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Selective Adsorption of Uranium on Activated Charcoal from Electrolytic Aqueous Solutions

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Selective Adsorption of Uranium on Activated Charcoal from Electrolytic Aqueous Solutions

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Abstract

Adsorption of uranium on activated charcoal has been studied as a function of shaking time, amount of adsorbent, pH, concentration of adsorbate, and temperature. Uranium adsorption obeys the Langmuir isotherm. ΔH° and ΔS° were calculated from the slope and intercept of plots of ln K_D vs $1/T$. The influence of different anions and cations on uranium adsorption has been examined. The adsorption of other metal ions on activated charcoal has been studied under specified conditions to check its selectivity; consequently, uranium was removed from Cs, Ba, Zn, and Co. More than 98% adsorbed uranium on activated charcoal can be recovered with 65 mL of 3 *M* HNO_3 solution. A wavelength dispersive x-ray fluorescence spectrometer was used for measuring uranium concentration.

INTRODUCTION

Preconcentration/separation procedures based on adsorption phenomena are important in nuclear/radiation chemistry, industry, medicine, and daily life. Adsorption of uranium onto various solids is important from purification, environmental, and radioactive waste disposal points of view. Activated carbon, due to its selective adsorption, high radiation stability, and high purity, is often used for the separation of ions from solutions. The adsorption of uranium on activated carbon has been the subject of several investigations in the past (*1–18*). The present communication describes our investigations of uranium adsorption on activated charcoal and

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illustrates the optimal conditions required for its preconcentration and separation.

EXPERIMENTAL

Reagent and Chemicals

The reagent and chemical used:

1) Activated charcoal (BDH, item no. 33032).
2) Uranyl nitrate $6H_2O$ (Riedel de Haen item no. 31638).
3) Sodium hydroxide (Merck, item no. 6498).
4) Hydrochloric acid (Riedel de Haen, item no. 30721).
5) Buffer tablet pH 4 (Fluka, item no. 82560).

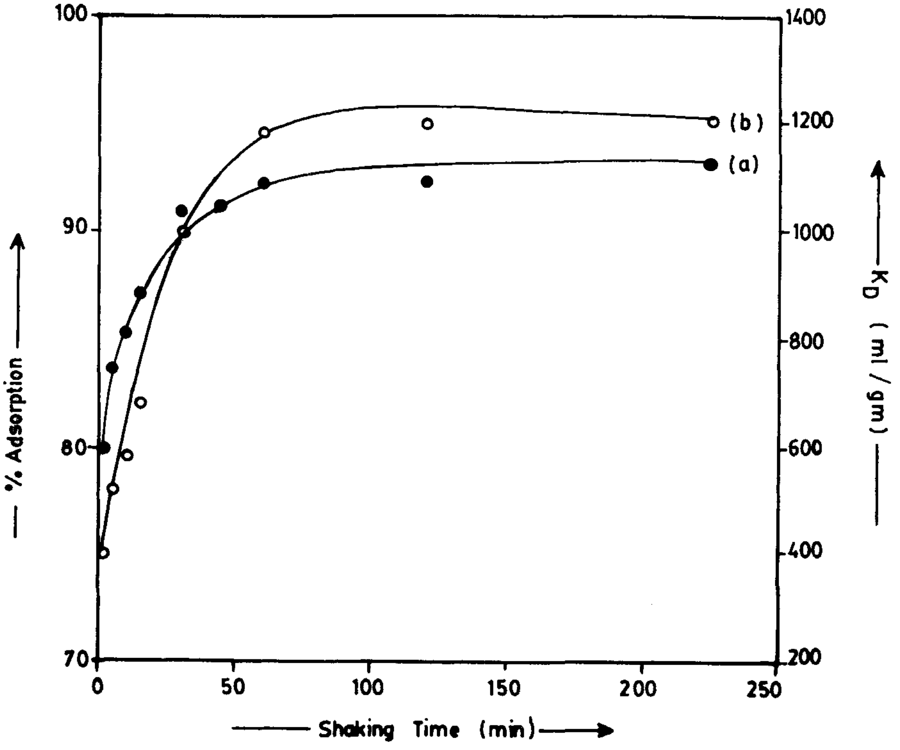

FIG. 1. Adsorption of uranium on activated charcoal as a function of shaking time: (a) % adsorption, (b) K_D.

INSTRUMENTS

Siemen's wavelength dispersive x-ray fluorescence spectrometer (WDXRFS)-SRS-200 with the following attachment: Cr-x-ray tube; Soller slit with angular divergence of 0.15; LiF (100) crystal; NaI(Tl) scintillation counter linked through a universal interface LC-200 to a PDP-11/04 computer was used for measuring uranium concentration. The pH measurements were made with a digital pH meter 605 from Metrohm. The pH of the solution was adjusted with 0.1 *M* HCl and 0.1 *M* NaOH. An Edmund Buhler SM25 shaker was used for shaking at a constant speed of 150 revolutions per minute.

PROCEDURE

Adsorption measurements were carried out by a batch technique at room temperature (21 ± 2°C) except where otherwise specified. Known amounts

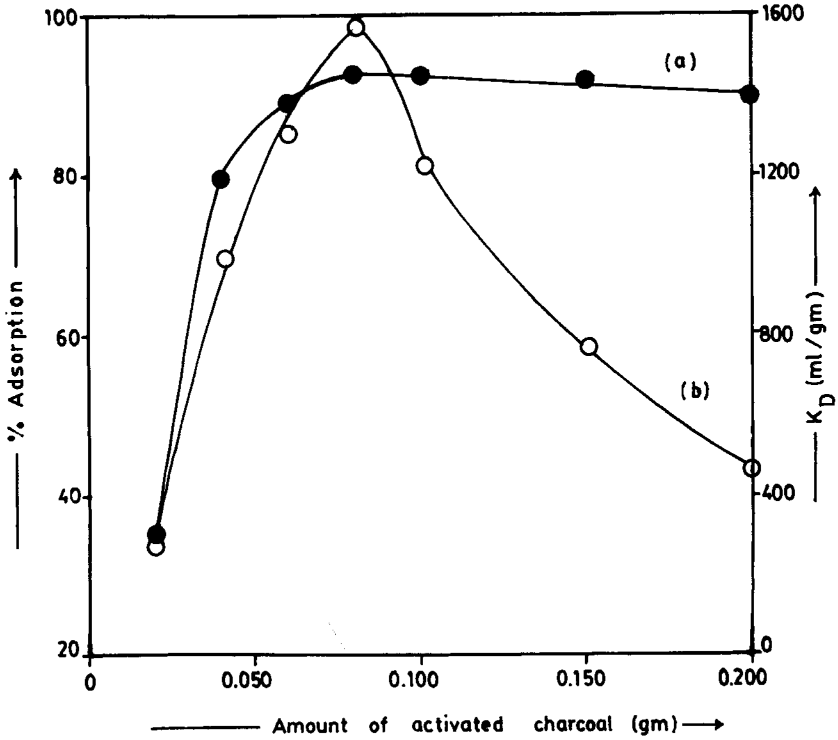

FIG. 2. Influence of amount of activated charcoal on the adsorption of uranium: (a) % adsorption, (b) K_D.

of activated charcoal in 250 mL reagent bottles containing 10 mL uranium solutions were shaken for a given time period. The solutions were then filtered, and the concentrations of uranium before and after shaking were measured by the WDXRFS technique. The sample solutions were presented to the spectrometer in polyethylene bottles with 0.1 mm thick walls (*19*, *20*). The percentage adsorption (%) and distribution coefficient (K_D) were computed by the usual methods (*21*).

RESULTS AND DISCUSSION

The adsorption of uranium on activated charcoal was studied as a function of shaking time. Ten milliliters of uranium solution (1000 μg/mL) was shaken with 100 mg of solid for different intervals of time ranging from 2 to 225 min. Figure 1 shows the variation of % adsorption and distribution coefficient (K_D) with shaking time. The adsorption increases with an increase of shaking time and attains a constant value at around 60 min where

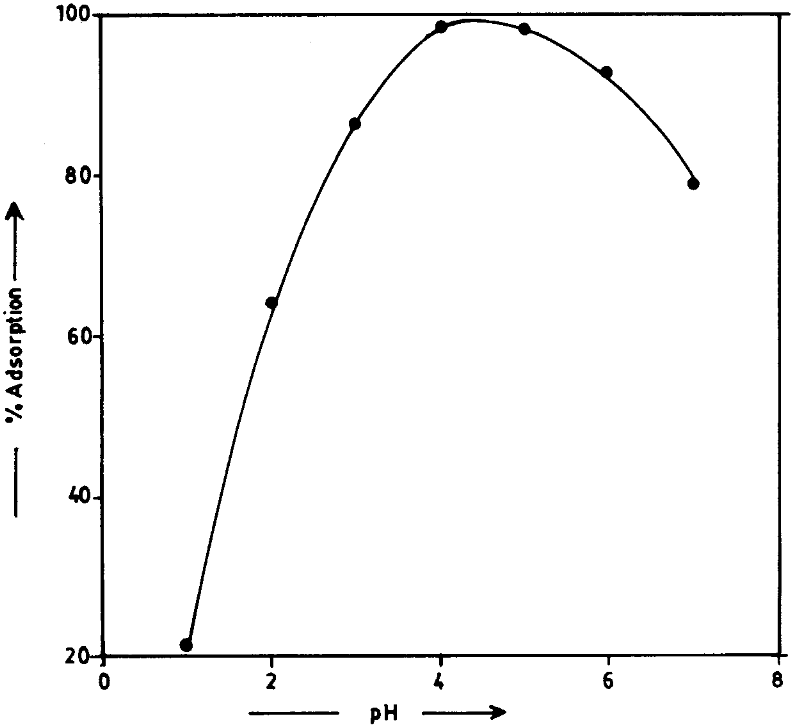

FIG. 3. Influence of pH on uranium adsorption on activated charcoal.

adsorption equilibrium is established. Therefore, 60 min shaking time was selected for all further studies.

The results of the dependence of uranium adsorption on the amount of activated charcoal are shown in Fig. 2. The concentration of uranium and shaking time were fixed as 1000 μg/mL and 60 min, respectively, while the amount of activated charcoal was varied from 20 to 200 mg. The % adsorption and distribution coefficient (K_D) increase with an increasing amount of adsorbent up to 800 mg. The % adsorption remains constant above 80 mg, but K_D decreases drastically. Therefore, 80 mg of activated charcoal was used for all further studies.

Figure 3 shows the influence of pH on the adsorption of uranium on activated charcoal. The percent adsorption increases with increasing pH up to 4 and then starts decreasing. Maximum adsorption occurs at pH 4,

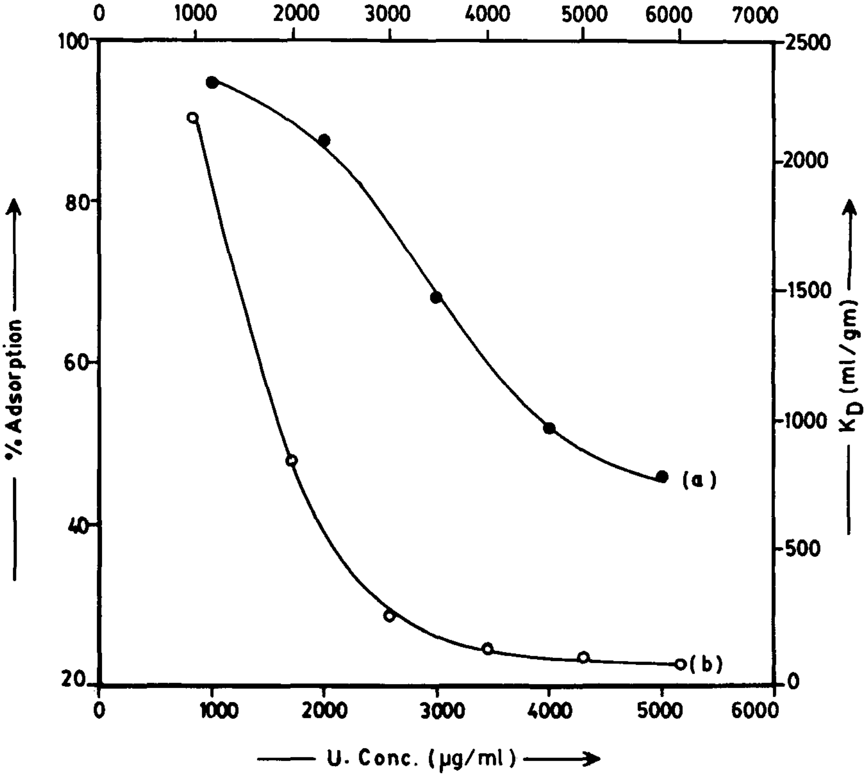

FIG. 4. Effect of uranium concentration on its adsorption on activated charcoal: (a) % adsorption, (b) K_D.

and hence a buffer of pH 4 was used in all further studies. The influence of pH on uranium adsorption can be explained in the following way: Hydrolysis of uranyl ion takes place as the pH varies from 1 to 4, and the availability of free uranium ions is maximum at pH 4 (*22*), and hence maximum adsorption. When pH increases beyond 4, precipitation starts due to the formation of complexes in aqueous solution and adsorption decreases since micropores are not formed.

The effect of uranium concentration on adsorption was studied under the optimized conditions of shaking time (60 min), pH (4), and amount of

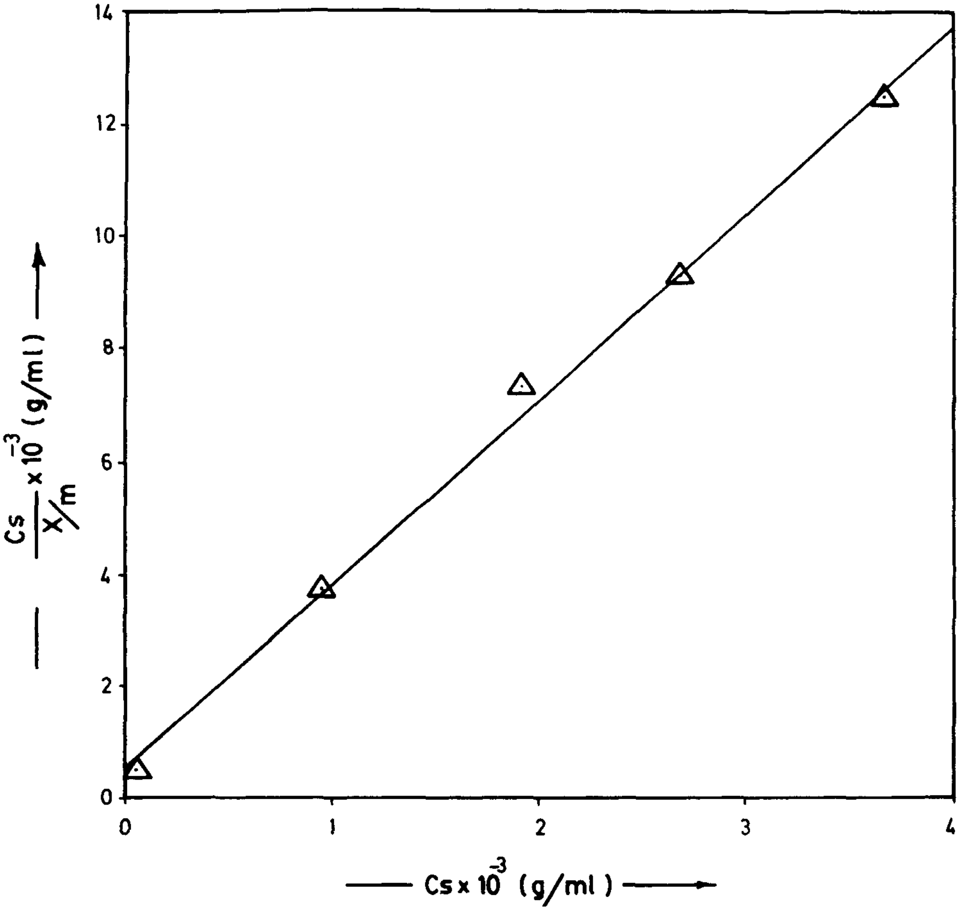

FIG. 5. Langmuir plot for uranium adsorption on activated charcoal.

adsorbent (80 mg). The concentration of uranium was varied from 1000 to 6000 μg/mL. The results in Fig. 4 show that the % adsorption and distribution coefficient (K_D) decrease as the uranium concentration increases. The increase of uranium concentration contributes to the formation of larger polymer particles that leads to decreasing adsorption (*7*). The results were analyzed in terms of Freundlich (*23*), Langmuir (*24*), and Dubinin–Radushkevich (D-R) (*25*) isotherms. The data do not fit the Freundlich and D-R equations. However, a straight line was obtained for Fig. 5 when Cs/(x/m) is plotted against Cs, showing that the Langmuir isotherm is obeyed.

Adsorption dependence on temperature was investigated for three different uranium solutions with concentrations of 2000, 4000, and 5000 μg/

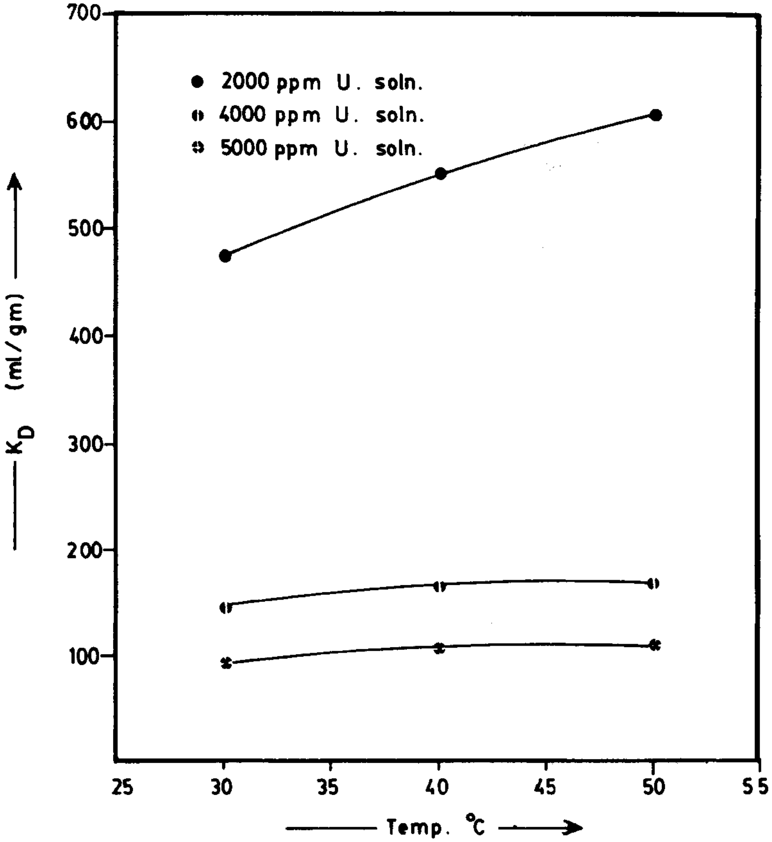

FIG. 6. Effect of temperature on uranium adsorption on activated charcoal.

mL. The temperature was varied from 30 to 50°C in steps of 10°C, while the other parameters were kept constant. Figure 6 shows that distribution coefficient (K_D) values increase with an increase in temperature, which may be due to a negative temperature coefficient or to a steep simultaneous decrease of real adsorption of the solvent (*26*).

The values of $\Delta H°$ and $\Delta S°$ were calculated from the slopes and intercepts of the linear variation of ln K_D with the reciprocal of the temperature, $1/T$ (see Fig. 7), by using the relation.

$$\ln K_D = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{1}$$

The values are given in Table 1. The free energy of specific adsorption, $\Delta G°$, is calculated from

$$\Delta G° = \Delta H° - T\Delta S° \tag{2}$$

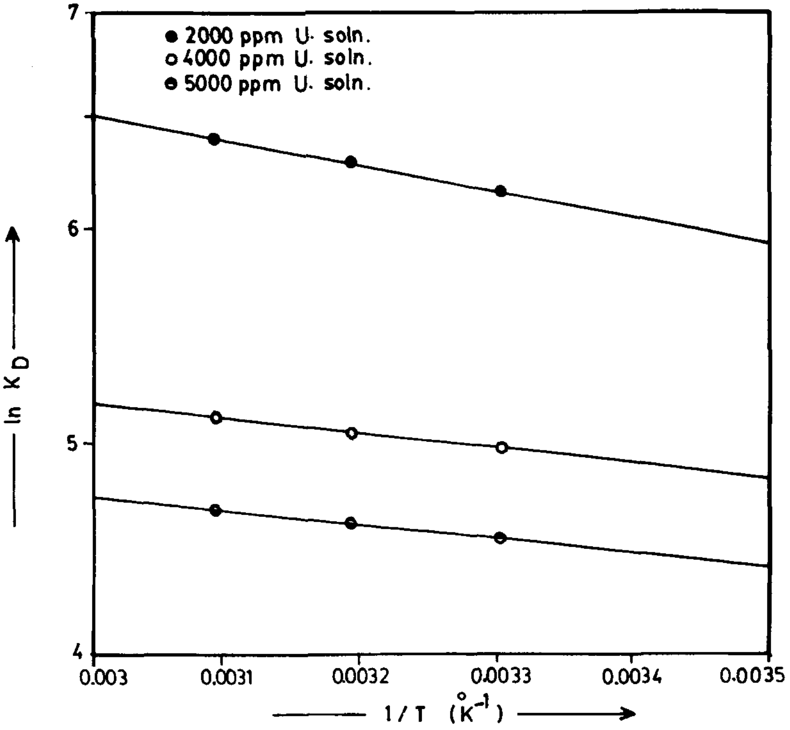

FIG. 7. Plot of ln K_D vs $1/T$ for uranium adsorption on activated charcoal.

TABLE 1
Thermodynamic Parameters for Uranium Adsorption on Activated Charcoal

U concentration (μg/mL)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/mol)	$\Delta G°$ (kJ/mol)		
			303 K	313 K	323 K
2000	9.9269	0.05401	−6.4351	−6.9751	−7.5151
4000	5.8971	0.0431	−7.1622	−7.5932	−8.0242
5000	5.5787	0.0395	−6.3898	−6.7848	−7.1798

$\Delta G°$ values are also given in Table 1. Both the positive value of $\Delta H°$ and the decrease in the value of $\Delta G°$ with the increase in temperature show that the reaction is more favorable at high temperature.

To examine the adsorption behavior of uranium in the presence of acetate, nitrate, fluoride, thiosulfate, and oxalate, the concentration of each anion was taken at 1000 μg/mL and the concentration of uranium was varied from 1000 to 6000 μg/mL. The results are shown in Figs. 8 and 9.

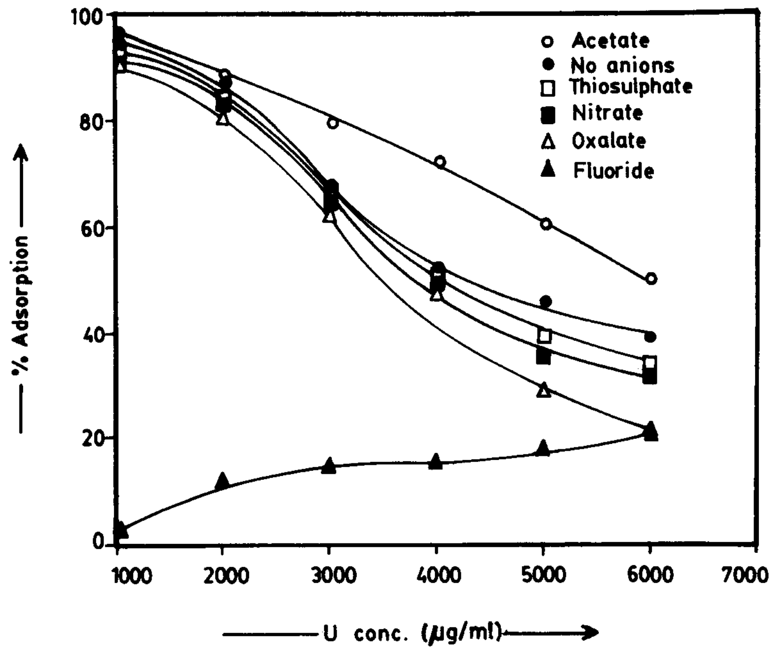

FIG. 8. Variation of % adsorption of uranium in the presence of some anions.

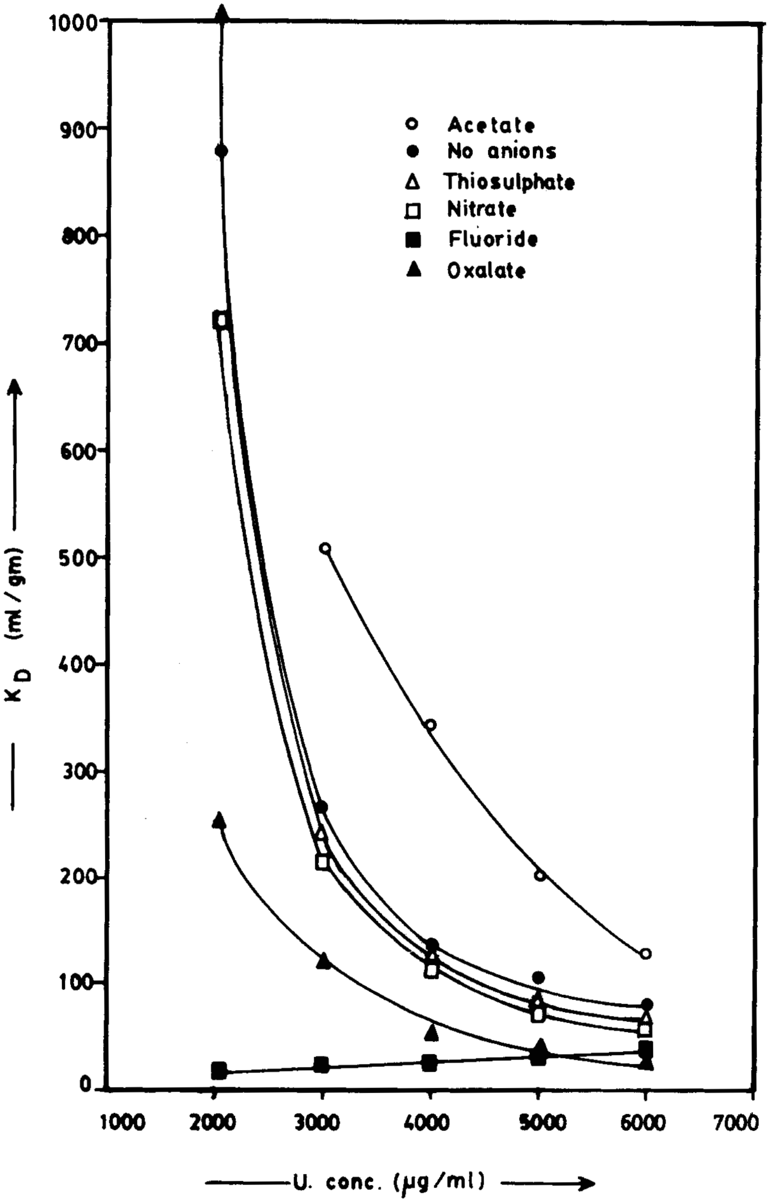

FIG. 9. Variation of K_D for the adsorption of uranium in the presence of some anions.

The acetate ion enhanced the adsorption of uranium while the other anions reduced the adsorption of uranium. This shows that the anionic complex of acetate ion with uranium is more strongly adsorbed on the activated charcoal than the uranium ions themselves. The decrease in adsorption in the presence of fluoride, nitrate, thiosulfate, and oxalate ion may be because of lower affinity of their complexes for adsorption. The anions reduce the adsorption in the order fluoride > oxalate > nitrate > thiosulfate. The influence of sodium, potassium, cobalt, cerium, and zinc cations on the adsorption of uranium on activated charcoal was investigated. Each cation was added as its nitrate with a fixed concentration of 1000 μg/mL and the uranium concentration was varied from 1000 to 6000 μg/mL. The results of these investigations are shown in Figs. 10 and 11. It is concluded that the greater the ionic potential (Z/r) of the added cation, the smaller is the adsorption of uranium. However, potassium is an exception. Similar observations were reported earlier (*21*).

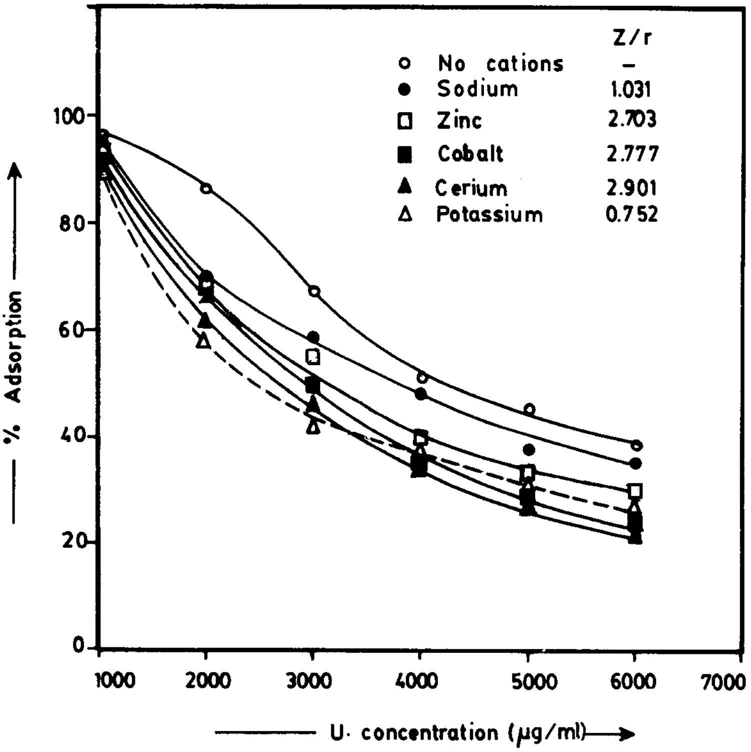

FIG. 10. Variation of % adsorption of uranium in the presence of some cations.

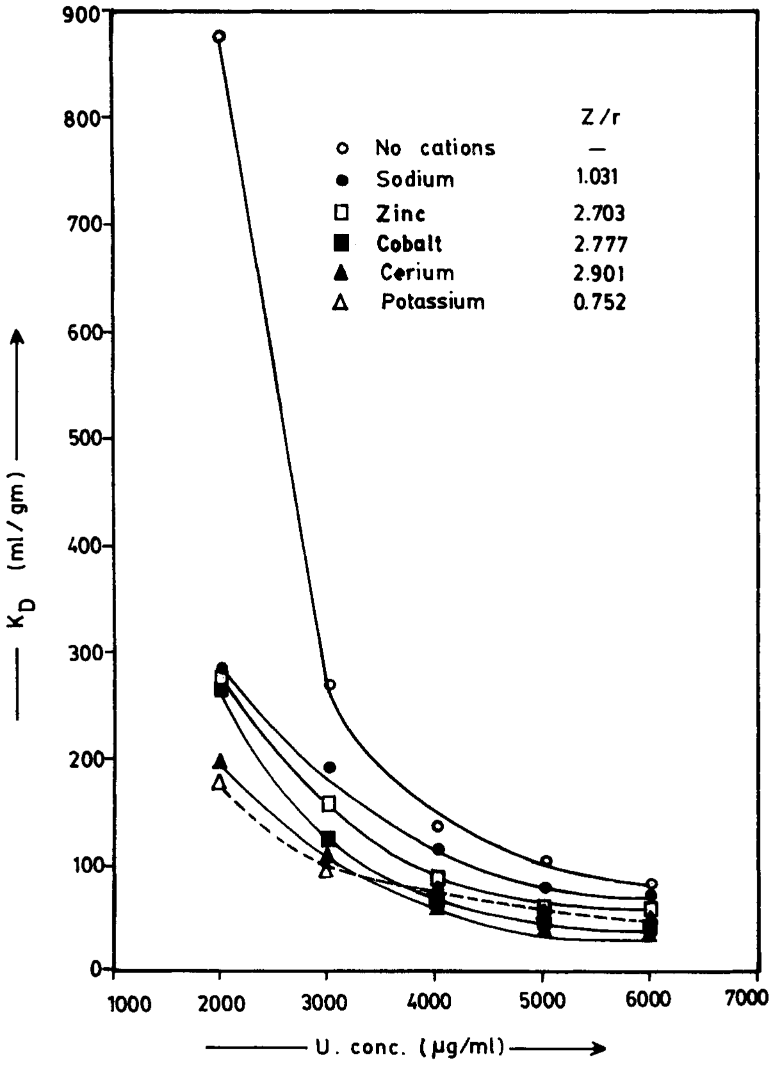

FIG. 11. Variation of K_D for uranium adsorption in the presence of some cations.

TABLE 2
Distribution Coefficient (K_D) of Other Metal Ions on Activated Charcoal

Metal	K_D (mL/g)
Gd	362.33
Er	358.56
Dy	276.28
Sm	204.82
Y	92.72
Eu	57.22
Ce	34.22
V	13.58
Cr	13.50
Sr	11.17
Cs	6.99
Zn	5.62
Ba	5.48
Co	0.313

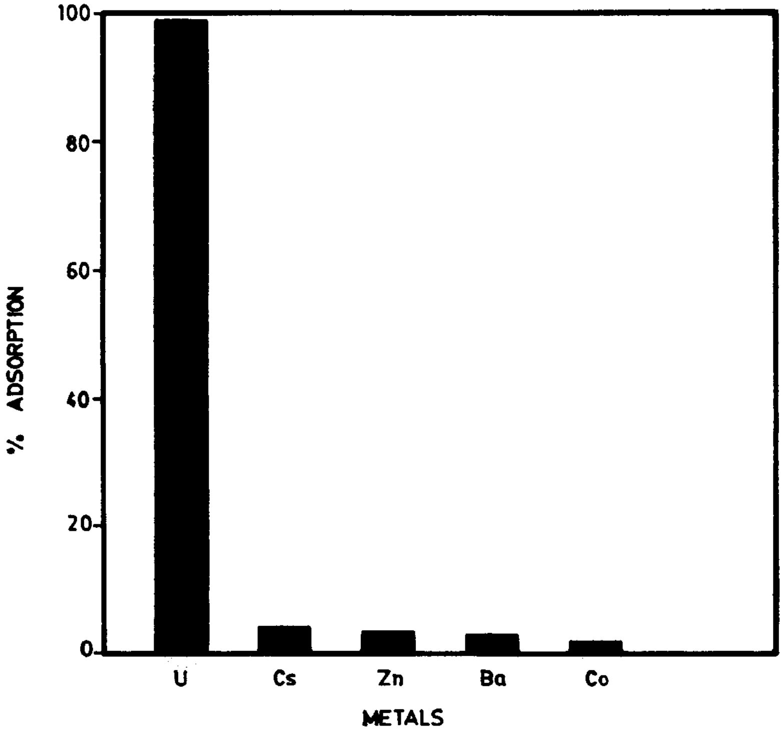

FIG. 12. Percent adsorption of U and other metals from a mixture containing U, Cs, Zn, Ba, and Co.

To check the selectivity of activated charcoal for uranium, the adsorption of Gd, Er, Eu, Ce, Dy, Sm, Y, Cs, Sr, Cr, V, Zn, and Co on the adsorbent was examined under specific conditions. The results are given in Table 2. It is obvious from the data that Gd, Er, Dy, and Sm have high K_D values, so they would be coadsorbed with uranium on activated charcoal. Er, Ce, Cs, Sr, Ba, Cr, V, and Zn are poorly adsorbed; hence separation of uranium from these metals can be achieved. The separation factor for uranium is larger in the presence of Cs, Ba, Zn, and Co because they have much lower K_D values. The separation of uranium in the presence of these metals is shown in Fig. 12.

The feasibility of using activated charcoal for preconcentration/separation of uranium was further assessed by elution studies. These studies were performed with H_2O, 3 *M* HNO, and 5% Na_2CO_3 solutions. Results are summarized in Fig. 13.

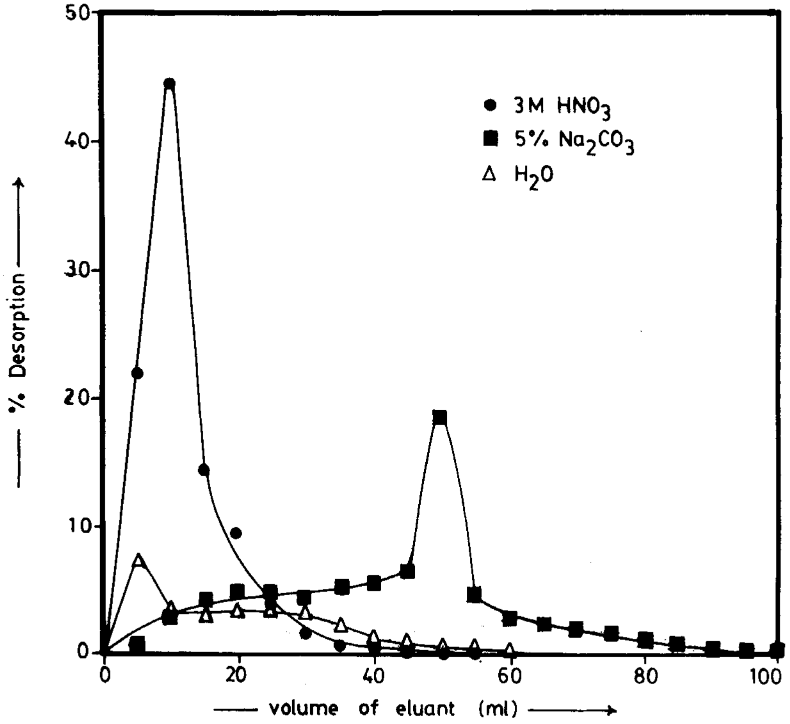

FIG. 13. Elution of adsorbed U from activated charcoal with various solvents.

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