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RESEARCH ARTICLE

Deflouridation from Aqueous Solutions Using Alum

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Abstract: This research work has been designed to remove the fluoride from aqueous solutions using alum by bench scale experiments. The defluoridating agent, which is easily available even in rural areas, has been selected. The known concentrations of fluoride solution were prepared. The removal of fluorides by the defluoridating agent was studied up to 4 hours for all the fluoride concentrations. The variations in the percentage removal and attainment of equilibrium were recorded. The solutions of 2, 4, 6, 8 and 10 mg/L were prepared. Each Fluoride concentration was tested with 100, 200 and 300 mg/L of alum. The removal of fluoride increased at the rate of 10% per hour up to 55% by 4 h for 100 and 200 mg/L while it rose from 40 to 60% by 4 h equilibration time in 300 mg/L alum solution it reaches 60%. The difference of fluoride removal between 100 and 300 mg/L alum concentrations was only 5% *i.e.* 0.9 and 0.8 mg/L of fluoride remained after 4 h equilibration time. All the concentrations of defluoridating agent have successfully reduced the fluoride content in waters to permissible limits.

Keywords: Deflouridation, Alum, Aqueous solutions, Equilibrium time, Batch tests

Introduction

Fluoride exists in many forms and the harmful nature of the fluoride is contingent upon the type of fluoride it is. Depending on its concentration, the fluoride in drinking water is known for both beneficial and detrimental effects on health, particularly to infants and young children. Fluoride is perhaps the only element whose deficiency (<0.5 ppm) as well as its presence in excess (>1.5 ppm) in drinking water has serious health implications. It is well known for its adverse health effects. It acts as an essential element up to 1.0 mg/L helping in teeth formation and strengthening of skeleton, beyond the limit it exerts negative impacts on the human health causing debilitating disease named "Fluorosis".

The optimum fluoride level in drinking water for general good health set by WHO is considered to be between 0.5 and 1.0 mg/L[1-3]. Fluoride concentrations in groundwater of some places in the world exceed the acceptable value; for example, in some area of Northeast China the fluoride concentration is about 4 mg/L. Fluoride removal from drinking water is presently a common practice worldwide.

To date, various methods to remove fluoride from groundwater have been proposed and applied in decades. Sedimentation with calcium and aluminum salts is one of the commonly used processes to eliminate fluoride. It can reduce the fluoride concentration to about 2 mg/L and can be used for fluoride-rich industrial wastewater treatment as well[4]. However, the process generates large amounts of fluoride-containing sludge and causes an unavoidable sludge treatment and disposal problem with increased costs[5]. Other methods, which include ion exchange, membrane (including reverse osmosis and nano-filtration), Donnan dialysis and integrated physiochemical and biological adsorption on active alumina, fly ash and carbon nano-tubbe *etc.*, have all been used for fluoride removal practice[6-12]. Among the various methods, it has been accepted that the ion exchange electro-dialysis and membrane processes are effective and can remove the fluoride to a suitable level. But they are expensive and require frequent regeneration of ion exchange beds or cleaning of the scaling and fouling on the membrane[5]. Although adsorption of defluoridation from drinking water by activated alumina was successfully demonstrated, the fluoride removal capacity changed significantly with pH value of water. In addition, it was found that the Al^{3+} ions released during the treatment process. Therefore, searching for cost-effective adsorbents remains an active theme in the research and practice of fluoride removal. In recent years, a lot of efforts have been devoted and some new cost-effective fluoride adsorbents, such as, zeolites and biomass material, like fishbone charcoal[13-14] as well as other novel adsorbents[15] have been identified and investigated.

The present work was initiated to find out an easy and practicable solution to the problem, more specifically with the following objectives (1) To remove fluorides from drinking water that contains 2,4,6,8 and 10 mg/L. (2) To study the defluoridating efficiency of alum and test the performance of this defluoridating agent at different concentrations *viz.*100, 200 and 300 mg/L. (3) To make defluoridation process user-friendly by avoiding complicated processes generally undertaken on bench scale experiments that are not practicable to the households.

Experimental

Alum was used to remove the fluorides from the drinking water. The concentrations of fluorides selected for removal from freshwater were 2, 4, 6, 8 and 10 ppm, that correspond to the levels of fluorides available in the natural waters of the fluoride infested areas in Guntur and Nalgonda districts of Andhra Pradesh. However, for the present study the distilled water was used to prepare the test solutions. The distilled water that was used for removal of fluorides did not contain more than 0.3 ppm and for every experiment a blank was also prepared.

The alum ($(Al_2SO_4)_3$ 18.H_2O) used for the experiments have been purchased in the commercially available form. For ascertaining consistency AR grade alum and other chemicals were used. Alum was administered as defluoridating agent in 100, 200 and 300 mg/L concentrations studied for the efficiency of fluoride removal. An optimum equilibration time has been identified for all the concentrations of fluorides with all the defluoridating agents. The experiment was run for all the fluoride concentrations and the quantum of fluorides removed from the respective concentrations by estimation after every 30 minutes up to 4 h. Many earlier workers have run the experiment for 120 minutes only. Since the present study is aimed at meeting the needs of the domestic sector with no addition of chemicals, maintenance of pH, additional contact time has been tried. In the pilot experiment from lowest to highest concentrations the removal continued to a considerable period beyond 120 minutes hence, the fluoride removal was tested up to four hours. The removal beyond 4 h was negligible and hence a four-hour equilibration time was adopted for all the series of experiments in the study.

The results of the fluoride removal are expressed as milligrams per litre (mg/L). After addition of defluoridating agent to all selected concentrations, the removal was measured for every half an hour up to 4 hours. The difference between the initial and final concentrations at every interval is reported as the fluoride removed. The removal efficiency of alum, was expressed in percent removals.

Estimation of fluoride concentrations

Estimation of fluoride concentrations has been carried out by adopting the procedure described in the NEERI Manual[16]. The reagents prepared for analysis are of AR grade and the solutions are prepared afresh whenever necessary. The procedure followed for estimation of fluoride is briefly described in the following account.

A standard curve (Figure 1) is prepared by plotting concentration of fluoride on x-axis and absorbance on y-axis with known concentrations of standard fluoride solutions of 1–15 mg/L at intervals of 1 mg/L (*i.e.* 1, 2, 3, 4, 5, ……. 15 mg/L). Standard stock solution of fluoride was prepared by dissolving 221.0 mg of anhydrous sodium fluoride in 1000 mL of distilled water to make a solution of each ml containing 1 mg.

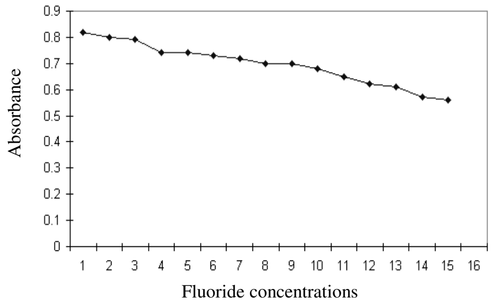

Figure 1. Calibration curve

To all the solutions containing a known concentration of fluorides, 10 mL of acid zyrconyl SPADNS reagent was added and the contents were mixed well and the optical density of the bleached colour was read in spectro-photometer (Elico Model No. 207/0535/II12) at 570 nm.

The same procedure was adopted for estimation of fluorides in the samples after administration of defluoridating agents at every half an hour up to 4 hours. Basing on the absorbance, the concentrations of the fluorides in the unknown samples are read from the calibration curve. The difference between two successive estimations was taken as the fluoride removed by the respective defluoridating agent. The pH during the experiments ranged between 7.2 to 7.6. The present study on defluoridation is only a bench scale experiment to select appropriate concentrations of defluoridating agents that suit to the requirements of the fluoride present in natural waters of various regions.

Results and Discussion

Fluorine in drinking waters is a detrimental factor to the standard of living and hence there have been many efforts to identify ways and means to decrease its concentrations in the drinking water. In the present study, the defluoridating agent, which was easily available even in rural areas, has been selected. The selected agent was tested for their defluoridation efficiency for the fluoride concentrations that are reported from natural waters. The known concentrations of fluoride solutions were prepared as per the procedures given in the literature[16].

During the experiment, removal of fluoride at half an hour intervals was calculated as described in the methodology. The removal of fluorides by the defluoridating agent was studied up to 4 hours for all the fluoride concentrations. The variations in the percentage removal and attainment of equilibrium are recorded. The solutions of 2, 4, 6, 8 and 10 mg/L were prepared as described in the method[16]. Each fluoride concentration was tested with 100, 200 and 300 mg/L of alum. The results of the defluoridation experiments for various concentrations are described in the following chapters.

Concentrations of alum on the defluoridation of water containing 2 mg/L fluoride

The water samples containing 2 mg/L fluoride has been treated with 100, 200 and 300 mg/L of alum concentrations. The concentration of the fluoride decreased to permissible limit within first half an hour. However, the percentage removal of fluoride was 35% for 100 and 40% for 200 mg/L of alum and the removal was 50% with 300 mg/L alum within half an hour (Table 1). The removal of fluoride increased at the rate of 10% per hour up to 55% by 4 h for 100 and 200 mg/L while it rose from 40 to 60% by 4 h equilibration time in 300 mg/L alum solution it reaches 60% shown in Figure 2. The difference of fluoride removal between 100 and 300 mg/L alum concentrations was only 5% *i.e.* 0.9 and 0.8 mg/L of fluoride remained after 4 h equilibration time. All the concentrations of defluoridating agents have successfully reduced the fluoride content in waters to permissible limits[17].

Table 1. Effect of different concentrations of alum on the defluoridation of water containing 2 mg/L fluoride

S. No.	Duration in hours	Alum concentration								
		100 mg/L			200 mg/L			300 mg/L		
		Fluoride remained	Fluoride removed	% Removal	Fluoride remained	Fluoride removed	% Removal	Fluoride remained	Fluoride removed	% Removal
1	0.5	1.3	0.7	35	1.2	0.8	40	1.0	1.0	50
2	1.0	1.2	0.8	40	1.2	0.8	40	1.0	1.0	50
3	1.5	1.2	0.8	40	1.1	0.9	45	0.9	1.1	55
4	2.0	1.1	0.9	45	1.1	0.9	45	0.8	1.2	60
5	2.5	1.1	0.9	45	1.0	1.0	50	0.8	1.2	60
6	3.0	1.0	1.0	50	0.9	1.1	55	0.8	1.2	60
7	3.5	0.9	1.1	55	0.9	1.1	55	0.8	1.2	60
8	4.0	0.9	1.1	55	0.8	1.2	60	0.8	1.2	60

Concentrations of alum on the defluoridation of water containing 4 mg/L fluoride

The alum concentrations when tried in 100, 200 and 300 mg/L concentrations to remove fluoride from the waters containing 4 mg/L concentration, the experiments showed a comparatively slower rate of removal with 20, 25.0 and 27.5%, respectively, by 100, 200 and 300 mg/L of alum solutions (Table 2). The highest removal in 100 mg/L of alum concentration was only 55% leaving behind 1.8 mg/L of fluoride in the sample and 1.8 mg/L of fluoride was left behind with 200 mg/L defluoridating solution while with 300 mg/L of alum concentration at 3.5 h of equilibration time, 2.4 mg/L of fluoride was removed leaving behind a fluoride content[18] of 1.6 mg/L (60% removal) shown in Figure 2.

Table 2. Effect of different concentrations of alum on the defluoridation of water containing 4 mg/L fluoride

S. No	Duration in hours	Alum concentration								
		100 mg/L			200 mg/L			300 mg/L		
		Fluoride remained	Fluoride removed	% Removal	Fluoride remained	Fluoride removed	% Removal	Fluoride remained	Fluoride removed	% Removal
1	0.5	3.2	0.8	20.0	3.0	1.0	25.0	2.9	1.1	27.5
2	1.0	3.1	0.9	22.5	2.9	1.1	27.5	2.3	1.7	42.5
3	1.5	3.0	1.0	25.0	2.8	1.2	30.0	2.2	1.8	45.0
4	2.0	2.8	1.2	30.0	2.6	1.4	35.0	2.0	2.0	50.0
5	2.5	2.5	1.5	37.5	2.2	1.8	45.0	1.8	2.2	55.0
6	3.0	2.0	2.0	50.0	1.9	2.1	52.5	1.6	2.4	60.0
7	3.5	1.9	2.1	52.5	1.8	2.2	55.0	1.6	2.4	60.0
8	4.0	1.8	2.2	55.0	1.8	2.2	55.0	1.6	2.4	60.0

Concentrations of alum on the defluoridation of water containing 6 mg/L fluoride

The fluoride removal was very slow initially from the water sample containing 6 mg/L of fluoride in all the three treatment concentrations of alum. However, it increased with increasing concentration of alum (Table 3). The maximum fluoride removed was 3.4, 3.6 and 3.7 in 100, 200 and 300 mg/L concentration of alum, respectively. The fluoride content after treatment in 300 mg/L at 4 h equilibration time was nearer to the permissible limit. There was a sudden increase of the rate of removal of fluoride from first half an hour to first one hour *viz*., from 10.0 to 15%, 16.7 to 26.7% and 21.7 to 30%. A maximum of 61.7% was removed with 300 mg/L of alum while 60% and 56.7% fluoride was removed with 200 and 100 mg/L of alum, respectively as shown in Figure 2.

Table 3. Effect of different concentrations of alum on the defluoridation of water containing 6 mg/L fluoride

S. No	Duration in hours	Alum concentration								
		100 mg/L			200 mg/L			300 mg/L		
		Fluoride remained	Fluoride removed	% Removal	Fluoride remained	Fluoride removed	% Removal	Fluoride remained	Fluoride removed	% Removal
1	0.5	5.4	0.6	10.0	5.0	1.0	16.7	4.7	1.3	21.7
2	1.0	5.1	0.9	15.0	4.4	1.6	26.7	4.2	1.8	30.0
3	1.5	4.4	1.6	26.7	3.6	2.4	40.0	3.1	2.9	48.4
4	2.0	3.3	2.7	45.0	2.9	3.1	51.7	2.9	3.1	51.7
5	2.5	3.1	2.9	48.3	2.6	3.4	56.7	2.7	3.3	55.0
6	3.0	2.8	3.2	53.3	2.5	3.5	58.3	2.6	3.4	56.7
7	3.5	2.6	3.4	56.7	2.4	3.6	60.0	2.5	3.5	58.5
8	4.0	2.6	3.4	56.7	2.4	3.6	60.0	2.3	3.7	61.7

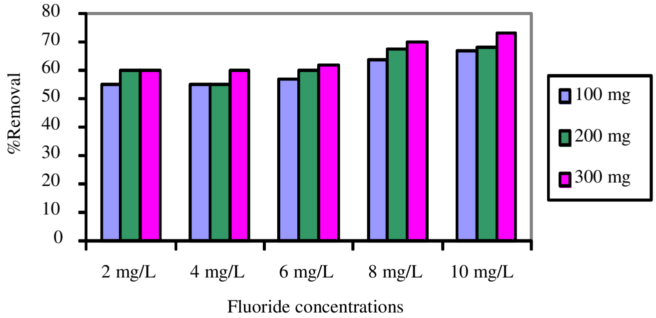

Figure 2. Graph showing the performance of alum, at 100, 200 and 300 mg/L concentrations in the defluoridation of 2, 4, 6, 8 and 10 mg/L fluoride concentrations from water

Concentrations of alum on the defluoridation of water containing 8 mg/L fluoride

The water sample containing 8 mg/L of fluoride has been subjected to defluoridation with 100, 200 and 300 mg/L of alum for a constant period of 4 h equilibration time. The rate of defluoridation was slow and less with 100 mg/L of alum in the initial stages however, at the equilibration time (4 h) there was only a difference of <10%. There was almost double the rate of removal of fluoride in 200 and 300 mg/L of alum concentrations (Table 4). The performance of 300 mg/L of defluoridating agent at 4 h equilibration time was comparatively better but the left over concentrations of the fluoride was about 2.4 mg/L higher than the permissible limit[19]. A maximum of 70% was removed with 300 mg/L of alum while 67.5% and 63.8% fluoride was removed with 200 and 100 mg/L of alum, respectively as shown in Figure 2.

Table 4. Effect of different concentrations of alum on the defluoridation of water containing 8 mg/L fluoride

S. No	Duration in hours	Alum concentration								
		100 mg/L			200 mg/L			300 mg/L		
		Fluoride remained	Fluoride removed	% Removal	Fluoride remained	Fluoride removed	% Removal	Fluoride remained	Fluoride removed	% Removal
1	0.5	6.7	1.3	16.30	5.8	2.2	27.5	5.2	2.8	35.0
2	1.0	6.0	2.0	25.0	5.2	2.8	35.0	4.8	3.2	40.0
3	1.5	5.5	2.5	31.3	4.7	3.3	41.3	4.2	3.8	47.5
4	2.0	4.7	3.3	41.3	4.0	4.0	50.0	3.7	4.3	53.8
5	2.5	3.4	4.6	57.5	3.3	4.7	58.5	3.0	5.0	62.5
6	3.0	3.3	4.7	58.8	3.1	4.9	61.3	2.7	5.3	66.3
7	3.5	3.2	4.8	60.0	3.0	5.0	62.5	2.6	5.4	67.5
8	4.0	2.9	5.1	63.8	2.6	5.4	67.5	2.4	5.6	70.0

Concentrations of alum on the defluoridation of water containing 10 mg/L fluoride

Defluoridation of water containing 10 mg/L of fluoride was tested with 100, 200 and 300 mg/L of alum for 4 h of equilibration time. Within first half an hour, 28, 34 and 41% of fluoride was removed from the water treated with 100, 200 and 300 mg/L of alum, respectively. Nearly one third of the fluoride was removed within half an hour. The removal increased with increasing concentration of alum (Table 5). A maximum of 73% was removed with 300 mg/L of alum while 68% and 67% fluoride was removed with 200 and 100 mg/L of alum[20], respectively as shown in Figure 2.

Table 5. Effect of different concentrations of alum on the defluoridation of water containing 10 mg/L fluoride

S. No	Duration in hours	100 mg/L			200 mg/L			300 mg/L		
		Fluoride remained	Fluoride removed	% Removal	Fluoride remained	Fluoride removed	% Removal	Fluoride remained	Fluoride removed	% Removal
1	0.5	7.2	2.8	28	606	3.4	34	5.9	4.1	41
2	1.0	6.5	3.5	35	6.0	4.0	40	5.5	4.5	45
3	1.5	6.0	4.0	40	5.4	4.6	46	4.0	6.0	60
4	2.0	5.1	4.9	49	4.3	5.7	57	3.9	6.1	61
5	2.5	4.3	5.7	57	3.9	6.1	61	3.7	6.3	63
6	3.0	3.9	6.1	61	3.5	6.5	65	3.5	6.5	65
7	3.5	3.5	6.5	65	3.2	6.8	68	3.3	6.7	67
8	4.0	3.3	6.7	67	3.2	6.8	68	2.7	7.3	73

Conclusion

The defluoridation from the aqueous solutions using low cost adsorbent (*i.e*., alum) has been carried out in batch experiments. The fluoride water samples were prepared with the known concentration of 2, 4, 6, 8 and 10 mg/L. Each fluoride concentration was tested with 100, 200 and 300 mg/L of alum. The removal of fluorides by the defluoridating agent was studied up to 4 hours for all the fluoride concentrations. The variations in the percentage removal and attainment of equilibrium were recorded. The higher concentrations of defluoridating agents proved effective in reducing the fluoride concentration in the water samples to the extent of 70%. In the lower concentrations of fluoride in water, 60% removal was recorded in the concentrations of defluoridating agent. Even at 60% removal, the left over fluorides were within the permissible limit for drinking water. All the concentrations of defluoridating agents have successfully reduced the fluoride content in waters to permissible limits. Based on the above said description, alum adsorbent could be used to remove fluoride selectively from aqueous solutions.

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