Adsorption of Uranium in the Presence of different cations on Activated Charcoal

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Summary: The adsorption of uranium in the presence of different cations namely Cd^{2+}, Zn^{2+}, La^{3+}, Y^{3+}, Sc^{3+} on activated charcoal from aqueous solution was studied at room temperature 23 ± 0.2°C. Their effect on uranium adsorption has been correlated with the ionic potential, z/r of cations. It was observed that the cations with larger (z/r) reduced the uranium adsorption more than the cation with smallest (z/r) value. The Langmuir and Dubinin-Radushkevich (D-R) isotherm equations have been applied to the data and the values of parameters of these isotherm equations were evaluated. The mean energy of adsorption, E was also calculated from the adsorption energy constant, K' values determined from D-R isotherm equation. Wavelength dispersive X-ray fluorescence spectrometer was used for measuring uranium concentration in solutions.

Introduction

Interest in the adsorption of metal ions for preconcentration and separation purposes has increased many fold in recent years. The adsorption process under certain condition has a definite edge over other method used for preconcentration because of its simplicity, selectivity and efficiency [1]. The primary requirement for an economic adsorption processes is an adsorbent with sufficient selectivity, adsorption capacity and life. Activated charcoal due to its large surface area, high adsorption capacity, microporous structure, selective adsorption, radiation stability and high purity has found many applications in industries for purification and separation purposes. In certain circumstances, it has also been used to remove the toxic and health hazardous particles and ions from solution [2-5].

The adsorption of uranium on solid is important from purification, environmental and radioactive waste disposal point of view. The adsorption of uranium on activated charcoal has been the subject of several investigations [6- 13]. In our recent communication, the effects of alkali metals, alkaline earth metals and lanthanides on uranium adsorption on activated charcoal from aqueous solutions were studied [14]. The present work describes our investigations of uranium adsorption in the presence of different cations namely Cd^{2+}, Zn^{2+}, La^{3+}, Y^{3+} and Sc^{3+} on activated charcoal with similar sort of purposes in mind.

Results and Discussion

Fig. 1 shows the adsorption isotherms of uranium in the presence of different cations namely Cd^{2+}, Zn^{2+}, La^{3+}, Y^{3+} and Sc^{3+} on activated charcoal from aqueous solution of pH 4. The value of pH 4 was selected in view of our earlier study where maximum adsorption of uranium on activated charcoal was observed at pH 4 [13]. In the present work the concentration of uranium was varied from 1000 µg/ml to 6000 µg/ml while the concentration of cation was fixed at 1000 µg/ml. It is obvious from Fig. 1

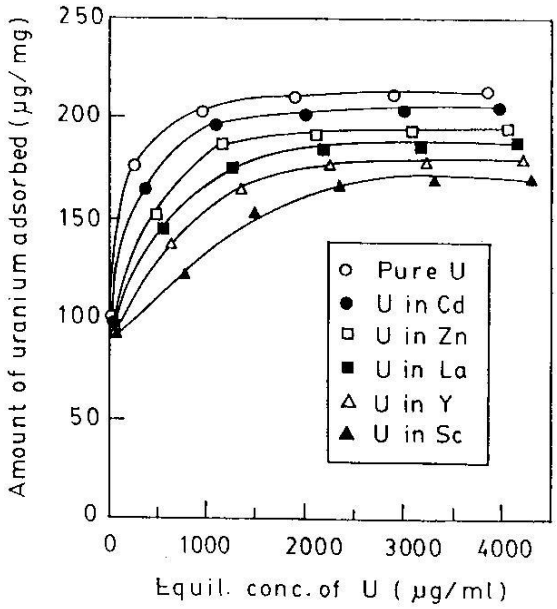

Fig. 1: Adsorption isotherms of uranium in presence of different cations.

that the adsorption isotherms of uranium on activated charcoal are L-type according to Giles classification

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[16]. In this type of isotherm, the initial portion provides information about the availability of the active site to the adsorbate and the plateau signifies the monolayer formation. The initial curvature indicates that large amount of uranium is adsorbed at lower concentration as more active sites of activated charcoal are available. As concentration increases, it becomes difficult for a uranium ions to find vacant sites so monolayer formation occur. It is also seen in Fig. 1 that the presence of aforementioned cations in solutions has reduced the adsorption of uranium on activated charcoal. The adsorption of uranium is lowered because these cations are coadsorbed alongwith uranium on activated charcoal. The cations reduced the adsorption of uranium in the order of:

$$Sc^{3+} > Y^{3+} > La^{3+} > Zn^{2+} > Cd^{2+}$$

The values of ionic potential (z/r) of the above mentioned cations varies in the order of:

$$Cd^{2+}\ (2.062) < Zn^{2+}\ (2.703) < La^{3+}\ (2.830) < Y^{3+}\ (3.226) < Sc^{3+}\ (3.704)$$

This indicate that the cation with larger Z/r values has greater effect on the adsorption of uranium as compare to the cation with smaller Z/r.

The data of Fig. 1 was applied to Langmuir isotherm equation in the form of

$$\frac{C_s}{(X/m)} = \frac{1}{K X_m} + \frac{C_s}{X_m} \qquad (2)$$

Where

C_s is the equilibrium concentration of uranium in solution (μg/ml)

X/m is the amount of uranium adsorbed per unit weight of activated charcoal (μg/mg)

X_m is the monolayer capacity (μg/mg).

K is the constant related to the heat of adsorption by relation $K = K_o e^{-qt}$, where q is the heat of adsorption.

Straight lines were obtained by plotting $C_s/(X/m)$ against C_s for the adsorption of uranium in the presence of different cations as shown in Fig. 2. This shows that uranium adsorption on activated charcoal obeys the Langmuir equation. The values of X_m and K were calculated from the slopes and intercepts of the Langmuir plots, are reported in Table 2. It can be seen from this table that the values of X_m and

Table 1: Instrumental conditions for measuring uranium concentration

Spectrometer	Siemen's SRS 200
Tube	Cr-target.
Detector	Scintillation, NaI (Tl)
Crystal	LiF-100
Collimator	Fine, 0.15°
Tube Voltage	50 kV
Tube Current	50 mA
Radiation path	Air
Analyte line	$Ul_{\alpha 1}$
LBG (2θ-value)	25.98
Peak (2θ-value)	26.18
HBG (2θ-value)	26.38
Counting time	40 sec at all 2θ-value.

Table 2: Langmuir isotherms constant for the adsorption of uranium in the presence of different cations

U in presence of	Ionic Potential of cation Z/r	X_m (μg/mg)	K (ml/mg)
Pure U (VI)	-	216.03	0.0230
Cd^{2+}	2.062	208.02	0.0165
Zn^{2+}	2.703	196.54	0.0139
La^{3+}	2.830	193.27	0.0089
Y^{3+}	3.226	185.19	0.0074
Sc^{3+}	3,704	178.70	0.0045

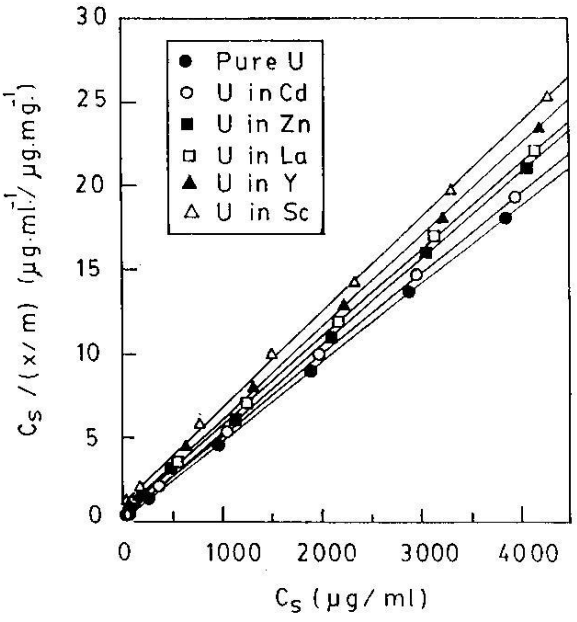

Fig. 2: Langmuir plots for uranium adsorption in presence of different cations.

K for the adsorption of uranium in the presence of different cation followed the sequence similar to that discussed above.

The adsorption data were also tested for another adsorption isotherm, the Dubinin-Radushkevich (D-R) [17]. The relationship between D-R and other types of adsorption isotherm is shown by Sokolowska and Szczpa [18]. This isotherm is more general than the Langmuir isotherm since it does not assume a homogeneous surface or constant sorption potential [19]. The D-R equation is

$$X/m = X'_m \exp(-K' \varepsilon^2) \quad (3)$$

where

ε (polanyi potential) = RT in $(1 + 1/C_s)$
X/m is the amount of uranium adsorbed per unit weight of activated charcoal (μg/mg)
X'_m is the adsorption capacity (μg/mg)
C_s is the equilibrium concentration of uranium in solution (μg/ml)
K' is the constant related to the adsorption energy (mol^2/kJ^2)
R is the gas constant ($kJ.deg^{-1}mol^{-1}$)
T is the temperature (K).

The D-R isotherm can be linearized as

$$\ln X/m = \ln X'_m - K' \varepsilon^2 \quad (4)$$

The plots of ln X/m against ε^2 is shown in Fig. 3. This shows that the uranium adsorption in presence of different cations obeys the D-R isotherm equation as well. The parameters X_m and K' obtained from the intercepts and slopes of these plots are given in Table 3. By making certain assumptions the mean energy of adsorption, E can be calculated from the K values [20-22], using the relation

$$E = (-2K')^{-0.5} \quad (5)$$

The determined values of E are also given in Table 3. This table shows that the change in X'_m, K' and E values are in line with the previous argument.

Table 3: D-R isotherm parameters and mean energy of the adsorption of uranium in the presence of different cations.

U in presence of	Z/r	X'_m (μg/mg)	K' x 10^{-3} (mol^2/kJ^2)	E ($kJ.mol^{-1}$)
Pure U (VI)		210.82	1.946	16.03
Cd^{2+}	2.062	202.96	4.861	10.14
Zn^{2+}	2.703	193.64	9.919	7.10
La^{3+}	2.830	186.98	12.99	6.20
Y^{3+}	3.226	180.37	18.36	5.2
Sc^{3+}	3.704	169.36	34.47	3.81

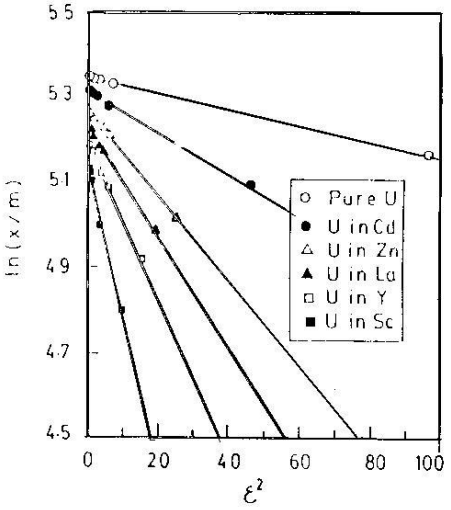

Fig. 3: D-R plots for the adsorption of uranium in presence of different cations.

Experimental

The chemical used during this study were activated charcoal (BDH: item No. 33032), uranyl-nitrate (Riedel de Haen; item No. 31638), cadmium nitrate (Fluka; item No. 20911), zinc nitrate (Fluka: item No. 96482) nitrates of lanthanum, yttrium and scandium (99.999%, Rare Earth Product).

Instruments

Siemen's wavelength dispersive X-ray fluorescence (WDXRF) spectrometer was used for measuring the uranium concentration in solutions. Emund Buhlar-SM25 shaker was used for shaking at a constant speed of 150 revolution per minutes.

Procedure

The adsorption of uranium in the presence of different cations were carried out by a batch technique at room temperature (23 ± 0.2°C) from aqueous solution of pH 4. 100 mg of activated charcoal in 250 ml reagent bottle containing known amount of

uranium and fixed concentration of cation were shaken for 60 minutes (equilibrium time). The solutions were then filtered through Whatman filter paper No. 40 (circular, 11.0 cm). First 2-3 ml portion of the filtrate was rejected because of the adsorption of uranium solution by filter paper. The concentration of uranium in the filtrate was measured by WDXRF spectrometer under conditions given in Table 1. The sample solutions were presented to the spectrometer in 0.1 mm thick walled polyethylene bottles [15]. The concentration of uranium was corrected for the adsorption loss of the uranium on the wall of the bottles by running blank experiment (without activated charocal added). The amount of uranium adsorbed per unit weight of an adsorbent, X/m, were calculated using the following formula:

$$X/m = \frac{(C_o - C_s)\,V}{M} \quad (1)$$

where

C_o is the initial concentration of uranium (μg/ml)
C_s is the equilibrium concentration of uranium in solution (μg/ml)
M is the weight of the activated charcoal (mg)
V is the volume of solution (ml)
X/m is the amount of uranium adsorbed per unit weight of activated charcoal (μg/mg).

The adsorption isotherms for uranium in presence of different cations on activated charcoal are given in Fig. 1.

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