Removal of fluoride from drinking water using activated carbon

Dissertation submitted in partial fulfillment for the requirement of degree of

Master of Technology
in
Environmental Science and Technology

By

Jasmine Kaur

(Roll No. 601101011)

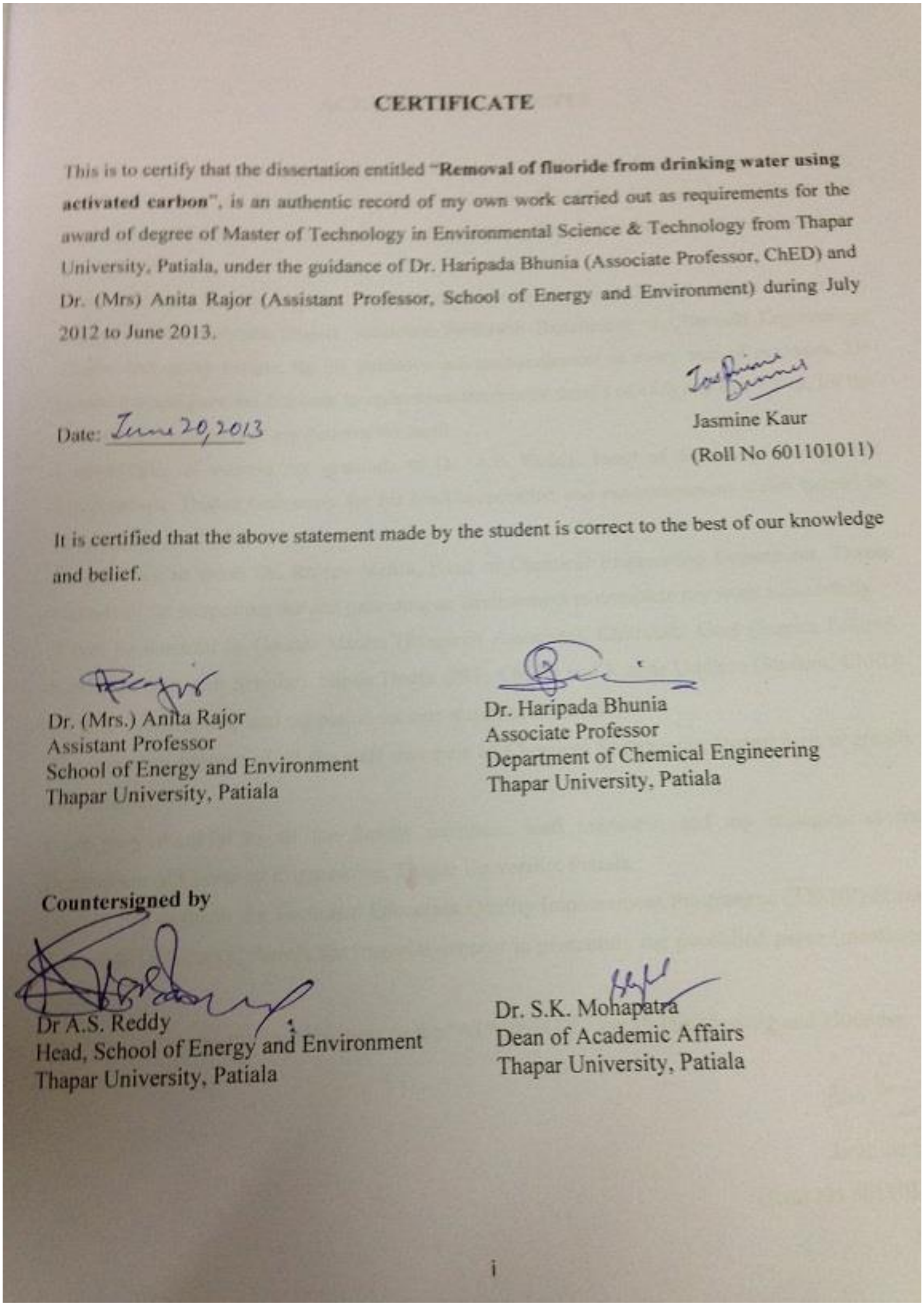
Under the supervision of

Dr. (Mrs.) Anita Rajor
Assistant Professor
School of Energy and Environment

Dr. Haripada Bhunia
Associate Professor
Department of Chemical Engineering

SCHOOL OF ENERGY AND ENVIRONMENT
THAPAR UNIVERSITY
PATIALA-147004

June 2013



CERTIFICATE

This is to certify that the dissertation entitled "**Removal of fluoride from drinking water using activated carbon**", is an authentic record of my own work carried out as requirements for the award of degree of Master of Technology in Environmental Science & Technology from Thapar University, Patiala, under the guidance of Dr. Haripada Bhunia (Associate Professor, ChED) and Dr. (Mrs) Anita Rajor (Assistant Professor, School of Energy and Environment) during July 2012 to June 2013.

Date: June 20, 2013

Jasmine Kaur
(Roll No 601101011)

It is certified that the above statement made by the student is correct to the best of our knowledge and belief.

Dr. (Mrs.) Anita Rajor
Assistant Professor
School of Energy and Environment
Thapar University, Patiala

Dr. Haripada Bhunia
Associate Professor
Department of Chemical Engineering
Thapar University, Patiala

Countersigned by

Dr A.S. Reddy
Head, School of Energy and Environment
Thapar University, Patiala

Dr. S.K. Mohapatra
Dean of Academic Affairs
Thapar University, Patiala

ACKNOWLEDGEMENTS

I express my sincere gratitude and regards to my supervisor Dr. Anita Rajor, Assistant Professor, School of Energy and Environment, Thapar University, Patiala for her valuable guidance and suggestions. Without her encouragement and guidance this dissertation would not have been materialized.

I feel privileged to offer my sincere thanks and owe an enormous deal of gratitude to my co-supervisor Dr. Haripada Bhunia, Associate Professor, Department of Chemical Engineering, Thapar University Patiala, for his guidance and encouragement at every step of my work. He guided me and gave me full time to understand the minute details of each and every step, for the successful completion of my dissertation work.

I would like to express my gratitude to Dr. A.S. Reddy, Head of School of Energy and Environment, Thapar University for his kind cooperation and encouragement which helped in the completion of this work.

I would like to thank Dr. Rajeev Mehta, Head of Chemical Engineering Department, Thapar University for supporting me and providing an environment to complete my work successfully.

I will be thankful to Gaurav Madhu (Research Associate), Chitrakshi Goel (Inspire Fellow), Kimi Jain (Reseach Scholar), Nipun Dogra (JRF, ChED) and Kumar Uddipto (Student, ChED) for their constant help and support at various stages of my work.

The generous support of all the staff members of Chemical Engineering Department is greatly appreciated.

I am very thankful to all the faculty members, staff members, and my collegues at the Department of Chemical Engineering, Thapar University, Patiala.

I would like to thank the Technical Education Quality Improvement Programme (TEQIP) Phase-II, Thapar University, Patiala for financial support in presenting the published paper (mentioned above)

Above all, I express my indebtedness to the "ALMIGHTY" for all His blessing and kindness.

Jasmine Kaur

(Roll No 601101011)

ABSTRACT

Fluoride in water above a certain limit is very toxic for human health. The prescribed limit for fluoride in drinking water is 0.5 – 1.5 mg/L. The major sources of exposure to fluoride are drinking water, food and pesticides. People can get fluoride exposure from atmospheric air and certain pharmaceuticals and consumer products. Intake of fluoride more than 1.5 mg/l can lead to fluorosis in both animals and humans. The early toxic effects of fluoride in humans are dental and skeletal fluorosis, which are endemic in areas with elevated exposure to fluoride. Fluoride is known to cross cell membranes and to enter soft tissues. There are many ways for fluoride removal viz Electrocoagulation, ion exchange, adsorption etc. But among them adsorption is the very popular, because of its simplicity and a lot of adsorbents available. Removal of pollutants from aqueous environments onto microporous active carbon is a favorite choice because of the high adsorption capacity. But high cost and irreversible nature of adsorption makes it difficult to use.

Activated carbon is a good adsorbent to remove fluoride as it has a large surface area and hence a large surface for the adsorption of fluoride. The more will be the surface, the more will be adsorption and more will be the removal. It is derived by crushing charcoal and having a high carbon content.

This work seeks the removal percentage for fluoride removal from drinking water using Activated Carbon as the adsorbent. It is a very effective and good method for the removal but having the disadvantage due to its irreversible nature.

The **1st chapter** is an introduction to the fluoride, its toxicity and the symptoms of toxicity and activated carbon (adsorbent).

The **2nd chapter** describes the review of literature based on fluoride removal and related studies

The **3rd chapter** gives all the materials and methods employed during the research work

The **4th chapter** discusses about the results and discussions

The **5th chapter** discusses about the conclusions of the work

The **6th chapter** gives the areas where work can be done in future.

CONTENTS

Title **Page No.**

Certificate i
Acknowledgments ii
Abstract iii
Contents iv
List of figures vi
List of tables vii
Abbreviations viii
Chemical formulae x

Chapter 1 Introduction 1-12

1.1 Introduction 1
  1.1.1 Effects of fluoride on health 4
  1.1.2 Symptoms of fluoride toxicity 6
  1.1.3 Fluoride deficiency 7
  1.1.4 Activated carbon 8
  1.1.5 Applications of activated carbon 9

Chapter 2 Literature review 13-24

2.1 International work 13
2.2 National work 18

Chapter 3 Materials and methods 25-31

3.1 Materials 25
  3.1.1 Chemicals and reagents 25
  3.1.2 Adsorbent 25
  3.1.3 Instruments/Equipment 25
    3.1.3.1 pH meter 25
    3.1.3.2 Centrifuge 25

3.1.3.3 Orion Ion Analyzer 26

3.1.3.4 Orbital Shaking Bath 26

3.2 Experimental procedure 27

3.2.1 Method for preparation of Sodium Fluoride solution 27

3.2.2 Optimizing the pH 27

3.2.3 Optimizing the carbon content 28

3.2.3 Optimizing the contact time 29

3.2.4 Testing for fluoride removal on drinking water sample 30

Chapter 4 Results and Discussion 32-34

4.1 Effect of pH 32

4.2 Effect of amount of adsorbent 33

4.3 Effect of contact time 33

4.4 Testing on Drinking Water Sample 34

Chapter 5 Conclusions 35

Chapter 6 Recommendations and future work 36

References 37-38

LIST OF FIGURES

Fig	Description	Page No
1.1	Fluoride affected areas of world	5
1.2	Excess fluoride affected teeth and also extent of infection	7
1.3	Defiency of fluoride effects on teeth	7
1.4	The enormous surface area of the activated carbon	8
1.5	Electron microscope view of activated carbon	9
4.1	Effect of different pH on fluoride adsorption	32
4.2	Effect of different amounts of carbon on fluoride adsorption	33
4.3	Effect of different contact time on fluoride adsorption	34

LIST OF TABLES

Table	Description	Page No
3.1	Various parameters for pH optimization	27
3.2	Removal of Fluoride by different pH	28
3.3	Various parameters for carbon content optimization	28
3.4	Removal of Fluoride by different amount of carbon	29
3.5	Various parameters for contact time optimization	29
3.6	Removal of Fluoride by different contact times	30
3.7	The parameters for sample testing	30
3.8	Concentration of fluoride before and after treating with carbon from a sample of drinking water and removal of fluoride	31

ABBREVIATIONS

AA	Activated alumina
ABC	Activated bagasse carbon
AC	Activated carbon
AIAA	Alum-impregnated activated alumina
AIST	Advanced industrial science and technology
AOCP	Aluminum oxide coated pumice
ASTM	American society for testing and materials
BDST	Bed depth service time
CAC	Commercially available activated carbon
EC	Electro coagulation
EDAX	Energy dispersive x-ray
EDTA	Ethylene diamine tetra acetic acid
EF	Electro flotation
EPA	Environmental protection agency
FTIR	Fourier transform infra red
IPAC	Indigenously prepared activated carbons
IQ	Intelligent quotient
K	Kelvin
LECCA	Ligand exchange cotton cellulose adsorbent
LED	Light emitting diode
MAAA	Magnesia-amended activated alumina
MCL	Maximum contaminant level
NMR Spectroscopy	Nuclear magnetic resonance spectroscopy
NOM	Natural organic matter
ppm	parts per million
RPM	Rotations per minute
SDR	Sawdust raw
SEM	Scanning electron microscopy
TRB	Titanium rich bauxite

US NRC	United states national research council
WHO	World health organization
WSR	Wheat straw raw
XPS	X-ray photoelectron spectroscopy
XRD	X- ray diffraction

CHEMICAL FORMULAE

NaF	Sodium fluoride
F^-	Fluoride
NaOH	Sodium hydroxide
HCl	Hydrochloric acid
HF^-	Bifluoride
AlF_x	Aluminum fluoride complexes
$FeCl_3$	Ferric chloride
SO_4^{2-}	Sulphate
Cl^-	Chloride
HNO_3	Nitric acid
H_2O_2	Hydrogen per oxide
$KMnO_4$	Potassium per manganate
H_3PO_4	Phosphoric acid

CHAPTER 1

INTRODUCTION

1.1 Overview

Fluorine is the most electronegative and the most reactive element as compared to all the halogens. As fluorine is very reactive it can't be found in nature in elemental state. It exists as inorganic fluorides and as organic fluoride compounds, always showing an oxidation state of -1. Fluorine is present in drinking water as fluoride (F-) ions and is an important nutrient for humans for calcification of dental enamel and bone formation, if present in low amount. The WHO recommended limit for fluoride in drinking water is 1.5 mg/l. The major sources of exposure to fluoride are drinking water, food and pesticides. People can get fluoride exposure from atmospheric air and certain pharmaceuticals and consumer products.

Fluoride is the anion F^-, the reduced form of fluorine formed as an ion or when bonded to another element. Inorganic fluorine having compounds are called fluorides. Fluoride, similar to other halides, is a monovalent ion (−1 charge). Its compounds often have properties that are distinct as compared to other halides. Structurally, and to some degree chemically, the fluoride ion looks like the hydroxide ion. Solutions of inorganic fluorides in water include F^- and bifluoride HF^-_2 **[1]**. Some inorganic fluorides are soluble in water without undertaking significant hydrolysis.

In terms of its reactivity, fluoride differs appreciably from chloride and other halides, and it is more strongly solvated because of its smaller radius/charge ratio. Its nearest chemical relative is hydroxide. If fluoride ions are relatively unsolvated, they are called "naked". Naked fluoride is a very strong Lewis base **[2].** The presence of fluoride and its compounds can be detected by ^{19}F NMR spectroscopy. Fluoride is usually found naturally in low concentration in drinking water and foods. The concentration of fluoride in seawater is approximately 1.3 parts per million (ppm). Fresh water supplies generally contains from 0.01 to 0.3 ppm, whereas the ocean contains between 1.2 and 1.5 ppm. **[3]**

Higher concentrations of fluoride in soil and ground water coming up from both natural source and anthropogenic activities are reported in many countries around the world, including India. The optimum fluoride level in drinking water should fall below 1.5 mg dm^{-3} as per WHO guidelines. Intake of fluoride more than this level for a prolonged period leads to fluorosis in both humans and animals. The most obvious early toxic effects of fluoride in humans are dental and skeletal fluorosis, which are common in areas with high exposure to fluoride. Fluoride is known to cross cell membranes and to enter soft tissues. Destruction of soft-tissue function has been demonstrated in fluoride- affected animals. In blood, brain, and animal liver, various changes occur after chronic administration of fluoride. These include abnormal behaviour patterns, altered neuronal cerebrovascular integrity, and metabolic lesions **[4-7].**

Generation of free radicals, lipid peroxidation, and altered antioxidant defence systems are considered to play important roles in producing toxic effects of fluoride **[8,9].** A cost-effective and technologically feasible method for the total removal or at least reduction of the load of fluoride in water is needed to control fluorosis. The treatment technology, based on the pollutant load, may be either physicochemical or biological. While the biological method is applicable to lower pollutant levels, physicochemical methods are applied for modium to high pollutant concentrations. Biological processes, may not always be possible in wastewater treatment because for of long-term biodegradation **[10].** The accepted technologies for fluoride removal from water are

(a) Electrocoagulation- Electrocoagulation (EC) is an electrochemical technique, in which a variety of useless dissolved particles and suspended matter can be effectively removed from an aqueous solution by electrolysis. In this fluoride makes complex with the coagulant (e.g. Alum) and becomes light and comes in froth and gets separated. As this process utilizes electricity so it can be a bit more expensive. Also it removes all the unwanted particles from drinking water**[11]**.

(b) Ion exchange- In ion exchange specific selective ion exchange resin are used to replace F^- from the drinking water to some ion in the resin and it can be taken out removing fluoride from drinking water. For example there can be a lot of Aluminium ions which have high affinity for fluorine and can bind fluorine very easily. So that fluoride is capable of removal.

(c) Adsorption- Adsorption techniques have been quite popular in latest years, due to their simplicity and the availability of large range of adsorbents. Removal of pollutants from aqueous environments onto microporous active carbon is a preferred choice because of the high adsorption capacity. However, the high cost and irreversible nature of adsorption accounts for its limited use. Several scientists have used a variety of low-cost adsorbents, both natural and synthetic, as well as of biomaterials

The quality of drinking water is very important for public safety and quality of life and toxic cations, for example heavy metals, have been a serious problem. While anions, for example nitric ions and nitrous ions, can cause methemoglobinemia **[12]**. Moreover, the fluoride ion must be removed from tap and ground water, because it causes teeth to become spotty. Fluoride derives from geological features and it is widely distributed in the natural world. Fluorine is found in coal; when it burns, the fluorine spreads in the atmosphere and then dissolves in water. Anybody who drinks drinking water containing the fluoride ion may suffer from spotted teeth and bone abortion **[13-14]**.

Widespread occurrence of fluoride above the given limit in groundwater meant for human consumption has caused multidimensional health problems, most common are dental fluorosis and skeletal fluorosis. Fluoride is one of the most abundant constituents found in groundwater in India and creates a major difficulty in safe drinking water supply **[15]**. Several methods of defluoridation of drinking water has been developed in India, precipitation and adsorption is the most preferred. Precipitation process is based on the adding up of chemicals and removal of insoluble compounds as precipitates. In adsorption method, many different types of adsorbents are used for defluoridation, e.g. activated alumina, coconut shell carbon, activated carbon, bone charcoal, natural zeolites, burnt clay and other low-cost adsorbents **[16]**.

The disadvantages of most of these methods are

(a) High operational and maintenance costs

(b) Low fluoride removal capacity

(c) Lack of selectivity for fluoride

(d) Undesirable after effects on water quality

(e) Generation of large amount of sludge

(f) Complicated procedure involved in the treatment.

Activated carbons are the most important commercial adsorbents. Their high surface area joined with their surface chemical structure allows them to be used in a large variety of industrial applications, some of the most significant dealing with the environmental field and particularly with water purification and industrial wastewater cleaning.

In these applications adsorption with activated carbon is most generally oriented towards the removal of species which are accepted as toxic pollutants like fluoride. Fluoride is a natural compound present in water, soils, plants and animals and is supposed to be essential for life **[17]**. A WHO experts committee considered fluorine to be one of the 14 elements that are necessary for animal life. WHO standards for drinking water are between 0.5 – 1.5 mg/L. Fluoride concentration below and above the permitted limit has an implication related to health. If fluoride is totally absent in water supply it is known to cause dental carries. Fluoride is more toxic than lead, and just like lead, even in minmium doses, accumulates in and is harmful to brain/mind development of children, i.e. produces abnormal behaviour in animals and lowrs IQ in humans .Fluorosis is a disease caused by ingestion of fluoride in excess through water, air, and food and is a serious health problem. Fluoride consumed with water goes on collecting in bones till the age of 55 years. At elevated doses fluoride can interfere with carbohydrates, vitamin, lipid protein, enzyme and mineral metabolism. Long term intake of water containing 1 mg of fluoride per liter leads to dental fluorosis. The procedure of removal of fluoride is generally termed as defluoridation. Several methods have been described employing various materials for the fluoride removal ever since 1930's **[18]**.

1.1.1 Effects of fluoride on health

When concentrations of fluoride are more then soluble fluoride salts are toxic. If skin or eye are contacted with elevated concentrations then it can be dangerous. For example the common salt of fluoride- Sodium Fluoride (NaF), the lethal dose for adults is said to be 5-10g, which is equivalent to 32 to 64 mg/kg elemental fluoride/kg body weight **[19-20]**. The slight ingestion of fluoride can cause gastrointestinal discomfort about 15-20 times a day at a concentration of 0.2–0.3 mg/kg or lower. Even though fluoride in lesser concentration helps to improve the teeth but in elevated concentrations it interferes with the bone formation. So the prime examples of fluoride poisoning come from fluoride containing ground water **[21]**. As most soluble materials, fluoride compounds are eagerly absorbed by the stomach and intestines, and excreted through the urine. Ingested fluoride at first acts locally on the intestinal mucosa, where it makes hydrofluoric acid in the stomach **[22]**.

Earlier the cases of fluoride toxicity were because of accidental ingestion of sodium fluoride based pesticides or insecticides **[23]**. But these days in largely countries the fluoride toxicity is owed to the ingestion of the fluoride based dental products. Even though contact to these products does not frequently cause toxicity, in one study only 30% of children exposed to fluoride dental products developed mild symptoms **[24]**.

A few of the man made sources of fluoride are **[25]**

(a) Glass-etching or chrome-cleaning agents like ammonium bifluoride or hydrofluoric acid
(b) Industrial exposure to fluxes used to promote the flow of a molten metal on a solid surface
(c) Volcanic ejecta
(d) Metal cleaners
(e) Malfunction of water fluoridation equipment
(f) Organofluorine compounds (Rare source)
(g) Flavored toothpaste

In India approximately 60 million people have been toxicated by well water infected by excessive fluoride, which is dissolved from granite rocks. The effects are mainly visible in the bone deformations of children. Comparable or larger problems are predicted in other countries including China, Uzbekistan, and Ethiopia. The generally established bad effect of fluoride at levels used for water fluoridation is dental fluorosis, which can change the appearance of children's teeth during tooth development; this is mostly meek and usually only an aesthetic concern. As compared to unfluoridated water, fluoridation upto 1 mg/L is approximated to origin fluorosis in one of every 6 people (range 4–21), and to cause fluorosis of aesthetic fear in one of every 22 people (range 13.6–∞) **[25]**. The fluoride affected areas in the world are

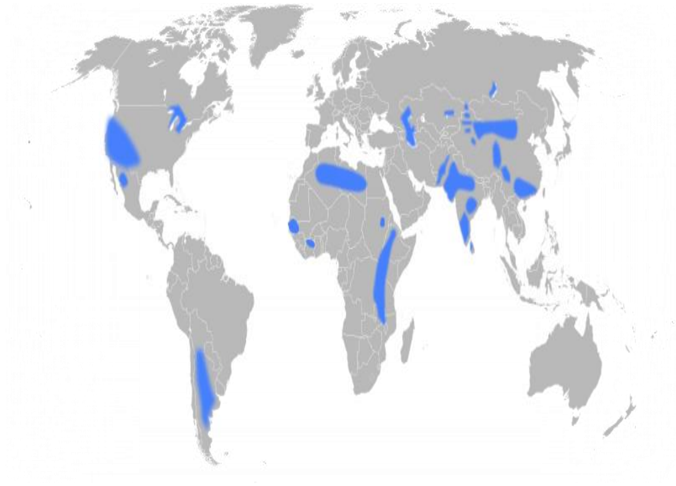


Figure 1.1 Fluoride affected areas of world

Intake of fluoride at levels higher than those used in fluoridated water for a extended period of time causes skeletal fluorosis. In some areas, mainly the Asian subcontinent, skeletal fluorosis is common. It is known to cause irritating-bowel symptoms and joint pain. Early stages are not clinically clear, and may be misdiagnosed as ankylosing spondylitis or (seronegative) rheumatoid arthritis **[26]**.

Other adverse effects may be possible at fluoride intake levels above the prescribed dosage, and defluoridation is recommended in these cases. In 1986, the United States EPA recognized a MCL for fluoride at a concentration of 4 milligrams per liter (mg/L), which is the official limit of fluoride allowed in the water. A review by the National Academy of Sciences ,in 1993, conducted at the request of EPA concluded that the 4 mg/L MCL was suitable. However, in 2006, a 12-person team of the USNRC reviewed the health risks connected with fluoride consumption and came to the differing conclusion that the MCL should be lowered. In reply to these studies, the EPA has made no change to the MCL. U.S. government officials lowered prescribed limits for fluoride in water on Friday Jan. 7, 2011, giving some children may be getting tooth damage from too much fluoride concentration. The

Health and Human Services Department reduced its prescribed levels to 0.7 milligrams of fluoride per litre of water – the lower limit of the current prescribed range of 0.7 to 1.2 milligrams.

1.1.2 Symptoms of fluoride toxicity

1) Bones become weak, leading to enhancing of wrist and hip bone fractures. The U.S. National Research Council says that, the number of fractures amplify when the concentration of fluoride increases from 1 mg/l to 4 mg/l, showing a continuous exposure-effect at these levels.

2) Kidneys get affected adversely. Effects on kidney are visible if the level of fluoride ingestion is higher than 12 mg/day, which is possible only if the fluoride concentration is around 4 mg/l. The people who already have problems with kidneys are more susceptible to get fluoride toxicity.

3) Four epidemiological studies have noted a association between increased fluoride and lower IQ. The most accurate of these compared an area with average water concentration of 0.36 ± 0.15 mg/L (range 0.18–0.76 mg/L) to an area with 2.47 ± 0.79 mg/L (range 0.57–4.50 mg/L). Most of the studies did not publish important details, making them difficult to measure. If these correlations are caused by fluoride, the procedure is not known, but the National Research Council considers that effects on the thyroid might lead to poor test results. Two Chinese meta-analyses which included the before mentioned studies have also noted this association. The high-fluoride areas studied had fluoride levels more those used in water fluoridation.

4) The NRC report said that "many of the untoward effects of fluoride are due to the formation of AlFx [aluminum fluoride] complexes". This topic has been recognized previously as cause for concern. The NRC noted that rats administered fluoride had 2 times as much aluminium in their brains. When water (1 ppm fluoride) is boiled in aluminum utensils more aluminum is leached and more aluminum fluoride complexes are created. Though, an epidemiological study found that a high-fluoride area had one-fifth the Alzheimer's that a lower-fluoride area had, and a 2002 study found that fluoride elevated the urinary excretion of aluminum

5) Fluoride's suppressive result on the thyroid are more harsh when iodine is lacking, and fluoride is linked with lower levels of iodine. Thyroid effects in humans were connected with fluoride levels 0.05–0.13 mg/kg/day when iodine ingestion was adequate and 0.01–0.03 mg/kg/day when iodine ingestion was inadequate. Its mechanism and effect on the endocrine system remain uncertain.

Figure 1.2 Excess fluoride affected teeth and also extent of infection

1.1.3 Fluoride deficiency

Fluoride deficiency is the situation in which fluoride is inadequate or is not utilized properly. Fluoride is a mineral stored in bones and teeth that strengthens them by heping in the retention of calcium. Studies have found that the enamel of sound teeth contains more fluoride than is found in the teeth of persons prone to dental caries, and the occurrence of dental caries is reduced in areas where natural fluoridation of water is moderate. For these reasons, fluoride is supplemented to water supplies in some areas to help decrease tooth decay, although such actions have in some cases aggravated controversy. Surplus amounts of fluoride may cause tooth mottling, which presents no trouble other than appearance **[28]**. The fluorine deficiency in diet can also influence teeth and bones. It can cause osteoprosis and dental caries. The teeth affected by dental caries look like:

Figure 1.3: Defiency of Fluoride effects on teeth

So it is very important to have the concentration of fluoride between optimal levels. Both ways it affects the teeth and bones.

1.1.4 Activated carbon

Activated carbon is a form of carbon accompanied with small, low-volume pores that increase the surface area available for adsorption and chemical reactions. Due to its higher degree of microporosity, only 1 gram of activated carbon has a surface area in surplus of 500 m^2, as observed by adsorption isotherms of carbon dioxide gas at room temperature or 0 °C temperature. An activation level sufficient for helpful application may be attained solely from high surface area; however, further chemical treatment often improves adsorption properties.

Activated carbon is usually formed from charcoal. The main raw material used for activated carbon is any organic material with higher carbon content (coal, peat, wood, coconut shells). Granular activated carbon media is commonly produced by grinding the raw material, adding an appropriate binder to give it re-compacting, hardness and crushing to the correct size **[29]**. The carbon-based material is transformed to activated carbon by thermal decomposition in a furnace by using a controlled heat and atmosphere. The resultant product has an extremely large surface area / volume, and a network of submicroscopic pores where adsorption takes place. The walls of the pores give the surface layer molecules that are essential for adsorption. Remarkably, one pound of carbon (a quart container) gives a surface area equivalent to six football fields.

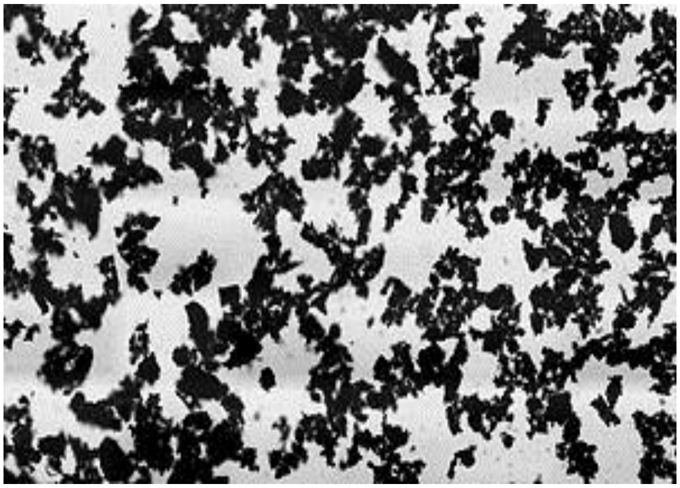


Figure 1.4 The enormous surface area of the activated carbon

Under an electron microscope, the higher surface-area structures of activated carbon are shown. Individual particles are strongly convoluted and display diverse kinds of porosity; there may be many areas where smooth surfaces of graphite-like material run parallel to each other, separated by just a few nanometers or so. These micropores give superb conditions for adsorption to occur, as adsorbing material can interact with a lot of surfaces simultaneously. Tests of adsorption behaviour are frequently done with nitrogen gas at 77 K under high vacuum, but in daily terms activated carbon is perfectly competent of producing the equivalent, by adsorption from the environment, liquid water from steam at 100 °C and a pressure of 1/10,000 of atmosphere.

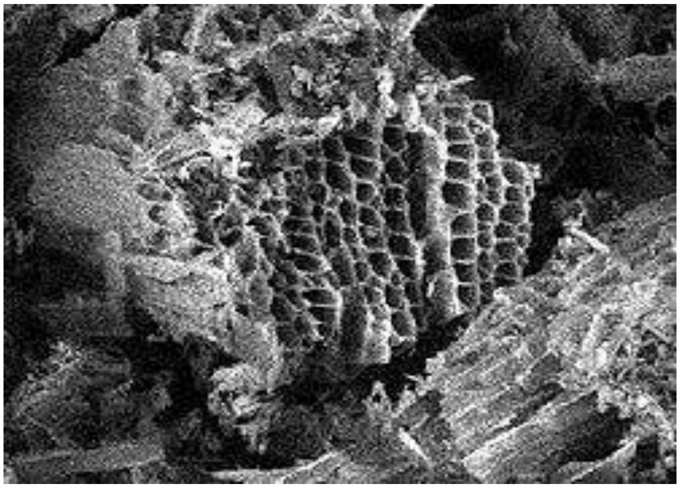


Figure 1.5 Electron microscope view of activated carbon

Activated carbon binds the materials by van der Waals force. Activated carbon doesn’t bind well to certain chemicals, including alcohols, strong acids, glycols and bases, metals and most inorganics, such as lithium, iron, sodium, lead, arsenic, fluorine, and boric acid. Activated carbon adsorbs iodine very well and in fact the iodine number, mg/g, (ASTM D28 Standard Method test) is taken as an indication of total surface area. Carbon monoxide is not well adsorbed by activated carbon **[30]**.

1.1.5 Applications of activated carbon

Activated carbon is used in

(a) Gas purification

Activated carbon's extremely porous nature and large surface area make it an ideal adsorbent for removing trace contaminants from gaseous and liquid streams. For a few inorganic contaminants encountered in gas processing operations, removal can be improved by impregnation of the activated carbon to encourage both physical adsorption and chemisorption.

(b) Decaffeination

The process used for decaffeination by activated carbon is called as “swiss water process of coffee decaffeination”. In it bean is soaked in water. The water is penetrated through activated charcoal, which shreds the caffeine from the bean. The beans are then put back in the water. In the water, the bean again absorbs the remaining flavour.

(c) Gold purification

The activated carbon adsorbs the dissolved gold from the percolated slurry thereby concentrating it onto a smaller solid mass. The carbon is then detached from the slurry by screening and sent for further treatment to recover the adsorbed gold.

(d) Water purification

Activated carbon (AC) is commonly used in water treatment for eliminating free chlorine and organic compounds. Removal of organics from potable water can be to prevent common organic acids such as fulvic or humic from reacting with chlorine to form trihalomethanes (a class of known carcinogens) or, to treat waste water to eliminate any number of organic compounds to make the water suitable for release.

(e) Medicine

Activated carbon is used to treat toxins and overdoses following oral ingestion. It is thought to bind the toxin and check its absorption by the gastrointestinal tract. In the cases of expected poisoning, medical personnel administer activated carbon on the scene or at a hospital's emergency division. Dosing is generally 1 gram/kg of body mass (for adolescents or adults, give 50–100 g), usually given just once, but depending on the medicine taken, it can be given more than once. In uncommon situations activated carbon is used in Intensive Care to sieve out harmful drugs from the blood stream of toxified patients. Activated carbon has become the cure of choice for many poisonings, and other decontamination mechanisms such as ipecac-induced emesis or stomach pumping are now used seldom.

(f) Sewage treatment

In taste and odour control applications activated carbon is used to eliminate chlorine or chloramines that are used broadly as disinfecting agents in water treatment process. Activated carbon also eliminates organic compounds from the water that cause bad taste and odour in drinking water.

(g) Air filters in gas masks and respirators

Activated carbon has been used for air purification and odour removal processes for centuries. Because of the high surface area of activated carbon the not desired molecules in the air are adsorbed and fixe in the pores of carbon. ACPL produces high grade virgin and impregnated activated carbon for adsorbing mercury, dioxins, and heavy metals from flue gases. Activated carbon is a established adsorbent in hazardous waste, waste-to-energy and clinical waste incineration plants.

(h) Stationary phase in low-pressure chromatographic separation of carbohydrates

Activated carbon, in 50% w/w combination with celite, is used as a stationary phase in low-pressure chromatographic separation of carbohydrates (mono-, di-trisaccharides) using ethanol solutions (5–50%) as the mobile phase in analytical or preparative protocols

(i) Spill cleanup

Activated carbon is the universal adsorbing material for most pesticides. Powdered activated carbon is made up of very small carbon particles that have high affinity for organic chemicals such as pesticides. Activated carbon has a large surface area to which organic molecules can bind. When activated carbon is applied to pesticide-toxicated soil, the pesticide molecules are attracted to the charcoal particles and bind to them when both of them come into contact.

(j) Groundwater remediation

The most common activated carbon used for remediation comes from bituminous coal. Activated carbon adsorbs volatile organic compounds from ground water by chemically binding them to the carbon atoms.

(k) Drinking water filtration

Activated carbon filtration can efficiently reduce certain organic compounds and chlorine in drinking water. It can also decrease the dissolved radon, quantity of lead and harmless taste- and odour-causing compounds

(l) Volatile organic compounds capture from painting, dry cleaning, gasoline dispensing operations, and other processes.

(m) Measurement of radon concentration in air

The inactive nature of the activated charcoal allows repetitive adsorption and desorption of radon. During the analysis period (typically two to seven days), the adsorbed radon experience radioactive decay. Therefore, the technique does not combine uniformly radon concentrations during the exposure period. As with all the devices that store radon, the average concentration is calculated using the mid-exposure time is subjected to error if the ambient radon concentration varies substantially during the analysis period

(n) Distilled alcoholic beverage purification

The properties of activated carbon allow it to entrap poisons, creosotes, heavy metals, insecticides, bad smell and taste, fusel oils, chemical substances and impurities, or unwanted substances in both liquids and gases.

(o) Mercury scrubbing

Activated carbon, often soaked with iodine or sulphur, is extensively used to trap mercury emissions from medical incinerators, coal-fired power stations and from natural gas at the wellhead. This carbon is a speciality product costing even more than US$4.00 per kg. However, it is regularly not recycled.

CHAPTER 2

LITERATURE REVIEW

2.1 International work

Abe et al, 2004, did work on the adsorption of fluoride ions on carbonaceous materials **[31]**. They observed the characteristics of fluoride ion adsorption on carbonaceous materials and were derived as adsorption isotherms at different temperatures and in different pH solutions. The fluoride ion was adsorbed into holes in carbonaceous materials produced from wood; the bigger the specific surface area, the more fluoride ions is adsorbed. Bone char was the most efficient adsorbent. The composition of bone char contains calcium phosphate, calcium carbonate etc. This tells that the phosphate ion in bone char was replaced with a fluoride ion. Likewise, the mechanism of fluoride ion adsorption on bone char is visibly chemical in nature because the quantity of fluoride ion adsorbed on bone char increased with increase in temperature and decrease in pH. The amount of fluoride ion adsorbed on bone char was also dependent on the concentration of NaCl in solution because of the "salting-out" effect. The adsorption of fluoride ion on bone char is endothermic. Bone char can be used to remove fluoride ions from the drinking water.

Matsunaga et al, 2006, carried out the studies on- fluorometric determination of fluoride ion by reagent tablets containing 3-hydroxy-2-sulfoflavone and zirconium(IV) ethylenediamine tetraacetate **[32].** They studied about a reagent tablet for determination of fluoride ion has been prepared using ethylenediamine-N,N,N,N-tetraacetate complex of zirconium (Zr-EDTA), 3-hydroxy-2-flavone (FS) and an appropriate pH buffer. Dissolving of the tablet into water exhibits an intense blue fluorescence ($\lambda max = 460$ nm) upon excitation at 377 nmand the fluorescence intensity decreases with the presence of fluoride ion. Hence, a simple fluorescent detection procedure for fluoride ion in aqueous media was successfully constructed with this tablet. The principle of this detection system is the ligand exchange reaction of FS bound to Zr-EDTA with fluoride ion. The present system provides an easy, rapid and selective determination method of fluoride ion ranging from 5×10^{-6} to 1×10^{-3} mol dm^{-3}. The measurement of real samples with this tablet showed the similar results as those by the common method with the Alfusone reagent

Tripathya et al, 2006, did studies on removal of fluoride from drinking water by adsorption onto alum-impregnated activated alumina **[33]**. They studied the ability of the alum-impregnated activated alumina (AIAA) for removal of fluoride from water through adsorption has been investigated in the present study. All the experiments are carried out by batch mode. The effect of various parameters viz. contact time, pH effect (pH 2–8), adsorbent dose (0.5–16 g/l), initial fluoride concentration (1–35 mg/l) has been investigated to determine the adsorption capacity of AIAA. The adsorbent dose and isotherm data are correlated to the Bradley equation. The efficacy of AIAA to remove fluoride from water is found to be 99% at pH 6.5, contact time for 3 h, dose of 8 g/l, when 20 mg/l of fluoride is present in 50 ml of water. Energy-dispersive analysis of X-ray shows that the uptake of fluoride at the AIAA/water interface is due to only surface precipitation. The desorption study reveals that this adsorbent can be regenerated following a simple base–acid rinsing procedure, however, again impregnation of the regenerated adsorbent (rinsed residue) is needed for further defluoridation process

Zhao et al, 2008, studied fluoride removal by Fe(III)-loaded ligand exchange cotton cellulose adsorbent from drinking water **[34]**. They studied that a novel bead adsorbent, Fe(III)-loaded ligand exchange cotton cellulose adsorbent [Fe(III)LECCA], was prepared, for fluoride removal from drinking water. The influence of pH, reaction time, temperature, foreign ions, flow rate, and regeneration were determined in batch and column systems. Adsorption–desorption–readsorption results indicated that Fe(III)LECCA has the potential to act as an adsorbent for the removal of fluoride because of its adsorption capacity and mechanical stability. The adsorption mechanism of fluoride removal was elucidated clearly by Fourier Transform Infra Red (FTIR) spectrum and chemical analysis. The results showed that Fe(III)LECCA would be a cost-effective and environmental benign adsorbent for fluoride removal from drinking water

Bhatnagara et al, 2011, did studies on fluoride removal from water by adsorption **[35]**. They observed Fluoride contamination in drinking water due to natural and anthropogenic activities has been recognized as one of the major problems worldwide imposing a serious threat to human health. Among several treatment technologies applied for fluoride removal, adsorption process has been explored widely and offers satisfactory results especially with mineral-based and/or surface modified adsorbents. In this review, an extensive list of various adsorbents from literature has been compiled and their adsorption capacities under various conditions (pH, initial fluoride concentration, temperature, contact time, adsorbent surface charge, etc.) for fluoride removal as available in the literature are presented along with highlighting and discussing the key advancement on the preparation of novel adsorbents tested so far for fluoride removal. It is evident from the literature survey that various adsorbents have shown good potential for the removal of fluoride. However, still there is a need to find out the practical utility of such developed adsorbents on a commercial scale, leading to the improvement of pollution control

Sun et al, 2011, studied the removal of fluoride from drinking water by natural stilbite zeolite modified with Fe(III) **[36]**. They found that the Stilbite zeolite , a natural zeolite with high crystallinity and an open pore system, was modified with $FeCl_3$ solution for the removal of fluoride from drinking water. The parent STI and modified STI (Fe(III)-STI) were characterized by FTIR, scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Adsorption of fluoride on modified STI (Fe(III)-STI) was studied as a function of contact time, adsorbent dose, initial concentration, pH and coexisting ions. Fluoride concentration can be reduced down to the lower level of 1 mg L−1 under the optimum condition (with solid/solution ratio of 1:100 and the contact time of 2 h and pH 6.94) when initial fluoride concentration of 10 mg L−1 is employed. The fluoride adsorption on Fe(III)-STI zeolite is well described by the Langmuir adsorption model, and the maximum fluoride adsorption capacity is 2.31 mg g−1. The kinetic result indicates that the adsorption of fluoride on the modified natural zeolite follows pseudo-first-order model

Montoya et al, 2012, did studies on optimizing the removal of fluoride from water using new carbons obtained by modification of nut shell with a calcium solution from egg shell **[37]**. They observed Carbons loaded with specific chemical moieties were prepared from pecan nut shells employing a natural modifier agent obtained from egg shell, which is rich in calcium, for the selective adsorption of fluoride from water. A L4 orthogonal array of the Taguchi method was used to optimize the synthesis conditions for obtaining these selective carbons. The samples obtained were characterized and the elemental composition, textural parameters and morphology were determined. Fluoride adsorption experiments were performed in synthetic and real groundwater samples. Results showed that carbons obtained from pecan nut shells modified with a calcium solution extracted from egg shells (CMPNS) were more effective for fluoride removal than those using the nut shell precursor as such. The calcium chemical species on the carbon surfaces were more important in the fluoride adsorption process than the carbon textural parameters. In addition, hydrogencarbonate was found to be the main competitor for the active sites of CMPNS during the fluoride removal process

Salifu et al, 2013, did studies on aluminum hydroxide coated pumice for fluoride removal from drinking water **[38]**. They studied that the Intake of excess fluoride (beyond 1.5 mg/L, WHO guideline) for long periods can result in the incidence of fluorosis. Adsorption is widely considered the most appropriate technology for water defluoridation, if a suitable adsorbent is available. Several studied adsorbents have shown certain degrees of adsorption capacity, however, applicability of most is limited either due to lack of socio-cultural acceptance, high cost or effectiveness only in extreme pH conditions. The search for alternative adsorbents thus remains of interest. Modification of pumice particle surfaces by aluminum oxide coating was found effective in creating hard surface sites for fluoride adsorption, in accordance with the hard and soft acids and bases (HSAB) concept. Aluminum oxide coated pumice (AOCP) reduced fluoride concentration in model water from 5.0 ± 0.2 mg/L to 1.5 mg/L in approximately 1 h, using an adsorbent dose of 10 mg/L. Contrary to expectations, thermal treatment of AOCP aimed at further improving its performance, instead reduced the fluoride removal efficiency. The equilibrium adsorption of fluoride by AOCP conformed reasonably to five isotherm models in the order: Generalized model > Langmuir type 2 > BET > Temkin > Dubinin–Radushkevich; with a maximum capacity of 7.87 mg/g. AOCP exhibited good fluoride adsorption within the pH range, 6–9, which makes it possible to avoid pH adjustment with the associated cost and operational difficulties, especially if it is to be used in remote areas of developing countries. Based on results from kinetic adsorption experiments, it was observed that at a neutral pH of 7.0 ± 0.1 which is a more suitable condition for groundwater treatment, fluoride adsorption by AOCP was quite comparable or perhaps fairly faster in the initial period of contact than that of activated alumina (AA), the commonly used adsorbent for water defluoridation. AOCP is thus promising and could also possibly be a useful fluoride adsorbent.

Zuo et al, 2008, studied the combined electrocoagulation and electroflotation for removal of fluoride from drinking water **[39]**. They found that a combined electrocoagulation (EC) and electroflotation (EF) process was proposed to remove fluoride from drinking water. Its efficacy was investigated under different conditions. Experimental results showed that the combined process could remove fluoride effectively. The total hydraulic retention time required was only 30 min. After treatment, the fluoride concentration was reduced from initial 4.0–6.0 mg/L to lower than 1.0 mg/L. The influent pH value was found to be a very important variable that affected fluoride removal significantly. The optimal influent pH range is 6.0–7.0 at which not only can effective defluoridation be achieved, but also no pH readjustment is needed after treatment. In addition, it was found that SO_4^{2-} had negative effect; Ca^{2+} had positive effect; while Cl^{-} had little effect on the fluoride removal. The EC charge loading, EF charge loading and energy consumption were 3.0 Faradays/m3, 1.5 Faradays/m3, and 1.2 kWh/m3, respectively, under typical conditions where fluoride was reduced from initial 4.0 to 0.87 mg/L.

Kamga et al, 2010, did their studies on preparation and characterization of charcoals that contain dispersed aluminum oxide as adsorbents for removal of fluoride from drinking water **[40]**. They studied that charcoals adsorbents that contain dispersed aluminum and iron oxides have been synthesized by impregnating wood with salt solutions followed by carbonization at 500 °C, 650 °C or 900 °C. The adsorbents were characterized and their performance for fluoride removal from aqueous solution was evaluated. Aluminum and iron oxides were well dispersed into the porous charcoals. The carbons were amorphous and highly porous. XRD of the adsorbents showed crystalline iron oxide but did not show any form of crystalline aluminum oxides. All the adsorbents showed acidic surface properties. The efficiency of defluoridation was found to depend on the carbonization temperature, the pH of point of zero charge (pHPZC), and the co-existing ions. Substrates prepared at 650 °C with aluminum and iron oxides exhibited the best efficiency with a fluoride sorption capacity of 13.64 mg g^{-1}. More than 92% removal of fluoride was achieved within 24 h from a 10 mg L^{-1} solution at neutral pH. Fluoride adsorption kinetic was well fitted by a pseudo-second order model. The amounts of residual Al and Fe in treated solution were pH dependant. At neutral pH, the amounts of dissolved Al and Fe were found to be 0.67 and 1.8 mg L^{-1}, respectively

Yadav et al, 2013, studied removal of fluoride from aqueous solution and groundwater by wheat straw, sawdust and activated bagasse carbon of sugarcane **[41]**. They studied to design and develop a novel cost effective strategy for fluoride removal, applicable to rural areas of developing countries. Most of the adsorbents based technologies for fluoride removal works at acidic pH which is not feasible condition for application to rural areas. This study investigates the feasibility of three low-cost agricultural biomass based adsorbents namely: activated bagasse carbon (ABC), sawdust raw (SDR), and wheat straw raw (WSR) for water defluoridation, at neutral PH range. Performance of these adsorbents was compared with commercially available activated carbon (CAC). The CAC, ABC, SDR, and WSR removed 57.6, 56.4, 49.8 and 40.2% respectively from an aqueous solution of 5 mg L−1 fluoride at pH 6.0, with the contact period of 60 min and a dose of 4 g L−1. All adsorption experimental data followed the Freundlich isotherm. The adsorption kinetic was also studied in terms of pseudo-first-order, pseudo-second-order and intraparticle diffusion models. Mechanism of fluoride removal was found to be complex. In addition, both surface adsorption and intra-particle diffusion contribute to the rate determining step. An updated list of biomass based adsorbents reported in scientific literatures was prepared and compared with adsorbents used in this study.

Daifullah et al, 2007, did their studies on adsorption of fluoride in aqueous solutions using KMnO4-modified activated carbon derived from steam pyrolysis of rice straw **[42]**. They studied that Fluoride in drinking water above permissible levels is responsible for human and skeletal fluorosis. In this study, activated carbons (AC) prepared by one-step steam pyrolysis of rice straw at 550, 650, 750 °C, respectively, were modified by liquid-phase oxidation using HNO_3, H_2O_2 and $KMnO_4$. Characterization of these 12 carbons was made by their surface area, porosity, acidity, basicity, pHpzc, pH and ability to remove fluoride anion. Based on the data of the latter factor, the $RS_2/KMnO_4$ carbon was selected. Along with batch adsorption studies, which involve effect of pH, adsorbate concentration, adsorbent dosage, contact time, temperature, and Co-ions ($SO4_2^-$, Cl^-, Br^-). The effects of natural organic matter (NOM) were also made to remove the fluoride from natural water. On the basis of kinetic studies, specific rate constants involved in the adsorption process using $RS_2/KMnO_4$ carbon was calculated and second-order adsorption kinetics was observed. Equation isotherms such as Langmuir (L), Freundlich (F), Langmuir–Freundlich (LF) and Dubinin–Radushkevich (DR) were successfully used to model the experimental data. From the DR isotherm parameters, it was considered that the uptake of F− by $RS_2/KMnO_4$ carbon proceeds by an ion-exchange mechanism (E = 10.46 kJ mol−1). The thermodynamic parameters of fluoride sorption were calculated and the sorption process was chemical in nature. The ability of $RS_2/KMnO_4$ to remove F^- from Egyptian crude phosphoric acid (P2O5 = 48.42%) was tested and the adsorption capacity of F^- in H_3PO_4 was greater than that in distilled water. This is may be due to fluoride adsorption enhanced at lower pH of crude acid.

2.2 National work

Emmanuel et al, 2008, carried out the studies on removal of fluoride from drinking water with activated carbons prepared from HNO_3 activation **[43]**. They found out that the removal of fluoride on commercial activated carbon (CAC) and indigenously prepared activated carbons (IPACs) from Pithacelobium dulce, Ipomoea batatas and Peltophorum ferrugineum have been studied. The effects of various experimental parameters like pH, dose of the adsorbent, adsorbate concentration and contact time have been investigated using a batch adsorption technique. The extent of fluoride removal increased with decrease in the initial concentration of fluoride and particle size of the adsorbent and also increased with increase in contact time, amount of adsorbent used and the initial pH of the solution. Adsorption data were modeled using the Freundlich and Langmuir adsorption isotherms and followed first order kinetic equation –dF/dt= Kr (F). The experimental data produced a straight line fit with a relatively good correlation coefficient (R^2) indicating the acceptability of the model for the studied indigenously prepared activated carbons (IPACs) fluoride system. $[R]^2$ values for PLDC=0.09967, IBC= 0.9953, PFC= 0.9946 and CAC=0.9946]. The kinetics of adsorption was found to be first ordered with regards to intra-particle diffusion rate. The adsorption capacities of PLDC (78.96), IBC (76.62), and PFC (74.48) have been compared with that of the CAC (39.20) in drinking water treatment for removal of fluoride.

Mohapatra et al, 2004, did study on use of mineral oxides to abate fluoride from water **[44]**. They studied The removal of fluoride from aqueous solutions has been investigated using various oxide ores such as refractory grade bauxite, feed bauxite, manganese ore, and hydrated oxides of manganese ores (WAD). The refractory grade bauxite showed promising results. The studies were carried out as functions of contact time, pH, concentration of adsorbents, concentration of adsorbate, and temperature. The adsorption was rapid during the initial 5 min but equilibrium was attained within 120 min. The adsorption followed first-order kinetics. The present system followed the Langmuir adsorption isotherm model. Various thermodynamic parameters such as free energy, enthalpy, entropy, and equilibrium constants were calculated. The isosteric heat calculations showed that the adsorption process followed a heterogeneous model

Das et al, 2005, carried out studies on defluoridation of drinking water using activated titanium rich bauxite **[45]**.They studied that the potential of thermally activated titanium rich bauxite (TRB) for adsorptive removal of excess fluoride from drinking water was examined. Adsorption with respect to variation of pH, adsorbent dose, initial fluoride concentration, presence of interfering ions and heat treatment were investigated by batch equilibrium experiments. Thermal activation at moderate temperatures (300–450 ◦C) greatly increased the adsorption capacity of TRB. The rate of adsorption was rapid and maximum level was attained within 90 min. The uptake of fluoride increased with increasing pH, reached to a maximum at pH 5.5–6.5 and thereafter decreased. The adsorption kinetics was found to follow first order rate expression and the experimental equilibrium adsorption data fitted reasonably well to both Langmuir and Freundlich isotherm models. The presence of common interfering ions in drinking water did not greatly affect the uptake of fluoride from aqueous solution indicating F specific sorption behaviour of TRB. Nearly complete desorption of adsorbed fluoride from loaded bauxite was achieved by treating with aqueous solutions of pH 11.1 ([NaOH] 0.015 mol/dm3).

Ghorai et al, 2005, studied equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina **[46]**. They studied that contamination of drinking water due to fluoride is a severe health hazard problem. Excess of fluoride (>1.5 mg/l) in drinking water is harmful to the human health. Various treatment technologies for removing fluoride from groundwater have been investigated in the past. Present investigation aims to remove fluoride by activated alumina. Adsorption isotherm has been modeled by Langmuir equation and isotherm constants. The dependence of the adsorption of fluoride on the pH of the solution has been studied to achieve the optimum pH value and a better understanding of the adsorption mechanism. It was found that maximum adsorption takes place at pH value of 7. Breakthrough analysis revealed that early saturation and lower fluoride removal takes place at higher flow rate and at higher concentrations. Predicted simulation results of one-dimensional model for isothermal, axially dispersed fixed bed on the assumption of pore-diffusion rate-control conditions matches with the experimental data in the initial zone of the breakthrough curve, but deviated marginally in the final tailing zone. Bed depth service time (BDST) model was also applied successfully

Sarkar et al, 2006, studied the use of laterite for the removal of fluoride from contaminated drinking water **[47]**. They studied that the effects of different operational variables on the mechanistic function of laterite in removal of fluoride have been investigated. Thermodynamic parameters such as free energy change, enthalpy, and entropy of the process, as well as the sorption isotherm, were evaluated. The extent of solute removal is determined by initial solute concentration, operational conditions, laterite dose, and solution pH. For a fixed set of experimental conditions, a model equation is developed from which the percent removal corresponding to each load of fluoride is determined. The mechanism of fluoride adsorption is governed by the zero point charge of laterite and follows a first-order rate equation. pH has a vital role influencing the surface characteristics of laterite. To simulate the flow dynamics, fluoride solution was run through a fixed bed column. The pattern of breakthrough curves for different influent fluoride concentration, pH, and column bed height was characterized. The column efficiency was tested from the bed depth–service time model. The elution of the retained fluoride was studied and the effectiveness of column operation was determined by the retention–elution cycles.

Yadav et al, 2006, studied the defluoridation of groundwater using brick powder as an adsorbent **[48]**. They studied that the deflouridation of groundwater using brick powder as an adsorbent was studied in batch process. Different parameters of adsorption, viz. effect of pH, effect of dose and contact time were selected and optimized for the study. Feasible optimum conditions were applied to two groundwater samples of high fluoride concentration to study the suitability of adsorbent in field conditions. Comparison of adsorption by brick powder was made with adsorption by commercially available activated charcoal. In the optimum condition of pH and dose of adsorbents, the percentage deflouridation from synthetic sample, increased from 29.8 to 54.4% for brick powder and from 47.6 to 80.4% for commercially available activated charcoal with increasing the contact time starting from 15 to 120 min. Fluoride removal was found to be 48.73 and 56.4% from groundwater samples having 3.14 and 1.21 mg l−1 fluoride, respectively, under the optimized conditions. Presence of other ions in samples did not significantly affect the deflouridation efficiency of brick powder. The optimum pH range for brick powder was found to be 6.0–8.0 and adsorption equilibrium was found to be 60 min. These conditions make it very suitable for use in drinking water treatment. Deflouridation capacity of brick powder can be explained on the basis of the chemical interaction of fluoride with the metal oxides under suitable pH conditions. The adsorption process was found to follow first order rate mechanism as well as Freundlich isotherm.

Maliyekkal et al, 2008, did the studies on enhanced fluoride removal from drinking water by magnesia-amended activated alumina granules **[49]**. They studied the fluoride removal potential of a novel sorbent, magnesia-amended activated alumina (MAAA) from drinking water. MAAA, prepared by calcining magnesium hydroxide impregnated alumina at 450 °C has shown high fluoride sorption potential than activated alumina from drinking water. Batch sorption studies were performed as a function of contact time, pH, initial fluoride concentration, and adsorbent dose. Studies were also performed to understand the effect of various other co-existing ions present in real ground water samples. X-ray powder diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray (EDAX) and a gas adsorption porosimetry analyses were used to characterize the physicochemical properties of MAAA. More than 95% removal of fluoride (10 mg l^{-1}) was achieved within 3 h of contact time at neutral pH. Sorption of fluoride onto MAAA was found to be pH dependant and a decrease in sorption was observed at higher pHs. Among the kinetic models tested, pseudo-second-order model fitted the kinetic data well, suggesting the chemisorption mechanism. Among the various isotherm model tested, Sips model predicted the data well. The maximum sorption capacity of fluoride deduced from Sips equation was 10.12 mg g^{-1}. Most of the co-existing ions studied have negligible effect on fluoride sorption by MAAA. However, higher concentrations of bicarbonate and sulfate have reduced the fluoride sorption capacity.

Ganvir et al, 2011, studied the removal of fluoride from drinking water using aluminum hydroxide coated rice husk ash **[50]**. They studied the fluoride content in groundwater that is greater than the WHO limit of 1.5 mg/L, causes dental and skeletal fluorosis. In India, several states are affected with excess fluoride in groundwater. The problem is aggravated due to the lack of appropriate and user friendly defluoridation technology. Several fluoride removal techniques are reported in the literature amongst which the Nalgonda technique and use of activated alumina have been studied extensively. However a simple, efficient and cost effective technology is not available for widespread use in many affected regions. In this paper, we present a novel cost effective defluoridation method that is based on surface modification of rice husk ash (RHA) by coating aluminum hydroxide. RHA is obtained by burning rice/paddy husk which is an abundantly available and is an inexpensive raw material. The results showed excellent fluoride removal efficiency and the adsorption capacity was found to be between 9 and 10 mg/g.

Meenakshi et al, 2006, studied the fluoride in drinking water and its removal **[51]**. They observed Excessive fluoride concentrations have been reported in groundwaters of more than 20 developed and developing countries including India where 19 states are facing acute fluorosis problems. Various technologies are being used to remove fluoride from water but still the problem has not been rooted out. In this paper, a broad overview of the available technologies for fluoride removal and advantages and limitations of each one have been presented based on literature survey and the experiments conducted in the laboratory with several processes. It has been concluded that the selection of treatment process should be site specific as per local needs and prevailing conditions as each technology has some limitations and no one process can serve the purpose in diverse conditions.

Mohapatra et al, 2009, studied the fluoride removal from drinking water **[52]**. They studied Fluoride in drinking water has a profound effect on teeth and bones. Up to a small level (1–1.5 mg/L) this strengthens the enamel. Concentrations in the range of 1.5–4 mg/L result in dental fluorosis whereas with prolonged exposure at still higher fluoride concentrations (4–10 mg/L) dental fluorosis progresses to skeletal fluorosis. High fluoride concentrations in groundwater, up to more than 30 mg/L, occur widely, in many parts of the world. They aimed at providing precise information on efforts made by various researchers in the field of fluoride removal for drinking water. The fluoride removal has been broadly divided in two sections dealing with membrane and adsorption techniques. Under the membrane techniques reverse osmosis, nanofiltration, dialysis and electro-dialysis have been discussed. Adsorption, which is a conventional technique, deals with adsorbents such as: alumina/aluminium based materials, clays and soils, calcium based minerals, synthetic compounds and carbon based materials. Studies on fluoride removal from aqueous solutions using various reversed zeolites, modified zeolites and ion exchange resins based on cross-linked polystyrene are reviewed. During the last few years, layered double oxides have been of interest as adsorbents for fluoride removal. Such recent developments have been briefly discussed.

Tomar et al, 2013, studied the adsorptive removal of fluoride from water samples using Zr–Mn composite material **[53]**. They observed that the toxicity of fluoride to mankind is very high. Thus there has always been need to treat fluoride contaminated water samples for its removal to make it safe for human consumption. A novel and efficient analytical method for the removal of fluoride using Zr–Mn composite material has been developed for water samples. The adsorption was confirmed by the use of various techniques like X-ray diffraction (XRD), Brunauer, Emmett and Teller (BET) and FTIR. The key parameters that influence analyte i.e. fluoride removal were investigated and optimized. Under the optimized conditions of the adsorbent dose 1.2 g/50 mL, pH 7, temp 29 °C and the contact time 145 min, an excellent fluoride removal up to 90% was achieved. The proposed material has successfully been applied to the removal of fluoride in different aqueous solutions having a broad concentration range of fluoride. The effectiveness of the sorption process on the adsorbent (Zr–Mn composite material) was verified by testing it on natural waters loaded with the proposed fluoride. The reproducibility of the method was validated by removing fluoride in various water samples by the proposed method in a different laboratory under the same condition. The simplicity of the proposed fluoride removal material, very high removal efficiency, short time and the use of safe chemicals demonstrate the high potential of the proposed method for routine fluoride removal from water samples. The process of adsorption by Zr–Mn composite material followed Freundlich as well as Langmuir isotherms but is favorable to Freundlich isotherm that provides best fit to the experimental data. The results obtained showed that adsorption on the Zr–Mn composite material could be an effective method for the removal of fluoride.

Srimurali et al, 1998, did studies on removal of fluorides from drinking water by adsorption onto low-cost materials **[54]**. They studied Various low-cost materials like kaolinite, bentonite, charfines, lignite and nirmali seeds were investigated to assess their capacity for removal of fluorides from water by batch adsorption studies. Studies were also conducted to determine optimum operating-system parameters; such as contact time, pH, dose and size of the adsorbent. Present study has indicated that materials like nirmali seeds and lignite are not effective (removal 6 to 8%); whereas removal by kaolinite clay was slightly higher (18.2%). Charfines and bentonite exhibited highest removal capacity of 38 and 46%, respectively, at optimum system conditions. Chemical pre-treatment of charfines did not result in enhanced removal of fluoride from water.

CHAPTER 3
MATERIALS AND METHODS

This chapter describes the materials as well as the methods used to conduct the experimental work

3.1 Materials

3.1.1 Chemicals and reagents

All chemicals used were of A.R. grade. These were purchased from Sigma-Aldrich chemicals PVT. Ltd. India, SD Fine and Merck, India. All chemicals were used as received in all experiments and distilled water was used.

The chemicals used were NaF (S D Fine Chemicals Limited), 1N HCl and 1N NaOH for adjusting pH, buffer solutions (pH=7 and pH=4) for caliberating pH meter.

3.1.2 Adsorbent

Activated Carbon was procured from “S D Fine Chemicals Limited”. Activated carbon is a form of carbon having low-volume pores that increase the surface area available for adsorption or chemical reactions. The structure of Activated carbon is shown in figure 1.

3.1.3 Instruments/Equipment

3.1.3.1 pH meter

The pH of the solution was measured using ELICO, India, model no. LI 120 pH meter.

3.1.3.2 Centrifuge

Samples were centrifuged after treatment in order to separate the Activated Carbon particles from the Sodium Flouride (NaF) solution. A compact laboratory centrifuge Hitachi High-Speed Micro Centrifuge, Model CF15RX II was used. Samples were centrifuged at a speed of 14,500 RPM until the solution appeared completely free of Activated Carbon particles.

3.1.3.3 Orion Ion Analyzer

Samples were sent to Orion Ion Analyzer for the analysis of fluoride and to get the amount of fluoride in the solution left after adsorption with activated carbon. It works on the principle of potential difference developed in the solution and measured with reference to a constant reference potential with a digital pH/mV.

3.1.3.4 Orbital Shaking Bath

A water bath with integral shaking, a choice of platform is available to provide linear or orbital shaking action. The platforms require no special fitting and use strong magnets, which couple to the drive unit underneath the stainless steel tank. Vessels are securely held in place on the stainless steel platforms by a series of high-tension springs, which will accommodate almost any size and combination of vessel. The heater is mounted underneath the tank to allow easy cleaning. A low-level water sensor causes a warning to flash on the display to indicate when the water level is low, cutting power to the heater to prevent the bath from boiling dry. A drain is also incorporated to aid emptying of the bath. The speed and temperature controls are easy to use. The shaking speed is adjustable and electronic feedback control ensures accurately maintained speed. The water bath temperature is set and monitored via the easy to read LED display. In addition, the design incorporates an over temperature protection system that tracks the set temperature and controls the heater in the event of a fault.

3.2 EXPERIMENTAL PROCEDURE

3.2.1 Method for preparation of Sodium Fluoride (NaF) solution

To make the solution of 20ppm Sodium Fluoride we calculate the amount of Sodium Fluoride that we need to put in 1L of water. After calculation the amount of Sodium Fluoride comes out to be as 20mg in 1L of water. The water used here is distilled water for the preparation of solution.

3.2.2 Optimizing the pH

For fluoride removal, pH is the most important parameter. For carrying out all the experiments, pH needs to be optimized first. So pH optimization is a very important step for carrying out Fluoride removal studies. To optimize the pH, we assume all other parameters to be constant. The values of the parameters for optimizing the pH are shown in Table 3.1

Table 3.1 Table showing various parameters for pH optimization

Parameter	**Value**
Initial Sodium Fluoride concentration	20 ppm
Temperature	25 C
Amount of carbon	0.2g
Contact Time	6 hours

To optimize the pH, 5 different plastic beakers are taken. 100ml of the sodium fluoride solution (20ppm) is taken in each beaker and keeping all the other parameters constant, pH is varied in each of them. The values of the different pH taken are- 6.71 (which is the original pH of the solution), 2, 4, 6, 9, 11. Then the beakers are kept in a batch shaker for 6 hours. After 6 hours the beakers are taken out and activated Carbon is removed using a glass fiber filter paper. The filtered solution is given for analysis of fluoride using Orion Ion Analyzer. The results of analysis are shown in Table 3.2

The values of fluoride removal by optimizing pH are shown in table 3.2

Table 3.2 Removal of fluoride by different pH

pH	Fluoride Conc (ppm)	Removal (in %age)
2	6.9	65.5
4	9.2	54
6	9.2	54
6.71 (Original)	9	55
9	9.5	52.3
11	10.1	49.3

The removal is calculated using the formula

$R= 100 (C_0 - C) / C_0$

3.2.3 Optimizing the carbon content

Carbon content is optimized to see at what amount of carbon the removal of fluoride is maximum. To optimize the carbon we keep all other parameters constant keeping the amount of carbon different for each beaker. The different parameters taken are shown in Table 3.3

Table 3.3 Table showing various parameters for carbon content optimization

Parameter	Value
Initial Sodium Fluoride concentration	20 ppm
Temperature	25 C
pH	6.71
Contact Time	6 hours

To optimize Carbon content 5 different plastic beakers are taken. 100ml of the sodium fluoride solution (20ppm) is taken in each beaker and all the above parameters are kept constant with different Carbon content as 0.2g, 0.4g, 0.6g, 0.8g, 1.0g. Then the beakers are kept in batch shaker for 6 hours. After that the contents of the beakers are filtered to remove the activated carbon using glass fiber filter paper. The filtered solution in beakers is sent for the analysis of Fluoride using Orion Ion Analyzer. The results obtained are shown in Table 3.4

Table 3.4 Removal of Fluoride by different amount of carbon

Amount of Carbon	**Fluoride Conc (ppm)**	**Removal (in %age)**
0.2	8	60
0.4	8.6	57
0.6	8.7	56.5
0.8	8.5	57.5
1.0	8.1	59.5

The removal is calculated using the formula

$R= 100 (C_0 - C) / C_0$

3.2.3 Optimizing the contact time

The contact time is the time for which the fluoride is in contact with the adsorbent. In adsorption fluoride gets adsorbed in the vacant spaces in the adsorbent, so when the spaces are filled and no more fluoride can go inside then adsorption stops and it is possible also that desorption may take place even and fluoride starts getting rem.oved. So contact time is very important for adsorption to take place properly. To optimize the contact time we keep all other parameters constant keeping the contact time different for each beaker. The different parameters are shown in table 3.5

Table 3.5 Table showing various parameters for contact time optimization

Parameter	**Value**
Initial Sodium Fluoride concentration	20 ppm
Temperature	25 C
pH	6.71
Amount of carbon	0.2g

To optimize Contact time, 5 different plastic beakers are taken and all the above parameters are kept constant with different Contact Time as 3hours, 6hours, 12hours, 24hours. Then the beakers are kept in batch shaker for all the different contact times. After that the contents of the beakers are filtered to remove the activated carbon using glass fiber filter paper. The filtered solution in beakers is sent for the analysis of Fluoride using Orion Ion Analyzer. The results obtained are shown in Table 3.6

Table 3.6 Removal of Fluoride by different contact times

Contact Time	**Fluoride Conc (ppm)**	**Removal (in %age)**
3 hours	8	60
6 hours	10.3	48.5
12 hours	10.0	50
24 hours	10.5	47.5

The removal is calculated using the formula

$R= 100 (C_0 - C) / C_0$

3.2.4 Testing for Fluoride Removal on Drinking Water Sample

Now as all the above parameters are optimized so we know that at what parameters the fluoride removal is maximum. So taking those parameters, we test the fluoride removal on the sample of drinking water. A sample of drinking water was taken and sent for analysis of Fluoride by the Orion Ion Analyser. Then keeping all the parameters constant we carry out the adsorption experiment. The parameters that are kept constant are shown in table 3.7

Table 3.7 Table showing the parameters for sample testing

Parameter	**Value**
Initial Sodium Fluoride concentration	20 ppm
Temperature	25 C
pH	6.71
Amount of carbon	0.2g
Contact Time	3 hours

The beakers are kept in batch shaker for 3 hours. After that the contents of the beakers are filtered to remove the activated carbon using glass fiber filter paper. The filtered solution in beakers is sent for the analysis of Fluoride using Orion Ion Analyzer. The results obtained are shown in table 3.8

Table 3.8 Concentration of fluoride before and after treating with carbon from some samples of drinking water and removal of fluoride

Sample	**F^- concentration before treatment with activated carbon (ppm)**	**F^- concentration after treatment with activated carbon (ppm)**	**Removal (%)**
Drinking water from lab	0.77	0.72	6.5
River water	0.9	0.6	33
Hostel drinking water	1.2	0.6	50
Domestic water from a house	1.6	1.1	31.3
Ground water	1.3	0.6	53.8
Domestic water from another house	2.6	1.5	42.3

CHAPTER 4

RESULTS AND DISUSSION

The results of the experiments are given in this chapter.

4.1 Effect of pH

The removal is maximum is at pH=2 so that should be the optimal pH. But as it is in highly acidic range and its not practically possible to carry out experiments in that conditions as it will cause the wear and tear to the apparatus. So we take the next value at which the removal is maximum i.e. at pH= 6.71, which is the pH without adjusting and normal pH of the Sodium Fluoride solution. The results are shown in Table 3.2

The graph representing the values is shown in figure 4.1

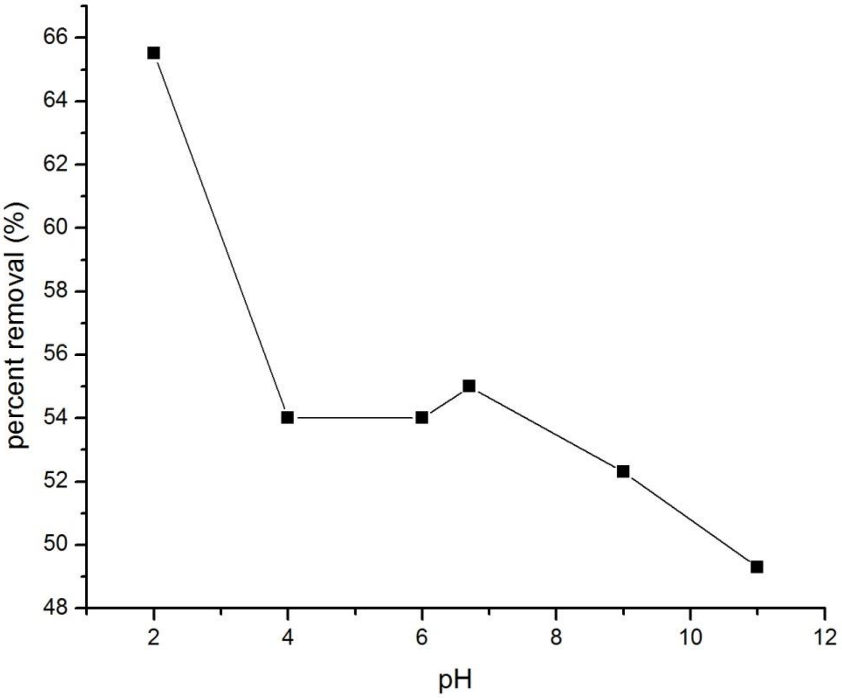


Figure 4.1 Effect of different pH on the removal of fluoride

4.2 Effect of amount of adsorbent

When the amount of carbon is 0.2g then removal is maximum i.e. 60% so that is optimum for fluoride removal. But the values follows a dome shaped graph and having lowest concentration at 0.2g and it keeps on increasing till 0.6g and after that the concentration decreases increases. The inverse trend is for fluoride removal, i.e. maximum at 0.2g and decreases till 0.6g and then increases but having a lower removal than at 0.2g. So 0.2g is chosen as the optimum removal. The results are shown in table 3.4

The graph showing the above results is shown in fig 4.2

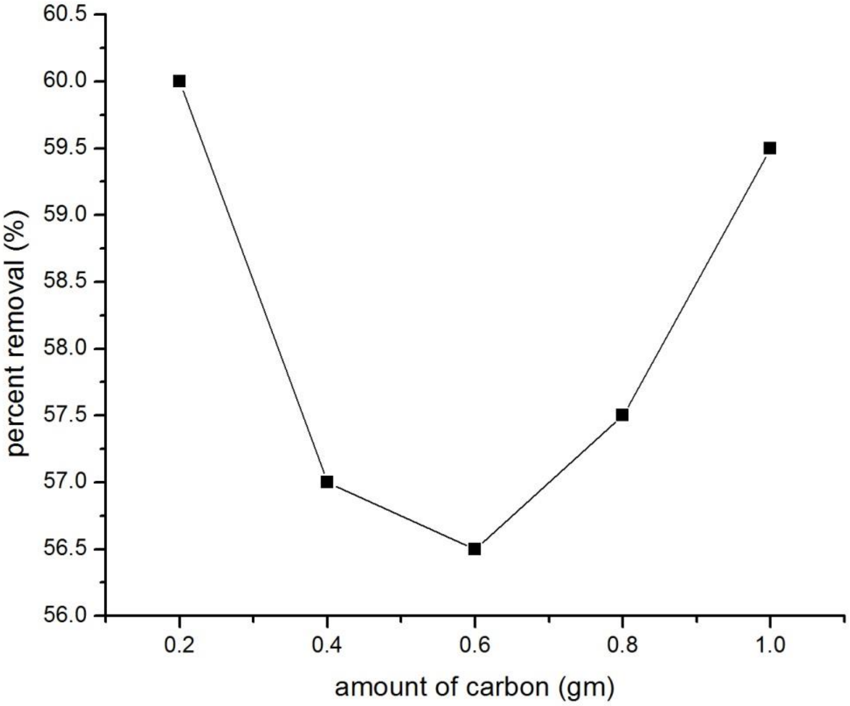


Figure 4.2 Effect of different amount of carbon on the removal of fluoride

4.3 Effect of contact time

The results of contact time optimization show that the removal is maximum at 3 hours and after that the removal starts to decrease. The reason may be that after that desorption starts to take place and the fluoride starts getting removed from the sites. The results are shown in table 3.6

The results are demonstrated graphically as shown in fig 4.3

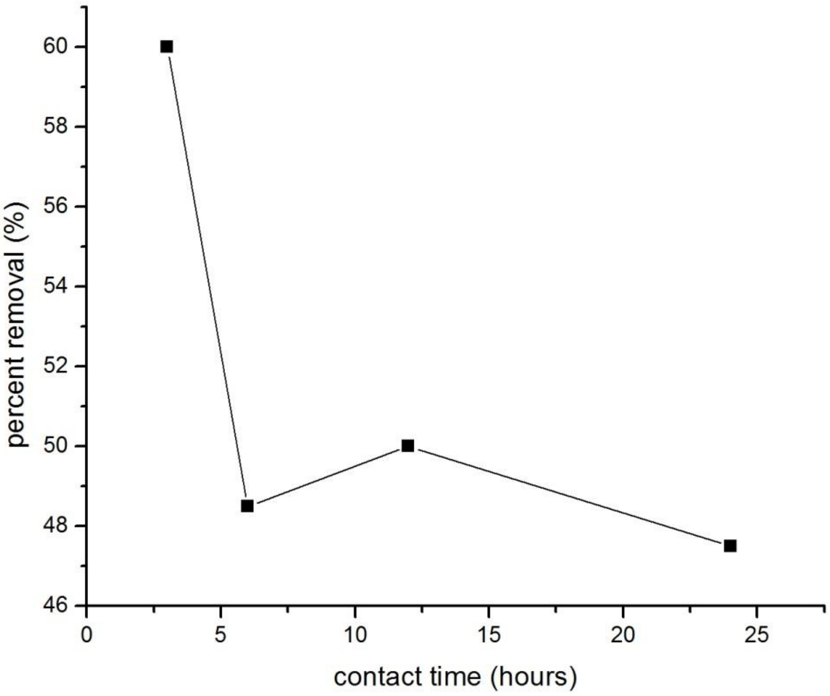


Figure 4.3 Effect of contact time on the removal of fluoride

4.4 Testing on Drinking Water Sample

Fluoride was tested on 6 different samples of different types of water that can be used as drinking water by some of the people. The samples taken were from the lab drinking water, river water, hostel drinking water, domestic water from a house, ground water, domestic water from another house and the respective removal was found out to be 6.5%, 33%, 50%, 31.3%, 52.8%, 42.3% . This is quite good and so Activated carbon can be used for the removal from drinking water.

CHAPTER 5

CONCLUSIONS

Activated carbon can effectively reduce the amount of fluoride present in drinking water. The removal of fluoride deceases with increase in pH with a dip at the original pH of the solution, i.e. 6.71 so that’s the optimum pH to carry out the experiments.

The removal of fluoride increases as the amount of adsorbent increases but with an exception at the lowest concentration of adsorbent as 0.2g. So that is the optimum for maximum removal.

The removal of fluoride showed a decrease as the contact time was increased from 3 to 6 hours but after that it showed some increase at 12 hours and again a decrease at 24 hours. This can be due to the start of desorption after 6 hours. But as at 3 hours the removal is maximum so we take that as the optimum contact time for removal of fluoride.

Then using all these optimum parameters the removal of fluoride was checked for six different samples of drinking water. The results were good and showed good removal of fluoride. So adsorption using activated carbon can be a technique to remove fluoride from drinking water.

CHAPTER 5

RECOMMENDATIONS AND FUTURE WORK

- The future work on removal of fluoride can be to study the kinetics of the adsorption and try to fit the curves in Langmuir and Frendlich Isotherms, to know which order reaction does it follow.
- This process is basically done on the small scale so it can be tried to extent it to large scale process, that way it can be used to remove fluoride from drinking water on a mass level.
- It will be worthwhile to study the suitability of different chemicals to regenerates the spent adsorbents and can be able to use the waste generated after adsorption. Activated carbon can be regenerated so this can make the process even more efficient.
- Finally the adsorbent can be tested on different types of water e.g sea water, industrial water etc.

REFRENCES

1) Holleman, Wiberg, Inorganic Chemistry 5 (2001) 87

2) Schwesinger, Reinhard; Link, Reinhard; Wenzl, Peter; Kossek, Sebastian, Chemistry—A European Journal 12 (2006) 438-445

3) Ramos, Turrubiartes, Castillo, Carbon 37 (1999) 609–617

4) Mullenix, Denbesten, Schunior, Kernan, Neurotoxicol. Teratol 17 (1995) 169

5) Singh, Fluoride 17 (1984) 81

6) Saralakumari, Rao, Toxicology 47 (1991) 834

7) Vani, Reddy, Fluoride 33 (2000) 17

8) Rzeuski, Chlubek, Machoy, Fluoride 31 (1998) 43

9) Sharma, Chinoy, Fluoride 31 (1998) 126

10) Miramontes, Margulis, Hernadez, Fluoride 36 (2003) 122

11) Apparao, Meenakshi, Karthikayan, Indian Journal of Environmental Protection, 10 (1990) 292.

12) Frith, Journal of Medical Associates 39 (1950) 258.

13) Bunder, Caries Res 7 (1973) 179

14) Mark, Neth, Chemical Technology 26 (1971) 413

15) Sreenivasulu, Sundaram, Reddy, Journal of Industrial Pollutants and Contaminants 15 (1999) 227

16) Larsen, Pearce, Caries Res 26 (1992) 22

17) Simons, Desalination 89 (1993) 325

18) Tanada, Kabayama, Kawasaki, Sakiyama, Nakamura, Araki, Tamura, Journal of Colloid Interface Science 257 (2003) 135

19) Gosselin, Smith, Hodge, Clinical toxicology of commercial products 3 (1984) 93-185

20) Baselt, Disposition of toxic drugs and chemicals in man 87 (2008) 636–40

21) Pearce, Fred, Journeys Into the Heart of the World's Water Crisis 41 (2006) 552-574

22) Baez, Ramon, Baez, Martha, Marthaler, Thomas, American Journal of Public Health 7 (2000) 242-248

23) Nochimson, Fluoride 28 (2008) 362- 378

24) Augenstein, Spoerke, Kulig ,Pediatrics 88 (1991) 907

25) Wu, Deng, Fan, Clinical Toxicology 48 (2010) 953-955

26) McDonagh, Whiting, Wilson, NHS Centre for Reviews and Dissemination 27 (2000) 855–859

27) Gupta, Kumar, Bandhu, Gupta, Rheumatol 36 (2007) 154–155

28) Aoba, Fejerskov, Dental fluorosis: chemistry and biology 13 (2002) 155-170

29) Romanos et al.,Nanotechnology 23 (2012) 103- 109

30) Saha, Tai, Streat, Process safety and environmental protection 79 (2 001) 211-217

31) Abe, Iwasaki, Tokimoto, Kawasaki, Nakamura, Tanada, Journal of Colloid and Interface Science 275 (2004) 35–39

32) Matsunaga, Kanno, Yamada, Takahashi, Suzuki, Talanta 68 (2006) 1000–1004

33) Tripathy, Bersillon, Gopal, Separation and Purification Technology 50 (2006) 310-317

34) Zhao, Li, Liu, Chen, Carbohydrate Polymers 72-1 (2008) 144- 150

35) Bhatnagar, Kumar, Sillanpää, Chemical Engineering Journal 171-3 (2011) 811-840

36) Sun, Fang, Dong, Cheng, Xu, Desalination 277 (2011) 121-127

37) Montoya, Petriciolet, Morán, Biochemical Engineering Journal 62 (2012) 1-7

38) Salifu, Petrusevski, Ghebremichael, Modestus, Buamah, Aubry, Amy, Chemical Engineering Journal 228 (2013) 63-74

39) Zuo, Chen, Li, Chen, Journal of Hazardous Materials 159 (2008) 452-457

40) Kamga, Alonzo, Njiki, Audebrand, Ngameni, Darchen, Carbon 48-2 (2010) 333-343

41) Yadav, Abbassi, Gupta, Dadashzadeh, Ecological Engineering 52 (2013) 211-218

42) Daifullah, Yakout, Elreefy, Journal of Hazardous Materials 147 (2007) 633-643

43) Emmanuel, Ramaraju, Rambabu, Rao, Rasayan, Chemical Engineering Journal 4 (2008),802-818

44) Mohapatra, Mishra, Mishra, Chaudhury, Das, Journal of Colloid and Interface Science 275 (2004) 355–359

45) Das, Pattanaik, Das, Journal of Colloid and Interface Science 292 (2005) 1–10

46) Ghorai, Pant, Separation and Purification Technology 42 (2005) 265–271

47) Sarkar, Banerjee, Pramanick, Sarkar, Journal of Colloid and Interface Science 302 (2006) 432–441

48) Yadav, Kaushik, Haritash, Kansal, Rani, Journal of Hazardous Materials B128 (2006) 289–293

49) Maliyekkal, Shukla, Philip, Nambi, Chemical Engineering Journal 140 (2008) 183-192

50) Ganvir, Das, Journal of Hazardous Materials 185 (2011) 1287-1294

51) Meenakshi, Maheshwari, Journal of Hazardous Materials 137 (2006) 456-463

52) Mohapatra, Anand, Mishra, Giles, Singh, Journal of Environmental Management 91 (2009) 67-77

53) Tomar, Prasad, Kumar, Microchemical Journal 111 (2013) 116-124

54) Srimurali, Pragathi, Karthikeyan, Environmental Pollution 99 (1998) 285-289