# DEVELOPMENT OF HYBRID ADSORBENT FOR SELECTIVE FLUORIDE REMOVAL FROM CONTAMINATED DRINKING WATER

**Thesis submitted in partial fulfillment of the requirements for the award of degree of**

**Master of Technology**
**in**
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**Submitted**
**By**

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# DECLARATION CUM CERTIFICATE

I hereby declare that the work embodied in thesis entitled, "**Development of Hybrid Adsorbent for selective fluoride removal of fluoride from ground water** ", is an original piece of work and was conducted in the Department of Biotechnology and Environmental Sciences, Thapar University, Patiala. The matter presented in this thesis has not been submitted in part or full, to this or any other University/Institute for any degree or diploma.

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

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Geetanjali

# ABSTRACT

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. Activated alumina and nanohydroxyapatite both have different physical and chemical characteristics regard to sorption behaviour for fluoride among other materials. Activated alumina has chemical stability, mechanical stability, selectivity, low cost, favourable hydraulic properties while nanohydroxyapatite possesses properties like high chemical reactivity, low selectivity, high surface area to volume ratio but it is non-regenerable. So the attempt is being made to take the advantage of their properties for defluoridation of ground water. The nanoparticle lacks chemical stability and mechanical strength. Though they are highly reactive yet exhibit a high pressure drop or head loss in fixed bed column operation hence they are not suitable for any continuous systems. Also nanoparticles have the tendency of aggregation; this reduces the high surface area to volume ratio and subsequently reduces the efficiency of process. By precipitating nano particles of within a host material, these scantinesses can be beaten out without compromising the parent properties of nanoparticles.

So an effort to synthesise a hybrid adsorbent, exploiting the properties of both activated alumina and nanohydroxyapatite was made by precipitating the hydroxyapatite within the nanosized pores of host material, activated alumina. Validation of this hybrid material was carried out in both, batch mode (adsorption isotherm) and continuous mode (column) at fluoride concentration 3mg/L to 10 mg/L having the background of Chloride(100 mg/L), sulphate(50 mg/L), bicarbonate(120 mg/L) and pH 7.5. Effect of different background condition was also studied and its applicability in real life was validated through its column performance. Up to 3 regeneration the adsorbent showed no decrease in its defluoridation capacity and it has more potential for fluoride removal if used after more regeneration.

**Keywords:** Activated alumina; nanohydroxyapatite; defluoridation; nanoparticles, breakthrough; regeneration; kinetics

# LIST OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

# CHAPTER -1

# INTRODUCTION

## 1.1 General Background

Groundwater, constituting 97% of global freshwater and used for drinking by more than 50% of the world populations, serves as the only economically viable option for many communities (Benefield, D.L et al 1982). In spite of receiving higher average annual rainfall (1,170 mm, 46 inches) as compared to the global average (800 mm, 32 inches), India is no exception. Use of surface water for drinking purposes in many developing nations including India is restricted by the wide range of microbial contamination caused by the absence of proper sanitation practices. Added to that, most of the rain falling on the surface tends to flow away rapidly, leaving very little for the recharge of groundwater. Lack of proper water-shed management leads to inefficient use of the available water resources. Due to poor water management, the huge amount of run-off is even remain unutilized for irrigation purposes. The agricultural demand for water in India is huge. With the advancement of well-drilling technologies it is easy to tap the water buried deep within the earth. Thus, groundwater reserves are being tapped and over-exploited to meet the demands of agriculture as well as domestic requirements, resulting in decline in groundwater levels.The use of groundwater in these regions is favored by its easy availability, microbial safety and absence of proper infrastructure for treatment and distribution of surface water. This over-exploitation of groundwater is taking its toll resulting in severe deterioration of its quality.

In the case of developing countries like India an estimated 80% of domestic consumption in rural and 50% in urban areas are met by groundwater sources alone (Maria A.,2003). But, due to various anthropogenic and natural factors coupled with indiscriminate withdrawal, the quality and quantity of groundwater have dwindled to alarmingly low levels. Therefore, in addition to scarcity, the entry of geogenic pollutants like fluoride into groundwater has become the most crucial and challenging environmental problem the world over, especially in developing countries. People in more than 35 nations across the globe face issues of excess fluoride in drinking water, the intensity and severity of which varies with the environmental settings in terms of their geographical and economical status.

### 1.2 Effects

Moderate amounts of fluoride ingestion can cause dental fluorosis, which is characterized by staining and pitting of the teeth. In more severe cases all the enamel may be damaged as depicted in **Figure 1.1 (a). (**Susheela, A.K. and Bhatnagar, M. 1999) Chronic high-level exposure to fluoride can lead to skeletal fluorosis. In skeletal fluorosis, fluoride accumulates in the bone progressively over many years. The early symptoms of skeletal fluorosis include stiffness and pain in the joints. In severe cases, the bone structure may change and ligaments may calcify, with resulting impairment of muscles and pain. Figure 1.1 (b) shows such a case of skeletal fluorosis affecting a young person**.** (www.who.int)

**Fig 1.1(a)** Mild effects

**Fig 1.1(b)** Chronic effects

Excess intake of fluoride leads to various diseases such as osteoporosis, arthritis, brittle bones, cancer, infertility, brain damage, Alzheimer syndrome, and thyroid disorder. Fluorosis is a common symptom of high fluoride ingestion manifested by mottling of teeth in mild cases and brittle nature of bones and neurological damage in severe cases. (Fan, X. et al, 2004). There are some reports indicating that fluoride may interfere with DNA synthesis. The excess concentrations of fluoride can also interfere with carbohydrates, lipids, proteins, vitamins and mineral metabolism. (Zhou,Y. et al,2004). Fluoride toxicity may occur by several ways. While ingested, fluoride initially acts locally on the intestinal mucosa, it can later form hydrofluoric acid in the stomach, which leads to gastro-intestinal irritation or corrosive effects. Following ingestion, the gastro-intestinal tractis the earliest and most commonly affected organ system. Fluoride can also interfere with a number of enzymes disrupting oxidative phosphorylation, glycolysis, coagulation, and neurotransmission. (Ismail, A.I., and Messer, J.G. 1996). It is well recognized that individuals with kidney disease have a heightened susceptibility to the cumulative toxic effects of fluoride. In addition, fluoride has been shown to poison kidney function at high doses over short-term exposures in both animals and humans. It has also been concluded by several research groups that fluoride has the ability to interfere with the functions of the brain and pineal gland. Pineal gland is a major site of fluoride accumulation within the body, with higher concentrations of fluoride than either teeth or bone. (http:.//www.fluoridealert.org/health/)

There is no medicine for fluorosis. It is necessary to avoid drinking of fluoride-contaminated water as far as possible. The control of drinking-water quality is therefore critical in preventing fluorosis. In India the regulatory limit for fluoride in drinking water is 1.5 mg/L (IS:10500). In places where fluoride levels are between 1.5 to 2 mg/l, some nutritional interventions can help. In these places it is advised to eat more of foods that are rich in iron, calcium and Vitamin C. The use of black salt (kalanamak) and products containing it, as well as the use of fluoridated toothpastes should be avoided in these areas (Mid-term appraisal of the eleventh five year plan, Planning Commission).

### 1.3 Fluoride situation in India:

According to the Department of Drinking Water Supply, out of 593 districts in India from which data is available, water in 203 districts has shown high fluoride .( Figure 1.2 shows the fluoride affected areas in India marked on the map, along with concentration ranges indicated for each state. As may be observed from the marked-up map, almost all states in India have districts where groundwater contains excessive levels of fluoride.

In India, occurrence of fluoride in top aquifer system is endemic in many places of Andhra Pradesh, Tamil Nadu, Karnataka, Gujarat, Rajasthan, Punjab, Haryana, Bihar and Kerala. (Rao, V.K., and Mahajan, C.L., 1988)A high concentration of 5.2 mg/L has been reported in Medak district, Andhra Pradesh, 15 mg/L in Nawabganj Block, Uttar Pradesh and 18 mg/l in Jaipur, Rajasthan as against its critical limit of 1.5 mg/L in drinking water. Nalgonda District in Andhra Pradesh is said to have the highest concentration of people affected by fluorosis. Nearly 500 villages in the district are under the grip of fluorosis resulting in twenty thousand fluorosis victims in the district. In contrast to the Indian standard of 1.5 mg/L fluoride in drinking water, the water contains up to 10 mg/L of fluoride in Nalgonda. Many adults and even young children have been irreversibly affected by skeletal fluorosis in this district.

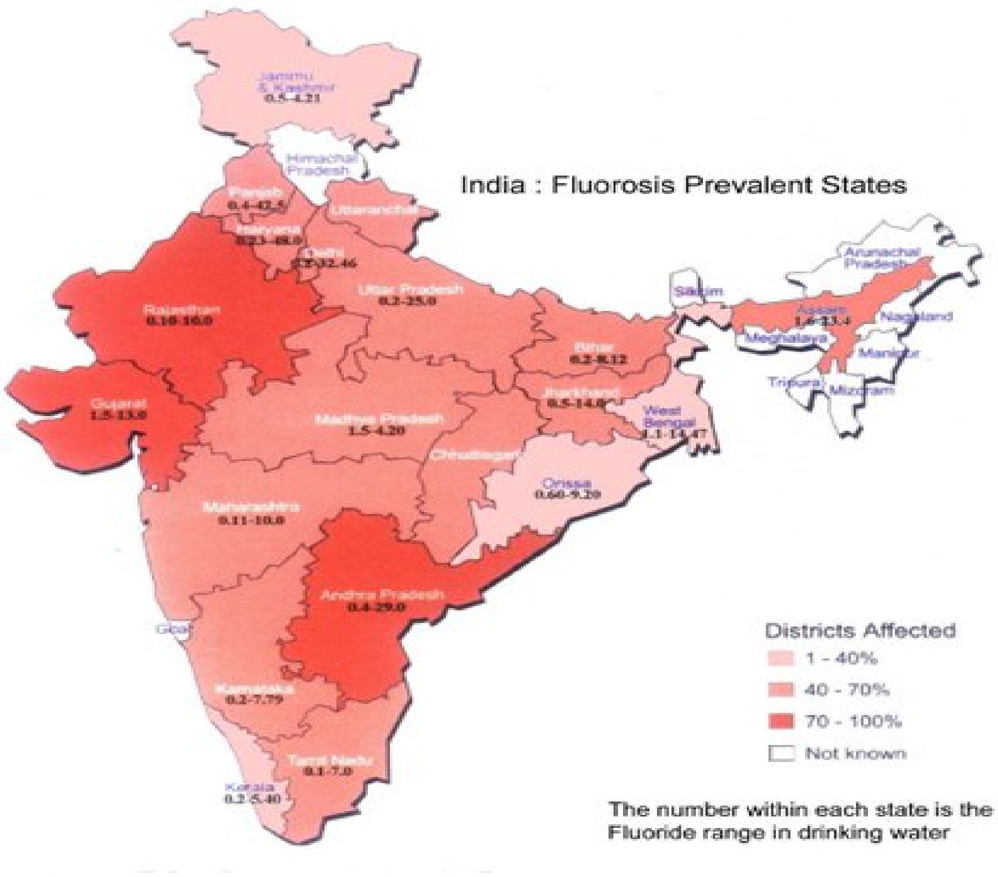


**Figure 1.2** Fluoride Affected States of India

**Source:** (www.who.net).

**1.4 Defluoridation Techniques- Needs and Overview:**

Surface water does not contain fluoride. While the best solution to the crisis is to switch over to treated surface water, development and maintenance of surface water-based drinking water system is expensive, time-consuming and investment-intensive. With all these difficulties, it is unlikely for a developing country to switch the source of water from ground water to surface water within a short period of time. In order to save people from suffering from the debilitating conditions of fluorosis before such a changeover is possible, it is imperative to build sustainable fluoride removal systems on an urgent basis.

Various efforts have been undertaken to develop an effective method for fluoride removal from drinking water. However, the prevailing nature of fluorosis in India and the continuously increasing number of fluorosis patients are a good indicator of ineffectiveness of the presently available techniques. While other toxic ions are significant in sub-mg/L concentration, fluoride normally is present in mg/L range in the contaminated waters. Therefore, simply considering the stoichiometry, it is much more difficult to develop a cost-effective removal process for fluoride than other trace contaminants such as arsenic.

Based on the nature of the mechanisms involved, defluoridation techniques can be generally grouped into coagulation, adsorption and/or ion exchange, electrochemical, and membrane processes. The coagulation technique involves precipitation or coprecipitation of fluoride by using suitable reagents like lime, calcium and magnesium salts, poly aluminum chloride, and alum (Ayoob, S.et al 2009) The precipitation method with aluminum salts, popularly known as Nalgonda technique, has number of drawbacks such as need for high residence time for the process-completion, sensitivity towards pH of water, production of bulky amount of sludge, high residual of aluminum in the treated water, etc. Electrocoagulation involves the use of aluminum electrodes that release $Al^{3+}$ ions by reaction at the anode, and the released $Al^{3+}$ ions that are found in excess near the anode then react with fluoride ions. As a result of the reaction between the aluminium and fluoride ions, precipitation of fluoride salt takes place, followed by removal of fluoride at the electrode/electrolyte interface. Another technique, electrosorptive technique basically involves activation of an adsorbent bed by the application of electric field and thereby resulting in the increasing in its adsorption capacity. Adsorption is another important technique most widely used for removal of several trace contaminants from aqueous solution. In this process, a packed bed of adsorbent in fixed columns is continuously used for cyclic sorption and/or desorption of pollutants by effectively utilizing the capacity of an adsorbent bed. From a relatively bulk liquid volume, the pollutant gets concentrated and confined on to a small adsorbent mass, which can invariably be regenerated, reused, or safely disposed of under control. The adsorbents generally used for fluoride removal include bone char, activated alumina, activated carbon, activated bauxite, ion-exchange resins, fly ash, super phosphate and tricalcium phosphate, clays and soils, synthetic zeolites, and other minerals. Apart from the above techniques, membrane-based removal techniques are of recent origin and include reverse osmosis, nano-ultrafiltration, electrodialysis, and Donnan dialysis. (Sarkar, S. et al, 2010) Excellent technologies for defluoridation based on a combination of two or more of these processes have also been reported. (Velizarov, S. et al, 2004)

### 1.5 Approach and Work Plan:

Among various methods used for defluoridation of water, the adsorption process is widely used and offers satisfactory results and seems to be a more attractive method for the removal of fluoride in terms of cost, simplicity of design and operation. (Mohpatra, M. et al, 2004). A plug-flow device such as an adsorption column is always user-friendly and desirable due to its inherent design supremacy compared to the completely-mixed reactors normally used in precipitation-type fluoride removal. Activated alumina (AA) is normally used as an adsorbent for such plug-flow type adsorption units. It is a regenerable media but considering the fact that fluoride occurs in mg/L concentration range, often the regeneration has to be done after 100-150 bed volumes of operation of the adsorption column. (Ghorai, S. and Pant, K.K., 2005) Although the regeneration can be done using commonly available chemicals, the frequent regeneration requirement tends to make the process cost-prohibitive, even in a community level with financial participation in operation and maintenance by the villagers. Therefore, it is necessary to develop an adsorbent media with comparable cost but a much superior adsorbent capacity so that an affordable and workable solution to the fluoride problem can be reached.

It was found that synthetic adsorbent hydroxyapatite can remove fluoride cheaply and effectively in poor, rural settings using locally available materials for synthesis. The mineral hydroxyapatite is the major component of our teeth and bones, and it transforms to fluorapatite, a softer mineral, when in contact with dissolved fluoride (Luke H. et al, 2011) transformation is one of the reasons fluoride weakens bones and can both help or harm teeth; thin layers of fluoroapatite prevent bacterially driven tooth decay, but thick layers lead to soft, pitted teeth (Aoba, T. 1997). While researchers recognize that hydroxyapatite holds potential as a possible solution to the fluoride problem (Sundaram, S.C. et al, 2008), no study has attempted to demonstrate fluoride removal with hydroxyapatite produced from in-expensive, low-grade materials available locally in rural areas afflicted with high fluoride. Finding a new low cost solution is particularly important in India because some more common low cost production methods are not appropriate. Hydroxyapatite substrate can be made from bone char, but consuming water filtered with animal bones conflicts with religious and culture taboos in India. Considering the potential of nano-sized hydroxyapatite for effective fluoride removal, it may be worth trying to develop and validate a hybrid adsorbent made by dispersal of nanoparticles of hydroxyapatite inside a suitable host material. The objective of the present work is to synthesize a hybrid adsorbent containing hydroxyapatite from inorganic ingredients, which can be used as a practical and viable filter media and should be scalable to communities of any size.

### 1.6 Aims and Objectives of the Study

#### 1.6.1 Aim of the Study

In order to achieve a higher efficiency for fluoride removal so that a reliable and cost-effective adsorption system can be designed, it is required to synthesize a new type of adsorbent that shall show better capability for fluoride removal than the commonly used adsorbent, activated alumina. The aim of the present study is therefore to synthesize an adsorbent which shall be a hybrid of activated alumina and hydroxyapatite so that the advantageous properties of both the adsorbents are kept intact, if not enhanced. The synthesis of the hybrid adsorbent also should ensure that their individual drawbacks are suppressed in the hybrid adsorbent. Thus, such an adsorbent shall prove to be highly efficient and cost-effective for fluoride removal from the contaminated groundwater.

#### 1.6.2 Objective of the Study

The primary objective of the present study is to develop and validate a highly efficient, regenerable, mechanically and chemically stable adsorbent that can be used for cost-effective removal of fluoride from contaminated drinking water. The above objective of the study is planned to be fulfilled by making the goal divided into three distinctive sub-steps or tasks. The tasks of the study were the following:

1. Synthesis of hybrid adsorbent
2. Characterization of the adsorbent
3. Validation of the performance of the adsorbent

##### 1.6.2.1 Synthesis of the hybrid adsorbent

The main goal in this task is to efficiently disperse nanoparticles of hydroxyapatite within the host materials, activated alumina granules, by using commonly available inexpensive chemicals. This is a challenging task because during the synthesis, not only the micropores of the host shall act like a micro-reactor for the reactions, the chemical nature of the functional groups of the host material shall also play a vital role in controlling the whole synthesis process. Some chemically diverse routes for the in-situ precipitation of hydroxyapatite have been identified and shall be used for the synthesis process.

#### 1.6.2.2 Characterization of the adsorbent

The characterization study obviously includes investigation of the internal structure of the hybrid adsorbent, including finding out the sizes of the dispersed nanoparticles within the host activated alumina granules, nature and structure of the nanoparticles inside the bead so as to find out whether the precipitates are amorphous or crystalline in nature. The characterization study should also include the quantification of available amount of internal pore area that will be useful for holding the adsorbed molecules. Available pore area obviously has a direct bearing on the adsorption capacity of the adsorbent. The internal morphology of the adsorbent also needs to be evaluated. Knowledge on the internal morphology shall help in the assessment of the kinetics of the adsorption process.

#### 1.6.2.3 Performance validation

The first step in the performance validation is to find out the performance of the adsorbent for selective fluoride removal from the contaminated water or from a synthetic solution containing different concentrations of fluoride with a background of other commonly occurring anions. Once an optimal synthesis pathway has been established so that synthesized adsorbent is observed to remove fluoride with the desired degree of satisfaction, further validation studies shall be undertaken. This will include the determination of fluoride adsorption capacity at different equilibrium conditions under batch mode of operation. The effect of pH and other commonly occurring anions on the adsorption capacity shall also be evaluated. Adsorption kinetics shall also be evaluated. This will be helpful for an optimum design of the real life adsorption devices and systems. Following the batch mode of determination of several adsorption parameters, column studies shall be undertaken. The characteristics of the fluoride adsorption shall be studied using bench-scale adsorption columns with an aim to finding out the parameters that shall help in future scaling up of the facilities in the real-life situations. Effective regeneration with low-cost chemicals is a necessity for a successful technology for field application. The study shall also optimize an effective regeneration protocol. The study shall also include performance validation for fluoride adsorption in columns that shall be run for multiple number of adsorption-regeneration cycles.

# CHAPTER-2

# LITERATURE REVIEW

## 2.1 General Background

In order to meet the daily needs and demands of population, both in terms of domestic and agricultural, ground water remains the only choice in many developed as well as developing countries like India. But weathering of rocks and over-exploitation of groundwater results in leaching of the mineral content into the groundwater causing high metal ion concentration in groundwater. Arsenic contamination of the groundwater used for drinking is currently the focus of the recent attention of the scientists and technologists around the world. Although Fluoride contamination in the drinking water is not as fatal as arsenic; however, the wide-spread nature and debilitating effect on the human beings have made the fluoride contamination problem as the one which needs to be urgently remediated.

One fourth countries of the world and a large fraction (28%) of rural population of the developing countries (India, Pakistan, Bangladesh etc.), are facing the problems of water supply with unsafe level of fluoride, resulting in a condition which demands an immediate and robust solution. There are many districts in Indian states where the community is compelled to use water having concentration of fluoride as high as 5mg/L to 49 mg/L while the permissible limit for fluoride intake decided by WHO is only 1.5 mg/L. (W.H.O., 2004)

## 2.2 Effects of Intake of Fluoride-contaminated Drinking Water

Healthy bones and teeth need right proportions of calcium and fluoride. Fluoride stimulates the bone and teeth formation and helps to prevent tooth decay. Fluoride also has been proven to strengthen the teeth. In minute concentrations it is beneficial to dental and skeletal health but at concentrations exceeding the maximum allowable range (1.5 mg/L - 2 mg/L), it becomes detrimental. Even the level at which the controlled fluoridation is performed in public water supply, usually at the rate of about 1 part fluoride for every million parts of water (1 ppm) by weight, has been known to cause severe problems. Dental fluorosis is one of the earlier signs of fluoride poisoning, appearing in mild cases as a chalky area on the tooth, and in more advanced cases, teeth become yellow brown or black and the tips break off. Fluoride in the drinking water leads to high fluoride levels in tissues and organs causing damage to the enzymes. Such damages of the enzymes result in a wide range of chronic diseases. Excessive fluoride weakens the immune system and may cause allergic type reactions including dermatitis, eczema and hives. It also causes birth defects and genetic damage. Fluoride is likely to aggravate kidney disease, diabetes and hypothyroidism. Excessive fluoride is known to lower the thyroid activity in humans. It also causes the breakdown of collagen which results in wrinkling of the skin and the weakening of ligaments, tendons and muscles. There are a number of ways that fluoride can be administered but the most insidious way is through the drinking water. The absorption of excessive fluoride in the body can result in several mild and chronic diseases like dental fluorosis, skeletal deformation, alzhimar, cancer, thyroid problems etc. (Figure 2.1)

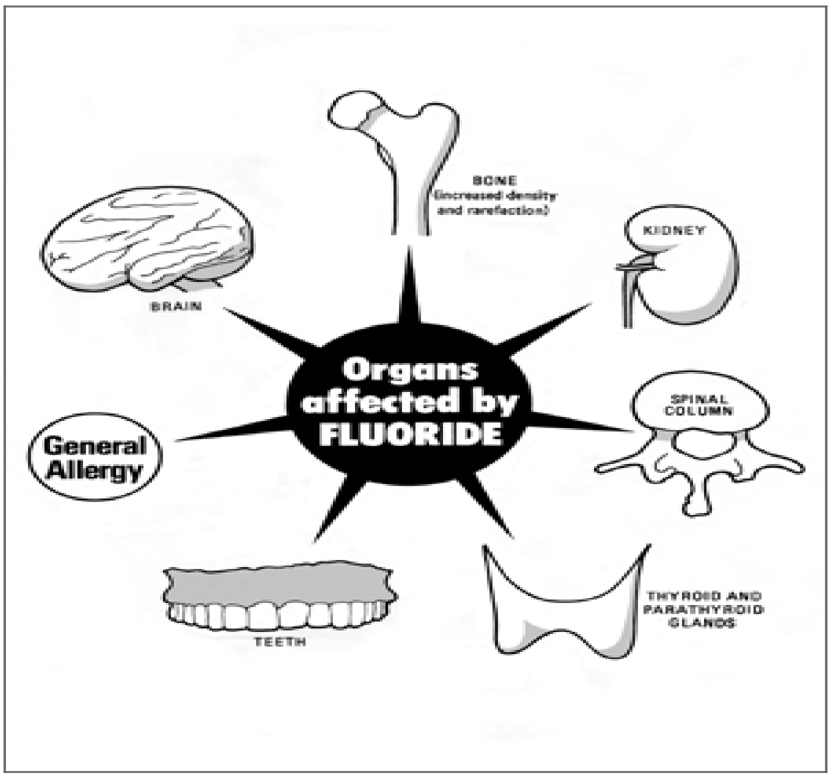


**Figure 2.1** Organs affected by Fluoride

**Source:** (www.who.net)

**2.2.1 Dental Fluorisis**: Dental fluorosis is a developmental disturbance of dental enamel caused by excessive exposure to high concentrations of fluoride during tooth development. In its mild forms (which are its most common), fluorosis often appears as unnoticeable, tiny white streaks or specks in the enamel of the tooth. In its most severe form, tooth appearance is marred by discoloration or brown markings. The enamel may be pitted, rough and hard to clean. The spots and stains left by fluorosis are permanent and may darken over time.

**2.2.2 Skeletal Fluorisis:** In advance stages fluorisis acquires severe form of skeletal fluorisis which is caused because by prolonged exposure of fluoride. Skeletal fluorosis is a bone disease caused by excessive consumption of fluoride. In advanced cases, skeletal fluorosis causes pain and damage to bones and joints. When fluorine enters the body it reacts with HCl in stomach and form HF which is a strong oxidizer and unable to be digested by liver. It passes through blood streams and get distributed to all tissues including bones. Bones are largely composed of Ca compounds particularly carbonated hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$); the reaction of Ca and HF forms an insoluble salt, $CaF_2$. This salt must be cleared by the body and as a result washes away some of the Ca that would be part of the bone matrix. This process results in increased density, but decreased strength in bones.

**2.2.3 Cancer:** In our body cells we have genetic material called DNA, and this DNA is double stranded, it has a helix shape and these two strands of DNA are held together by semi strong bonds called hydrogen bonds. Hydrogen bonds also hold proteins together. Fluoride goes in and breaks those hydrogen bonds, and consequently destabilizes DNA. It can't cause a lesion in the DNA itself, but if it is in a site of the cell that regulates cell growth, it will cause uncontrolled cell growth. A few minor modifications will produce first a tumour, and secondly an invasive tumour or cancer. So fluoride has the ability to actually cause the cancer.

**2.2.4 Reduction in Immunity:** Fluoride causes the lesion; it inhibits the DNA repair enzyme, and then inhibits our immune system by 30 to 70% and that occurs at only one part per million. Our immune system is composed of white blood cells including phagocyte cells that are carried in the blood system. If there is an infection or cancer or some foreign agent, these phagocytes will go to that area and start engulfing and destroying this bad agent whether it is a cancer cell or a bacterium or virus. It engulfs it in a little pocket called a lysosome which squirts enzymes and breaks down the bad agent into little pieces. They have other things called peroxisomes which burn that agent with free radicals and either destroy it or use it for building new and healthy cells. These phagocytes will actually eat up bacteria or viruses, and toxic substances are just thrown off. Fluoride inhibits these white blood cells and causes a chronic release of these free radicals from the white blood cell out into the blood stream where it starts slowly damaging your body by increasing free radicals and functions as the ageing factor.

**2.2.5 Effect on Brain:** Fluoride has the ability to damage the brain, fluoride accumulates in the brain of the foetus, causing damage to cells and neurotransmitters and has found a correlation between exposure to fluoride during fatal development and behavioural while adult exposures to fluoride may result in central nervous system disturbances. Some direct toxic effects of fluoride on brain tissue, even at low level of fluoride in water. These effects include:

-- reduction in nicotinic acetylcholine receptors;
-- reduction in lipid content;
-- impaired anti-oxidant defence systems;
-- damage to the hippocampus;
-- damage to the purkinje cells;
-- increased uptake of aluminium;
-- formation of beta-amyloid plaques (the classic brain abnormality in Alzheimer's disease);
-- exacerbation of lesions induced by iodine deficiency; and
-- accumulation of fluoride in the pineal gland.

**2.2.6 Effect on Thyroid Gland**: The thyroid gland produces hormones which control our metabolism – the rate at which body fuel is burnt and if it does not function properly people become tired, cold, overweight, depressed, constipated; they suffer artheoscerosis and chronic illness. Fluorides damage the thyroid system on four levels.

1. The process by which iodine is attached to the amino acid tyrosine and converted to the two significant thyroid hormone, thyroxin and liothyronine, is slowed.
2. The stimulation of certain proteins whose function is to govern uptake of substances into each of cell of the body switch off the uptake into cell of the active thyroid hormone.
3. The thyroid control mechanism is compromised as the thyroid stimulating hormone output from the pituitary gland is inhibited and thus reducing thyroid output of thyroid hormones.

4. Fluoride competes for the receptor sites on the thyroid gland which respond to the thyroid stimulating hormone; so less of this hormone reaches the thyroid gland and so less thyroid hormone is manufactured.

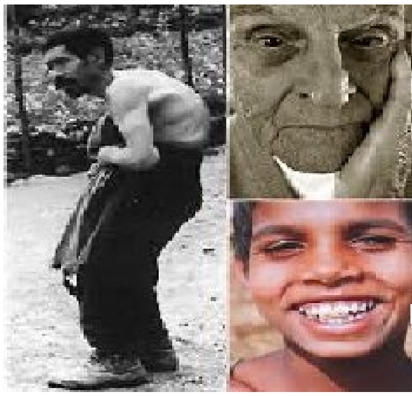

**Figure 2.2 (a)** Few patient of fluorisis

**Figure 2.2 (b)** Dental Fluorisis

**Source: (**www.who.net)

**2.2.7 Effect on Plants:** Natural contamination of groundwater by fluoride causes irreparable damage to plant and human health. High fluoride level inhibits germination causes ultrastructural malformations, reduces photosynthetic capacities, alters membrane permeability, reduces productivity and biomass and inflicts other physiological and biochemical disorders in plants. These damaging effects, all of which occur with small concentration of fluoride, have obvious and easily identifiable effects on individual's health.

## 2.3 Current Situation of Fluoride Contamination

### 2.3.1 Global Scenario

All over the world fluoride in ground water is becoming a serious issue which is not getting a proper solution. Groundwater with high fluoride concentrations occur in many areas of the world including large parts of Africa, China, the Eastern Mediterranean and southern Asia (India, Sri Lanka). One of the best-known high fluoride belts on land extends along the East African Rift from Eritrea to Malawi. There is another belt from Turkey through Iraq, Iran, Afghanistan, India, northern Thailand and China. The Americas and Japan have similar belts. Argentina, Brazil, Canada, China, Eretria, Germany, India, Indonesia, Israel, Kenya, Mexico, Niger, Nigeria, Norway, Pakistan, Saudi Arabia, Senegal, South Africa, Spain, Sri Lanka, Sudan, Thailand, Turkey, Uganda, United States of America etc are the countries suffering from the diseases and disorders caused by fluoride excess. Around 19% of the world's population is facing the problem of excess fluoride in ground water (figure 2.2).

**Figure 2.2.** Geographical ares associated with groundwater having over 1.5 mg/l of naturally occuring fluoride,which is above recommended level (Yeung CA,2009)

### 2.3.2 Indian Scenario

From the figure above it is clear that is one of the countries which are under the threat of excessive concentration of fluoride varying from 4 mg/L to 50/L,in water was used to meet out the daily needs of the people. The problem of excessive fluoride in ground water wasfirst repoeted in 18 out of 32 constituents states of India.Nearly 117 districts have been confirmed as fluoride affected areas.The existence of fluoride as a fluoride in water first reported in 1973 in India.Recent studies show approximately 62 million children people including 6 million children suffer from fluorisis because of consumption of water containing high concentration of fluoride. In Rajasthan the existence of fluoride was first detected from Jobner near Jaipur city during 1964 in the villages of Nagpur and in 1976 high fluoride content in drinking water were observed in Bhilwara district and the prevelence of fluorisis in fluorisis in Ajmer district was reported (Yadav, A.K. and Khan, P. 2010)

High concentration of fluoride in ground water is common in some of the semi arid regions of Rajasthan, southern Punjab and southern Haryana. Several areas of Andhra Pradesh have high concentration of fluoride in ground water (exceeding 1.5 mg/L). In several parts of Karnataka, Tamil Nadu, U.P. and other areas, fluoride concentrations in ground water are more than permissible level of 1.5 mg/L. Around 25 million people in rural areas consume water with fluoride content more than this limit. Concentration of fluoride in different parts of the country varies from 0.5 to 50 mg/L.

**Table 2.1** States and Districts affected by the excessive concentration of fluoride in ground water

| S. No. | State | Fluoride | |
|---|---|---|---|
| | | No.of districts affected | Districts (in parts) |
| 1. | Andhra Pradesh | 19 | Adilabad, Anantpur, Chitoor, Guntur, Hyderabad, Karimnagar, Khammam, Krishna, Kurnool, Mehboobnagar, Medak, Nalgonda, Nellore, Prakasham, Rangareddy, Vishakhapatnam, Viziangaram, Warangal, West Godawari |
| 2. | Assam | 4 | Goalpara, Kamrup, Karbi Anglong, Naugaon |
| 3 | Bihar | 9 | Aurangabad, Banka, Buxar, Jamui, Kaimur, Munger, Nawada, Rohtas, Supaul |
| 4. | Chhattisgarh | 12 | Bastar, Bilaspur, Dantewara, Janjgir-Champa, Jashpur, Kanker, Korba, Koriya, Mahasamund, Raipur, Rajnandgaon, Suguja |
| 5. | Delhi | 6 | East Delhi, New Delhi, Northwest Delhi, South Delhi, Southwest Delhi, West Delhi |
| 6. | Gujarat | 18 | Ahmedabad, Amreli, Anand, Banaskantha, Bharuch, Bhavnagar, Dahod, Junagarh, Kachchh, Mahesana, Narmada, Panchmahals, Patan, Rajkot, Sabarkantha, Surat, Surendranagar, Vadodara |
| 7. | Haryana | 14 | Bhiwani, Faridabad, Gurgaon, Hissar, Jhajjar, Jind, Kaithal, Kurkshetra, Mahendragarh, Panipat, Rewari, Rohtak, Sirsa, Sonepat |
| 8. | Jammu & Kashmir | 2 | Rajauri, Udhampur |
| 9. | Jharkhand | 6 | Bokaro, Giridih, Godda, Gumla, Palamau, Ranchi |
| 10.. | Karnataka | 20 | Bagalkot, Bangalore, Bellary, Belgaum, Bidar, Bijapur, |

| | | | |
|---|---|---|---|
| | | | Chamarajnagar, Chikmagalur, Chitradurga, Devangere, Dharwar, Gadag, Gulbarga, Haveri, Kolar, Koppala, Mandya, Mysore, Raichur, Tumkur. |
| 11. | Kerala | 1 | Palakkad |
| 12. | Madhya Pradesh | 19 | Bhind, Chhatarpur, Chhindwara, Datia, Dewas, Dhar, Guna, Gwalior, Harda, Jabalpur, Jhabua, Khargone, Mandsaur, Rajgarh, Satna, Seoni, Shajapur, Sheopur, Sidhi. |
| 13. | Maharashtra | 8 | Amrawati, Chandrapur, Dhule, Gadchiroli, Gondia, Jalna, Nagpur, Nanded, |
| 14. | Orissa | 11 | Angul, Balasore, Bargarh, Bhadrak, Boudh, Cuttack, Deogarh, Dhenkanal, Jajpur, Keonjhar, Suvarnapur |
| 15. | Punjab | 11 | Amritsar, Bhatinda, Faridkot, Fatehgarh-Saheb, Firozpur, Gurdaspur, Mansa, Moga, Muktsar, Patiala, Sangrur, |
| 16. | Rajasthan | 30 | Ajmer, Alwar, Banswara, Barmer, Bharatpur, Bhilwara, Bikaner, Bundi, Chhittorgarh, Churu, Dausa, Dholpur, Dungarpur, Ganganagar, Hanumangarh, Jaipur, Jaisalmer, Jalore, Jhunjhunu, Jodhpur, Karauli, Kota, Nagaur, Pali, Rajasamand, SawaiMadhopur, Sikar, Sirohi, Tonk, Udaipur |
| 17. | Tamil Nadu | 16 | Coimbatore, Dharmapuri, Dindigul, Erode, Karur, Krishnagiri, Namakkal, Perambalur, Puddukotai, Ramnathpuram, Salem, Shivaganga, Theni, Thiruvannamalai, Vellore, Virudunagar |
| 18.. | Uttar Pradseh | 10 | Agra, Aligarh, Etah, Firozabad, Jaunpur, Kannauj, Mahamayanagar, Mainpuri, Mathura, Maunathbhanjan, |
| 19. | West Bengal | 8 | Bankura, Bardhhman, Birbhum, Dakhin Dinajpur, Malda, Nadia, Purulia, Uttar Dinajpur |

**Table 2.2** Permissible limits of fluorides in water prescribed by various organisations

| Name of the Organisation | Desirable Limit (mg/L) |
|---|---|
| Bureau of Indian standard(BIS) | 0.6-1.2 |
| Indian Council of Medical Research (ICMR) | 1.0 |

| | |
|---|---|
| The Committee on Public Health Engineering Manual and Code of Practice, Government Of India | 1.0 |
| World health Organisation (International Standard for Drinking water) | 1.5 |

**Source:** www.nih.ernet.in/rbis/India_Information/fluoride.htm

From the above data it is clear that intake of fluoride in affected areas is far higher than the level that can benefit individuals health. So it becomes mandatory to come up with a proper solution for fluoride problem that can reduce its concentration up to desirable limits.

**2.4 Technological Options for Fluoride Removal from Contaminated Drinking Water**

Based on the nature of the mechanisms involved, defluoridation techniques can be generally grouped into coagulation, adsorption and/or ion exchange, electrochemical, and membrane processes.

**2.4.1. Coagulation Techniques:**

Chemical coagulants are effective in removing a broad range of impurities from water, including colloidal particles and dissolved organic substances. Two mechanisms essentially operate: charge neutralization of negatively charged colloids by cationic hydrolysis products, and incorporation of impurities in an amorphous precipitate of metal hydroxide, generally known as "sweep flocculation." Charge neutralization is a simple mechanism for destabilization of negatively charged particles by the adsorption of cations from solution and this adsorption of positively charged species on negative surfaces may occur for simple electrostatic reasons or by formation of some types of surface complexes. "Sweep flocculation" refers to the "sweeping out" of particles from water by the hydroxide precipitate and generally gives improved particle removal. Thus, coagulation by hydrolyzing coagulants may involve both charge neutralization and sweep flocculation as essential steps in particle removal. (J. Gregory and Duan J., 2001)

Defluoridation processes by coagulation are of two types:

1. Precipitation of fluoride by a suitable reagent through a chemical reaction.

2. Co-precipitation of fluoride, which involves its simultaneous precipitation with a macro component from the same solution through the formation of mixed crystals, by adsorption, occlusion, or mechanical entrapment.

#### 2.4.1.1. Precipitation of Fluoride:

**2.4.1.1.1. Lime.** Addition of lime ($Ca(OH)_2$) or other calcium salts ($CaSO_4$, $CaCl_2$) can be used to precipitate fluoride as insoluble $CaF_2$ (Ksp = 3 × 10−11 at 25◦C) and is the cheapest and most commonly used precipitation technique for defluoridation, but is principally used for high-fluoride-containing wastewaters.( C.J. Huang et al,1999)The precipitation reaction using lime is as follows:

$$Ca(OH)_2 + 2F^- \rightarrow CaF_2 + 2OH^- \qquad (2.1)$$

Precipitation processes are governed by the solubility of the salt formed. It has been reported

that liming normally gives residual fluoride concentrations of 10–20 mg/L, which is not satisfactory for drinking-water purposes. So subsequent defluoridation processes must be undertaken to remove the residual amount, which necessitates additional requirements of reagents, chemicals, and processes.(C. Castle et al,2000) enhancing the treatment costs, and thereby contributing to large volumes of additional sludge.(S.A.Wassey et al,1996)

**2.4.1.1.2. Magnesium Oxide.** In addition to lime, magnesium oxide has also been used for fluoride removal from drinking water. (Lislie, A.L. 1967) Addition of magnesium oxide to fluoride-bearing water results in the hydration of magnesium oxide to magnesium hydroxide as:

$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad (2.2)$$

The magnesium hydroxide formed in reaction combines with fluoride ions to form practically insoluble magnesium fluoride as:

$$Mg(OH)_2 + 2F^- \rightarrow MgF_2 \downarrow + 2OH^- \qquad (2.3)$$

The use of magnesium oxide increases the pH of treated water samples to between 10 and 11.

**2.4.1.1.3. Calcium and Phosphate Compounds.** The precipitation of fluoride from drinking water by using the chemicals calcium chloride ($CaCl_2{\cdot}2H_2O$) and monosodium phosphate ($NaH_2PO_4{\cdot}H_2O$) as calcium fluoride and/or fluorapatite is theoretically feasible as shown by Equations. :

$$CaCl_2 \cdot 2H_2O \rightarrow Ca^{2+} + 2Cl^- + 2H_2O \quad (2.4)$$

$$NaH_2PO_4 \cdot H_2O \rightarrow PO_4^{\ +} + Na^+ + 2H^+ + 2H_2O \quad (2.5)$$

$$Ca^{2+} + 2F^- \rightarrow CaF_2 \quad (2.6)$$

$$10Ca^{2+} + 6PO^- + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2 \quad (2.7)$$

It has recently been reported that the slow reaction kinetics of this process can be easily catalyzed in a contact bed (using a saturated bone charcoal medium) that acts as a filter for the precipitate, (E., Dahi, 1996) terming the process as "contact precipitation."

**2.4.1.2. Co-precipitation of Fluoride:**

**2.4.1.2.1. Alum:** When aluminium (Al) salts are dissolved in water in sufficient quantities to exceed the solubility limit of the metal hydroxide, the metal ion $Al^{3+}$ is hydrated to form an aquometal ion $Al(H_2O)_3^{+\ 6}$ , which( Qureshi, N. and Malmberg, R.H. 1985) then undergoes further hydrolysis to mononuclear, binuclear, and possibly polynuclear hydroxo complexes like $Al_{13}(OH)^{5+}$ , $Al_7(OH)4^+$ ,$Al_8(OH)_4^+$ , and $Al_6(OH)_3^+$ , ultimately precipitating the metal hydroxide Al(OH)3.

The hydrolytic reactions can be written as:

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + 2H^+ \quad (2.8)$$

$$Al^{3+} + 2H_2O \rightarrow Al(OH)^{2+} + 2H^+ \quad (2.9)$$

$$17Al^{3+} + 17H_2O \rightarrow Al_7(OH)^{2+} + 17H^+ \quad (2.10)$$

$$Al(H_2O)_3 + 6H_2O \rightarrow Al(H_2O)_5(OH)_2 + H_3O^+ \quad (2.11)$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3(s) + 3H^+ \quad (2.12)$$

In the co precipitation using Al salts, fluoride ions were considered to be removed from solution by getting enmeshed onto the gelatinous Al(OH)3 flocs. Since water containing fluoride concentrations greater than 10 mg/L requires higher doses of alum, this can lead to an increase of sulphate and aluminium concentrations in treated water to unacceptable levels.

**2.4.1.2.2. Alum and Lime (Nalgonda Technique)**: Defluoridation practices in India have had its genesis from Nalgonda Technology (Nalgonda is one of the poorest and most drought prone districts of the state of Andhra Pradesh in southern India affected by severe fluorosis, where the first community defluoridation plant was constructed). It involves the addition of prescribed quantities of alum, lime, and bleaching powder to raw water, followed by rapid mixing, flocculation, sedimentation, filtration, and disinfection, as represented by the line diagram shown in Fig. 2.1. Sodium aluminate or lime hastens settlement of precipitate, and bleaching powder ensures disinfection. Lime is cheaper than aluminates and is preferred since its dose is only 1/20th to 1/25th that of filter alum.

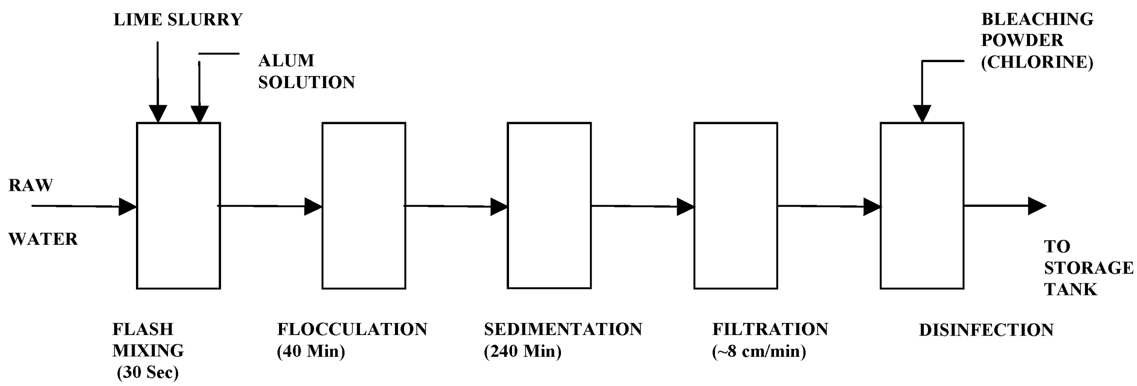


**Figure 2.3** Schematic Diagram of Defluoridation Process by Nalgonda Technique.

The process involves coagulation with alum in an alkaline aqueous environment and, as described in defluoridation by alum treatment previously, it involves adsorption and charge neutralization. Fluoride may be adsorbed onto the sticky gelatinous Al(OH)3 flocks during sweep coagulation and get co precipitated with it.

The entire operation of a commonly used “fill and draw type” defluoridation unit for small community (around 200 persons) can be completed within 2–3 h, with a number of batch performances in a day. The absence of regeneration of media, use of readily available chemicals, easy operation and maintenance, and other economic considerations made this technique popular. Since the process involves the mechanism of coagulation, flocculation, settling or sedimentation, and disinfection, simultaneous removal of colour, odour, turbidity, bacteria, and organic contaminants Moreover, the sludge generated is convertible to alum for use in the removal of excess turbidity of surface waters. Thus this technique is considered preferable at all levels because of the low cost and ease of handling. (RGNDWM, Rajiv Gandhi National Drinking Water Mission. 2001)

**2.4.2. Adsorption Techniques:** Adsorption is defined as change in the concentration of a component in the surface layer in comparison with the bulk phase related to unit surface area. It involves interface accumulation of substances at a surface or interface. The process can occur at an interface between any two phases, such as liquid–liquid, gas–liquid, gas–solid, or liquid–solid interfaces. The material adsorbed is known as the adsorbate and the adsorbing phase is the adsorbent. Adsorption occurring as a result of van der Waals forces is termed "physical adsorption" or "physisorption." If the adsorbate undergoes chemical interaction with the adsorbent the phenomenon is referred to as "chemisorptions." The chemisorbed molecules are not free to move on the surface since they form strong localized bonds at the active centres of the adsorbent. Chemisorption exhibits high energies of adsorption and is favoured at higher temperatures. A third category of adsorption is known as "exchange adsorption," in which ions of one substance concentrate at a surface as a result of electrostatic attraction to charged sites at the surface.(Weber,W. J., Jr. 1972)

**2.4.2.1. Bone and Charcoal:** The fluoride-scavenging potential of degreased, caustic-and-acid treated bone material is good and it can effectively reduce fluoride concentration from 3.5 to less than 0.2 mg/L. The removal mechanism of ion exchange in which the carbonate radical of the apatite ($Ca_9$(PO4)6·CaCO3) comprising bone can be replaced by fluoride to form an insoluble fluorapatite, as:

$$Ca_9(PO_4)_6 \cdot CaCO_3 + 2F^- \rightarrow Ca(PO_4)_6 \cdot CaF_2 + CO_2 \qquad (2.13)$$

**Table 2.3.** Typical Properties of Bone Char

| Constituent | Content |
|---|---|
| Ca3(PO4)2 | 73.5% |
| CaCO3 | 8.5% |
| Iron and aluminium oxide | 0.4% |
| Magnesia | 0.2% |
| Acid insoluble ash | 0.3% |
| Total volatile | 16.5% |
| Apparent density (g/cc) | 0.64–0.74 |

**Source:** (Benefield, D.L. et al 1982).

But the high cost of bone, became an inhibiting factor for its wider use. However bone char, produced by carbonizing bone at temperatures of 1100–16000C, had superior scavenging potential to unprocessed bone. Thereafter, bone char replaced bone as a defluoridating agent. (Sorg, T.J. 1978)

The simplicity, local availability, and local processing facilities made this method more appropriate. A combination of bone char with Nalgonda technique has also been proven to be good. (Mjengera, H., and Mkongo, G. 2003) but at the application level, the success of this technique hinges mainly on the quality of bone charcoal.

**2.4.2.2. Clays and Soils:** The excess fluoride in water could be removed to different degrees by adsorption onto a variety of soil and mineral types and thereafter, fluoride adsorption onto soils and clays both in natural and modified activated is found to be good.

**Table 2.4.** Adsorption Capacity of Different Soils

| **Sorbents Type** | **Place Description** | **pH** | **Initial Fluoride Concentration(mg/L)** | **Maximum Adsorption Capacity(mg/g)** |
|---|---|---|---|---|
| Gibbsite | Australia | 5-7 | 10 | 0.40 |
| | South Africa | 5-7 | 10 | 0.25-0.40 |
| Goethite | South Africa | 5-7 | 10 | 0.0 |
| | China | 5-7 | 10 | 0.23 |
| | Sri Lanka | 5-7 | 10 | 0.40 |
| Palygorksite | South Africa | 5-7 | 10 | 0.21-0.29 |
| Bentonite | South Africa | 5-7 | 16-630 | 63.3 |

Fluoride removal is believed to occur via multiple mechanisms, including electrostatic attraction, anion exchange, ligand exchange (with surface hydroxyl groups and water molecules), and precipitation. The use of different clays for defluoridation in columns is possible, but troublesome mainly because of difficulties in packing the columns and controlling the flow (S. Ayoob et al, 2008). The clay process would be of no use, or at least much less use, if the water contains higher concentrations of fluoride or if better removal efficiencies are required.

**2.4.2.3. Alumina-Based Adsorbents:** Alumina has been widely used for catalyst and separation applications in which it has been identified that the acidity–basicity properties are the major determinants of the adsorption behaviour on alumina. Surface structure and adsorption play an important role. The two main models for explaining adsorption on alumina from aqueous solutions are the ion exchange model and the ligand exchange model. Ion exchange properties are based on the ability of surface hydroxyls to dissociate or to be protonated depending on the pH. (Nawrocki, J. et al 2004)

$$M - OH + H^{+} \leftrightarrow M - OH^{2+} \qquad (2.14)$$

$$M - OH + OH^{-} \leftrightarrow M - OH^{-} + H_2O \qquad (2.15)$$

M represents the metal oxide metal.

**2.4.2.3.1. Activated Alumina**. Activated alumina (AA) is a granular, highly porous material consisting essentially of aluminium oxide, $Al_2O_3$. The surface area per unit weight is quite high, normally in the range of 200– 300 $m^2$/g. The application of AA in the removal of fluoride from drinking water is regarded as one of the best available technologies worldwide. The major factors affecting fluoride removal are pH, surface loading (the ratio of total fluoride concentration to the alumina dosage), and presence of other interfering ions.

**Table 2.5.** Characteristics of Activated Alumina

| **Serial no** | **Physical characteristics** | **Value** |
|---|---|---|
| 1 | Particle form | Sphere |
| 2 | Particle size(mm) | 2-5 |
| 3 | Bulk density (mg/cm3) | 800 |
| 4 | Pore volume(cm3/g) | 0.42 |
| 5 | Bed crushing strength(wt%)(minimum) | 92 |
| 6 | Water adsorption capacity at 30$^{o}$c by weight | 21 |

Table 2.5 displays the characteristics of activated alumina. **(**Ghorai, S., and Pant, K.K. 2005). The specific affinity of AA for fluoride coupled with excellent exchange capacity makes it an ideal candidate for defluoridation. The uptake capacity and reuse potential are considered important parameters for the application of AA for defluoridation in the field. The minimum interference from counter–ions is the added advantages for AA-based systems.

**2.4.2.3.2. Modified Activated Alumina:** In order to enhance the adsorption efficacy of activated alumina, the surface of activated alumina is modified with lanthanum, manganese oxide, copper, magnesia etc. The efficiency was increased up to 95% using different modifying material at optimum conditions. The adsorption capacity of original alumina was in the range of 0.170–0.190 mM/g, whereas for alumina impregnated with lanthanum hydroxide, the adsorption capacity was found higher (0.350 mM/g) (Puri B.K. and Balanis S. 2011). The alumina surface was modified by impregnating with alum and the modified adsorbent was used for defluoridation. The adsorption of fluoride increased with the rise in pH and reached a maximum of 92.6% at pH 6.5. The Langmuir sorption capacity of fluoride was found to be 40.68 mg/g at pH 6.5 (Tripathy, S.S. et al 2006). Alumina treated with manganese oxide to prepare manganese-oxide-coated alumina (MOCA) and the potential of sorbent was investigated for defluoridation of drinking water by batch and continuous mode experiments. Adsorption of fluoride on to MOCA was found to be much faster than that of AA at the initial period of time. The Langmuir maximum sorption capacity of MOCA for fluoride was about 2.65 times higher than that of AA (2.851 mg/g). Mesoporous alumina was modified by coating copper oxide to enhance the defluoridation of water. (Teng S.X. et al 2009) The adsorption capacity of copper oxide coated alumina (COCA) for fluoride obtained from the Langmuir model was 7.22 mg/g, which was three times higher than that of unmodified AA (2.232 mg/g). (Bansiwal A. et al 2010) Activated alumina was modified using the sol gel technique. Coating of calcium oxide (CaO) or manganese oxide ($MnO_2$) was done to improve the surface functionality of alumina. The results of the adsorption studies showed that the calcium oxide-modified activated alumina (CaO-AA) adsorbent had the maximum adsorption capacity for fluoride. CaO-AA was found to adsorb 5 and 10 times more fluoride than sol–gel AA and MnO2-AA at the same initial concentration. (Camacho L.M. et al 2010) Alkoxide origin alumina sorbent showed lower equilibrium fluoride concentration as compared to the activated alumina. The maximum fluoride removal efficiency was observed in the pH range of 5–7. Carbonate, bicarbonate and sulphate reduced the fluoride sorption due to the change in solution pH and competition for active sorption sites. (Kamble S.P. et al 2010)

**2.4.2.4. Calcium-based sorbents:** Fluoride removal was conducted by using crushed limestone (99% pure calcite) by batch studies and surface-sensitive techniques from solutions with high fluoride concentrations ranging from 3 to 2100 mg/L. The fluoride adsorption occurred immediately over the entire calcite surface with fluorite precipitating at step edges and kinks. The removal of fluoride was 80.6% at optimum conditions from the synthetic solution when initial fluoride concentration was 50 mg/L. The anions reduced the fluoride adsorption in the order, (Turner B.D. et al 2005)

$$PO_4^{3-} \rangle SO_4^{2-} \rangle NO^{3-}$$

**2.4.2.5. Iron-based sorbents for defluoridation of water:** Most of the adsorbents for fluoride removal have been tested for drinking water, and would not be stable at extreme pH values unless the pH is adjusted. Thus, polishing industrial wastewaters containing excess fluoride stands as a major problem. Owing to the stability at low pH and its magnetic properties, granular ferric hydroxide (GFH) for the removal of various ions including fluoride was used for the treatment of fluoride contaminated wastewater. (Mohapatra, D. et al 2004)

**2.4.2.6. Other metal oxides/hydroxides/oxyhydroxides, mixed metal oxides, metal-impregnated oxides as sorbents for defluoridation of water:** The metal oxyhydroxides have surface oxygen which differs in the number of coordinating metal ions to facilitate the adsorption of different cations and anions. This property of oxide minerals was considered as an advantage for fluoride removal. Refractory grade bauxite (RGB), feed bauxite (FB), manganese ore, magnesia-amended silicon dioxide granules (MAS), titanium oxysulfate TiO(SO4), and hydrated oxides of Zirconium ores (WAD) (Blackwell, J. A. and Carr, P.W 1991) were taken as test adsorbents for fluoride removal from aqueous solutions. These adsorbent were able to remove fluoride in real waste water at very low concentration. Fluoride ions were easily desorbed using a high pH solution, completely regenerating for further removal process at acidic pH and the capacity for fluoride adsorption remained almost unchanged three times after repeated adsorption and desorption. (Biswas, K. et al 2009)

**2.4.2.7. Carbon based sorbents for defluoridation of water:** Few carbon based sorbents have also been explored for fluoride Removal. The optimization and application of the regenerated bone char media for the defluoridation of drinking water was found to be very good. . Results indicated that the highest fluoride removal and adsorption capacity were good. Fluoride adsorption capacity of impregnated activated charcoals was 3–5 times higher to that of plain activated charcoal. The adsorption capacities of the carbon can be doubled by impregnation, with a maximum capacity of defluoridation, 1.07 mg/g. The activated carbons used were based on wood, coal, and petroleum coke. The adsorption potential and chemistry of different types of carbon represents that the removal is only by physical adsorption depending only on the specific surface area. Also, the numbers of carboxyl and phenolic hydroxide groups on the carbonaceous material surface are found to play no role in fluoride uptake. (Gupta, A. K. et al 2009)

**2.4.2.8. Natural materials as sorbents for defluoridation of water:** Various naturally occurring materials available abundantly free of charge have been explored as adsorbents for the removal of fluoride from water. The efficacy of three different coal based sorbents, lignite (LN), fine coke (FC), raw laterite and bituminous coal (BC) was evaluated for fluoride sorption from water and found to be good if they are given treatment. (Ma, Y. Et al 2009)

**2.4.2.9. Biosorbents for defluoridation of water:** Biosorption is an emerging technique for water treatment utilizing abundantly available biomaterials. Various biosorbents have been developed for fluoride removal and among those chitin and chitosan-derivatives have gained wide attention as effective biosorbents due to their low cost and high contents of amino and hydroxyl functional groups which show significant adsorption potential for the removal of various aquatic pollutants. Algal biomass pretreated with $Ca^{2+}$ was also evaluated for the biosorption of fluoride from polluted waters. The fluoride sorption phenomenon on fungal biosorbent was attributed to the chemical type of interaction. Collagen fiber, a profuse natural biomass, has abundant functional groups and is capable of chemically reacting with many type of metal ions, and can be used as a carrier of metal ions. A novel biosorbent was developed by the crosslinking of an anionic biopolymer, calcium alginate, with glutaraldehyde. The glutaraldehyde-crosslinked calcium alginate (GCA) was examined for its potential for fluoride removal by batch equilibrium and column flow adsorption studies and was proved to be very good. (Jagtap, S. et al 2011)

**2.4.2.10. Agricultural wastes as sorbents for defluoridation of water:** Agricultural waste materials being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewable nature and low cost are viable option for water and wastewater remediation. Low cost adsorbents from different agricultural waste materials such as coconut shell, coconut shell fibers and rice husk were developed and employed for the removal of various pollutants in industrial wastewater including fluoride. (Alagumuthu, G. Rajan M. 2007)

**2.4.2.11. Industrial wastes as sorbents for defluoridation of water:** Widespread industrial activities generate huge amount of solid waste materials as by products and these products can be used as defluoridating agents. Various industrial wastes have the potential with or without treatment for fluoride removal from water. Fly ash (a thermal power plant waste), carbon slurry (a fertilizer industry waste), red mud, original waste mud (o-WM), acid-activated (a-WM) and precipitated waste mud (p-WM), Spent bleaching earth (SBE), a solid waste from edible oil processing industry, alum sludge are the some wastes that can be used for defluoridation purposes after some treatment. (Kemer, B. et al 2009)

**2.4.2.12. Layered double hydroxides (LDHs)/ hydrotalcite-like compounds (HTlcs)/apatite and hydroxypatite as sorbents for defluoridation of water:** Layered double hydroxides (LDHs) have also been explored for their potential for fluoride removal because the main advantage in using LDHs as adsorbents is that unlike other chemical treatment methods (for example, precipitation), no chemical sludge is produced and they reconstruct their original layered structure after adsorption of various anions. The presence of sizable interlayer spaces and large quantity of exchangeable anions, make HTlCs and their calcined products excellent adsorbents for removal of toxic anions from contaminated waters. HTlCs have also found promising for fluoride removal from water. Synthetic nano-hydroxyapatite (n-HAp), biogenic apatite (bone meal; B), treated biogenic apatite (bone meal prepared by H2O2 oxidation, BH2O2) and geogenic apatite (rock phosphate) were also found to have good efficiency for fluoride removal. (Lv, L. et al 2011)

**2.4.2.13. Nano-sorbents for defluoridation of water:** Nanotechnology has emerged as a promising technology in past decade in various fields and use of nanoparticles as sorbents for water treatment is also gaining wide attention in recent years. Aligned carbon nanotubes (ACNTs), prepared by catalytic decomposition of xylene using ferrocene as catalyst, and proved their good performance for fluoride removal from water. Both the surface and inner cavities of ACNTs were found to be readily accessible for fluoride sorption. A variety of nano-sized inorganic oxides prepared through thermolysis of a polymeric based aqueous precursor were capable to give the solution of the desired inorganic ions. A combination of Al(OH)3 and magnetic nanoparticles to fabricate nano-sized adsorbents with advantage of high surface area, high affinity towards fluoride and good magnetic separability was used to develop a new kind of magnetic fluoride adsorbent.(Sarkar S.et al 2007) Like this various efforts in this field have been made to take the advantage of nanoparticles. (Ayoob, S. and Gupta, A.K. 2009)

**2.4.3. Electrochemical Techniques:**

**2.4.3.1. Electrocoagulation:** Electrocoagulation (EC) utilizes an electrolytic process to generate a coagulant in-situ by oxidation of an appropriate anodic material. The coagulant ions then react with the target pollutant ions, initiating normal coagulation. When an electric current passes through the aluminium electrodes, an anodic reaction releases Al(III) ions, which then react with hydroxide ions produced at the cathode and with fluoride ions in solution.

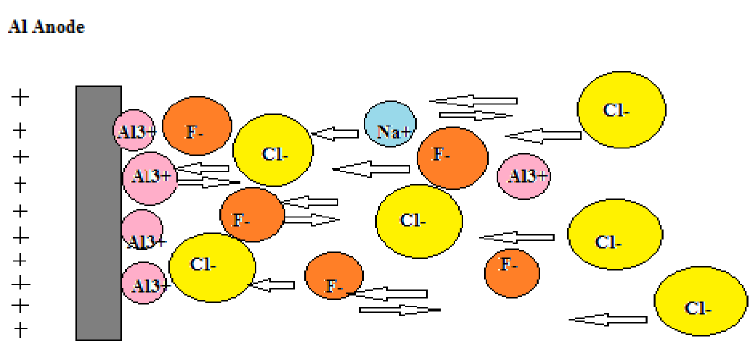


**Figure 2.4.** Diagram representing the electro-condensation effect [Hu, C.Y. et al 2003].

Defluoridation efficiency of the EC system may exceed that of the traditional coagulation process because of electrocondensation. Since fluoride ions are attracted to the anode, fluoride concentration near the anode exceeds that in the bulk solution, which may lead to higher efficiency (condensation effect) for the EC process. The modification of the process was done by introducing bipolar electrodes. A conductive plate without any electric connection, placed between two electrodes having opposite charges, will develop bipolarity and hence it is known as the bipolar electrode. (Mameri, N. et al 1998)

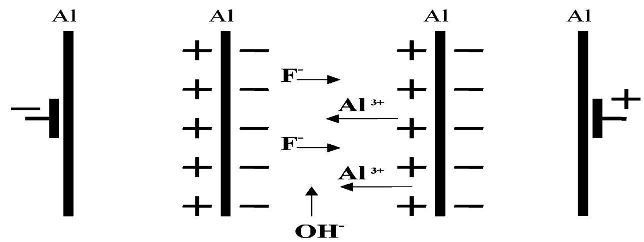


**Figure 2.5.** Schematic diagram of bipolar electrode system [Mameri, N. et al 1998].

Anodic reaction will take place on the positive side of the bipolar electrode and cathodic reactions at the negative side.

**2.4.3.2. Electrosorption:** Electrosorptive techniques have been used to treat various contaminated waters and also to enhance sorption capacity of the conventional systems. Electrochemical cell, equipped with two stainless-steel electrodes, was introduced into a polyvinyl chloride (PVC) column (2 cm in diameter and 20 cm long) to produce an electrical field in the activated alumina bed. Normally, chemical desorption and regeneration result in reduced sorption capacities. But the electrodesorption techniques are found to be better. 90% less cleaning agent (NaOH) was used as compared to conventional regeneration techniques. A 95% recovery of the adsorption capacity was realized with the electrosorption system and the volume of water required to regenerate the saturated bed was only 6% of the treated water volume, a much lower value than with current regeneration techniques. (Lounici, H. et al 2004)

**2.4.4. Membrane Techniques:** A membrane is an interface between two adjacent phases, which acts as a selective barrier controlling material transport between them. The main advantage of membrane technology in separation science relates to the transport selectivity of the membrane.

**Table 2.6** Classification of Membranes and Membrane Processes for Separations via Passive Transport

| Sl No. | Membrane Barrier Structure | Transmembrane Gradient | | |
|---|---|---|---|---|
| | | **Concentration** | **Pressure** | **Electric Field** |
| 1 | Non Porous | | Reverse Osmosis(Ro) | Electro Dialysis(Ed) |
| 2 | MICROPOROUS (Dp<= 2nm) | DIALYSIS | nanofiltration (nf) | |
| 3 | Mesoporous Pore (Dp=2-50nm) | Dialysis | Ultrafiltration | Electro Dialysis(Ed) |
| 4 | Macroporous Size (Dp=50-500nm) | | Microfiltration | |

**Source: [**Ulbricht, M. 2006].

The membrane shapes generally used are flat sheet, hollow fiber, or hollow capsule types. The driving force for passive transport operating in membrane separations is generally a difference in chemical potential created due to a concentration or pressure gradient across the membrane, or, by an electric field. . In an ion-exchange membrane, ions are exchanged between a solution and the ionic groups attached to the membrane. These membranes can be either cation exchangers for positively charged cations or anion exchangers for negatively charged anions. The type of attached ionic groups in the membrane matrix imparts its anion exchange or cation exchange character. Since the process is reversible these membranes can be regenerated or loaded by washing with an excess of ions to be exchanged. The distinguishing characteristic of ion exchange membranes is their permeability to ions of opposite charge (counter–ions) while excluding ions of the same charge (co-ions). The unique feature of an ion exchange membrane system is that it is more energy-efficient and sustainable, which recovers many of the useful effluents that otherwise flow along with the liquid stream. (Ulbricht, M. 2006)

**2.4.4.1. Nanofiltration:** NF is also a pressure-driven membrane process, which is generally used for separating multivalent ions from monovalent species. It is also possible to achieve separation of ions of same valence by selecting a proper membrane and operating conditions. NF membranes are essentially low pressure RO membranes. Because NF membranes provide higher water fluxes at lower transmembrane pressures than traditional RO membranes, they are sometimes referred to as "low-pressure RO membranes" or "loose RO membranes." The NF membranes are usually asymmetric with negative charge at neutral and alkaline environment and also have a "loose" polymer structure. The origin of surface charge on NF membranes are the anions adsorbed on its surface, whereas in ion exchange membranes it is due to various fixed charged groups bonded to the polymer structure. So in the NF process, in addition to the convection and diffusive mechanisms, repulsion (Donnan exclusion) between anions in solution and the surface groups becomes significant in retention, which will obviously be higher for multivalent anions. As a result of this additional mechanism of ion exclusion (in addition to size based exclusion), high degrees of ion separation (ion rejections) similar to those in RO, but with higher water fluxes through the NF membranes could be achieved. But the NF process is much more sensitive than RO to pH and ionic strength of source water. (Velizaros, S 2004)

**2.4.4.2. Electrodialysis:** Electrodialysis (ED) is an electromembrane process developed for desalting and demineralization of water. In this process, the transport of ions present in contaminated water is accelerated due to an electric potential difference applied externally.

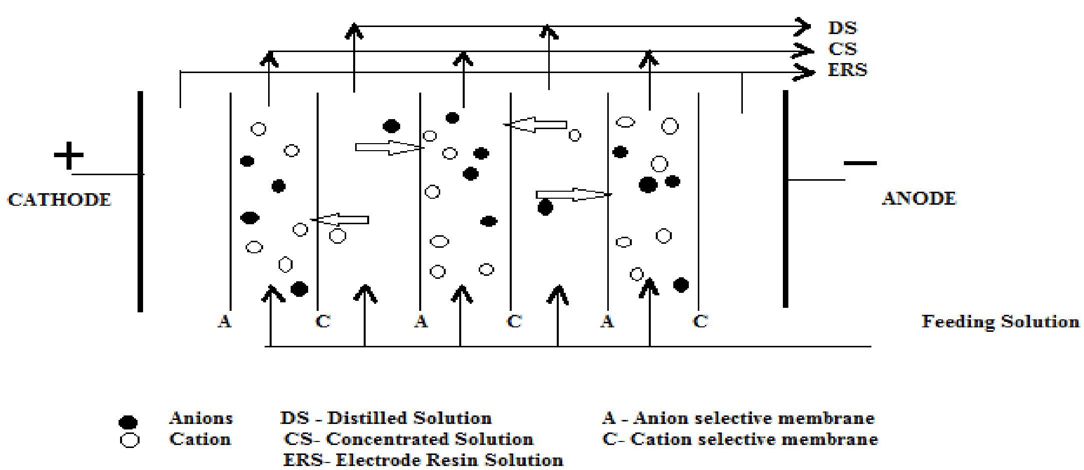


**Figure 2.5** Schematic diagram of a typical ED cell (Marder, L. et al 2003).

The separation is accomplished by alternately placing cation- and anion-selective membranes in a parallel fashion across the current path to form an ED cell. A schematic representation of a typical ED cell is given in Figure 13. (Marder, L 2003)

When voltage is applied, cations pass through the cation exchange membrane toward the cathode and anions pass through the anion exchange membrane in the opposite direction. Thus in alternating spaces between the membranes, salinity decreases in one space and increases in the next, throughout the stack of parallel membranes, ED costs are directly proportional to salinity of the water sample and membrane fouling, as with RO, is largely attributed to colloidal matter and precipitation of sparingly soluble salts such as calcium carbonate, calcium sulfates, and ferric hydroxides.

**2.4.4.3. Donnan Dialysis:** Donnan dialysis (DD) is a membrane separation process that uses an ion exchange membrane similar to electro-membrane processes but with a concentration gradient as driving force rather than applying an external electric potential difference across the membrane. Its operation requires addition of a so called driving counter ion to stripping solution, which is transported in a direction opposite to that of the target ion in order to maintain electro neutrality. The ions which are permeable to the membrane will equilibrate until the conditions of Donnan equilibriums are satisfied. (Sarkar, S. et al, 2010)

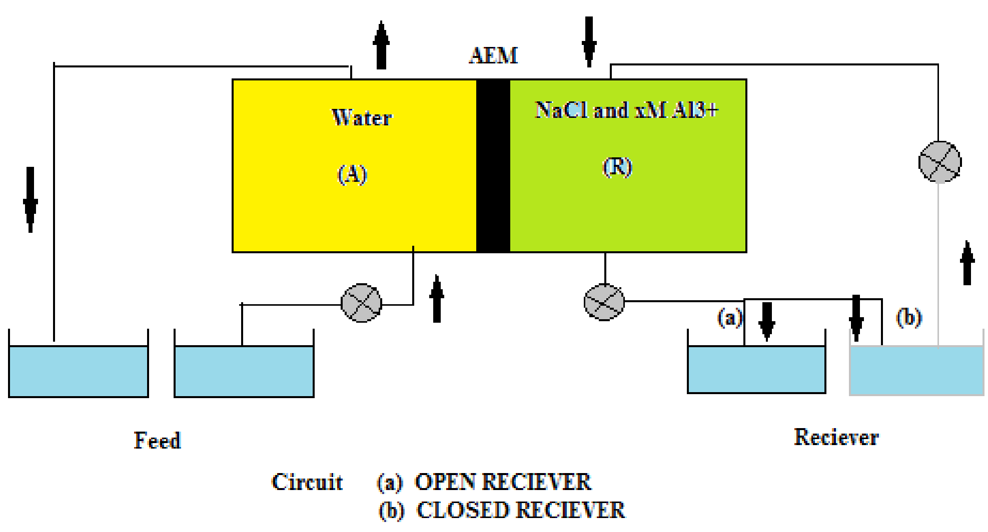


**Figure 2.6** Schematic flow diagram of DD system (Hichour, M. 2000).

The DD process mechanism involves three steps:

1. At the beginning of the experiment, between 0 and 1 h, the fluoride ions were mainly transferred to the receiver compartment.
2. Between 1 and 7 h, the transfer rate declined while the concentration at the outlet of the feed compartment increased.
3. After 7 h, the transfer rate became equal to zero.

DD has shown potential for removal of inorganic anions, from drinking water, especially from waters of low salinity. (Hichour, M. 2000)

**2.5 Comparison of different defluoridation technologies used**

Different processes have been developed for removal of fluoride from drinking water. The major techniques include coagulation, adsorption and/or ion exchange, electrochemical methods, and membrane techniques. Though coagulation methods are generally effective in defluoridation, they are unsuccessful in bringing fluoride to desired concentration levels. Ion exchange and/or adsorption are widely accepted technologies utilized on a full-scale basis.

The traditional methods discussed below (table 2.6) being used for the defluoridation purposes are very limiting and have the drawback of fluoride precipitation. The precipitation and coagulation processes with iron, activated alumina, alum sludge and calcium have been widely investigated and ion exchange, reverse osmosis and electrodialysis have also been studied for the removal of excess amounts of fluoride from drinking water.

The shortcomings of most of these methods are high operational and maintenance costs, secondary pollution (generation oftoxic sludgse, etc.) and complicated procedure involved in the treatment. If a comprehensive study is done over the technologies and methods that are being used for defluoridation purposes and the comparisons is made on the basis of strength and limitations of different methods used for defluoridation purposes then a most suitable solution for the problem can be drawn.

Sorption methods are more effective in reducing fluoride concentration than precipitation methods; usually well below permissible limits. Though a number of adsorbents with very high potential have had been developed as cited in this article, only activated alumina and bone char were reported successful at the implementation level. (Table 2.7)

Coagulation methods have generally been found effective in defluoridation but they are unsuccessful in bringing fluoride to desired concentration levels. Furthermore, membrane processes do not require additives but these are relatively expensive to install and operate and

**Table 2.7** Comparison of techniques used for defluoridation

| Defluoridation Techniques | Defluoridation Capacity/ Dose | Strength | Limitations |
|---|---|---|---|
| **Electrochemical methods** | | | |
| Electrocoagulation | Efficiency 100% | Emerging technique. Efficiency of EC system is very high compared to the traditional coagulation process. | Interference from other anions like sulphate. Need for regular replacement of sacrificial electrodes, due to high consumption of electric power. |
| Electrosorption | Highly efficient | Emerging technique. Capacity of adsorbent enhanced by more than 0%.Excellent regeneration potential. | Costly due to high consumption of electric power. |
| **Membrane Processes** | | | |
| Reverse osmosis | Highly efficient | Well-studied and established technology. Immense commercial applications. Dominant in many developed countries. Small foot print. Organics and salts are also removed. | Sensitive to polarization Phenomenon. Chances of biological and mineral fouling. Treated water may lack the right balance of minerals. Poor water recoveries. High cost. |
| Nanofiltration | Highly efficient | Well-accepted membrane separation process. Handles higher water fluxes at lower trans-membrane pressures than RO. | More sensitive than RO to pH and ionic strength. Leaves large conc. of retentate fraction. Expensive technique. Skilled operators required. |
| Electrodialysis | Highly efficient | Excellent technique for simultaneous defluoridation and desalination. Commercially established. More economical than RO. More resistant to fouling. | Require high degree of pretreatment. Ineffective in removing low-molecular-mass non charged compounds. Membrane scaling. |

| | | | |
|---|---|---|---|
| | | | Treated water quality is inferior to that of RO. |
| Donnan dialysis | Highly efficient | Recently, received attention in treating fluoride. Electro-membrane processes but with concentration gradient as driving force. A permanent separation between solutions which is not reversed even if the system is closed to the surroundings. | Operation requires addition of a so-called driving counter-ion to stripping solution. Reduced efficiency in high-salsine waters. Expensive technique. |
| **Adsorption** | Efficient | Widely used | Easy in operation |

**Table 2.8** Comparison of adsorption capacity different adsorbent

| **Adsorbent** | **Defluoridation Capacity/ Dose** | **Strength** | **Limitations** |
|---|---|---|---|
| Bone | 0.9mg F/g | Long established technique for local applications. | Impart taste to water. Limited social acceptance. |
| Bone char | 2–4 mg F/g | Well known and established technique. Good potential. Local availability and processing facilities aids local applications. Ability to remove fluoride to very low levels. | Capacity reduces drastically after successive regenerations. More expensive than coagulation techniques. The use is constrained by the religious beliefs in many societies and communities. Limited social acceptance. |
| Clays | 0.03–0.35 mg F/g | Economical. Very limited local Application. | Defluoridation potential is generally low. Regeneration is very difficult. |
| Activated Alumina | 1.0 mg F/g | Very well established technique. Regarded as one | Costly compared to coagulation processes and |

| | | | |
|---|---|---|---|
| | | of the best available technologies worldwide. Best performance at pH 5.Minimum interference from counter-ions with consistent potential. | bone char. High pH reduces potential. Regeneration result in a reduction of about 5–10% in material, and 30–40% in capacity with increased presence of aluminium (>0.2 mg/L). |
| Modified Activated Alumina | Up to 3 mg F/g | Good performance in comparison to Activated Alumina. | Affected by the presence of counter ions. Sensitive to variation in pH. |
| Calcium Based Adsorbent | Up to 84.8 mg F/g | Can defluoride highly contaminated water. Very quick action. | Cannot be regenerated easily. Do not work in acidic conditions.(pH<3) |
| Iron Based Sorbents | Up to 58.6 mg F/g | Stable at low pH have magnetic properties. Insensitive to temperature change. Do not affect the adsorption of arsenate. | Very sensitive in high pH range (>8). |
| Metaloxides/ hydroxides/ oxyhydroxide, mixed metal oxides, metal-impregnated oxides. | Up to 98 mg F/g | Cost effective alternative, removal can occur at low pH(3). | Impart other ions to the defluoridated water. Phosphate and Sulphate ions put adverse affect. Efficiency decreases at high pH(>10). |
| Carbon Based adsorbents | Up to 3.13 mg F/g | Cheap, easily available | Low defluoridation capacity. |
| Natural Materials | 3-5 mg F/g | Almost free of cost, easily available, do not impart any contaminant to the treated water. | Can treat water having low concentration of fluoride. |

| | | | |
|---|---|---|---|
| Biosorbents | Up to 4 mg F/g | Emerging technique, low cost and high concentration of amino and hydroxyl group that can remove other contaminants too. | Low removal capacity, affected by pH variation. |
| Agricultural wastes | Up to 18.9 mg F/g | Economic, eco-friendly, Available in abundance, renewable in nature, low cost. | Removal is affected by the presence of carbonates, sulphates, and nitrate and bicarbonate ions. |
| Industrial wastes | Up to 11.8 mg F/g | Waste materials and by-Products can be reused, cheap and easily available. | Large amount of sludge generated, highly sensitive to pH change. |
| Layered double hydro-oxides(LDHs)/ hydrotalcite-like compound (HTlcs)/apatie & hydroxy-apatite. | Up to 13.4 mg F/g | No sludge is produced and they gain their original layered structure when they adsorb various ions. | Temperature and pH dependent, presence of counter ions like sulphate, carbonates, nitrate and chloride put adverse effect. |
| Building materials | Up to 3.91 mg F/g | Waste products can be reused. | pH sensitive (3-11), phosphate, silicates, bicarbonaets, carbonates affects removal |
| Nano-sorbents | Up to 28.7 mg F/g | Small size, large surface area, high mechanical strength and conductivity. | High pressure drop if used in column, Phosphate, Chloride, nitrate etc. |

addition of prescribed quantities of alum, lime, and bleaching powder to raw water, followed by rapid mixing, flocculation, sedimentation, filtration, and disinfection. After adding alum bottom and co-precipitate fluoride and bleaching powder ensures disinfection during the process. The entire operation of a commonly used “fill and draw type” defluoridation unit for small community (around 200 people) can be completed within 2–3 h, with a number of batch performances in a day. However, some disadvantages of this technique have also been reported are high residual aluminium concentration (2–7 mg/L) in the treated water than the set WHO standard: 0.2 mg/L). (Ayoob S. 2011)

Among methods discussed above for defluoridation of water, the adsorption process is found to be used extensively and offers satisfactory results and seems to be a quite appealing method for defluoridation in terms of cost, simplicity of design and operation. Various conventional and non-conventional adsorbents have been assessed for the removal of fluoride from water.

The manner in which to contact adsorbent most effectively with the water to be treated and the efficiency of adsorbent is of great significance for large-scale treatment of water. (Bhatnagar A. et al 2011)

Rates of adsorption from solution on granular adsorbents have been found to be dependent upon the particle size of the adsorbent and the type of contact process. It is therefore desirable to employ particles of as small a diameter as conditions of efficient operation allow with suitable contact process, so that high rates of adsorption may be obtained.

In batch-type contact processes a quantity of adsorbent is mixed continuously with a specific volume of water until the contaminants have been decreased to a desired level. The adsorbent is then removed and either discarded or regenerated for use with another volume of solution. If finely adsorbent is used in this type of system, separation of the spent adsorbent from the water may be difficult. Conversely, the use of large particles of adsorbent which are removed more rapidly when exhausted, requires longer periods of contact between solution and adsorbent, necessitating larger basins or tanks in which to retain the water during treatment.

Column-type continuous-flow operations have an advantage over batch type operations because rates of adsorption depend on the concentration gradient between solute and solution being treated. For column operation the adsorbent is continuously in contact with a fresh solution and concentration gradient always remain high which results in better adsorption. For the best performance of adsorption, a media with high capacity and properties which make it feasible to be used in continuous flow process is needed which can make its real life application feasible. (Ghorai, S and Pant, KK 2005)

Activated alumina is an adsorbent which has been extensively used for fluoride removal in the field. Activated alumina is manufactured from aluminium hydroxide by dehydroxylating it in a way that produces a highly porous material; this material can have a surface area significantly over 200 square metres/g. It has a very high surface-area-to-weight ratio. That means it has a lot of very small pores, almost like tunnels, that run throughout it. But if we consider the sorption capacity of fluoride on active alumina near neutral pH; the sorption capacity of fluoride on active alumina in distilled water is 2.41 mg/g, which means that active alumina is far less effective at removing fluoride for drinking purposes, especially given the comparably higher concentration of fluoride in groundwater. (Jaffe, P.R. et al 2011)

Synthetic hydroxyapatite can also remove fluoride cheaply and effectively in poor, rural

settings using locally available materials for synthesis. The mineral hydroxyapatite when come in contact with dissolved fluoride it transforms to fluorapatite, a softer mineral. So hydroxyapatite holds potential as a possible solution to the fluoride problem. It has good specific surface area 150 $m^2/g$ resulting in large capacity of HA for element substitution and this has triggered the use of HA for water purification, for waste stabilization, contaminated soil remediation, and heavy metal adsorption( Bailliez S. et al, 2004) For widespread use, natural apatites available in large quantities such as phosphate rock and natural fish bones have been investigated and subjected to field trials but naturally occurring substances vary in nature and cannot have well tailored properties. So hydroxy apatite with good and tailored properties can be synthesized by using cheap and locally available inorganic materials easily.

The sorption capacity of any adsorbent depends upon its physical characteristics, for example high specific surface area, fine grain size and size distribution including small in particle agglomeration. Nanoparticles offer unique properties as sorbents, catalysts, sensors, reducing agents, and bactericides. High surface area to volume ratio imparts nanoparticles a power to offer a very fast kinetics and multiplied sorption capacity. (Sarkar S. et al, 2011) However the nanoparticles are not suitable for direct application in fixed bed columns, reactive barriers, or any plug-flow like application due to their poor durability and excessive pressure drop across the column. Furthermore, the nanoscale particles typically tend to aggregate, a property that negates many of the benefits associated with the nanoscale dimension for utilizing the benefits of the nanoparticles for applications in the environmental remediation and sensing, it is necessary to overcome the disadvantages associated with the use of it. One way to make nanoparticles fit for the field-applications is to encapsulate them inside a matrix. (Sarkar S. et al, 2010) As a host material activated alumina can be a good choice for encapsulation of hydroxy apatite nanoparticles. As a host material activated alumina can bring several advantages to the hybrid nanocomposite material. Porous activated alumina granules impart the excellent mechanical strength, durability, and hydraulic properties to the hybrid material so that they can be used in different critical environmental applications. The morphology of the host materials, such as pore size and its distributions influence the size and aggregation nature of the nanoparticles dispersed within the pores. Stabilization of the nanoparticles within the pores helps to conserve their superior performance over multiple cycles of operation. (Sarkar, S. et al 2011)

So developing a hybrid adsorbent having the properties of both the material like high mechanical strength, and hydraulic properties of activated alumina along with the high removal capacity of fluoride of nano hydroxyapatite can be a far better and cheaper solution for defluoridation of water for poor communities. (Sarkar, S. et al 2007)

# CHAPTER- 3

# MATERIALS AND METHODS

## 3.1. Materials:

**3.1.1. Activated alumina:** Activated alumina in **Figure 3.1**, used in this study was procured **from Oxide India Pvt. Ltd., Durgapur, West Bengal**. Usually it is manufactured from aluminum hydroxide by dehydroxylating it in a way that it produces a highly porous structure. The principal use of this material is as desiccant and catalyst in petroleum industries. It is made of aluminium oxide (alumina; $Al_2O_3$), but because of its porous structure, it offers a very high surface-area-to-weight ratio Together with its favorable amphoteric and Lewis acid characteristics, it is often used as an adsorbent for effective removal of anionic contaminants such as arsenate and fluoride ions from contaminated water. Table 4.1 provides a few physical properties of the activated alumina used in this study.

**Figure 3.1** Virgin activated alumina

**Table 3.1.** Properties of activated alumina used, Grade (Oxide India Ltd.)

| S. No. | Characteristics | Value |
|---|---|---|
| 1 | Particle form | Sphere |
| 2 | Particle size(micron) | 600-900 |
| 3 | Water adsorption capacity at $30^{o}C$ by weight | 21 |
| 4 | Surface area ($m^2/g$)(minimum) | 250 |
| 5 | Pore volume($cm^3/g$) | 0.42 |

| | | |
|---|---|---|
| 6 | Bulk density(g/cm3) | 800 |
| 7 | Bed crushing strength (wt. %)(minimum) | 92 |

**3.1.2. Activated carbon:** Activated carbon from Gongyi Boyuan **Wear Resistant Materials Co., Ltd., China** in **Figure 3.2** was used in this study. It is also called activated charcoal, activated coal or carboactivatus, is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions. Due to its high degree of micro-porosity, just 1 gram of activated carbon has a surface area in excess of 500 $m^{2.}$ . Sufficient activation for useful applications may come solely from the high surface area, though further chemical treatment often enhances the adsorbing properties of the material. Activated carbon is usually derived from charcoal. However, due to the relative absence of charged functional groups in activated carbon makes it less suitable for adsorption of inorganic anions or cations from contaminated water.

**Figure 3.2** Virgin activated carbon

**Table 3.2.** Properties of activated carbon used.

| S. No. | Characteristics | Value |
|---|---|---|
| 1 | Iodine value (mg/g) | 350 |
| 2 | Apparent density ($kg/m^3$) | 620 |
| 3 | CTC adsorption (%) | 15 |
| 4 | Ash content (%) | 5 |
| 5 | Hardness (%) | 95 |
| 6 | pH | 8-10 |

**3.1.3. Polymer Resin:** IRA67 polymer resin **from Rohm and Hass Co. Ltd** in **Figure 3.3** was used in our study. It is a weak base anion resin is used for water softening in the Na cycle and for demineralization when the temporary hardness in the feed is < 40%.A weak base polymer resin IRA67 was used for defluoridaton in our study.

**Figure 3.3** Polymer resin IRA-67

**Table 3.3** Properties of polymer resin used, IRA-67

| S. No. | Characteristics | Values |
|---|---|---|
| 1 | Physical form | Translucent white spherical beads |
| 2 | Matrix | Cross-linked acrylic gel structure |
| 3 | Functional group | Tertiary amine |
| 4 | Moisture holding capacity | 56- 64% |
| 5 | Particle size | 0.500- 0.750 mm |
| 6 | Reversible swelling | FB $\rightarrow Cl^-$ <= 30% |

**3.1.4. Chemicals and Glass and Plastic wares:** The following table contains chemicals, reagents and other materials used for the study.

**Table 3.4** Different chemicals, reagents, glass wares and plastic wares used in study

| S. No. | Chemical / Reagents/Glass wares/Plastic wares | Sources |
|---|---|---|
| 1. | Zirconium oxychloride octahydrate AR, Spadns GR, activated carbon granular, HCl. | Loba Chemicals |
| 2. | Sodium hydroxide pellets, Ammonium dihydrogen | HIMEDIA |

| | | |
|---|---|---|
| | phosphate, Calcium Chloride. | |
| 3. | Activated alumina | Grade OA-25 (Oxide India Ltd.) |
| 4. | Polymer Resin IAR-67 | Roam and Hass Co. |
| 5. | Broad mouthed bottles 250 ml and 500 ml capacity. | TARSONS |
| 6. | Glass cuvettes | Lianyungang Highborn Technology Co., Ltd. |

**3.1.5. Instruments used:** The following instruments are used for the studies.

**3.1.5.1. Spectrophotometer:** A double beam UV-visible/NIR spectrophotometer model **U-2900** from **Hitachi** in **Figure 3.4** was used for fluoride estimation.

**Figure 3.4** Spectrophotometer (U-2900, Hitachi)

**3.1.5.2. Distilled Water Unit**: Distilled water unit from **Millipore Water Purification system** in **Figure 3.5** was used for distilled water.

**3.1.5.3. Shaker**: A horizontal shaker from **Lab-therm (kuhner)** in **Figure 3.6** was used for maintaining shaking condition.


**Figure 3.5** Millipore water purification system

**Figure 3.6** Horizontal shaker (Kuhner)

### 3.2. Methods

#### 3.2.1. Chemicals preparation:

**SPADNS Solution:** 958 mg SPADNS (sodium 2-(parasulphophenylazo)-1, 8-dihydroxy-3,6-naphthalene disulphonitrate) was dissolved to make up a final volume using distilled water.

**Zirconyl–acid Reagent:** 133 mg of zirconyl oxide octahydrate was dissolved in 25 ml water. Then 350 ml of conc. HCl was added and finally diluted to 500 ml.

**Reference Solution:** 10 ml SPADNS solution was taken and 100 ml distilled water was added to it. A 7 ml of conc. HCl was diluted to 10 ml and was added to SPADNS solution.

**Fluoride Stock Solution:** A 100X solution was prepared using sodium fluoride.

**Chloride Stock Solution:** A 100X solution was prepared using sodium chloride.

**Sulphate Stock Solution:** A 100X solution was prepared using sodium sulphate.

**Bicarbonate Stock Solution:** A 100X solution was prepared using sodium bicarbonate.

**Ammonium Di Hydrogen Phosphate Solution:** A strong 5% (wt by volume) solution of Ammonium Di hydrogen phosphate was prepared.

**Calcium Chloride Solution:** A strong 5% (wt by volume) solution of calcium chloride was prepared.

**3.2.2. Conditioning of polymer IRA-67**: The conditioning involves the following steps:

1) The resin is dipped in water and using HCl and pH was adjusted to 6.
2) The above resin then put in strong (4%) solution of NaCl and was kept on shaker for15 minutes.
3) The pH increased and again adjusted to 6 using HCl.
4) These steps were repeated until the pH become constant.
5) The resin is washed and dried under normal temperature.

**3.2.3. Synthesis of Modified Adsorbent**: Following steps as shown in **Figure 3.7** were involved:

1) Virgin activated alumina was washed by distilled water and dried under normal temperature (room temperature).

**Loading of adsorbent for first cycle**

2) The washed and dried activated alumina was put in calcium chloride (5%) solution and pH was adjusted to 4 (acidic) and the solution with activated alumina was kept on a shaker for 8 hours.
3) The solution was decanted and the material was poured in a 5% solution of ammonium di hydrogen phosphate and pH was adjusted to 11. The solution along with activated alumina was kept on a shaker for 8 hours.

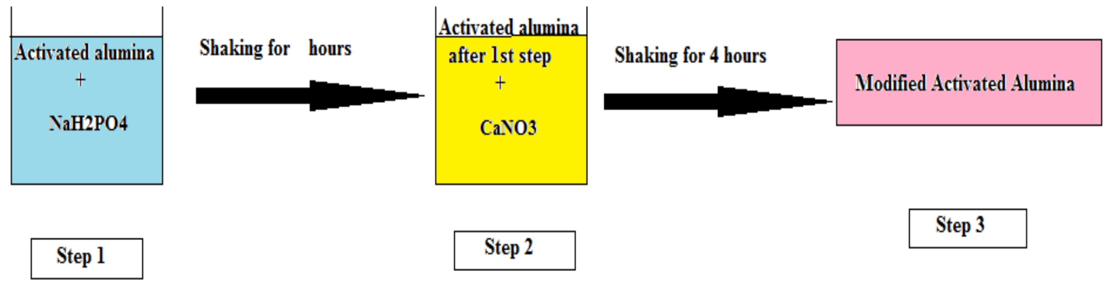


**Figure.3.7** Preparation steps for the synthesis of modified adsorbent

1) The solution was decanted and the material was dried under normal temperature conditions.
2) Steps (2-4) were repeated for second loading.

May be following equations were involved in this reaction

Step 1

$$\equiv AlOH_2^{\ +} + Na\,H_2\,PO_4 \rightarrow \equiv AlOH_2^{\ +}(H_2PO_4)^- + NH_4^{\ +} \quad (3.1)$$

Step 2

$$\equiv AlOH_2^{\ +}(H_2PO_4) + CaNO_3 \rightarrow \equiv AlOH + Ca_{10}(PO_4)_6(OH)_2 \quad (3.2)$$

Activated alumina is microporus in nature and these pores acts as micro-reactor for precipitation of hydroxyapatite. Physical characteristics like size, surface area, porosity and shape of pores decide the size and the nature of nanoparticles dispersed within it. As the micropores offer a very small volume, the precipitated particles get less freedom to agglomerate, resulting in the formation of nano-sized precipitates. Because of lack of infrastructure we could not perform Scanning Electron Microscopy (SEM) analysis but the probable structure of the hybrid material is like the one shown below in **Figure 3.8**.

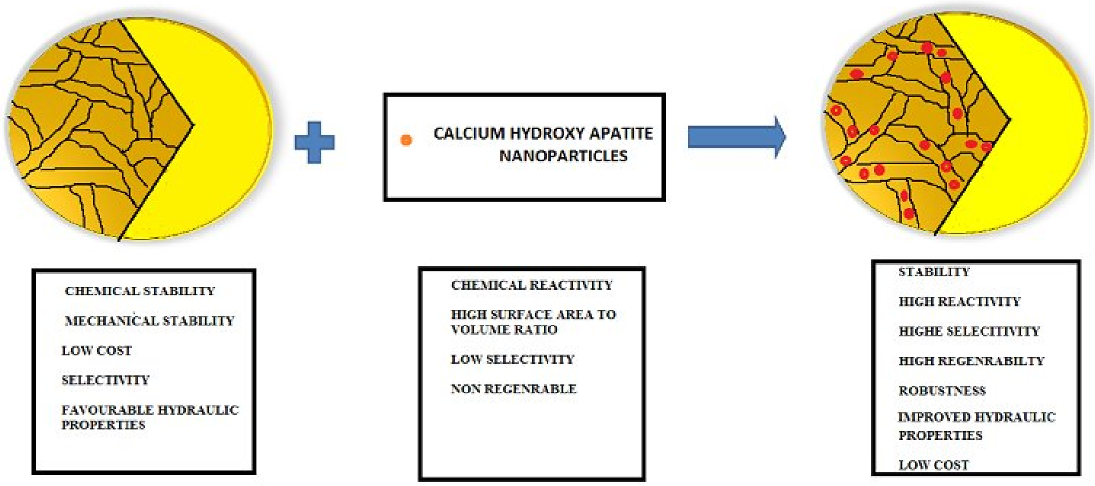


**Figure 3.8** Possible structure and enhanced properties of modified adsorbent

**3.2.4. Calibration Curve Preparation:** Following steps were involved:

1) Fluoride solutions with different concentrations ranging from 0 to 2mg/L was prepared from a stock solution that was prepared by dissolving 221mg anhydrous sodium fluoride in 1000 ml distilled water(100 $\mu g / ml$ as F).
2) Spectrophotometer was set at auto zero using reference solution or distilled water at a wavelength of 570 nm.
3) 50 ml of the sample was taken and 10 ml SPADNS and 10 ml zirconyl acid reagent was mixed and shaken.
4) Absorbance was recorded at different concentration.
5) A calibration curve showing straight line correlation between between absorbance and fluoride concentration was plotted.

**3.2.5. Determination of Fluoride** : Following steps were involved:

1) 50 ml of sample or aliquot was taken and 10 ml SPADNS and 10 ml zirconyl acid reagent was added to it. The aliquot was thoroughly mixed and absorbance was recorded at 570 nm.
2) Using the calibration curve, concentration corresponding to the absorbance was noted.
3) Fluoride concentration in the samples was found out by multiplication with the dilution factors.

**3.2.6. Adsorption Isotherm Preparation**: Following steps were involved:

1) Different known amounts of the adsorbent were weighed (from 0 to 90 mg).
2) A sample solution having constant fluoride concentration 10 mg/l and background concentrations of competing anions (chloride=100 mg/L, Sulphate=50 mg/L and Bicarbonate=120 mg/L) was prepared.
3) pH was adjusted to 7.2.
4) Different amount of adsorbent was put in flasks/ bottles containing a constant volume of the above solution (200 ml).
5) All the sample bottles/ flasks were placed on a horizontal shaker for 8 hours.
6) After 8 hours, concentration in different samples was calculated using spectrophotometer.
7) A graph between solid phase (qe) concentration and liquid phase concentration (Ce) was plotted. Solid phase uptake of fluoride on the activated alumina was calculated using the following relationship:

Where, Ce = concentration of fluoride in the solution in mg/L.

qe = amount of fluoride adsorbed by the adsorbent in mg/g.

$$\boxed{q_e = \frac{V(C_0 - C_e)}{m}}$$

Co = initial concentration of fluoride of the solution mg/L.

Ce = Equilibrium concentration of fluoride in solution in mg/L.

V = Volume of solution in ml.

m = Mass of adsorbent in g

**3.2.7. Kinetic Study**: Following steps were involved:

1) A sufficient amount of adsorbent (9 g) was added to a plastic container containing sample solutions of volume 750 ml and with different concentration of fluoride with the same background concentration of competing anions mentioned above were placed in .

2) The plastic containers with the solution and adsorbents were put on a shaker.
3) Concentration of fluoride in the liquid phase was analysed at different time intervals (5 min,10 min,30 min,1 hour,2 hours,4 hours,8 hours,12 hours and 24 hours). The solid phase fluoride concentration was estimated from the mass balance using the liquid phase concentration of fluoride measured at different time intervals.
4) A curve between time (t) and solid phase (qe) concentration was plotted. Also, the data were analyzed using different adsorption kinetic models.

**3.2.8. Study of the Effect of pH on the Adsorption capacity**: Following steps were involved.

1) A solution containing 10 mg/L with e background concentration of commonly occurring ions (fluoride = 10 mg/L, chloride = 100 mg/L, sulphate 50 mg/L and bicarbonate = 120 mg/L) was taken and divided into 200 mL portions with each portion kept either in a plastic bottle or inside a 250 mL capped flask.
2) Different pH was adjusted in the range from 4 to 13 using a concentrated solution of HCl or NaOH.
3) A fixed same amount of adsorbent (9 g) was put in each of the containers. and the containers were put on a shaker for 6 hours followed by sampling and analysis of liquid phase fluoride concentration

**3.2.9. Study for Assessment of Interferences of Different Competing Species on the Adsorption Capacity**: Following steps were included. Same amount of adsorbents were added to 200 mL solutions at constant pH of 7.2 and containing 10 mg/L of fluoride but with varying concentration of background competing anions (chloride, sulphate and bicarbonate). Plastic bottles/ flasks containing 200 mL of solutions and adsorbents were put on a shaker for 6 hours after which samples were taken and analyzed for liquid phase fluoride.

**3.2.10. Column Study:**

In the real life, adsorbents are always used in flow-through systems using plug-flow configurations such as adsorption columns. Batch studies for the adsorbents are useful for a comparative analysis of the performance of the adsorbents. However, unless column studies are performed, it is difficult to predict the performance of the adsorbents in the adsorption columns generally employed in the field. The column studies with the adsorbents were performed using a glass column of internal diameter 11 mm (ACE Glass, USA). Figure 3.9 shows a photograph of the column set up at laboratory level. At the bottom of the glass column, a thin bed of glass wool was provided to lie below the adsorbent bed such that finer particles get arrested and cannot escape the bed. A peristaltic pump is used for continuous transfer of solution inside a column containing the adsorbent. The column is run in a down flow mode. A measured amount of adsorbent was used in each study. Samples were collected from the column outlet at pre-determined interval of time for further analysis for its fluoride content. Different column runs were performed at different inlet fluoride concentrations. The column runs were continued either to the point of exhaustion (when the inlet and outlet concentrations become equal) or upto the breakthrough of 1.5 mg/L of fluoride (Permissible value of fluoride in drinking water in India).

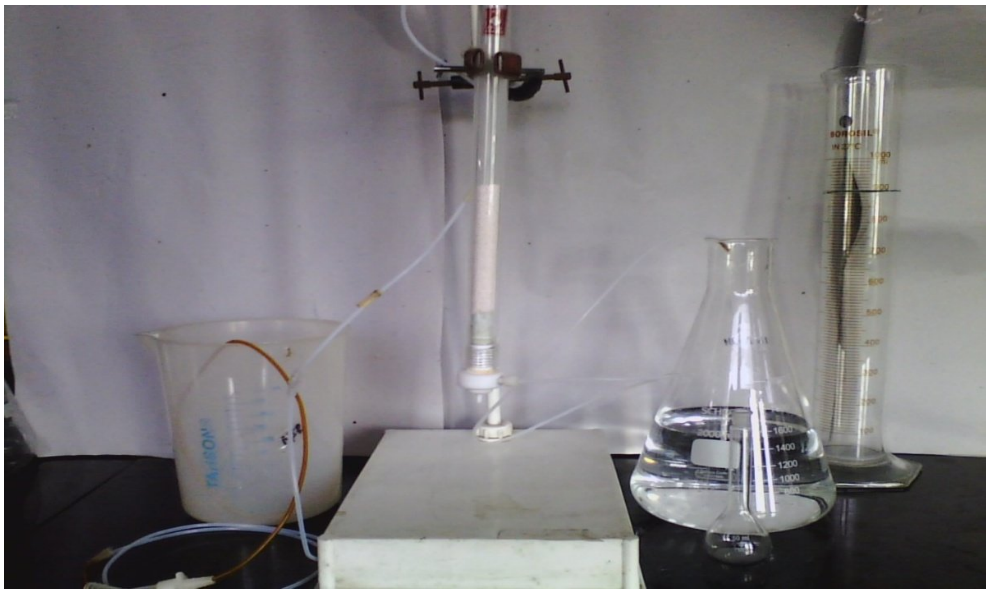

**Figure 3.9** Adsorption column set up at laboratory level

### 3.2.11 Regeneration Studies

The exhausted adsorbent was regenerated by using a solution of 1N NaOH. The exhausted adsorbent was kept inside the column while the regenerant solution was pumped inside the column in down-flow mode. The effluent samples were collected at every 0.5 bed volume. The samples were appropriately diluted and analyzed for fluoride concentration. After the regeneration the adsorbent bed was subjected to about 0.5N HCl solution until the effluent pH becomes slightly acidic. The acid addition step was performed to protonate the functional groups on the adsorbent. A thorough rinse with 5-7 bed volumes of de-ionized water was performed before restarting the bed for the next cycle of operation.

# CHAPTER-4

# RESULTS AND DISCUSSION

### 4.1. Batch studies

Different types of adsorbents such as granulated activated alumina, activated carbon, weak base anion exchange resin IRA67 and modified activated alumina were used in this study. Synthetic fluoride solution for the study was prepared by adding appropriate quantity of sodium fluoride to distilled water. For resemblance with the groundwater, in all the studies appropriate background concentration of competing anions were maintained in the synthetic fluoride solution. Batch experiments were carried out in different sets by taking the adsorbents in the range of 1-10 g/l of synthetic fluoride sample of desired initial concentration (2.0–10 mg/l) in a series of plastic reagent bottles at an optimum pH. The adsorption capacity at different pH was studied using synthetic solutions at a varying pH (4–13). Unless otherwise stated, all the batch adsorption studies were carried out at constant speed of 130 rpm in a mechanical shaker. pH was adjusted using either dilute NaOH or HCl. Samples were collected at different time intervals and analyzed using SPADNS photometric method for fluoride concentration.

### 4.1.1. Equilibrium studies and adsorption isotherms

Equilibrium studies were carried out to determine equilibrium fluoride adsorption by different types adsorbents and ion exchangers. When a fixed volume of solution containing a solute is allowed to remain in contact with an adsorbent, it was observed that after a time period the adsorption capacity reaches an equilibrium value beyond which there is negligible change in the residual concentration of the solute in the solution phase. The distribution of the solute or the sorbent between the liquid phase and the solid phase is a measure of the position of equilibrium in the adsorption process and can be expressed by the Freundlich and Langmuir models. The Freundlich model indicates the surface heterogeneity of the adsorbent. It is more applicable when the adsorption is more attributable to chemisorption rather than being a physical adsorption process. The model is defined per the following general equation:

$$q_e = k_f C_e^{\frac{1}{n}} \tag{4.1}$$

Where $k_f$ and 1/n are Freundlich constants related the adsorption capacity and adsorption intensity, respectively. $q_e$ and $C_e$ are the equilibrium concentration of the adsorbate in adsorbent and aqueous phase, respectively.

Taking natural logarithm on the both sides, the above equation transforms to the following linear form,

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \tag{4.2}$$

If the experimental data shows a good correlation with the above equation, the adsorption process is said to follow the Freundlich model and can be considered to be taking place through chemisorption rather than physical sorption.

The Langmuir model, on the other hand assumes that adsorption takes place through monolayer sorption onto a surface with a finite number of identical sites. The Langmuir model is given by the following equation,

$$q_e = \frac{q_o b C_e}{1 + bC_e} \qquad (4.3)$$

Where $q_0$ is the maximum amount of the fluoride uptake per unit weight of adsorbent to form a complete monolayer on the surface bound at a very high $C_e$ and $b$ is a constant related to the affinity of the binding sites. $q_0$ represents a particle limiting adsorption capacity when the surface is fully covered with adsorbate ions and assists in the comparison of adsorption performance, particularly in case where the sorbent did not reach its full saturation in experiments. A reorganization of the terms yields the following equation,

$$\frac{1}{q_e} = \left(\frac{1}{q_0 b}\right)\left(\frac{1}{C_e}\right) + \left(\frac{1}{q_0}\right) \qquad (4.4)$$

The linear plot of $1/C_e$ versus $1/q_e$ for the experimental data indicates the applicability of Langmuir adsorption isotherm for the adsorption process. In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter was determined by using the following equation (Namasivayam, C. 1995)

$$r = \left(\frac{1}{(1 + bC_0)}\right) \qquad (4.5)$$

where $C$o is the initial concentration values of $r < 1$ represent favourable adsorption.

#### 4.1.1.1. Adsorption Isotherm for different Adsorbents

Equilibrium adsorption capacity of different adsorbents were assessed by employing batch isotherm studies by contacting the adsorbents to a solution containing fluoride at concentration 10 mg/L and with a background of 100mg/L chloride, 50 mg/L sulphate,120 mg/L bicarbonate and pH 7.2. **Figure 4.1** shows the result obtained from the equilibrium batch studies.

It was observed that activated alumina showed the maximum fluoride uptake capacity among the commonly used adsorbents. For example, at equilibrium fluoride concentration of 8 mg/L activated alumina has the highest fluoride adsorption capacity of 2.9 mg/g in comparison to 0.832mg/g of activated carbon and 2.3 mg/g for anion exchange resin IRA 67. All these adsorbents are porous in nature and can act as a good host material which can be further modified by dispersing nano-hydroxyapatite within their micropores. Activated alumina showed a good performance for fluoride uptake because of the presence of active functional groups on its surfaces. Also, activated alumina has functional groups that are amphoteric in nature. Therefore, surface charges of the activated alumina surfaces can be changed from positive to negative and vice versa by changing the solution pH, resulting in ease of synthesis of the hydroxyapatite-modified hybrid adsorbent. Therefore, activated alumina was chosen as the host material for further synthesis and adsorption studies.

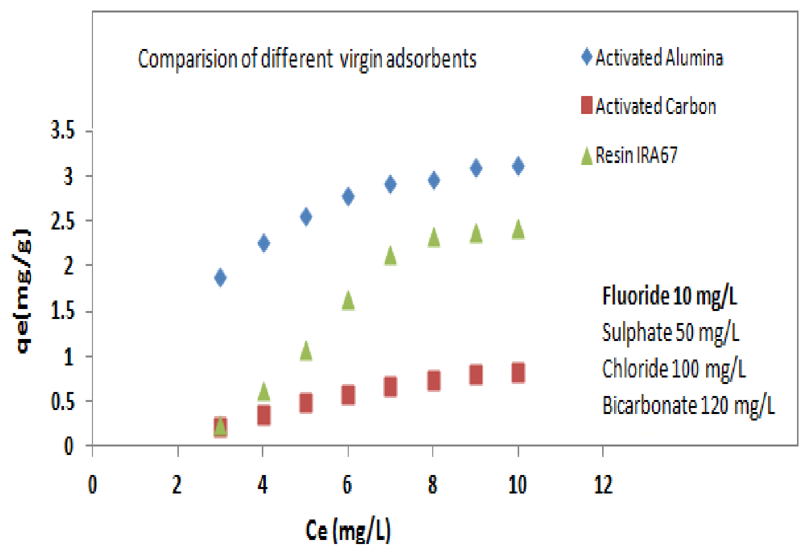


**Figure 4.1** Adsorption isotherm for fluoride uptake by different commonly used adsorbent and ion exchange resins.

#### 4.1.1.2. Adsorption Isotherm for Virgin and Modified Activated Alumina

In order to determine the equilibrium adsorption capacities of the virgin activated alumina and modified activated alumina, equilibrium isotherm studies were carried out experimentally following the protocol described earlier. Following the experiments, the experimental data were analyzed for investigation of fit to the two equilibrium adsorption models, Freundlich model and Langmuir's model. **Figures 4.2** and **Figure4.3** show the linear fit for the data obtained during equilibrium isotherm study of virgin activated alumina.

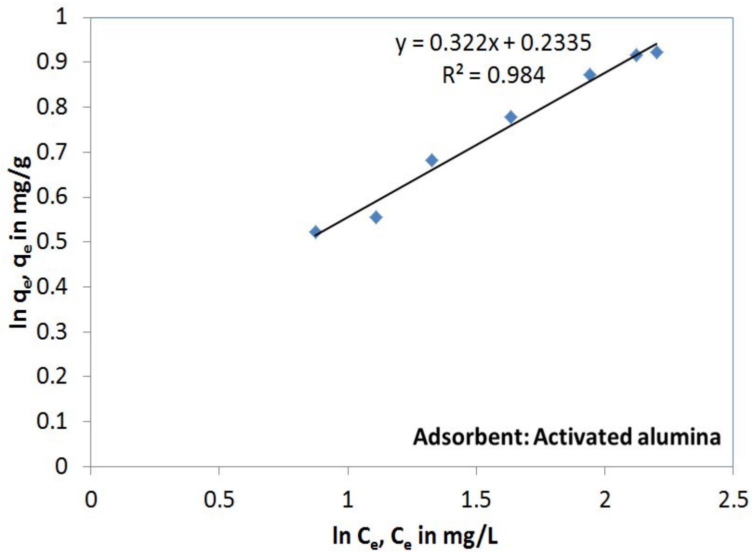


**Figure 4.2** Freundlich plot for adsorption of fluoride on virgin activated alumina.

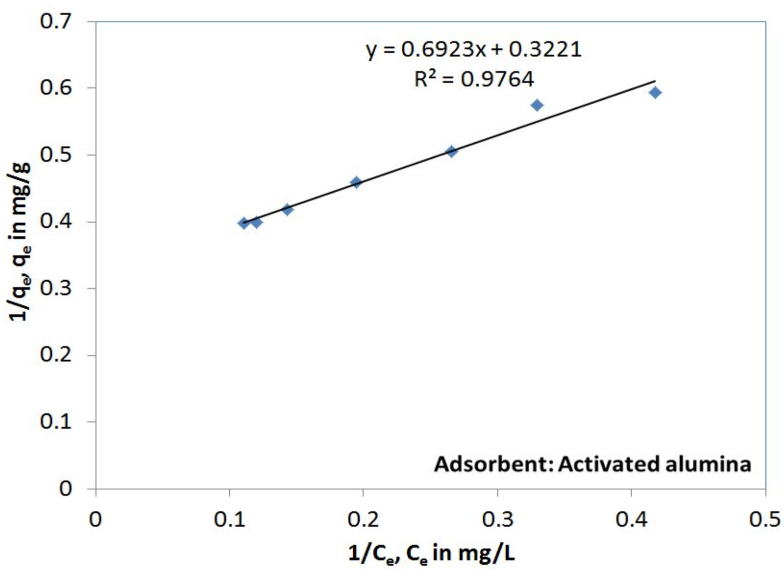


**Figure 4.3** Langmuir plot for adsorption of fluoride on virgin activated alumina.

Values of Langmuir constants $k_f$ and $n$ for virgin activated alumina are 1.263 mg/g and 3.105 respectively. Since the value of $\frac{1}{n}$ is less than unity, it indicates a favourable adsorption. Values of Langmuir constants $q_0$ and $b$ are 3.1046 mg/g and 0.465 L /mg respectively while the value of $r$ is 0.4092 which also indicates a favourable adsorption.

Langmuir model points out to a maximum achievable fluoride adsorption capacity of 3.1 mg/g by virgin activated alumina. The values of the constants are consistent to those found by other researchers (Ghorai and Pant, 2005).

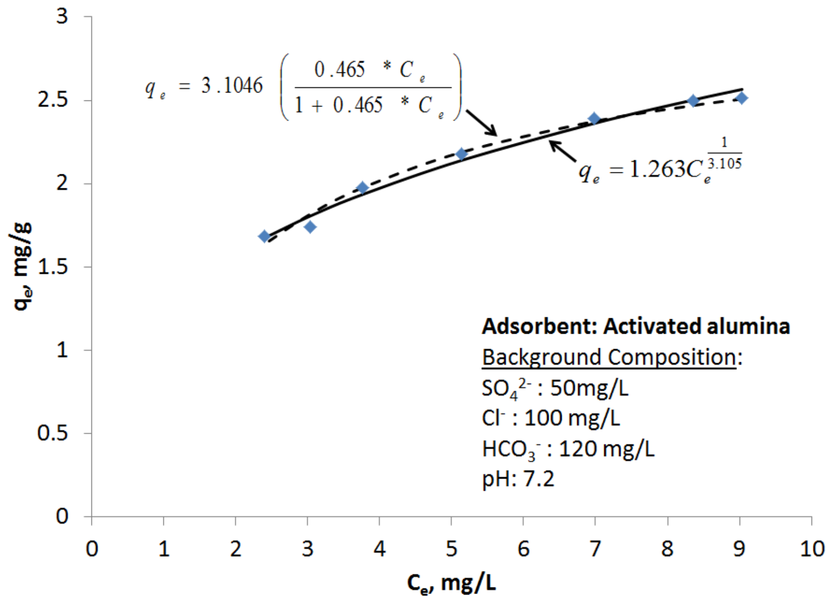


**Figure 4.4** Adsorption behaviour of fluoride onto virgin activated alumina and models describing the equilibrium adsorption capacities.

**Figure 4.4** shows the equilibrium adsorption isotherm of activated alumina along with the fitted models showing closeness of the fit. From the **Figure 4.4** it is clear that the adsorption behaviour of virgin activated alumina closely resembles both the Langmuir and Freundlich model equations, which is a confirmation of surface heterogeneity as well as validation for monolayer sorption onto surface of activated alumina. **Figures 4.5** and **Figure 4.6** are the straight line fits of Freundlich and Langmuir model, respectively for the experimentally observed data from the equilibrium adsorption isotherms for adsorption of fluoride on modified activated alumina. The values of Freundlich adsorption model constants $k_f$ and $n$ were observed to be 2.79 mg/g and 1.67, respectively. Since the value of $n$ is greater than unity the adsorption is favourable.

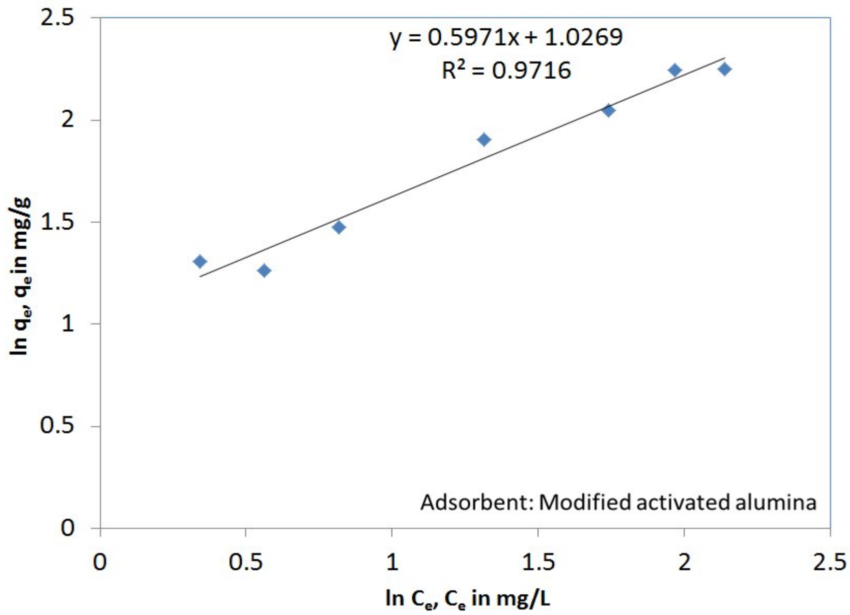


**Figure 4.5** Freundlich plot for adsorption of fluoride on modified activated alumina

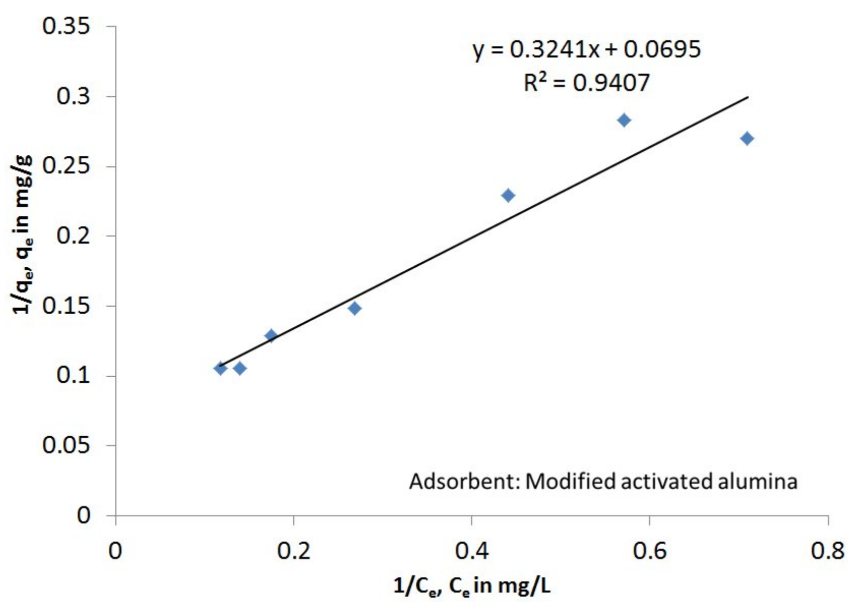


**Figure 4.6** Langmuir plot for adsorption of fluoride on modified activated alumina

A close fit with Freundlich model indicates the heterogeneity of surface. Langmuir constants $q_0$ and $b$ observed were 14.39 mg/g and 0.2144 L/mg respectively while value of $r$ was 0.2447 which indicates a favourable adsorption process. A comparison between the $q_0$ values of activated alumina and modified activated alumina indicates that the modified activated alumina has a much higher fluoride adsorption capacity compared to virgin activated alumina.

**Figure 4.7** shows the equilibrium adsorption isotherm of modified activated alumina along with the fitted models showing closeness of the fit. From the **figure 4.7** it is clear that the adsorption behaviour of modified activated alumina closely resembles both the Langmuir and Freundlich model equations, which is again a confirmation of surface heterogeneity as well as validation for monolayer sorption onto surface of activated alumina.

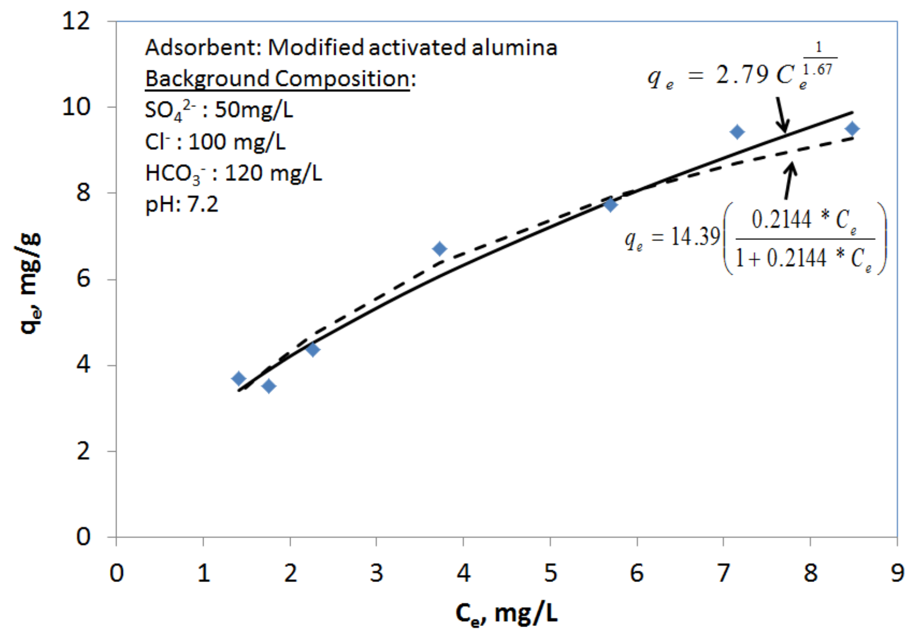


**Figure 4.7** Adsorption behaviour of fluoride onto modified activated alumina and adsorption models describing the equilibrium adsorption capacities.

Figure 4.8 shows comparative values of the equilibrium fluoride adsorption capacities of the virgin and modified activated alumina observed under identical experimental conditions. The modified activated alumina has been prepared by loading the hydroxyapatite in two consecutive cycles. The comparison indicates that the fluoride adsorption capacity in the activated alumina has received at least five-fold boost as a result of dispersal of hydroxyapatite within its pores. In absence of the proper characterization studies it is difficult to conclude about the size of the dispersed hydroxyapatite particles. However, as the hydroxyapatite synthesis took place within micropores of activated alumina, it may be concluded that the dispersed hydroxyapatite particles are nano-sized. Because of the very high surface area to volume ratio, nano-sized hydroxyapatite particles within the modified activated alumina can be considered to provide a tremendous boost to the adsorption capacity of activated alumina.

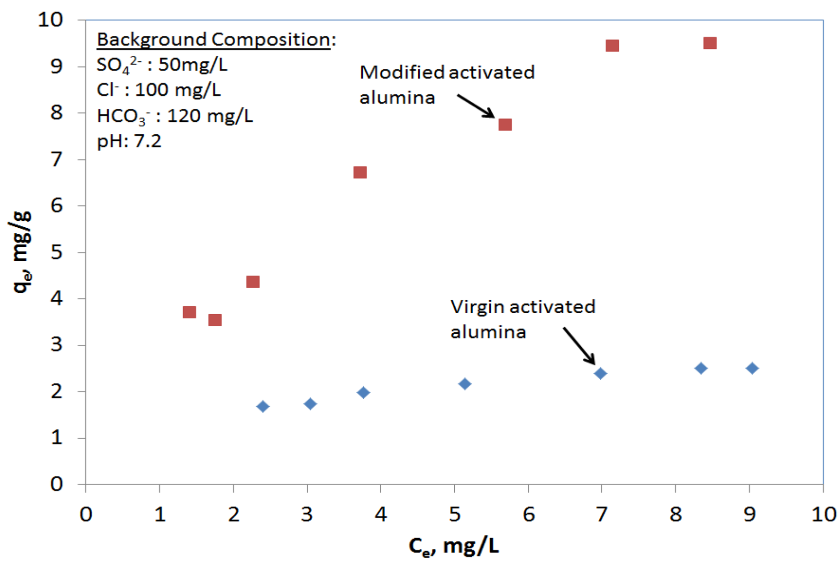


**Figure 4.8** Comparison of adsorption capacity of virgin and modified activated alumina

It was worthwhile to investigate the effect of the number of loading cycles on the adsorption capacity of modified activated alumina. Modified activated alumina prepared using different cycles of loading were subjected to equilibrium isotherm study under identical experimental conditions. From the individual adsorption isotherm curves (not shown here), equilibrium adsorption capacity of the adsorbents were determined. **Figure 4.9** shows the adsorption capacities of the adsorbents prepared at different loading cycles, at equilibrium aqueous phase fluoride concentration of 7 mg/L. After the first loading, the adsorption capacity increased from 2.8 mg/g to 5.324 mg/g and in second loading cycle the value increased significantly from5.324 mg/g to 8.893 mg/g. Further loading cycles were found to add only marginal increase in the adsorption capacity. In third cycle it increased from 8.893 mg/g to 8.954 mg/g and in fourth cycle the increment was from 8.954 mg/g to 9.032 mg/g. Based on the above results it was concluded that two cycle loading provides the optimum adsorption capacity. Further studies were performed with modified activated alumina prepared through two cycles loading of hydroxyapatite.

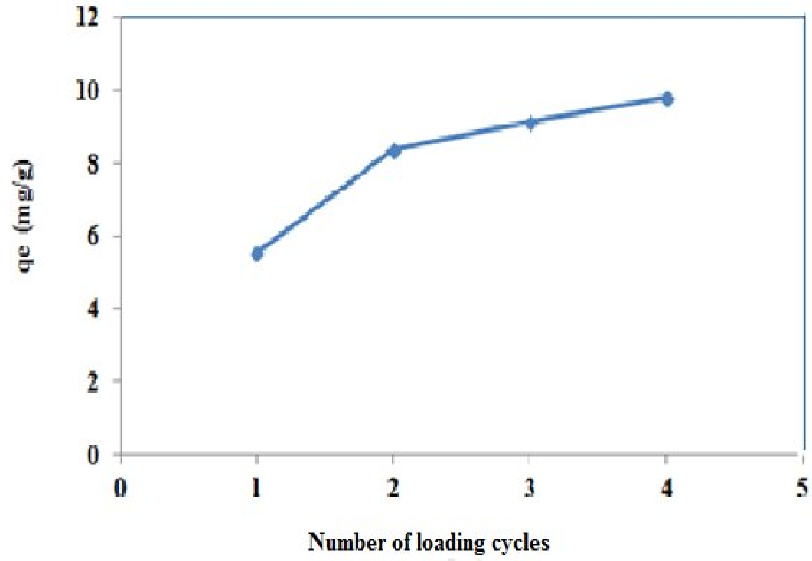


**Figure 4.9** Increase in capacity of modified adsorbent after each loading

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### 4.1.2 Effect of pH

In order to study the effect of pH on the adsorption, batch adsorption experiments were carried out with solution containing initial fluoride concentration of 9.0 mg/l with background concentration of competing anions. The solutions were adjusted to different pH in the range of 4–10. The adsorbent dose was kept as 7g/L. **Figure 4.10** shows the percentage adsorption of fluoride from the solution at different equilibrium pH of the resultant solution.

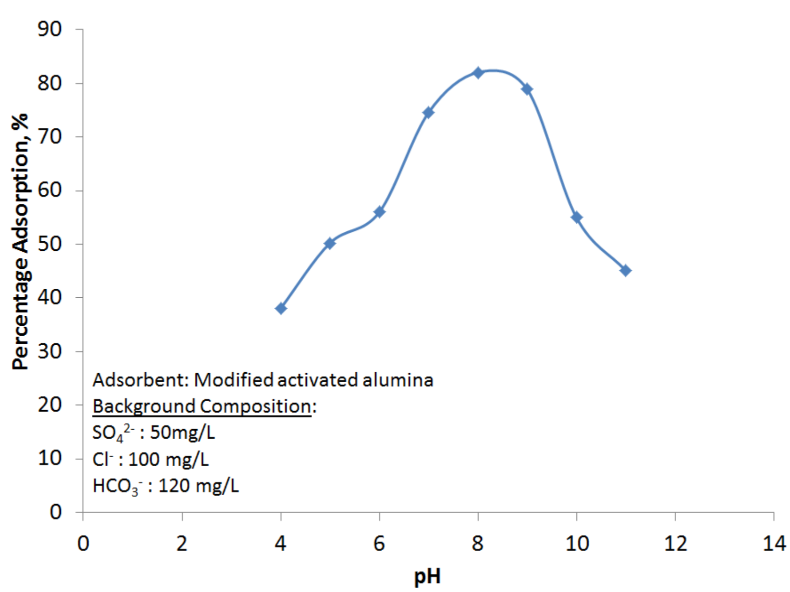


**Figure 4.10** Effect of pH on the adsorption of fluoride by modified activated alumina

The adsorption capacity was found to be the maximum at a pH of 8.5. (Ghorai and Pant 2005) indicated that activated alumina showed maximum adsorption capacity around a pH of 7. Here an apparent shift of the pH of a maximum capacity is observed to take place towards alkaline region. The dispersed hydroxyapatite phase was observed to give a boost to the adsorption capacity of the modified activated alumina. The pH shift for maximum adsorption capacity is also attributable to the hydroxyapatite phase which actually exchanges $OH^-$ ions for the take up of fluoride ions from the aqueous phase.

### 4.1.3 Effect of competing Ions

To study the effect of competing ions a synthetic sample with fluoride concentration 8-10 mg/L was taken with amount of adsorbent 7-9 g.

#### 4.1.3.1 Effect of Sulphate ions

Effect of sulfate ions on the adsorption of fluoride was observed in synthetic solutions having fluoride concentration 10 mg/L and amount of adsorbent 9 g/L but with varied initial sulfate ion concentration. **Figure 4.11** shows the percentage adsorption of fluoride at different initial sulfate ion concentrations. The adsorption capacity was found to be the highest at low sulfate concentrations indicating that there is a competition by sulfate ions for the adsorption sites.

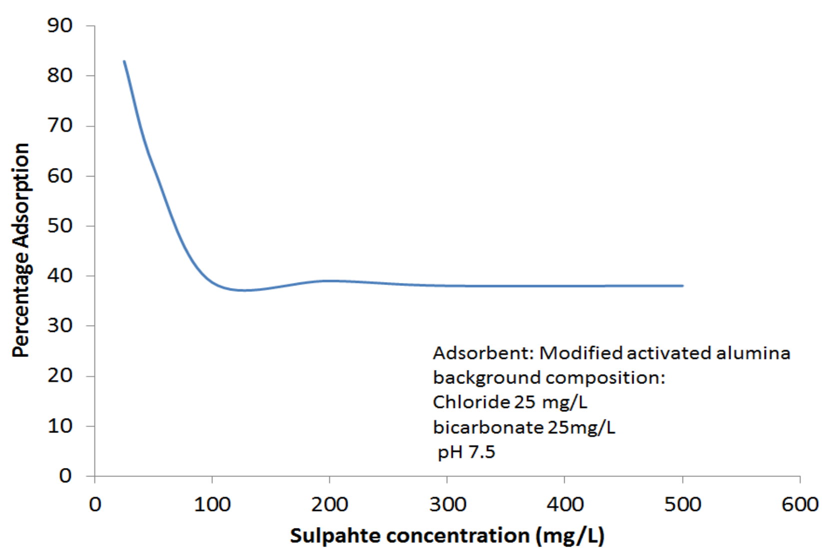


**Figure 4.11** Adsorption behaviour of fluoride on modified activated alumina at varying concentration of sulphate ions.

However, as the sulphate ion concentration increases the competition subsides and the percentage fluoride uptake remains unaffected at a sulphate ion concentration greater than 100 mg/L.

### 4.1.3.2 Effect of Chloride ions

Impact of chloride ion on fluoride adsorption was observed in synthetic sample with 10 mg/L of fluoride and 9g of modified adsorbent. It was observed that there is a variation in adsorption capacity of adsorbent at different initial chloride ion concentration. **Figure 4.12** shows the percentage adsorption of fluoride ions with variation in chloride concentration. The adsorption capacity was found to be the maximum at chloride concentration 200 mg/L

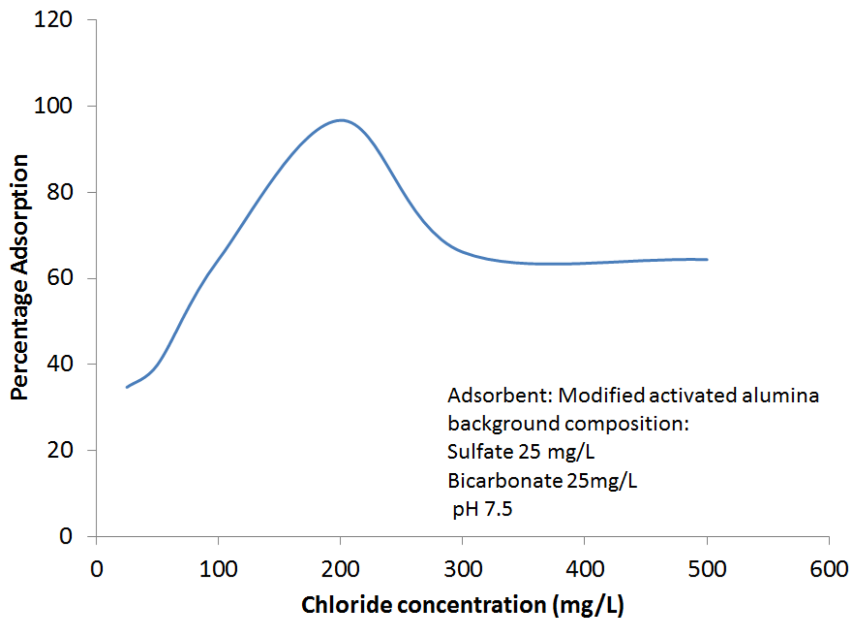


**Figure 4.12** Adsorption behaviour at varying concentration of chloride ion

### 4.1.3.3 Effect of bicarbonate ions

Impact of bicarbonate ion on adsorption on fluoride was observed using a synthetic sample of 10 mg/L of fluoride with 7 mg of modified adsorbent .Variation in adsorption capacity with different initial concentration of bicarbonate ions was observed. **Figure 4.13** shows the effect on percentage of adsorption of fluoride ion with variation in bicarbonate concentration. There is no change in adsorption capacity with variation in bicarbonate concentration.

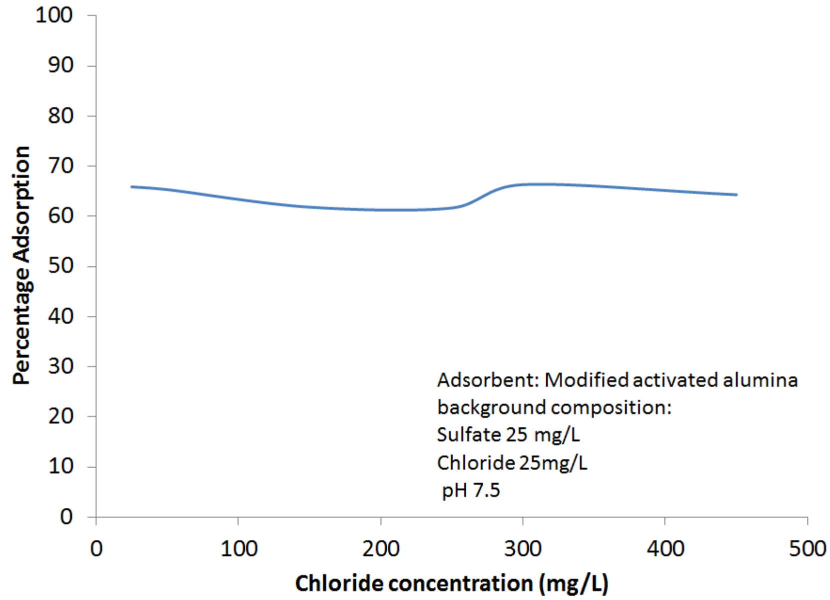


**Figure 4.13** Adsorption behaviour at varying concentration of bicarbonate ions

**4.2 Column Studies**

The adsorption isotherms do not give accurate scale-up data in fixed bed systems therefore the practical applicability of activated alumina was ascertained in the column operations. A column (ACE Glass, USA) of length 550 mm and internal diameter 11 mm was used to which the flow was controlled from a feed reservoir of 20 L capacity at the top using a flow controller. The effluent was collected at the bottom through an orifice. The column experiments were aimed at studying the effect of process parameter, initial fluoride concentration. Samples of the outlet bulk solution were collected at definite intervals of time and examined for fluoride concentration.

**Breakthrough analysis**

The general position of the breakthrough curve along the volume axis depends on the capacity of the column with respect to the feed concentration, flow rate and bed height. In a fixed bed adsorption column, the adsorbent located closest to the feed water gets saturated first and reaches in equilibrium with the inlet concentration of fluoride. The subsequent thin layer of adsorbents receives gradually lower concentration of fluoride and comes in equilibrium with the solution. Thus there exists a zone within the adsorbent bed with varying amount of adsorbate sorbed onto it. This is a called a mass transfer zone and as the column run progresses the mass-transfer zone moves to the exit of the column at a slower speed than the liquid phase. When the adsorption zone has moved completely through the column, the concentration of the adsorbate at the exit becomes equal to the feed concentration. A plot of exit concentration as a function of volume throughput reacted is known as breakthrough curve. The characteristic shape of the breakthrough curve depends on the inlet flow rates, concentration and other properties such as column diameter and bed height. The area under the breakthrough curve gives the total quantity of fluoride that came out of the bed for a given feed concentration. The area contained by the breakthrough curve and the influent fluoride concentration provides the amount of fluoride adsorbed in the bed.

### 4.2.1 Column Study at Influent Fluoride Concentration of 2.8 mg/L

First column run was performed at influent fluoride concentration of 2.8 mg/L. **Figure 4.13** shows the fluoride concentration profile in the effluent from the column. The breakthrough of fluoride was observed to occur around 285 bed volumes. The breakthrough of 1.5 mg/L fluoride, the permissible limit in India, was observed to occur at 450 bed volumes. The column was allowed to run until exhaustion when the influent and effluent fluoride concentrations became equal. At exhaustion, thus the whole column is supposed to come under equilibrium with the influent fluoride concentration. The area ABCDEA bound by the breakthrough curve in **Figure 4.14** represents the amount of fluoride adsorbed by the adsorbent in the column when it reached equilibrium with influent fluoride solution.

Area of ABCDEA was calculated and amount of fluoride absorbed by bed is found to be

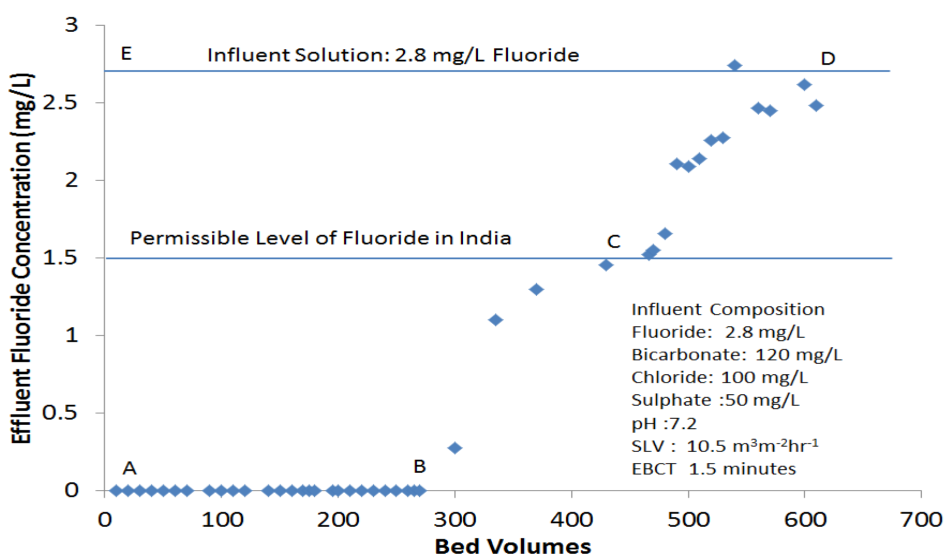


**Figure 4.14** Fluoride concentration profiles during a column run with modified activated alumina as adsorbent at influent fluoride concentration of 2.8 mg/L.

approximately equal to 32.87 mg. Value of $q_e$ at concentration 2.8 mg/L from column run therefore was approximately 1.5 mg/g from while from the isotherm model it was found to be 5.05 mg/g.

### 4.2.2 Column study at influent fluoride concentration of 5 mg/L

In this run the initial concentration of fluoride was 5 mg/L along with a background concentration of commonly occurring anions. **Figure 4.15** shows the breakthrough profile of fluoride from the column. Breakthrough from the column took place at 350 bed volumes. Breakthrough of 1.5 mg/L fluoride was observed to take place at around 415 bed volumes. The complete exhaustion of the bed was found to occur at 600 bed volumes. A calculation of area enclosed by the breakthrough curve indicated that the amount of fluoride adsorbed by the bed was approximately 60 mg. The volume of the bed was 25 mL. The fluoride uptake by the adsorbent in the column was found to be equal to 2.4 mg/g whereas the equilibrium capacity of the adsorbent from the adsorption model was found to be equal to 7.05 mg/g.

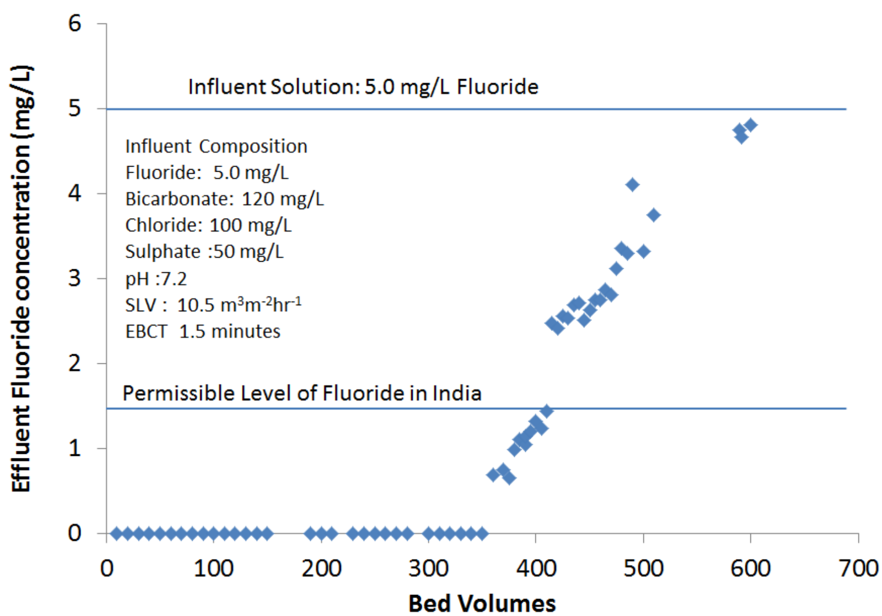


**Figure 4.15** Fluoride concentration profiles during a column run with modified activated alumina as adsorbent at influent fluoride concentration of 2.8 mg/L

### 4.2.3 Column study at influent fluoride concentration of 7 mg/L

Adsorption column containing 25 mL of modified activated alumina was run with an influent solution containing 7.0 mg/L of fluoride with background of other commonly occurring anions. **Figure 4.16** shows the breakthrough profile of fluoride from the column. The breakthrough was observed to occur at 265 bed volumes. Breakthrough of 1.5 mg/L fluoride occurred at 360 bed volumes. The column was exhausted at 680 bed volumes. At exhaustion fluoride uptake by the bed was determined to be 78.33 mg. This means that the equilibrium adsorption capacity during column run was 3.13 mg/g whereas, the value of $q_e$ from column the adsorption model was found to be 8.63 mg/g.

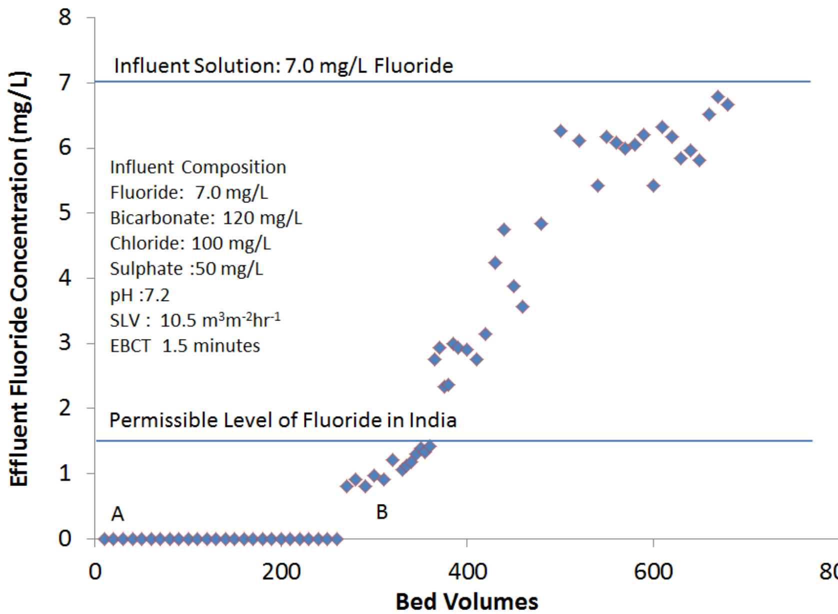


**Figure 4.16** Fluoride breakthrough profile of modified activated alumina column run with influent solution with 7 mg/L fluoride.

### 4.3 Regeneration studies

Exhausted modified activated alumina bed in the column was regenerated in situ using 1 N NaOH. Being a relatively inexpensive chemical the cost of regeneration with NaOH would be much cheaper than that using other regenerants. After the regeneration the bed was rinsed with one bed volume of distilled water followed by passage of 0.5N HCl until the effluent pH reaches a value of 7.0. The acid wash was necessary to protonate the bed before proceeding with another adsorption run. After regeneration, a quantification of the amount of fluoride eluted out of the bed gives us an idea about the efficiency of regeneration. The amount desorbed by the regenerant can be determined from the area under the effluent history of fluoride during the regeneration.

**4.3.1 First Regeneration:** The column run was performed at concentration of fluoride 5 mg/L up to exhaustion at effluent concentration 4.8 mg/L. The exhausted column was then made to undergo desorption process so that the exhausted material can be regenerated and can further be used for next adsorption cycle ($2^{nd}$ cycle).The column was subjected to regeneration using IN NaOH following the protocol discussed in Subsection **3.2.13** in chapter material and methods. The amount of fluoride adsorbed by the bed can be calculated by finding out the area under the regeneration curve ABCDEF in **Figure 4.17** . The bed capacity in first regenerationwas found to be 30.9375 mg.

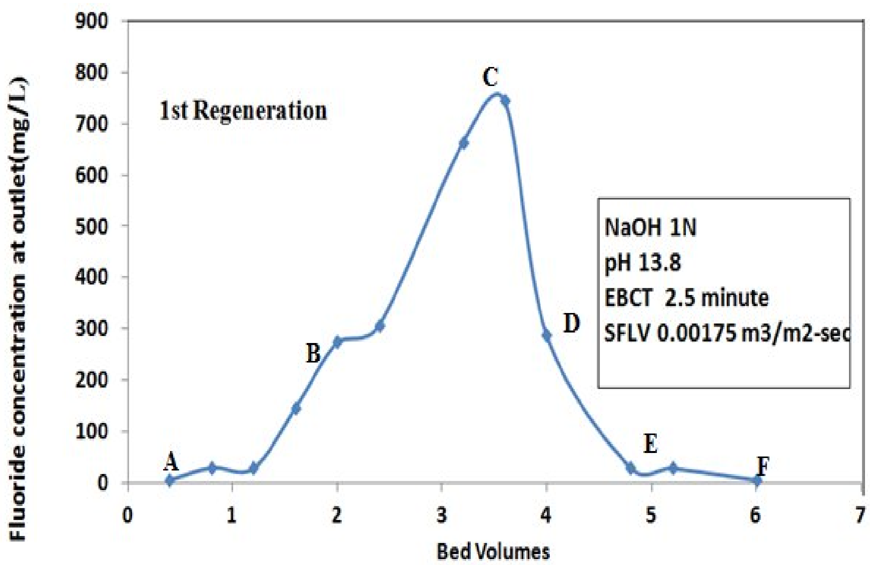


**Figure 4.17** $1^{st}$ Regeneration curve

**4.3.2 Second adsorption cycle after $1^{st}$ regeneration:** The first regenerated column was then subjected to next adsorption column run at influent fluoride concentration 5 mg/L after conditioning using 0.5 N HCl. **Figure 4.18** shows the breakthrough profile of fluoride column. The breakthrough was observed to occur at 190 bed volumes. The column was made to run till breakthrough of 1.5 mg/L fluoride and it occurred at 305 bed volumes. The amount of fluoride adsorbed by the column was found to be 11.25 mg.

**4.3.3 Second Regeneration**: Column exhausted after second adsorption cycle was subjected to next regeneration after exhaustion similarly as done in previous cycles. The effluent profile of second regeneration is shown in **Figure 4.19**. The amount of fluoride that came out of the column was found to be 23.96 mg which is less than the amount came out from first regeneration cycle which indicates that the effeciency of second regeneration is decreased.

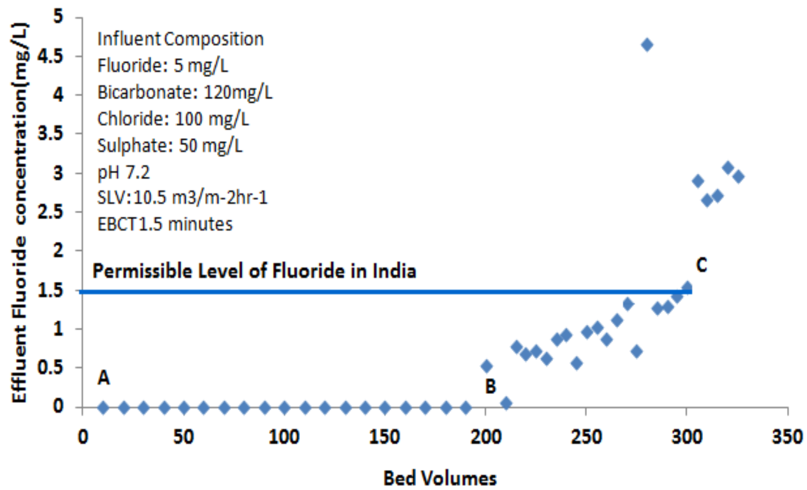


**Figure 4.18** Column behaviour of modified adsorbent after 1st regeneration

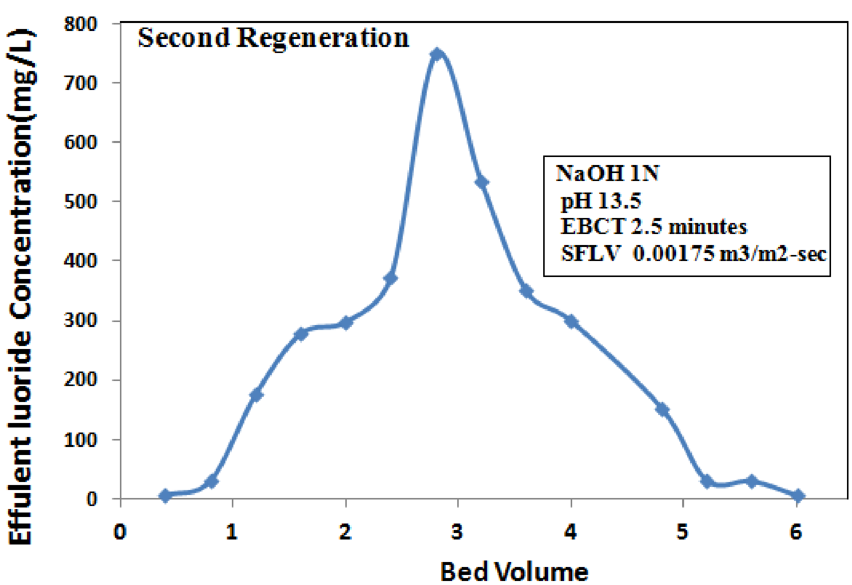


**Figure 4.19** 2nd Regeneration curve

**4.3.4 Third adsorption cycle after 2nd regeneration:** For the third adsorption cycle the column was subjected to run at influent concentration 5 mg/L. The effluent profile of the column shows breakthrough occurred at 170 bed volume. The column was continued to run till breakthrough of 1.5 mg/L which occurred at 265 bed volume. This indicates that the bed capacity decreasing as we proceed for more regenerations cycles in next than that of the previous one (1st cycle). It may be due to reduction in the adsorption capacity. **Figure 4.20** shows the amount of fluoride adsorbed till breakthrough in the second run after regeneration was 10.125 mg.

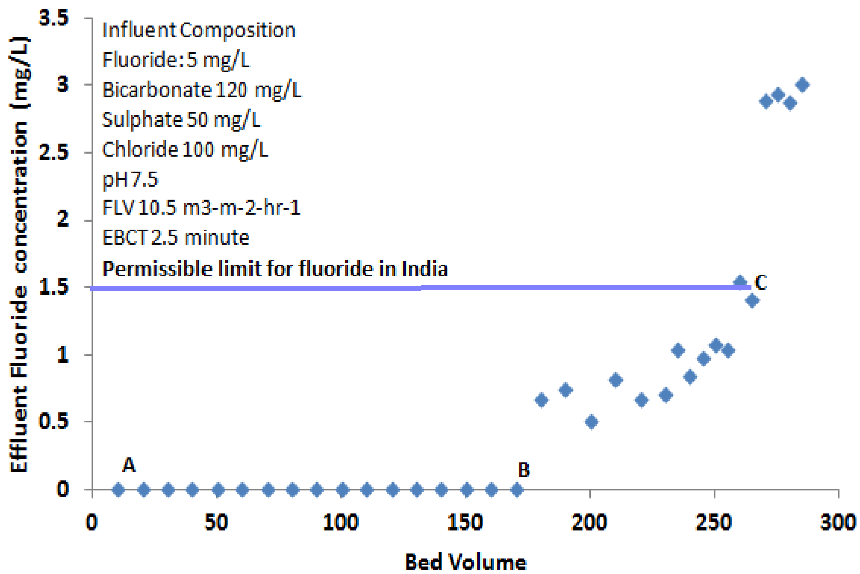


**Figure 4.20** Column behaviour of modified adsorbent after 2nd regeneration

**4.3.5 Third Regeneration**: In third regeneration the column exhausted upto breakthrough (1.5 mg/L) was subjected to regeneration and from **Figure 4.21** the concentration profile of effluent fluoride gives the information about the desorbed by the column. This time for regeneration few more bed volume of regenerants (1.5 bed volumes) were used until the effluent concentration came around 0.1 mg/L. The amount of fluoride came out from this column was found to be 37.53 mg, because of almost complete regeneration.

**4.3.6 Fourth adsorption cycle after 3rd regeneration:** After 3rd regeneration the adsorption capacity of the bed was increased. **Figure 4.22** shows the concentration profile of fluoride at outlet. Breakthrough occurs at 230 bed volume which shows increase in bed capacity. The breakthrough of 1.5 which is Indian permissible limit occurred at 230 bed volume. The amount desorbed by the column was found to be 11.8 mg.

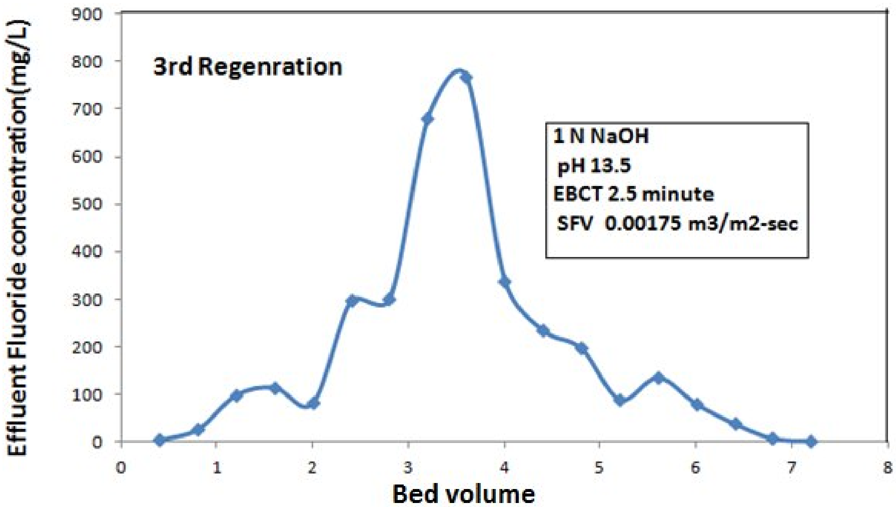


**Figure 4.21** 3rd Regeneration curve

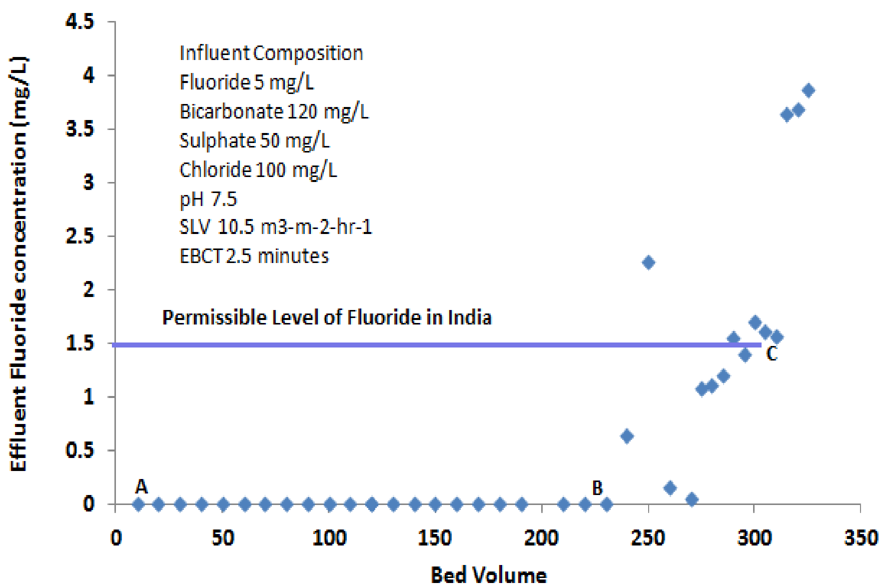


**Figure 4.22** Column behaviour of modified adsorbent after 3rd regeneration

**4.3.7 Comparison of Regeneration Cycles:** It was observed that even after three regenerations the capacity of bed was not decreased too much which indicates the capacity of adsorbent did not vary too much after each regeneration. **Figure 4.20** shows the difference in capacity of column with each regeneration.

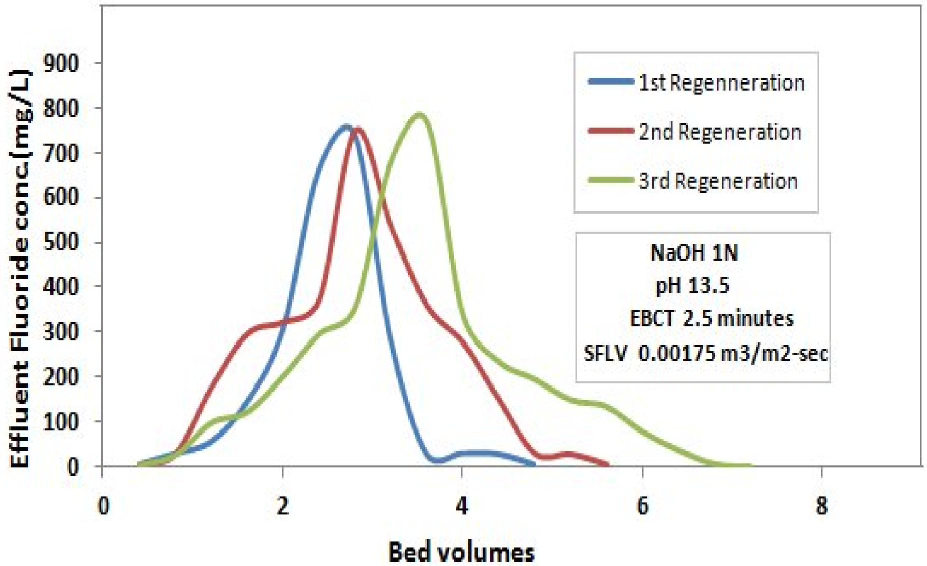


**Figure 4.23** Comparison of different regeneration cycle

### 4.4 Adsorption Kinetics

An adsorption study should include both equilibrium as well as kinetic aspects of adsorption so that a complete behaviour of the adsorbents can be fully assessed before designing a practical process applicable in the field. The kinetic study of the adsorption process indicates the rate of adsorption of the target species by the adsorbent over a wide range of time period. Once the solute uptake rate is determined for a particular adsorption process, the engineered adsorption facilities such as the fixed-bed column type systems, batch or semi-batch type systems can be adequately and optimally designed.

The kinetic studies were carried out in batch reactors which contained finite volume of fluoride contaminated solution having a background of commonly-occurring anions. A small amount of adsorbent was added in the batch reactors and the fluoride concentration in the solution phase was measured at regular time intervals. From the mass balance, the fluoride concentration in the solid phase was determined. Kinetic studies were carried out at three different initial fluoride concentrations. **Figure 4.24** shows the solid (adsorbent) phase fluoride concentrations or the extent of fluoride uptake over time. It has been observed that the fluoride uptake reaches equilibrium after 6 hours.

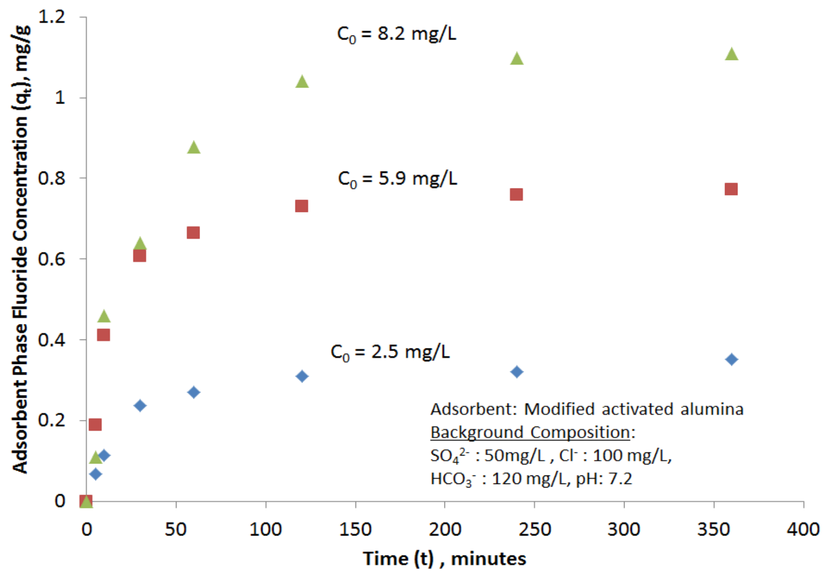


**Figure 4.24** Adsorbent-phase fluoride concentrations during at different times during kinetic tests run at three different initial aqueous phase fluoride concentration.

An analysis of the adsorption kinetics data not only helps to determine the optimum time of contact for the adsorption devices, it also helps to have an insight into the fundamental process how adsorption is taking place. In order to have the insight, it is always preferable to analyze the data with the help of well-known adsorption models.

The adsorption models can be classified into two major groups, namely, adsorption reaction models and adsorption diffusion models. The adsorption diffusion models consider that the whole adsorption procedure consists of three distinct steps:

1) Diffusion of the solute across a thin liquid film surrounding the adsorbents, which is known as film diffusion or external diffusion;

2) Adsorption and desorption between the adsorbate and the active sites on the adsorbent, which is also known as mass action;

3) Adsorbent-phase (or solid-phase) diffusion of the solute or intraparticle diffusion.

Slowest of the above three steps is known to control the whole kinetics of adsorption process. Usually the mass action step is so fast compared to the other two steps, it is considered to be the quickest among the three steps. Therefore, either intraparticle diffusion or film diffusion is the slowest among the steps for adsorption. Depending upon which is the slowest step in the whole adsorption process, the adsorption process is known to be film-diffusion controlled or intraparticle diffusion controlled. The adsorption reaction models, however, originate from chemical reaction kinetics and therefore, does not take a fragmented view of the adsorption process. Rather, they consider the process as a whole reaction similar to chemical reactions and try to explain the kinetics based on that.

Two types of adsorption reaction models are known to be applicable for explaining the adsorption reactions, namely, pseudo first-order and pseudo second-order rate reaction models.

The pseudo first-order models, as the name suggests, considers that the rate of adsorption at any instant of time is proportional to the available number of adsorption sites. The mathematical description of the model is indicated below:

$$\frac{dq_t}{dt} \propto (q_e - q_t) \tag{4.6}$$

Where, $q_e$ and $q_t$ are the solid (adsorbent) phase concentration of the solute at equilibrium and at any time t (minutes) during the adsorption, respectively.

The above equation can be written as,

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \tag{4.7}$$

Where, $k_1$ is the pseudo-first order reaction rate constant ($min^{-1}$).

Thus,

$$\int_{q=0}^{q=q_t} \frac{dq_t}{(q_e - q_t)} = k_1 \int_{t=0}^{t=t} dt \tag{4.8}$$

This yields,

$$\ln \frac{q_e}{(q_e - q_t)} = k_1 t \tag{4.9}$$

The above equation can be re-arranged as,

$$\ln \frac{q_e}{(q_e - q_t)} = k_1 t \tag{4.10}$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (4.11)$$

Therefore, a plot of experimental data as $\ln(q_e - q_t)$ versus time t (minutes) shall yield a straight line and the slope of the line should be negative of the pseudo first order reaction rate. The correlation coefficient of the straight line fit shall indicate whether or not the adsorption follows the first order kinetics.

Similarly for a pseudo second order reaction model, the rate of adsorption at any time t shall be proportional to the square of the available sites. Therefore,

$$\frac{dq_t}{dt} \propto (q_e - q_t)^2 \qquad (4.12)$$

This means that,

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \qquad (4.13)$$

Where $k_2$ is the pseudo second order rate constant of adsorption.

Integration and rearrangement of the above equation yields the following:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \qquad (4.14)$$

Which can be rearranged as follows:

$$\frac{t}{q_t} = \frac{1}{V_0} + \frac{t}{q_e} \qquad (4.15)$$

Where, $V_0 = k_2 q_e^2$, $V_0$ is the initial adsorption rate and the constants can be found out by plotting $t/q_t$ versus t.

A plot of $(q_e - q_t)^{-1}$ versus t shall yield a straight line for the adsorption reactions that follow the second order model. The value of the pseudo second order rate constant can be found out from the slope of the straight line.

**Figure 4.25** shows the pseudo first order straight line fit of the kinetics data obtained in the initial period of 30 minutes of the experiment. The equilibrium adsorption capacity for each time instant were obtained using the Freundlich's model and its parameters that showed the.

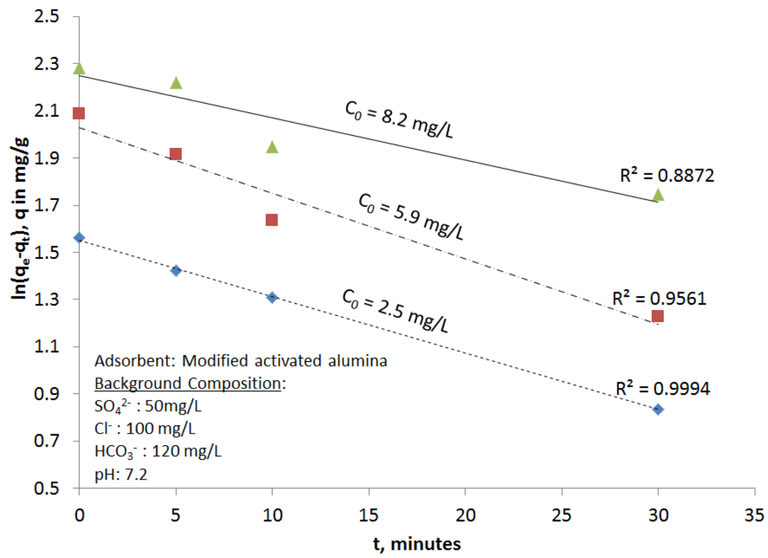


**Figure 4.25** Pseudo first order straight line fit of the data obtained from initial 30 minutes of the batch kinetic test for fluoride adsorption by modified activated alumina

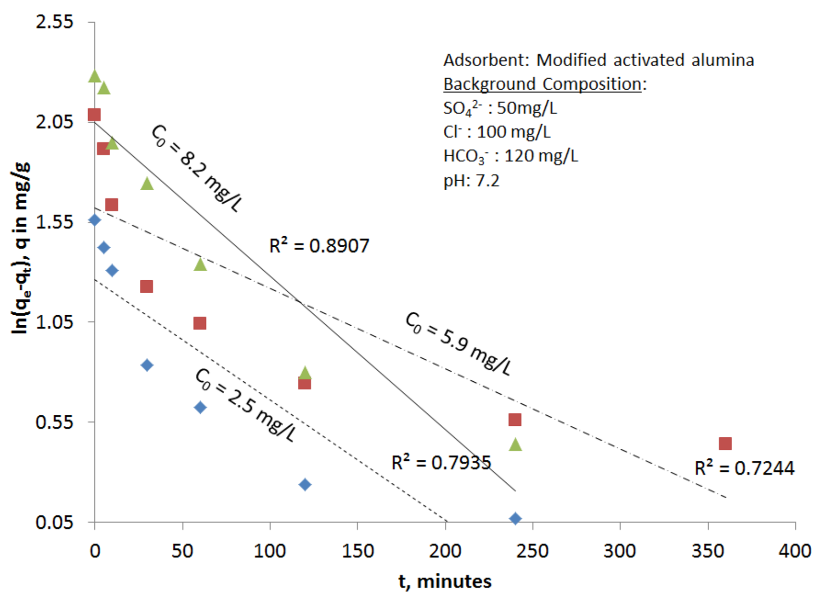


**Figure 4.26** Pseudo first order straight line fit of the data obtained during the batch kinetic test for fluoride adsorption by modified activated alumina.

best fit during the equilibrium isotherm studies. **Figure 4.26** shows the pseudo first order straight line fit for the entire period of six hours during the experiment. It may be observed that there was a good correlation between the data and the model during the initial period of the adsorption. As the time progressed, the adsorption deviated from the pseudo first order kinetics so that the overall data from the six hours experiment did not correlate with the first order rate model. This implies that the adsorption is driven by at least two mechanisms. The adsorption in the initial periods was by and large a monolayer sorption onto a surface with finite number of identical adsorption sites. However, later as the solute started diffusing inside the internal pores of the adsorbent, the process was not controlled by the monolayer sorption process. The whole process was then controlled by a slower adsorption process that occurred inside the sorption sites residing on the surface monolayer.

Figure 4 shows a pseudo-second order fit for the adsorption kinetics data obtained from the experiments. The data was plotted as $t/q_t$ versus t and there was excellent correlation between the data and the pseudo-second order adsorption models. The pseudo-reaction rate constants ($k_2$) were calculated from the curve and they were found to be 0.128 $g.mg^{-1}$min-1, 0.106 $g.mg^{-1}min^{-1}$ and 0.03 $g.mg^{-1}min^{-1}$ for the initial concentrations of 2.5 mg/L, 5.8 mg/L and 8.2 mg/L, respectively. The values of equilibrium adsorption capacity obtained from the experiments differed significantly with those that were found from the Freundlich's model obtained from equilibrium experiments.

In an extensive study involving activated alumina for the fluoride removal from synthetic solutions done earlier (Ghorai and Pant, 2005), the kinetics of adsorption was found to follow a pseudo-first order adsorption reaction. In the present study, the pseudo-first order fit was found to remain valid for initial period of adsorption but the kinetics deviated significantly from the model when entire period of adsorption was considered. Rather, a nearly-perfect second order fit with the experimental data points out to the complex nature of this adsorption reaction where the rate-limiting step may be chemical sorption or chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate or may be the intraparticle diffusion or the liquid film diffusion. In the first step, the sorbate molecules are adsorbed on the free surface and also, the sorbate–sorbate interaction is absent, leading to the formation of a monolayer. As this monolayer approaches saturation over time, a process of rearrangement such as intraparticle diffusion may start causing some adsorption sites fall vacant, which can accommodate further sorbate molecules causing an increase in the sorption capacity. This constitutes the second step. It is presumed that such complex nature of adsorption stems out from the fact that there were two types of adsorption sites, namely activated alumina as well as nanoparticles of hydroxyapatite. **Figure 4.27** is a reconstruction

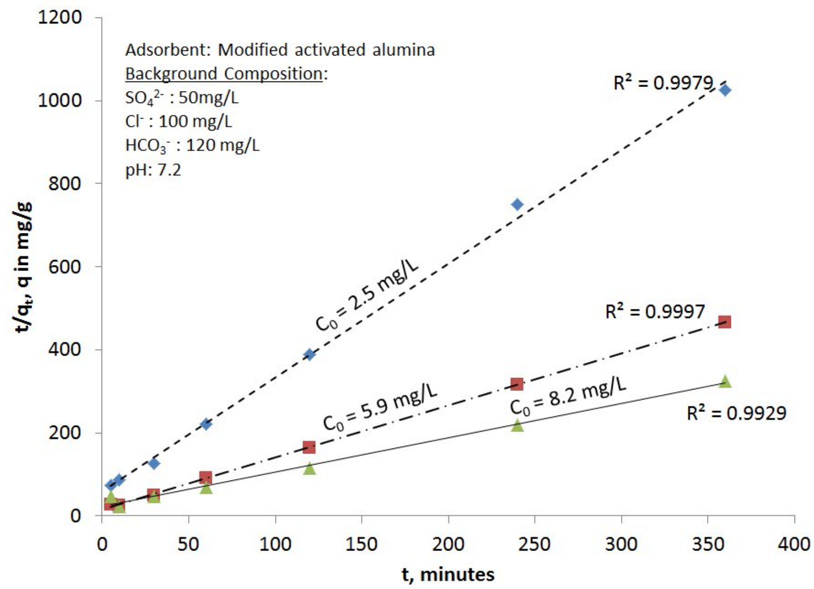


**Figure 4.27** Pseudo second order straight line fit of the data obtained from the batch kinetic test for fluoride adsorption by modified activated alumina.

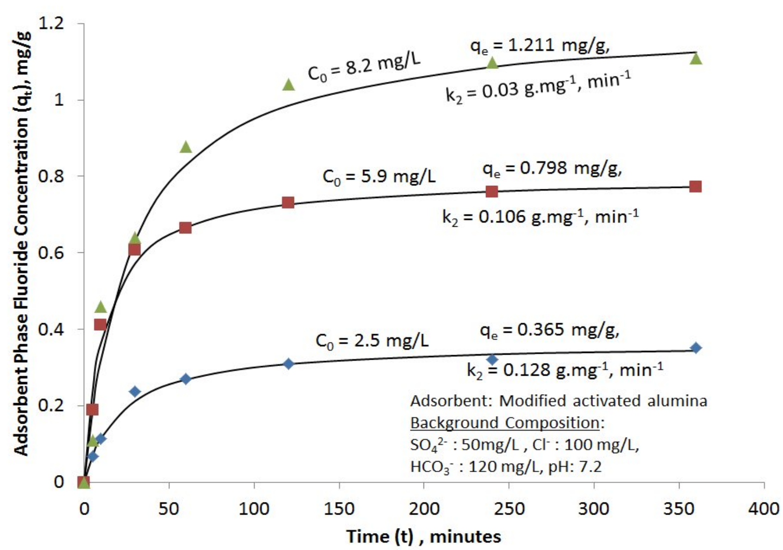


**Figure 4.28** Adsorbent-phase fluoride concentration with the best-fitting models and its parameters at different time instants during kinetic test.

of the kinetic data obtained from the experiment with a curve showing the pseudo-second order models and the rate constants and equilibrium capacities indicated on the curve. The pseudo second order adsorption reaction model as established above pointed out to a complex nature of the adsorption process for the adsorption of fluoride on to the modified activated alumina. It also hints towards a possibility that the overall adsorption rate may either be controlled by an intraparticle or liquid film diffusion controlled step. With respected to adsorption on to an adsorbent, the different process steps controlling the overall adsorption reaction are depicted in **Figure 4.28**

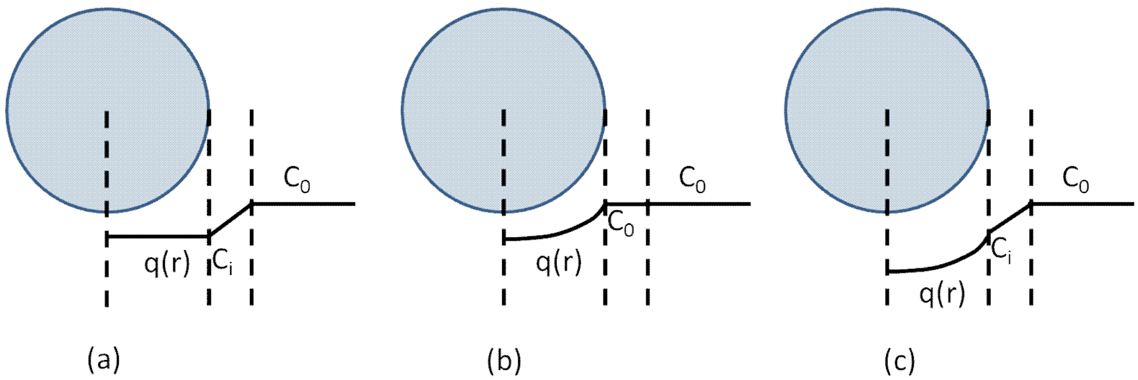


**Figure 4.29** (a) A film diffusion controlled adsorption process, (b) An intraparticle diffusion controlled process and (c) a process controlled by both intraparticle and film diffusion steps.

In a film diffusion controlled process, solute takes a long time to diffuse through the thin liquid film surrounding the particle. As soon as the solute reaches the surface of the adsorbent, the adsorption reaction being a very fast process, the solute immediately gets adsorbed to the surface. If the intraparticle diffusion process is also fast, then the solute reaches to the internal pores of the adsorbent almost instantaneously. So, at any instant before the equilibrium is reached, there shall remain a concentration gradient across the liquid thin film surrounding the adsorbent particle. But, there remains no solid-phase concentration gradient inside the adsorbent.

In order to determine which of the diffusion steps, intraparticle or liquid film diffusion step controls the process, a simple confirmatory test was performed following the technique proposed by Helfferich. This test is known as an "interruption test". In this test, modified activated alumina column run was intentionally paused for an interval of 12 hours about mid-way of the run. After such a pause, the column run was resumed with the flow rate same as before. **Figure 4.30** shows fluoride breakthrough pattern from the outlet of a column containing modified activated alumina when a solution containing 5 mg/L fluoride with other competing anions were passed through it. As the fluoride gradually started exiting from the column, the influent flow was deliberately discontinued for 12 hours. This interruption during the column run is marked with a circle. **Figure 2.31** shows the blown up detail of the portion of the fluoride breakthrough history for the region of interruption marked with a circle in **Figure 4.30**. It may be observed from **Figure 4.31** that when the flow was resumed, the effluent fluoride concentration dropped significantly compared to that before the pause in the column run. Following the passage of a few more bed volumes of the influent after the restart, fluoride concentration at the exit of the column reached to the level same as prior to interruption.

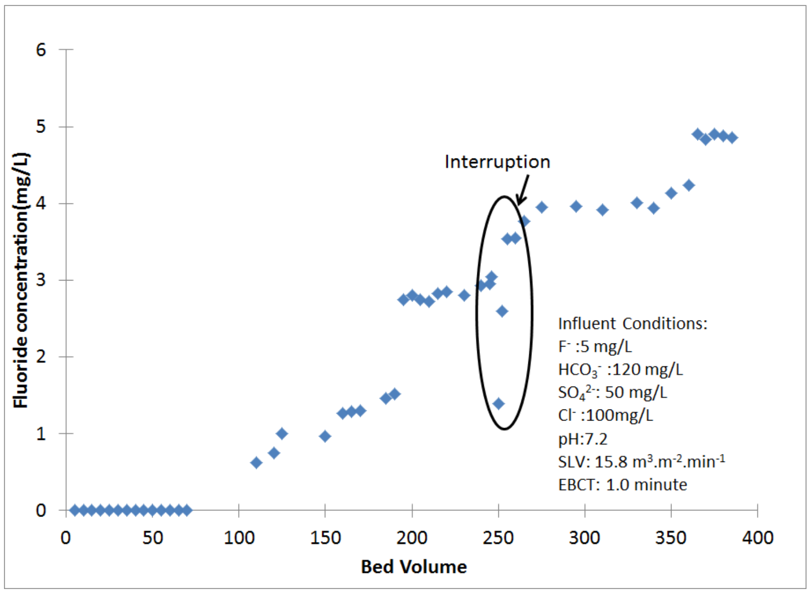


**Figure 4.30** Fluoride breakthrough history with interruption during a column run.

Such a situation arises when intraparticle diffusion is the slowest step in the adsorption process and it thus controls the kinetics of the adsorption process as a whole. For intraparticle diffusion controlled sorption process, the concentration gradient within the adsorbent particle serves as the driving force and governs the overall rate. The concentration gradients existing in the adsorbent phase before, during and after the interruption are indicated in **Figure 4.31**. When the column run is in progress, this concentration gradient continuously attenuates. The interruption allows the adsorbed fluoride to get evenly spread out within the adsorbent bead. As a result, the concentration gradient immediately at restart is greater than that prior to the

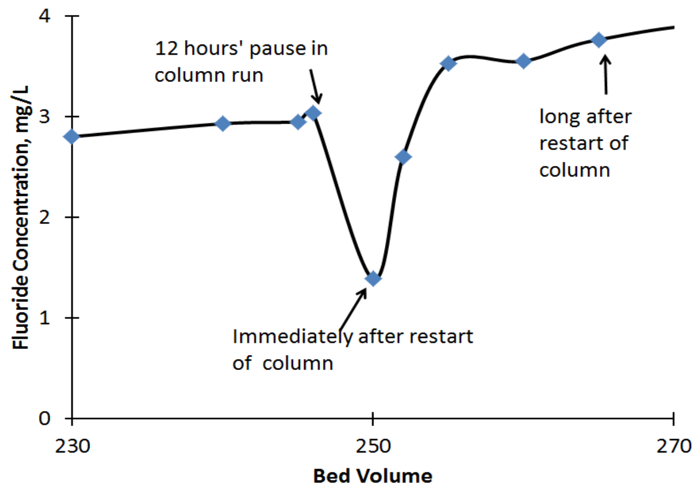


**Figure 4.31** Effect of interruption on the fluoride breakthrough history of a column containing modified activated alumina.

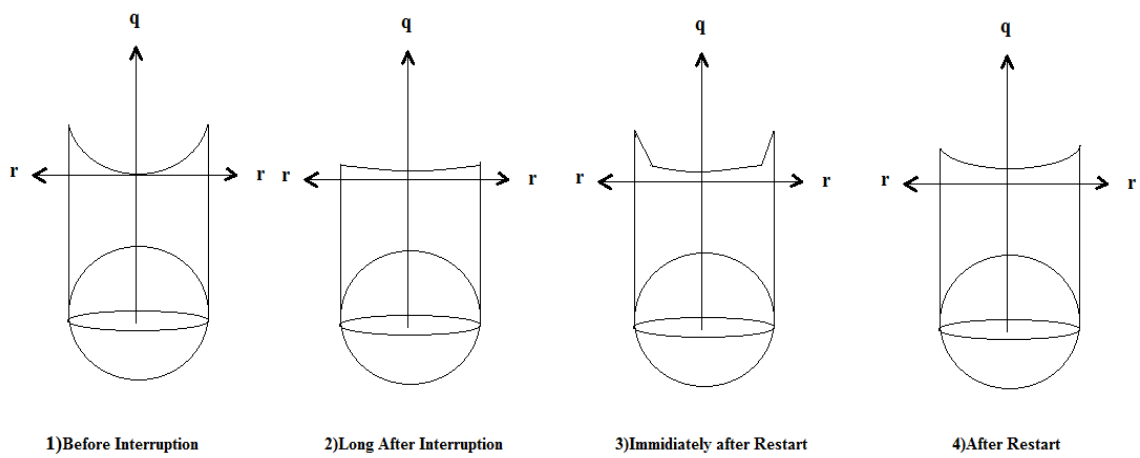


**Figure 4.32** Schematic view of the internal concentration gradient within an adsorbent before, during and after the interruption in column run.

interruption. As the driving force for adsorption is the concentration gradient within the bead, therefore the fluoride uptake rate immediately after the column restart is greater than the uptake rate prior to the interruption. A faster uptake shall cause a drop in the aqueous phase fluoride concentration at the exit of the column immediately after restart. If the process is kinetically controlled by slower film diffusion process, according to **Figure 4.29** there is no concentration gradient within the particle. If there is no concentration gradient within the particle then there should not be any effect of interruption on the effluent fluoride concentration immediately after restart. This confirms that the adsorption of fluoride on modified activated alumina is intraparticle diffusion controlled process. The steeper concentration gradient established after the restart quickly attenuates as the column run progresses. Fluoride concentration at the column effluent thus comes back to the level prior to the interruption. However, because of the even spread of the adsorbate within the adsorbent bead during the interruption, the concentration gradient within the particle becomes gradual long after restart than that prior to the interruption. Therefore, the slope of the breakthrough curve after the interruption test becomes steeper than prior to the interruption. **Figures 4.30** and **4.31** show confirmation of such phenomenon. Thus, it is proven that the adsorption process of fluoride on to modified activated alumina is controlled by intraparticle diffusion.

# CONCLUSION

In this study, we were able to synthesize a high capacity, cost-effective, mechanically and chemically stable, regenerable and reusable hybrid adsorbent for selective removal of fluoride from contaminated water. The hybrid adsorbent was synthesized by precipitation of nanoparticles of hydroxyapatite within activated alumina granules using inexpensive and commonly available chemicals. Activated alumina itself is a good adsorbent for fluoride removal but its modification by nanoparticles of hydroxyapatite gave it a tremendous boost in its adsorption capacity. The hybrid adsorbent was found to be superior in terms of high capacity, selectivity and robustness, better mechanical and chemical stability, regenerability, and better hydraulic properties and cost-effectiveness.

The further studies on the defluoridation performance of the adsorbent revealed that the performance is influenced by a small extent by the presence of commonly occurring competing anions present in the groundwater. The adsorption capacity was found to be also dependent on pH of the solution, pH around 8 to 8.5 being suitable for the best performance. The adsorption process was found to follow a second order kinetics and the regression analysis of the equilibrium data fitted well with both the Langmuir and Freundlich isotherms, indicating the presence of both monolayer sorption as well heterogeneous surface sorption processes. The kinetic study data revealed that fluoride removal on hybrid adsorbent is a complex process and was controlled by both the surface adsorption as well as intra-particle diffusion process, the latter was found to contribute to be the rate determining step. Column studies involving modified activated alumina revealed that it treated much more volume of contaminated water compared to activated alumina before reaching a breakthrough concentration of 1.5 mg/L of fluoride. Under identical influent conditions of 5mg/L of fluoride, modified activated alumina treated 410 bed volumes of contaminated water before there is a breakthrough of 1.5 mg/L whereas virgin activated alumina column run lasted for only 125-150 bed volumes. Regeneration with 1N NaOH was found to be effective. Multiple consecutive adsorption and desorption cycles proved that there was no loss of fluoride removal capacity over multiple number of cycles of operation. A suitable pilot scale model for the removal of fluoride from ground water may well be developed from the results obtained during the present study.

Following points from our studies are worth highlighting:

1. Modified activated alumina showed promising results for selective removal of fluoride from the contaminated water.
2. During column runs, the hybrid adsorbent performed much better than the popular and commonly used adsorbent activated alumina.
3. The hybrid adsorbent is regenerable and efficient regeneration is possible using inexpensive regenerant such as 1N NaOH solution.
4. There was no change in the adsorption capacity even after three cycles of operation, each involving one adsorption run followed by a regeneration run.

The characterization studies could not be largely performed because the relevant instruments were either not available or not accessible within the time period of the study. If more time was available, adsorption desorption cycles in the column could be continued for up to atleast 10 cycles, which would prove the applicability of the material in real life situation.

Future studies definitely should include a detailed characterization of the hybrid adsorbent as was envisaged in the objectives of the current study. It is suggested that few more column experiments under varying experimental parameters like different flow rates, inlet fluoride concentrations, bed heights, etc. should be carried out to achieve a better understanding on the adsorption process, its dynamics and the process parameters. Following such bench scale runs with synthetic contaminated water, column runs should be carried out with contaminated groundwater to check its performance under real life conditions. Further model and prototype studies may be performed at the field-level. This hybrid adsorbent showed a great promise for future commercial applications.

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