TEMPERATURE AND CONCENTRATION DEPENDENCE OF KINETICS OF THORIUM ADSORPTION ON ACTIVATED CHARCOAL FROM AQUEOUS SOLUTIONS

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SUMMARY: The batch kinetics of thorium ions adsorption on activated charcoal from aqueous solution has been investigated at temperatures within the range of 283-313K and concentration (0.5-3.0 g/1). The thorium ions adsorption obeys a first order rate law, with an activation energy 13.40 kJ/mol. Various thermodynamic quantities (namely $\triangle H$, $\triangle S$, $\triangle G$) were computed from the equilibrium constant, kc values calculated at different temperatures. The results indicate that the process has an endothermic heat of adsorption. Moreover, thorium ions adsorption obeys the Freundlich and Langmuir equations especially the latter provide the better fit over the entire range of concentration studied.

Key Words : Thorium, adsorption, activated charcoal, kinetics, aqueous solutions.

INTRODUCTION

The time dependence study of metal ions adsorption on solids provide valuable information about the adsorption process and its mechanism. The adsorption process can be broken down into three consecutive steps : transport of the metal ions to the adsorbent : the adsorption process itself i.e., the formation of the adsorption bond, and transport of metal ions to the deeper layers of the adsorbent. The rate of each of these step is dependent on number of factors such as agitation of the solution, the state of metal ions in solution, age the solution, concentration of metal ions and adsorption temperature etc (1). Thorium is an important element in the nuclear industry and its adsorption on solids for pre-concentration point of view is particularly important from purification, trace metal analysis, and waste treatment. Owing to the large surface area, micro-porous structure, high adsorption capacity, radiation stability and high purity, we have used the activated charcoal for the adsorption of thorium ions and optimized various parameters for its pre-concentration from aqueous solutions (2). This communication reports results of the effect of temperature and concentration on the kinetics of thorium ions adsorption on activated charcoal. The results are important in relation to the recovery of thorium ions from solutions.

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EXPERIMENTAL

A commercial activated charcoal (B D H; item No. 33032) was used as an adsorbent. The values of surface area, pore volume, particle diameter, porosity, density of activated charcoal have been measured and are reported earlier (3). Thorium nitrate (Fluka; item No. 27103) was used to make thorium solutions in doubly distilled water.

Siemen's wavelength dispersive X-ray fluorescence

(WDXRF) spectrometer, SRS-200, was used for measuring the concentration of thorium in solutions with variation <2.0%. A Hetofrig shaker (M/S Heto Birkerod -Denmark) was used for temperature controlled studies. The fluctuation in the measurement of temperature is within ±0.1 K.

The adsorption of thorium ions on activated charcoal from aqueous solutions was carried out via a batch technique. The details of adsorption procedure is similar as described earlier (4). The fraction of thorium ions adsorbed at any time, F (t) was calculated using the following relation :

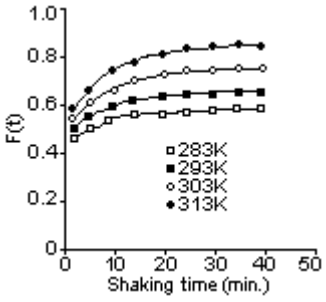
$$F(t) = (C_i - C_t) / C_i \qquad (1)$$

where C_i is the initial concentration of thorium ions (g/l) and C_t is the concentration of thorium ions in solutions at time t, (g/l).

RESULTS AND DISCUSSION

Figure 1 shows the variation of thorium ions adsorption on activated charcoal with shaking time at different temperatures. This study was performed by shaking 10 ml thorium solution of 1.0 g/1 (pH=3.60) with 0.1 g dry activated charcoal in 250 ml glass reagent bottles. This figure indicates that initially the adsorption of thorium ions increases rapidly, but then the process slow down and subsequently attain a constant value around 30 minutes. In the initial stages the surface coverage is too low and adsorptive species accumulate rapidly at the activated charcoal surface and occupy active sites, resulting in the higher uptake in the early shaking time.

Figure 1: Thorium ions adsorption on activated charcoal against shaking time at different temperatures.



As a consequence, some portion of the active adsorbent sites may be blocked with the passage of time, hence the rate becomes slower and reaches equilibrium when the surface become almost saturated. Figure 1 also shows that the general time dependence of thorium ions adsorption process is essentially independent of temperature. However, temperature variations influence the amount of thorium ions adsorption, which increases with a rise in adsorption temperature.

The adsorption of thorium ions on activated charcoal may be explained by a mechanism involving prior hydrolysis of thorium ions to give hydrolyzed species $Th(OH)^{3+}$ releasing H^+ into the solution. This hydrolyzed species is then adsorbed on the activated charcoal which possesses acidic functional groups (5). The release of H^+ results in the lowering of pH of the solution. The pH determined of thorium solution is 3.6 which confirm the above argument.

The adsorption of thorium ions on activated charcoal from aqueous solution can be considered as a reversible reaction with an equilibrium between two phases :

$$\underset{\text{Activated charcoal}}{S} + \underset{\text{Thorium ions}}{M} \underset{k_2}{\overset{k_1}{\rightleftarrows}} S-M \qquad (2)$$

where k_1 and k_2 are the rate constants for the adsorption and desorption processes. The values of overall rate constant, k, k_1 and k_2 were calculated using the following equations (6) :

$$\log(q_e - q_t) = \frac{-k\,t}{2.303} + \text{constant} \qquad (3)$$

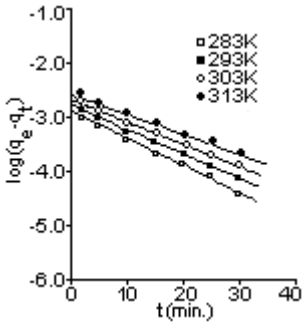
$$k = k1\,(1+1/k_c) = k_1 + k_2 \qquad (4)$$

and

$$k_c = \frac{C_{AC}}{C_{SN}} = \frac{k_1}{k_2} \qquad (5)$$

where q_e and q_t are the amounts of thorium ions adsorbed on activated charcoal at equilibrium and at time t respectively, k is the overall rate constant, k_c is

Figure 2: Plots of log (q_e-q_t) vs. t for thorium ions adsorption on activated charcoal at different temperatures.



the equilibrium constant, C_{AC} is the equilibrium concentration of thorium on the activated charcoal (g/1). Straight lines are obtained by plotting log (a_e-a_t) against t, as shown in Figure 2, which indicates that thorium ions adsorption on activated charcoal proceeds as a first order process. The values of overall rate constant, k obtained from the slopes of the aforementioned curves are given in Table 1. Other constants k_1, k_2 and k_c were calculated using equations 4 and 5 and are also given in Table 1. The activation energy for the thorium ions adsorption process on activated charcoal is determined from the slope of a straight line plot of ln k vs 1/T and is found to be 13.40 kJ/mol. Table 1 shows that the k_c values increase with an increase in adsorption temperature, thus implying a strengthening of the adsorbate-adsorbent interactions at higher temperature. The thermodynamic quantities △H, △S and △G were calculated from the k_c values using the following relations :

$$\triangle G = -RT \ln k_c \quad (6)$$

$$\ln kc = -\triangle H/RT + \text{constant} \quad (7)$$

$$\text{and} \quad \triangle S = (\triangle H - \triangle G)/T \quad (8)$$

The variation of ln k_c with reciprocal of temperature is given in Figure 3. From the slope of this curve, the quantity △H is calculated and is given Table 2, along with the values of △G and △S calculated using equation 6 and 8 respectively. The positive values of △H show that the thorium ions adsorption on activated charcoal is an endothermic process. The possible explanation of endothermicity is given in our earlier communication (3). The values of △G are negative as expected for a spontaneous process. The decrease in △G values with increasing temperature reveals that thorium ions adsorption on activated charcoal is favorable at higher temperature. The △S values are positive and no appreciable change in △S values is observed with increasing temperature, which means that the magnitude of △S is not affected by the temperature. It is concluded that, since the thorium ions adsorption process is endothermic, the driving force for adsorption must come from an entropy effect.

Figure 4 depicts the adsorption of thorium ions on activated charcoal in different concentration ranges (0.5-3.0 g/l) from aqueous solutions at 293K. These observations are similar to the temperature dependent studies of thorium ions adsorption, as shown in Figure 1. It is quite evident from Figure 4 that the fraction of thorium ions adsorbed at equilibrium as well as prior to the equilibrium decreases with an increase in thorium ions concentration. The data concerning the dependence of the extent of adsorption of thorium ions concentration at equilibrium (Table 3) were fitted using the Freundlich and the Langmuir isotherm equations. The Freundlich and the Langmuir plots were obtained, Figure 5, using well known equations :

$$x = A \; C^{1/n} \quad \text{(Freundlich)} \quad (9)$$

and

$$C/X = 1/K_{ads} X_m + C/X_m \quad \text{(Langmuir)} \quad (10)$$

Figure 3: Plots of ln k_c vs. 1/T for thorium adsorption on activated charcoal.

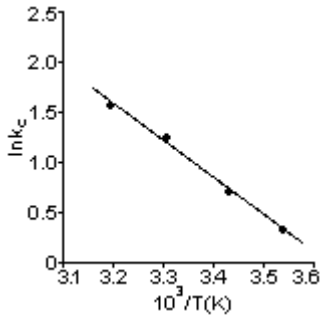


Figure 4: Thorium ions adsorption on activated charcoal as a function of shaking time at different concentration of thorium ions.

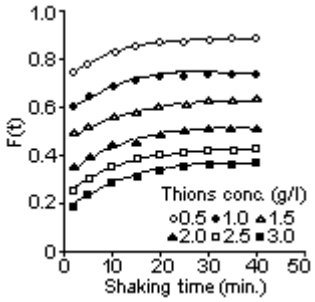


Table 1: Calculated values of rate constants and equilibrium constants for thorium ions adsorption on activated charcoal at different temperatures.

Tempera k	k (min^{-1})	k_1 (min^{-1})	k_2 (min^{-1})	k_c
283	0.131	0.076	0.055	1.39
293	0.105	0.070	0.035	2.00
303	0.090	0.068	0.022	3.08
313	0.080	0.066	0.014	4.88

where X is the amount of thorium ions adsorbed per gram of the activated charcoal (g/g), C is the equilibrium concentration of thorium ions in solution (g/l). A and n are the constants that can be related to the strength of the adsorptive bond and bond distribution respectively. X_m is the adsorption capacity at monolayer and K_{ads} is the constant that is related to the heat of adsorption. Figure 5 reveal that the adsorption of

Table 2: Determined values of thermodynamic parameters for thorium ions on activated charcoal.

Tempera k	△G kJ.(mol^{-1})	△H kJ.(mol^{-1})	△SK kJ.deg^{-1}(mol^{-1})
283	-0.774	30.86	0.1117
293	-1.688		0.1110
303	-2.834		0.1112
313	-4.125		0.1118

Table 3: Equilibrium data for thorium ions adsorption on activated charcoal as a function of its own concentration.

Initial thorium concentration C_i(g/l)	Equilibrium concentration of thorium insolution C(g/l)	Concentration of thorium adsorbed at equilibrium (g/l)	*Amount of thorium adsorbed at equilibrium per gram of activeted charcoal X (g/g)
0.5	0.06	0.44	0.044
1.0	0.26	0.74	0.074
1.5	0.57	0.93	0.093
2.0	0.96	1.02	0.102
2.5	1.44	1.06	0.106
3.0	1.91	1.09	0.109

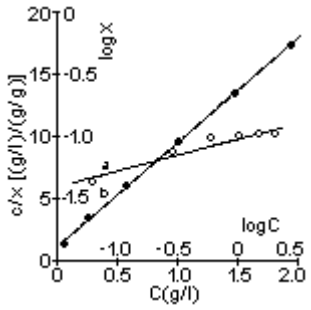
*Amount adsorbed. $X(g/g)= \frac{(C_i-C)V}{M}$; where V is the volume of the solution and M is the weight of the activated charcoal.

thorium ions on activated charcoal obeys the Freundlich and the Langmuir isotherm equation. The Langmuir equation provide the better fit over the entire range of study.

CONCLUSION

The adsorption of thorium ions on activated charcoal from aqueous solutions proceeds as a first order process, with an activation energy 13.40 kJ/mol. High temperature favors the adsorption of thorium and

Figure 5: (a) Freundlich and (b) Langmuir plots for thorium ions adsorption on activated charcoal.



attained equilibrium within 30 minutes. Moreover Langmuir equation provide a better fit in the whole concentration range studied. Thermodynamic quantities $\triangle H$, $\triangle S$ and $\triangle G$ were computed from the equilibrium constant, k_c values. The results show that the thorium adsorption on the activated charcoal is an endothermic process. The data are important for the recovery of thorium ions from solutions.

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