf) + \frac{1}{n}log(Ce) \quad (4)$$

Where q = the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg g-1)

Ce = the equilibrium solute concentration (mg L-1)

KF = the measurement of the adsorption capacity (mg g-1) based on freundlich isotherm

n = the adsorption equilibrium constant

The ability of Freundlich model to fit the experimental data was examined. Plot between logCe and logqe was drawn to generate the intercept value of kf and the slope of n as shown in the Figure 4.13 and 4.14

Table 4.12 Calculations of Freundlich qe using sawdust

Dose	Initial concentration Co	final concentration Ce	(C0-Ce) mg/l	Qe (mg/g)	Ln Ce	Ln qe	qe freundlich
2g/l	5	2.3	2.7	1.35	0.832	0.3	1.23
2g/l	10	2.72	7.28	3.64	1	1.29	5.059
2g/l	15	2.82	12.18	6.09	1.036	1.806	6.859
2g/l	20	2.85	17.15	8.57	1.047	2.14	7.499
2g/l	25	2.91	22.09	11.04	1.068	2.401	8.938
2g/l	30	3.05	26.95	13.4	1.115	2.59	13.28

qe freundlich was calculated in table 4.12 using Kf and n determined from the slope and intercepts of the plot given below in figure 4.13

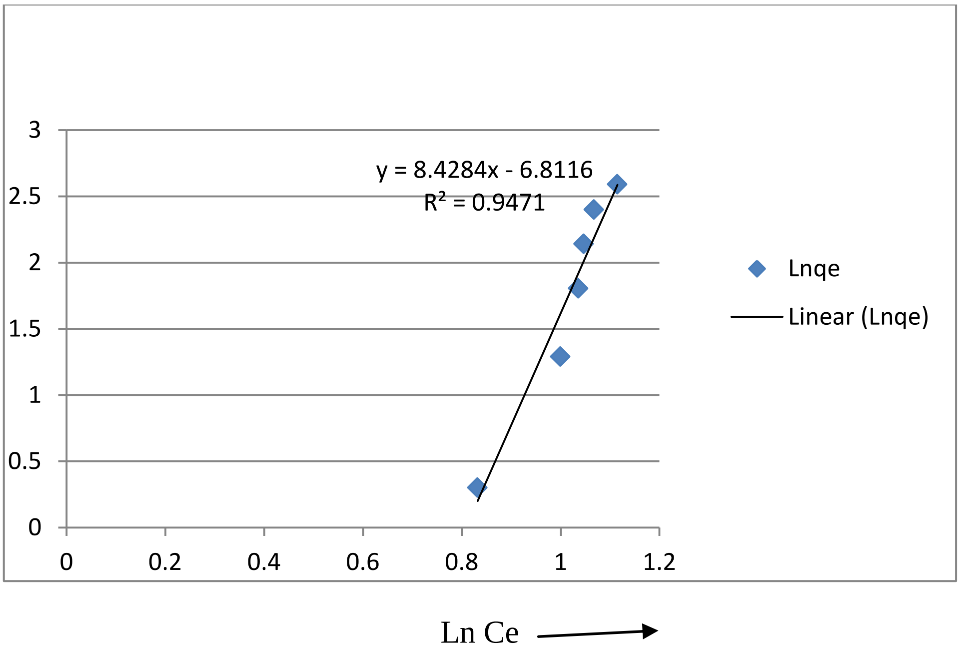


Figure4.13:Freundlich isotherm for adsorption of fluoride using sawdust

The values of KF=0.0011 (measurement of the adsorption capacity (mg g-1)) based on freundlich isotherm and n =0.1186 (the adsorption equilibrium constant) is determined from the plot shown in figure 4.13, giving the coefficient of correlation as 0.9471.

Table 4.13 Calculations of Freundlich qe using Banana peel powder

Dose	Initial concentration Co	final concentration Ce	(C0-Ce) mg/l	Qe (mg/g)	Ln Ce	Ln qe	qe freundlich
5g/l	5	2	3	0.6	0.693	-0.51	0.85
5g/l	10	2.36	7.64	1.52	0.858	0.418	0.957
5g/l	15	7.4	7.6	1.52	2.001	0.4187	2.171
5g/l	20	8.12	11.8	2.37	2.094	0.862	2.32
5g/l	25	9.5	15.5	3.1	2.251	1.131	2.596
5g/l	30	13	17	3.4	2.564	1.223	3.25

qe freundlich was calculated in table 4.13 using Kf and n determined from the slope and intercepts of the plot given below in figure 4.14

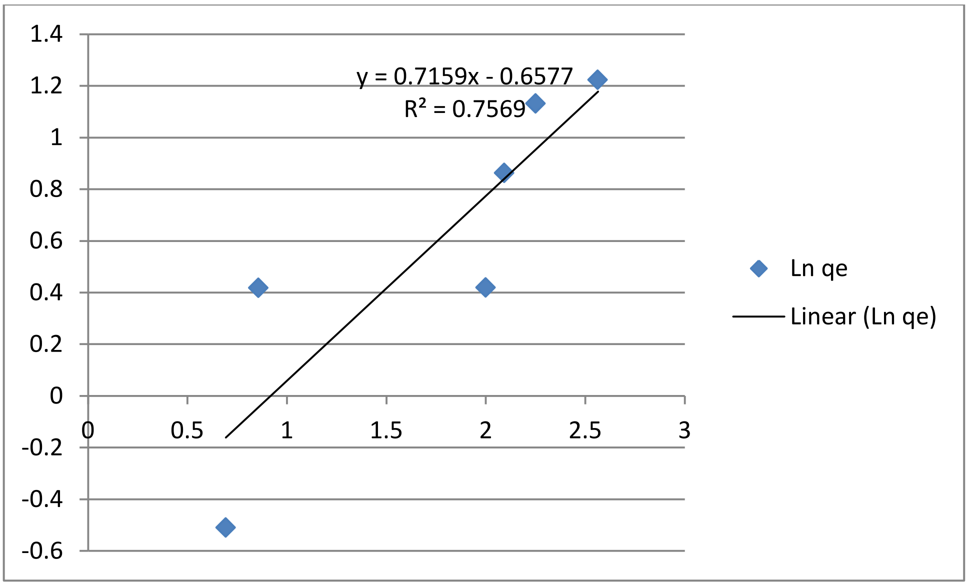


Figure 4.14: Freundlich isotherm for adsorption of fluoride using Banana peel powder

The values of *K*F and 1/*n* were obtained from the slope and intercept of the linear Freundlich plot of log *q*e versus log*C*e and were found to be 0.518mg/g and 0.7163 respectively, with regression coefficient (*R*2) of 0.7569. Since the value of adsorption intensity (heterogeneity factor) is less than unity, it indicates that system shows favorable adsorption.

4.6.3 Tempkin isotherm

The Tempkin isotherm (Wasewar et al., 2009) contains a factor that explicitly takes in account adsorbing species- adsorbate interactions. This isotherm assumes that

(i)the heat of adsorption of all molecules in the layer decreases with coverage due to adsorbate-adsorbent interaction, and

(ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The Tempkin isotherm is represented by the following equation:

qe = RT ln (KT Ce) / b (5)

Equation (5) can be linearized as in equation (6).

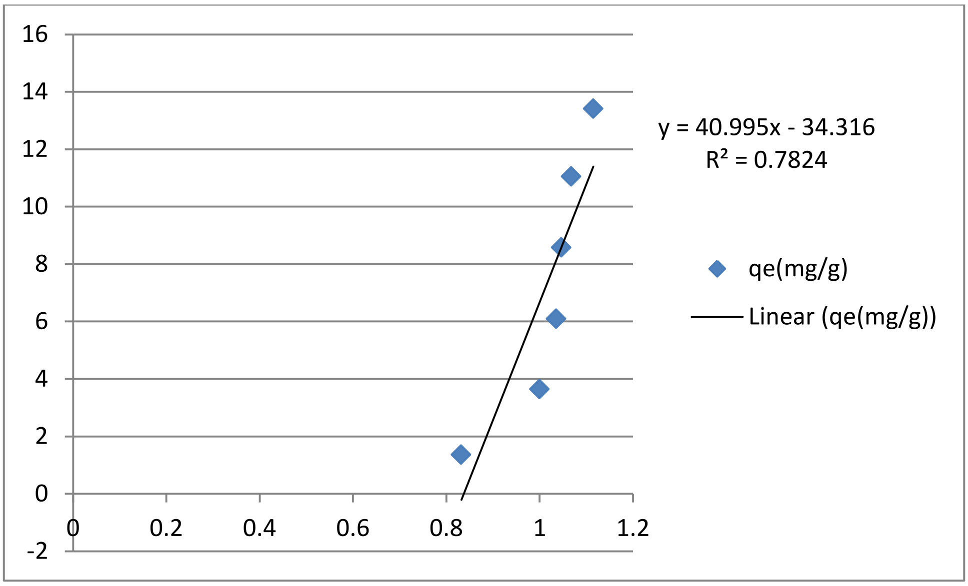
qe = B1 ln KT + B1 ln Ce (6)

Where, B1 = RT / b

Regression of qe versus ln Ce enables the determination of isotherm constants KT and B1.

Table 4.14:Calculation of Tempkin qe using sawdust

Dose	Initial concentration Co	final concentration Ce	(C0-Ce) mg/l	Qe (mg/g)	Ln Ce	Temp qe
2g/l	5	2.3	2.7	1.35	0.832	.025
2g/l	10	2.72	7.28	3.64	1	6.896
2g/l	15	2.82	12.18	6.09	1.036	8.377
2g/l	20	2.85	17.15	8.57	1.047	8.810
2g/l	25	2.91	22.09	11.04	1.068	9.66
2g/l	30	3.05	26.95	13.4	1.115	11.59



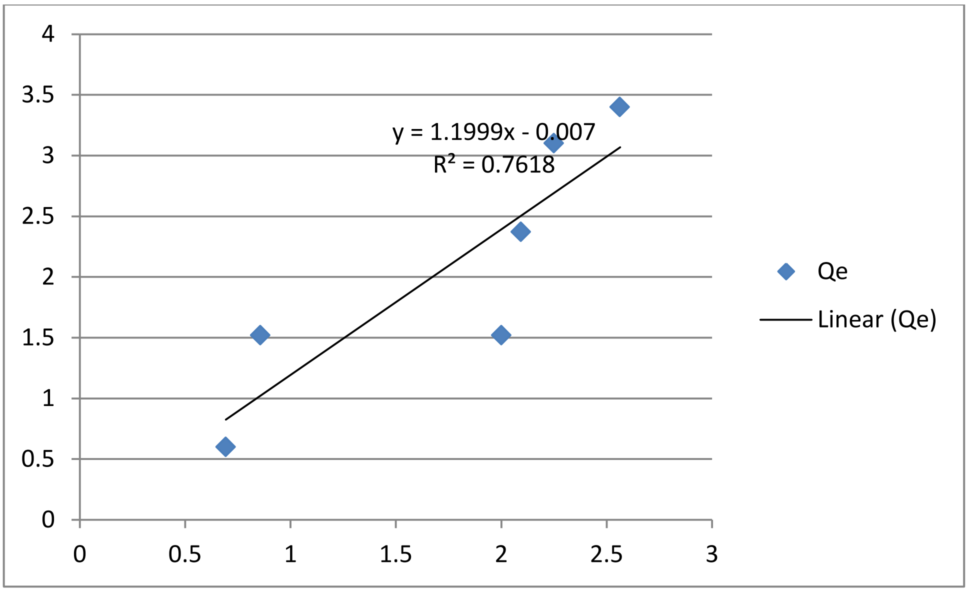
ln Ce →

Figure 4.15: Tempkin isotherm for adsorption of fluoride using sawdust

Isotherm constants KT= 0.435 and B= 40.995 are calculated from the plot in figure 4.15. The coefficient of correlation of the linear plot between ln Ce and qe is determined as 0.7824.

Table 4.15:Calculation of Tempkin qe using Banana peel powder

Dose	Initial concentration Co	final concentration Ce	(C0-Ce) mg/l	Qe (mg/g)	Ln Ce	Temp qe
5g/l	5	2	3	0.6	0.693	0.824
5g/l	10	2.36	7.64	1.52	0.858	1.0233
5g/l	15	7.4	7.6	1.52	2.001	2.394
5g/l	20	8.12	11.8	2.37	2.094	2.506
5g/l	25	9.5	15.5	3.1	2.251	2.694
5g/l	30	13	17	3.4	2.564	3.07



Ln Ce →

Figure 4.16:Tempkin isotherm for adsorption of fluoride using Banana peel powder

Isotherm constants KT= 0.9942and B= 1.199 are calculated from the plot in figure 4.16. The coefficient of correlation of the linear plot between ln Ce and qe is determined as 0.7618.

The values of sorption capacities and coefficient of correlation (R^2) for various sorbents and equilibrium models are as shown in the Table 4.16.

Table 4.16 Comparision of sorption capacities and coefficient of correlation

Adsorbent	Langmuir isotherm		
Sawdust	a	b	R^2
	0.457	0.326	0.9754
	Freundlich isotherm		
	Kf	1/n	R^2
	0.0011	8.4284	0.9471
	Tempkin isotherms		
	KT	B1	R^2
	0.435	40.995	0.7824
Banana peel powder	Langmuir isotherm		
	a	b	R^2
	7.097	.0605	0.6998
	Freundlich isotherm		
	Kf	1/n	R^2
	0.518	0.7163	0.7569
	Tempkin isotherms		
	KT	B1	R^2
	0.9942	1.1999	0.7618

From Table above, The values of coefficient of correlation (R^2) was obtained as 0.9754 for sawdust giving a best fit for Langmuir equation compared to Freundlich Isotherm and Tempkin isotherm. The monolayer capacity (a) and adsorption energy (b) calculated from the linear plot are given in the same table.

It follows from the data the equilibrium adsorption of fluoride follows Langmuir isotherm model onto sawdust, which reflects the formation of a monolayer of sorbate over a homogeneous surface of uniform energy and that the adsorbed layer is unimolecular.

It may also be observed that the isotherm fits of sawdust have negative intercepts which indicates that the removal is good at lower concentrations, but not as good, at higher concentrations.

Whereas the values of R^2 for Banana peel powder is 0.7618 giving best fit to Tempkin isotherm, indicating that the heat of adsorption of all molecules in the layer decreases with coverage due to adsorbate-adsorbent interaction.

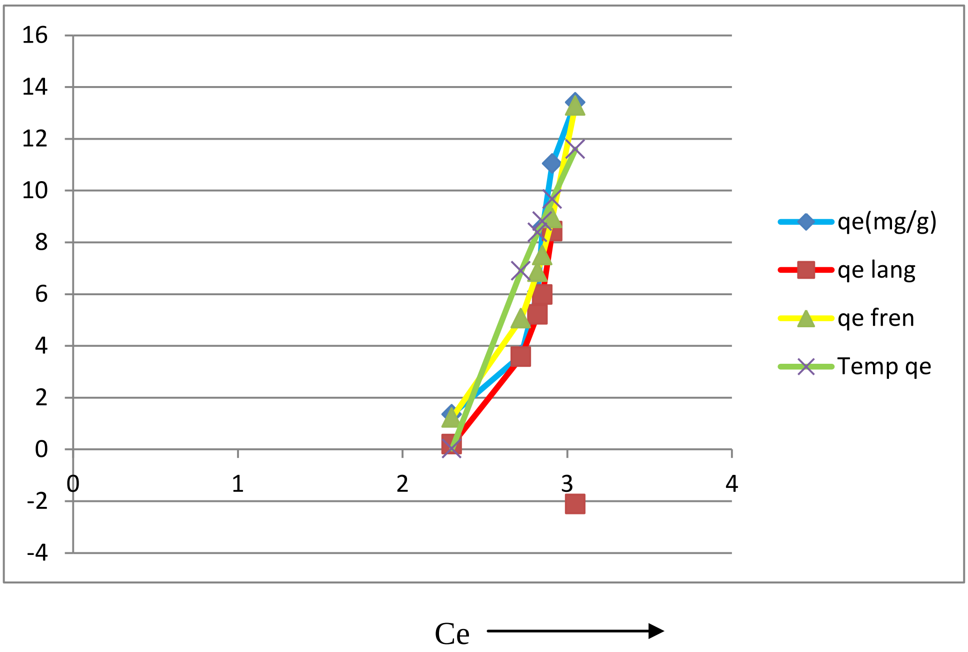


Figure 4.17: Comparison between the measured and modeled isotherm profiles for the adsorption of fluoride onto sawdust

From the figure 4.17 it is clear that the Langmuir isotherm models follows the experimental procedure best.

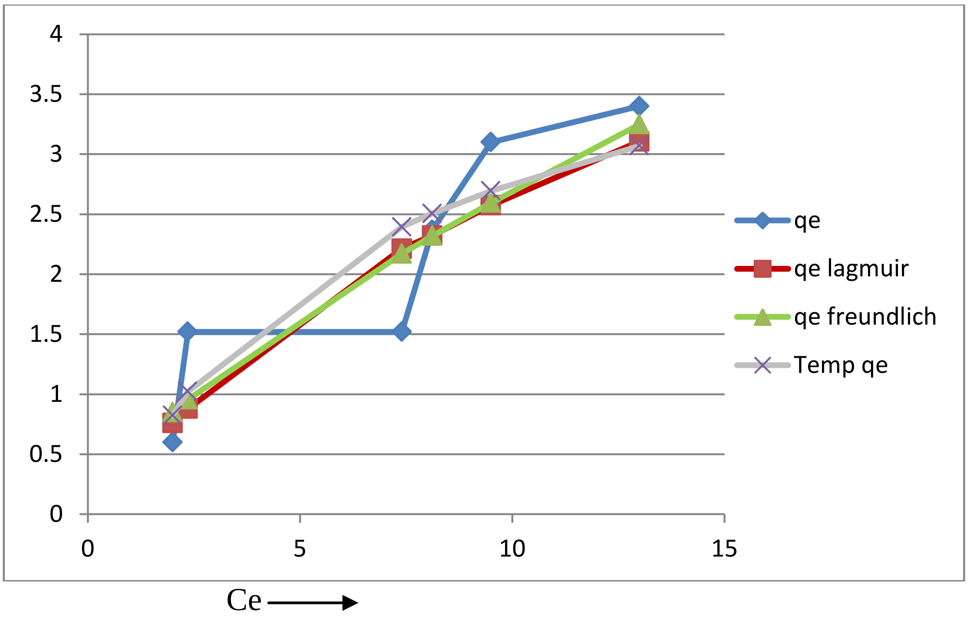


Figure 4.18: Comparison between the measured and modeled isotherm profiles for the adsorption of fluoride onto Banana peel powder

From figure 4.18 it is clear that the adsorption onto banana peel powder follows the Tempkin isotherm models best.

4.7 Kinetic model of adsorption

4.7.1 Pseudo-first-order model

In order to determine the controlling mechanism of adsorption process such as mass transfer and chemical reaction, the first order kinetic model is used to test the experimental data. A simple kinetics of adsorption is given by Lagergren rate equation.

$$\frac{dqt}{dt} = K1(qe - qt)$$

where K1 is the rate constant of first order adsorption; qe is the amount of flouride adsorbed at equilibrium and qt is the amount of flouride adsorbed at time.

Applying conditions:

qt = 0 at t = 0
qt = qt at t = t

$log(q_e\text{-}q_t) = logq_e - (k_1t/2.303)$

Table 4.17: Calculations of Pseudo-first-order sorption kinetics of fluoride onto sawdust

Time(min)	qe	Qt	qe-qt	log(qe-qt)
30	3.65	3.26	0.39	-0.4
60	3.65	3.55	0.1	-1
90	3.65	3.63	0.02	-1.69
120	3.65	3.65	0	
150	3.65	3.65	0	

Based on experimental results, linear plots of log (qe-qt) versus t suggest the applicability of Lagergren first order equation. The rate constant was calculated from the slopes and values are given in Table 4.23. The effect of fluoride concentration on rate constants (k1) helps to describe the mechanism of removal of fluoride from aqueous solution.

Table 4.18:Calculations of Pseudo-first-order sorption kinetics of flouride onto Banana peel powder

Time(min)	qe	Qt	qe-qt	log(qe-qt)
30	1.62	1.52	0.1	-1
60	1.62	1.58	0.04	-1.397
90	1.62	1.6	0.02	-1.698
120	1.62	1.62	0	
150	1.62	1.62	0	

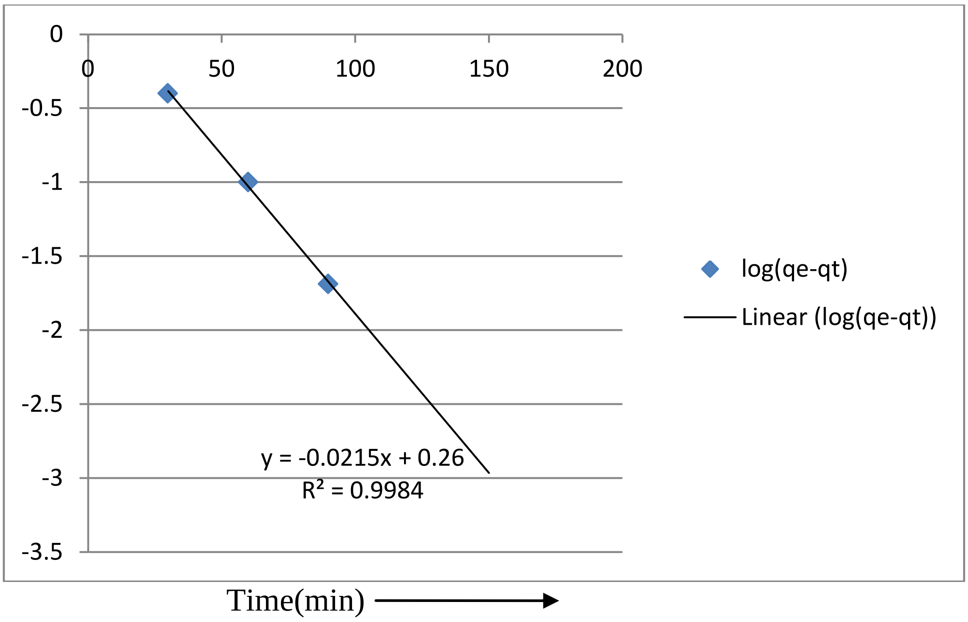


Figure4.19: Pseudo-first-order sorption kinetics of flouride onto sawdust

From Pseudo first order isotherm model shown in figure 4.19 it was calculated that that the qe,exp= 3.65 and qe,cal = 1.26 values from the pseudo-second order kinetic model are not close to each other therefore it does not follows the pseudo first order rate kinetics.

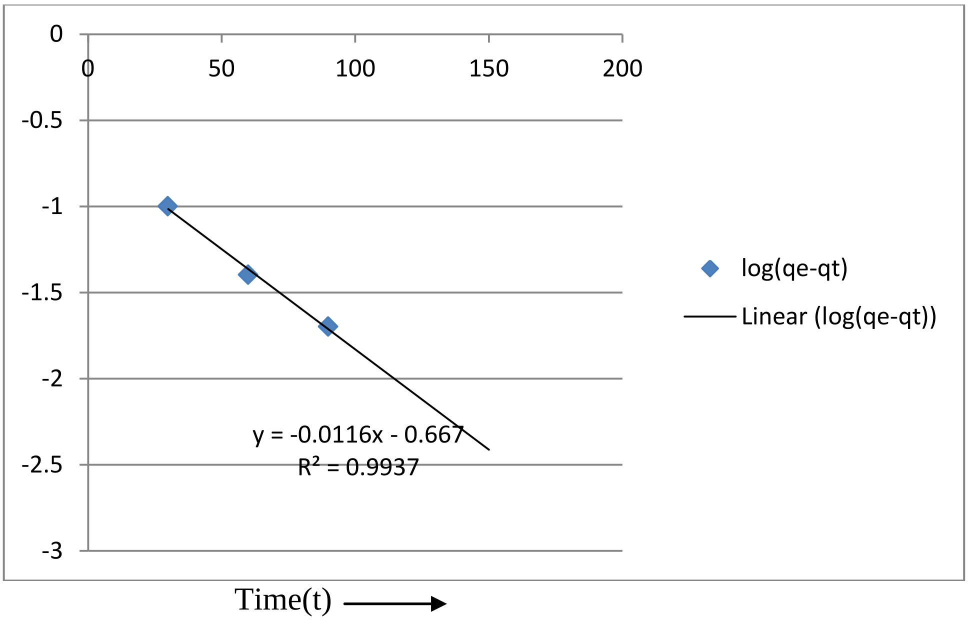


Figure4.20: Pseudo-first-order sorption kinetics of fluoride onto Banana peel powder

It was observed from the figure 4.20 that the pseudo-first-order model did not fit well. It was found that the calculated *q*e values do not agree with the experimental *q*e values (Table 4.23). This suggests that the adsorption of fluoride does not follow first-order kinetics.

4.7.2 Pseudo-second-order model

In this model, the rate-limiting step is the surface adsorption that involves chemisorption, where the removal from a solution is due to physicochemical interactions between the two phases.

The pseudo-second-order kinetics may be expressed in a linear form as

$$\frac{t}{qt} = \frac{1}{K2qe2} + \frac{1}{qet}$$

where the equilibrium adsorption capacity (*q*e), and the second order constants *k*2 (g/mg h) can be determined experimentally from the slope and intercept of plot *t*/*q*t versus *t* (Fig).

Table 4.19: Calculations of Pseudo-second-order sorption kinetics of flouride onto sawdust

Time(min)	qe	qt	t/qt
30	3.65	3.26	9.24
60	3.65	3.55	16.9
90	3.65	3.63	24.7
120	3.65	3.65	32.87
150	3.65	3.65	41.09

Table 4.20: Calculations of Pseudo-second-order sorption kinetics of flouride onto Banana peel powder

Time(min)	qe	qt	t/qt
30	1.62	1.52	19.736
60	1.62	1.58	37.974
90	1.62	1.6	56.25
120	1.62	1.62	74.074
150	1.62	1.62	92.592

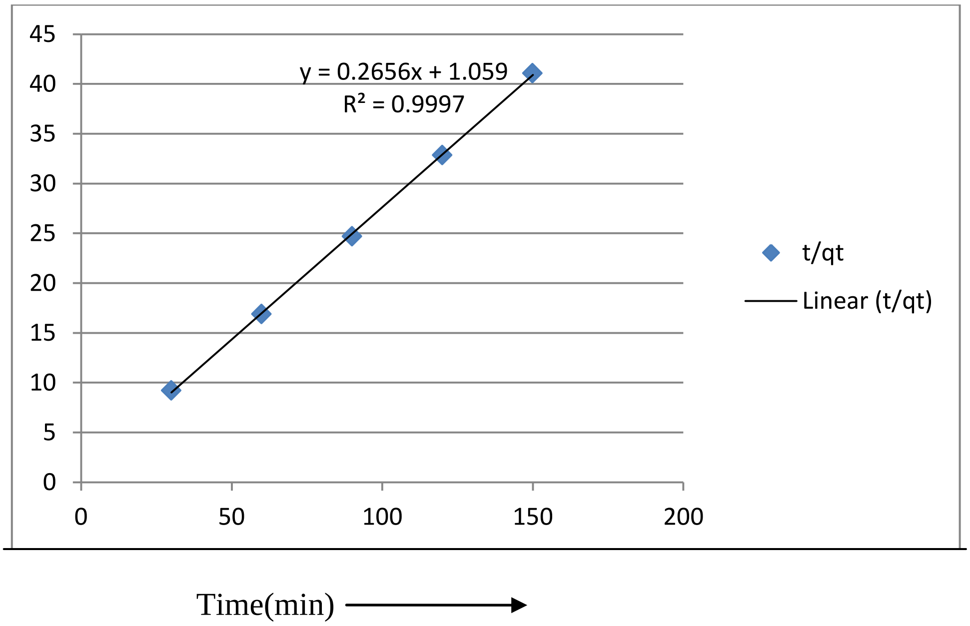


Figure4.21: Pseudo-second-order sorption kinetics of fluoride on sawdust

The constant calculated from the slop and intercept of the plots in figure 4.21 are given in Table 4.23. shows that R^2 values are higher than those obtained from the first-order kinetics. In addition, theoretical and experimental qe values are in agreement. Therefore, it is possible to prove that the adsorption process using Sawdust followed the second-order kinetic model.

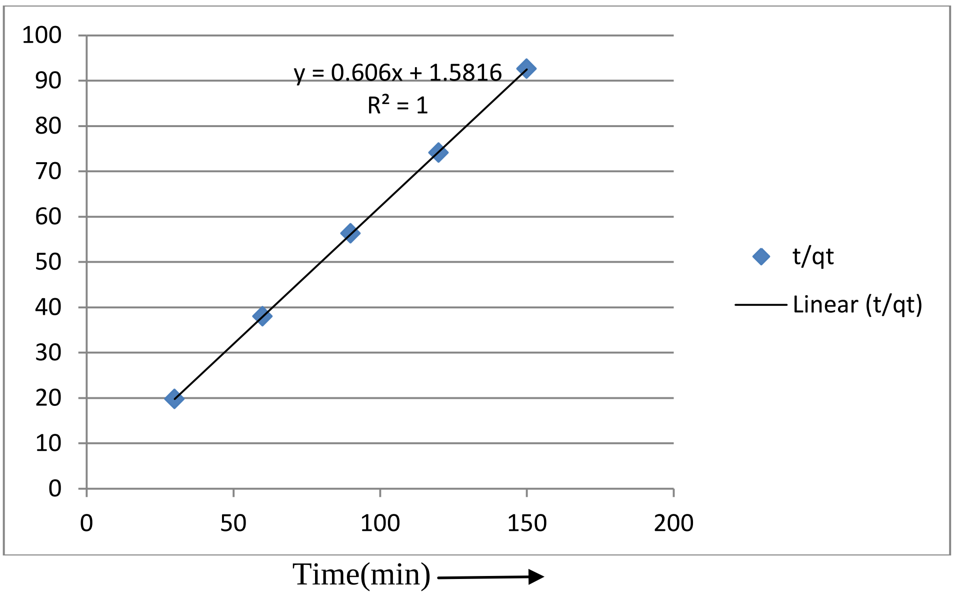


Figure4.22: Pseudo-second-order sorption kinetics of fluoride on Banana peel powder

The $k2$ and qe determined from the model for adsorption onto Banana peel powder are presented in Table 4.23 along with the corresponding correlation coefficients. The values of the calculated and experimental qe are also represented in Table 4.23 .

It can be seen from Table that there is an agreement between qe experimental and qe calculated values for the pseudo-second-order model. Hence, the pseudo-second-order model better represented the adsorption kinetics.

4.7.3 Intraparticle diffusion model

The intraparticle diffusion model describes adsorption processes, where the rate of adsorption depends on the speed at which adsorbate diffuses towards adsorbent (i.e., the process is diffusion-controlled), which is presented by Equation

$$q_t = K_3 t^{1/2} + c$$

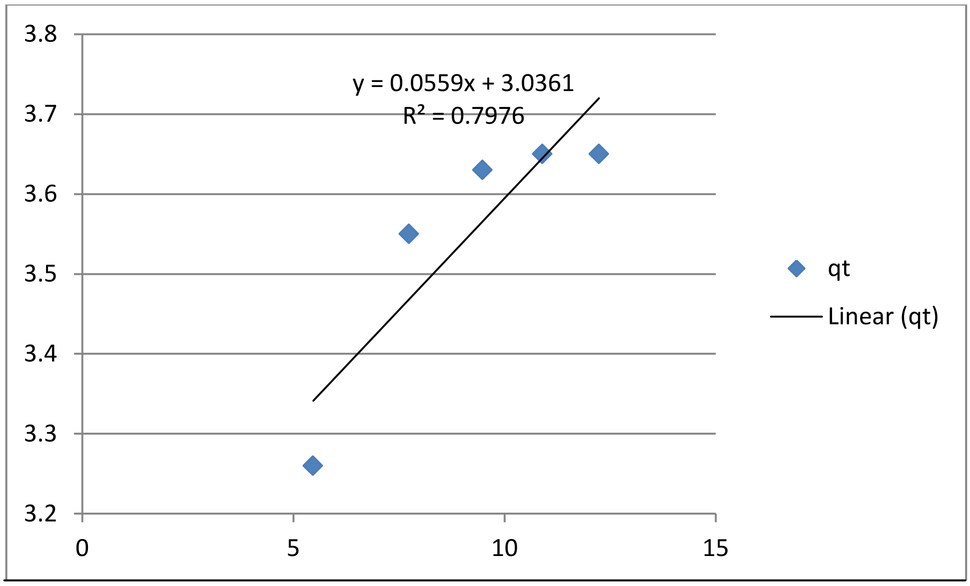
where, k_3 is the rate constant of the intraparticle transport (g/mg/min) and c is the intercept. The intraparticle diffusion model as fitted with the experimental data is presented in the plot of qt versus $t^{1/2}$ depicted in Figure and the values of k_3 and correlation coefficients are given in Table.

Table4.21: Calculations for intraparticle transport model kinetics of fluoride on sawdust

Time(min)	qe	qt	$t^{0.5}$
30	3.65	3.26	5.47
60	3.65	3.55	7.74
90	3.65	3.63	9.48
120	3.65	3.65	10.9
150	3.65	3.65	12.24

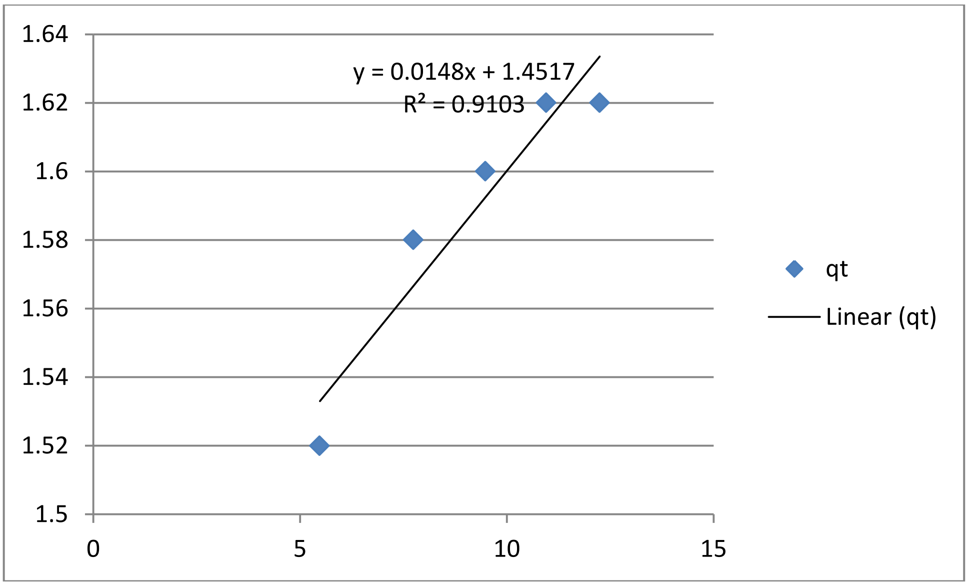
Table4.22: Calculations for intraparticle transport model kinetics of fluoride on Banana peel powder

Time(min)	qe	qt	$t^{0.5}$
30	1.62	1.52	5.477
60	1.62	1.58	7.745
90	1.62	1.6	9.486
120	1.62	1.62	10.954
150	1.62	1.62	12.247



Time(min) $t^{0.5}$ →

Figure4.23: Plots for evaluating intraparticle diffusion rate constant for sorption of fluoride onto sawdust



Time(min) →

Figure4.24: Plots for evaluating intraparticle diffusion rate constant for sorption of fluoride onto Banana peel powder

The data shown in Fig4.23 and 4.24 have an initial curved shape that is followed by a straight line. The curved shape of the plot is due to the diffusion of fluoride through the solution to the external surface of Sawdust and Banana peel powder. The straight line portion suggests a gradual adsorption stage, where intra-particle diffusion of fluoride on the Sawdust surface takes place. However, the extrapolated linear plot at different time did not pass through the origin which suggests that the intra-particle diffusion was not the rate-controlling step.

4.7.4. Elovich model:

A kinetic model of chemisorption was developed by Zeldowitsch in 1934. Previously Elovich's equation has been widely used to describe the adsorption of gas onto solid systems. Recently it has also been applied to describe the adsorption process of pollutants from aqueous solutions. The Elovich model equation is usually expressed as follows.

$$Dqt/dt = \alpha \exp(-\beta\, qt)$$

$$qt = \beta \ln(\alpha\beta) + \beta \ln t$$

Where qt is the sorption capacity at time t (mg/g), α is the initial sorption rate (mg/g/min) and β is the desorption constant (g/mg). The constants can be obtained from the slope and the intercept of a straight line plot of qt vs lnt.

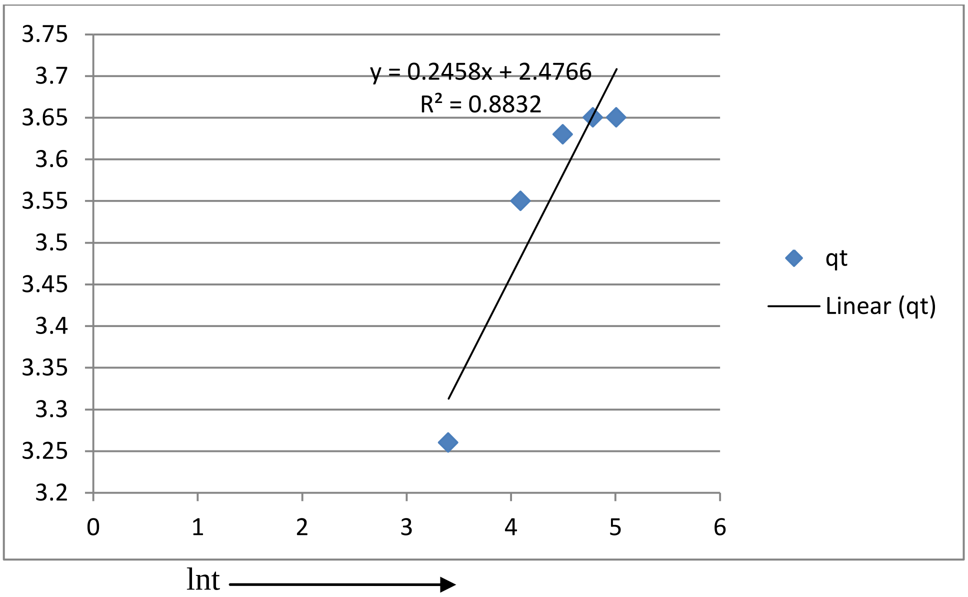


Figure4.25: Elovich model for adsorption of fluoride on to sawdust

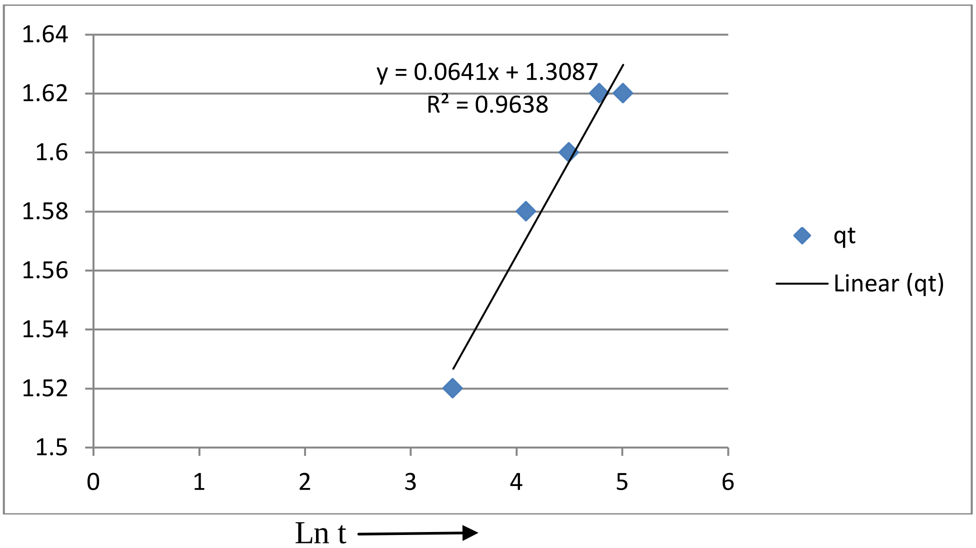


Figure4.26: Elovich model for adsorption of fluoride on to Banana peel powder

Elovich kinetic model constants α and β are calculated in Table 4.23 from the intercept and slope of plot qt against ln t, Figure 4.25 and 4.26. Constant α depends upon initial rate of adsorption which is found to be high but constant β which is desorption constant has the low value for the same adsorbent. α is initial rate constant which is found to be high for sawdust and Banana peel powder and thus better adsorbent of fluoride ions.

Table4.23: Comparison of the pseudo-first-order, pseudo-second-order, Intraparticle diffusion model and Elovich model for their adsorption rate constants and calculated and experimental qe values obtained

Sawdust			
Pseudo-first-order kinetic model			
qe Expt (mg/g)	K1 (l/min)	qe ,calc (mg/g)	R^2
3.65	0.0495	1.26	0.9984
Pseudo-second-order kinetic model			
qe Expt (mg/g)	K2 (l/min)	qe,calc (mg/g)	R^2
3.65	0.066	3.76	0.9997
Intraparticle diffusion model			
qe Expt (mg/g)	K3	qe,calc (mg/g)	R^2
3.65	0.0559	3.64	0.7976
Elvich model			
qe Expt (mg/g)	α	β	R^2
3.65	92.34	0.2458	0.8832
Banana peel powder			
Pseudo-first-order kinetic model			
qe Expt (mg/g)	K1 (l/min)	qe ,calc (mg/g)	R^2
1.62	0.026	0.5132	0.9937
Pseudo-second-order kinetic model			
qe Expt (mg/g)	K2 (l/min)	qe,calc (mg/g)	R^2
1.62	0.383	1.65	1
Intraparticle diffusion model			
qe Expt (mg/g)	K3	qe,calc (mg/g)	R^2
1.62	0.0148	1.613	0.9103
Elovich model			
qe Expt (mg/g)	α	β	R^2
1.6	735	0.0641	0.9638

The qe,exp and the qe,cal values from the pseudo-second-order kinetic model are very close to each other for both the adsorbents. The calculated correlation coefficients are also closer to unity for pseudo-second-order kinetics than that for the pseudo first-order kinetic model , intraparticle diffusion model and Elovich model. Therefore, the sorption can be approximated more appropriately by the pseudo-second-order kinetic model than the pseudo-first-order kinetic model and intraparticle diffusion model for the adsorption of fluoride onto sawdust and Banana peel powder.

Chapter-5

CONCLUSION

Fluoride removal from aqueous solution using Sawdust and Banana peel powder were studied using batch adsorption process. This study demonstrated the applicability of low cost waste material for removal of fluoride. Moreover, adsorption process for fluoride removal was investigated in this research.

5.1. Fluoride removal by Sawdust

5.1.1. Batch adsorption process for fluoride removal by Sawdust

In the present study, sawdust is used as the adsorbent and the following conclusion are made:

1) The adsorption of fluoride by using sawdust is very effective and its adsorption capacity is 3.63 mg/g at 10mg/L initial fluoride concentration. That indicates the adsorbent of sawdust is applicable for the removal of fluoride from underground water or drinking water.

2) Among different pH, an optimum fluoride removal was observed in the pH range of 6-8. That pH is very suitable and reasonable for practical application.

3) Fluoride adsorption was very rapid during the first 60minutes and after that gradually reached the pseudo-equilibrium value in 120min. Adsorption kinetics followed pseudo-second-order model and that may indicate the process of fluoride adsorption is mainly a chemisorptions process.

4) Langmuir isotherm model can fit the equilibrium data well in this study, whereas the other two isotherm models could not predict the equilibrium data well.

5) Briefly, the adsorbent is very cost effective, efficient and novel for the removal of fluoride from underground water or drinking water.

5.2. Fluoride removal by Banana peel powder

This study had proven that Banana peel powder have a good potential as a fluoride adsorbent since it able to adsorb fluoride quite effectively.

1)The optimum operating pH of the fluoride itself is maximized around pH 8 to pH 9 giving 78% fluoride removal, which can be easily maintained and can be easily converted back to drinkable pH after treatment of fluoride removal.

2) The adsorption capacity of Banana peel powder for fluoride was 1.52 mg/g at 30 ^{0}c. The sorption process was fitted well with Tempkin isotherm model.

3) Kinetic study results indicate that the adsorption process followed a pseudo-second-order kinetic model with coefficient of correlation as unity.

4) However due to the cheapness of Banana peel it can be easily replaced, a further study needed to be done to see which option is more feasible whether to replace it or to regenerate it.

The present research work established that Sawdust and Banana peel powder were excellent low-cost adsorbents for the removal of fluoride.

Future scope for study

The human curiosity to know the unknown things are the fundamental basis for scientific development. Based on the finding of present investigation, the following areas are recommended for further study.

1) The characterization of the adsorbents should be performed in order to provide a better understanding of the adsorption mechanism of fluoride on to the adsorbents.

2) An investigation using continuous process in terms of adsorbent particle size, column diameter and the presence of competitor ions have to be performed.

3) The process cost should be evaluated in order to make the application feasible.

4) An investigation of the chemistry of treated water must be carried out in order to reduce the health effect on the people who uses it.

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2) Suman mann, Dr.Anubha mandal, **Removal of Fluoride from Drinking Water Using Sawdust,** *Int. Journal of Engineering Research and Applications ISSN : 2248-9622, Vol. 4, Issue 7(Version 2), July 2014, pp.116-123*

Appendix