Adsorption of fluoride onto magnesia—Equilibrium and thermodynamic study

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Batch sorption system using magnesium oxide as an adsorbent was investigated to remove fluoride ions from aqueous solutions. The system variables studied include initial concentration of the sorbate, agitation time, adsorbent dose, pH, co-ions and temperature. The experimental data fitted well to the Freundlich isotherm while, poorly to the Langmuir isotherm. Thermodynamic parameters such as ΔH°, ΔS° and ΔG° were calculated indicating that the adsorption was a spontaneous, endothermic and a physical process. Kinetic studies reveal that the adsorption is first order. A mechanism involving three stages (external surface adsorption, intraparticle diffusion and final equilibrium) has been proposed for the adsorption of fluoride ions onto MgO. XRD patterns of the adsorbent were recorded to get a better insight into the mechanism of the adsorption process.

Keywords: Defluoridation, Isotherm, Adsorption

Fluoride is an essential constituent for both humans and animals depending on the total amount ingested or its concentration in drinking water. The presence of fluoride in drinking water, within permissible limits of 0.5-1.0 mg/L, is beneficial for production and maintenance of healthy bones and teeth, while excessive intake of fluoride causes dental or skeletal fluorosis which is a chronic disease manifested by mottling of teeth in mild cases, softening of bones and neurological damage in severe cases.

Current methods used to remove fluoride from water can be divided into two categories: precipitation and adsorption. Precipitation of fluoride with calcium and aluminium salts has been used to remove fluoride from industrial wastewater. Typically, lime is used as a calcium source and the Ca(II) ions released interact with fluoride and form CaF₂ precipitate. The aluminium salts interact with fluoride in water and form AlF₃⁻ and Al(OH)₃·nFₙ etc. Adsorption is another technique, in which fluoride is adsorbed onto a membrane, or a fixed bed packed with resin or other mineral particles.

Many techniques have been reported, such as reverse osmosis, electro dialysis, Donnan dialysis, ion exchange, limestone rector and activated alumina column. The efficiency of this technique mainly depends on adsorbents. Recent attention of researchers has been devoted to the study of low cost, but effective materials. The objective of the present endeavour, therefore, is to study the adsorption behaviour of fluoride onto MgO, an easily available, non-toxic colourless compound.

Experimental Procedure

Materials

All the reagents and the adsorbent, MgO, used were of commercially available high purity Analar grade (Sd-fine, India). Stock solutions of fluoride were prepared by dissolving sodium fluoride in doubly distilled water.

Apparatus

The concentration of fluoride was measured using a fluoride ion-selective electrode (Orion USA, Model EA94-09). The pH measurements were made with Systronic digital pH meter. The particle size of the adsorbent was determined using the Carl Zeiss Light microscope (Axioskop Plus) as reported earlier. The particle size of the adsorbent employed in the present study is 0.02 mm. The XRD patterns of the adsorbent, before and after treatment with fluoride ions, were recorded at the Regional Research Laboratory, Thiruvananthapuram, India.

Batch adsorption experiments

Adsorption experiments were performed by agitating 3 g of adsorbent with 50 mL of fluoride solution of desired concentrations at 30±1°C in different stoppered bottles in a shaking thermostat.
machine. At the end of pre-determined time intervals, the sorbate was filtered and the concentration of fluoride was determined. All experiments were carried out twice and the average values are given. Adsorbed fluoride concentrations were the means of the duplicate experimental results. Experimental variables considered were: (i) initial concentration of fluoride ions: 2-10 mg L$^{-1}$; (ii) contact time between adsorbent and the fluoride solution: 5-45 min; (iii) pH: 3-11; (iv) dosage of the adsorbent: 0.1-3.5 g/50 mL; (v) temperature: 30-50°C; and (vi) co-ions: Cl$,\,\text{SO}_4^{2-},\,\text{NO}_3^-,\text{and HCO}_3^-$. 

Data analysis

The experimental data were analyzed using Microcal Origin (version 6) computer software. The goodness of fit was discussed using coefficient of determination, $r^2$, and standard deviation, $sd$.

Error analysis

In the single-component isotherm studies, the optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the isotherm to the experimental equilibrium data. In this study, linear coefficients of determination and a non-linear Chi-square test, as described in the literature, were used.

The Chi-square test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models. The equivalent mathematical statement is:

$$\chi^2 = \Sigma \frac{(Q_e - Q_{e,m})^2}{Q_{e,m}} \quad \ldots \quad (1)$$

where $Q_{e,m}$ is the equilibrium capacity obtained by calculating from the model (mg g$^{-1}$) and $Q_e$ is experimental data of the equilibrium capacity (mg g$^{-1}$). If data from the model are similar to the experimental data, $\chi^2$ will be a small number; if they are different, $\chi^2$ will be a large number. Therefore, it is necessary to also analyze the data set using the Chi-square test to confirm the best-fit isotherm for the sorption system.

Results and Discussion

Effect of agitation time and initial concentration

Figure 1 shows the effect of agitation time and initial concentration on the adsorption of fluoride ions on the adsorbent. It is clear from the figure that the uptake of fluoride ions increases slowly with the lapse of time and reaches to saturation in 25 min, which is fixed as the optimum contact time for other experiments. The equilibrium time was independent of initial fluoride ions concentration. The results in Table 1 revealed that, the amount adsorbed increases sharply while the percentage removal exponentially

<table>
<thead>
<tr>
<th>[F]$^-$o</th>
<th>$C_e$ (mg L$^{-1}$)</th>
<th>$Q_e$ (mg g$^{-1}$)</th>
<th>Fluoride removed (%)</th>
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<td>40$^\circ$</td>
<td>50$^\circ$</td>
</tr>
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<td>2</td>
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<td>0.32</td>
<td>0.21</td>
</tr>
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<td>0.89</td>
<td>0.33</td>
</tr>
<tr>
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<td>1.55</td>
<td>1.14</td>
<td>0.71</td>
</tr>
<tr>
<td>8</td>
<td>1.94</td>
<td>1.60</td>
<td>1.19</td>
</tr>
<tr>
<td>10</td>
<td>2.60</td>
<td>2.18</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Fig. 1—Effect of agitation time and initial concentration (mg/L) for the adsorption of fluoride on MgO.
decreases with the increase in initial concentration of fluoride ions. This indicates that there exists a reduction in immediate solute adsorption owing to the lack of available active sites on the adsorbent surface, compared with the relatively large number of active sites required for the high initial concentration of fluoride.

The percentage uptake is highly dependent on initial concentration of fluoride ions in the solution and it increase, at a fixed concentration of fluoride, with increase in temperature. This may be due to the fact that with increase in temperature the rate of adsorption may increase i.e. the adsorption process is endothermic in nature. Further, the fluoride ions uptake versus time curves are single, smooth and continuous leading to saturation, suggesting the possible monolayer coverage of fluoride ions on the surface of the adsorbent.

**Effect of adsorbent dosage**

Figure 2 shows the amount of fluoride removed as a function of adsorbent dosages at 4 mg L\(^{-1}\) of initial fluoride concentration and at 30°C. Adsorbent dosages was varied from 100 mg to 3.5 g per 50 mL and equilibrated for 45 min. From the result it is evident that optimum adsorbent dosage of 3 g/50 mL is required for maximum removal of fluoride. It is interesting to note that, in the same range of dosage silica gel, as adsorbent, exhibits comparatively very low fluoride removal capacity.

**Adsorption isotherms**

The adsorption isotherms generally used for the design of adsorption system. The Langmuir\(^7\) and Freundlich\(^8\) equations are commonly used for describing the adsorption isotherm. The linear equation of Langmuir and Freundlich are represented as follows Eqs (2) and (3), respectively.

\[
\frac{C_e}{Q_e} = \left(\frac{C_e}{Q^o}\right) + \left(\frac{1}{Q^o b}\right) \quad \ldots (2)
\]

\[
\log Q_e = \frac{1}{n} \log C_e + \log K \quad \ldots (3)
\]

where \(Q_e\) and \(C_e\) has the usual meanings and \(Q^o\) and \(b\) are the Langmuir constants, indicating the adsorption capacity and energy of adsorption, respectively. \(K\) and \(n\) are the empirical constants of the Freundlich isotherm measuring the adsorption capacity and intensity of adsorption, respectively.

To quantify the adsorption capacity of the chosen adsorbent for the removal of fluoride ions from water, the Langmuir adsorption equation was applied. The adsorption isotherms were studied at 30, 40 and 50°C. The plots (Fig. 3) of \(C_e/Q_e\) versus \(C_e\) at different temperatures indicate the non-applicability of the Langmuir adsorption isotherm. The statistical parameters are given in Table 2.

The adsorption data have been fitted to the Freundlich isotherm. The linear plots of \(\log Q_e\) versus \(\log C_e\) (Fig. 4) at different temperatures indicate the applicability of the Freundlich adsorption isotherm. The results (Table 2) indicate that the adsorption
capacity (measured by \( K \)) of the adsorbent increases with increase in temperature. Further, the value of intensity of adsorption \((n)\) is greater than unity signifies that the forces within the surface layer are attractive\(^9\).

The Langmuir model makes several assumptions, such as monolayer coverage and constant adsorption energy while Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces. The applicability of Freundlich isotherm to MgO implies that heterogeneous surfaces conditions exist under the experimental conditions used. The adsorption properties of MgO are thus likely to be complex, involve more than one mechanisms\(^10\).

Non-linear analysis

The Chi-square statistic, \( \chi^2 \), and coefficient of determination, \( r^2 \), were obtained and are shown in Table 2. The Freundlich isotherm exhibited very low \( \chi^2 \) values \((0.4 \times 10^{-3}, 2.0 \times 10^{-3} \) and \(4.8 \times 10^{-3}\) at 30, 40 and 50\(^\circ\)C, respectively). Therefore, drawing conclusion from the non-linear Chi-square analysis, the Freundlich isotherm was best fitting isotherm.

Thermodynamic parameters

The standard free energy change \((\Delta G^o)\), enthalpy change \((\Delta H^o)\) and entropy change \((\Delta S^o)\) were calculated from the variation of the thermodynamic equilibrium constant \( K_o \). The values of \( K_o \) for the adsorption process were determined by the reported method\(^11\). The thermodynamic parameters were calculated using the following equations.

\[
\ln K_o = \left( \frac{\Delta S^o}{R} \right) - \left( \frac{\Delta H^o}{RT} \right) \quad \ldots (4)
\]

\[
\Delta G^o = -RT \ln K_o \quad \ldots (5)
\]

\( \Delta H^o \) and \( \Delta S^o \) were determined from the slope and intercept of the plot of \( \ln K_o \) versus \( 1/T \) (figure not shown).

The standard free energy change, enthalpy and entropy changes along with equilibrium constants were given in Table 3. The endothermic nature of adsorption is indicated by an increase in \( K_o \) with rise in temperature. The results in Table 3 indicate that \( \Delta G^o \) values are negative which mean that the reaction is spontaneous. The values of enthalpy of a sorption process may be used to distinguish between chemical and physical sorption\(^12\). For chemical sorption,
enthalpy values range from 83 to 830 kJ mol\(^{-1}\), while for physical sorption they range from 8 to 25 kJ mol\(^{-1}\). On the basis of the above distinction, it is concluded that fluoride ion sorption by MgO is a physical process. Positive values of \(\Delta H^o\) suggest that the process is endothermic, so an increase of temperature encourages fluoride ion adsorption. Enhancement of adsorption capacity of MgO at higher temperatures may be attributed to the enlargement of the pore size and/or activation of the adsorbent surface and to the increase in the mobility of the fluoride ions. As indicated in Table 3, \(\Delta S^o\) values for the adsorption process are positive. This observation suggests a high degree of disorderliness at the solid-solution interface during the adsorption of fluoride onto MgO. This may be due to the fact that the adsorbed water molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system\(^{13}\).

Effect of pH

The effect of initial pH of the fluoride solution on the amount of fluoride ions adsorbed was studied. The percent removal of fluoride ion (by 3 g of adsorbent per 50 mL of the solution at 4 mg L\(^{-1}\) of initial fluoride ion concentration) at pH values 3, 5, 7, 9, 11 and 13 are 77, 75, 75, 72, 71, and 70\%, respectively. The results indicate that the adsorbent exhibits a commendable defluoridation capacity in wide range of pH. However, at very high pH the defluoridation capacity decreases slightly. This may be due to the competition between hydroxide and fluoride ions in this pH range\(^{14}\).

Effect of co-ions

The effect of added co-ions viz. Cl\(^-\), NO\(_3\)^-, SO\(_4\)^2- and HCO\(_3\)^- on the percentage of adsorption is given in Table 4. The results indicate that the addition of co-ions, in the range investigated, has no appreciable effect on the amount of fluoride ions removed. However, increase in the concentration of bicarbonate ions slightly decreases the adsorption efficiency. This may be due to the competition between bicarbonate and fluoride ions for the active sites on the adsorbent and a similar observation was made in the adsorption fluoride onto activated alumina\(^{14}\).

Kinetics of adsorption

Kinetics of sorption describes the solute uptake rate which in turn governs the residence time of sorption reaction. It must be remembered that the two important physico-chemical aspects for parameter evaluation of sorption process as unit operation are the kinetics and the equilibria. Hence in the present study, the kinetics of fluoride removal has been carried out to understand the behaviour of the adsorbent employed.

The sorption of fluoride from a liquid phase to solid phase may be expressed as Eq. (6).

\[
\begin{align*}
\frac{k_1}{k_2}A & \quad B \quad \ldots \quad (6)
\end{align*}
\]

where \(k_1\) is the forward rate constant and \(k_2\) is the backward rate constant. A represents fluoride remaining in the solution and B represents fluoride retained on the surface of the adsorbent. Since the reaction in both directions is of first order, the rate constant of adsorption, \(k_{ad}\), was determined using the following rate expression given by Natarajan and Khalaf\(^{15}\), Eq. (7).

\[
\log \left(\frac{C_o}{C_t}\right) = \frac{k_{ad}}{2.303} \cdot t \quad \ldots \quad (7)
\]

where \(C_o\) and \(C_t\) are the concentration in mg L\(^{-1}\) of fluoride initially and at time \(t\), respectively. Linear plots \((r>0.97)\) of \(\log \left(\frac{C_o}{C_t}\right)\) versus \(t\) suggest the applicability of the Natarajan and Khalaf equation. A representative plot is given in Fig. 5. The rate constants were calculated from the slope and the values, for an initial fluoride ion concentration of 4 mg/L, are \(10.13 \times 10^{-3}\), \(20.04 \times 10^{-3}\) and \(27.18 \times 10^{-3}\) min\(^{-1}\) at 30, 40 and 50°C, respectively. The values of \(k_{ad}\) were found to increase with increase in the temperature indicating the endothermic nature of the adsorption process.

Intraparticle diffusion studies

The contact time experimental results can be used to study the rate determining step in the adsorption process.
process, as shown by Weber and Morris. Since, the particles are vigorously agitated during the adsorption period, it is probably reasonable to assume that mass transfer from the bulk liquid to the particle external surface does not limit the rate. One might then postulate that the rate determining step may be either film or intraparticle diffusion. As they act in series, the slower of the two will be the rate-determining step.

In a rapidly stirred batch reactor, the adsorbate species are most probably transported from the bulk of the solution to the solid phase through intraparticle diffusion, which is often the rate-limiting step in many sorption process. Applying the intraparticle diffusion model tests the presence of intraparticle diffusion process in the present adsorption system. The intraparticle diffusion equation can be described as:

\[ Q_e = k_p t^{0.5} + C \]  \hspace{1cm} ...(8)

where \( Q_e \) is the amount of fluoride adsorbed per unit mass of the adsorbent (mg g\(^{-1}\)) at time \( t \) and \( k_p \) is the intraparticle diffusion rate constant (mg g\(^{-1}\) min\(^{-0.5}\)). The plot of \( Q_e \) versus \( t^{0.5} \) is shown in Fig. 6. The initial curved portions represent the boundary layer diffusion. The value of intraparticle diffusion rate constant \( k_p \) calculated from the slopes of the linear portion of the curves, for 1.5, 2.5 and 3.5 g/50 mL of the adsorbent doses are 0.44, 0.66 and 0.85, respectively. The value of \( k_p \) increase with the dose of the adsorbent, as more active binding sites are available for fluoride ions to diffusion into it.

**Time dependence of the fraction of adsorption**

The plots of \( Y_t \) versus \( t^{0.5} \) (Fig. 7) for different doses have three stage shapes. The first, sharp portion...
of the curves corresponds to the external surface adsorption stage or instantaneous adsorption stage. The second, gradual linear portion corresponds to intraparticle diffusion and the final, linear portion represents the equilibrium stage\textsuperscript{18}. In this model, the adsorbent is treated as being surrounded by a boundary layer film of water molecules through which the fluoride ions must diffuse prior to adsorption. The second portion of the curve indicates the intraparticle diffusion, which is predominant in the rate-controlling step where the diffusive transport of fluoride ions occurs through the internal pores of the adsorbent. As the bulk and surface fluoride ion concentrations start to decrease, the third section of the Fig. 7 shows a decrease in the rate of diffusion reaching a point of equilibrium\textsuperscript{18}.

**X-Ray diffraction (XRD) studies**

Adsorption reaction may lead to changes in molecular and crystalline structure of the adsorbent and hence an understanding of the molecular and crystalline structures of the adsorbent and the resulting changes thereof would provide valuable information regarding adsorption reaction. Hence, XRD patterns of the adsorbent before and after treatment with fluoride ions have been studied.

The XRD patterns of the adsorbent before and after treatment with fluoride ions are shown in Fig. 8. The XRD data for selective/predominant peaks are given in Table 5. It is evident that the XRD pattern of loaded MgO exhibits no variation in the crystal structure and this suggests that the fluoride ions might diffuse into micropores and macropores and sorb mostly by physisorption without altering the structure of the adsorbent\textsuperscript{19}. The above observation corroborated well with batch sorption experiments and thermodynamic results.

![Fig. 8—XRD pattern of the adsorbent: (a) before adsorption and (b) adsorbent loaded with fluoride ions](image)

**Table 5**—X-ray diffraction details of the adsorbent before and after treatment with fluoride ions

<table>
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<tr>
<th>d-spacing (Å)</th>
<th>Relative intensity (%)</th>
<th>Angle (°2Theta)</th>
<th>Peak height (counts)</th>
<th>(hkl)</th>
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</thead>
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<td>Before adsorption</td>
<td></td>
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<td></td>
<td></td>
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<tr>
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Conclusion

In batch adsorption studies, data show that MgO has considerable potential for the removal of fluoride ions from aqueous solutions. Wide range of pH and high temperature ranges were found as the optimum conditions for maximum fluoride adsorption by the adsorbent. The results gained from this study were extremely well described by the theoretical Freundlich isotherm. The thermodynamics of the system pointed out the system was spontaneous and endothermic. On the basis of the kinetic and XRD studies a mechanism involving three stages has been proposed for the physisorption of $F^-$ onto the MgO in which the pore diffusion is the rate-limiting step.

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References