Kinetics of Strontium Ions Adsorption on Activated Charcoal from Aqueous Solutions

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Summary: Batch kinetics of strontium ions adsorption on the activated charcoal from aqueous solutions was studied within the temperature rang 283-313K. It is observed that the hydrolyzed strontium diffuses into the micropores of the activated charcoal and the film diffusion, with an activation energy 6.80 kJ/mol, is the rate determining step.

Introduction

A major problem associated with the nuclear industry is the production of health hazardous radioactive waste solutions containing soluble metal ions and radionuclides. Strontium is an important element in nuclear industry. One of its isotope Sr^{90} is produced during the irradiation of the nuclear fuel as a fission fragment, and is a principal source of radioactivity due to its long half life ($t_{1/2}$ = 29.1 years) and has ability to substitute for calcium in bone tissue of human being. This adverse situation has demands attention to condition the waste effluent before discharging into the environment. Interest in the adsorption process for preconcentration/recovery of metal ions has increased many fold in recent years, because of its simplicity, selectivity and efficiency [1]. The time dependence study of metal ions adsorption on solids provides valuable informations about the adsorption process and its mechanism. The rate of adsorption process is dependent on number of factors such as an agitation of the solution, the state of metal ions in solutions, age of the solution, concentration of metal ions, pH of the solution, and adsorption temperature etc. [2]. Previously [3] we have studied the adsorption of strontium on activated charcoal and optimized different parameters for its preconcentration/removal from aqueous solutions. This communication reports results of the effect of temperature on the kinetics of strontium uptake by the activated charcoal. These results are important in relation to the recovery of strontium ions from solutions.

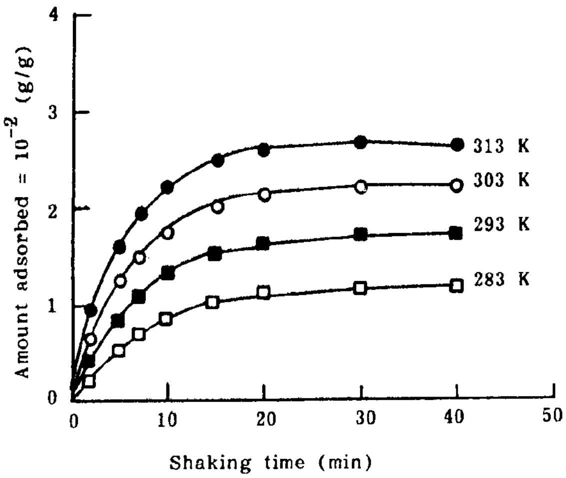

Fig. 1: Variation of strontium adsorption on activated charcoal with shaking time at different temperatures.

Results and Discussion

Figure 1 shows the variation of strontium ions adsorption on activated charcoal with shaking time at different temperatures. This study was performed by shaking 10 ml strontium solution of 1.0 g/l (pH = 3.9) with 0.1 g dry activated charcoal. This figure indicates that initially the adsorption of strontium ions increases with shaking time, then the process slows down and subsequently attains a constant value around 30 minutes. The slow adsorption may be due to the diffusion of the ions into the micropores of the activated charcoal. The general time dependence of strontium ions adsorption process is essentially independent of temperature. However, heating influence the amount of adsorbed strontium which increases with temperature.

The adsorption of strontium may be explained by a mechanism involving prior hydrolysis of strontium ions to give a hydrolyzed species $Sr(OH)^+$, releasing H^+ into the solution. This hydrolyzed species is then hydrolytically adsorbed on the activated charcoal surface (X) which usually have OH^- group [6-7]. The adsorbed strontium then diffuses into the micropores of the activated charcoal, which is a slow process hence controls the kinetics of strontium adsorption.

$$Sr^{2+} + H_2O \xrightleftharpoons{k_1 = 10^{-13.4}} Sr(OH)^+ + H^+ \qquad (2)$$

$$Sr(OH)^+ + X \rightleftharpoons Sr(OH)X \longrightarrow \text{Adsorbed strontium diffused into the micropores of the activated charcoal} \qquad (3)$$

The release of H^+ results in the lowering of the pH of the solution. The pH determined of strontium solution is 3.9 which conform the above argument.

The Bangham equation as suggested by Ahroni *et al.* [8] has been applied to the above process in the form:

$$\log\log\frac{\varphi_o}{\varphi_o - q_t W} = \frac{k_o W}{2.303\ V} + \alpha \ \log t \qquad (4)$$

where φ_o is the original concentration of strontium present in the solution (g/l), α (<1) and k_o are constants and W and V have been defined earlier. Straight lines were obtained by plotting the quantity log log $\varphi_o/\varphi_o - q_t w$ versus log t (Fig. 2). The reduced α and k_o values are given in Table-1. It results that the diffusion of strontium ions into the micropores of the activated charcoal controls the adsorption process [8].

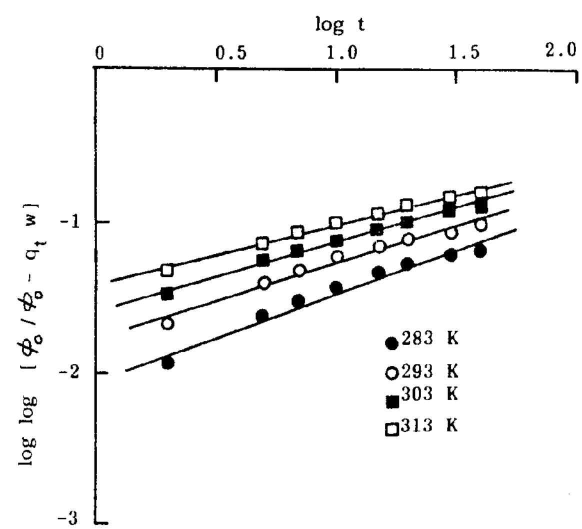

Fig. 2: Bangham's equation plots for strontium adsorption at different temperatures.

The adsorption of strontium ions from aqueous solution is supposed to occur in three steps [9]: bulk transport of the ions in the solution, Table-1: Determined α and k_o values for strontium ions adsorption on activated charcoal at different temperatures.

Temperature K	α	k_o
283	0.577	1.99×10^{-3}
293	0.502	3.80×10^{-3}
303	0.464	5.76×10^{-3}
313	0.403	8.58×10^{-3}

transfer of ions through a hypothetical film boundary layer, and diffusion of the ions within the pore volume of the activated charcoal and/or along the pore wall surfaces to an active adsorption site. The actual adsorption on the inner surface sites is generally considered to be very rapid, and hence is not a rate determining step. Therefore film and intra particle diffusion may controls the rate of adsorption. To ascertain the rate controlling step of strontium ions adsorption on activated charcoal, the equation of film diffusion was applied to the adsorption data [10] as:

$$- \ln (1-F) = kt \quad (5)$$

where $F = (q_t/q_e)$ is the fraction attainment of adsorption and k is the rate constant of film diffusion, q_e and q_t are the amount of metal ions adsorbed on activated charcoal at equilibrium and at time, t respectively. Straights lines are obtained by plotting -ln (1-F) versus t (Fig. 3) indicates that the film diffusion controls the kinetics of strontium ions adsorption on activated charcoal. The values of rate constants for film diffusion process are determined from the slopes of lines of Fig. 3 and are given in Table-2. This shows that the rate constant values increase with the rise in temperature. This may be due to the fact that the diffusion process become fast at higher temperature. The activation energy of the film diffusion process has been calculated with the Arrhenius equation. Plot of ln k vs. 1/T is shown in Figure 4., from the slope of which the values of 6.80 kJ/mol is obtained.

Table-2: Determined values of the film diffusion rate constants at different temperatures.

Temperature K	k (min^{-1})
283	0.125
293	0.144
303	0.152
313	0.167

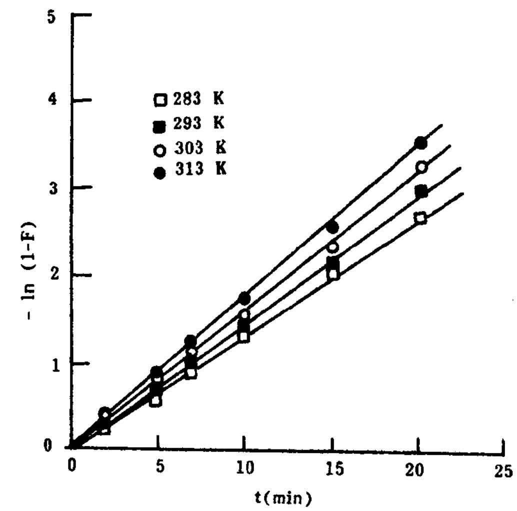

Fig. 3: Plot of -ln (1-F) vs. t for strontium adsorption.

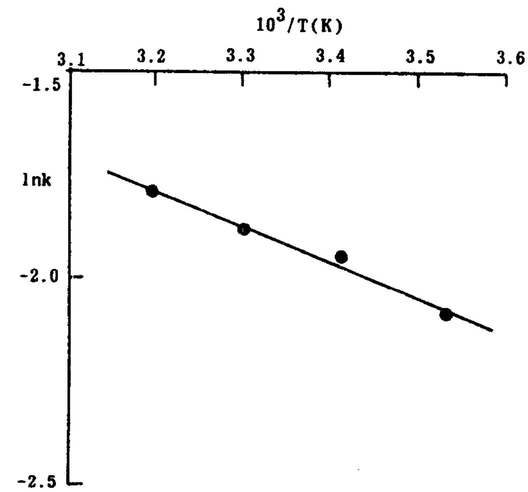

Fig. 4: Arrhenius plot for film diffusion of strontium ions.

Experimental

A commercial activated charcoal (BDH; item No. 33032) was used as an adsorbent. The values of surface area, pore volume, particle diameter, porosity, densities of activated charcoal have been measured and are reported earlier [4]. Strontium nitrate (Merck, item No. 7872) was used to make strontium ions solutions in doubly distilled water.

Siemen's wavelength dispersive x-ray fluorescence (WDXRF) spectrometer, SRS-200, was used for measuring the concentration of strontium in solutions. The variation in the measurement is <2.0%. A Hetofrig shaker (M/S Heto Birkerod, Denmark) was used for temperature controlled adsorption studies. The fluctuation in the temperature measurement is within ± 0.1K.

The adsorption of strontium ions on activated charcoal from aqueous solutions was carried out via a batch technique in the temperature range 283-313 K. The details of the adsorption procedure is similar as described earlier [5]. The amount of strontium ions adsorbed at any time, t was calculated using the following relation:

$$\text{Amount adsorbed, } qt = \frac{(C_i - C_t)V}{W} \quad (1)$$

where C_i is the initial concentration of strontium (g/l), C_t is the strontium concentration at time t (g/l), V is the volume of solution [l] and W is the weight of the activated charcoal (g)

Conclusion

High temperature favours the adsorption of strontium ions on activated charcoal from aqueous solutions. The diffusion of adsorbed strontium into the micropores controls the kinetics of adsorption process and the film diffusion is the rate determining step.

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