REMOVAL OF FLUORIDE IN DRINKING WATER BY GREEN CHEMICAL APPROACH

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ABSTRACT

Aluminum oxalate as adsorbent was used by authors for preparing traditional soil pots to minimize fluoride content in drinking water samples. The adsorbent dose was varied in the range of 2 g to 8 g per 500 g soil. Langmuir and Freundlich isotherms curves were also plotted. pH, TDS, hardness, fluoride and aluminum parameters were also examined in residual water samples. Maximum fluoride removal efficiency of adsorbent was studied.

Aluminum oxalate

Key words: Fluorosis, Defluoridation, Adsorption.

INTRODUCTION

The prolonged intake of water containing excess of fluoride (> 1.5 ppm WHO limit) causes the crippling disease called fluorosis. The first case of endemic fluorosis in India was reported from Andhra Pradesh in 1937. At least 17 Indian states including Rajasthan have been identified as having excess fluoride in drinking water. All the 33 districts in Rajasthan are endemic for fluorosis. According to WHO 20% villages out of total fluoride affected village in the world are found in India and out of total affected villages in India 52% are in Rajasthan. It is to be noted that not only India but also several other nations in the world are severely affected by the problem of fluorosis.

Fluorosis, a disease caused by excessive intake of fluoride, Fluorosis disease is mainly of two types: Dental and Skeletal Fluorosis.

• Dental fluorosis (Fluoride intake > 1.5 ppm)
• Skeletal fluorosis (Fluoride > 3.0 ppm)
Chemical change of bone & teeth minerals is shown in Eq. 1.

\[
\begin{align*}
[3\text{Ca}_3(\text{PO}_4)_2\text{Ca}(\text{OH})_2] + 2\text{F}^- & \rightarrow [3\text{Ca}_3(\text{PO}_4)_2\text{CaF}_2] \\
\text{Hydroxyapatite} & \rightarrow \text{Calcium fluoroapatite}
\end{align*}
\]

(1)

Commonly used domestic defluoridation processes various defluoridation methods are used for removal of fluoride from drinking water. These exiting methods for defluoridation of drinking water is expensive, slow, in efficient, unhygienic and highly technical.

1. Nalgonda technique (Flocculation and Sedimentation)
2. Activated alumina process (Adsorption)
3. KRASS Process
4. Other processes (Bio-remedial, Ion exchange, R.O. etc.)

**New defluoridation method by- green chemical approach**

A comparative study of degree of toxicity of NaF, NaSiF₆, CaF₂, CaSiF₆, MgF₂, ZnF₂, AlF₃ and CuF₂ showed that calcium and aluminum fluoride are less toxic than other fluoride³. Therefore, in present paper authors used aluminum oxalate as defluoridating agents in soil pots and developed a new defluoridation method.

**EXPERIMENTAL**

The following investigations were conducted to find out the fluoride minimizing capacity of aluminum oxalate in the water samples kept in the soil pots.

**Determination of different physical and chemical parameters of water samples**

The pH, TDS and Al ion concentration were determined by the standard procedures. Result of these parameters shows that the values of all parameters in water samples are in their desirable limits.

**Preparation of soil pots**

Four soil pots (A, B, C and D) were prepared after incorporation of aluminum oxalate (2 g., 4 g., 6 g and 8 g.) in 500 g. of soil respectively as shown in flow chart given below²,⁵-⁷.

**Determination of fluoride concentration**

Fluoride concentration of untreated sample and the treated fluoride water samples was determined as per the standard procedure by ion selective method by Orion 720⁺ after time interval of 3, 24, 48 and 72 hours. Results are given in Fig. 1

![Proposed defluoridated Soil Pots](image)

**Fig. 1: Proposed soil pots**
RESULTS AND DISCUSSION

Investigation pertaining to the effect of increasing of aluminum oxalate in the soil pot on the fluoride concentration in Fig. 2 shows that the fluoride concentration of water sample (10 mg/L fluoride) decreases in the all soil pots with increasing amounts of aluminum oxalate at contact time periods. It is noticed that soil pot No-1 (having 2 g C₆Al₂O₁₂), decreases the fluoride concentration of the water sample about 20% but in case of soil pot No. 3 (having 6 g C₆Al₂O₁₂), the concentration of fluoride decreases about 70% at time interval 72 hours. This can be explained on the basis of surface chemistry. It is a general phenomena of surface chemistry that more the surface area of adsorbent more the adsorbate are adsorbed on the surface of adsorbent to form a unimolecular layer (Langmuir isotherm limitation) of adsorbent during chemsorption process. Result shows that a certain amount of aluminum oxalate reduces the fluoride concentration in the water sample.

Fig. 2: Concentration of fluoride ions in different soil pots

The removal of fluoride from water sample (10 mg/L) is expected due to the formation of polyhydroxide aluminum complex (e.g. [Al(H₂O)₃(OH)₃] [Al(H₂O)₂(OH)₄] etc.) with fluoride and adsorption of fluoride on polymeric aluminum oxalate.

\[
\text{Aluminum oxalate + Fluoride contaminated} \quad \text{effective hydrolysis} \quad \text{Polyfluro polyhydroxide water}
\]

\[
\text{aluminum complex (10 mg/LF')} +
\]

\[
\text{Adsorption of fluoride on Polymeric aluminum hydroxide}
\]

The linear Langmuir plots between Ce/x and Ce are shown in the Fig. 3-6. The linear Freundlich isotherm models are shown in the Fig. 7-10 by plotting log x/log Ce. The constant values of the both isotherms for each soil pot are given in the Table 1. It is observed from the curves and the correlation coefficient data that the fluoride adsorption follows neither Langmuir isotherm nor Freundlich isotherm in a perfect way. However, it follows Langmuir isotherm in a better way. The value of n is always less then unity, which indicates that, none of the soil pots have completely energetically homogeneous surface. This can be explained that all the four soil pots are associated with certain amounts of aluminum oxalate at certain specific sites having different activation energy. The adsorption involves attractive electrostatic interaction between the negative sites created by the ionization of the sodium fluoride and the positively charged Al³⁺ cations.
Figure 3: Linear Langmuir plot for soil pot no A

Figure 4: Linear Langmuir plot for soil pot no B

Figure 5: Linear Langmuir plot for soil pot no C

Figure 6: Linear Langmuir plot for soil pot no D
Figure 7: Linear Freundlich plot for soil pot no A

Log x vs Log Ce

Log x: 0.954242509, 0.903632516, 0.848189117, 0.838849091
Log Ce: 0.954242509, 0.903632516, 0.848189117, 0.838849091

Figure 8: Linear Freundlich plot for soil pot no B

Log x vs Log Ce

Log x: 0.963787827, 0.905256049, 0.843855423, 0.838219222
Log Ce: 0.963787827, 0.905256049, 0.843855423, 0.838219222

Figure 9: Linear Freundlich plot for soil pot no C

Log x vs Log Ce

Log x: 0.926342447, 0.755112256, 0.671172843, 0.567026366
Log Ce: 0.926342447, 0.755112256, 0.671172843, 0.567026366

Figure 10: Linear Freundlich plot for soil pot no D

Log x vs Log Ce

Log x: 0.931457871, 0.939019776, 0.969814644, 0.841984805
Log Ce: 0.931457871, 0.939019776, 0.969814644, 0.841984805
(1) Dried in sun light
(2) Crushed and sieved

Particle of appropriate size (0.164 Å)

Dried in hot air over at 80°C–100°C

(1) Incorporating of Aluminum oxalate
(2) Preparation of soil pots and fired

Soil ready for use

Soil pots ready for defluoridation

Added fluoride water Sample in soil pots

Testing of fluoride after 3 hrs, 24 hrs, 48 hrs and 72 hrs

Fig. 11: Flow chart of adsorbent (soil pots) preparation and fluoride adsorption on to soil pots

Table 1: Langmuir and Freundlich equation constants for adsorption of fluoride ions on different soil pots

<table>
<thead>
<tr>
<th>Soil Pots No.</th>
<th>C₆Al₂O₁₂ in soil pots (g/500 g soil)</th>
<th>Langmuir equation constants</th>
<th>Freundlich equation constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>xₘ (mg/g)</td>
<td>k</td>
</tr>
<tr>
<td>1</td>
<td>2 g</td>
<td>0.487075</td>
<td>-0.17016</td>
</tr>
<tr>
<td>2</td>
<td>4 g</td>
<td>0.46465</td>
<td>-0.16922</td>
</tr>
<tr>
<td>3</td>
<td>6 g</td>
<td>1.807318</td>
<td>-0.36847</td>
</tr>
<tr>
<td>4</td>
<td>8 g</td>
<td>0.203617</td>
<td>-0.13747</td>
</tr>
</tbody>
</table>

CONCLUSION

(i) Adsorption isotherm of fluoride ions follows the mixed model of the Langmuir and Freundlich isotherm. The adsorption does not depend on the BET surface area of the pots and takes place on certain specific site.

(ii) Aluminum oxalate can be used as defluoridating agent in soil pots without effecting the environment as a Green Chemical Approach.

REFERENCES


