Fluoride removal from water using crushed limestone

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An examination of defluoridation by industrial grade limestone indicated that a combination of precipitation and adsorption of fluoride can be more effective for defluoridation of water. Pre-acidified fluoride water using two edible acids, viz., acetic acid (AA) and citric acid (CA) have been used for treatment by crushed limestone of diameter 3-4 mm to precipitate fluoride as CaF$_2$ in addition to adsorption of fluoride on limestone. The study has been carried out in batches by varying the acid concentration and contact time. Addition of the acids to the water before treatment with the crushed limestone in batch tests significantly improved the fluoride removal and this increased with the increase in the concentrations of the acids. The concentration of CA and AA required bringing down the fluoride concentration from 10 to 1.5 mg/L, are 0.05 M and 0.033 M, respectively, when the crushed limestone chips sample was used for the first time with contact time of 12 h. The acids are neutralized by limestone during the defluoridation process and the resulting final pH of the treated water was found to be in the ranges of 6.2 and 7.0 for CA and 5.7 and 7.0 for AA.

Keywords: Defluoridation, Limestone, Calcite, Acetic acid, Citric acid

Fluoride contamination of groundwater is a serious problem in several countries spread throughout the world as ingestion of excess fluoride, most commonly, through drinking contaminated groundwater causes fluorosis. Mainly two factors are responsible for contamination of groundwater with fluoride – geological and anthropogenic. Rock geochemistry has a major control on geological fluoride contamination. Physiological conditions of rock, like decomposition, dissociation and subsequent dissolution along with long residence time may be the responsible factors for F leaching. Among anthropogenic factors industrialization, urbanization and improper utilization of water resources are of prime importance, in case of the developing countries. Fluoride can be released in higher concentrations to the atmosphere than it occurs naturally, through a number of industrial processes. Some of them are the manufacture of cement and bricks, electronic industries, the refining of aluminium and the processing of slag from electric furnaces and from steel manufacture, where a fluoride flux is used.

Long term ingestion of fluoride in high doses can lead to severe skeletal fluorosis. In India the groundwater of most of the states contains high concentration of fluoride. Multidimensional health problems, mainly dental and skeletal fluorosis are prevalent in these states. The prevention of fluoride contamination of water is critical; however, fluoride removal from water is under practice for several decades to prevent fluorosis.

The principles underlying the fluoride removal are based on adsorption, precipitation–coagulation, ion-exchange, membrane separation process, electrolytic defluoridation, electrodialysis, etc. Some recently used adsorbent for fluoride are laterite, waste residue from alum manufacturing plant, activated carbon prepared from Morringa indica bark and Neem (Azadirachta indica) bark & Kikar leaves (Acacia arabica), alum-impregnated activated alumina, etc. Beyond these methods, there are miscellaneous methods for fluoride removal, e.g., nanofiltration, reverse osmosis, use of different adsorbent like bone char, sunflower (Helianthus annuus) plant dry powder, etc. Although some of these fluoride removal methods have the potential for use in treating wastewater, either due to low efficiency, high cost or production of huge amount of sludge containing fluoride they may not be preferable for application in fluoride removal from groundwater.

Calcium containing compounds/materials have been tried by several workers to remove fluoride from water due to the potentiality of this metal for this purpose. Addition of lime to precipitate fluoride can lower the fluoride concentration to about 1 mg/L but it increases the pH of water. Nalgonda technique, a
low cost method of fluoride removal which uses lime and alum also suffers from some disadvantages, viz., it adds toxic aluminium to the water and adjustment of the pH of water is necessary. Similarly, the method developed at the IISc, India also uses alkaline MgO and CaO followed by adjustment of pH with NaHSO₄ 31,32. Calcium hydroxide [Ca(OH)₂], calcium chloride [CaCl₂] and calcium sulphate [CaSO₄] have already been tried for fluoride removal 33. Calcium chloride and hydroxide 34, cement paste 35 and combined use of calcium salts as precipitant and polymeric aluminium hydroxide as coagulant have been studied for the fluoride removal by precipitation method. Another fact is that, when initial concentration of fluoride is large it is easier to precipitate fluoride as CaF₂ since it attains supersaturation level easily. However, when fluoride concentration is low, it is difficult to precipitate 36. So, it is a challenge to decrease the fluoride from lower strength, i.e., from 10-20 mg/L to drinking water level by precipitation method alone.

Limestone filtration as such has been found to reduce F⁻ concentration to 4 mg/L. Reardon and Wang 14 achieved F⁻ removal to below 2 mg/L by passing CO₂ through crushed limestone columns during filtration. Precipitation of CaF₂ by an increased Ca³⁺ activity in the limestone column due to dissolution of calcite by CO₂ was reported to be the main mechanism for the observed F⁻ removal. However, it may not be practical to have CO₂ canisters in remote rural areas. Thus, although there have been several attempts with different techniques on de-fluoridation of groundwater, the area still remains quite topical in view of the world-wide fluoride contamination in groundwater. This is mainly because a method which can be easily used by a layman and at the same time is cheap and effective in long term has yet to be definitely proven. It appears that the above mentioned precipitation or adsorption processes alone, without increasing the pH or adding other impurity to the water, are not capable of bringing fluoride level in water to below 2 mg/L, which is safe for drinking according to WHO and BIS 37,38. Therefore, it was thought worthwhile to carry out a systematic investigation of de-fluoridation of water by combination of precipitation and adsorption method with limestone. The studies on de-fluoridation by crushed limestone using acidified synthetic fluoride solutions in batches have been carried out. Two edible acids, viz., acetic acid (AA) and citric acid (CA) have been used in this study for pre-acidifying the fluoride containing water to generate high concentration of Ca²⁺ in the crushed limestone pack in situ due to dissolution of CaCO₃ by the acids. These edible acids have been chosen because they do not add any harmful contaminants or unpleasant taste to the treated water 39. The organic anions of the acids remaining, after neutralization by limestone, in the water also should not affect the acidity of gastric juice which is due to dissociation of HCl. Acetic acid can eliminate fatigue, because it is changed to citric acid by combining with oxaloacetic acid with the help of Coenzyme A and ATP (adenosine triphosphate) 39. Acetic acid has 1/60 power of hydrochloric acid, while citric acid has 1/180 power of hydrochloric acid. So, it is classified scientifically as one of the weaker acids, having no power to cause a heart burn 39.

**Experimental Procedure**

**Materials**

Acetic acid, citric acid and sodium fluoride (AR Grade, Merck Ltd.) were used. Distilled water was used for the preparation of F⁻ solutions (10 mg/L) by dissolving anhydrous sodium fluoride. Crude limestone and powdered limestone of particles size <170 µm were obtained from Bokajan Cement Factory, Bokajan, Assam, India. The crude limestone was crushed and the 3-4mm size segment was used for the experiments. The composition of limestone based on chemical analysis is given in Table 1.

**Analysis of fluoride, calcium and pH**

Concentrations of fluoride were measured on an Orion Multiparameter Kit ion meter using an Orion ion selective electrode for fluoride. TISAB-III was used to control ionic strength and de-complex fluoride. The calibration was done at 10, 1.0 and 0.1 mg/L standard sodium fluoride solutions. Calcium was determined by using an atomic absorption spectrophotometer - Perkin Elmer AA200. The pH was measured on a Systronics µ-pH System.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Composition</th>
<th>% Weight of dried material</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Calcium carbonate CaCO₃</td>
<td>85.0-90.0</td>
</tr>
<tr>
<td>2</td>
<td>Magnesium carbonate MgCO₃</td>
<td>0.8-1.6</td>
</tr>
<tr>
<td>3</td>
<td>Calcium oxide CaO</td>
<td>40.0-45.0</td>
</tr>
<tr>
<td>4</td>
<td>Magnesium oxide MgO</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>5</td>
<td>Silica SiO₂</td>
<td>10.0-14.0</td>
</tr>
<tr>
<td>6</td>
<td>Aluminium oxide Al₂O₃</td>
<td>4.0-5.0</td>
</tr>
<tr>
<td>7</td>
<td>Iron oxide Fe₂O₃</td>
<td>2.5-3.5</td>
</tr>
<tr>
<td>8</td>
<td>Loss on ignition</td>
<td>33.5-37.5</td>
</tr>
</tbody>
</table>
Defluoridation by limestone using acid treated water

Batch tests were carried out with crushed limestone using synthetic fluoride solutions pre-acidified with varying amounts of AA and CA. In the first batch tests with crushed limestone, a set of half liter size bottles were filled with 3-4 mm size limestone particles and 10 mg/L F⁻ solutions having varying concentrations of 0.016 to 0.20 M of AA were added to fill up to the top level of limestone. They were allowed to stand without shaking. Parts of the solutions were withdrawn after 3, 6 and 12 h by decantation; filtered using Whatman 42 filter paper and the concentration of F⁻ and final pH in the solutions were measured. The remaining solutions of the bottles were drained out. Fresh F⁻ solutions were put into the respective bottles for the next day containing the limestone packs. This experiment was repeated once a day for five consecutive days. The experiments were repeated with CA of varying concentrations from 0.01 to 0.10 M and crushed limestone chips of 3-4 mm.

Results and Discussion

Defluoridation by limestone using acid treated water

Batch test with added CA

The results of batch experiments of F⁻ removal with crushed limestone chips of 3-4 mm size, as a function of initial concentrations of CA up to 0.1 M are shown in Fig. 1. It can be seen from the figure that addition of the acid to water before treatment with crushed limestone lowers the F⁻ concentration from its initial value of 10 mg/L to below 2 mg/L, which is much better compared to the fluoride removal by limestone filtration alone. The ability of the crushed limestone chips to remove F⁻ increased with increasing the acid concentration. However, the removal became poorer with the number of repeated use (\(\eta\)) of the same lot of limestone chips. This happens due to the adsorption of fluoride onto the surface of the limestone. Turner et al. have shown that limestone can precipitate as well as adsorb fluoride. As the acid reacts with limestone generated Ca²⁺ and it precipitates as CaF₂. At the same time new surfaces of limestone are created and fluoride also gets adsorbed onto the surface. With increase in number of repeated use (\(\eta\)), adsorption of fluoride and calcium citrate on the limestone surface decreases the ability of the limestone for fluoride adsorption. An initial CA concentration of 0.05 M is required to bring the F⁻ concentrations from 10 to 1.98 mg/L when the crushed limestone chips sample was used for the first time with residence time (t) of 12 h. CA was added only up to 0.1 M because above that concentration, excessive precipitation of calcium citrate was observed as confirmed from IR and XRD data. Although this precipitate makes the water turbid, those were settled down on the bottom of the container on standing for 2-3 h. Thus the turbidity of the solution can be removed by filtration.

Batch test with added AA

The results of the batch experiments with AA and crushed limestone are shown in Fig. 2. Lowering of the F⁻ concentration from 10 to 1.5 mg/L was achieved with an initial concentration of 0.033 M of AA, which is not only better than limestone filtration alone but also better than limestone filtration with CO₂ bubbling. These batch test results also indicated a slightly better efficiency of AA in comparison to CA in F⁻ removal at equal concentration of the acids.
Moreover, one can see from Fig. 2 that the remaining F⁻ concentration can be further reduced to 1 mg/L on increasing [AA]₀ to 0.2 M. The F⁻ removal ability of the crushed limestone chips gradually decreased with η in the case of AA also. An important point to be noted here is that the in situ generation of high concentration Ca²⁺ ions by dissolving limestone with CA and AA can lower the F⁻ concentration much more than the crushed limestone chips alone as is evident from the results in Figs 1 and 2. Another interesting observations from the batch tests with crushed limestone and added acid is that the final pH of the water which come to the near neutral range and is acceptable for drinking. The final pH of the treated water was found to be between 7.0 to 6.2 and 7.0 to 5.7 for water pre-acidified with CA and AA, respectively, as shown in Figs 1 and 2 for η=1, 3 and 5. The slightly lower values of pH can be brought to the acceptable range for drinking by passing the water through a limestone column after this treatment. The final pH may also be maintained within the acceptable limit by optimization of the process parameters. Thus, the present method also has an advantage over use of MgO or CaO for defluoridation needing subsequent pH correction by adding more chemicals. It can be mentioned here that no odor of vinegar was observed in the treated water which can be attributed to the neutralization of the acetic acid by the limestone. Occurrence of precipitation of CaF²⁻ in the experiment can be proved by calculation of saturation index from the concentration of Ca²⁺ and F⁻ in the treated water which has been elaborated in the next section.

Saturation index of fluorite (SIₙ)

Saturation index of fluorite (CaF₂) in the water after the batch tests with the crushed limestone chips can be used to know whether precipitation of CaF₂ is a major mechanism of fluoride removal or not. A positive saturation index of fluorite (CaF₂), SIₙ in the water after treatment of the acidified water with crushed limestone indicates precipitation to control the F⁻ removal. The SIₙ of the solutions have been calculated using Eq. (1),

\[ \text{SI}_n = \log_{10}(Q/K_{sp}) \] (1)

where, \( Q = (\text{activity of Ca}^{2+})(\text{activity of F}^{-})^2 \) and \( K_{sp} = \text{fluorite solubility product} \).

The SI values for acetic acid have been found within the range of 0.07 to 0.2 and for citric acid the range was 0.01 to 0.7. All the values are positive, which indicates precipitation to control the F⁻ removal. However, since adsorption of fluoride from water over calcite has been already known, the same may also take place along with precipitation in the present case.

The excess free Ca²⁺ ions generated by the dissolution of limestone by the acids combine with the F⁻ present in water are precipitated. The Ca²⁺ concentration in the treated water was found to be within the range of 8 mg/L initially which increased to 109 mg/L on repeated use of the same limestone sample for both the acids. Thus the values of Ca²⁺ concentration remain within soft or moderately soft range of total hardness. The moderate hardness can be removed by simple methods by using water softeners. However, the slight increase in [Ca²⁺] above the desirable limit can be removed or may be acceptable as the increased Ca²⁺ concentration may also work as a potential calcium supplement for patients of fluorosis and osteosporosis. An analysis of the treated water showed that no harmful chemicals such as Pb or Hg were leached from the limestone during the process.

Effect of contact time

The dependence of the removal of F⁻ on contact time, t with crushed limestone in the batch was examined by measuring remaining F⁻ concentration in water samples withdrawn from the containers after t = 3, 6 and 12 h and the results are presented in Fig. 3. The removal of F⁻ was found to increase with increasing the contact time. In the case of CA, the slope rapidly decreased to almost zero at 0.10 M. This means, the fluoride removal attains equilibrium fast on the first use of the crushed limestone and the equilibration time increases with η in the case of CA. In the case of AA the removal continued to improve even beyond 12 h up to the acid concentration of 0.10 M. The remaining F⁻ concentration decreased almost linearly with time within the experimental range of 12 h. The slope slightly decreased with increasing the concentration of the acid. This indicates that at higher concentration of the acid the F⁻ removal is not only more but also quicker. It can be seen from Figs 3 and 4 that the equilibration times for F⁻ removal in the presence of 0.1 M CA and AA are about 6 and 12 h, respectively and the equilibration time increases with decrease in the concentration of the acids in both cases.
Cost effectiveness and suitability

Limestone is a very low-cost material. Therefore, the cost of the present fluoride removal method is practically due to the cost of the acid only. Considering the present market price of AA and CA as Rs. 100/- and 125/- per kg, respectively, the cost of fluoride removal by the present method should be within Rs. 0.50 per liter of water. Moreover, availability of limestone near some fluoride affected areas, e.g., that of central Assam, is an added advantage of the present method.

Conclusions

The results of the batch study with crushed limestone and fluoride solutions acidified with the edible acids show that both CA and AA can reduce the fluoride concentration from 10 to 1.74 mg/L and 0.977 mg/L, respectively, without affecting the taste and colour. Although, adsorption of fluoride on limestone surface takes place, precipitation is the major mechanism of fluoride removal in the batch tests with acidified fluoride containing water and crushed limestone. Therefore, limestone defluoridation of fluoride containing water pretreated with CA and AA can be potential ways of removing fluoride from water.

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