A comprehensive treatment method for defluoridation of drinking water

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The fluoride concentration in ground water is increasing at an alarming rate. Poor ground water recharge, excessive consumption of water and other geological factors contribute to this effect. Conventional reverse osmosis (RO) membrane system has failed because fluoride concentration in permeate is not consistently below 1 mg/L. Moreover, the reject stream of the RO process containing higher fluoride concentration is left untreated. A treatment method has been devised with an objective to reduce fluoride concentration to less than 1 mg/L from fluoride contaminated water using calcium carbonate pretreatment and reverse osmosis. Also a passive adsorption system to treat the reject stream of membrane process has been developed wherein the fluoride concentration in the final effluent is below ambient concentration. This combined system can be used to treat fluoride contaminated water without generating secondary wastes.

Keywords: Fluoride, drinking water, defluoridation

Scarcity of safe drinking water and contamination of water bodies is a major problem at present in India. Fluoride contamination in potable water is one of these and is prevalent in many states like Andhra Pradesh, Rajasthan and Tamilnadu. As per Indian standards, the desirable concentration of fluorine as fluoride ions in drinking water is less than 1 mg/L and the permissible limit in the absence of any other sources is 1.5 mg/L. However, in contaminated regions the fluoride concentrations are as high as 48 mg/L. Consumption of fluoride contaminated water causes dental and skeletal fluorosis. Several processes have been reported on fluoride removal from drinking water. Table 1 gives a comparison of the different methods. Experiments have been reported in literature regarding the use of cement paste for fluoride uptake from acidic effluents. However, these methods were not applied to raw water and the fluoride levels could not be reduced to less than 1 mg/L. A complete review of the recent defluoridation techniques including membrane methods and adsorption technique has been reported. The various adsorbents that have been used for fluoride removal are alumina, alumina in combination with manganese dioxide, iron oxide, calcium minerals. Also several clays and soils have been tried as an adsorbent medium for defluoridation elsewhere. A technology for the granulation of Fe-Al-Ce nano-adsorbent (Fe-Al-Ce) in a fluidized bed has also been developed.

Defluoridation works based on membrane techniques have also been reported in Finland. Similarly experiments have also been reported on the use of reverse osmosis (RO) membranes for fluoride removal from contaminated water sources. However, this technique has not been successful due to low permeate fluxes. Moreover, the process also generates more concentrated waste as reject. This paper describes the use of a combination of calcium carbonate pretreatment followed by membrane separation to reduce the final fluoride concentrations to 1 mg/L. Also an innovative adsorption system for treatment of the reject water is described in this paper. Effects of space velocity and coexisting ions have been investigated elsewhere in packed column filled with calcite. This total system ensures efficient water management, wherein there is minimal wastage of ground water.

Experimental Procedure

Experiments were conducted with feed solutions containing about 10 to 30 mg/L fluoride ions. All reagents used for simulation and analysis were of LR grade. The simulated water was then pumped through a water purification set-up. The schematic of the set-up is shown in Fig. 1. The purification unit consisted of a calcium carbonate column for pretreatment, a 5 micron prefilter to remove the suspended solids and

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a reverse osmosis membrane. Commercial grade calcium carbonate crystals were used for pre-treatment. The membrane is a standard domestic spiral wound polyamide membrane with pore size 0.1 nm. The raw water was first analysed for anions and cations using an ion chromatograph of Metrohm make. A typical chromatogram indicating the concentrations of anions and cations in a feed solution is shown in Figs 2 and 3, respectively. The permeate stream of the membrane is collected separately and is analysed for fluoride periodically. The analyses of fluoride ions in permeate and reject samples were also determined by using ion specific electrode (PHM 240 pH/ionmeter, Radiometer Analytical). The reject stream of the membrane is collected in an overhead reject storage tank. The reject from here is passed through a percolation pit. As shown in Fig. 4, the pit consists of concentric pipes. The pit is filled with commercial grade calcium carbonate. The solution flows from top at the centre and subsequently flows upward in the next chamber as shown. The pit is designed in such a way that the reject solution spends sufficient residence time within it, such that the fluoride levels at the outlet are lowered considerably below the ambient concentrations in a short volume.

Results and Discussion

Initial experiments were done by passing fluoride containing feed solutions (9.6 to 22 mg/L) through the RO membrane set-up without passing through the calcium carbonate pretreatment column and it was found that the maximum rejection of fluoride was only 65.5% at lower feed fluoride concentrations. The results obtained are shown in Table 2. It was also observed that the fluoride levels in the permeate was greater than 1 mg/L. By introducing a calcium carbonate pretreatment column before the RO membrane, it was found that the fluoride rejection increased to a maximum of 93.5%. The results obtained are shown in Table 3. The calcium carbonate aids in increasing the alkalinity of the feed water, which in turn helps in effective combination of fluoride ions with calcium. This increases the

<table>
<thead>
<tr>
<th>Technique</th>
<th>Removal efficiency</th>
<th>Working pH</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Precipitation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alum</td>
<td>&gt;90%</td>
<td>Non-specific</td>
<td>Sludge produced treated water is acidic, residual aluminium present</td>
</tr>
<tr>
<td>Lime</td>
<td>&gt;90%</td>
<td>Non-specific</td>
<td>Sludge produced treated water is alkaline</td>
</tr>
<tr>
<td>Alum+lime (Nalagonda)</td>
<td>70-90%</td>
<td>6.5</td>
<td>Sludge produced high chemical dose, residual aluminium present</td>
</tr>
<tr>
<td>Calcium chloride</td>
<td>&gt;90%</td>
<td>6.5 – 8.0</td>
<td></td>
</tr>
<tr>
<td><strong>Adsorption/Ion exchange</strong></td>
<td></td>
<td>&lt;3.0</td>
<td></td>
</tr>
<tr>
<td>Activated carbon</td>
<td>&gt;90%</td>
<td></td>
<td>Many interferences large pH changes before and after treatment</td>
</tr>
<tr>
<td>Zeolites</td>
<td>&gt;90%</td>
<td>Non-specific</td>
<td>Poor capacity</td>
</tr>
<tr>
<td>Activated alumina</td>
<td>85-95%</td>
<td>5.5</td>
<td>Spent regenerated solution contains fluoride, chemical and sludge handling needed, efficiency depends on source water</td>
</tr>
<tr>
<td><strong>Other methods</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electro dialysis</td>
<td>85-95%</td>
<td>Non-specific</td>
<td>High water loss high energy consumption high capital costs</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>85-95%</td>
<td>Non-specific</td>
<td>High water loss high energy consumption high capital costs</td>
</tr>
</tbody>
</table>

Fig. 1– Schematic of the water purification process
Table 2 – Experimental results for fluoride rejection with RO only and without calcium carbonate pretreatment

<table>
<thead>
<tr>
<th>Sl.no.</th>
<th>Fluoride concentration (mg/L)</th>
<th>Fluoride rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.2</td>
<td>14.8</td>
</tr>
<tr>
<td>2</td>
<td>20.0</td>
<td>14.5</td>
</tr>
<tr>
<td>3</td>
<td>14.0</td>
<td>8.2</td>
</tr>
<tr>
<td>4</td>
<td>22.0</td>
<td>7.6</td>
</tr>
<tr>
<td>5</td>
<td>20.0</td>
<td>14.2</td>
</tr>
<tr>
<td>6</td>
<td>9.6</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Table 3 – Experimental results for fluoride rejection with RO and calcium carbonate pretreatment

<table>
<thead>
<tr>
<th>Sl.no.</th>
<th>Fluoride concentration (mg/L)</th>
<th>Fluoride rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>4.0</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>4.5</td>
</tr>
<tr>
<td>3</td>
<td>32</td>
<td>3.5</td>
</tr>
<tr>
<td>4</td>
<td>22</td>
<td>2.4</td>
</tr>
<tr>
<td>5</td>
<td>14</td>
<td>0.91</td>
</tr>
<tr>
<td>6</td>
<td>13</td>
<td>0.98</td>
</tr>
<tr>
<td>7</td>
<td>12.6</td>
<td>1.1</td>
</tr>
<tr>
<td>8</td>
<td>8.74</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Table 4 – Typical concentrations of anions in permeate and reject solutions after calcium carbonate pretreatment and RO

<table>
<thead>
<tr>
<th>pH</th>
<th>Permeate</th>
<th>Reject</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conductivity (µS/cm)</td>
<td>Conductivity (µS/cm)</td>
</tr>
<tr>
<td>7.4</td>
<td>19.8</td>
<td>600</td>
</tr>
</tbody>
</table>
molecular size, higher than the molecular weight cutoff of the membrane and hence higher rejection is obtained. A typical anion analysis of permeate and reject streams of the RO membrane with calcium carbonate pretreatment is shown in Table 4. It can be seen that the fluoride concentration in the permeate is 0.2 mg/L, which is less than the prescribed limit of 1 mg/L. It was also observed that the conductivity of permeate after the RO membrane was in the range 15 to 20 μS/cm. In order to increase the conductivity of the final permeate to 100 μS/cm, remineralisation was done by dosing sodium bicarbonate and calcium chloride. In order to minimize excessive water loss as reject, experiments were done with hollow fiber ultrafiltration membranes in the same set-up with calcium carbonate pretreatment. But it was found that the fluoride rejection was only 26 to 41.2%. The results are shown in Table 5.

Experiments were conducted with a percolation pit designed to reduce the fluoride concentrations in reject water and it was found that a residence time of 48 h is required to lower the concentrations of fluoride in the reject to less than 1 mg/L. Table 6 shows results for fluoride uptake for various residence times within the percolation pit. The reject solution entering the percolation pit contains about 14 mg/L fluoride. The flow rate to the pit is maintained at 20 mL/min under these operating conditions, the adsorption capacity of calcium carbonate was found to be 0.03 mg/g compared to 0.2 mg/g for natural aluminium hydroxide and 1.08 mg/g for activated alumina. The low adsorption capacities of calcium carbonate is due to the operation of the columns in non-equilibrium conditions. Equilibrium and kinetic studies have also been well investigated. Figure 5 shows the fluoride concentration breakthrough at the outlet of the percolation pit for a residence time of 48 h. It was observed that the fluoride levels gradually increases from 1.4 mg/L to 3.6 mg/L after 11 days of continuous operation.

**Conclusions**

When hollow fiber ultrafiltration membranes were used with calcium carbonate pretreatment, there was no significant fluoride rejection. Thus, RO membrane with pore size of 0.1 nm was essential for significant rejection of fluoride. Also, with RO alone and no calcium carbonate pretreatment, there was only 18 to 65% rejection of fluoride. When the fluoride concentrations in the feed are higher, the fluoride rejection is insignificant. But finally when the fluoride contaminated solution was passed through the calcium carbonate pretreatment column followed by RO membrane, 78 to 93.5% fluoride rejection was observed. The fluoride rejection was consistently above 85% irrespective of feed concentration and the fluoride concentrations in the permeate was consistently below 1 mg/L. This established the fact that calcium carbonate pretreatment followed RO was essential for effective fluoride removal. The outlet of

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**Table 5 – Experimental results for fluoride rejection with hollow fiber ultrafiltration membrane**

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Feed fluoride concentration (mg/L)</th>
<th>Permeate fluoride concentration (mg/L)</th>
<th>Fluoride rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.5</td>
<td>4.41</td>
<td>32.0</td>
</tr>
<tr>
<td>2</td>
<td>6.5</td>
<td>3.82</td>
<td>41.2</td>
</tr>
<tr>
<td>3</td>
<td>6.5</td>
<td>4.53</td>
<td>30.3</td>
</tr>
<tr>
<td>4</td>
<td>6.5</td>
<td>4.49</td>
<td>30.9</td>
</tr>
<tr>
<td>5</td>
<td>6.5</td>
<td>4.82</td>
<td>26.0</td>
</tr>
</tbody>
</table>

**Table 6 – Results of percolation pit experiments (effect of residence time)**

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Initial fluoride concentration (mg/L)</th>
<th>Flow rate (mL/min)</th>
<th>Residence time (h)</th>
<th>Final fluoride concentration (mg/L)</th>
<th>Percent removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.8</td>
<td>20</td>
<td>46</td>
<td>0.4</td>
<td>97.1</td>
</tr>
<tr>
<td>2</td>
<td>13.8</td>
<td>100</td>
<td>9.2</td>
<td>2.4</td>
<td>82.6</td>
</tr>
<tr>
<td>3</td>
<td>13.8</td>
<td>225</td>
<td>4.0</td>
<td>4.5</td>
<td>67.4</td>
</tr>
</tbody>
</table>
the RO process which also releases a concentrated reject stream was passed through percolation pits filled with calcium carbonate. Here the fluoride concentrations can be lowered to values much lower than ambient levels when the solution spends a residence time of 48 h. Fluoride ions get precipitated as calcium fluoride in the central portion of the concentric pipe system and it gets adsorbed in the outermost pipes.

However, it was also observed that the outlet fluoride concentration gradually increases with time and indicates bed exhaustion. The regeneration of the calcium carbonate is carried out with 0.1 N hydrochloric acid and rinsing with water. The calcium fluoride that precipitates in the pit can be used as a raw material in cement, glass fluorspar and steel industries\textsuperscript{10}. Thus an economical procedure for fluoride removal from contaminated drinking water has been devised, wherein there is no secondary waste generation.

References
1 Drinking water specification Indian Standard IS 10500: 1991 Ed 2.2