Removal of fluoride ion from aqueous bodies by aluminium complexed amino phosphonic acid type resins

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Three resins, namely Purolite S940, Purolite S950 and Duolite ES467 were studied for the removal of fluoride ion under different equilibrium conditions. The adsorption data of Purolite S940 and Purolite S950 closely fitted in Freundlich and Langmuir equations, respectively. Validity of the Lagergan equation for the sorption of fluoride ion was proved and the data showed that the process followed first order kinetics. The performance of Purolite S940 and Purolite S950 showed good promise for removing fluoride from water whereas the performance of Duolite ES467 was comparatively poor under dynamic conditions.

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Adsorption at solid–solution interface is an important means for controlling the extent of pollution due to metallic/non-metallic species of industrial effluents/polluted water. Numerous techniques exist for removal of toxic ions, such as chemical precipitation as an insoluble salt, sorption (adsorption, ion-exchange, and precipitation/co-precipitation), distillation, reverse osmosis, electro osmosis, solvent extraction and foam flotation have been reported to be promising and effective.

Among other different toxic ions, fluoride is one of potentially very toxic ion whose presence in water causes diseases in living organism. During the past few years, interest has been increasing in the problem of excessive fluoride in drinking water, which causes fluorosis a disease affecting teeth and bones. In India cattle and human fluorosis was detected in 1930 and 1957, respectively. People of about 177 districts in 20 states of India are suffering from excessive fluoride in water. Some states like Rajasthan, Gujarat, Andhra Pradesh have large number of villages where ground water contains excessive fluoride1. Permissible limit of fluoride in drinking water suggested by World Health Organization (WHO) is 1.5 mg/L. A voluminous work has been reported by several authors using different adsorbents like amorphous alumina supported on carbon nanotubes2, zirconium(IV) complexes of the chelating resins functionalized with amine N-acetate ligands3, activated alumina4, calcium phosphate5, zirconium(IV) arsenate vanadate6, coal based sorbents7, cationic synthetic resins8, D412 resin loaded with Ce(IV) ions9, and cerium-poly(hydroxamic acid) resin complex10 etc.

This paper describes the removal of fluoride ions from drinking water under different equilibrating conditions such as concentration of fluoride ions, pH, temperature, time, dissolved salts in fluoride bearing water by using commercially available ion-exchange resins, Purolite S940, Purolite S950, and Duolite ES467.

Experimental Procedure

Materials

Sodium hydroxide, hydrochloric acid, aluminum sulphate, sodium fluoride, sodium acetate, acetic acid, sodium sulphate, sodium chloride, sodium hydrogen carbonate were of AR quality. Resin Purolite S940 and Purolite S950 were received from Purolite International Limited, Duolite ES467 was purchased from market. The stock solutions used in this work were prepared with laboratory reagent chemicals using RO-deionized water.
Method

Commercial resins Purolite S940, Purolite S950 and Duolite ES467 were conditioned by following standard procedures adopted for ion-exchange resins. All these resins were converted to Na\(^+\) form with 4\% NaOH solution and then to Al\(^{3+}\) form by equilibrating with 5\% of aluminium sulphate solution and used for the uptake of fluoride ions from water.

Uptake of fluoride ions

Equilibrium studies under static conditions were carried out by contacting separately 150 mL of fluoride ion containing solution of pre-decided concentration (10 to 50 ppm) with about 0.5g of ion exchange resin with occasional shaking at 30 °C for 16 h. The concentration of fluoride ion in equilibrating solution was evaluated by Ion Analyzer (Orion EA 940)\(^{11}\). The same procedure was repeated to check the effect of different parameters such as pH of equilibrating solution, concentration of fluoride ions in solution, kinetics, temperature and dissolved salts on the uptake of fluoride ion by the resins. In the case of studies involving the effect of dissolved salts in equilibrating solution on the sorption of fluoride ions, the concentration of fluoride ion was tentatively fixed at 10 ppm.

The uptake of fluoride ion was also studied under dynamic conditions by percolating 10 ppm of aqueous fluoride ion solution through the resin bed at different service flow rates, till 1 mg/L leakage of fluoride ions in the effluent was detected. The adsorbed fluoride ions on the resin were desorbed by passing 5\% alum solution.

Results and Discussion

Effect of fluoride ion concentration on its uptake

The uptake of fluoride ions from water having different concentrations of fluoride (10 ppm to 50 ppm) by ion-exchange resins is given in Table 1. The examination of data revealed that the uptake of fluoride ion increased with the increase in concentration of fluoride ion in solution. At lower concentration of fluoride ions, the number of ions available in solution was less as compared to the available sites on the resin. However, at higher concentrations the available sites of sorption remained the same whereas more fluoride ions were available for sorption and subsequently the sorption became almost constant after a particular equilibrium concentration level reached.

<table>
<thead>
<tr>
<th>Fluoride concentration (ppm)</th>
<th>Purolite S940</th>
<th>Purolite S950</th>
<th>Duolite ES467</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>4.80</td>
<td>4.27</td>
<td>0.46</td>
</tr>
<tr>
<td>20</td>
<td>9.56</td>
<td>5.14</td>
<td>0.57</td>
</tr>
<tr>
<td>30</td>
<td>11.18</td>
<td>4.93</td>
<td>0.57</td>
</tr>
<tr>
<td>40</td>
<td>11.64</td>
<td>5.47</td>
<td>1.15</td>
</tr>
<tr>
<td>50</td>
<td>12.17</td>
<td>6.02</td>
<td>1.73</td>
</tr>
</tbody>
</table>

Effect of pH on fluoride ion uptake

Separation of ions from aqueous solutions was highly dependent on pH of the equilibrating aqueous solution, as it altered the surface charge on the sorbent/resin\(^{12}\). The equilibrium studies at different pH were performed to determine the optimum pH at which maximum adsorption occurred. Results are shown in Fig.1. Adsorption of fluoride ions decreased with increase in pH of solution and maximum sorption took place in pH range 2 to 3. Adsorption of fluoride decreased with increase in pH of solution, which could be attributed to the formation of aluminium hydroxide which contained higher negative charge that led to the reduction in electrostatic attraction resulting in less sorption of fluoride ions.

Effect of dissolved salts

The effect of dissolved salts on uptake of fluoride ions as well as the nature of the resin is shown in Fig. 2. Evidently dissolved salts such as NaCl and Na\(_2\)SO\(_4\) had no remarkable effect on fluoride uptake. Substantial quantity of SO\(_4^{2-}\) and Cl\(^-\) did not affect fluoride uptake, while at higher concentration of NaHCO\(_3\), CO\(_3^{2-}\) increased in solution, thereby resulting into pH increase of solution. As shown in Fig. 1 at higher pH, uptake of fluoride decreased because higher deprotonation of the co-ordinated water took place leaving an increased negative charge around Al\(^{3+}\), which probably repelled fluoride ions. It
was observed that there was no remarkable change in uptake of fluoride with increasing concentration of dissolved salts.

**Adsorption isotherms**

To determine the adsorption capacity of Purolite S940, Purolite S950, and Duolite ES467 resins, a study of adsorption isotherms was attempted by analyzing adsorption data to fit the models of Freundlich and Langmuir isotherms (Figs 3 and 4). The coefficients of these models were computed using linear least squares fitting.

**Freundlich isotherm**

The equilibrium data were analyzed using the following linear equation13,

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e$$  \hspace{1cm} (1)

where $C_e$ is the equilibrium concentration (mg/L), $Q_e$ is the amount adsorbed at equilibrium (mg/g), $K_f$ and $1/n$ are Freundlich constants related to adsorption capacity and intensity, respectively. A linear relationship was observed between $\log Q_e$ and $\log C_e$ from plotted parameters indicating the applicability of Freundlich equation (Fig. 3).

**Langmuir isotherm**

The equilibrium data were analyzed using the following linear equation for the Langmuir adsorption isotherm14,

$$\frac{C_e}{Q_e} = \frac{1}{Q_0 b} + \left(\frac{C_e}{Q_0}\right)$$  \hspace{1cm} (2)

where $C_e$ is the equilibrium concentration (mg/L), $Q_e$ is the amount adsorbed at equilibrium (mg/g) and $Q_0$ and $b$ are Langmuir constants related to the capacity and energy/intensity of adsorption respectively, determined from the slope and intercept of the linear plot.

To judge the fitting of the above equations 1 and 2 to adsorption data of Purolite S940 and Purolite S950 an absolute relative percent deviation (RD) as described elsewhere was calculated15. Freundlich constants $1/n$ and $K_f$ were calculated as 1.731 and
1.474 for Purolite S940 and 5.376 and 2.827 for Purolite S950, respectively. Langmuir constants $Q_0$ (maximum sorption capacity) and $'b'$ energy/intensity constants were calculated as 18.86 mg/g and 22.96 L/mg for Purolite S940 and 6.523 mg/g and 0.1736 L/mg for Purolite S950, respectively. From these calculations it was found that adsorption data of Purolite S940 and Purolite S950 closely fitted to Freundlich and Langmuir equations respectively. Similar inferences are derived in the recent studies on adsorption of nickel and copper by crosslinked methacrylic acid copolymers by using Freundlich and Langmuir isotherms16.

**Rate constant**

The specific rate constant, $K_r$ for the adsorption of fluoride ion on the resins was determined by Lagergan equation17.

$$\log (q_e - q) = \log q_e - (K_r/2.303) t$$

...(3)

where $q_e$ and $q$ (mg/g) are amounts of fluoride ion adsorbed at equilibrium and at time $t$, respectively. The straight line plot (Fig. 5) of $\log (q_e - q)$ versus $t$ at 30°C indicated the validity of the Lagergan equation for the present system and explained that the process followed first order kinetics. The values of $K_r$ were calculated from the slope of the plot and were 0.05191/min and 0.0115/min for Purolite S940 and Purolite S950 respectively.

**Effect of temperature**

At higher temperatures mobility of fluoride ions increased so the complex formation also increased. As shown in Fig. 6, with the increase of temperature uptake of fluoride ion also increased. The reason was that at higher temperature fluoride ions formed more complex with aluminium, thereby resulting into higher uptake.

**Complex formation on the resin**

The resins studied formed complex with fluoride ion in water when these were taken in aluminium form. The probable structure of complex formation is shown in Fig. 7. These resins are insoluble/infusible polymeric materials and the phenomenon cannot be ascertained by any physico-chemical means.

**Column operations**

The performance of resins in continuous column operations was studied by conducting loading runs using 30 mL bed volume of resins and an influent having 10 ppm fluoride ion concentration. The capacities of resins for 1 ppm leakage at different influent flow rates such as 5 B.V./h, 10 B.V./h and 15 B.V./h were determined. As the flow rate increased the adsorption capacity of resins decreased because of the lesser contact time with the resin. Purolite S940 treated 6500, 5750 and 4500 mL, 10 ppm fluoride containing water whereas Purolite S950 treated 5000, 4750 and 4500 mL, 10 ppm fluoride containing water at 5, 10, and 15 B.V./h, flow rate respectively.
Conclusions

All the three studied resins namely, Purolite S940, Purolite S950 and Duolite ES467 showed promise in removing fluoride from drinking water under varying conditions of water quality. The sorption phenomenon followed Langmuir and Freundlich isotherm pattern. The rate constants followed first order Lagergeran phenomenon. Purolite S940 and Purolite S950 showed very good performance under dynamic conditions.

References