Adsorption 11: 51–55, 2005

Kinetic Study of Erbium Ion Adsorption on Activated Charcoal from Aqueous Solutions

RIAZ QADEER
Pakistan Atomic Energy Commission, P.O. Box 1611, Islamabad, Pakistan

Received March 23, 2004; Revised October 26, 2004; Accepted January 3, 2005

Abstract. The kinetics of the adsorption of erbium ions on activated charcoal from aqueous solutions has been studied in the temperature range of 10 to 40°C. It was observed that the diffusion of erbium ions in to the pores of activated charcoal controls the kinetics of the adsorption process, and the values of intra-particle diffusion rate constant, k_d (g/g · min$^{1/2}$) were evaluated as 0.7×10^{-3} to 1.6×10^{-3} in the temperature range studied. Various thermodynamic parameters ΔH, ΔG and ΔS were also computed from values of the equilibrium constant K_C. The results showed that the adsorption of erbium ions on activated charcoal is an endothermic process.

Keywords: activated charcoal, erbium ions, adsorption, kinetics, aqueous solutions

Introduction

The time dependence study of metal ions adsorption on solids provides valuable information about the adsorption process and its mechanism. Generally, 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 layer of the adsorbent. The rate of each of these steps is dependent on many factors such as agitation of solution, the state of metal ions in solution, age of the solution, concentration of metal ions and temperature etc. (Benes and Majer, 1980). The adsorption of erbium ions is important for pre-concentration for use in nuclear and metallurgical industries. Due to its thermal neutron absorption cross section (168 b) and high melting point (1529°C), erbium along with other material is used to make nuclear control rods. Earlier reports have dealt with the adsorption of erbium ions on molybdenum surface (Shakirova et al., 1990) and resin (Yuan et al., 1996), but no data are available on its adsorption on activated charcoal. This communication reports the results of a temperature dependence study of erbium ion adsorption on activated charcoal from aqueous solutions.

Experimental

Materials

The chemicals used in this study were erbium nitrate (Rare Earth Product, 99.999%) and a commercial activated charcoal (M/S British Drug House BDH; item No. 33032). The B.E.T. surface area, determined by nitrogen adsorption, was found to be 980 ± 10 m^2/g. The porosity and pore volume were found to be 75.75 ± 2% and 1.43 ± 0.12 cm^3/g respectively, and average particle size was 3.7 ± 0.2 μm.

Instruments

An energy dispersive X-ray fluorescence (EDXRF) spectrometer, XR 500 from Links System, U.K., equipped with an 860 analyzer, a Si (Li) detector and an X-ray tube K5012 with tungsten anode, was used for measuring the erbium ions concentration in solution with an error of ±1.5%. A Hetofrig shaker from Heto Birkerod, Denmark was used for temperature controlled adsorption studies with temperature variations of ±0.1 K.

Procedure

Adsorption measurements were carried out via a batch technique. Accordingly, 10 ml of erbium solutions of 2.0 g/l concentration were added to 250 ml glass reagent bottles and shaken with 0.1 g of dry activated charcoal in a thermostat shaker, the temperature of which was pre-adjusted to a desire value. After a predetermined time, the solution was filtered through Whatman filter paper No. 40 (Circular, 14.0 cm). The first 2–3 ml portion of the filtrate was rejected because of the adsorption of erbium ions on filter paper. The concentration of erbium ions in measuring filtrate was determined by means of the EDXRF spectrometer and was corrected for losses due to adsorption on the walls of the glass bottles by running blank experiments (i.e., without activated charcoal added). The amount of erbium ions adsorbed on activated charcoal was computed using the following relation:

$$\text{Amount adsorbed (g/g)} = (C_o - C_t)V/W \tag{1}$$

Results and Discussion

Figure 1 represents the variation of erbium ions adsorption on activated charcoal with shaking time at different temperatures. This figure indicates that initially the amount of erbium ions adsorbed increases rapidly, but then the process slows down and subsequently attains a constant value after 60 minutes (i.e., when adsorption equilibrium is established). As an approximation, the adsorption of erbium ions on activated charcoal can be said to take place in two distinct steps, a relatively fast one followed by a slower one. The slow adsorption is explained by the diffusion of erbium ions into the pores of activated charcoal.

An equation proposed by Aharoni et al. (1979) was employed to study the kinetics of erbium ions adsorption on activated charcoal, and is given below:

$$dq_t/dt = k\alpha t^{\alpha-1} \tag{2}$$

k is a factor that depends on the concentration of solutions and is given as:

$$k = k_o(q_o - q_t W)/V \tag{3}$$

On substituting k values from Eq. (3) into Eq. (2) and integrating Eq. (2) becomes:

$$\ln[q_o/(q_o - q_t W] = k_o W/V \cdot t^{\alpha} \tag{4}$$

To apply Eq. (4) to the experimental data of the adsorption of erbium ions on activated charcoal given in Fig. 1, Eq. (4) is re-arranged as follows:

$$\log\log[q_o/(q_o - q_t W)] = \log(k_o W/2.303V) + \alpha \log t \tag{5}$$

Straight lines were obtained by plotting log log $[q_o/(q_o - q_t W]$ against log t, as shown in Fig. 2, indicating that the system acts in accordance with the Eq. (5). The values of α may be calculated from the slopes of the straight lines in Fig. 2 using least square method and are given in Table 1. The applicability of

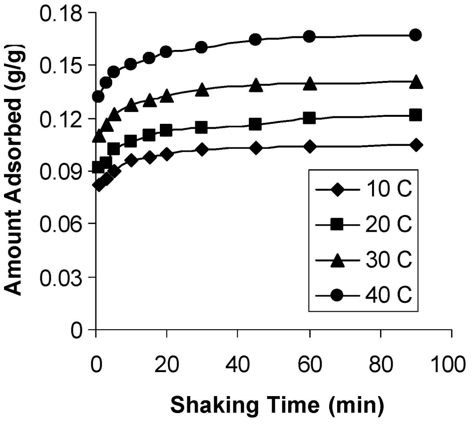

Figure 1. Variation of amount of erbium ions adsorbed on activated charcoal with shaking time at different temperatures.

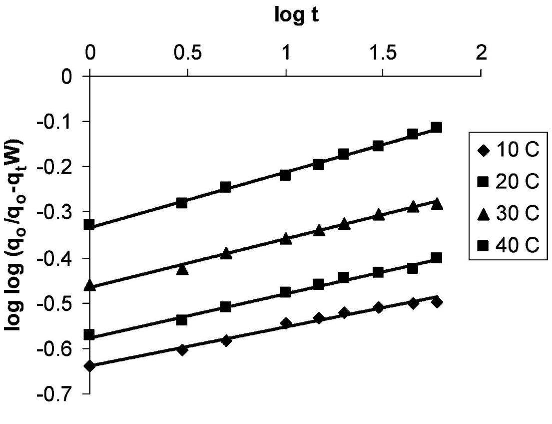

Figure 2. Plot of log log $[q_o/(q_o - q_t W)]$ versus log t for erbium ions adsorption on to activated charcoal at different temperatures.

Table 1. Calculated values of α and k_d for the adsorption of erbium ions on activated charcoal.

Temperature (°C)	α	k_d (g/g · min$^{1/2}$)
10	0.085	0.7×10^{-3}
20	0.097	1.1×10^{-3}
30	0.105	1.3×10^{-3}
40	0.123	1.6×10^{-3}

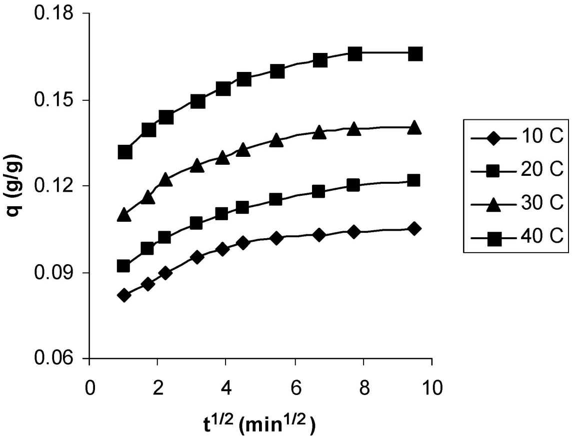

Figure 3. Amount of erbium ions adsorbed, q_t (g/g) on activated charcoal as a function of $t^{1/2}$ at different temperatures.

Eq. (5) to the erbium ions adsorption data shows that the diffusion of erbium ions into the pores of the activated charcoal controls the adsorption process (Aharoni et al., 1979).

The Weber and Morris equation (Akhtar and Qadeer, 1997):

$$q_t = k_d(t)^{1/2} \tag{6}$$

was also employed to the experimental data depicted in Fig. 1. Figure 3 indicates that the boundary layer and the intra-particle diffusion plays significant role in the adsorption process. The values of the rate constant for intra-particle diffusion, k_d, were evaluated from the slopes of the data at higher time and are also given in Table 1.

The adsorption of erbium ion on activated charcoal can be expressed as:

$$S + M \underset{k_2}{\overset{k_1}{\leftrightarrow}} S - M \tag{7}$$

where S is the activated charcoal; M is the erbium ion; k_1 and k_2 are the rate constant for the adsorption and desorption processes, respectively. The equilibrium constant, K_C can be calculated as:

$$K_C = k_1/k_2 = C_{\mathrm{M,AC}}/C_{\mathrm{M,SN}} \tag{8}$$

where $C_{\mathrm{M,AC}}$ and $C_{\mathrm{M,SN}}$ are the equilibrium concentrations of erbium ions on activated charcoal and in solution, respectively. Mathematically these concentrations can be expressed as:

$$C_{\mathrm{M,AC}} = C_{\mathrm{Mi}}(F) \tag{9}$$

and

$$C_{\mathrm{M,SN}} = C_{\mathrm{Mi}}(1 - F) \tag{10}$$

where C_{Mi} is the initial concentration of erbium ions and F is the fractional attainment of adsorption equilibrium. On substituting the values of $C_{\mathrm{M,AC}}$ and $C_{\mathrm{M,SN}}$, Eq. (8) becomes:

$$K_C = F/(1 - F) \tag{11}$$

The values of the equilibrium constant, K_C for the adsorption of erbium ions on activated charcoal were calculated at different temperatures at 60 minutes of equilibrium time and are given in Table 2. This shows that K_C values increase with an increase in adsorption temperature.

The thermodynamic quantities such as ΔG, ΔH and ΔS of erbium ions adsorption on activated charcoal were calculated using the following relations:

$$\ln K_C = -\Delta H/RT + \Delta S/R \tag{12}$$

and

$$\Delta G = \Delta H - T\Delta S \tag{13}$$

The variation of ln K_C with reciprocal temperature, 1/T is shown in Fig. 4. From the slope and intercept of

Table 2. Equilibrium constant K_C and F values for erbium adsorption on activated charcoal.

Temperature (°C)	10	20	30	40
F	0.52	0.60	0.70	0.83
K_C	1.09	1.50	2.34	4.89

Table 3. Calculated values of the thermodynamics parameters for erbium ions adsorption on activated charcoal.

ΔH	ΔS	ΔG (kJ/mol)			
(kJ/mol)	(kJ/deg · mol)	283 K	293 K	303 K	313 K
31.20	0.11	−0.07	−1.03	−2.13	−3.23

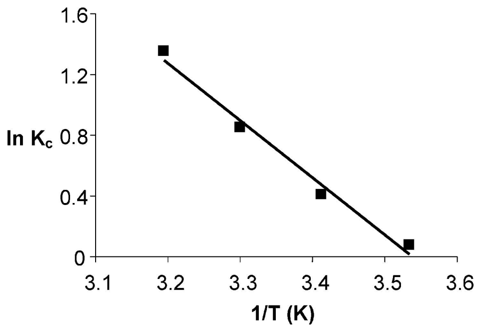

Figure 4. Plot of ln K_C versus $1/T$ for erbium ions adsorption on activated charcoal.

this linear plot, the quantities ΔH and ΔS are calculated and are given in Table 3 along with the values of ΔG. The positive values of ΔH show that the erbium ions adsorption on activated charcoal is endothermic in nature. Similar observations have been reported earlier for different metal ions adsorption on activated charcoal (Qadeer et al., 1993). A possible explanation of the endothermic process is given in our earlier communication (Qadeer et al., 1993) which is reproduced here as a reference. The endothermicity of the adsorption process may be due to the fact that erbium ions are well solvated in aqueous solution. In order for these ions to adsorb, they are to some extent denuded of their hydration sheath. This dehydration process of ions requires energy. It is assumed that after adsorption the environment of the meatl ions is less aqueous than it was in solution state. The removal of water from ions is is essentially an endothermic process, and it appears that the endothermicity of the desolvation process exceeds that of heat of adsorption by a considerable extent. The values of ΔG are negative as expected for a spontaneous process. The decrease in ΔG value with increasing temperature reveals that adsorption of erbium ion on activated charcoal becomes favorable at higher temperature, because erbium ion are more readily de-solvated. The positive value of ΔS reveals the increased in randomness at solid-solution interface during the fixation of erbium ion on the active site of the adsorbent. Since the adsorption process is endothermic; it follows that under these conditions the process becomes spontaneous because of positive entropy change.

Conclusion

Higher temperature favors the adsorption of erbium ions on to activated charcoal from aqueous solutions. Equilibrium is attained within 60 minutes. Diffusion of erbium ion into the pores of the activated charcoal controls the adsorption process. Erbium ion adsorption on to activated charcoal is an endothermic process in nature. The data are important for the recovery of erbium ions from solutions.

Nomenclature

C_o	the initial concentration of erbium ions solution (g/l);
C_t	the concentration of erbium ions in solutions (g/l) at time t;
V	the volume of the solution taken (l)
W	the weight of the activated charcoal taken(g)
q_t	the amount of erbium ions adsorbed per g of activated charcoal at time t;
α	is a constant and usually has a value <1;
q_o	the initial amount of erbium ions in solution (g);
k_o	the proportionality constant;
k_d	the intra-particle diffusion rate constant (g/g · min$^{1/2}$)
ΔG	free energy change for erbium ions adsorption (kJ/mol)
ΔH	the enthalpy change for erbium ions adsorption (kJ/mol)
ΔS	the entropy change for the adsorption of erbium ions adsorption (kJ/deg · mol)

References

Aharoni, C., S. Sideman, and E. Hoffer, “Adsorption of Phosphate Ions by Collodion-Coated Alumina,” *J. Chem. Tech. Biotechnol.*, **29**, 404–412 (1979) .

Akhtar, S. and R. Qadeer, “Active Carbon as an Adsorbent for Lead Ions,” *Adsor. Sci. Technol.*, **15**, 815–824 (1997).

Benes, P. and V. Majer, *Trace Chemistry of Aqueous Solutions*, p. 207, Elsevier Scientific Publishing Co., 1980.

Qadeer, R., J. Hanif, M. Saleem, and M. Afzal, "Surface Characterization and Thermodynamics of Adsorption of Sr^{2+}, Ce^{3+}, Sm^{3+}, Gd^{3+}, Th^{4+}, $UO_2{}^{2+}$ on Activated Charcoal from Aqueous Solutions," *Colloid. Polym. Sci.*, **271**, 83–90 (1993).

Shakirova, S.A, V.A. Pleshkov, and G.A. Rump, "Adsorption of Erbium Atoms on the Molybdenum (110) Surface," *Poverkhnost*, **11**, 40–45 (1990); *Chemical Abstract*, **114**, 109346r (1991).

Yuan, M., S. Meng, Li, Deqian, and Sho. Chuanlin, "Adsorption of Heavy Rare-Earths (III) with Levextrel Resin Cynax 302," *Fenxi Huaxue*, **24**, 882–885 (1996); *Chemical Abstract*, **125**, 264449x (1996).