FLUORIDE REMOVAL USING ALUMINA NANOPARTICLES

By

ECROLIEN LIBERTY LOPOG

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ABSTRACT

The presence of fluoride in drinking water, in quantities in excess of permissible limits is a serious matter of concern from a public health point of view. High concentration of fluoride can lead to fluorosis. Various adsorbents for removing fluoride from drinking water have been studied in the past. In this research, alumina nanoparticles was proposed for the removal of fluoride from drinking water. Batch experiments were conducted to determine the efficacy of alumina nanoparticles in fluoride removal from water. The fluoride removal performance was investigated as a function of pH, contact time, initial fluoride concentration and adsorbent dosage. The dependence of the adsorption of fluoride on the pH of the solution has been studied to achieve the optimum pH value. It was found that the maximum adsorption takes place at pH 2.5. Contact time analysis revealed that the percent fluoride removal increases initially as contact time increases, but then it gradually approaches a more or less constant value, indicating that the equilibrium has been attained. The experiments showed that 120 minutes was the suitable contact time. In kinetic study, the Second Order Integral model was found to express the sorption kinetics of fluoride better. Study on the influence of adsorbent dosage showed that the efficiency of the fluoride removal increases with the increase of adsorbent dosage. The removal efficiency for 2, 4, 6, 8, and 10 g/l of alumina nanoparticles is 15, 24.80, 33.87, 41.33, and 48.53 % respectively. Adsorption isotherms have been modeled by Langmuir and Freundlich equations and isotherm constants for both isotherms were calculated. In isotherms studies, both models were found to be suitable to describe the adsorption of fluoride onto the alumina nanoparticles. The capacity of alumina nanoparticles is 4.4033 mg/g which can be obtained from the Langmuir isotherm.

ABSTRAK

Kewujudan fluorida dalam kuantiti yang melebihi had dibenarkan adalah perkara yang perlu diambil perhatian serius. Kandungan fluorida yang tinggi akan mengganggu kesihatan dan menyebabkan penyakit *fluorosis*. Beberapa bahan penjerap yang digunakan untuk menyingkirkan fluorida dari air telah dikaji. *Alumina nanoparticles* digunakan dalam kajian ini untuk menyingkirkan fluorida. Ujikaji secara kelompok dijalankan untuk mengkaji keberkesanan *alumina nanoparticles* dalam penyingkiran fluorida dari air. Kajian terhadap pengaruh pH, masa tindakbalas, kepekatan awal fluorida dan dos bahan penjerap ke atas penyingkiran fluorida dilakukan. Pergantungan penjerapan fluorida terhadap nilai pH larutan dikaji untuk mendapatkan nilai pH yang optimum. Kadar penjerapan yang maksimum diperolehi apabila nilai pH adalah 2.5. Analisa ke atas masa tindakbalas menunjukkan peratusan penyingkiran fluorida pada mulanya meningkat dan beransur-ansur menjadi malar dengan peningkatan masa. Ini menunjukkan bahawa proses penjerapan telah mencapai keseimbangan. 120 minit adalah masa tindakbalas yang sesuai. Dalam kajian kinetik, model Tertib Kamiran Kedua adalah lebih sesuai digunakan untuk menyatakan kinetik penjerapan fluorida. Kajian terhadap dos bahan penjerap menunjukkan kecekapan penyingkiran fluorida meningkat dengan penambahan dos bahan penjerap. Kecekapan *alumina nanoparticles* pada dos 2, 4, 6, 8, dan 10g/l adalah 15, 24.80, 33.87, 41.33, dan 48.53% masing-masing. Isoterma penjerapan dimodelkan dengan menggunakan persamaan Langmuir dan Freundlich dan nilai pemalar untuk kedua-dua isoterma dikira. Kedua-dua model tersebut sesuai digunakan untuk menghuraikan penjerapan fluorida ke atas a*lumina nanoparticles*. Kapasiti alumina nanoparticles adalah 4.4033 mg/g.

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1   RESEARCH BACKGROUND

Water is one of the major compounds essential for the sustenance of all forms of life
and is available in abundance in nature covering approximately three fourths of the
surface of the earth. The chemical nature of water is one of the most important criteria
that determines its usefulness for a specific need and as such not all waters are fit for
drinking.

The ever growing population, urbanization, industrialization and unskilled utilization
of water resources have led to the degradation of water quality and the reduction in its
per capita availability in various developing countries. Due to various ecological
factors either natural or anthropogenic, groundwater is getting polluted because of
deep percolation from intensively cultivated fields, disposal of hazardous wastes,
liquid and solid wastes from industries, sewage disposal, surface impoundments etc.
During its complex flow history, groundwater passes through various geological
formations leading to consequent contamination of shallow aquifers.

Presence of various hazardous contaminants like fluoride, arsenic, nitrate, sulfate,
pesticides, heavy metals etc. in groundwater has been reported. The presence of
fluoride, in quantities in excess of permissible limits is a serious matter of concern
from a public health point of view. High concentration of fluoride (F^-) can lead to
fluorosis. Fluorosis is caused by an excess ingestion of fluoride. Severe forms of the

disease typically develop only when the F^- concentration in drinking water is greater than 5–10 mg/l. Children metabolize a higher percentage of F^- than adults and are, therefore, particularly vulnerable to fluorosis. Like many other pollutants, fluoride pollution can also occur due to both natural and man made reasons (Meenakshi and Maheshwari, 2005).

The amount of fluoride in groundwater is in excess in many regions. It has been found that the fluoride concentrations in many places in Africa, America, Europe and Asia do not comply with the national requirements. Studies have been conducted on the physiological effects of fluoride on human health since the early part of the 20th century. Several reports and studies established both the risks of high fluoride dosing and the benefits of minimal exposure (Ghorai and Pant, 2004).

In many cases, water sources have been rendered unsafe not only for human consumption but also for other activities such as irrigation and industrial uses. Therefore, there is a need to focus greater attention on the future impact of water resources planning and development taking into consideration all the related issues.

1.2   RESEARCH OBJECTIVES

Mainly, this research is conducted to study the removal of fluoride from aqueous solution using alumina nanoparticles as an adsorbent. Other objectives of this study are:

1. To study the effects of various parameters such as pH, agitation time, initial fluoride concentration and adsorbent dosage on fluoride adsorption onto alumina nanoparticles.

2. To determine the conditions for maximum fluoride removal using alumina nanoparticles.

3. To investigate the effectiveness of alumina nanoparticles in the removal of excess fluoride from water.

1.3   SCOPE OF STUDY

The scope of study for this project is to analyse the adsorption of fluoride onto the alumina. The proposed project will indicate whether alumina nanoparticles can be used as an adsorbent in the removal of fluoride from water. Batch will be conducted in the environmental laboratory to study the effect of several factors affecting the adsorption process. The results will be analyse and the efficiency of alumina nanoparticles to remove fluoride from aqueous solution can be determined.

1.4   THESIS OUTLINE

The first chapter generally describes the background of the research and its objectives. The problem statement has been mention in the research background in this chapter.

Chapter 2 presents the literature review for this study. This chapter discusses about the sources of fluoride and its effect on human health. The methods of how to prevent fluoride poisoning and the fluoride removal technologies that have been used are discussed in this chapter.

Chapter 3 explains the materials that were used, the methodology and procedure, and the apparatus specifications.

The results of the experiments are presented and discussed in Chapter 4. Important aspects discussed in this chapter are the adsorption capacity of alumina nanoparticles, the adsorption kinetics and the factors affecting the adsorption.

Finally, the conclusions of the research and some recommendations for future studies are presented in chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1   INTRODUCTION

Leaching of fluoride from the earth crust is the main source of fluoride in groundwater. Water with high fluoride content is generally soft, has high pH and contains large amount of silica. In groundwater, the natural concentration of fluoride depends on the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of the soil and rocks, temperature, the action of other chemicals and depth of wells. Due to the large number of variables involved, the fluoride concentration in groundwater varies from below 1.0 mg/liter to more than 35.0 mg/liter.

Other sources like food items also increase the overall ingestion of fluoride into the human body. Fluoride is purposely added to water supply, toothpaste and sometimes other products to promote dental health because it is believed that fluoride in small doses has no adverse effect on health to offset its proven benefits in preventing dental decay. High dose of fluoride can cause permanent dental and skeletal fluorosis.

2.2   SAFE LIMIT

According to the 1984 guidelines published by the World Health Organization (WHO), fluoride is an effective agent for preventing dental caries if taken in optimal amounts. Water is a major source of fluoride intake. The 1984 WHO guidelines

suggested that in areas with a warm climate, the optimal fluoride concentration in drinking water should remain below 1 mg/liter (1 ppm), while in cooler climates it could go up to 1.2 mg/litre. The guideline value (permissible upper limit) for fluoride in drinking water was set at 1.5 mg/l, considered a threshold where the benefit of resistance to tooth decay did not yet shade into a significant risk of dental fluorisis. (Climatic conditions, volume of water consumed, and intake from other sources should be considered when setting national standards). The WHO guideline for Chemicals of health significance in drinking water (Inorganic Constituents) is enclosed in Appendix 1.

As the amount of water consumed and consequently the amount of fluoride ingested is influenced by air temperature, US Public Health Service (USPHS) (1962) has set a range of concentrations for maximum allowable fluoride in drinking water for communities based on the climatic conditions as shown in Table 2.1 (Meenakshi and Maheshwari, 2005).

Table 2.1: USPHS recommendations for maximum allowable fluoride in drinking water

Annual average of maximum daily air temperature (°C)	Recommended fluoride concentration (mg/L)			Maximum allowable fluoride concentration (mg/L)
	Lower	Optimum	Upper	
10 – 12	0.9	1.2	1.7	2.4
12.1 – 14.6	0.8	1.1	1.5	2.2
14.7 – 17.7	0.8	1.0	1.3	2.0
17.8 – 21.4	0.7	0.9	1.2	1.8
21.5 – 26.2	0.7	0.8	1.0	1.6
26.3 – 32.5	0.6	0.7	0.8	1.4

2.3 FLUORIDE SOURCES

2.3.1 Fluoride In The Environment

Fluorine is one of the 92 naturally occurring elements. It is a member of the halogen family, which also includes chlorine, bromine, iodine and astatine. It is a pale yellow gas which is extremely reactive. As a result it is never found free in nature but only in combined form with other elements. These compounds are called fluorides. Fluorine readily forms compounds with all elements except helium and neon. Fluoride exists fairly abundantly in the earth's crust and can enter groundwater by natural processes; the soil at the foot of mountains is particularly likely to be high in fluoride from the weathering and leaching of bedrock with high fluoride content. Fluoride can be found in minerals such as shown in Table 2.2 (Rao, 2003). Besides water, fluoride can be found in the air. Natural fluoride concentration in air is 0.5 ng/m^3. If anthropogenic emissions are included, worldwide background concentration is 3 ng/m^3.

Table 2.2: Fluoride Bearing Minerals (Rao, 2003)

MINERAL	CHEMICAL FORMULA	% FLUORIDE
Sellaite	MgF_2	61
Villianmite	NaF	55
Fluorite (Fluospar)	CaF_2	49
Cryolite	Na_3AlF_6	45
Bastnaesite	$(Ce,La)(CO_3)F$	9
Fluorapatite	$Ca_3(PO_4)_3F$	3 – 4

2.3.2 Fluoride In Food

Almost every food contains at least some fluoride. Plants take it up from the soil and from the air. From soil, fluoride is transmitted through fine hair rootlets into stems, and some reaches the leaves. Fluoride can be found in our daily food especially when we cook our meal with fluoridated water. Unlike chlorine, fluoride does not enter the steam when water is boiled. Thus during cooking the fluoride increases in concentration. Fluoride can also be found in infant formulas, and processed food and beverages. The fluoride content of some major food products is given in Appendix 2.

2.3.3 Fluoride-Containing Products

Fluoridated drinking water is an effective, safe and inexpensive way to prevent tooth decay. Fluoride works by stopping or even reversing the tooth decay process. It keeps the tooth enamel strong and solid by preventing the loss of important minerals from it. The success of fluoride in controlling dental caries has led to the production of fluoride-containing products. Examples of fluoride-containing products are toothpastes, mouth rinses and professionally applied gels or varnishes.

2.4   EFFECTS ON HEALTH

Community water fluoridation is an effective, safe, and inexpensive way to prevent tooth decay. Children and adults who are at low risk of dental decay can stay cavity-free through frequent exposure to small amounts of fluoride. This is best gained by drinking fluoridated water and using fluoride toothpaste twice daily. But excessive

fluoride intake carries serious toxic effects. Consumption on a long term basis, of water containing fluoride in concentrations of 2 mg/l and 5 mg/l can cause dental and skeletal fluorosis respectively.

"Fluorosis is a disease caused by ingestion of fluoride in excess through water, food, and air and is a serious health problem. Fluoride ingested with water goes on accumulating in bones up to the age of 55 years. At high doses fluoride can interfere with carbohydrates, lipid protein, vitamin, enzyme and mineral metabolism." (Rao, 2003)

When consumed in excess, fluoride can cause several ailments besides skeletal and dental fluorosis such as:

- Neurological Manifestations

- Muscular Manifestations

- Allergic Manifestations

- Gastro intestinal problems

- Head-ache

- Loss of teeth at an early age

The relationship between concentration of fluoride and its biological effects are summarized in Table 2.3.

Table 2.3: Concentrations of fluorides and its biological effects (Rao, 2003)

CONCENTRATION OF FLUORIDE, ppm*	MEDIUM	EFFECT
0.002	Air	Injury in vegetation
1	Water	Dental caries reduction
2 or more	Water	Mottled enamel
8	Water	10% osteosclerosis
50	Food and water	Thyroid changes
100	Food and water	Growth retardation
120	Food and water	Kidney changes
*In dilute aqueous solutions, ppm is equivalent to mg/L		

2.5   PREVENTING FLUORIDE POISONING

The chronic toxic effects of excessive intake of fluoride on human health have been studied intensively and fluoride in the range 0.5 – 1.5 mg/l is generally considered to be beneficial to human being (Ghorai and Pant, 2003). Many scientists have studied on how to reduce excess fluoride in drinking water and different techniques have been adopted.

Fluoride poisoning can be prevented or minimized by using alternative water sources, by removing excessive fluoride from drinking water, and by improving the nutritional status of populations at risk.

2.5.1 Alternative Water Sources (Qian et al., 1999)

Surface water. Fluoride concentrations in surface water are usually low – 0.01 ppm to 3 ppm. Since it is often heavily contaminated with biological and chemical pollutants, particular caution is required when opting for surface water. Surface water should not be used for drinking without treatment and disinfection.

Rainwater. Rainwater is usually a much cleaner water source and may provide a low-cost simple solution. Large storage reservoirs are needed because annual rainfall is extremely uneven in tropical and subtropical regions.

Low-fluoride groundwater. Fluoride content can vary greatly in wells in the same area, depending on the geological structure of aquifer and the depth from which water is drawn. The problem with high fluoride concentrations in groundwater can be solved by deepening tube wells or sinking new wells at another site.

2.5.2 Better Nutrition

An adequate calcium intake is directly associated with a reduced risk of dental fluorosis and vitamin C also safeguards against the risk. Improving the nutritional status of an affected population should be an effective supplement to the technical solutions of the problem (Meenakshi and Maheshwari, 2005).

2.5.3   Current Treatment Methods

The amount of fluoride in groundwater is in excess in many regions. Removal of fluoride from water is needed to make it safe to use as drinking water. Many methods have been developed to remove fluoride such as adsorption, ion exchange, electrodialysis, and precipitation. The materials studied in each are tabulated as shown in (Materials and Methods for Defluoridation) Appendix 3.

2.5.3.1 Precipitation

Fluoride removal by precipitation involves addition of chemicals (coagulants and coagulant aids) and formation of fluoride precipitates or simultaneous co-precipitation of fluoride with a resulting precipitate (Ghorai and Pant, 2005). Fluoride removal is accomplished with solids separation from liquid. Lime, alum, alum and lime, poly aluminium chloride, poly aluminium hydroxyl sulphate and polyelectrolyte are the chemicals involved in the precipitation process.

Stainless Steel Candle Filter (Nalgonda Technique) uses the precipitation process to remove fluoride (Mariappan and Vasudevan, 2004). The Nalgonda technique involves addition of aluminium salt, lime and bleaching powder followed by rapid mixing, flocculation, sedimentation, filtration and disinfection. The lime dose required to be added is empirically 1/20th that of the dose of alum. Lime facilitates the formation of denser flocs and thus rapid settling. This method has been adopted in several areas of India and requires careful control of pH, failing which the coagulation process will not be complete resulting in high residual Al levels in the product water. The

quantities of alum and lime depend upon the quantity, alkalinity, pH and fluoride content of water. The amount of alum needed increases with alkalinity and initial fluoride concentration.

The Nalgonda technique has been claimed as the most effective technique for fluoride removal. However, the process removes only a smaller portion of fluoride (18 – 33%) in the form of precipitates and converts a greater portion of ionic fluoride (67 – 82%) into soluble aluminium fluoride complex ion, and therefore this technology is erroneous. The soluble aluminium fluoride complex is toxic, this make the Nalgonda technique for defluoridation not desirable. Regular analysis of feed and treated water is required to calculate the correct dose of chemicals to be added, because water matrix keeps on changing with time and season (Meenakshi and Maheshwari, 2006).

2.5.3.2 Adsorption

Adsorption processes involve the passage of the water through a bed where fluoride is removed by ion exchange or surface chemical reaction with the solid bed matrix (Ghorai and Pant, 2005). Among all the methods that have been used, adsorption is a widely used method for defluoridation. Many different fluoride adsorbents have been investigated and have shown that large surface area and physicochemical interaction between adsorbate and adsorbent were important factors affecting fluoride adsorption from water.

Adsorption can be conducted in either batch or column study. In the batch process, the adsorbent and the fluoride solution are mixed together and are agitated until the

desired level of removal is achieved. The column or continuous-flow adsorption system is operated in columns using up-flow or down-flow techniques. In the adsorption process, the transfer of adsorbate from solution to adsorbent continues until the concentration of the adsorbate remaining in the solution is in equilibrium with the concentration of the adsorbate adsorbed by the adsorbent. An adsorption isotherm can be used to determine the adsorption capacity of an adsorbent. Fluoride removal by adsorption has been described in more detail in Section 2.7 as it is directly related to the present research.

Adsorption can remove fluoride up to 90% and the treatment is cost effective but the process is highly dependent on pH and works best only in a narrow pH range (5-6) (Meenakshi and Maheshwari, 2006).

2.5.3.3 Reverse Osmosis (RO)

RO is a physical process in which contaminants are removed by applying pressure on the feed water to direct it through a semi permeable membrane. The process is the "reverse" of natural osmosis (water diffusion from dilute to concentrate through a semi permeable membrane to equalize ion concentration) as a result of the applied pressure to the concentrated side of the membrane, which overcomes the natural osmotic pressure. RO membranes reject ions based on size and electrical charge. The raw water is typically called feed, the product water is called permeate, and the concentrated reject is called concentrate. Common RO membrane materials include asymmetric cellulose acetate or polyamide thin film composite. Common membrane construction includes spiral wound or hollow fine fiber. Each material and

construction method has specific benefits and limitations depending upon the raw water characteristics and pretreatment (Water Treatment Engineering and Research Group, U.S.A, 2001).

There are many advantages of using RO membrane. The advantages are as stated below (Meenakshi and Maheshwari, 2005):

- The process is highly effective for fluoride removal. Membranes provide an effective barrier to suspended solids, all inorganic pollutants, organic micropollutants, pesticides and microorganisms etc.

- It ensures constant water quality.

- No chemicals are required and very little maintenance is needed.

- Life of membrane is sufficiently long, so problems of regeneration or replacement are encountered less frequently.

- It works under a wide pH range.

However, this method also has its limitations. This method removes all ions present in water, though some minerals are essential for proper growth, remineralizaliton is required after treatment. It is expensive in comparison to other options. The water becomes acidic and needs pH correction.

2.5.3.4 Ion-Exchange

Fluoride can be removed from water with a strong basic anion-exchange resin containing quarternary ammonium functional groups. The removal takes place according to the following reaction:

$$\text{Matrix - NR}_3{}^+\text{Cl}^- + \text{F}^- \rightarrow \text{Matrix - NR}_3{}^+\text{F}^- + \text{Cl}^-$$
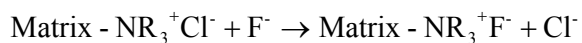
The fluoride ions replace the chloride ions of the resin. This process continues until all the sites on the resin are occupied. The resin is then backwashed with water that is supersaturated with dissolved sodium chloride salt. New chloride ions then replace the fluoride ions leading to recharge of the resin and starting the process again. The driving force for the replacement of chloride ions from the resin is the stronger electronegativity of the fluoride ions.

The advantages of this method are that it can remove fluoride up to 90 – 95% and it can keep the taste and colour of the water intact. However, this method has its limitations. In ion-exchange, the efficiency of fluoride removal is reduced in the presence of other ions like sulfate, carbonate, phosphate and alkalinity. This technique is expensive because of the cost of resin, pretreatment is required to maintain the pH, for regeneration and for waste disposal.

2.5.3.5 Other Methods of Fluoride Removal

Other methods that have been studied to remove fluoride from water are electrodialysis for brackish water (Amor et al., 1998); Donan dialysis (Hichour et al., 2000); electrochemical removal of fluoride ions from industrial wastewater (Shen et al., 2003); and combination of an activated alumina column and an electrochemical system (Loucini et al., 2004).

The performance for the adsorption, Nalgonda and Reverse Osmosis processes has been tested and compared by Meenakshi and Maheshwari (2005) in their laboratory experiments. The results are presented in Table 2.4.

Table 2.4: Comparative analysis of various techniques for fluoride removal
(Meenakshi and Maheshwari, 2006)

No.	Initial Fluoride Concentration (mg/L)	Fluoride concentration after treatment (mg/l)			
		Activated Alumina	Activated Saw Dust	Nalgonda	Reverse Osmosis
1	4.2	1.13 (73.10)	1.42 (66.19)	1.32 (68.57)	0.32 (92.38)
2	5.6	2.23 (74.07)	2.56 (70.23)	2.47 (71.30)	0.78 (90.93)
3	6.8	1.81 (73.38)	2.16 (68.24)	1.95 (71.32)	0.56 (91.76)
4	7.8	1.96 (74.87)	2.32 (70.26)	2.24 (71.29)	0.63 (91.93)
5	8.2	2.17 (73.54)	2.43 (70.37)	2.34 (71.46)	0.77 (90.61)
6	9.3	2.11 (77.31)	2.42 (73.98)	2.31 (71.16)	0.88 (90.54)

2.6 FLUORIDE REMOVAL BY ADSORPTION

2.6.1 Activated Alumina

Fluoride adsorption by an activated alumina (AA) column appeared to be an interesting process compared to other techniques (Lounici et al., 1997). The main characteristics of AA indicate interesting chemical and mechanical properties. Activated alumina is a granular, highly porous material consisting essentially of aluminium trihydrate (Rao, 2003).

Removal of fluoride from water depends on the contact time, pH, and dose of adsorbent. According to Ghorai and Pant (2004), AA is an efficient fluoride remover from natural water and its efficiency for fluoride removal is reported to be in the range of 1–9 g of fluoride per liter of the material. Table 2.5 shows typical characteristics of AA (Ghorai and Pant, 2004)

Table 2.5: Properties of AA, grade OA – 25 (Oxide India Ltd.)

No.	Characteristics	Value
1.	Particle form	Spheres
2.	Particle size, mm	2 – 5
3.	Water adsorption capacity at 30°C by wt.%	21
4.	Surface area, m^2/g (minimum)	250
5.	Pore volume, cm^3/g	0.42
6.	Bulk density, g/cm^3	800
7.	Bed crushing strength, wt.% (minimum)	92
8.	Loss on attrition, wt.% (maximum)	0.3
9.	Loss on ignition (250 - 1000°C) (%)	7.5

2.6.2 Activated Carbon

Activated carbons suitable for water process applications are produced from a variety of raw materials, including bituminous coal, peat, lignite, petrol coke, wood and coconut shells (Casey, 1997). Most of the carbons prepared from different carbonaceous sources showed high fluoride removal capacity after alum impregnation. Alkali digested alum impregnated paddy husk carbon was an efficient

defluoridating agent. Alkali digested (1% KOH) and alum soaked (2% alum) carbon removed 320 mg fluoride per kg and showed maximum removal efficiency at pH 7.0. Investigations have shown that carbonized saw dust when quenched in 2 % alum solution forms an excellent defluoridating carbon (Rao, 2003).

2.6.3 Low-cost Materials

Low-cost materials, such as kaolinite, bentonite, charfines lignite and nirmali seeds, were investigated as adsorbent to remove fluoride (Srimurali et al., 1998). These materials were investigated so that they can be used to remove fluoride instead of using a high cost material. Bentonite and kaolinite used as adsorbents are clay minerals which are disintegration products of volcanic ash and are hydrous alumininum silicate. Charfines are the byproduct obtained during making of coke from lignite coal, whereas lignite is a low rank coal and is the youngest in the coalification process. Nirmali (*Strychnos potatorium*) seed is a natural product and is used for the removal of pollutants like turbidity, color, etc. from water (Srimurali et al., 1998).

The studies according to Srimurali et al. (1998), showed that at the optimum system conditions, charfines and bentonite exhibited highest removal capacity. Removal of fluoride increased with time and approached a more or less constant value. It decreased with the increasing pH of the solution. The fluoride removal increased with decreasing size of the sorbent and with increasing sorbent dose.

2.6.4 Other Adsorbents

Adsorption is a method scientist generally used in their research to remove fluoride from water with different materials as adsorbents. Amorphous alumina supported on carbon nanotubes or Al_2O_3/CNTs (Li et al., 2001) and Aligned carbon nanotubes or ACNTs (Li et al., 2003) are new materials that have been studied and have shown to be useful adsorbents. Other materials that have been studied are the acid treated spent bleaching earth (Mahramanlioglu et al., 2002); electro-activated alumina (Loucini et al., 2003); carbonaceous materials such as activated carbons (ACs), carbon black (CB), charcoals (CCs), and bone char (BC) (Abe et al., 2004); bone charcoal, processed bone, tricalcium phosphate, activated magnesia, tamarind gel, serpentine, plant materials, and burnt clay (Karthikeyan and Sundarraj, 2000); fired clay chips (Moges et al., 1996); gas concrete materials (Oguz, 2005); alum sludge (Sujana et al., 1998) and electrochemical generation of aluminium sorbent for fluoride adsorption (Yang and Dluhy, 2002). Table 2.6 shows the fluoride adsorption capacities of some of the adsorbents mentioned above.

Table 2.6: Fluoride adsorption capacity

Adsorbent	Adsorption Capacity (mg/g)
Fired Clay Chips	0.285
Al2O3/CNTs	14.900
Acid Treated Spent Bleaching Earth	7.752
ACNTs	1.990
Alum Sludge	5.394

2.7 ADSORPTION

Physical adsorption is a process in which solute molecules (adsorbate) become attached to a solid surface under the attracting influence of surface forces (van der Waals force). Good adsorbents have a very high specific surface area which is relatively free of adsorbed materials (Casey, 1997). Adsorption can be operated on either batch or continuous-flow basis. In the batch processes, the adsorbate and wastewater are mixed together in a reaction vessel until the desired level of treatment is achieved.

Generally, adsorption is the process where the matter dispersed in solution accumulates at an interface on the adsorbent surface. A generally accepted model of adsorption kinetics consists of two main steps. The first step is the transport of particles from bulk solution near the adsorbent, which can take place due to one or more contributions such as convection and/or diffusion. The second step (attachment step) is the formation of bonds between adsorbate and adsorbent. An activation energy barrier is the main factor determining the adsorption rate as it can decrease the rate of attachment (Kasprzyk-Hordern, 2004).

The transfer of adsorbate from solution to adsorbent continues until the concentration of the adsorbate remaining in the solution is in equilibrium with the concentration of the adsorbate adsorbed by the adsorbent. The kinetics of the system describes the rate at which this equilibrium is reached and determines the retention time required for the treatment (Ibrahim, 2005).

2.7.1 Adsorption Isotherm Equations

The Langmuir isotherm describes the dependence of the equilibrium surface concentration of an adsorbed molecule on its gas-liquid phase concentration at constant time. The Langmuir isotherm is based on the following assumptions:

- The solid surface is made up of a uniform array of energetically identical adsorption site;

- A maximum of one monolayer can be adsorbed; and

- There are no interactions between the adsorbed molecules.

The Langmuir adsorption model can be expressed by the following equations:

$$q_e = \frac{q_0 b C_e}{1 + b C_e} \tag{2.1}$$

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \tag{2.1a}$$

or

$$\frac{1}{q_e} = \frac{1}{q_0 b} \times \frac{1}{C_e} + \frac{1}{q_0} \tag{2.1b}$$

Where,

q_o = the maximum amount of adsorbate adsorbed per unit weight of adsorbent

b = constant

q_e = quantity of adsorbate adsorbed per unit weight of adsorbent

C_e = equilibrium concentration of adsorbate in solution, mg/l.

The coefficient q_o and b can be obtained by plotting $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ on arithmetic paper from the results of a batch adsorption test (Lee et al., 1999).

The Freundlich isotherm assumes that the heat of adsorption decreases exponentially with surface coverage (q_e) (Kasprzyk-Hordern, 2004). The Freundlich equation is an empirical equation which is commonly used to describe adsorption of pollutants in water. The equation is written as:

$$q_e = kC_e^{1/n} \tag{2.2}$$

or
$$\log q_e = \log k + \left(\frac{1}{n}\right) \log C_e \tag{2.2a}$$

Where,

q_e = quantity of adsorbate adsorbed per unit weight of adsorbent

C_e = equilibrium concentration of adsorbate in solution, mg/l.

k = Freundlich adsorption coefficient (mg/g)

n = empirical coefficient

The constant k is related to the adsorption capacity of the adsorbent for the adsorbate. $\frac{1}{n}$ is a function of the strength of adsorption. For an adsorption isotherm with fixed values of K and C_e, the smaller the value of $\frac{1}{n}$, the stronger the adsorption bond. When $\frac{1}{n}$ becomes very small, the adsorption tends to be independent of C_e. For fixed values of C_e and $\frac{1}{n}$, the larger the K value, the greater the adsorption capacity C_e.

The application of both isotherms, is generally restricted to chemisorption (when an ionic or covalent chemical bond is formed between adsorbent and adsorbate). The isotherm can be applied to physisorption if the amount physically adsorbed does not exceed monolayer coverage (Kasprzyk-Hordern, 2004).

2.7.2   Adsorption kinetics

The rate involved in batch adsorption can be considered using First-Order Integral Method and Second-Order Integral Method models. The First-Order Integral and Second-Order Integral models can be expressed as Equation 2.5 and Equation 2.6 respectively (Weber, 2001).

$$\frac{dC_R}{dt} = k_1 \left(C_0 - C_R \right) \tag{2.5}$$

$$\frac{dC_R}{dt} = k_2 \left(C_0 - C_R \right)^2 \tag{2.6}$$

The following linearised time dependent functions can be obtained by integrating and rearranging Equation 2.5 and 2.6:

For First-Order Integral:

$$\ln \left(C_0 - C_R \right) = \ln \left(C_0 \right) - k_1 t \tag{2.5a}$$

or
$$\log \left(C_0 - C_R \right) = \log \left(C_0 \right) - \frac{k_1}{2.303} t \tag{2.5b}$$