DEFLUORIDATION OF WATER USING NEEM (AZADIRACHTA INDICA) LEAF AS ADSORBENT

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ABSTRACT

Fluoride is often called a two- edge sword. In the human system this fluoride has a dual personality, a destructive effect when fluoride concentration is greater than 1.5 ppm – dental & skeletal fluorosis and a beneficial effect when concentration is upto 1.0 ppm – caries prevention and health promotion. World Health Organization (WHO) and IS: 10500 recommend that the fluoride content in drinking water should be in the range of 1.0 to1.5 ppm. Fluoride concentrations beyond the standards cause dental and skeletal fluorosis. This mini project presents the findings of an investigation on the use of neem leaf powder for the defluoridation of water. Here the study presents the suitability of inexpensive leaf adsorbents to effectively remediate fluoride-contaminated water. The efficiency of the sorption of fluoride ion is affected by contact time, pH and concentration of adsorbents. Treated leaf powder was studied at various pHs, adsorbent dosage and contact time with aqueous solutions containing 10mg /l fluoride ion. The maximum adsorption of fluoride is at pH 2. For pH greater than 2 fluoride removal decreases sharply. The sufficient time for adsorption equilibrium of fluoride ions is 120 min and maximum removal efficiency obtained is 85% at adsorbent dose 10 g/l.

Keyword:- Fluoride, Fluorosis, World Health Organization (WHO), Adsorption.

1. INTRODUCTION

Water is one of the most important elements for all forms of life and is indispensable to the maintenance of life on earth. Water is frequently referred to as a universal solvent, because it has the ability to dissolve almost all substance; that comes in its contact. Safe drinking water is the primary need of every human being. Pure water is scarce and is not easily available at all. Water may be contaminated by natural sources or industrial effluents. Some elements are essential in trace amount for human being while higher concentration of the same can cause toxic effects. One such contaminant is fluoride [2].

Due to rapid urbanization and growth of modern industries (anthropogenic source of fluoride) as well as geo chemical dissolution of fluoride bearing minerals (natural source of fluoride), fluoride concentration is increasing in the environment including water resources. The high concentration in the drinking water leads to destruction of enamel of teeth and causes a number of conditions referred to collectively as fluorosis. The problem of high fluoride

in groundwater has now become one of the most important toxicological and geo environmental issues in India. During the last three decades high fluoride concentrationin water resources resulting in the disease called "Fluorosis" is being highlighted considerably throughout the world [1].

Fluoride is an essential constituent for both humans and animals depending on the total amount ingested or its concentration in drinking water. It is purposely added to drinking water in small quantities to prevent dental caries. The presence of fluoride in drinking water, within the permissible limits of 0.5-1.0 mg L-1, is beneficial for the production and maintenance of healthy bones and teeth [3, 4, 8, 11]. An intake of more than 6 mg of fluorine per day results in fluorosis and causes dental or skeletal fluorosis which is a chronic disease manifested by mottling of teeth in mild cases, softening of bones and neurological damage are severe cases. Fluorine being cumulative boneseeking mineral, the resultant skeletal changes are progressive. Fluoride increases the stability of crystal lattice in bone, but makes the bone more brittle. Drinking fluoridated water will double the number of hip fractures. The International Society for Fluoride Research (ISFR) has reported studies implicating fluoride in the rising rates of Down's syndrome, chronic fatigue syndrome and sleep disorder [2]. Because of its health risks, defluoridation of drinking water is the best practicable option to overcome the problem of excessive fluoride in drinking water, where alternate source is not available. Research of several researchers during the last 5–6 years has proved that lifelong impact and accumulation of fluorides cause not only human skeletal and teeth damage, but also changes in the DNA-structure, paralysis of volition, cancer, etc. Mainly two factors are responsible for contamination of ground water with fluoride:one is geological and second is anthropogenic. Although both geological and manmade sources contribute to the occurrence of fluoride in water, the major contribution comes from geological resources. During the years following the discovery of fluoride as the cause of fluorosis, extensive research has been done on various methods for removal of fluoride from water and wastewater [9].

The popular technologies for the removal of fluoride from water include: coagulation followed by precipitation, membrane processes, ion exchange and adsorption. In coagulation, trace amounts of fluoride ions tend to remain in solution due to solubility restriction. Other shortcomings include the resulting high pH of the treated water and the generation of large amount of wet bulky sludge.

The Nalgonda technique, based on precipitation processes, is also a common defluoridation technique. The limitations of the process are: daily addition of chemicals, large amount of sludge production, and low effectiveness for water having high total dissolved solids and

hardness. Further, increase in residual aluminum in the treated water has been reported. This may endanger human health as concentrations of aluminum, a neurotoxin, as low as 10–2 mg/l in drinking water have been associated with Alzheimer's disease. Membrane processes, though effective in fluoride removal, demineralise water completely, besides the high initial and maintenance costs.

Ion exchange methods are efficient for fluoride removal, but a tedious and difficult process of preparation of resins as well as the high cost necessitates a search for an alternative technique.

Adsorption techniques have been quite popular in recent years due to their simplicity, as well as the availability of wide range of adsorbents. Research has focused on various types of inexpensive and effective adsorption media, such as different clays, solid industrial wastes like red mud, spent bleaching earths, spent catalysts and fly ash, activated alumina, carbonaceous materials, bone charcoal, natural and synthetic zeolites and other low-cost adsorbents, with various degrees of success.

Here, this study presents an investigation on the use of leaf powder from neem trees for the defluoridation of water.

2. METHODOLOGY

2.1 Materials

The adsorbent which is used is neem leaf for the removal of fluoride from the water. The natural adsorbent is collected from the neem tree.

2.2 Methods

Adsorbent Preparation

Fresh leaves chosen based on their crude fiber content and tress were obtained from neem (*Azadirachta indica*) trees. The fresh leaves were sun-dried for 3–4 days, put in a cotton jute bag and crushed manually. This process can save the energy expended in hot air oven drying and mechanical crushing. The powder was sieved to get various particle sizes. Leaf powder biomass was further digested by chemical methods.

Preparation of Stock Solution

Fluoride stock solution was prepared by dissolving 221 mg anhydrous sodium fluoride in 1000 ml distilled water in volumetric flask. Fluoride standard solution was prepared by diluting 100ml stock solution to 1000 ml distilled water in volumetric flask. This 1 ml solution has 0.1 mg of fluoride.

Alkali treatment

Leaf biomass powder sample (40 gm) and 400 ml 0.5 N NaOH were taken in 1000-ml conical flask. Then mixture was gently heated on burner for 20 min after boiling started. Using distilled water, the treated biomass was washed which continued until maximum colour was removed and clear water obtained.



Fig – 1 : Alkali treated leaf powder

Preparation of reagent

Zirconyl – SPADNS reagent is used for the analysis of fluoride.

a) SPADNS solution : Dissolve 958 mg SPADN (sodium 2-1,8-dihydroxy-3,6-naphthalene disulfate) in distilled water and dilute to 500 ml.

b) Zincronyl – acid reagent : dissolve 133mg zincronyl chloride octahydrate in about 25ml distilled water. Add 350 ml conc. Hcl and dilute to 500 ml with distilled water.

c) Acid Zincronyl - SPADNS reagent : Mix equal volume of SPADNS and zincronyl - acid reagent.

2.3 Experimental setup

Jar Test Apparatus

To study the effect of pH jar apparatus has been used. The jar apparatus has the six beakers and six steel paddles which helps in the agitation process. The initial speed of agitation is 100 rpm for 2 min, followed by 40 rpm for 30min. The settling time applied for coagulation process is 60 min. The pH is determined by pH meter.

Spectrophotometer

Flouride ions is detected using spectrophotometer. Spectrophotometry is a method to measure how much a chemical substance absorbs light by measuring the intensity of light passes through sample solution. Basic principle is that each compound absorbs or transmits light over a certain range of wavelength of 570 nm.

2.4 Development of Standard Curve

0.2

0

2

The fluoride standard sample in the range of 1 mg/lit to 12 mg/lit was prepared by taking appropriate quantities of standard fluoride solution with distilled water. Then pipette 5 ml each of SPADNS solution and zirconyl acid solution to each standard and mixed well. Contamination avoided. The spectrophotometer was set to zero absorbance with reference solution and absorbance readings of standard were obtained. Reference solution was used as a blank solution. Spectrophotometer used at 570 nm wavelength was taken as per standard method procedure.

	Sl. no	Initial fluoride concentration (mg/l)	Absorbance reading	
	1	2	0.345	
	2	4	0.480	
£., 1	3	6	0.670	
×.	4	8	0.865	
1	5	10	1.035	
	1.2			
	1			
e C	0.8 —			
sorban	0.6			
Ade	0.4			

 Table – 1 : For the Development of Standard Curve

Fig - 2 : Standard curve

6

Fluoride ion concentration (mg/l)

8

10

4

3. RESULTS AND DISCUSSIONS

Successful application of the adsorption technique demands innovation of cheap, nontoxic, easily and locally available material. Bio adsorbents meet these requirements. Knowledge of the optimal conditions would herald a better design and modeling process. Thus, the effect of some major parameters like pH, contact time, initial adsorbate concentration and adsorbent dosage was investigated from kinetic viewpoint. Adsorption studies were performed by batch technique to obtain the rate and equilibrium data. Experiments were carried out by shaking 10 g/l of adsorbent dose with 100 ml of aqueous solution containing known concentration of fluoride ions and by agitating the samples at a speed of 200 strokes/min. Samples containing fluoride ions were maintained at a desired pH by adding 0.5 N HNO₃. All the experiments were conducted at room temperature ($27 \pm 0.5^{\circ}$ C).

3.1 Effect of initial adsorbate concentration

For a strictly adsorptive reaction, in the optimized period of contact, the rate varies directly with the concentration of adsorbate. The capacity of the adsorbent materials gets exhausted sharply with increase in initial fluoride ion concentration. The adsorption capacity of treated biosorbents was systematically studied by varying the initial concentration of fluoride ions between 2 and 12 mg/l.

Operating	condition
Adsorbant dosage	10 g/l
Time of contact	120 min
Temperature	27°C
pH	2
Volume of sample	100 ml

Table -2: Operating condition for effect of initial adsorbate concentration

 Table – 3 : Effect of initial adsorbate concentration

S1. no	Initial adsorbate concentration (mg/l)	Final concentration (mg/l)	% Removal of fluoride ion
1	2	0.04	98
2	4	0.28	93
3	6	0.96	84
4	8	1.6	80
5	10	2	80
6	12	4.8	60



Fig - 3: Effect of initial adsorbate concentration

The percent removal of fluoride ion is a function of initial concentration at different initial pH values. Treated biosorbents may be seen fairly active in reducing fluoride ions from 100 to 60 % when the initial concentration of fluoride ion concentration was increased from 2 to 12 mg/l with a constant sorbent dose of 10 g/l at pH of 2.

3.2 Effect of contact time

For study the effect of contact time on the removal efficiency of fluoride from water using adsorbent, the following operating conditions are used.

Operatin	ig condition
Adsorbant dosage	10 g/l
pH	2
Initial adsorbate concentration	10 mg/l
Temperature	27°C

 Table - 5 : Effect of contact time

Sl. no	Time	Initial	Final concentration	% Removal of
	(min)	concentration	(mg/l)	fluoride ion
		(mg/l)		
1	30	10	4.5	55
2	60	10	3.6	64
3	90	10	1.5	85
4	120	10	1	90
5	150	10	1	90
6	180	10	1	90



Fig - 4 : Effect of contact time on the removal of fluoride ion

It is found that the removal of fluoride ions increases with increase in contact time to some extent. Further increase in contact time does not increase the uptake due to deposition of fluoride ions on the available adsorption sites on adsorbent material. Preliminary investigations on the uptake of fluoride ions on the adsorbent material at their optimum pH values indicate that the processes are quite rapid. Typically, 80% of the adsorption occurs within the first hour of the contact for fluoride ions with an initial concentration and adsorbent dose of 10 mg/l for treated biosorbents. This initial rapid adsorption subsequently gives way to a very slow approach to equilibrium and saturation is reached in 1.5 to 3 h. For further optimization of other parameters, this contact time was considered as the equilibrium time.

3.3 Effect of pH

The pH of the aqueous solution is a controlling factor in the adsorption process. Thus, the role of hydrogen ion concentration was examined at pH values of 2, 4, 6, 8. This was adjusted by adding 0.5N HNO3 with 100 ml of standard solution of 10 mg/l of fluoride for a contact time of 60 min with a dose of 10 g/l of treated bioadsorbent.

We have observed decrease in the extent of removal of fluoride ions with increase in the pH of the solution. This was investigated as 80% at pH 2 and 75% in the case of pH 4. Hence further studies were conducted within these pH values. In the case of treated biosorbents, the percentage of adsorption increased almost linearly between 2.0 and 8.0, attaining a maximum removal at pH 2.0 in 60 min of contact time.

Operating condition		
Adsorbant dosage	10 g/l	
Time of contact	120 min	
Initial adsorbate concentration	10 mg/l	
Temperature	27°C	
Volume of sample	100 ml	

Table - 6 : Operating condition for effect of pH

Sl. no	P^{H}	Initial concentration	Final concentration (mg/l)	% Removal of fluoride ion
		(mg/l)		
1	2	10	2	80
2	4	10	2.5	75
3	6	10	3.2	68
4	8	10	4	60
		participant and a second		
9	0			
8	0			
7	0			
× 6	0			
λ ₂ 5	0			

Table – 7 : Effect of pH



Fig - 5: Effect of pH on the removal of fluoride ion.

In this case, the result may be due to neutralization of the negative charges at the surface of the treated biosorbents by greater hydrogen ion concentration at lower pH values. This reduces hindrance to diffusion of the negatively charged fluoride ions on to the increased active surface of treated biosorbents.

3.4 Effect of adsorbent dosage

It is observed that the removal of fluoride ions increases with an increase in the amount of adsorbent. For all these runs, initial fluoride ion concentration was fixed at 10 mg/l. The amount of adsorbent dose was varied between 2 and 12 g/l in aqueous solution at their optimal pH values.

Operating condition		
Time of contact	120 min	
Initial adsorbate concentration	10 mg/l	
Temperature	27°C	
pH	2	

Table - 8 : Operating condition for effect of adsorbent dosage

Sl. no	Amount of adsorbent (g/l)	Initial concentration (mg/l)	Final concentration (mg/l)	% Removal of fluoride ion
1	2	10	6.5	35
2	4	10	5.6	44
3	6	10	4.2	58
4	8	10	3.5	65
5	10	10	2	80
6	12	10	1.5	85

 Table – 9 : Effect of adsorbent dosage



Fig - 6: Effect of adsorbent dose on the removal of fluoride ion

Results showed that treated bioadsorbent was efficient for 58% removal of fluoride ions, 65% at 6 g/l and 8 g/l and maximum removal of 85%, and 80% was observed at 12 and 10 g/l, respectively, at a room temperature of 27° C.

4. CONCLUSIONS

Results show that these low-cost bioadsorbent could be fruitfully used for the removal of fluoride over a wide range of concentrations. Treated bio adsorbents were observed to be efficient for the uptake of fluoride ions between 2.0 and 8.0 pH. Fluoride removal for a given bio adsorbent size increased with time attaining equilibrium within 2 h. The percentage of fluoride removal was found to be a function of adsorbent dosage and time at a given initial solute concentration.

Treated biosorbents can be disposed off safely by burning after use. Treated biosorbents are locally available and hence involve no expenditure on transportation and have a very low cost for pretreatment. There is no need to

regenerate the exhausted treated biosorbents as they are available abundantly, easily, cheaply and locally.

5. REFERENCES

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