EVALUATION OF DEFLUORIDATION OF WATER WITH FEW ADSORBENTS BY BATCH SORPTION STUDIES

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CERTIFICATE

Certified that the work contained in the thesis entitled "Evaluation of Defluoridation of water with few adsorbents by sorption studies" submitted by Kumar Chand Behera (112CH0070), has been carried out under my guidance and supervision and this work has not been submitted elsewhere for a degree.

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DECLARATION OF ORIGINALITY

I, *Kumar Chand Behera*, Roll Number 112CH0070 hereby declare that this dissertation entitled "Evaluation of Defluoridation of water with few adsorbents by sorption studies" represents my original work carried out as a undergraduate student of NIT Rourkela and, to the best of my knowledge, it contains no material previously published or written by another person, nor any material presented for the award of any other degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela or elsewhere, is explicitly acknowledged in the dissertation. Works of other authors cited in this dissertation have been duly acknowledged under the section "Bibliography". I have also submitted my original research records to the scrutiny committee for evaluation of my dissertation.

May 11, 2016   Kumar Chand Behera
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ABSTRACT

Over the excessive intake of fluoride, generally through drinking water is a valid flourishing danger influencing people the worldwide. There are two or three systems utilized for the Defluoridation of drinking water, of which adsorption strategies are for the most part thought to progress in light of their possibility, effectiveness, convenience, environmental reasons. In this, we exhibit an expansive and a key composed work survey on different adsorbents utilized for defluoridation, their relative adequacy, instruments and thermodynamics of adsorption and suggestions will be settled on the decision of adsorbents for different circumstances. Impacts of pH, temperature, imperativeness and existing together anions on Fluoride adsorption are like way assessed. Laboratory studies were done to review the chemical behavior of activated alumina and magnesium oxide as a defluoridating materials by the Batch studies.

Since the adsorption is phenomenally delicate into an extremely low or high pH values, depending upon the adsorbent, acids or salts are utilized to desorb Fluoride and recover the adsorbents for reuse. Regardless, adsorption capacity largely decreases with the rehashed utilization of the recovered adsorbent. Future examination is to look into astoundingly convincing, inconsequential effort adsorbents that can be effortlessly recovered for reuse more than a couple cycles of the operations without first loss of adsorptive limit.

Key words: Activated alumina; Fluoride; Defluoridation capacity; Regeneration; Sorption mechanism

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CHAPTER I

INTRODUCTION

1.1 Fluoride and its occurrence

Fluoride is a typical constituent of characteristic water tests. Its focus, be that as it may, shifts fundamentally relying upon the water source. Although both land and man-made sources add to the event of fluoride in water, the main contribution originates from geographical assets. But in secluded cases, surface waters from time to time have fluoride levels surpassing 0.3 mg/l. Illustrations are streams streaming over stone rich in fluoride minerals and waterways that get untreated fluoride-rich mechanical wastewater. There are a few fluoride bearing minerals in the world's outside layer. They happen in sedimentary (limestone and sandstone) and molten (stone) rocks. Weathering of these minerals alongside volcanic and fumarolic forms lead to higher fluoride levels in groundwater. Disintegration of these scarcely dissolvable minerals relies on upon the water arrangement and the season of contact between the source minerals and the water. Utilization of water having overabundance fluoride over a drawn out time period prompts an unending disease known as fluorosis. Occurrence of high-fluoride groundwater has been accounted for from 23 countries around the world. It has prompted endemic fluorosis, which has turned into a noteworthy geo-natural wellbeing issue in numerous creating nations. As indicated by a late gauge, 62 million individuals are influenced by different degrees of fluorosis in India alone. (Savinelli et.al, 1958)

1.2. Fluoride as an essential ion for health

It is well known that fluoride ion within the limit is essential for the formation of caries resistant dental enamel and for the normal process of mineralization in hard tissues. This element in the form of a compound has been used as a therapeutic agent in atherosclerosis, osteoporosis and in dental caries in human beings. Because of the beneficial role of fluoride, WHO Expert Committee on 'Trace elements in human nutrition' included fluoride in its list as one of the trace elements essential for human health. (Meenakshi R et.al, 2006)

1.3. Fluoride toxicity

Though the beneficial effects of fluoride have been questioned, its toxicity has never been. When the fluoride concentration exceeds a certain limit, it causes a disease called 'Fluorosis'. Three kinds of fluorosis are identified and they are:

1. Dental fluorosis
2. Skeletal fluorosis
3. Non-skeletal fluorosis

1.3.1. Dental fluorosis

A condition known as dental fluorosis or mottled enamel characterized by minute white flacks, yellow or brown spot areas scattering irregularly over the tooth surface. Dental fluorosis is usually of endemic nature. The incidence as well as severity of mottling was found to increase with increasing concentration of fluoride in drinking water. Mottling occurs only when the dentition is permanently exposed to excessive fluoride during the development and calcification of the teeth. The permanent teeth are affected more frequently and to a greater extent than the milk teeth. (Meenakshi R et.al, 2006)

1.3.2. Skeletal fluorosis

Unlike dental fluorosis, the skeletal fluorosis is not clinically obvious until the advanced stage of crippling fluorosis occurs. Skeletal fluorosis affects bones causing stinging pain in the back and joints, followed by progressive restriction of movement. The vertebral column is affected and fluoride gets accumulated in the intervertebral discs. This causes stiffness of the back bone and hip joints. Calcification of ligaments affects the movement of muscles also. At this stage, the affected persons have stiff-necks, bow-legs and bent frame and after some time their movement becomes totally restricted. This stage is known as skeletal fluorosis. (Meenakshi R et.al, 2006)

1.3.3. Non-skeletal fluorosis

Fluoride when consumed in excess can cause several ailments besides skeletal -and dental fluorosis. It also affects the non-calcified tissues. The soft tissue organs affected by fluoride are aorta, thyroid gland, lungs, kidneys, heart, pancreas, brain and spleen. Fluoride content in non-calcified tissues before and after ingestion has been studied in rabbits and it was found that fluoride is incorporated into non-calcified tissues like skeletal muscle, liver, kidney, thyroid gland and erythrocytic membrane in excess. (Meenakshi R et.al, 2006)

CHAPTER II

LITERATURE REVIEW

2.1 Tolerance Limits of Fluoride in Drinking Water

The fluoride in drinking water is known to prevent the development of dental caries and this level appears to lie between 0.5 and 1.0 mg/l.

Table 2.1 Drinking water standards for fluoride ion prescribed by various authorities.

Authority	Permissible limit (mg F-/1)
Bureau of Indian Standards	1.0
I.C.M.R.	1.0
Committee on Public Health Engineering Manual code of practice constituted by Government of India	1.0
U.S. Public Health Standards	0.8
W.H.O. International Standards	0.5

However, at these levels, which are apparently safe in some countries, dental mottling is seen. In parts where drinking water contains 8 mg F^-/l, skeletal fluorosis does not occur. This suggests that there can be no uniform concentration of fluoride that can be called 'Permissible'. However, the incidence of caries and mottled enamel vary considerably to nearly the same amount of fluoride in drinking water. The reason for this is the role of a number of other factors which determine the fluoride toxicity. The severity of fluorosis has a definite relationship to the following factors.

1. Amount of fluoride.

2. Length of time of contact.

3. Meteorological factors (for e.g. temperature)

4. Total fluoride ingestion

5. Nutritional status

6. Interaction with other trace elements

People exposed to 0.51 mg/1 fluoride water are affected and such reports are scanty in India. There is prevalence of dental fluorosis among the people of Nilakkottai and Dindigul of Tamil Nadu in India consuming water with 0.51 mg/1 fluoride only and food with 4.0 to 4.6 mgF^-/kg. (Meenakshi R et.al, 2006)

2.2 Levels of Fluorides in Drinking Water All Over the World

2.2.1 Range of fluorides in drinking water in several countries

Distribution of fluoride bearing waters in different countries are shown in the table below.

Table 2.2.1 Fluoride levels in natural waters in different countries. (Thole B., 2011)

CONTINENT	COUNTRY	RANGE OF FLUORIDE LEVELS, mg/l	
Africa	Kenya	0	800
	Nigeria	0	6.2
	South Africa	0	53
	Tanganyika	0	95
America	Argentina	0	1.6
	Canada	0	1.2
	Chile	0	1.5
	Equador	0	1.5
	Peru	0	1.4
	USA	0	16.0
Asia	China	0	13.0
	India	0	21.0
	Isreal	0.3	1.5
	Japan	0	20.0
	Korea	0.8	10.0
	Taiwan	1.5	1.5
	Thailand	0	1.5
Australia	Australia	0.0	13.5
	USSR	0.0	7.0
	Sweden	0.0	10.0
	Spain	0.0	6.3
	England	0.0	5.8
	France	0.0	7.0
	Germany	0.0	4.9

2.2.2. Fluorides in surface waters in India

In Peninsular India, Archaean granites and gneisses are dominant covering 2.068 million sq.km. Cuddapah and Vindhyan sand stone, shales and lime stone occupy about 0.189 million sq.km. The peninsular rivers flow over one or more and the incidence of fluoride is related to the hydrogeological conditions. (Thole B., 2011)

Table 2.2.2 Fluoride in surface waters of peninsular India

S.No.	NAME OF RIVER/STREAM/SPRING	LOCATION	FLUORIDE (mg/l)
1.	Ganga	Rajmahal, Bihar	0.35
2.	Hooghly	Dakshineswar, WB	0.35
3.	Narmada	Jamtara, Jabalpur, MP	0.10
4.	Indravati	Chitakut, MP	0.40
5.	Vekkilsvagu	Chagla marri, AP	1.50
6.	Paleru	Rajapet, AP	1.50
7.	Godavari bed	Gundala, AP	3.00
8.	Munera	Khammam, AP	2.00
9.	Chitravati	Dharmavaram, AP	3.50
10.	Pennar	Pamidi, AP	1.50
11.	Kongal	Nalgonda, AP	12.0
12.	Vaigai	Madurai, TN	>1.00
13.	Amaravati	Darapuram, TN	1.00
14.	Bhima	Yadgir, Karnataka	1.50
15.	Tambra parani	TN	>1.00

2.3 Ground water fluorides and fluoride bearing rocks in india

Fluoride bearing minerals in India

Table 2.3 Fluoride bearing minerals, their formulae and fluoride content in percentage

NAME	FORMULA	% FLUORIDE CONTENT
FLUORIDES		
Fluorite	CaF_2	48.18-48.61
Fluocerite	$(Ce, La, Dy)F_3$	19.49-29.44
Cryolite	Na_3AlF_6	53.55-54.88
Sellaite	MgF_2	60.99
PHOSPHATES		
Fluor-apatite	$Ca_5(PO_4)_3F$	2.57-5.60
Wagnerite	$Mg_2(PO_4)F$	5.06-11.48
Triplite	$(Mn, Fe, Mg, Ca)_2FPO_4$	6.02-9.09
SILICATES		
Topaz	$Al(F, OH)_2SiO_4$	13.23-20.37
Humite	$Mg(OH, F)_2\, nMg_2\, SiO4$	Upto 13.55
Sphene	$Ca\, Ti\, (SiO)_4\, (O, OH, F)$	0.61-1.40
MICA GROUP		
Phlogopite(Magnesium mica)	$K\, Mg\, Al\, Si_4\, O_{10}\, (OH, F)_2$	0.56-9.20
Lepidolite(Lithium mica)	$K\, Li_2\, Al\, (Si_4\, O_{10})\, (OH, F)_2$	4.93-8.08

The main contributors of fluoride among igneous rocks are fluorite and fluorapatite apart from topaz, amphibole and micas. In sedimentary rocks, it is related to fluorapatite while some amount is absorbed by the clay minerals.

2.3.1 Fluoride leaching from fluoride bearing minerals into ground water

Leaching is a process by which a certain constituent of a mineral is dissolved without destroying the mineral lattice. Leaching of sedimentary rocks is active in oxidizing environment. As the leaching proceeds, water dissolves the fluorapatite in the rock phosphates. Then, the fluoride present in these minerals goes into ground water. Igneous rocks are not directly subjected to the leaching, but due to prolonged chemical weathering process. The presence of water is basic for chemical weathering. The ground water charged with carbon dioxide, acts as weathering agent and able to break up nearly all minerals forming new compounds. (Swope, G.H., 1937)

Factors that tell the release of fluoride into natural water from the fluoride bearing minerals are given below.

1. Basic chemical composition of water

2. Presence and accessibility of the fluoride

3. Contact time between source minerals and water.

2.4 VARIOUS DEFLUORIDATING AGENTS

Many methods have been given from time to time for removing excessive fluorides in water. Various defluoridating agents studied so far are reviewed here. The defluoridating agents may be divided into three basic types depending upon the process of removal of fluoride.

1. Based on adsorption process.

2. Based on ion - exchange process.

3. Based on chemical reaction with fluoride.

2.4.1 Defluoridating agents based on adsorption process

Bone charcoal: The bone is processed by burning in air and pulverising it to fine powder. The fluoride removal capacity of the product is found to be 1000 mg F-/1. Processed bone The bone is dried and pulverised to 40 - 60 mesh size. The powder is carbonised in a closed retort at 748.8 to 948.8°C. The product contains tricalcium phosphate and has a capacity to remove 1000 - 1500 mg F~ /l of the medium. After saturation it is recalcined at around 398.8°C under restricted air supply to restore the adsorption capacity of the material. Alternatively, the bed is regenerated by sodium hydroxide solution. (Karthikeyan et.al, 1998)

Florex: It is a trade name for a mixture of tricalcium phosphate and hydroxy apatite. The fluoride removal capacity of the medium is found to be 600 mg F- /l and is regenerated with 1.5% sodium hydroxide solution. Without much success owing to high attritional losses and the plants were abandoned. (Karthikeyan et.al, 1998)

Activated alumina: Here, bed was regenerated with a 2% solution of sodium hydroxide, followed by neutralisation of the excess alkali with dilute hydrochloric acid. The capacity of the medium was found to be about 800 mg F"/l of alumina. The capacity of activated alumina to remove fluoride is proportional to the amount of filter alum. The fluoride removal capacity of activated alumina was reported to vary considerably, apparently caused by difference in the physio-chemical characteristics of activated alumina and regeneration procedure. (Karthikeyan et.al, 1998)

Table 2.4 Overveiw of Defluoridation Technologies

Material	Typical capacity, mg/g	The science	Strengths	Limitations
Nalgonda	0.7-3.7	Reactions of Alum, $Al_2(SO_4)_3$ and Lime	Same chemicals used for ordinary water treatment	High chemical dose, high sludge disposal required
Activated alumina	3.5-10.0	Precipitations involving Al_2O_3 and F^- ions	High selectivity for fluoride	Lower pH of water, residual Al^{3+}
Bone char	2.3-4.7	Filtration and ion exchange in $Ca_5(PO_4)_3OH$ structure	Availability of raw materials	Not universally acceptable
Bauxite	3.0-8.9	Precipitations involving Al_2O_3 and F^-, Fe_2O_3 ions in water	Available locally in some areas, high capacity	Residual color and turbidity in treated water if used raw
Gypsum	1.1-6.8	Ion exchange involving $CaSO_4$, F^-, $Ca(OH)_2$	Locally available in some areas	High Residual calcium sulphate
Magnesite	1.0-3.7	Ion exchange and precipitate involving MgO, F^-, $Mg(OH)_2$	Simple technique	High pH and residual Mg
HAP	0.5-2.9	Ion exchange and precipitation involving $Ca_5(PO_4)_3OH$, F^-, $Ca_5H(PO_4)_3(OH)_2$	Naturally available in some areas	Residual phosphate
Bauxite,gypsum,magnesite composite	4.2-11.3	Ion exchange and precipitation in reactions of $Al_2O_3,CaSO_4,MgCO_3$,MgO	Simple and versatile, better then use of each of materials	Energy intensive, fairly novel technique

Zoelites	28-41	Ion exchange and surface complexation reactions	High capacity	Limited availability
Other advanced techniques	High	Nano-filtration, reverse osmosis, precipitation, electrolysis	High capacity	High cost

2.4.2 Defluoridating agents based on chemical reaction with fluoride

Lime: This consists of treatment of water with sodium aluminate or lime and filter alum followed by flocculation, sedimentation and filtration. This is used for defluoridation of water at domestic level. The raw water taken and mixed with the adequate amounts of lime and alum. Bleaching powder for disinfection can be added simultaneously. The quantities of alum and lime required depend on dissolved solids, alkalinity and fluorides in the raw water. Lime powder and bleaching powder are sprinkled first and mixed well with the water. Alum solution is then poured and the water is stirred for ten minutes (Meenakshi et.al, 2004). Contents are allowed to settled for an hour and the clear water is removed without disturbing the sediment. The average fluoride concentration varied from 4.1 to 4.8 mg F-/1 in raw water and 0.70 to 1.20 mg F'/l in treated water. In Nalgonda technique using aluminium sulphate for defluoridation, the sulphates are increased in treated water. In order to overcome this difficulty aluminium chloride is recommended to supplement aluminium sulphate in treating water. (Meenakshi et.al, 2004)

2.5 MECHANISM OF DEFLUORIDATION OF WATER USING DIFFERENT ADSORBENTS

2.5.1 Activated Alumina

With reference to fluoride removal by activated alumina is made to explain the process in terms of adsorption at the activated alumina / solution interface. Stern Model of the alumina course of action interface is delineated in taking after figure. The ability of zero charge for activated alumina happens to warm a pH estimation of 9 and the surface charge of establish d alumina may be controlled or settled by a potential choosing molecule. The potential choosing ion in activated alumina is shown an impression of being the hydrogen ion. That infers when the centralization of hydrogen molecule is more noticeable i.e. if the pH is les s than 9, the alumina surface gets a positive charge and this quite charged surface adsorbs unfavorably charged fluoride particles from course of action. Therefore, as the pH reduces further and help, that

infers hydrogen ion center forms, that means hydrogen ion concentration increases, the positive charge on the activated alumina also increases, and hence adsorption of fluoride becomes more pronounced at lower pH values. (M.D. Smith et.al, 2003)

Thus, one sort of the forces responsible for adsorption of fluoride on activated alumina is the coloumbic forces between the positive charged aluminum oxide and negative charged fluoride ions. Regardless, the charge alone does not choose the adsorption technique in the twofold layer. Another segment responsible is the specificity. This 'specificity " component distinguishes fluoride and the other two ions, chloride and sulfate. Thus, this charged aluminum oxide favors fluoride ions and accordingly there is no adsorption of chloride or sulfate particles. This specificity is fundamental in all the examples of chemisorption. Along with fluoride ions there is a large segment of water molecules in the twofold/double layer. Activated alumina adsorbs bicarbonate particles to some degree however the order is F^-/HCO_3^- (Karthikeyan, J.et.al, 1998) In the basic medium when the activated alumina requires a negative charge, still there is sufficient defluoridation limit which can't be elucidated with respect to forces of chemisorption. In this manner, at pH more than 7 it makes the fluoride removal by activated alumina maybe given by the physisorption. Infact fluoride adsorption through Vander waals kind of forces perhaps striking some degree all through the pH range. This can be maintained by the way that Defluoridation capacity reaches saturation after a minimum contact time of 20 minutes. As we go to pH range lower than 9, chemisorption similarly starts happening and with decreasing pH the level of chemisorption increases at a much higher rate and this explains the increase in defluoridation capacity of activated alumina in acidic medium. (Karthikeyan, J. et.al, 1998)
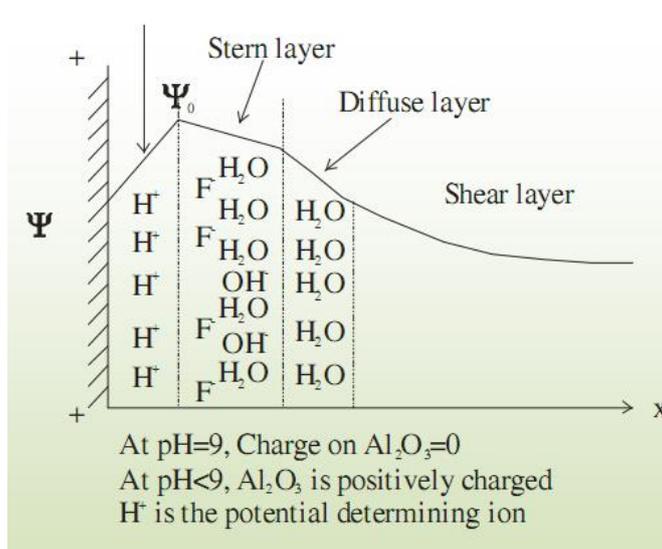

Fig.2.5.1 Model of the double layer between Al_2O_3/solution interface

2.5.2 Magnesium oxide

There is one distinction in the defluoridation mechanism of magnesium. Magnesium oxide responds with water first and structures a floe of finely separated magnesium hydroxide which ensnares the fluoride particles present in the arrangement. This floe arrangement is substantially less in the acidic locale and expansions with expanding alkalinity. Since the degree of floe development is (Very les s in acidic locale, the defluoridation limit of magnesium oxide is les s in acidic district in contrast with pH 7. Presently on the off chance that we consider its defluoridation limit between pH 7 or more a continuous diminishing is found. In the event that fluoride expulsion is controlled just by the floe development it ought to really increment with expanding pH. Be that as it may, the genuine perception is in opposition to this (Karthikeyan, J. et.al, 1998).

The colloidal magnesium hydroxide additionally should have the purpose of zero charge at some pH in the soluble reach. In this manner, at high pH the surface of magnesium hydroxide might be contrarily charged and there is no chemisorption of fluoride particles. At those pH values capturing of fluoride might be simply by physisorption. As we go towards pH 7 magnesium hydroxide might gain a positive charge at first glance and chemisorption evacuates some more fluoride (M.D. Smith et.al, 2003). At the point when the pH is under 7, the degree of floe arrangement itself is diminished, it implies the accessible surface region for fluoride evacuation is lessened and thus the decrease in the defluoridation limit. All the above dialog clarifies the most extreme defluoridation limit of magnesium oxide at pH 7. Water adsorption on these two materials can be effectively found in the swelling impacts of the two materials (Karthikeyan, J. et.al, 1998). The rate of fluoride expulsion by magnesium oxide is moderate when contrasted with initiated alumina. Another imperative perception connected with defluoridation of water with magnesium oxide is that notwithstanding when the crude water is acidic (pH = 5) the treated water turned basic with a pH 9. This is basically due to the dissolvability of magnesium hydroxide to the degree of around 0.5 x 10-5 mol/l under the conditions which prompt a grouping of 1 x 10-5 mol/l of hydroxide particle identical in a fundamental medium. (Karthikeyan, J. et.al, 1998)

2.5 OBJECTIVES

Right now, Nalgonda technology is the only available method in India for defluoridation of water. But, this technology suffers from certain limitations. The limitations are given below.

1. Fluoride in water samples containing total dissolved solids (TDS) above 1,500 mg/1 cannot be brought down to the permissible levels.

2. This technology is not applicable to Defluoridation water sources with total hardness below 250 mg/1.

3. Water sample requires to be analyzed for fluoride, alkalinity, TDS and hardness before fixing the dosages of alum and lime.

Beside these, practical implementation of Nalgonda technique has been found to be extremely difficult. At domestic level, it is difficult to maintain the required alkalinity by adding the necessary chemicals to water and to add the exact dosages of alum and lime for Defluoridation as most of the affected people belong to rural areas and they are illiterate. Most of these failed due to several operational and technical reasons (Meenakshi et.al, 2004).

1. Fluoride reduction is so low that the aim of installing defluoridation plants and spending high amounts on installation, maintenance not justified.

2. Treated water is found to be turbid not accepted by the people.

3. Preparation of alum solution of required concentration, filtration and frequent filling of overhead tank and the maintenance of the dozer pump are difficult in remote areas.

4. The cost as compared to the cost of a hand pump is quite high.

5. Spare parts are such that they are not easily available in the local market. Therefore, their replacement is expensive and time taking. (Meenakshi et.al, 2004)

Hence, the objective of the present study is therefore two fold

1. To carry out laboratory studies on defluoridation of water with selected adsorbents viz. magnesium oxide, activated alumina.

2. Based on the results of the laboratory studies, to select a suitable adsorbent with the following characteristics.

a. It uses only indigenously available materials.

b. Materials must have good fluoride removal capacity.

c. Capital and running costs must be low.

d. Operation of the unit must be easy.

CHAPTER III

DEFLUORIDATION EXPERIMENTS

3.1 Materials used as adsorbents: Magnesium oxide, activated aluminium oxide (activated alumina) are the adsorbent materials used for defluoridation studies.

3.2 Evaluation of Defluoridation capacity

Defluoridation experiments were carried out by the batch equilibration method. Here 0.5 g of the adsorbent material (0.1 g in case of magnesium oxide) was added to 100 ml of water sample at a fluoride concentration of 10 mg F"/l, the contents were shaken and the solution was then filtered through Whatmann 42 filter paper and the filtrate was analyzed for fluoride content. The adsorbent in the residue was dried in an oven at 110°C and then used for defluoridation of another fresh sample of 100 ml solution at the same fluoride concentration. The experiments were repeated with the same amount of the adsorbent till it was unable to remove any fluoride further. The defluoridation capacity of the adsorbent was calculated as follows (Srimurali, M. et.al, 1998).

$$\text{Defluoridation capacity (mg F}^-/\text{kg)} = \frac{\textbf{(mg of fluoride removed)}}{\textbf{(Amount of Adsorbent taken in grams)}} \times \textbf{1000}$$

Besides the calculation of defluoridation capacities of the adsorbents, the effect of the following variables on their defluoridation capacities was also investigated.

a. Time period of contact

b. Particle size of the adsorbent

c. pH of the environment

d. Concentration of fluoride ion

e. Temperature

f. Presence of other ions like chloride and sulphate.

3.2.1 Time as variable

In order to find out the effect of time period of contact on the fluoride removal capacity of the adsorbents in a single cycle, the defluoridation capacity of the adsorbents was investigated by keeping other parameters as constant. (Srimurali, M. et.al, 1998)

(i) Particle size   (iii) Fluoride concentration of raw water sample = 10 mg F/l

(ii) pH = 7   (iv) Concentration of other ions = Nil

3.2.2 pH as variable

Defluoridation experiments were also carried out to study the effect of pH of the environment on the defluoridation capacities of the absorbent materials. The acidic and alkaline pH values of the medium were maintained by adding the required amount of dilute hydrochloric acid in first case and sodium hydroxide solution in other case. Following parameters were kept constant while carrying out the experiments under different pH environments. (Srimurali, M. et.al, 1998)

(i) particle size   (iii) Fluoride concentration of the water sample = 10 mg/l

(ii) temperature = 30°C   (iv) concentration of other ions = Nil

3.2.3 Temperature as variable

Defluoridation experiments were carried at different temperatures viz. 30°C, 40°C, 50°C and 60°C in order to find the effect of the temperature. While doing this experiment, the following parameters were kept constant. (Srimurali, M. et.al, 1998)

(i) particle size   (iii) fluoride ion concentration of the water sample = 10 mg/l

(ii) pH = 7   (iv) concentration of other ions = Nil

3.2.4 Concentration of fluoride ion as variable

Preparation of various concentrations of fluoride solutions. Here 0.221 g of sodium fluoride dissolved in fluoride free double distilled water and then made up to one litre standard measuring flask. This solution contains fluoride equivalent to 100 mg F-/l and was used as the stock solution.

Samples prepared at different fluoride concentrations (i.e. 2,5,10,15,20,25mg/l) from right

Figure 3.2.4 Samples at different fluoride concentrations

From this stock solution, different volumes of fluoride solutions like 250 ml, 200 ml, 150 ml, 100 ml, 50 ml and 20 ml were put into six separate 1000 ml standard measuring flasks and the solutions were made up to 1000 ml using fluoride free double distilled water. The solutions then have

fluoride concentration of 25 mg/1, 20 mg/1, 15 mg/1, 10 mg/1, 5 mg/1 and 2 mg/1. The defluoridation experiments were repeated with water samples at all these concentrations of fluoride. (Srimurali, M. et.al, 1998)

3.2.5 Concentration of chloride, sulphate ions as variables

The Defluoridation experiments were performed using the adsorbents in the presence of each of these ions at one time. The experiments were done at different concentrations of each ion in the environment viz. 0.000, 0.002, 0.004, 0.006, 0.008, 0.010 and 0.014 mol/l. Preparation of standard chloride solution 1.6363 g of sodium chloride mixed in one litre flask. This solution has chloride concentration of 0,028 mol.1"1. Preparation of standard sulphate solution 3.97 g of sodium sulphate mixed in a one litre flask. This solution has sulphate concentration of 0.028 mol/l. (Srimurali, M. et.al, 1998)

3.3 DETERMINATION OF VARIOUS PARAMETERS

3.3.1 Determination of Fluoride in water sample

SPADNS colorimetric method is based on the reaction between fluoride and a zirconium-dye lake. Fluoride reacts with the dye lake, dissociating it into a colorless complex anion (ZrF_6^{2-}) and the dye. As the amount of fluoride increases, the color produced is lighter. The reaction rate between fluoride and zirconium ions is influenced by the acidity of the reaction mixture. If the proportion of acid in the reagent is increased, the reaction can be made almost instant. (Mary Ann. H. Franson, 1985)

 Procedure: Stock Fluoride solution is prepared by dissolving 0.2210 g anhydrous NaF in distilled water and diluting it to 1000 mL (100 ppm). Then work solution is made by taking 10 ml from stock, complete to 100 ml distilled water to get 10 ppm. SPADNS solution is prepared by dissolving 958 mg SPADNS, sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate, in distilled water and dilute to 500 ml and Zirconyl-acid reagent by dissolving 133 mg zirconyl chloride octahydrate, ZrOCl2·8H2O, in about 25 mL distilled water and adding 350 mL conc HCl and dilute to 500 mL with distilled water. Acid zirconyl-SPADNS reagent is then made by mixing equal volumes of SPADNS solution and zirconyl-acid reagent. Use a prepared standard of 0 mg F–/L as a reference solution. (Mary Ann. H. Franson, 1985) Avoid contamination. Set photometer to zero absorbance with the reference solution and obtain absorbance readings of standards. Plot a curve of the milligrams fluoride-absorbance relationship.

$$\text{mg F}^- \text{/L} = \frac{A}{\text{mL sample}} \times \frac{B}{C}$$

where: A = mg F⁻ determined from plotted graph

B = final volume of diluted sample, mL

C = volume of diluted sample used for colour development, mL

3.3.2 REGENERATION OF ADSORBENTS

Regeneration experiments were carried out using hydrochloric acid (1% and 2%) and sodium hydroxide solution (1% and 2%). After the defluoridation experiments, the adsorbent residue on the filter paper was treated with aliquots of 50 ml of the regenerant solution till the fluoride adsorbed on the adsorbent was eluted to the maximum extent possible. The fluoride content of each aliquot was determined after bringing down the pH to 7. (Pranab kumar, 2004)

Calculation of elution capacity

Total amount of fluoride eluted from the adsorbent with several 50 ml portions of the eluant was calculated first. Then the elution capacity of each eluant was calculated using the formula (Pranab kumar, 2004),

$$\text{Elution capacity of the eluant (\%)} = \frac{\textbf{Amount of fluoride eluted from the adsorbent}}{\textbf{Amount of fluoride adsorbed on the adsorbent}} \times \textbf{100}$$

CHAPTER IV

EXPERIMENTAL OBSERVATION AND RESULTS

For Magnesium Oxide

Table 4.1 Variation of removal of Fluoride by MgO with Time.

S.No.	Time, min	Fluoride concentration after treatment, mg/L	Fluoride removed,mg/L
1.	5	9.00	1.0
2.	10	8.16	1.84
3.	30	7.75	2.25
4.	60	5.97	4.03
5.	120	3.68	6.32
6.	180	2.95	7.05
7.	240	2.02	7.98
8.	300	0.77	9.23
9.	330	0.45	9.55
10.	360	0.25	9.75
11.	390	0.25	9.75
12.	420	0.25	9.75

Table 4.2 Variation of defluoridation capacity of MgO with Time period

S.No.	Time, min	Defluoridation capacity, mgF^-/kg
1.	30	2250
2.	60	4030
3.	120	6320
4.	180	7950
5.	240	7980

Table 4.3 Variation of defluoridation capacity of MgO with Temperature

S.No.	Temperature (°C)	Fluoride concentration, mg/L	Defluoridation capacity, mgF^-/kg
1.	30	1.72	8280
2.	40	2.12	7880
3.	50	1.81	8190
4.	60	2.02	7980

Table 4.4 Defluoridation capacity of MgO with concentrations of Fluoride

S.No.	Fluoride concentration, mg/L	Fluoride concentration after treatment, mg/L	Defluoridation capacity, mgF^-/kg
1.	2	8.79	1210
2.	5	7.22	2780
3.	10	4.62	5375
4.	15	3.89	6105
5.	20	1.60	8396
6.	25	1.29	8710

Table 4.5 Defluoridation capacity of MgO with concentrations of Chloride

S.No.	Chloride concentration, mol/l		Fluoride concentration, mg/L	Defluoridation capacity, mgF⁻/kg
	Before treatment	After treatment		
1.	0.000	0.000	8.713	12862
2.	0.002	0.002	8.721	12795
3.	0.004	0.004	8.724	12767
4.	0.006	0.006	8.725	12757
5.	0.008	0.008	8.733	12672
6.	0.010	0.010	8.739	12618
7.	0.014	0.014	8.724	12795

Table 4.6 Defluoridation capacity of MgO with concentrations of Sulphate

S.No.	Sulphate concentration, mol/l		Fluoride concentration, mg/L	Defluoridation capacity, mgF⁻/kg
	Before treatment	After treatment		
1.	0.000	0.000	7.75	22500
2.	0.002	0.002	7.95	20500
3.	0.004	0.004	7.85	21500
4.	0.006	0.006	7.85	21500
5.	0.008	0.008	8.27	17300
6.	0.010	0.010	8.58	14200
7.	0.014	0.014	8.16	22500

For Activated Alumina

Table 4.7 Variation of removal of Fluoride by Activated Alumina with time

S.No.	Time, min	Fluoride concentration after treatment, mg/l	Fluoride removed, mg/l
1.	2	3.79	6.21
2.	10	3.49	6.51
3.	20	3.37	6.63
4.	30	2.64	7.36
5.	60	2.33	7.67
6.	120	2.33	7.67

Table 4.8 Defluoridation capacity of Activated alumina with time period

S.No.	Time, min	Defluoridation capacity, mgF⁻/kg
1.	10	1302
2.	20	1326
3.	30	1472
4.	60	1534

Table 4.9 Defluoridation capacity of Activated alumina with Fluoride concentration

S.No.	Fluoride concentration, mg/l	Fluoride concentration after treatment, mg/l	Defluoridation capacity, mgF$^-$/kg
1.	2	1.60	80
2.	5	2.43	514
3.	10	2.95	1410
4.	15	1.29	2741
5.	20	0.97	3804
6.	25	0.97	3804

Table 4.10 Defluoridation capacity of Activated alumina with Temperature

S.No.	Temperature (˚C)	Fluoride concentration, mg/l	Defluoridation capacity, mgF$^-$/kg
1.	30	3.16	1368
2.	40	3.06	1388
3.	60	3.27	1346
4.	80	3.16	1368
5.	100	3.27	1346

Table 4.11 Defluoridation capacity of Activated alumina with temperature (pH < 7)

S.No.	Temperature (˚C)	Fluoride concentration, mg/l	Defluoridation capacity, mgF$^-$/kg
1.	30	5.45	910
2.	40	5.77	846
3.	60	5.14	972
4.	80	4.62	1076
5.	100	4.62	1076

Table 4.12 Defluoridation capacity of Activated alumina with concentrations of Fluoride (pH < 7)

S.No.	Fluoride concentration, mg/l	Fluoride concentration after treatment, mg/l	Defluoridation capacity, mgF$^-$/kg
1.	2	7.43	514
2.	5	6.29	742
3.	10	5.14	976
4.	15	2.95	1410
5.	20	2.12	1526
6.	25	1.18	1764

Table 4.13 Defluoridation capacity of Activated alumina with Chloride concentrations

S.No.	Chloride concentration, mol/l		Fluoride concentration, mg/L	Defluoridation capacity, mgF⁻/kg
	Before treatment	After treatment		
1.	0.000	0.000	6.18	3820
2.	0.002	0.002	6.08	3920
3.	0.004	0.004	6.08	3920
4.	0.006	0.006	6.08	3920
5.	0.008	0.008	6.08	3920
6.	0.010	0.010	6.08	3920
7.	0.014	0.014	5.97	4030

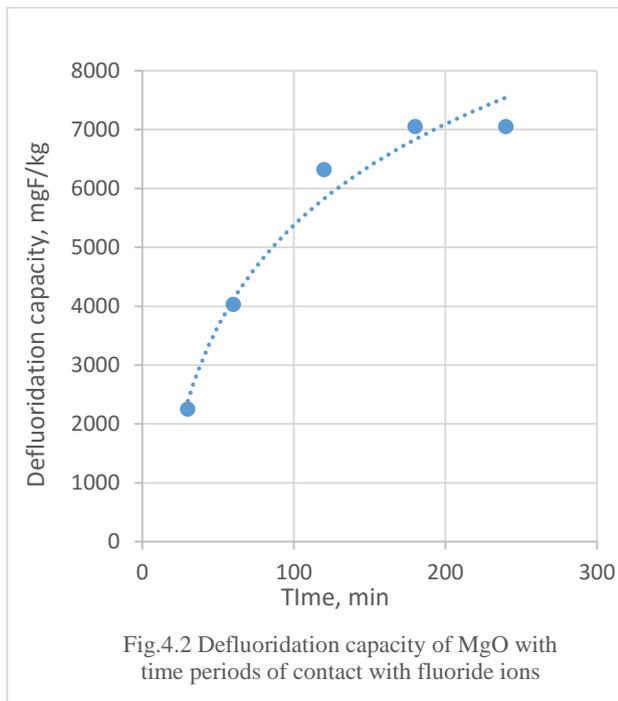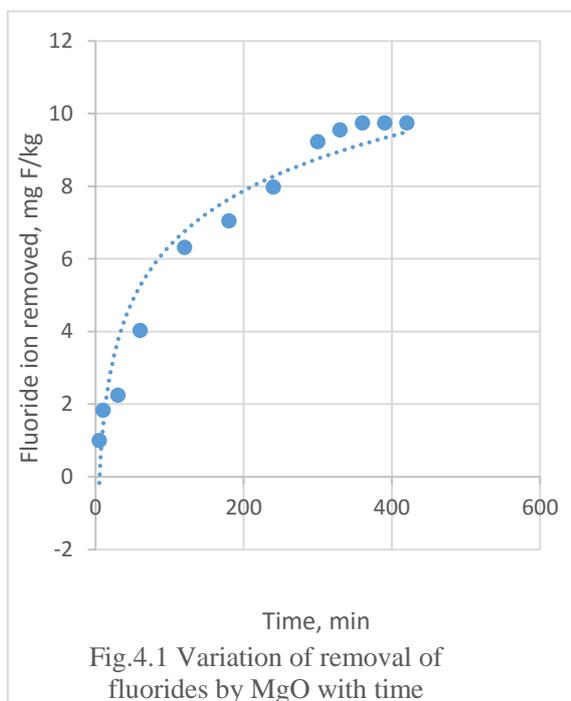Table 4.14 Defluoridation capacity of Activated alumina with Sulphate concentrations

| S.No.	Sulphate concentration, mol/l		Fluoride concentration, mg/L	Defluoridation capacity, mgF⁻/kg
	Before treatment	After treatment		
1.	0.000	0.000	4.62	5325
2.	0.002	0.002	4.41	5590
3.	0.004	0.004	4.72	5820
4.	0.006	0.006	4.62	5325
5.	0.008	0.008	4.62	5325
6.	0.010	0.010	4.41	5590
7.	0.014	0.014	4.62	5325

4.2 RESULTS AND DISCUSSION

The results of defluoridation experiments with magnesium oxide and activated alumina are presented in this section. Variation of fluoride removal in single cycle and also change of defluoridation capacity of the adsorbent with time, particle size, pH and temperature on defluoridation capacity are shown in tables 4.1 to 4.14. Influence of concentration of fluoride ions and also concentrations of other ions like chloride, sulphate on defluoridation capacities are shown in the figures 4.1 to 4.14 and the related data are given in tables corresponding to it. The figures representing the results are given in the text itself wherever they are found relevant. Experimental data in the form of tables are given at the end of presentation of the results of each adsorbent. These tables are quoted in the text as and when found required. The details of the conditions maintained in each experiment are given in the respective tables.
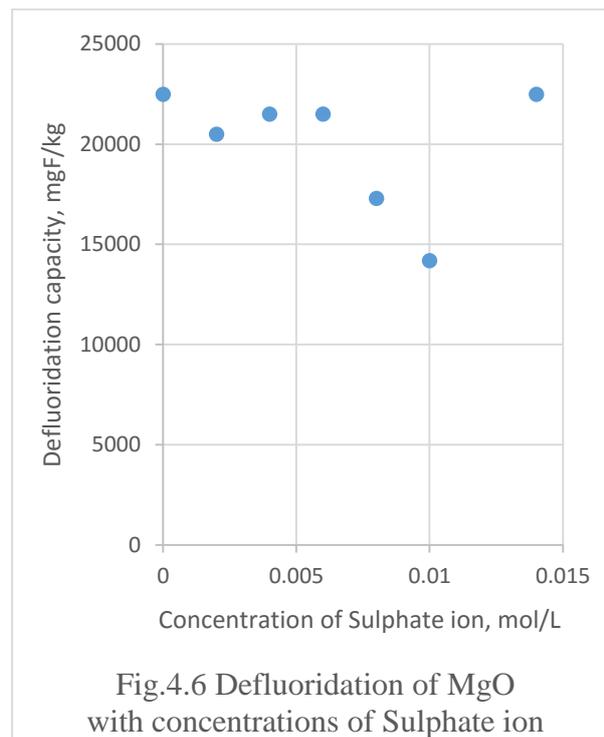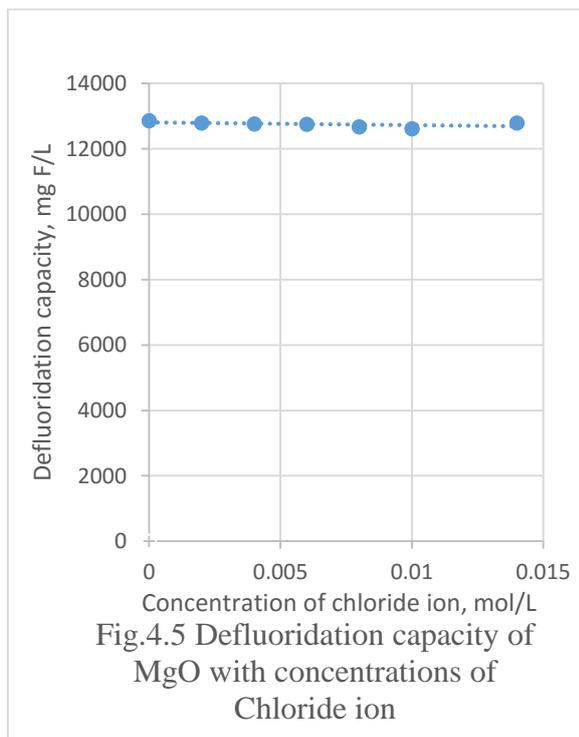
4.2.1 MAGNESIUM OXIDE AS ADSORBENT

The results shown in fig. indicate that the process of fluoride removal by magnesium oxide is very slow. It reaches completion only after a period of 300 minutes. At the end of 5th minute fluoride removal is just 900 mg/kg and at the end of 5th hour it increases by more than 10 times. It is interesting to note that the defluoridation capacity of magnesium oxide reaches saturation much earlier and that too at the 60th minute itself. Defluoridation capacity is the efficiency of the material to remove fluoride till it gets completely saturated. The results are based on the batch equilibration method. Therefore, it is obvious that after a large number of cycles when the material actually gets saturated there should not be any difference between the defluoridation capacities with time.

Fig.4.1 Variation of removal of fluorides by MgO with time

Fig.4.2 Defluoridation capacity of MgO with time periods of contact with fluoride ions

It has been observed that magnesium oxide recorded the maximum defluoridation capacity of 28,300 mg F$^-$/kg at pH 7. There is a slight decrease as the pH is towards the acidic region. There is a gradual decrease of defluoridation capacity from pH 7 as we go towards more alkaline range and it reaches the minimum of 19,000 mg F-/kg at higher pH. The values beyond pH 9 are only of academic interest as the pH of naturally occurring drinking water sources rarely exceeds 9.

Fig.4.3 Defluoridation capacity of
MgO with Temperatures

Fig.4.4 Defluoridation capacity of
MgO with concentrations of
Fluoride ion
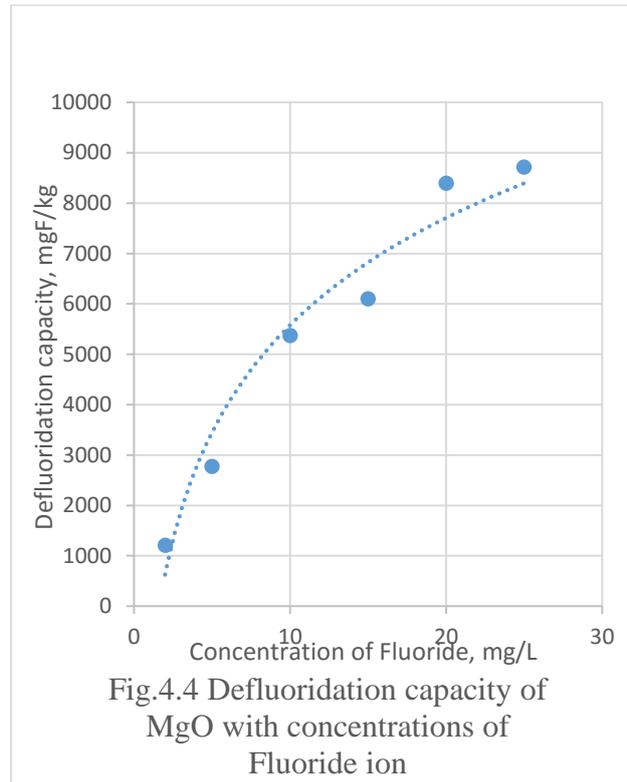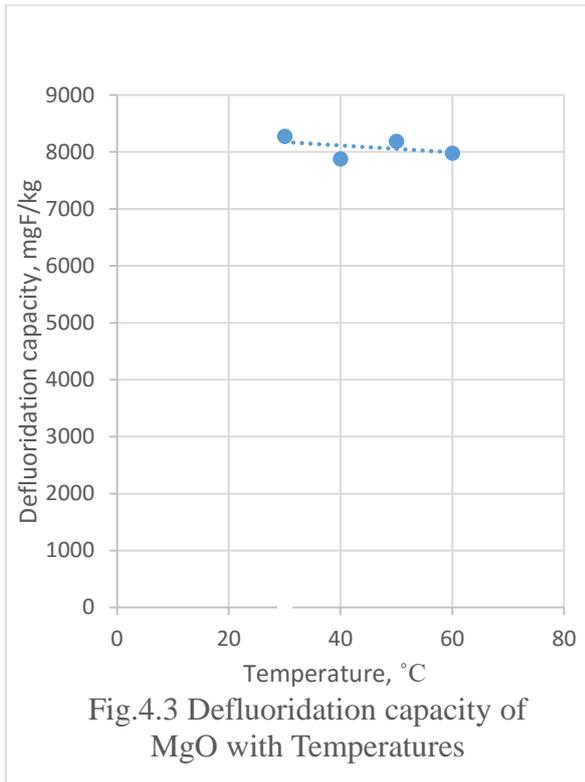
From the results shown in table 4.3 and figure 4.3, it is evident that there is no influence of temperature within the range of 30°C to 60°C on the defluoridation capacity of the magnesium oxide. This is not at all surprising because, defluoridation capacity shows the total number of available sites for fluoride for the adsorption. There could be influence of temperature definitely on the kinetics of the adsorption of fluoride which is also observed in the present study.

Fig.4.5 Defluoridation capacity of
MgO with concentrations of
Chloride ion

Fig.4.6 Defluoridation of MgO
with concentrations of Sulphate ion

It is observed that at higher temperature adsorption is faster and the material reaches its state of saturation earlier than when compared to adsorption at a lower temperature. But there cannot be any increase in the total number of sites available for adsorption and hence the defluoridation capacity is independent of temperature.
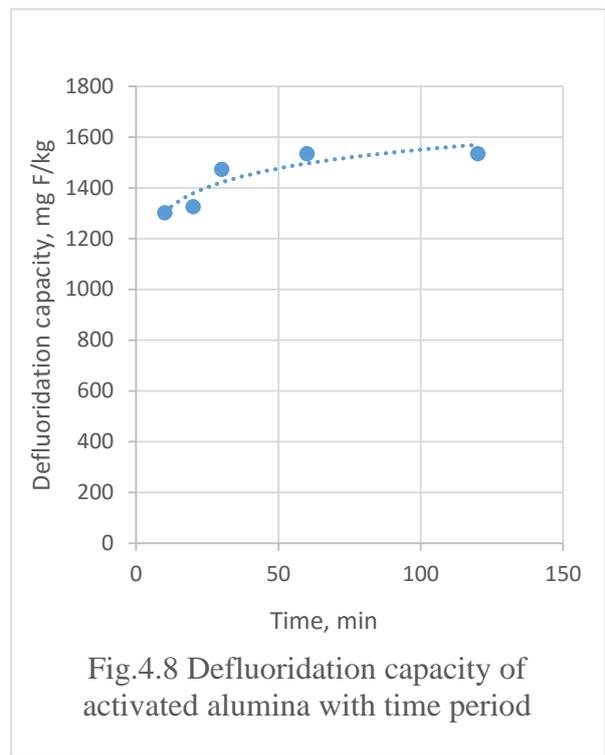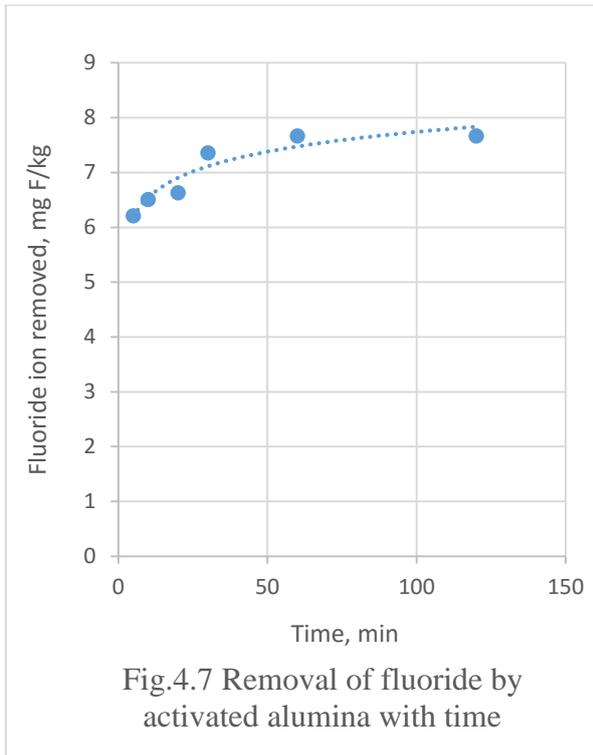
Variation of defluoridation capacity with the change in concentration of fluoride in the range of 2 to 25 mg/1 are presented in table 4.4 and also in fig 4.4. These concentrations of fluoride are chosen as the ground water fluorides are reported to be within this range. The curve is linear up to a concentration of 10 mg/1 and then gradually tends to reach saturation beyond 25 mg/1. At a low concentration the chemisorption naturally obeys Langmuir' s adsorption isotherm as there is little possibility of ion-ion interaction s or ion-solvent interactions at that condition.

Figures and as well as tables 4.5-4.6 reveal that there is absolutely no influence of concentration of chloride ions and sulphate ions on defluoridation capacity of magnesium oxide. This is given by the fact that there is no difference in the concentration of these ions before and after defluoridation. The concentrations chosen are in the range of 2×10^{-3} to 1.4×10^{-3} mol/l which is much higher than the concentration of the fluoride. To conclude, in comparison to chlorides and sulphates, fluoride is selectively adsorbed on magnesium oxide.

4.2.2 ACTIVATED ALUMINA AS ADSORBENT

Fluoride removal for the time dependence is given in figures 4.7-4.8 and also tables 4.7-4.8 for activated alumina. The defluoridation capacity of activated alumina reaches saturation after a time period of 20 minutes though a period of 60 minutes is required for attaining maximum fluoride removal capacity in a single cycle. This difference is in accordance with the observed difference in case of magnesium oxide also. Though it takes a little longer time for attaining the maximum efficiency in the first batch process, the total defluoridation capacity of the adsorbent attained its maximum after 20 minutes itself. That means, if we provide greater time of contact, greater amount of fluoride will get adsorbed and the material gets saturated in less number of batches.

At pH 7, the defluoridation capacity of 80 mg F^-/kg which was observed to have been increased by nearly four times to a value of 514 mg F^-/kg in acidic medium. On the other hand, it decreases to a value of 3,000 mg F'' /kg as we go to higher alkaline range. This extremely higher defluoridation capacity of this material at acidic medium makes it a very promising material for defluoridation.

Fig.4.7 Removal of fluoride by activated alumina with time

Fig.4.8 Defluoridation capacity of activated alumina with time period

There is no temperature dependence on defluoridation capacity of activated alumina in the range of pH 3-7. This observation is in accordance with the results reported earlier in case of magnesium oxide also. Though there is a tendency for reaching saturation beyond the concentration of 25 mg/1 at pH 7, there is no such tendency at pH 3. The adsorption of fluoride on activated alumina obeys Langmuir's adsorption isotherm.
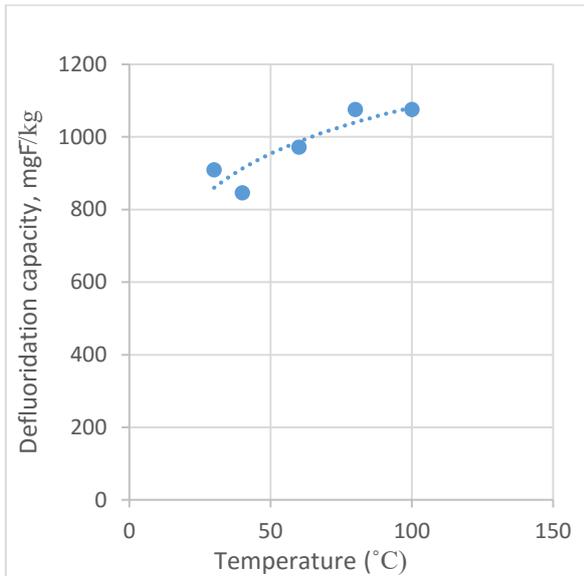

Fig.4.9 Defluoridation capacity of activated alumina with concentrations of fluoride ion

Fig.4.10 Defluoridation capacity of activated alumina with temperatures
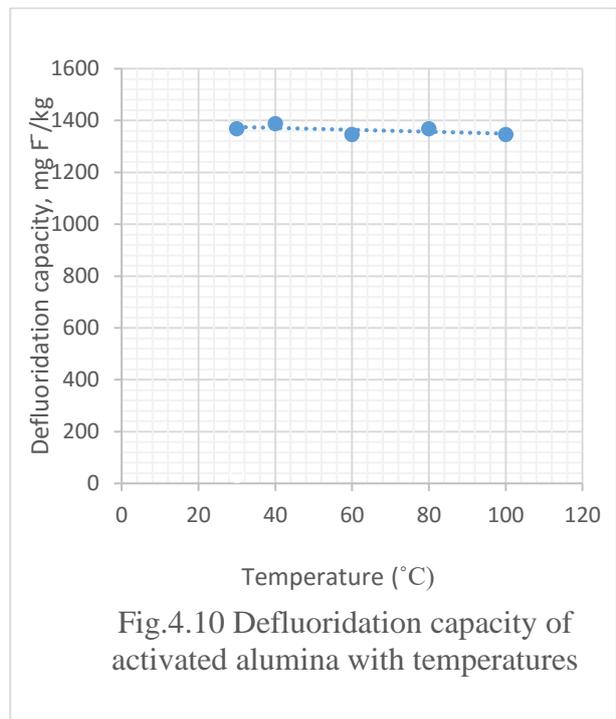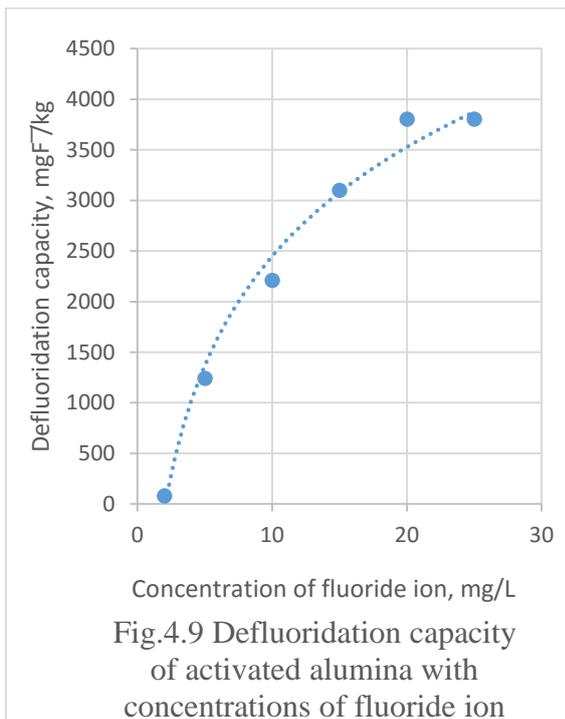
Fig.4.11 Defluoridation capacity
of activated alumina with
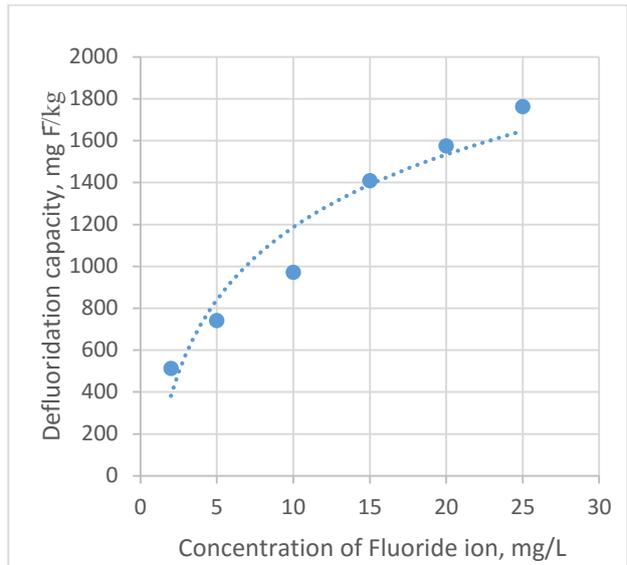temperatures (pH<7)

Fig.4.12 Defluoridation capacity of
activated alumina with
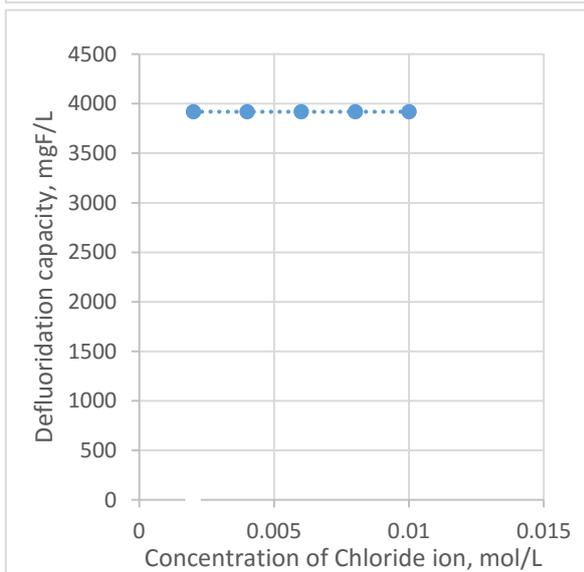concentrations of fluoride ion
(pH<7)

Fig.4.13 Defluoridation capacity
of Activated alumina with
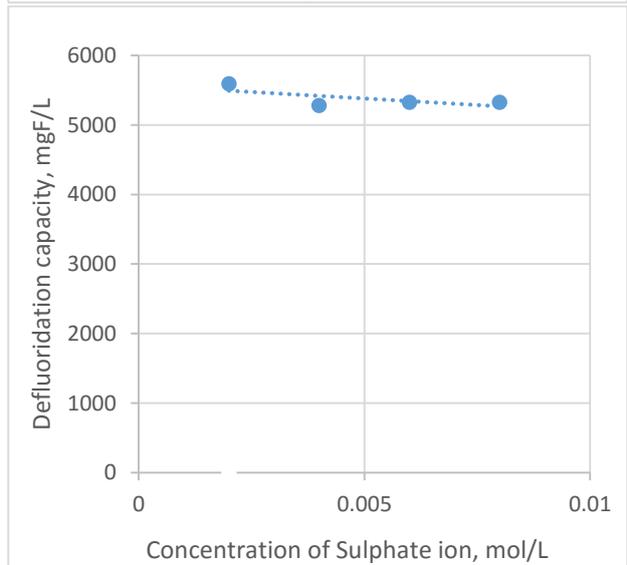concentrations of Chloride ion
(pH=7)

Fig.4.14 Defluoridation capacity of
Activated alumina with
concentrations of Sulphate ion
(pH=7)

Figures 4.13-4.14 clearly indicate that there is no dependence of chloride or sulphate on defluoridation capacity of activated alumina in the range of pH 3-7. Tables 4.13-4.14 also indicate that there is no change in the concentrations of the chloride or sulphate ions before and after treatment.

4.2.3 ELUTION CAPACITY OF THE ELUANTS

Table 4.15 Elution capacity of the eluants

S.No.	Adsorbent	Eluant	Elution capacity (%)
1.	Magnesium oxide	2% Hydrochloric acid	Magnesium oxide dissolves completes at this condition
2.	Activated alumina	2% Hydrochloric acid	80.1
3.	Magnesium oxide	2% Sodium Hydroxide	22.54
4.	Activated alumina	2% Sodium Hydroxide	61

These results of elution capacities of solutions indicate that 2% hydrochloric acid cannot be used as the eluant for magnesium oxide but good eluant for activated alumina. On using 2% Sodium hydroxide solution, percentage of elution of fluoride for various adsorbents found to be in order as: Magnesium oxide < Activated alumina. From these results, it is clear that after one cycle of defluoridation magnesium oxide cannot be regenerated significantly. This advantage overweighs the advantage of high defluoridation capacity of Magnesium oxide. Regeneration of adsorbents at least to the extent of above 8-10% is necessary to bring down the cost of defluoridation of water.

4.3 DISCUSSION

Based on the results of delfluoridation capacities of two adsorbents viz. magnesium oxide and activated alumina, the following conclusions has been derived.

1. Defluoridation capacity of each material depends upon the time period of contact for the adsorption. This time period varies from one material to other in following order: Activated alumina < Magnesium oxide.

2. The Defluoridation capacity is completely independent of temperature in case of both the adsorbents.

3. There is no influence of chlorides and sulphates on the defluoridation capacities of the materials studied.

4. The defluoridation capacity is pH dependent. In both the adsorbents, a decrease in the defluoridation capacity with increasing pH (or basicity) is observed. The rate of increase of defluoridation capacity with decrease in pH is highest in case of Activated alumina.

5. The defluoridation capacity increases in both the cases with an increase in the fluoride concentration.

CONCLUSION

Based on the results and discussion above, the selection of a suitable adsorbent for defluoridation unit can be made at a domestic level. Magnesium oxide showed extremely high defluoridation capacity. However, it suffers from the following limitations:

1. It cannot be regenerated. Therefore, once exhausted it should to be discarded.
2. The cost of magnesium oxide is much higher compared to that of activated alumina.
3. Magnesium oxide is not readily available in a bulk quantity.
4. The alkalinity of the treated water is high to an objectionable extent, neutralization of which is not practically feasible.

Activated alumina does not suffer from any attritional losses during regeneration, the percentage of regeneration of activated alumina is higher and the cost is relatively low. Besides it needs lowest contact time with fluoride when compared to magnesium oxide. Hence, in view of these advantages of activated alumina it is concluded to be a chosen adsorbent for the development of indigeneous plant.

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