SELECTIVE ADSORPTION OF STRONTIUM ON ACTIVATED CHARCOAL FROM ELECTROLYTIC AQUEOUS SOLUTIONS

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The adsorption of strontium on activated charcoal has been studied as a function of shaking time, pH, concentration of adsorbate and temperature. Wavelength dispersive X-ray fluorescence spectrometer was used for measuring strontium concentration. The adsorption of strontium obeys Freundlich and Langmuir isotherms. Quantities ΔH^0 and ΔS^0 were calculated from the slope and intercept of plot $\ln K_D$ vs $1/T$. The influence of different cations and anions on strontium adsorption has been examined. The adsorption of other metal ions on activated charcoal has been studied under specific conditions to check its selectivity. Consequently strontium was removed from Rh, Pr, Rb and Cs. More than 95% adsorbed strontium on activated charcoal can be recovered with 65 ml 3M HNO_3 solution.

The adsorption of strontium on various solids is important because it has numerous application in industries such as glass, electrical, sugar, paint and nuclear. Much work has been done on the adsorption of strontium on tungsten[1 - 4], zeolite[5], soil and clay[6,7], mica[8], hydroxylapatite[9,10], gels[11], MnO_2 (refs[12 - 14]), salts and precipitates[15 - 18], Mo-crystal[19], cation exchanger[20,21], sediment[22], chiolite[23], sodium titanates[24], hydrous ceria[25], immobilized microorganism[26], copper and nickel[27,28] and activated carbon and graphite[29 - 32]. The present communication describes our investigations of adsorption of strontium on activated charcoal, which led to the determination of optimal conditions required for its preconcentration and separation.

EXPERIMENTAL

Chemicals and reagents. Activated charcoal supplied by M/s BDH (item No. 33032) and strontium nitrate supplied by M/s Merck (item No. 7872), were used during these studies. Buffer solutions of diffe-

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rent pH supplied by M/s Fluka were used for studying the affect of pH on the adsorption of strontium on activated charcoal.

Instruments. Siemen's wavelength dispersive X-ray fluorescence spectrometer (WDXRFS) SRS-200 was used with the following attachments: Cr X-ray tube; LiF(100) crystal; soller slit with angular divergence of 0.15°; NaI(Tl) scintillation counter linked through an universal interface LC-200 to a PDP-11/04 computer, for measuring strontium concentration. The pH measurements were made with a digital pH-meter 605 from M/s Metrohm. Edmund Buhler-SM25 shaker was used for shaking at a constant speed of 150 revolution per minute.

Procedure. Adsorption measurements were carried out by a batch technique at room temperature (17 ± 1 °C) except where otherwise specified. Known amount of activated charcoal in 250 ml reagent bottles containing 10 ml of strontium solution were shaken for a given time period. The solution were then filtered and concentration of strontium before and after shaking was measured by WDXRFS technique. The sample solutions were presented to the spectrometer in a 0.1 mm thick walled polyethylene bottle[33 - 34]. The distribution coefficients (K_D in ml/g) were computed in the following way[35]

$$K_D = C_1 / C_2 , \qquad (1)$$

where C_1 is amount of adsorbed Sr(II) ions per gram of solid and C_2 is concentration of Sr(II) ion per ml of the aqueous solution.

RESULTS AND DISCUSSION

The adsorption of strontium on activated charcoal was studied as a function of shaking time. An amount of 10 ml of strontium solution (1 000 μg/ml) was shaken with 100 mg of solid for different intervals of time ranging from 5 to 60 min.

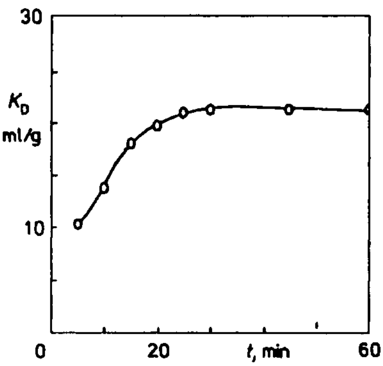

FIG. 1
Distribution coefficient (K_D) as a function of shaking time for Sr adsorption on activated charcoal

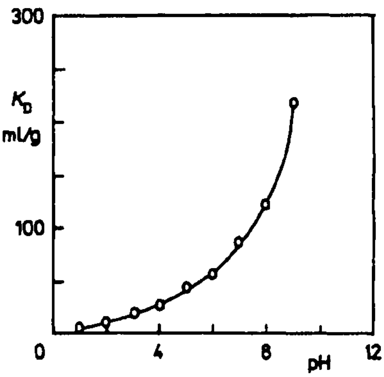

FIG. 2
Influence of pH on distribution coefficient (K_D) for Sr adsorption on activated charcoal

Figure 1 shows the variation of K_D with shaking time. The K_D value increases with an increase of shaking time and attains a constant value around 30 min when adsorption equilibrium is established. Shaking time 30 min was selected for all further studies.

Figure 2 shows the influence of pH on the adsorption of strontium on activated charcoal. The K_D value increases with the increasing pH upto 9.2. Above pH 9.2, the precipitation starts due to the formation of complexes in aqueous solution. Maximum adsorption occur at pH 9.2; hence buffer of pH 9.2 (Fluka, item No. 82562) was used for all further studies. The influence of pH on strontium adsorption is well explained by Hasany and Chaudhary[14].

The effect of strontium concentration on the adsorption was studied under optimized condition as determined above. The concentration of strontium was varied from 1 000 μg/ml to 6 000 μg/ml. The results in Fig. 3 show that K_D values decrease as the strontium concentration increases, indicating that energetically less favourable sites became involved with increasing strontium concentration. The results are then analyzed in terms of Freundlich, Langmuir and Dubinin–Radushkevish[36] (D–R) isotherms. The data does not fit the D–R equation. Freundlich and Langmuir plots were obtained, Figs 4 – 5, using the well known equations[37].

$$X/m = K C_s^{1/n} \quad \text{(Freundlich)} \tag{2}$$

and

$$C_s/(X/m) = 1/(K_1 K) + C_s/K_1, \quad \text{(Langmuir)} \tag{3}$$

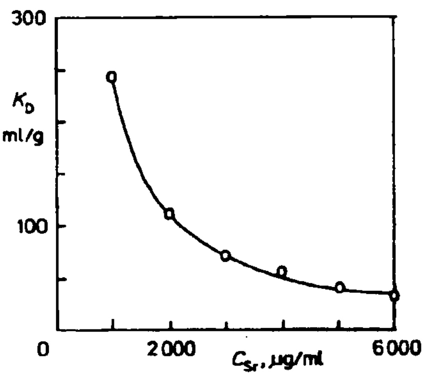

FIG. 3
Effect of Sr concentration on distribution coefficient (K_D) for its adsorption on activated charcoal

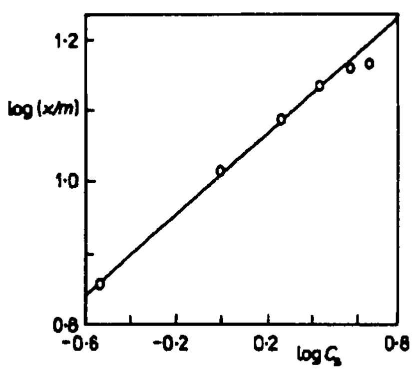

FIG. 4
Freundlich plot for Sr adsorption on activated charcoal

where X is amount of Sr(II) ions adsorbed (in g), m is weight of activated charcoal (in g), C_s is equilibrium concentration of Sr(II) ions (in g/l) and $1/n$, K, $1/K_1$ and $1/K_1K$ are constants. Constant $\log K$ and $1/n$ from Freundlich plot (Fig. 4) and $1/K_1$ and $1/K_1K$ from Langmuir plot (Fig. 5) were evaluated and are 1.014, 0.2853, 0.06323 and 0.2678, respectively. The Langmuir equation provides the best fit for the data in the whole range of strontium concentration.

The dependence of strontium adsorption on temperature was investigated. The temperature was varied from 10 ± 0.01 °C to 60 ± 0.01 °C in a step of 10 °C, while

TABLE I
Thermodynamic parameters for strontium adsorption on activated charcoal

C_{Sr} μg/ml	ΔH^0 kJ mol^{-1}	ΔS^0 kJ deg^{-1} mol^{-1}	ΔG^0, kJ mol^{-1}					
			283 K	293 K	303 K	313 K	323 K	333 K
1 000	42.0	0.191	-12.1	-14.0	-15.9	-17.8	-19.7	-21.6
2 000	16.8	0.098	-10.9	-11.9	-12.9	-13.9	-14.7	-15.8
3 000	12.5	0.079	-9.9	-10.6	-11.4	-12.2	-13.0	-13.8
4 000	12.4	0.076	-9.1	-9.9	-10.6	-11.4	-12.1	-12.9
5 000	12.1	0.073	-8.6	-9.3	-10.0	-10.7	-11.5	-12.2
6 000	11.4	0.068	-7.8	-8.5	-9.2	-9.9	-10.6	-11.2

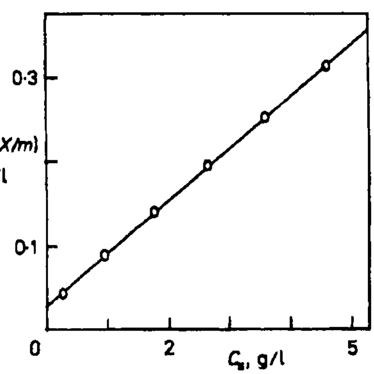

FIG. 5
Langmuir plot for Sr adsorption on activated charcoal

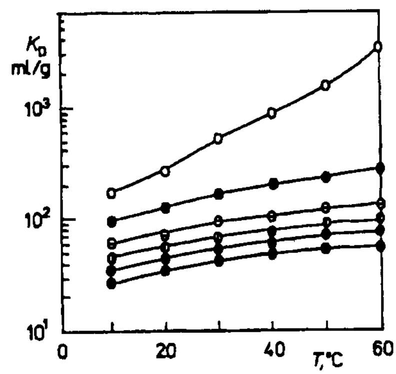

FIG. 6
Effect of temperature on distribution coefficient (K_D) for Sr adsorption on activated charcoal. C_{Sr}, μg/ml: O 1 000, ⊙ 2 000, ⊖ 3 000, ⦶ 4 000, ⊕ 5 000, ⊗ 6 000

other parameters were kept constant. Figure 6 shows that K_D values increase with the rise in temperature. This increase may be due to a negative temperature coefficient or to a steep simultaneous decrease of real adsorption of solvent[38]. The values of ΔH^0 and ΔS^0 were calculated from the slopes and intercepts of the linear variation of $\ln K_D$ with the reciprocal of temperature, $1/T$, Fig. 7, using the relation

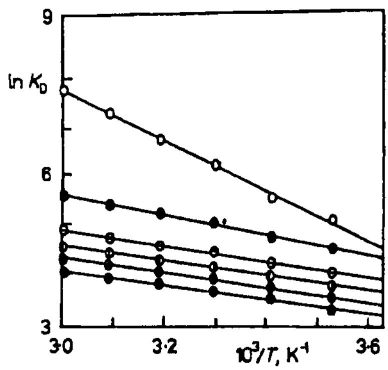

FIG. 7
Plot of $\ln K_D$ vs $1/T$ for Sr adsorption on activated charcoal. C_{Sr}, µg/ml: O 1 000, ⊙ 2 000, ⊖ 3 000, ⦶ 4 000, ⊕ 5 000, ⊛ 6 000

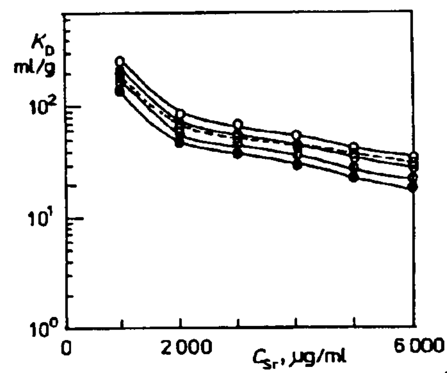

FIG. 8
Variation of K_D for Sr adsorption on activated charcoal in presence of some cations. Cation (Z/r): O NIL (–), ⊙ Na^+ (1.031), ⊖ K^+ (0.752), ⦶ Li^+ (1.471), ⊕ Cr^{3+} (4.762)

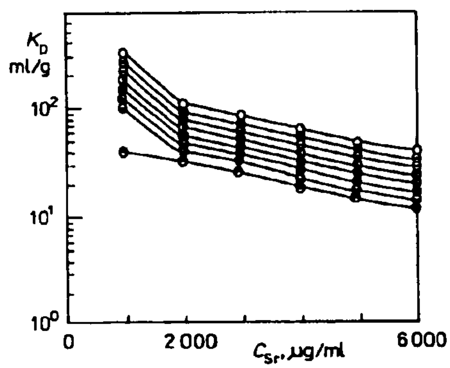

FIG. 9
Variation of K_D for Sr adsorption on activated charcoal in presence of some anions. Anion: O CH_3COO^-, ⊙ NIL, ⊖ $S_2O_3^{2-}$, ⦶ I^-, ⊕ Br^-, ⊛ Cl^-, ● NO_3^-, ● EDTA

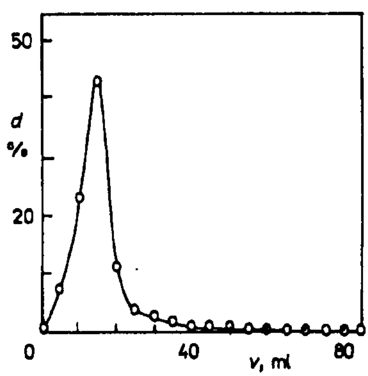

FIG. 10
Elution of adsorbed Sr from activated charcoal with 3M HNO_3 solution. Desorbed amount d as a function of the eluant volume v

$$\ln K_D = \Delta S^0 / R - \Delta H^0 / (R T) \qquad (4)$$

and ΔG^0 using equation

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 . \qquad (5)$$

The values of ΔH^0, ΔS^0 and ΔG^0 are given in Table I. Positive values of ΔH^0 and decrease in the value of ΔG^0 with rise in temperature show that the adsorption of strontium is more favourable at high temperature.

The influence of added cations (Li^+, Na^+, K^+ and Cr^{3+}) on the adsorption of strontium on activated charcoal was also investigated. The concentration of each cations was fixed at 1 000 μg/ml and strontium concentration was varied from 1 000 μg/ml to 6 000 μg/ml. The results of these investigation are shown in Fig. 8. It is seen that the greater is the ionic potential (Z/r) of the added cations, the smaller is the adsorption of strontium, potassium being the exception. Similar observation have been reported earlier[39].

To examine the adsorption behaviour of strontium on activated charcoal in the presence of acetate, thiosulfate, chloride, bromide, iodide, nitrate and EDTA, the concentration of each anion was taken as 1 000 μg/ml and the concentration of strontium was varied from 1 000 μg/ml to 6 000 μg/ml. The results are shown in Fig. 9. The acetate ion enhanced the adsorption of strontium while the other anions reduce the adsorption.

To check the selectivity of activated charcoal for adsorption of strontium, the adsorption of V, Cr, Mn, Ni, Cu, Rb, Zr, Ru, Rh, Cd, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er, U and Th on the adsorbent was examined under the optimum conditions for Sr. V, Mn, Ni, Cu, Zr, Cd, Cs, La, Ce, Sm, Eu, Gd, Dy, Er, U and Th were precipitated in pH 9.2 buffer solution. The K_D values for Cr, Rb, Rh, Cs, Ba, Pr, Nd are given in Table II. It is obvious from the data that Cr, Ru, Ba, Nd, have considerably high value of K_D, and hence would be coadsorbed alongwith strontium on activated charcoal. Rb, Rh, Cs and Pr are poorly adsorbed, therefore separation of strontium from these metals can be achieved. The separation factor for strontium is larger in presence of Rb and Cs,

TABLE II

Distribution coefficient (K_D) for Sr and other metals on activated charcoal at optimized condition for strontium. Concentration of all metals fixed at 1 000 μg/ml. The order of entries is on the basis of decreasing K_D value

Metal	Ba	Cr	Sr	Ru	Nd	Rh	Pr	Rb	Cs
K_D, ml/g	400.00	334.78	250.88	173.97	138.19	63.40	60.26	26.42	17.37

because they have much lower K_D values. The feasibility of using activated charcoal for preconcentration of strontium was further assessed by elution studies. This study was performed with 3M HNO_3 solution and result is shown in Fig. 10.

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