Adsorption of U(VI) has been studied as a function of time, temperature and initial concentration of uranium on kaolinite. The adsorption data were fitted to Freundlich, Langmuir and Dubinin-Radushkevich(D-R) adsorption isotherms. The mean energy of adsorption was calculated by using D-R isotherm. It was found 6.51 kJ/mole which does not corresponds to the energy of ion-exchange reactions. Although Freundlich isotherm does not take the solid’s finite capacity for adsorption at high concentrations of solute into account, it has been shown in many experimental studies that it can describe the experimental data well on a phenomenological basis[1]. Lagergren equation has been used for dynamic modelling of process and the rate constants for kaolinite type clay were calculated at 293 K, 313 K and 333 K at the solution concentration of 1.10^{-2} M. The results show that as the temperature increases the rate constant increases too. This shows that the rate of uptake increases rapidly with increasing temperature. Using the experimental datas obtained at 5 different temperatures, thermodynamic constants ΔH^0, ΔS^0 and ΔG^0 were calculated. The results show that the adsorption process on kaolinite is endothermic.

INTRODUCTION

Adsorption of uranium onto clay minerals is one of the significant reaction affecting the transport of uranium in the environment. Interest in the adsorption of metal ions for recovery purposes has increased manyfold in recent years, because of its simplicity, selectivity and efficiency [2].

In this study kaolinite type clay was chosen as an adsorbent and the kinetics of uranium adsorption on kaolinite have been investigated. Thermodynamic investigations were carried out to get more information about the adsorption of uranium.

MATERIAL AND METHOD

Kaolinite type clay was crushed and sieved through 250 μm sieve. X-ray diffraction spectrometry was used to elucidate the structure of the clay. The initial concentration of uranyl nitrate solution (Merck., item no. 8476) ranged from 1.10^{-2} to 1.10^{-1} M and distilled water was used throughout the experimental work. Adsorption measurements were carried out by batch technique at 293 K, 313 K and 333 K, in a thermostatic shaker. 0.05 g clay sample was
put into contact with 5 mL of uranyl nitrate solution for 1, 3, 5, 15, 30 and 60 minutes. Time period sufficient to reach equilibrium is found to be 60 minutes. Therefore all the adsorption results obtained at 60 minutes. Dublicate samples were suspended in polypropylene centrifuge tubes in known volumes of solutions. The two phases were separated by centrifuging at 3000 rpm for 15 minutes. The change in β activity of supernatant was determined with an ERD Mullard G-M tube type MX 123 system. The adsorption percentage (Ads.,%) and distribution coefficient (Kd) was calculated as:

\[ K_D = \frac{c_0 - c_d}{c_d} \frac{V}{m} \]  

(2)

\[ Ads.\% = \frac{A_i - A_f}{A_i} \times 100 \]  

(1)

where, \( A_i \) and \( A_f \) are the initial and final activities \( (\text{bq/cm}^3) \) of solution phase, respectively. \( c_0 \) and \( c_d \) are the initial and final solution concentration \( (\text{M}) \). \( V \) is volume of solution \( (\text{mL}) \) and \( m \) is amount of adsorbent \( (\text{g}) \).

RESULTS AND DISCUSSION

Datas obtained from adsorption experiments were fitted to Freundlich isotherm (Fig. 1). The linearized Freundlich equation is,

\[ \log X = \log A + n \log c \]  

(3)

Where, \( X \) – amount of solute adsorbed per unit weight of solid \( (\text{mole/g}) \)

\( c \) – equilibrium concentration of solute in solution \( (\text{mole/L}) \)

\( A,n \) – Constants

From the slopes and intercepts of the straight lines parameters \( n \) and \( A \) were calculated and their values are given in Table I. The Freundlich equation provides the best fit for the data in the whole range of uranium concentration.

As an alternative to the Freundlich isotherm, the data were fitted also to the D-R equation\[1\]. (Fig. 2)

\[ X = X_m \exp (-Kc^2) \]  

(4)

Where, \( X \) - amount of solute adsorbed per unit weight of solid \( (\text{mole/g}) \)

\( X_m \) – adsorption capacity of adsorbent Per unit weight \( (\text{mole/g}) \)
\[ E = (-2K)^{1/2} \quad (5) \]

The data obtained from D-R isotherm is shown in Table I. The value \( E \) is lower than the energy range 8-16 kJ/mole, of ion exchange reactions.

Kinetic studies of adsorption of uranium on kaolinite showed that Lagergren’s first order rate equation[3].

\[ \ln \frac{q_e - q}{q_e} = -k_{ads} \cdot t \quad (6) \]

Where, \( q_e \) and \( q \) are the equilibrium and initial adsorbate concentrations in the adsorbent respectively, \( t \) is the time (min.) and \( k_{ads} \) is the first order rate constant. \( q \) value calculated as follows;

\[ q = (c_0 - c_f) \frac{V}{m} \quad (7) \]

Where, \( c_0 \) and \( c_f \) are the initial and final concentrations of the adsorbate in solution (mg/L), \( V \) is volume (L) of solution and \( m \) is the amount of adsorbent (g). Straight line was obtained by plotting \( \ln (q_e - q) \) versus \( t \) (Fig.3). The adsorption rate constants were determined from the slopes of the straight lines and were found as 0.185, 0.189 and 0.199 min\(^{-1}\) for kaolinite type clay at 293 K, 313 K and 333 K respectively. The first order rate constants computed at 99 % confidence level.

The experiments were carried out at 293 K, 303 K, 313 K, 323 K and 333 K shows that the distribution coefficient \( K_D \) values increased with increase the temperature indicating the endothermic nature of adsorption. The values of \( \Delta H^0 \) and \( \Delta S^0 \) were calculated from the slopes and intercepts of linear variation of \( \ln K_D \) vs. \( 1/T \) using the relation (Fig.4):
\[
\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]  

(8)

Where \( K_D \) is the distribution coefficient, \( T \) is the absolute temperature (K), \( R \) is the universal gas constant (kJ/mole). The positive value of \( \Delta H^0 \) confirms the endothermic nature of the process. The positive \( \Delta S^0 \) shows the existence of some structural changes at solid-liquid interface. The standart free energy values for all the systems are negative and the decrease in the value of \( \Delta G^0 \) with the increase in the temperature shows that the reaction is more spontaneous at high temperature (Table2).

**Table 1.** Constants calculated by using the Freundlich and D-R adsorption isotherms

<table>
<thead>
<tr>
<th>A</th>
<th>n</th>
<th>r</th>
<th>X_m (mole/g)</th>
<th>E (kJ/mole)</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,994</td>
<td>0,660</td>
<td>0,982</td>
<td>0,0121</td>
<td>6,51</td>
<td>0,999</td>
</tr>
</tbody>
</table>

**Table 2.** Thermodynamic constants calculated for adsorption of uranium on kaolinite

<table>
<thead>
<tr>
<th>( \Delta H^0 ) (kJ/mole)</th>
<th>( \Delta S^0 ) (kJ/Kmole)</th>
<th>( \Delta G^0 ) (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293K</td>
<td>303K</td>
<td>313K</td>
</tr>
<tr>
<td>6,79</td>
<td>0,0719</td>
<td>-14,27</td>
</tr>
</tbody>
</table>

**REFERENCES**


Figure 1. Freundlich adsorption isotherm for uranium adsorption on kaolinite

Figure 2. D-R adsorption isotherm for uranium adsorption on kaolinite

Figure 3. Lagergren equation for uranium adsorption on kaolinite

Figure 4. The relationship between $\ln K_D$ and $1/T$