Kinetics and Thermodynamics of Some Metal Ions Adsorption on Activated Charcoal from Aqueous Solutions

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Summary: The kinetics and thermodynamics of metal ions (Sr^{2+}, Sm^{3+}, Gd^{3+}, Th^{4+} and UO_2^{2+} adsorption from aqueous solutions on activated charcoal have been investigated. The adsorption process of metal ions proceeds via two stages, the first stage is rather fast followed by a much slower one Bangham equation was applied to study the kinetics of metal ions adsorption. It is observed that the diffusion of metal ions into the micropores of the activated charcoal controls the kinetics of the adsorption process. Various thermodynamic quantities, ΔH, ΔS, ΔG, were computed from equilibrium constant, k_c values. The results show that the adsorption of the metal ions on activated charcoal is an endothermic process.

Introduction

The discharge of toxic metal ions and radionuclides from industrial and nuclear effluents in the environment cause pollution and the prolonged exposure to the metal ions is hazardous for all living organisms. This adverse situation has necessitated the importance of controlling and removing these metal ions and other radionuclides from effluents before discharging into the environment. It is therefore considered necessary to develop a simple and cheap method to clean up the nuclear/industrial effluents before discharging into water stream. For this purpose many processes are being utilized such as precipitation, ion-exchange, solvent extraction and adsorption on solids. The adsorption process under certain conditions has a definite edge over other methods used for metal ions recovery because of its simplicity, selectivity and efficiency [1]. Owing to its large surface area, microporous structure, high adsorption capacity, radiation stability and high purity, activated charcoal has been extensively used to remove the metal ions from solutions [2-5].

The adsorption of metal ions namely strontium (Sr^{2+}), samarium (Sm^{3+}), gadolinium (Gd^{3+}), thorium (Th^{4+}) and uranium (UO_2^{+2}) is important from the environmental and waste disposal point of view. Previously we have used the activated charcoal for the adsorption of these metal ions from aqueous solutions [6-10]. As an extension of our previous work, the present communication reports results of kinetic and thermodynamic investigations of the metal ions on activated charcoal from aqueous solution. The results are important in relation to the recovery of metal ions from solutions.

Results and Discussion

Figure 1 shows the variation of Sr^{2+}, Sm^{3+}, Gd^{3+}, Th^{4+}, and UO_2^{2+} ions adsorption on the activated charcoal with shaking time. This figure indicates that initially the amount of metal ions adsorbed increases rapidly, but then the process slow down and subsequently attains a constant value when adsorption equilibrium is established. The equilibration time for different metal ions is given below:

Metal ion	Sr^{2+}	Sm^{3+}	Gd^{3+}	Th^{4+}	UO_2^{2+}
Equil.time (min)	30	45	45	30	45

As an approximation, the adsorption of metal ions can be said to take place in two distinct stages, a relatively fast one followed by a slower one. The slow adsorption is explained by the diffusion of metal ions into the micropores of the activated charcoal.

The Bangham equation as suggested by Aharoni *et al.* [11], has been applied to the above processes in the form:

$$\log \log \frac{\phi_o}{\phi_o - q_t W} = \log \frac{k_o W}{2.303\ V} + \alpha \log t \qquad (2)$$

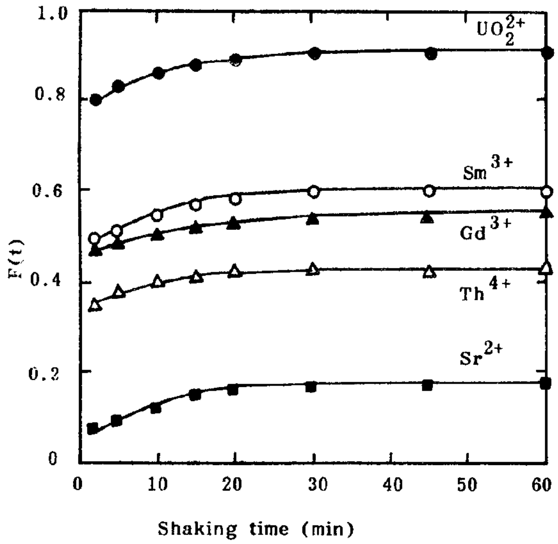

Fig. 1: Metal ions adsorption on the activated charcoal from aqueous solution against shaking time.

where ϕ_o is the initial concentration of metal ions in the solution, V is the volume of the solution, W is the weight of the activated charcoal, q_t is the amount of metal ions adsorbed at time t, α (<1) and k_o are constants.

Straight lines were obtained by plotting log log $\phi_o/\phi - q_tW$ against log t, as shown in Figure 2, indicating that the Bangham equation describes the systems very well. The values of α and k_o, calculated from the slopes and intercepts of plots shown in Figure 2, are given in Table 1. It indicates that the diffusion of metal ions into the micropores of the activated charcoal control the adsorption process [1].

Table-1: Kinetic parameters of Bangham equations for metal ions adsorption on the activated charcoal.

Metal ions	conc. (g/L)	α	k_o
Sr^{2+}	1.0	0.196	0.0101
Sm^{3+}	2.0	0.098	0.0639
Gd^{3+}	2.0	0.057	0.0637
Th^{4+}	2.0	0.064	0.0436
UO_2^{2+}	1.0	0.138	0.1442

The rate constants of two stages adsorption process of metal ions on activated charcoal are determined using the equation [12].

$$(1\text{-}F) = A_1e^{-k_1t} + A_2e^{-k_2t} \tag{3}$$

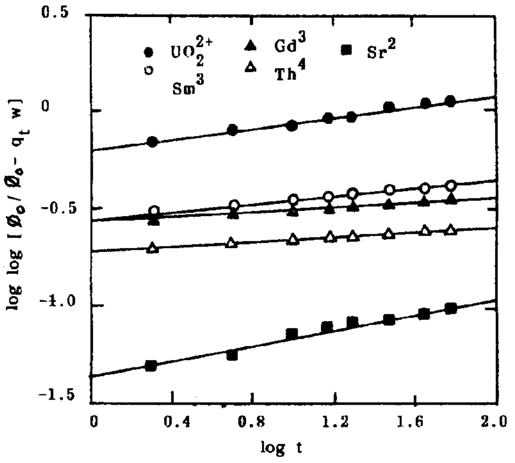

Fig. 2: Plots of log log $\phi_o/(\phi_o - q_tW)$ vs logt for metal ions adsorption on the activated charocal.

where k_1 is the rate constant for the first stage of adsorption k_2 is the rate constant for the second stage; and A_1 and A_2 are constants. Plots of ln (1-F) versus t for metal ions adsorption on activated charcoal are given in Figure 3. The values of k_1, k_2, A_1 and A_2 were determined as suggested by Mekhail *et al.* [12] and are given in Table 2.

Table-2: Values of rate constants for metal ions adsorption on the activated charcoal.

Metal ions	conc. (g/L)	$k_1(min^{-1})$	A_1	$k_2(min^{-1})$	A_2
Sr^{2+}	1.0	$6.751x10^{-3}$	0.9394	$3.465x10^{-4}$	0.8374
Sm^{3+}	2.0	$1.272x10^{-3}$	0.5188	$1.122x10^{-3}$	0.4195
Gd^{3+}	2.0	$5.692x10^{-3}$	0.5222	$1.625x10^{-3}$	0.4861
Th^{4+}	2.0	$5.206x10^{-3}$	0.6367	$4.212x10^{-4}$	0.5825
UO_2^{2+}	1.0	$3.204x10^{-2}$	0.2033	$7.884x10^{-3}$	0.1236

The adsorption of metal ions on activated charcoal can be expressed as a reversible process with an equilibrium between two phases [13].

$$S + M \underset{k'_2}{\overset{k'_1}{\rightleftarrows}} S - M \tag{4}$$

where S is the activated charcoal; M is metal ions, k'_1 and k'_2 are the rate constants for the adsorption and desorption processes respectively. It follows:

$$k_c = k'_1/k'_2 = C_{M.AC}/C_{M.SN} = C_{Mi}\,F/C_{Mi}\,(1\text{-}F) = F/(1\text{-}F) \tag{5}$$

where $C_{M.AC}$ is the equilibrium concentration of metal ions on activated charcoal and

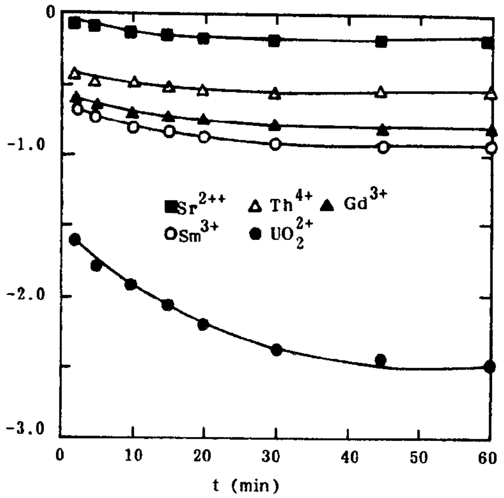

Fig.3: Plots of ln (1-F) vs. t for metal ions adsorption on the activated charocal.

C_{MSN} is the equilibrium concentration of metal ions in solution, k_c is the equilibrium constant and F is the fractional attainment of metal ions at equilibrium.

The equilibrium constant, k_c for the adsorption of Sr^{2+}, Sm^{3+}, Gd^{3+}, Th^{4+} and UO_2^{2+} ions on activated charcoal from aqueous solution was evaluated, using equation 5, at different temperatures. For such determinations, the concentration of metal ions and the V/m ratio were kept at 2.0 g/L and 100 mL/g respectively. The determined values of k_c at different temperatures are given in Table 3. This table show that k_c values increase with an increase in adsorption temperature. This is because at higher temperatures, the diffusion of metal ions into charcoal pores is faster and can proceed to a larger extent.

Table-3: Equilibrium constant, k_c values for metal ions adsorption on the activated charcoal at different temperature

Metal ions	Temperature °C					
	10	20	30	40	50	60
Sr^{2+}	0.98	1.22	1.67	2.03	2.33	2.85
Sm^{3+}	6.46	9.00	13.29	19.00	21.22	22.81
Gd^{3+}	4.68	5.94	7.20	8.85	10.11	-
Th^{4+}	1.26	1.60	1.66	1.93	2.13	2.33
UO_2^{2+}	-	-	3.78	4.41	4.48	-

The thermodynamic quantities such as ΔG, ΔH and ΔS of metal ions adsorption were calculated from the equilibrium constant, k_c values using the following relations

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

$$\ln k_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{7}$$

The values of ΔH and ΔS were obtained from the slopes and intercepts of linear variation on ln k_c with 1/T,. (see Figure 4) and are given in Table-4 along with the values of ΔG for metal ions adsorption on activated charcoal.

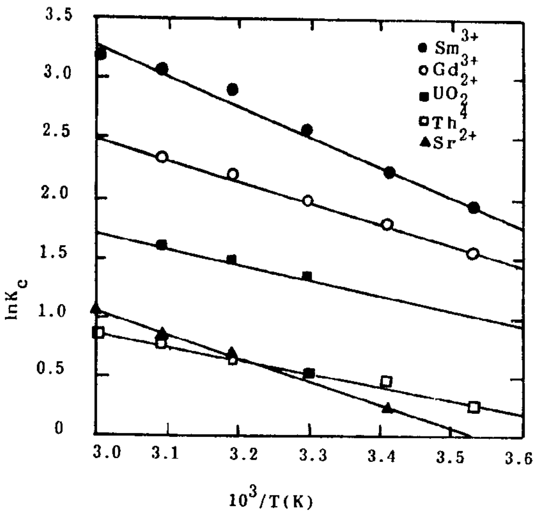

Fig. 4: Plots of ln k_c vs 1/T for metal ions adsorption on the activated charcoal.

It is evident that the values of ΔH for Sr^{2+} Sm^{3+}, Gd^{3+}, Th^{4+} and UO_2^{2+} ions are positive *i.e.*, endothermic, which is quite contrary to the usual observations of exothermicity. Such behaviour has been reported earlier for thorium and cerium ions [14-15], but no explanation has been given for the observed endothermicity. The possible explanation of endothermic heat of adsorption is given in our earlier communications [16-17]. The values of ΔG are negative as expected for a spontaneous process. The decrease in ΔG values for different metal ions with increasing temperature shows that the

Table-4: Calculated values of thermodynamic quantities of metal ions adsorption on activated charcoal.

Metal ions	ΔH ($kJ.mol^{-1}$)	ΔS ($kJ.deg^{-1}.mol^{-1}$)	ΔG($kJ.mol^{-1}$)					
			10°C	20°C	30°C	40°C	50°C	60°C
Sr^{2+}	16.49	0.0583	-	-0.60	-1.17	-1.76	-2.34	-2.93
Sm^{3+}	20.88	0.0898	-4.53	-5.93	-6.33	-7.23	-8.13	-9.02
Gd^{3+}	14.74	0.0651	-3.68	-4.33	-4.99	-5.64	-6.29	-
Th^{4+}	9.18	0.0347	-0.64	-0.99	-1.33	-1.68	-2.03	-2.38
UO_2^{2+}	10.37	0.0453	-	-	-3.36	-3.81	-4.26	-

adsorption of metal ions on activated charcoal is favourable at high temperature. It is therefore concluded that since the adsorption processes of Sr^{2+}, Sm^{3+}, Gd^{3+}, Th^{4+} and UO_2^{2+} ions on activated charcoal are endothermic, the driving force for adsorption must come from an entropy effect.

Experimental

The chemicals used in this study are strontium nitrate (Merck; item No. 7872); nitrates of samarium and gadolinium (Rare Earth Products; 99.999%); thorium nitrate (Fluka; item No. 27103); uranyl-nitrate (Riedel de Haen; item No. 31638) and a commercial activated charcoal (BDH: item No. 33032). Values of various parameter determined for the activated charcoal are reported elsewhere [16].

A Siemen's wavelength dispersive X-ray fluorescence (WDXRF) spectrometer, SRS-200, was used for measuring the concentration of metal ions in solution with an error within 3%. An Edmund Buhler-SM 25 shaker was used for shaking the sample solutions at a constant speed of 150 rev/min.

The adsorption of metal ions on activated charcoal from aqueous solutions was carried out by a batch technique at room temperature. Accordingly, 10 mL solutions of known concentration were added to 250 mL glass reagent bottles and shaken with about 100 mg of dry activated charcoal. After a predetermined time, the solution was filtered through Whatman filter paper No. 40. The initial 2-3 mL portions of the filtrates were rejected because of the adsorption of metal ions by filter papers. The concentration of metal ions was measured using WDXRF spectrometer and corrected for the loss of metal ions through adsorption on the walls of the glass bottles by running blank experiments (i.e., without activated charcoal) at each time. The fraction of metal ions adsorbed at any time, F(t) was calculated using the following relation.

$$F(t) = \frac{(C_i - C_t)}{C_i} \qquad (1)$$

where F(t) Fraction of metal ions adsorbed at time, t on activated charcoal.

C_i Initial concentration of metal ions in solutions (g/L).

C_t Concentration of metal ions in solutions at time, t (g/L).

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