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Adsorption of ruthenium ions on activated charcoal: influence of temperature on the kinetics of the adsorption process

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Abstract: Influence of temperature on ruthenium adsorption on activated charcoal from 3 mol/L HNO_3 solutions was investigated in the temperature range of 288 K to 308 K. It was observed that the rise in temperature increases the adsorption of ruthenium ions on activated charcoal and follows the kinetics of first order rate law with rate constant values 0.0564–0.0640 min^{-1} in the temperature range of 288 K to 308 K respectively. The activation energy for the adsorption process was found to be 1.3806 kJ/mol. Various thermodynamics quantities namely ΔH, ΔS and ΔG were computed from the equilibrium constant K_C values. The results indicated a positive heat of adsorption, a positive ΔS and a negative ΔG.

Key words: Ruthenium, Activated charcoal, Adsorption, Kinetics, Thermodynamic parameters, Nitric acid solution
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INTRODUCTION

Time dependence study of metal ions adsorption on solids provides valuable information on the adsorption process and its mechanism. Rate of metal ions adsorption process is dependent on a number of factors such as agitation of the solution, the state of metal ions in solution, concentration of metal ions and temperature (Benes and Majer, 1980). Temperature is the parameter generally ignored in most adsorption studies (Bangash and Hanif, 1992; Afzal *et al.*, 1993; Atun and Kilislioglu, 2003; Esumi *et al.*, 2004; Ko *et al.*, 2004).

^{106}Ru ($t_{½}$=386 d) is an important radioisotope in the nuclear industry and its adsorption on solid is important for purification, trace metal analysis and waste treatment. This paper reports results of our investigation of temperature's influence on the kinetics of ruthenium ions adsorption on activated charcoal from 3 mol/L HNO_3 solution. Activated charcoal is used due to its well known adsorptive characteristics and radiation stability (Qadeer and Hanif, 1994). The results are important in relation to the recovery of ruthenium ions. Some workers studied the adsorption of ruthenium on various solids/substrate (Legin and Kuznestsov, 1974; Qian and Yang, 1986; Che *et al.*, 1987; Jiang and Anson, 1992; Kavan *et al.*, 1993; Lin *et al.*, 1993; Chen *et al.*, 1993; Vrublevs'ka *et al.*, 1999; Lazarin and Sernaglia, 1999). Only few data are available on its adsorption on graphite/carbon (Che *et al.*, 1987). These studies were investigated from different points of view.

MATERIALS AND METHODS

The chemicals used in this study were ruthenium (III) chloride (MERCK, product No. 119246), a commercial activated charcoal (M/S British Drug House BDH; Item No. 33032, BET surface area 980 m^2/g) and nitric acid (MERCK, Product No. 100441).

Adsorption measurements were carried out via batch technique. Accordingly, 10 ml of ruthenium solutions of known concentration in 3 mol/L HNO_3 were added to 50 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 desired value. After a predetermined time, each 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 ruthenium ions on the filter paper. The concentration of ruthenium ions in measuring filtrate was determined by means of a wavelength dispersive X-rays fluorescence spectrometer (Siemens SRS200) 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 ruthenium ions adsorbed on the activated charcoal was computed using the following relation:

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

where C_0 is the initial concentration of ruthenium ions solution (g/L); C_t the concentration of ruthenium ions in solutions (g/L) at time t; V the volume of the solution taken (L) and W the weight of the activated charcoal taken (g).

RESULTS AND DISCUSSION

Investigations were conducted to ascertain the time required to reach equilibrium between ruthenium ions and the activated charcoal as a function of temperature. This study involved shaking of 10 ml of a solution containing 5×10^{-3} g/L of ruthenium in 3 mol/L HNO_3 with 0.1 g of activated charcoal for different time intervals from 2 to 100 min at temperatures of 288 K to 308 K. Fig.1 represents the variation of ruthenium ions adsorption on activated charcoal with shaking time. This figure indicates that initially the amount of ruthenium ions adsorbed increases rapidly, but then the process slows down and subsequently attains a constant value after 80 min i.e., when adsorption equilibrium is established. The slow adsorption is explained by the diffusion of ruthenium ions into the pores of the activated charcoal. Fig.1 also shows that the general time dependence of the ruthenium ions adsorption process is essentially independent of temperature. However, the temperature variations influence the amount of ruthenium ions adsorption, which increases with the rise in the adsorption temperature. This is because at higher temperature, the diffusion of ruthenium ions through the charcoal pores is faster and can proceed to a larger extent (Qadeer and Hanif, 1994).

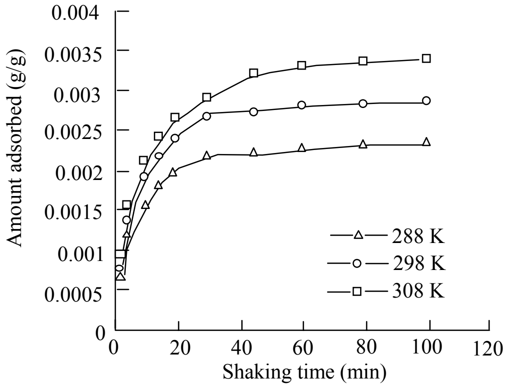

Fig.1 Influence of temperature on the adsorption of ruthenium ions on activated charcoal from 3 mol/L HNO_3

The Lagergren equation (Lagergren, 1898) employed for studying the rate constant of the process of ruthenium ions adsorption on activated charcoal is in the form:

$$\log(q_e-q_t)=\log q_e-K_{ads}t/2.303 \qquad (2)$$

where q_e is the amount of ruthenium ions adsorbed per gram of activated charcoal at equilibrium; q_t is the amount of ruthenium ions adsorbed at time t and K_{ads} is the rate constant for ruthenium ions adsorption (min^{-1}). The linear plot of $\log(q_e-q_t)$ versus t, Fig.2, shows the appropriateness of the above equation and subsequently the first order nature of the process involved. The values of the rate constant K_{ads} were calculated from the slopes of the afore-mentioned curves and are given in Table 1. The activation energy

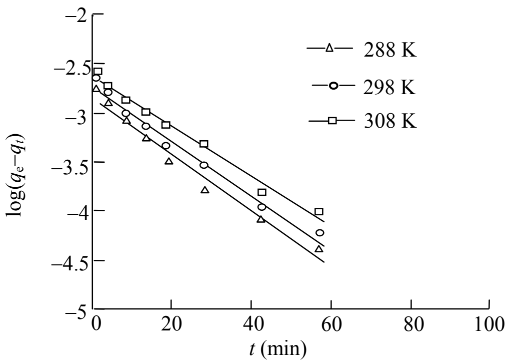

Fig.2 Plots of $\log(q_e-q_t)$ versus time at different temperature for ruthenium adsorption on activated charcoal from 3 mol/L HNO_3

for the ruthenium ions adsorption process was determined from the slope of a linear plot of $\ln K_{ads}$ versus $1/T$ and was found to be 1.3806 kJ/mol.

Table 1 Values of K_{ads} for the adsorption of ruthenium on activated charcoal from 3 mol/L HNO_3

Temperature (K)	K_{ads} (min^{-1})
288	0.0640
298	0.0619
308	0.0564

The adsorption of ruthenium ions on activated charcoal can be expressed as:

$$S+M \underset{k_2}{\overset{k_1}{\leftrightarrow}} S\text{-}M \quad (3)$$

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

$$K_C=k_1/k_2=C_{M,AC}/C_{M,SN} \quad (4)$$

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

$$C_{M,AC}=C_{Mi}(F) \quad (5)$$

and

$$C_{M,SN}=C_{Mi}(1-F) \quad (6)$$

where C_{Mi} is the initial concentration of ruthenium ions and F is the fractional amount of adsorption at equilibrium. On substituting the values of $C_{M,AC}$ and $C_{M,SN}$ into the Eq.(4), it becomes:

$$K_C=F/(1-F) \quad (7)$$

The values of the equilibrium constant (K_C) for the adsorption of ruthenium ions on activated charcoal were calculated at different temperatures at equilibrium time (i.e. 80 min). The variation of K_C with temperature is shown in Fig.3 showing that K_C values increase with increase in adsorption temperature, thus implying a strengthening of the adsorbate-adsorbent interactions at higher temperatures. This also indicates that the ruthenium ions dehydrate considerably at higher temperature before adsorption and thus their size during adsorption is smaller yielding higher K_C values (Qadeer *et al.*, 1995). The thermodynamic quantities such as ΔG, ΔH and ΔS of ruthenium ions adsorption on activated charcoal were calculated using the following relations:

$$\ln K_C=-\Delta H/RT+\text{constant} \quad (8)$$

$$\Delta G=-RT\ln K_C \quad (9)$$

$$\Delta S=(\Delta H-\Delta G)/T \quad (10)$$

where ΔH, ΔG, ΔS and T are the enthalpy, Gibbs free energy, entropy and temperature in K respectively; R is the gas constant (8.314 J/(mol·K)). Value of ΔH was computed from the slope of the linear variation of $\ln K_C$ with the reciprocal of temperature, $1/T$ (Fig.4) according to Eq.(8). The estimated ΔH value for the present system was 34.1642 kJ/mol. This value matches fairly well with the ΔH value determined by

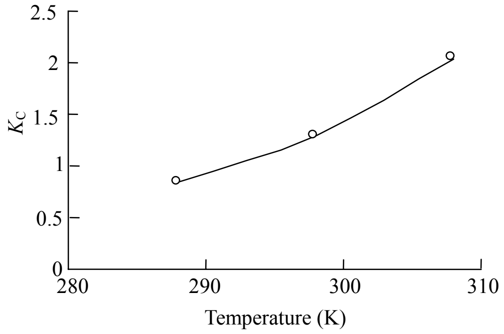

Fig.3 Variation of K_C with temperature for ruthenium adsorption on activated charcoal from 3 mol/L HNO_3

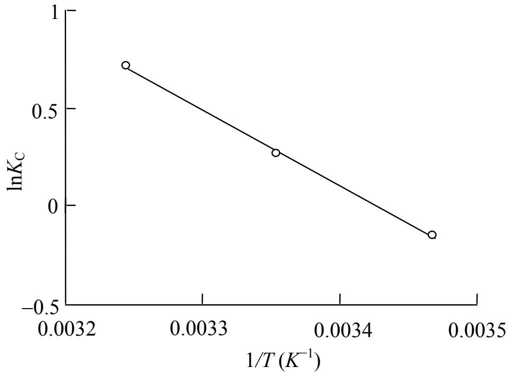

Fig.4 Plot of $\ln K_C$ versus reciprocal of temperature ($1/T$) for the adsorption of ruthenium on activated charcoal from 3 mol/L HNO_3

Chen and coworkers for the adsorption of ruthenium on resin as 22.59 kJ/mol (Chen *et al.*, 1993). The values of the free energy of specific adsorption, ΔG and entropy ΔS at various temperatures were calculated by using Eq.(9) and Eq.(10) respectively and are listed in Table 2. The positive value of ΔH shows that the adsorption of ruthenium ions on activated charcoal is an endothermic process. A possible explanation of the endothermic process is given by Qadeer *et al.*(1993). The values of ΔG are negative at 298 K and 303 K as expected for a spontaneous process. The decrease in ΔG value with increasing temperature reveals that adsorption of ruthenium ion on activated charcoal becomes better at higher temperature, because ruthenium ions are more readily de-solvated. The positive value of ΔS reveals the increased randomness at the solid-solution interface during the fixation of the ruthenium 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 the positive entropy change.

Table 2 Thermodynamic parameters for the adsorption of ruthenium adsorption on activated charcoal from 3 mol/L HNO_3

Temperature (K)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (kJ/(K·mol))
288	34.1642	0.3838	0.1172
298	34.1642	−0.6478	0.1168
308	34.1642	−1.4492	0.1156

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