REMOVAL OF FLUORIDE FROM DRINKING WATER USING LOW COST WASTE ADSORBENTS

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF

MASTER OF TECHNOLOGY
IN
ENVIRONMENTAL ENGINEERING

Submitted by:
ANUJ KUMAR
2K12/ENE/03

Under the supervision of
Dr. ANUBHA MANDAL

DEPARTMENT OF ENVIRONMENTAL ENGINEERING
DELHI TECHNOLOGICAL UNIVERSITY
(FORMERLY DELHI COLLEGE OF ENGINEERING)
New Delhi-110042

REMOVAL OF FLUORIDE FROM DRINKING WATER USING LOW COST WASTE ADSORBENTS

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF

MASTER OF TECHNOLOGY

IN

ENVIRONMENTAL ENGINEERING

Submitted by:
ANUJ KUMAR
2K12/ENE/03

Under the supervision of
Dr. ANUBHA MANDAL

DEPARTMENT OF ENVIRONMENTAL ENGINEERING
DELHI TECHNOLOGICAL UNIVERSITY
(FORMERLY DELHI COLLEGE OF ENGINEERING)
New Delhi-110042

DELHI TECHNOLOGICAL UNIVERSITY
(formerly DELHI COLLEGE OF ENGINEERING)
MAIN BAWANA ROAD, NEW DELHI-110042

DEPARTMENT OF ENVIRONMENTAL ENGINEERING

CERTIFICATE

This is to certify that the research work embodied in this dissertation entitled "**Removal of fluoride from drinking water using Low cost waste adsorbents**" has been carried out in the Department of Environmental Engineering, Delhi Technological University, New Delhi. The work is approved for submission.

Date:
Place:

Dr. Anubha Mandal
(Supervisor)

DELHI TECHNOLOGICAL UNIVERSITY
(formerly DELHI COLLEGE OF ENGINEERING)
MAIN BAWANA ROAD, NEW DELHI-110042

DEPARTMENT OF ENVIRONMENTAL ENGINEERING

CERTIFICATE

This is to certify that the research work embodied in this dissertation entitled "**Removal of fluoride from drinking water using Low cost waste adsorbents**" has been carried out in the Department of Environmental Engineering, Delhi Technological University, New Delhi. This work is original and has not been submitted in part or full for any other degree or diploma to any university or institute. The work is approved for submission.

Date:
Place:

Anuj Kumar
(Candidate)

Acknowledgement

First and foremost I would like to thank my parents for their blessings, support and guidance throughout my academic career.

I sincerely convey my thanks to our HOD – Department of Environmental Engineering, **Dr. S.K. Singh,** for all the support and guidance. I would also like to thank my guide **Dr. Anubha mandal**, inspiration from her made my work enjoyable and I learned a lot during my master's degree. She has given me valuable insight in many aspects of research. Dr. Anubha Mandal's wide knowledge and her logical way of thinking have been of great value in shaping up my dissertation.

I express my sincere gratitude to all the faculty of Environment Engineering Department. Their moral support and encouragement has played an important part in completion of my master's degree.

My dissertation shall be incomplete if I do not thank my family. They have provided me support at every step during my master's degree, in my life. My friends have been a constant support and encouragement throughout.

It was my mother's dream, my father's vision which has brought me this far. I dedicate my thesis to my parents.

Anuj Kumar
M.Tech-Environmental Engineering

Dedicated to my parents…

Table of Contents

List of Tables

List of figures

Figure 4.13 Pseudo second order plot of effect of contact time for removal of fluoride by Pineapple peel powder

Abstract

Fluoride is a poison that accumulates in our bones. It has been associated with cancer in young males; osteoporosis; reduced I.Q; and hip fractures in the elderly, to name a few. Fluoride in nature exists as mineral deposits and, naturally, contaminates our ground water resources. Besides, surface water is also being polluted by fluoride due to various anthropogenic activities. The permissible limit of fluoride concentration in drinking water is 1.5mg/L according to WHO guidelines. Therefore, knowledge of its removal, using best technique with maximum efficiency is needed. Among various techniques adsorption occupies a prominent place in fluoride removal. As cost is an important consideration in most developing countries, efforts have been made to explore the possibility of using various low cost adsorbents that are abundant, readily available and are derived from waste materials.

In this study, the adsorption behavior of Lemon peel powder and Pineapple peel powder has been studied in order to consider its application for fluoride removal. The batch adsorption method was employed: Laboratory investigation of the potential of Lemon peel powder and Pineapple peel powder to remove fluoride from aqueous solution has been studied. The effects of various experimental parameters such as pH , adsorbent dosage and contact time were investigated . The equilibrium data have been analyzed by the Langmuir and Freundlich models.

Key words: Fluoride, Adsorption, Pineapple peel powder, Lemon peel powder, Batch adsorption

CHAPTER 1

INTRODUCTION

CHAPTER 1

INTRODUCTION

Pure water is scarce and is not easily available to all. Most sections of the society consume contaminated water and fall ill periodically, often resulting in epidemics. The water may be contaminated by natural sources or by industrial effluents. One such contaminant is fluoride. Fluoride is a salt of the element fluorine. Fluorine is the most highly reactive element of halogen family. Small amounts of it are found in seawater, bone, teeth and in ground water mainly as fluoride ion. Most fluoride associated with monovalent cations such as NaF and KF is water soluble, while the one formed with divalent cations such as CaF_2 and PbF_2 is generally insoluble. Fluoride is "more toxic than lead and less toxic than arsenic" and is an accumulative toxin. Fluoride has dual significance; if its content is less then it may result in problems like dental caries. World Health Organisation (WHO) recommend sit 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. Thus the requirement of fluoride content varies among countries and depends on the geography and the age of people involved.

International Status. The problem of excessive fluoride in drinking water has engulfed many parts of the world, and today many millions of people rely on groundwater with concentrations above the World Health Organization (WHO) guideline value .There are >20 developed and developing nations in which fluorosis Is endemic. High fluoride concentrations in groundwater are also found in the USA, Africa, and Asia. The most severe problem associated with high fluoride waters occurs in China, India, Sri Lanka ,and Rift Valley countries in Africa. High fluoride groundwater have been studied in detail in Africa, in particular in Kenya and Tanzania. High fluoride groundwater is also found in the East Upper Region of Ghana. In the early 1980s, it was estimated that ~260 million people worldwide (in 30 countries) were drinking water with >1 mg/L of fluoride.

Current Status in India. In India, fluoride was first detected in drinking water at Nellore district of Andhra Pradesh in 1937. At present, it has been estimated that fluorosis is prevalent in 17states of India, indicating that endemic fluorosis is one of the most alarming public health problem of the country, especially in Rajasthan, Madhya Pradesh, Andhra Pradesh, Tamil Nadu, Gujarat, and Uttar Pradesh. The state of Art Report of UNICEF confirms the fluoride problem in 177 districts of 20 states in India. At present, in India, endemic fluorosis is thought to affect approx. 1 million people.

1.1 Effects of fluoride

An intake of more than 6 mg of fluorine per day results in fluorosis. Fluorine being cumulative bone-seeking mineral, the resultant skeletal changes are progressive. Fluoride increases the stability of crystal lattice in bone, but makes the bone more brittle. Drinking fluoridated water will double the number of hip fractures. Exposure to excessive consumption of fluoride over a lifetime may lead to increased likelihood of bone fractures in adults, and may result in effects on bone leading to pain and tenderness. Children aged 8 years and younger exposed to excessive amounts of fluoride have an increased chance of developing pits in the tooth enamel, along with a range of cosmetic effects to teeth.

1.2 De-fluoridation is the process of removal of fluoride ion in drinking water. The process may be classified broadly into two categories:-

1. Additive methods
2. Adsorptive methods.

The different methods so far tried for the removal of excess fluoride from water can be broadly classified into four categories:

1. Adsorption methods,
2. Ion exchange methods,
3. Precipitation methods, and
4. Miscellaneous methods.

Some de-fluoridation techniques developed to control fluoride content in water are reverse osmosis, adsorption using sunflower plant dry powder, steam of phytomass, Holly Oak, neem bark powder, activated cotton jute carbon, bagasse ash, burnt bone powder, phosphate-treated saw dust, bone char, etc. as adsorbents, Nalgonda technique, activated alumina process and ion exchange process. However, due to high cost or lower efficiency or no applicability on mass scale these techniques are not much in use.

1.3 Problem Statement

India has 29 states and more than 18 states are affected by fluorosis. . Fluoride content in ground water in these states are above permissible limits. People in many parts of Rajasthan , Andhra Pradesh ,etc. consume water with fluoride above 10 mg/L. People of all age groups have mottled teeth, skeletal fluorosis, painful and restricted joint, deformities in limbs and hunch back. It is challenge to provide clean and safe water to the people who are consuming unsafe water. Efforts have been taken to overcome this problem but most of the rural areas are still fighting with these problem.

1.4 Objective of the study:

1. To study the removal of fluoride by batch process using Lemon peel powder and pineapple peel powder.
2. To compare the fluoride removal efficiency of Pineapple peel powder and Lemon peel powder.
3. The experimental data is to be fitted in the different adsorption isotherms , Freundlich and Langmuir .
4. To study the adsorption kinetics for fluoride removal by lemon peel and pineapple powder.

CHAPTER 2
LITERATURE REVIEW

CHAPTER-2

LITERATURE REVIEW

2.1 Introduction

There are many scientists in the world who have studied about the de-fluoridation using low cost materials and contributed in solving the problem of drinking water and fluoride content in water. These studies helps in understanding the occurrence , circulation and its effects on earth.

Naba Kumar Mondal, RIA Bhaumik, Tanmoy Baur, Biswajit Das, Palas Roy and Jayanta Kumar Datta (2012)[1] 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

C.M.Vivek Vardhan and J.Karthikeyan (2011)[2]The experimental investigations clearly suggestted that abundantly available and low-cost materials like Rice Husk, seed extracts of Moringa Oleifera (Drum stick) and chemicals like Manganese Sulphate and Manganese Chloride are effective in removing Fluoride from water to acceptable levels. Equilibrium isothermal sorption experiments suggested that sorbent dosages of 6g/l of rice husk accomplished a removal of 83% of Fluoride. The time to reach equilibrium was observed to be 3 hours. pH does not have any significant impact in the range of 3-10, whereas pH of more than 10 resulted in a steep decrease in Fluoride removal. Manganese Sulphate, Manganese Chloride exhibited good percentage removal of Fluoride. Acid extract of natural Polyelectrolyte Moringa Oleifera seed is very effective as a coagulant for removal of Fluoride. A dose of 1000 mg/l removed 88% of Fluoride.

Ibrahim M, Asimrasheed M, sumalatha M and Prabhakar P (2011)[3]They studied about the quality of ground water and different ions present in it.After this study they got to know that some ions are above their permissible limits.. Fluoride concentration in groundwater vary range form 0.5-5.0 ppm. They obseverd that there is two different relationship between ground water level and fluoride level in ground water.at low level fluoride concentration is high and at deep the concentration is low. They also studied about the fluorosis and their effects. They studied about the methods that can reduce fluoride content in drinking water and also compared the methods.

Suman Mann, Dr.Anubha Mandal (2014)[4]The paper briefly highlighted the importance of adsorption process and its benefits. Also the overview of various papers publishes in various journals on removal of fluoride ions from water or wastewater by adsorption using various low cost adsorbents instead of expensive commercial adsorbents. The efficiency of different adsorbents in the removal of fluoride depends on dose of adsorbate, charac teristics of adsorbent, pH, temperature, contact time, speed of agitation, etc. A review of various low cost adsorbents presented here shows a great potential for the fluoride removal. The use of commercially available adsorbents can be replaced by the inexpensive and effective low cost adsorbents. There is need for more studies to better understand the process of low-cost adsorption and to demonstrate the technology effectively.

Pali Shahjee, B.J.Godboley , A.M.Sudame (2013)[5] 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 fluorideremoval 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.

Vaishali Tomar and Dinesh Kumar (2013)[6] Studies for the removal of fluoride by using different adsorbents and the efficacy of each adsorbent has been examined and discussed. They have studied about activated alumina activated for adsorption process. This process is very efficient but expensive also. Some earth oxide based materials are found to be very efficient but they are expensive also.they have also studied about carbon based adsorbent which have applications in small scale .but they do not used in column process .some natural materials have good potential for removal of fluoride but they cannot regenerate . they have also studied about the nano-adsorbent who have high potential. the effect of pH, agitation time, initial fluoride concentration, temperature, particle size, surface area and nature of counter ions and solvent dose were studied for de-fluoridation with various adsorbents. Adsorption isotherms and kinetics were also studied by them.

G. Alagumuthu, V. Veeraputhiran and R. Venkataraman (2011)[7] investigated the removal of fluoride 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 fluoride 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 de-fluoridation works using natural adsorbents was most effective.

Bhagyashree M Mamilwar, A.G.Bhole, A.M.Sudame (2012)[8] investigated the adsorption of Fluoride usingbark 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. Thepseudo-second-order kinetic model fitted well as compared to pseudo first-order model.

N. Gandhi, D. Sirisha, K.B. Chandra Shekar and Smita Asthana (2012)[9] 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 indicate 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%

R. Bhaumik, N. K. Mondal, B. Das , P. Roy, K. C. Pal, C. Das, A. Banerjee, and J. K. Datta (2012)[10] Studied the role of eggshell powder as an adsorbent for removal of fluoride from aqueous solution using batch technique. The maximum adsorption was achieved 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 120 minutes. 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.

Naba Kr Mondal, Ria Bhaumik, Arnab Banerjee, Jayanta Kr Datta, Tanmoy Baur(2011)[11] 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.

C.M.Vivek Vardhan and J.Karthikeyan(2011)[12] carried out investigations for removal of Fluoride from water employing physico-chemical processes of adsorption and coagulation employing abundantly available and lowcost 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 favourable for Fluoride removal by Manganese sulphate, Manganese Chloride and MOE.

S. T. Ramesh, R. Gandhimathi, P. V. Nidheesh and M. Taywade (2012)[13] 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.

S. Kagne, S. Jagtap, P. Dhawade, S.P. Kamble, S. Devotta, S.S. Rayalu (2008)[14] 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 initialfluoride concentration 5.9 mg/l.The experimental data generated from batch adsorption experiments fitted well into the linearly transformed Freundlich and Langmuir isotherms.

Das Kumar Malay and Attar J. Salim (2011)[15] 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.

Veeraputhiran V. and Alagumuthu G (2011)[16] studied fluoride 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.

Mohammad Mehdi Mehrabani Ardekani, Roshanak Rezaei Kalantary, Sahand Jorfi, Mohammad Nurisepehr (2013)[17] 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.

S. A. Valencia-Leal, R. Cortés-Martinez, R. Alfaro-Cuevas-Villanueva (2012)[18] Evaluated the Guava Seeds (Psidium Guajava) as Low-Cost Bio sorbent 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 pseudosecond 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.

Kaushik Bandyopadhyay, Chandrima Goswami, Devaleena Chaudhuri, Arunabha Majumdar, Amal. K. Misra (2009)[19] 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 minutes 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.

Dwivedi Shubha, Mondal Prasenjit and Balomajumder Chandrajit (2014)[20] 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 orde r rate equation and the estimated equilibrium concentration falls within ~ 6 % error limit.

In all the studies it was observed that removal of fluoride is possible by adsorption using different adsorbents such as activated alumina, charcoal, peanut hull, rice husk, etc . Hence, the following study includes the adsorption of fluoride present in drinking water using waste materials as adsorbents i.e. lemon peel and pineapple peel and study of various parameters such as adsorbent dose, contact time and pH in batch process is done.

CHAPTER 3
MATERIALS AND METHODS

CHAPTER -3

MATERIALS AND METHODS

Corning glassware of good quality and analytical reagent grade chemicals were used. The glassware was soaked for 5-6 hours in a 5.0 mg/L of Fluoride solution to minimize the possibility of Fluoride getting absorbed by the glassware.. The glassware was washed off with nitric acid and distilled water before use. First, a stock solution of 100 mg was prepared by dissolving appropriate amount of sodium fluoride (NaF) in distilled water and desired concentrations of working solutions were then prepared from stock solution. Sulphuric acid (0.1N) and sodium hydroxide (0.1 N) were used for adjusting the pH values either to acidic or alkaline conditions.

Naturally occurring and abundantly available low cost materials or we can say waste materials like Pineapple peel and lemon peel powder were used.

3.1 Adsorbent collection

The adsorbents used in this study are pineapple peel powder and Lemon peel powder. These adsorbents are waste and can be utilise in de-fluoridation.

Pineapple peel obtained from juice shops , canteen ,etc. and was sieved through IS sieves of 150 µm and 300 µm size and the material passing through 150 µm and retained on 300 µm which has a geometric mean size is in the range of 150-300 microns was used in all experiments.

Lemon peel Lemon peel sites are canteen, Juice shops, houses, etc. Juice shops and canteens use lemon for Nimbu pani and pickle. Lemon peel chemical composition as well as some trace elements, ascorbic acid, carotenoids dietary fibre , total polyphenols and their antiradical efficiency, using the 2,2-diphenyl-1-picrylhidracyl (DPPH) were assessed in the dried peels of Lemon (Citrus sinensis),due to certain porosity of orange peel powder adsorbs fluoride from aqueous solution.

3.2 Synthesis of adsorbents

Lemon peels are collected from sampling sites and dried in the sunlight for a day. It should be taken care of that dirt or any other impurity did not get mix with adsorbents. Weight of the adsorbent had taken before drying. Then these peels were oven dried at a temperature of 105 Celsius for half an hour. After oven drying process adsorbents were weighed again to know the moisture content in the adsorbents. Dried peels then crushed to fine particles with the help of mortar and pestle and was sieved through IS sieves of 150 μm and 300 μm size and the material passing through 150 μm and retained on 300 μm which has a geometric mean size is in the range of 150-300 microns was used in all experiments.

Figure 3.1 Oven dried lemon peal

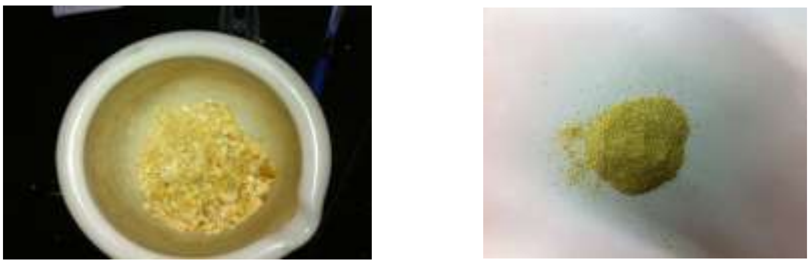

Figure 3.2: Converting lemon peel to smaller particles.

Similarly for Pineapple. Lemon peels are collected from sampling sites and dried in the sunlight. then these peels were oven dried at a temperature of 105 Celsius. Peel was dried and crushed to fine particles and was sieved through IS sieves of 150 µm and 300 µm size and the material passing through 150 µm and retained on 300 µm which has a geometric mean size is in the range of 150-300 microns used in all experiments.

Figure 3.3: Fine particles of Pineapple

3.3 preparation of adsorbate solution

Dry 3-5 grams of AR grade sodium fluoride (NaF), (molecular weight of compound is 41.99 and purity is 97%) in a 110°C oven to a constant weight and cool in a desiccator. Weigh 2.2105 g of the NaF and quantitatively transfer to a 1,000 ml volumetric flask. Dissolve and dilute to volume with distilled water. Mix and transfer to a polyethylene bottle for storage. Label as 1000 ppm Fluoride Stock Solution in distilled water. For a 100 ppm fluoride solution, use 0.2210 g NaF and for a 10 ppm fluoride solution, use 0.0221 g of NaF .

3.4 Apparatus required

1. shaker or Jar Test apparatus

2. Spectrophotometer

3. Fluoride meter

4. Weighing machine

5. beakers

6. PH meter and PH paper

3.5 Experimental procedure (Methodology)

- Preparing stock solution with NaF salt. This stock solution will be used for experiment purpose.
- 0.221g NaF salt is added to 1000ml distilled water to prepare 100ppm stock solution.
- This stock solution stored in the plastic bottle for further use.
- 100 ppm stock solution is diluted to 10 ppm and 5 ppm.

Figure 3.4 : Fluoride meter

3.5.1 Time Optimization

- Take 100 ml NaF stock solution of 5 ppm/10ppm concentration in 250 ml conical flask and add 0.1 g/1g of adsorbent in it.
- This flask is put into shaker. The shaker is set at 150 RPM because the equilibrium time was found to be less.
- Sample is measured at every 15 minutes/10 minutes by fluoride meter and final concentration can be check . As a result percentage removal can be find.
- This process is repeated until the percentage removal become constant.

- Then the time after which the percentage removal becomes constant is the optimum contact time.

3.5.2 Dose Optimization

- Take conical flask ,250ml with 100ml NaF stock solution of 5ppm/10ppm initial fluoride concentration in each flask.
- Add adsorbent in each flask with varying weights i.e. 0.1g, 0.2g, 0.4g, 0.6g, 0.8g, 1.0g, 1.2g, 1.4g,1.6g,1.8g,2.0g
- Level these flask according to their weights.
- These flasks are put into shaker and allow to shake these samples for optimum time interval at 150 RPM.
- After completion of optimum time each sample is measured with fluoride meter.
- We will get the optimum dose at which maximum removal takes place.
- Plot the graph between dose in gram/100mL and percentage removal of fluoride.

3.5.3 pH Optimization

- Take conical flask of 250 ml with 100ml NaF stock solution in each flask.
- Add optimum dose which is calculated in each flask.
- PH of every flask is changed range from 2 to 10.
- Level the flask according to the pH values i.e 2, 3, 4, 5, 6, 7, 8, 9, 10.
- The flasks are put into the shaker for optimum contact time at 150 RPM.
- Then these samples measure with fluoride meter and final concentration of fluoride is known.
- We can find the percentage removal of fluoride.
- Plot the graph between percentage removal and PH values.

CHAPTER 4
RESULTS AND DISCUSSION

CHAPTER-4

RESULTS AND DISCUSSION

Two materials have been used for experiment for removal fluoride. The bio adsorbents used are Pineapple and Lemon peel powder. In order to study the effect of different controlling parameters like pH, contact time, dosage etc. on de-fluoridation capacity of Pineapple peel powder and Lemon peel powder, adsorption studies are carried out by a batch process.

4.1 Pineapple Peel Powder

In this study, Pineapple peel powder has been used for de-fluoridation by batch process. The variation in the percentage removal by varying various parameters like adsorbent dose, pH and contact time were studied.

4.1.1 Effects of contact time:-

The effect of contact time on batch experiments was studied by varying contact time from 10 minutes to 80 minutes. The data was observed and graph was plotted. Table 4.1 shows the value of percentage removal of fluoride with initial concentration of 10 ppm and adsorbent dose of 0.4 g/ 100ml. The value of removal of fluoride increases with increase in contact time and it becomes constant after contact period of 60 minutes.

Table 4.1 Contact time reading of Pineapple peel powder

Fluoride (initial conc.)	Fluoride (final conc.)	Time (Minutes)	% Removal
10	8.4	10	16
10	7.6	20	24
10	7	30	30
10	6.6	40	34
10	6.4	50	36
10	6.2	60	38
10	6.2	70	38
10	6.2	80	38

The effect of contact time on removal on Fluoride using Pineapple is presented graphically as percentage Fluoride removal at different contact time. It may be observed from the Figure 4.1 that as contact time increases, percentage removal also increases initially and starts reducing gradually with time and then attains almost an equilibrium state in 60 minutes and remains more or less constant.

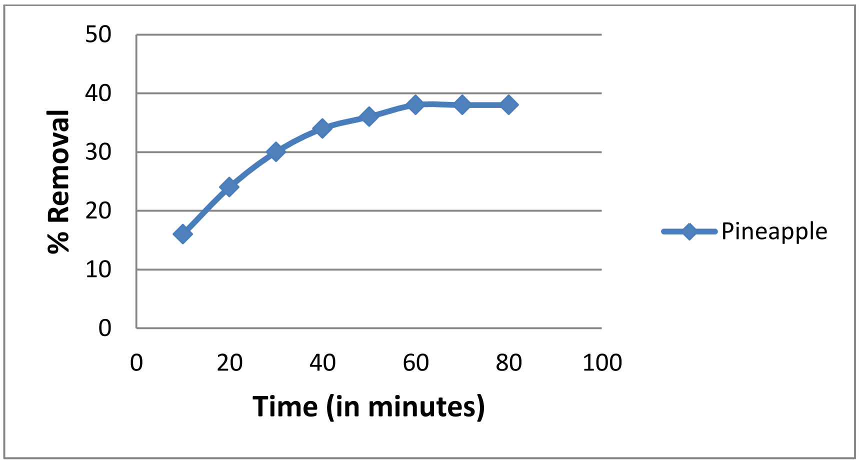

Figure 4.1: Effect of contact time on fluoride removal, 10mg/L initial concentration, dose is 0.4g/100mL and pH is 7

Further increase in contact time does not increase the uptake due to deposition of fluoride ions on the available adsorption sites on adsorbent material. A maximum of 38% removal can be done by Pineapple peel powder with 0.4g/100ml of adsorbent at 7 pH . To see the effects of various other factors on removal of fluoride, this contact time i.e. 60 minutes is considered.

4.1.2 Identification of Optimum dose

The dose at which maximum removal is observed is called optimum dose which can be obtained by varying the quantity of adsorbent. Batch experiment were conducted with initial concentration of fluoride 10 ppm, contact period of 60 minutes and varying the adsorbent dose from 0.1 g/100ml cumulatively increasing till 1.6gm/ 100ml.

Table 4.2: Adsorbent Dose readings of Pineapple peel powder

Fluoride (Initial conc.)	Fluoride (Final conc.)	Dose	% removal
10	7.1	0.1	29
10	6.8	0.2	32
10	6.6	0.4	34
10	6.2	0.6	38
10	6	0.8	40
10	5.92	1	40.8
10	5.811	1.2	41.89
10	5.79	1.4	42.1
10	5.76	1.6	42.4

Table 4.2 shows the value of percentage removal of fluoride with initial dose of 0.1g/100ml .As the dose increases the removal increases. But results showing less significant results. Removal with pineapple has maximum removal at 7 pH is 41%.

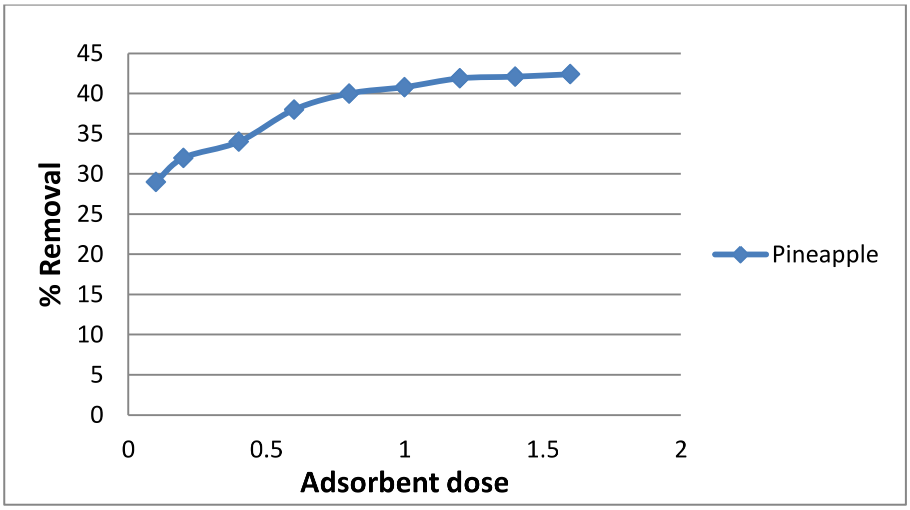

Figure 4.2: Effect of dose on fluoride removal, contact time is 60 min and pH is 7.

To find the optimum dose experiments were conducted with fluoride solution of concentrations 10.0 mg /L. At initial stage the fluoride uptake is increases because of increase in the active sites due dose increase. A maximum of 42% removal is done by the pineapple peel powder at 1.2g/100ml in optimum time of 60 minutes. After a dose of 1.2g/100ml there is no increase in fluoride removal. The reason of this decrease in removal is non-availability of active sites due overlapping of active sites. After 1-1.6 g/100ml of dose very less change is observed in fluoride uptake. Hence removal is constant at 1.2g/100ml.

4.1.3 Effect of pH

pH is an important factor to study and its effects on adsorption capacity. The effect of pH on adsorption by batch experiments was studied by varying pH from 2 to 10. The data was observed and graph was plotted.

Table 4.3 shows the value of pH of fluoride with initial concentration of 5 ppm, contact time 60 min, adsorbent dose of 1.2 g/ 100ml and varying pH from 2 to 10.

Table 4.3: pH readings of pineapple peel powder

Fluoride (initial conc.)	Fluoride (final conc.)	pH Value	%Removal
5	3.15	2	48
5	3.195	3	47.2
5	3.25	4	46.3
5	3.315	5	44
5	3.43	6	42.1
5	3.55	7	41
5	3.7	8	37.3
5	4.27	9	26
5	4.88	10	2.3

Removal of fluoride by pineapple is decreases as the pH of water increases. Initially the curve shows removal in the range from 2.0-8.0 pH but after 8.0 pH there is sudden drop in percentage removal of fluoride. The number of positively charged sites decreased and number of negatively charged sites increased. Due this reason there is competitive

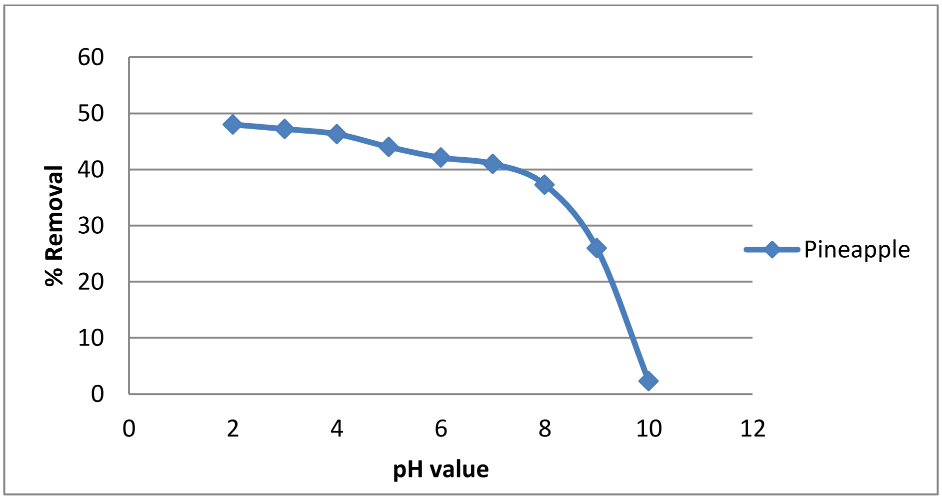

Figure 4.3 Effect of pH on fluoride removal, Fluoride initial concentration is 5mg/L, dose is 1.2g/100mL and contact time is 60 minutes.

adsorption starts with anionic fluoride for opposite charged particles to get stabilized. In acidic medium hydrogen ions easily combined with active functional groups like –OH, C=O and become positively charged and increases adsorption. In basic medium the hydroxyl ions neutralizes the functional groups and decreases adsorption due repulsive forces .Thus, Pineapple adsorption capacity at low pH is more than at high pH value. Hence the uptake is higher at 2-6 pH .

4.2 Lemon peel powder

In this study, lemon peel powder has been used for de-fluoridation by batch process. The variation in the percentage removal by varying various parameters like adsorbent dose and contact time were studied.

4.2.1 Effects of contact time

The effect of contact time on batch experiments was studied by varying contact time from 15 min to 120 minutes and the data was observed and graph was plotted. Table 4.4 shows the value of percentage removal of fluoride with initial concentration of 5 ppm and adsorbent dose of 1 g/ 100ml and varying contact time from 15 to 120 minutes. At contact time 45-75 minutes there is removal of 54-58% i.e. the removal is very less in this range of contact time.

Table 4.4: Contact time readings of Lemon peel powder

Fluoride (initial conc.)	Fluoride (final conc.)	Contact time(min)	%Removal
5	2.4	15	52
5	2.4	30	52
5	2.3	45	54
5	2.2	60	56
5	2.1	75	58
5	2.1	90	58
5	2.1	105	58
5	2.1	120	58

The effect of contact time on removal on Fluoride using Lemon peel powder is presented graphically as percentage Fluoride removal at different contact time. It may be observed from the Figure 4.4 that as contact time increases, percentage removal also increases initially and starts reducing gradually with time and then attains almost an equilibrium state in 75 minutes and remains more or less constant. . Further increase in contact time does not increase the uptake due to deposition of fluoride ions on the available adsorption sites on adsorbent material.

80% of the adsorption occurs within the first hour of the contact. 58% is maximum removal could be accomplished by Lemon peel powder at pH 7 with dose of 1g/100ml.

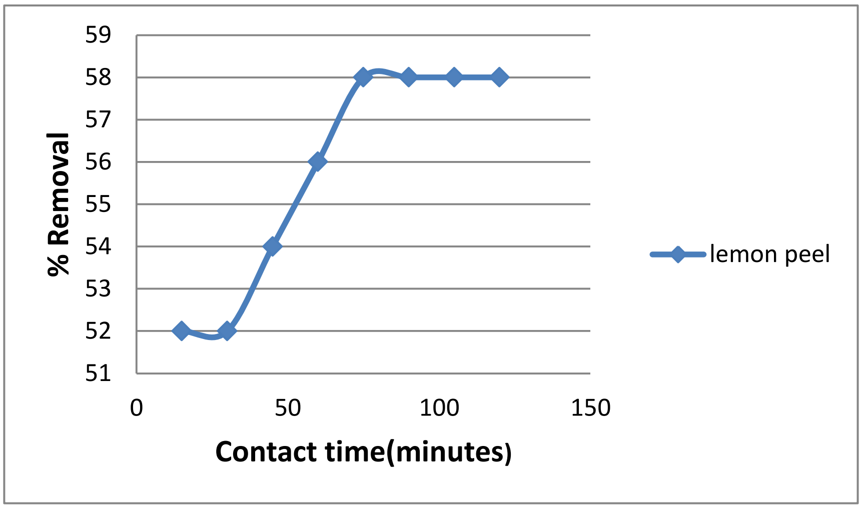

Figure 4.4: Effect of contact time on fluoride removal, Fluoride initial concentration is 5mg/L , adsorbent dose is 1g/100mL and pH is 7

considered for further study.

4.2.2 Identification of Optimum dose:

The dose at which maximum removal is observed is called optimum dose which can be obtained by varying the quantity of adsorbent dose. Batch experiments were conducted with initial concentration of fluoride 5 ppm taking contact period of 75 min and varying the adsorbent dose from 0.1-2g/100ml.

Table 4.5: Dose optimisation readings of Lemon peel powder

Fluoride (initial conc.)	Fluoride (final conc.)	Adsorbent dose(m)	% Removal
5	3.4	0.1	32
5	2.7	0.2	44
5	2.8	0.4	50
5	2.2	0.6	56
5	2	0.8	60
5	1.9	1	62
5	1.8	1.2	64
5	1.75	1.4	65
5	1.6	1.6	66
5	1.6	1.8	68
5	1.6	2	68

Table 4.5 shows the value of percentage removal of fluoride with initial concentration of 5 ppm, contact time in minutes and varying adsorbent dose of 0.1 g/ 100ml to 2 g/100ml. The value shows that the adsorptions is increases with increase in adsorbent dose. The removal of fluoride increased from 32% to 68% for 0.1-2g/100ml dosages of lemon peel powder.

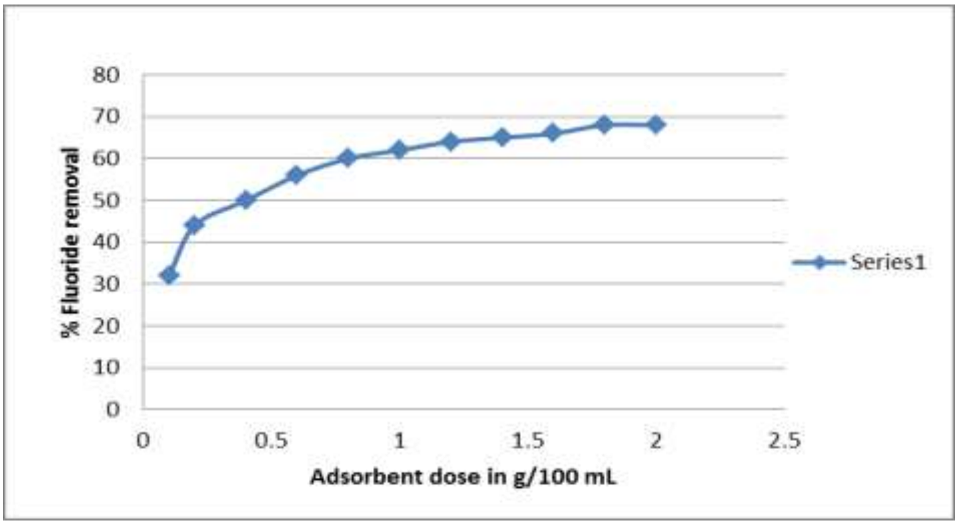

Figure 4.5: Effect of dose on fluoride removal, contact time is 75 min and pH is 7

It is hereby observed that after 1.8 and 2g/100ml there was no significant change in the percentage removal of fluoride. It is due to overlapping of active sites (Killedar. D.J.1990) at higher dosage ,thus reducing the net surface area. So 1.8 grams per 100ml was taken for further study.

Table 4.6: Comparison of percentage removal between Lemon peel powder and pineapple peel powder

Lemon Peel Powder			**Pineapple peel powder**		
Parameter		**% Fluoride Removal**	**Parameter**		**% Fluoride Removal**
Optimum contact time	75 minutes	58%	**Optimum contact time**	60 minutes	38%
Optimum Dose	1.8g/100mL	68%	**Optimum Dose**	1.2g/100mL	42%
pH	7	68%	**pH**	7	41%

This table shows that the comparison between lemon peel powder and pineapple peel powder of percentage removal of fluoride at optimum contact time, optimum dose and pH . As the readings inferred that the lemon peel powder is more efficient than pineapple peel powder.

4.3 Adsorption isotherms:

An adsorption isotherm is a curve relating the equilibrium concentration of a solute on the surface of an adsorbent, qe, to the concentration of the solute in the liquid, Ce, with which it is in contact. The adsorption isotherm is also an equation relating the amount of solute adsorbed onto the solid and the equilibrium concentration of the solute in solution at a given temperature. The adsorption data was fitted on Langmuir and Freundlich isotherm equations to find out the maximum R^2.

4.3.1 Lemon peel powder :

The data collected from batch experiments performed on lemon peel powder with contact period of 75 min and optimum dose of 1.8 gm /100ml were analysed for adsorption isotherms, i.e., Langmuir's and freundlich's isotherms.

Table 4.7: Adsorption data for removal of fluoride by lemon peel powder

Fluoride (initial conc.) Co	Fluoride (final conc.) Ce	Adsorbet dose(m)	% Removal	q_e	$1/Ce$	$1/q_e$	logq_e	logCe
5	3.4	0.1	32	1.6	0.29	0.62	0.204	0.531
5	2.7	0.2	44	1.15	0.37	0.86	0.060	0.431
5	2.8	0.4	50	0.55	0.357	1.81	-0.259	0.447
5	2.2	0.6	56	0.466	0.454	2.2	-0.330	0.342
5	2	0.8	60	0.375	0.5	2.66	-0.425	0.301
5	1.9	1	62	0.31	0.526	3.22	-0.508	0.278
5	1.8	1.2	64	0.266	0.555	3.75	-0.574	0.255
5	1.75	1.4	65	0.232	0.571	4.30	-0.634	0.243
5	1.6	1.6	66	0.212	0.625	4.70	-0.672	0.204
5	1.6	1.8	68	0.188	0.625	5.29	-0.723	0.204
5	1.6	2	68	0.17	0.625	5.88	-0.76	0.204

Table 4.6 represents that on keeping the initial concentration of 5 mg/l as the adsorbent dose i.e lemon peel powder increases the percentage removal of fluoride ions also increases but the value of q_e, i.e., the adsorption of fluoride over lemon peel on equilibrium decreases. So, it can be inferred that adsorption of fluoride over lemon peel is directly proportional to the concentration of adsorbent i.e. lemon peel and is indirectly proportional to value of q_e , which is the amount of adsorption of fluoride over lemon peel on equilibrium.

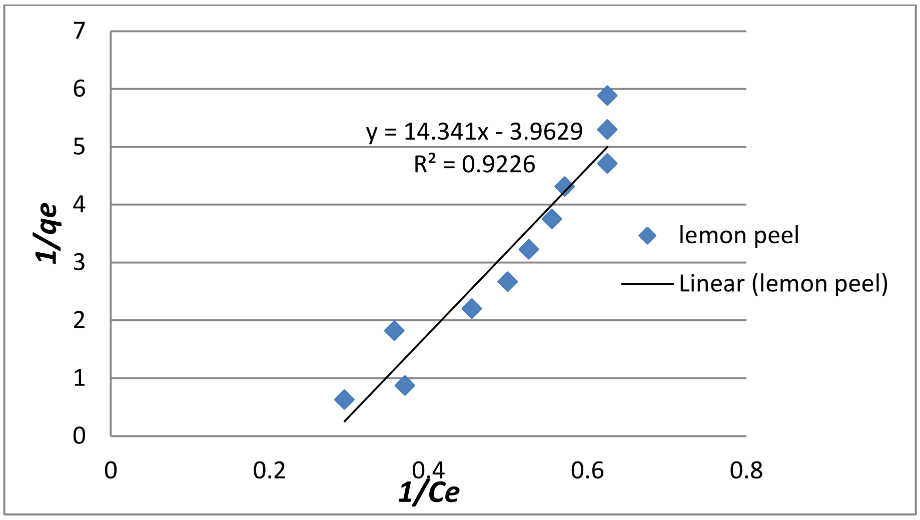

Figure 4.6: Plot of Langmuir's isotherm for adsorption of Fluoride by Lemon peel powder

.

Langmuir isotherm has linear form and is represented by the following equation

$$C_e \,/\, q_e = 1/\,(q_m \text{ b}) + C_e \,/q_m$$

As per the Langmuir isotherm a graph is drawn between $\frac{1}{q_e}$ and $\frac{1}{C_e}$, using values from table 4.6, as shown in figure 4.6. The coefficient of correlation, R^2 was obtained as 0.9226.

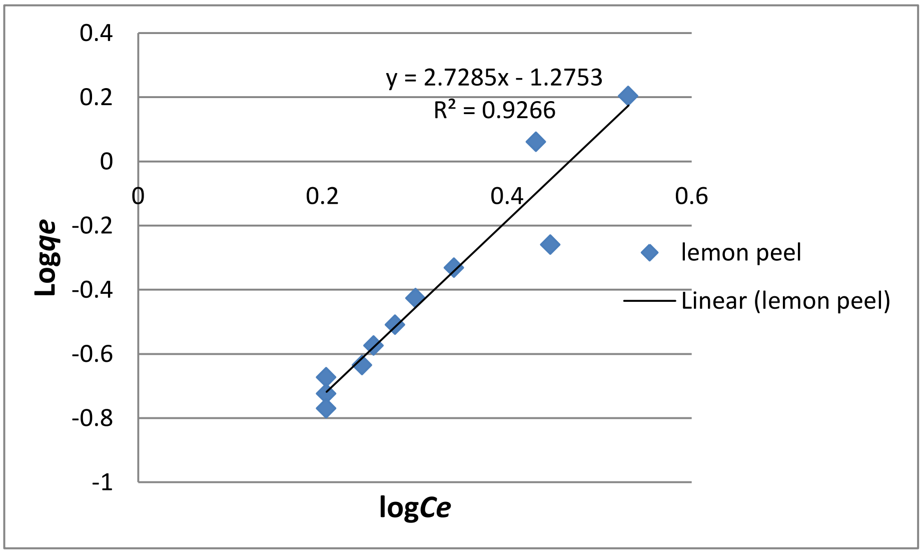

Figure 4.7: Plot of Freundlich isotherm for adsorption of Fluoride by Lemon peel powder

As per the freundlich isotherm a graph is drawn between log q_e and log C_e using values from table 4.6, as shown in figure 4.7.

The equation employed for fluoride adsorption is represented by

$$\log q_e = \log K_f + 1/n \log Ce$$

K_f and n are constant affecting the adsorption capacity and intensity of adsorption these can be calculated from the intercept and slop of the graph. The value of coefficient of correlation, R^2 obtained for the graph is 0.9266.

4.3.2 Pineapple peel powder :

The data collected from batch experiments performed on pineapple peel with contact period of 120 min and optimum dose of 0.8 gm /100ml were analysed for adsorption isotherms, i.e., Langmuir and freundlich's isotherm.

Table 4.8: Adsorption data for removal of fluoride by Pineapple peel powder

Fluoride Initial conc. (Co)	Fluoride Final conc.(Ce)	Dose	% removal	q_e	$1/q_e$	$1/Ce$	logCe	logq_e
10	7.1	0.1	29	2.9	0.344	0.140	0.851	0.462
10	6.8	0.2	32	1.6	0.625	0.147	0.832	0.204
10	6.6	0.4	34	0.85	1.176	0.151	0.819	-0.070
10	6.2	0.6	38	0.633	1.579	0.161	0.792	-0.198
10	6	0.8	40	0.5	2	0.166	0.778	-0.301
10	5.92	1	40.8	0.408	2.450	0.168	0.772	-0.389
10	5.811	1.2	41.89	0.349	2.865	0.172	0.764	-0.457
10	5.79	1.4	42.1	0.300	3.325	0.172	0.762	-0.521
10	5.76	1.6	42.4	0.265	3.773	0.173	0.760	-0.576

Table 4.6 represents that on keeping the initial concentration of 10 mg/l as the adsorbent dose i.e. pineapple peel powder increases the percentage removal of fluoride ions also increases but the value of q_e , i.e., the adsorption of fluoride over pineapple peel on equilibrium decreases. So, it can be inferred that adsorption of fluoride over pineapple peel is directly proportional to the concentration of adsorbent i.e. pineapple peel and is indirectly proportional to value of q_e , which is the amount of adsorption of fluoride over pineapple peel on equilibrium.

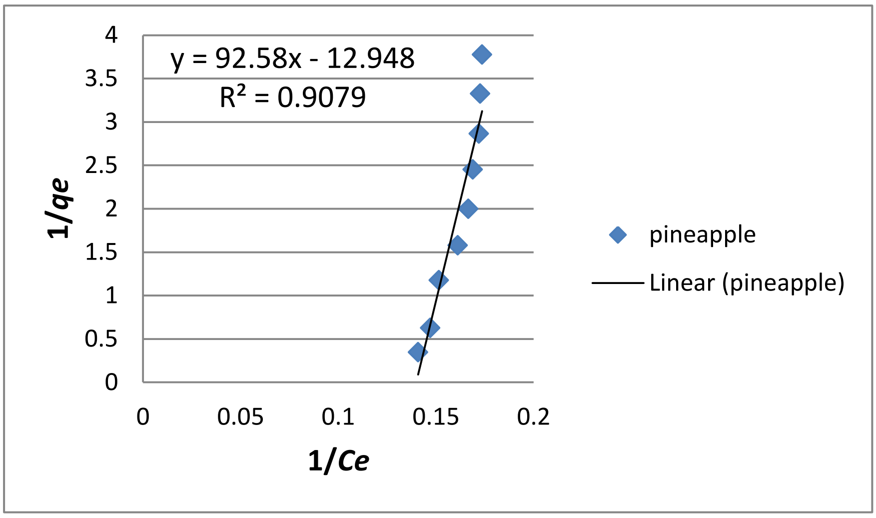

Figure 4.8: Plot of Langmuir's isotherm for adsorption of Fluoride by Pineapple peel powder

Langmuir isotherm has linear form and is represented by the following equation

$$C_e / q_e = 1/ (q_m \text{ b}) + C_e /q_m$$

As per the Langmuir isotherm a graph is drawn between $\frac{1}{q_e}$ and $\frac{1}{C_e}$, using values from table 4.8, as shown in figure 4.8. The value of R^2 obtained is 0.9079.

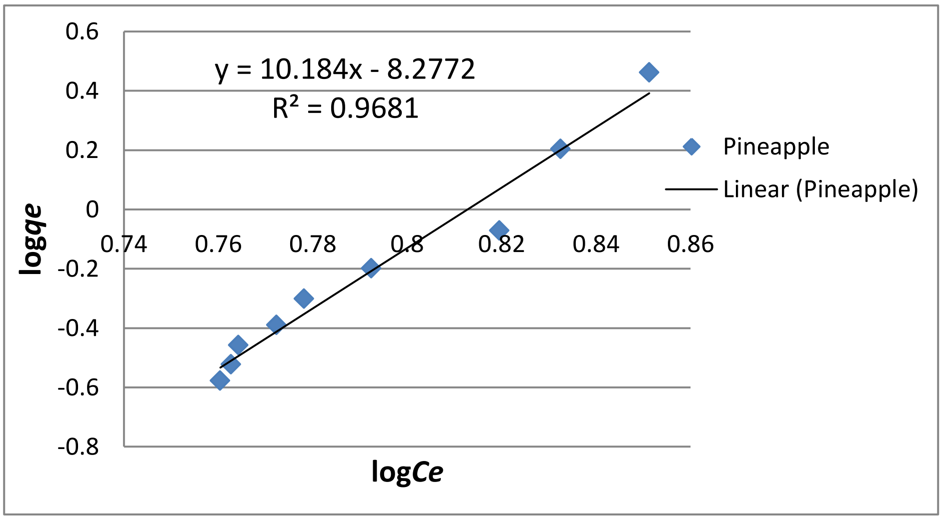

Figure 4.9: Plot of Freundlich's isotherm for adsorption of Fluoride by Pineapple peel powder

As per the freundlich isotherm a graph is drawn between log q_e and log C_e using values from table 4.8, as shown in figure 4.9. The equation employed for fluoride adsorption is represented by

$$\log q_e = \log K_f + 1/n \log Ce$$

K_f and n are constant affecting the adsorption capacity and intensity of adsorption these can be calculated from the intercept and slop of the graph. The value of coefficient of correlation, R^2 obtained for the graph is 0.9681.

Table 4.9: Coefficients of Langmuir and Freundlich's isotherm

Adsorbents	Freundlich			Langmuir		
	K_f	n	R^2	q_m	b	R^2
Lemon peel powder	0.95	0.3665	0.9266	0.252	0.278	0.9226
Pineapple peel powder	0.95	0.098	0.9681	0.0772	0.139	0.9079

From table 4.9 it can be inferred that the adsorption of fluoride over pineapple peel powder and lemon peel powder follows Freundlich isotherm as the value of R^2 for Freundlich is greater than that of Langmuir isotherm. Hence, assumptions by Freundlich shall be applicable. Freundlich isotherm is based on the following assumptions:-

- Each surface site can be occupied singly,
- There are no lateral interactions between adsorbed species.
- The enthalpy of adsorption is independent of surface coverage
- Energy of adsorption is constant thus creating homogeneity of energy on the surface (there is dynamic equilibrium between the adsorption and desorption processes).

4.4 Adsorption Kinetics:

In batch process the kinetics of fluoride uptake on pineapple peel powder and lemon peel powder has done .Kinetic modelling not only allows estimation of sorption rates but also leads to suitable rate expressions characteristic of possible reaction mechanisms. In this respect, several kinetic models including the pseudo-first-order kinetics model and pseudo-second-order kinetics models were studied.

4.4.1 Lemon peel powder

The kinetic behaviour of lemon peel powder was studied on data obtained from batch experiments. The equilibrium analysis was done on pseudo first order and pseudo second order kinetics.

Table 4.10: Pseudo first order kinetics data for removal of fluoride by Lemon peel powder

Fluoride (initial conc.)	Fluoride (final conc.)	Contact time(min)	%Removal	dose	q_e	q_t	log(q_e-q_t)
5	2.4	15	52	1	0.29	0.26	-1.522
5	2.4	30	52	1	0.29	0.26	-1.522
5	2.3	45	54	1	0.29	0.27	-1.698
5	2.2	60	56	1	0.29	0.28	-2

This table represents that as contact time increases ,percentage removal is also increasing but attain equllibrium after some period of time. q_t value is increasing initially and attain 0.29 value after 75 minutes hence value of q_e is 0.29. Dose of adsorbent with different contact time is constant i.e 1gm/100mL.

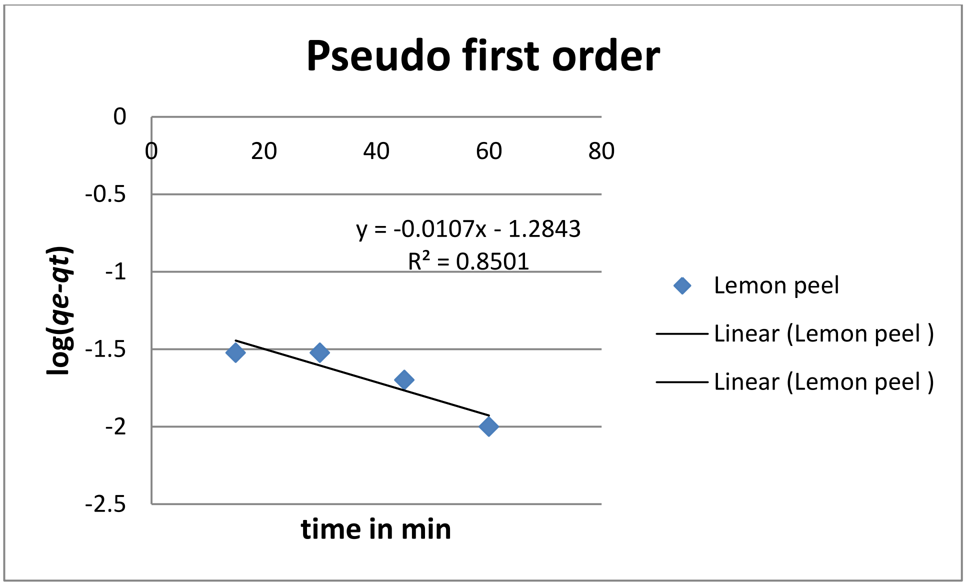

Figure 4.10: Pseudo first order plot of effect of contact time for removal of fluoride by Lemon peel powder

Pseudo first order plot shows a linear graph till equilibrium time is achieved with R^2 value 0.8501 .This indicates that Lemon peel powder followed first order kinetics and adsorption is taking place because of weak vander waal forces.

Table 4.11: Pseudo second order kinetics data for removal of fluoride by Lemon peel powder

Fluoride (initial conc.)	Fluoride (final conc.)	Contact time(min)	%Removal	dose	q_e	q_t	t/q_t
5	2.4	15	52	1	0.29	0.26	57.69
5	2.4	30	52	1	0.29	0.26	115.3
5	2.3	45	54	1	0.29	0.27	166.66
5	2.2	60	56	1	0.29	0.28	214.28

This table represents that as contact time increases, percentage removal is also increasing but attain equllibrium after some period of time. q_t value is increasing initially and attain 8.3 value after 75 minutes hence value of q_e is 0.29. Dose of adsorbent is constant i.e 1gm/100mL.

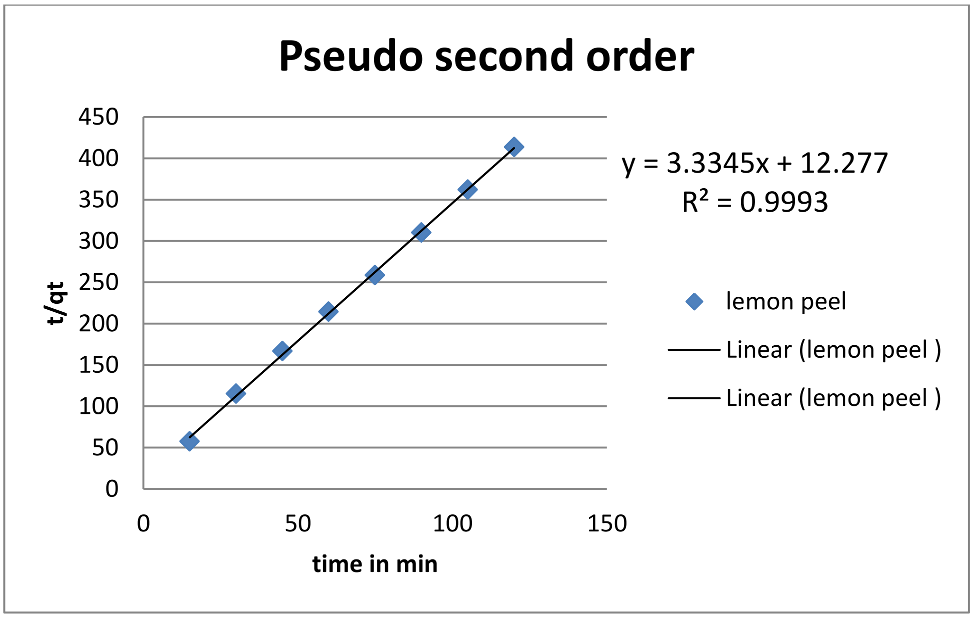

Figure 4.11: Pseudo second order plot of effect of contact time for removal of fluoride by Lemon peel powder

The value of coefficient of correlation R^2 for second order adsorption model has high value for lemon peel powder and $q_e^{(the)}$ and $q_e^{(exp)}$ are consistent, showed that pseudo second order adsorption equation fit good with maximum range of contact time and adsorption of fluoride ion appears to follow chemisorptions. This showed the adsorption is of pseudo second order kinetics.

4.4.2 Pineapple Peel Powder

The kinetic behaviour of lemon peel powder was studied on data obtained from batch experiments. The equilibrium analysis was done on pseudo first order and pseudo second order kinetics.

This table represents that as contact time increases ,percentage removal is also increasing but attain equilibrium after some period of time. q_t value is increasing initially and attain 0.95 value after 60 minutes hence value of q_e is 0.95. Dose of adsorbents is constant for contact time i.e. 0.4 g/100mL.

Table 4.12: Pseudo first order kinetics data for removal of fluoride by Pineapple peel powder

Fluoride (initial conc.)	Fluoride (final conc.)	Time(Min)	%Removal	dose	q_e	q_t	$\log(q_e-q_t)$
10	8.4	10	16	0.4	0.95	0.4	-0.259
10	7.6	20	24	0.4	0.95	0.6	-0.455
10	7	30	30	0.4	0.95	0.75	-0.698
10	6.6	40	34	0.4	0.95	0.85	-1
10	6.4	50	36	0.4	0.95	0.9	-1.301

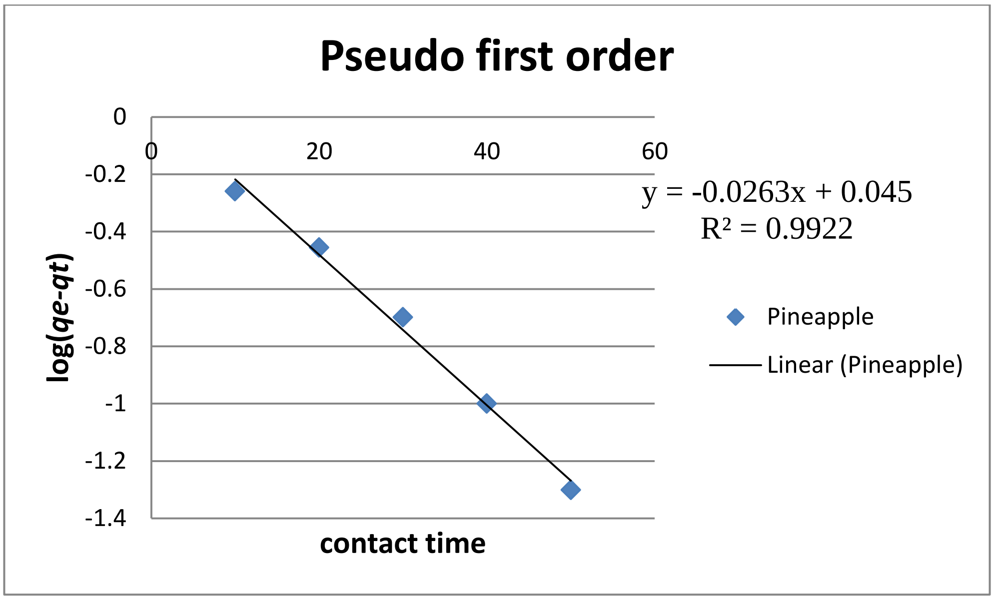

Figure 4.12: Pseudo first order plot of effect of contact time for removal of fluoride by Pineapple peel powder

Pseudo first order plot shows a linear graph till equilibrium time is achieved with R^2 value 0.9922 .This indicates that Pineapple peel powder followed first order kinetics and adsorption is taking place because of weak vander waal forces i.e physisorptions.

Table 4.13: Pseudo second order kinetics data for removal of fluoride by Pineapple peel powder

Fluoride (initial conc.)	Fluoride (final conc.)	Time (Min)	% Removal	dose	q_e	q_t	t/qt
10	8.4	10	16	0.4	0.95	0.4	25
10	7.6	20	24	0.4	0.95	0.6	33.33
10	7	30	30	0.4	0.95	0.75	40
10	6.6	40	34	0.4	0.95	0.85	47.058
10	6.4	50	36	0.4	0.95	0.9	55.55

This table represents that as contact time increases ,percentage removal is also increasing but attain equllibrium after some period of time. q_t value is increasing initially and attain 0.95 value after 60 minutes hence value of q_e is 0.95. Dose adsorbent is contstant i.e. 0.4 g/100mL.

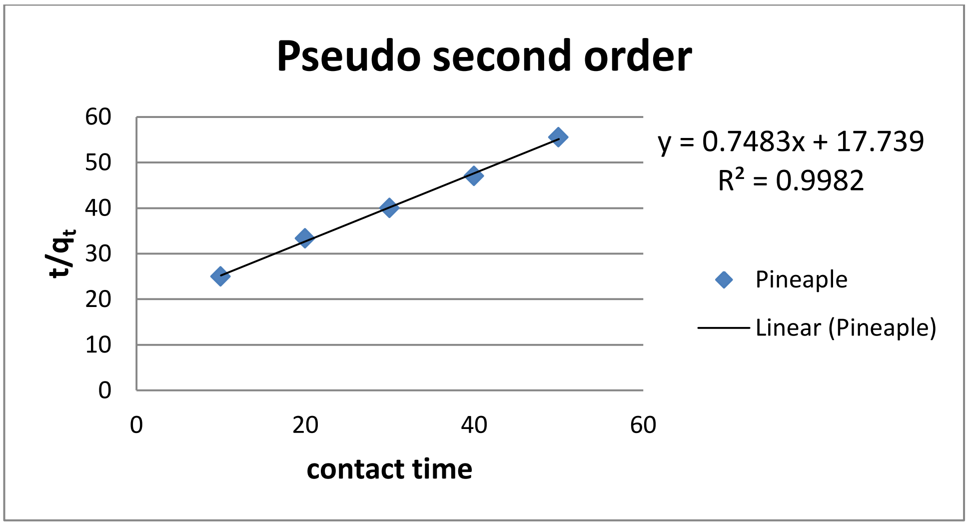

Figure 4.13: Pseudo second order plot of effect of contact time for removal of fluoride by Pineapple peel powder

The value of coefficient of correlation for second order adsorption model is 0.9982. q_e (the) and q_e (exp.) are consistent and showed that pseudo second order adsorption equation of Langergen approx fit well with maximum range of contact time and adsorption of process may be controlled through chemisorption.This showed that adsorption of the fluoride ion on adsorbents follow pseudo second order kinetics.

CHAPTER 5

CONCLUSIONS

Chapter 5

Conclusions

In this study, pineapple peel powder and lemon peel powder have been used for de-fluoridation. The conclusions drawn from the above study are given below:

1. Fluoride uptake by lemon peel powder at pH 7 is 58% and by pineapple peel powder is 38% at pH 7. This inferred that the lemon peel powder is more efficient than pineapple peel powder. The reason for fluoride to adsorb more fluoride is the porosity of lemon peel powder is more than in pineapple peel powder.
2. Adsorption of fluoride on pineapple peel powder shows that it has very less adsorption capacity. It removes fluoride at low pH value i.e. 2.0-6.0 more than at high pH value. Hence it will be difficult to use pineapple peel powder for fluoride removal at every place. Effective Fluoride removal percentage at pH 7 is 30%-38% and optimum dosage of 1.2 grams per 100 mL and contact time is 60 minutes.
3. Lemon peel powder has capacity to remove fluoride its optimum dose is 1.8 grams per 100 ml and optimum time is 75 minutes. pH variation with lemon peel powder was not considered. So for treating water the pH variation should be done to check the variation in adsorption process.
4. Lemon peel powder and pineapple peel powder both are following Freundlich isotherm with R^2 values 0.9266 and 0.9681 respectively.
5. Kinetics of lemon peel powder with R^2 value of pseudo first order and pseudo second order are 0.9922 and 0.9982 respectively. Result inferred that lemon peel powder follows pseudo second order kinetics.
6. Kinetics of pineapple peel powder with R^2 value of pseudo first order and pseudo second order are 0.8501 and 0.9993 respectively. Result inferred that Pineapple peel powder follows pseudo second order kinetics.

REFERENCES

References

[1] Naba Kumar Mondal, Ria Bhaumik, Tanmoy Baur, Biswajit Das, Palas Roy and Jayanta Kumar Datta (2012),"Studies on Defluoridation of Water by Tea Ash: An Unconventional Biosorbent," Chem Sci Trans volume 1-issue 2, page 239-256.

[2] C.M.Vivek Vardhan and J.Karthikeyan (2011), " Removal of fluoride from water using low-cost materials", International Water Technology Journal, IWTJ Vol. I - Issue 2.

[3] M Ibrahim, SM Asim Rasheed, P Prabhakar (2011)," Effects of Fluoride Contents in Ground Water: A Review" International Journal of Pharmaceutical Applications, 2011 vol. 2 - issue2. PP(128-134)

[4] Suman Mann, Dr.Anubha Mandal (2014), "Performance of Low-Cost Adsorbents for the Removal of fluoride ions – An overview", International Journal of Engineering Science and Innovative Technology (IJESIT) Volume 3, Issue 3, 2014.

[5] Pali Shahjee, B.J.Godboley, A.M.Sudame (2013), "removal of fluoride from aqueous solution by using low cost adsorbent", International Journal of Innovative Research in Science, Engineering and Technology Vol. 2, Issue 7.

[6] Vaishali Tomar and Dinesh Kumar (2013),"A critical study on efficiency of different materials for fluoride removal from aqueous media", Chemistry Central Journal. Vol. 111, page 116-124.

[7] Alagumuthu, G., V. Veeraputhiran and R. Venkataraman (2011)," Fluoride sorption using Cynodon dactylon based activated carbon" . Hem. Ind., 65: 23-35.

[8] Bhagyashree M Mamilwar , A.G.Bhole , A.M.Sudame (2012), "Removal Of Fluoride From Ground Water By Using Adsorbent", International Journal of Engineering Research and Applications (IJERA) Vol. 2, Issue 4, pp.334-338.

[9] N. Gandhi1, D. Sirisha, K.B. Chandra Shekar and Smita Asthana (2012), "Removal Of Fluoride From Water And Waste Water By Using Low Cost Adsorbents", International Journal of ChemTech Research ISSN : 0974-4290 Vol.4, No.4, pp 1646-1653.

[10] R. Bhaumik, N. K. Mondal, B. Das ,P. Roy, K. C. Pal, C. Das, A. Banerjee, and J. K. Datta(2012), ""Eggshell Powder as an Adsorbent for Removal of Fluoride from Aqueous Solution: Equilibrium,Kinetic and Thermodynamic Studies", E-Journal of Chemistry,volume 9(issue3),pg1457-1480.

[11] Naba Kr Mondal, Ria Bhaumik, Arnab Banerjee, Jayanta Kr Datta, Tanmoy Baur (2011), "A comparative study on the batch performance of fluoride adsorption by activated silica gel and activated rice husk ash ", International Journal of Environmental Sciences, Volume 2, No 3.

[12] C.M.Vivek Vardhan and J.Karthikeyan(2011), " Removal of fluoride from water using low-cost materials", Fifteenth International Water Technology Conference, IWTC-15.

[13] S. T. Ramesh, R. Gandhimathi, P. V. Nidheesh and M. Taywade (2012),"Batch and Column Operations for the Removal of Fluoride from Aqueous Solution Using

Bottom Ash", Environmental Research, Engineering and Management, 2012. No. 2(60), P. 12-20.

[14] S. Kagne, S. Jagtap,P. Dhawade, S.P. Kamble, S. Devotta, S.S. Rayalu (2008), "Hydrated cement: A promising adsorbent for the removal of fluoride from aqueous solution", Journal of Hazardous Materials, Volume 154, Issues 1–3, Pages 88–95.

[15] Das Kumar Malay and Attar J. Sali (2011),"Comparative Study of Batch Adsorption of Fluoride Using Commercial and Natural Adsorbent ",Research Journal of Chemical Sciences,Volume 1(Issue7), pg 68-75.

[16] Veeraputhiran V. and Alagumuthu G. (2011),"Treatment of High Fluoride Drinking Water Using Bioadsorbent", Research Journal of Chemical Sciences, Volume 1 (issue 4), pg 49-54.

[17] Mohammad Mehdi Mehrabani Ardekani, Roshanak Rezaei Kalantary, Sahand Jorfi, Mohammad Nurisepehr (2013), "Comparison the Efficiency of Bagas, Modified Bagas and hitosan for Fluoride Removal from Water by adsorption", Journal of Environmental Treatment Techniques, Volume 1, issue 1, pp. 1-7.

[18] S. A. Valencia-Leal, R. Cortés-Martínez, R. Alfaro-Cuevas-Villanueva (2012) , "Evaluation of Guava Seeds (Psidium Guajava) As a Low-Cost Biosorbent for the Removal of Fluoride from Aqueous Solutions", International Journal of Engineering Research and Development, Volume 5, Issue 4 ,PP. 69-76.

[19] Kaushik Bandyopadhyay , Chandrima Goswami , Devaleena Chaudhuri , Arunabha Majumdar , Amal. K. Misra (2009), "Removal of fluoride from groundwater using broken concrete cubes as the adsorbing media", IGC 2009, Guntur, INDIA.

[20] Dwivedi Shubha, Mondal Prasenjit and Balomajumder Chandrajit (2014)," Removal of Fluoride using Citrus limetta in batch Reactor: Kinetics and Equilibrium Studies", Research Journal of Chemical Sciences Vol. 4(1), 50-58, January (2014).