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The effect of *Amaranthus hybridus* on fluoride removal by iron (III) salts as fluoride coagulants

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The use of iron (Fe) (III) salts as fluoride coagulants in water is challenged by the requirement of high pH for maximum efficiency. At their natural pH, these salts have low fluoride removal efficiency. This study examines the effect of amaranth plants on enhancement of the defluoridation efficiency of Fe (III) salts as coagulants. *Amaranthus hybridus* plants were suspended in fluoride water treated with varying concentrations of Fe (III) with its roots immersed completely in fluoride water for varying time from 720 to 1440 min. The study shows that fluoride coagulation by Fe (III) in the absence of plants is limited to 10%, whereas when plants were introduced, it increased from 10 to 40%. These results suggest that amaranth plants enhance the defluoridation efficiency of Fe (III). This enhanced removal may be attributed to increased coagulation effected by exudates released by plant root which contain organic compounds and CO_2 or charged root surfaces by the formation of Fe (III) oxide film. The exact factor that has a major contribution to enhanced removal observed remains to be subject of further studies.

Key words: Coagulation, defluoridation, iron (III) salts, phytoremediation, plant exudates.

INTRODUCTION

Fluoride occurrence in surface and ground water is a global problem and is a cause of fluorosis in both humans and animals (Fawell et al., 2006) with over 200 million people at risk (Fawell et al., 2006). Ingestion of fluoride concentrations greater than 1.5 mg/L is associated with health problems, the more notable being dental fluorosis (Murray, 1986). Even though fluoride rich food materials such as fresh vegetables, meat, milk and some of the cereals can contribute to the total ingestion of fluoride (Radha et al., 2010), it is drinking water which is identified as the main contributor to fluorosis occurrence in humans (McClure, 1936; Ruiz-Payan et al., 2005).

There are several options imaginable to evade fluorosis, namely, (i) using water sources with fluoride level less than 1.5 mg/L, (ii) dilution of fluoride water with fluoride free water and (iii) defluoridation of drinking water. Defluoridation of drinking water however, is the only practical option to overcome the problem of

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excessive fluoride in drinking water, where alternative water source is not available. The widely studied fluoride removal methods include coagulation by alum and lime (Fawell et al., 2006; Emamjomeh and Sivar, 2009; Behbahani et al., 2011), ion exchange/adsorption (Bhatnagar et al., 2011; Zhong et al., 2013) and membrane filtration (Alkan et al., 2008; Sehn, 2009). Other methods tested include phyto-remediation by aquatic plants such as *Hydrilla verticillata* under laboratory and field conditions (Sinha et al., 2000) and a combination of these methods. Defluoridation by phytoremediation method did not receive considerable attention from researchers, understandably due to low fluoride uptake by used plants reported (thence low defluoridation efficiency) (Sinha et al., 2000), although some plants in general are reported to have good fluoride bioaccumulation property (Njenga et al., 2005; Khadare and Rao, 2006; Yadav et al., 2012; Patil et al., 2014). Phytoremediation is well-known in municipal wastewater and heavy metals contaminated soils and water (Wuana and Okieimen, 2011). In these plants, introduction of chemicals that form complexes with destined contaminant has enhanced its removal (Nowack et al., 2006; Wuana and Okieimen, 2011).

On the other hand, water defluoridation by coagulation is widely applied in what is commonly known as the Nalgonda technique (Fawell et al., 2006). In this technique, a mixture of alum and lime are employed to flocculate/coagulate and precipitate fluoride from water (Fawell et al., 2006). Challenges associated with this technique include (i) alkalinity of the treated water and (ii) presence of fluoro-alumino complexes in the treated water. Fe (III), tricalcium phosphate and Moringa seed powder are among the studied fluoride coagulants (Boruff, 1934; He and Cao, 1996; dos Santos Bazanella et al., 2012). The use of Fe (III) in fluoride coagulation is not widely reported in literature even though it is a potent fluoride coagulant. Since the optimal conditions for Fe (III) coagulation is in alkaline media, the low Fe (III) fluoride coagulation efficiency reported by Boruff (1934) could be due to this factor. This alkaline media is achieved when Fe (III) is used in combination with lime (Kerslake et al., 1946). This implies that the high pH challenge associated with the use of alum as coagulant cannot be avoided when Fe (III) is used instead. However, Fe (III) stands a better chance for acceptability and wide application as Fe is less toxic than Al.

Since the combination of phytoremediation and chemical action in water decontamination is already known to increase decontamination efficiency (Braen and Weinstein, 1985; Nowack et al., 2006; Wuana and Okieimen, 2011), this study investigated the combined effect of phytoremediation (by *Amaranthus hybridus*) and Fe (III) coagulation in defluoridation of water. *Amaranthus* species was selected based on its higher fluoride bioaccumulation reported (Njega et al., 2005; Yadav et al., 2012) and higher growth rate. The motivation for this was the fact that plants roots releases dissolved CO_2 and O_2 through respiration and photosynthesis, respectively, in species which are known to effect coagulation of Fe (III) in aqueous media (Devonshire, 1890; Kerslake et al., 1946).

Experimental procedures

The fluoride stock solution (1000 mg/L) was prepared from NaF by using standard procedures using distilled water (Anonymous, 1999). Lower concentrations were prepared by standard dilution of the stock solution to obtain 5, 10, 15, 20 and 25 mgF/L concentrations using tap water. The Fe(III) stock solution of concentration 1 M Fe(III) was prepared by standard procedures using reagent grade anhydrous ferric chloride (Anonymous, 1999). Other concentrations were obtained by appropriate dilution of this stock solution. The total ionic strength adjustment buffer (TISAB 2) was prepared by standard method using 1,2 cyclohexylene-diaminetetraacetic acid (1,2-CDTA).

Experimentation

To determine the effect of time, the roots of the 10 days old amaranth seedlings were washed carefully with tap water until visually clean wash water was obtained. The roots were then blotted by a clean and dry blotting paper such that no droplets were observable in root parts. Then 9 seedlings were immersed in 50 mL of 10 mg/L fluoride solution contained in 100 mL plastic beaker in triplicate. The setting was such that only roots of the nine seedlings were immersed completely into the containers with solution. The containers with plants were exposed to the sun light and left for up to 24 h. During this time, 10 mL of fluoride water were drawn from the reactor at intervals of 12, and 24 h for fluoride analysis by pH/ISE OrionMeter fluoride meter. Standard procedures were adhered to during fluoride analysis (Anonymous, 1999).

The effect of initial fluoride concentration was determined by putting 50 mL of the solutions whose concentrations were 0, 5, 10, 15, 20 and 25 mgF/L, into different containers in triplicate. Then, the roots of about nine amaranth seedlings were immersed completely in fluoride solution in each container for 12 h. The containers were exposed to the sun light and left for observation for 12 has stated above.

In determining the effect of pH on the fluoride removal efficiency, fluoride solution with pH and fluoride concentration of 5 and 10 mgF/L, respectively was prepared and filled in the three separate 50 mL plastic containers. Nine seedlings were introduced in each separate container and left in the sun light for 12 h after which the samples were analyzed as stated above. The procedure was repeated for pH 7 and 8. The various pHs were obtained by adjusting pH using 0.1 M NaOH and HCl.

The effect of Fe(III) on the extent of fluoride coagulation and precipitation was obtained by preparing the Fe (III) solution of concentration 10 mgF/L by diluting 10 mL of 1000 mgF/L fluoride standard to 1 L using 0.1 mM $FeCl_3$ aged solution in a 1 L plastic volumetric flask. This procedure was repeated using 1 and 10 mM $FeCl_3$ aged solutions. Then, 50 mL of each solution was treated with 9 seedlings for up to 12 h undisturbed as explained above. Then, the fluoride concentration of the residue solution was analyzed as explained above. To isolate the effect of iron (III) coagulation of fluoride, parallel experiments were conducted in the absence of plants for equal amount of time as experimental

Table 1. The effect of time, initial fluoride, pH and Fe (III) on fluoride removal.

Initial F (mg/L)	FRE1 (%)	FRE2 (%)	FRE3 (%)	Average	SD	SE	r
0	0	0	0	0	0	0	0.523915
5	0	2	0	0.666667	0.942809	0.544331	
10	1	4	3	2.666667	1.247219	0.720082	
15	13.33	6.77	13.33	11.14333	3.092414	1.785406	
20	25	30	20	25	4.082483	2.357023	
25	4	0	4	2.666667	1.885618	1.088662	
Time (hours)				**Mean**			
0	0	0	0	0	0	0	-0.188982
12	2	3	3	2.666667	0.471405	0.272166	
24	0	-1	-1	-0.66667	0.471405	0.272166	
pH				**Mean**			
5	10	20	20	16.66667	5.773503	3.333333	-0.96682
7	5	0	1	2	2.645751	1.527525	
8	0	2	0	0.666667	1.154701	0.666667	
Fe(III) concentration (mM)				**Mean**			
0.1	30	20	19	23	6.082763	3.511885	0.803581
1	30	40	40	36.66667	5.773503	3.333333	
10	30	50	50	43.33333	11.54701	6.666667	

FRE = Fluoride removal efficiency, SD = standard deviation, SE = relative standard deviation, r = correlation coefficient.

reactors.

RESULTS AND DISCUSSION

When the equilibration time was increased from 0 to 12 then to 24 h, the fluoride concentration in the remnant solution showed no significant change in concentration as shown in Table 1. The slight increase in fluoride concentration observed at 24 h could be associated with the leaching out of the previously up taken fluoride from the plant. The inability of the amaranthus to uptake fluoride from the solution to the extent of reducing its concentration regardless of its reported fluoride bioaccumulation capacity (Njega et al., 2005; Khadare and Rao, 2006) could be attributed to the fact that fluoride is not among the essential elements for plant growth/survival (Tucker, 1999; Silva and Uchida, 2000). It could also imply that the 3% removal efficiency after 12 h could be due to adsorption of fluoride on root surfaces which are later released. Plant showed slight wilting during the day time but regained their vigor next morning. As fluoride initial concentration was varied from 0 (tap water), 5, 10, 15, 20 to 25 mgF/L, the fluoride removal efficiencies varied from 2 to 25% with highest removal at 20 mg/L as shown in Table 1.

When the pH was varied from 5, 7 to 8 and the reactors left undisturbed for 12 h, the removal efficiency ranged from 2 to 10, with highest removal being 10% at pH 5. This implies that fluoride removal is higher in the acidic media than in alkaline media as shown in Figure 1. This enhanced removal in acidic media could be due to the charged root surfaces (Fawell et al., 2006; Bhatnagar et al., 2011) in acidic media or increased fluoride uptake (Jagtap et al., 2012).

When the seedling roots of the Amaranths were immersed in the fluoride solution with 0.1 mM $FeCl_3$ solution, the removal efficiency after 12 h was about 20%, for 1 mM $FeCl_3$ solution, the removal efficiency after 12 h was about 37%, for 10 mM $FeCl_3$ solution, the removal efficiency after 12 h was about 40% as shown in Table 1. When fluoridated solution of 10 mM Fe (III) was tested in open air but without plants for fluoride coagulation, it was found that only 10% of fluoride was removed. Therefore, some other processes than normal Fe (III) fluoride coagulation is involved to bring about increased fluoride removal when plants were immersed in fluoridated iron (III) solutions. Results of analyses of fluoride complexed by Fe (III) in variable time indicate that over 95% of fluoride present is analyzable by 1,2 CDTA prepared TISAB 2 as indicated in Figure 3.

On the other hand, the 0.1 Mm fluoridated Fe(III)

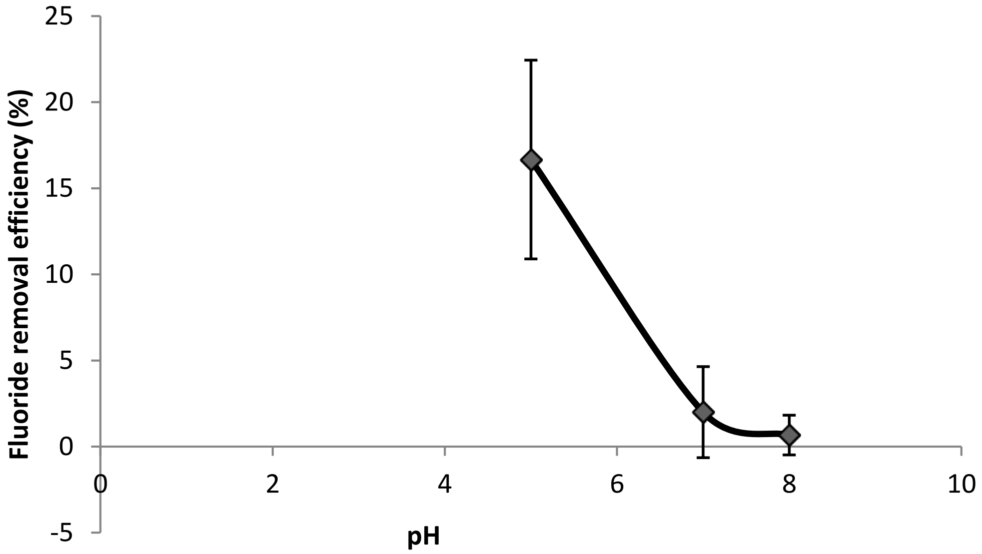

Figure 1. The effect of pH on fluoride removal by amaranth.

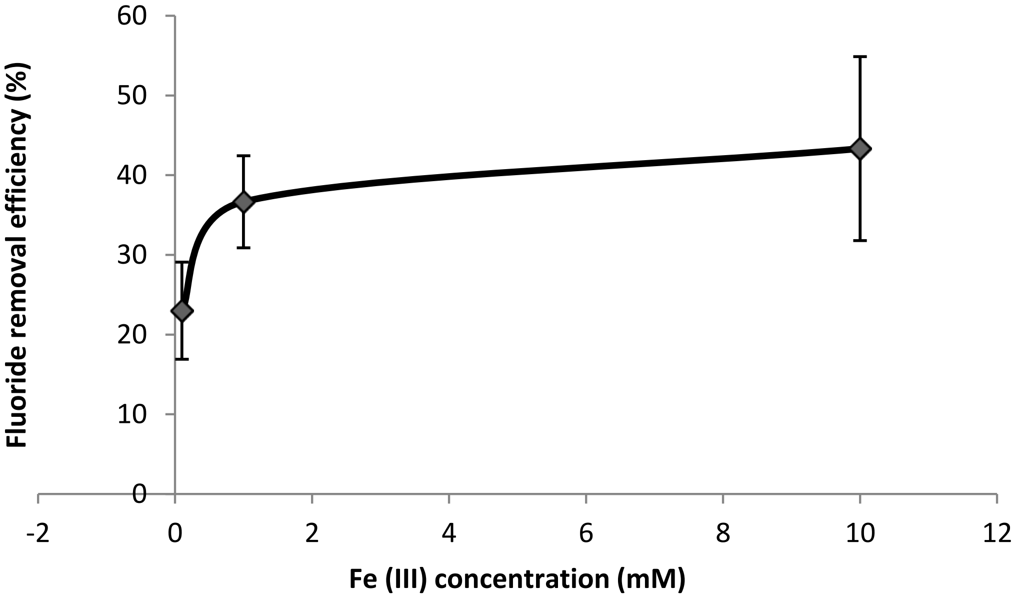

Figure 2. The effect of Fe (III) concentration on fluoride removal.

solution had pH reading of 5 at the start of experiments (Figure 2). Thus, the effect of pH could be suspected as the dominant factor for fluoride removal. However, comparison of the HCl induced and Fe (III) induced pH 5 showed that for HCl induced pH 5, only 10% fluoride removal efficiency was obtainable after 12 h while in Fe (III) induced pH 5, the removal rose to 20%. It can thus be fairly stated that the higher removal in Fe (III) is not from the effect of pH alone. The added efficiency of in Fe (III) treated fluoride may be contributed by a number of factors including plant exudates induced coagulation of Fe (III) and adsorption onto charged Fe (III) oxide film on root surfaces (Devonshire, 1890). This was supported by appearance of the solution in the plant treated reactor as compared to those that were not exposed to plants. The plant treated solution was flocculated at the end of the reaction and appeared slightly decolorized (with a decrease in absorbance from 2.88 to 1.06 at

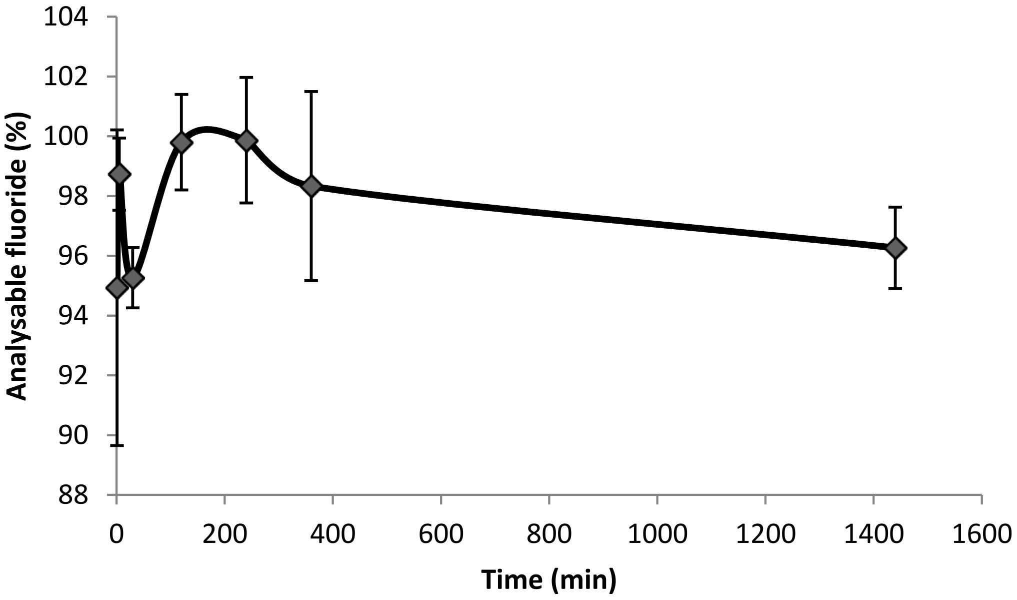

Figure 3. Effect of time on percentage analyzable fluoride in Fe (III) solution.

wavelength 425 nm) than the ones not exposed to plants.

From Table 1 and Figure 2, it is clear that there was high removal of fluoride by amaranthus when the Fe (III) was added. However, the amaranth plant wilting was higher at low pH and when Fe (III) was added. Since amaranth is not an aquatic and can thus not withstand water logging, the experiments could not be extended for times longer than 24 h.

CONCLUSION AND RECOMMENDATION

This work investigated the effect of amaranth plant roots in enhancing defluoridation efficiency of Fe (III) in batch reactors. From this work, it was found that, the peak fluoride removal efficiency at initial fluoride concentration of 10 mg/L was only 3%. Fe (III) increased this fluoride removal efficiency to about 40% with removal efficiency increasing with increasing concentration of Fe (III) in fluoride water. These findings suggest that fluoride coagulants such as Fe salts could be used in what is called chemical assisted phytoremediation of fluoride from water. Since amaranth is not an aquatic plant, further experiments are needed using a variety of aquatic plant species. It is thus recommended that further experiments be conducted using different types of aquatic plants, especially those that bioaccumulate Fe.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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