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Equilibrium Study On The Adsorption Of Cesium And Europium On Zirconium Molybdate Ion Exchanger

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ABSTRACT

The present work is an investigation of the adsorption behavior of cesium(I) and europium(III) on zirconium molybdate at different pHs, different metal concentrations and different alcohol concentrations. The uptake percentages were found to depend on both the alcohol content and metal concentration. The effect of particle size with time was studied. It was found that the rate of adsorption of Cs(I) is chemically controlled and no diffusion along the particles takes place. In case of Eu(III) the particle size showed a marked effect on the rate of exchange.

KEYWORDS

Ion Exchange;
Sorption;
Cs^+;
Eu^{+3} ions;
Zirconium molybdate.

INTRODUCTION

Recovery of valuable elements from the waste is a subject of growing interest to many waste management professionals because of the precious nature and potential applications[1,2] of valuables present in the waste. Actually, this subject is very appropriate to the separation of precious metal ions present in high-level waste of purex origin. Long-lived gamma emitting radionuclides such as $Cs^{134,\ 137(2Y),\ 30(1Y)}$ and $Eu^{152,\ 154(12Y,\ 16Y)}$ were regarded as waste few decades ago. Now they are being termed as valuables owing to the utilization of these radioisotopes in the area of food irradiation[3,5] and sewage treatment technologies[6] in recent years. Several countries have installed various irradiation facilities for processing of food and clean up of sewage waste[7-8]. The potential applications of these radionuclides have made everyone to reconsider the existing disposal options and examine the possibility of recovering these useful radionuclides from HLLW for real applications. Also the stringent safety regulations demand the separation of these long-lived radiotoxic hazardous metal ions from a large volume of waste and concentrate them into small volumes by a suitable technology.

Inorganic compounds are extremely proven candidates for the separation and recovery of cesium and europium from aqueous waste streams[9,10]. A number of inorganic solvents show selectivity to Cs^{134} and $Eu^{152+154}$ from alkaline waste solution, but so far only few sorbents[11,13] were reported to be selective to these radioisotopes from acid radioactive streams. Zirconium phosphate(ZrP) has been prepared and studied in the amorphous, semi crystalline and crystalline states. A tremendous amount of literature has appeared on its ion exchange behavior in aqueous solutions. Of this literature we mention the books and review articles[14,18]. N.Souka studied the adsorption behavior of some actinides on zirconium phosphate from mineral acid-alcohol media (6)[19].

Zirconium molybdate shows high sorption efficiency and exhibits different affinity for Cs(I), Zn(II) and Eu(III). This fact allows the sorption of these elements from their aqueous solutions and their separation from each other. Under appropriate conditions, Zirconium molybdate shows high selectivity to both europium and cesium ions[20]. In this work, the adsorption of Cs(I) and Eu(III) on zirconium molybdate was studied. The effect of various parameters such as contact time, metal concentration, particle size and effect of different alcohols on the uptake were investigated.

EXPERIMENTAL

Irradiation

The radionuclides used Cs(I) or Eu(III) were produced by irradiating weighed amounts of their salts or oxides in the second research reactor at Inchas ERE2, Egypt.

Solutions

Stoke solutions of cesium and europium(10^{-1}M) have been prepared by dissolving known amounts of Chloride salts in redistilled water. Each solution was then diluted to the required concentration and then labeled with the corresponding radioisotopes(Cs^{134}, $T^1/_2$=2.06y) and ($Eu^{152,154}$, $T^1/_2$= 12y).

Exchanger

Zirconium molybdate was synthesized and characterized (IR and XRD) as methods reported before [20]. The ion exchange capacity was determined by repeated batch equilibration of the prepared exchanger till saturation with 10^{-2}M CsCl or $EuCl_3$ by shaking in a water bath adjusted to 25°C±1°C. The capacity was then calculated by the following equation[21,22]:

$$\text{Capacity} = \frac{\%\text{uptake}}{100} \times \text{Co} \times \frac{V}{m} \times Z(\text{meq/g})$$

where C_0 = initial concentration of the counter ions; V = volume of solution (ml); m = mass of exchanger (g); Z = valency of the tested ion. The capacity of Cs^{+1} and Eu^{+3} were found 0.413 meq/g and 0.285 meq/g respectively.

Uptake method

A portion of the prepared molybdate (m) was mixed with a certain volume(v) of a solution containing the specified ion then shacked at 25°C±°C. After certain time, the solution was separated and the concentration of the sorbed ion was determined radiometrically using NaI scintillation detector connected with an ST6 scaler timer. The counting rates were at least 10 times as that of the background. The distribution coefficient K_d and the uptake percent B were determined as follows:

$$K_d = [(A_i - A_f)/A_f] \times v/m \ (\text{mlg}^{-1})$$

$$B = [(A_i - A_f)/A_i] \times 100$$

where: A_i = area of the γ-ray peak of the corresponding isotope before contacting the ion exchanger; A_f = area of the same peak after contacting the ion exchanger; V = volume of the aqueous phase (ml); and m = mass of the dry ion exchanger (g).

RESULTS AND DISCUSSION

Effect of pH

The pH dependence of the adsorption of Cs^{+1} and Eu^{+3} on zirconium molybdate is shown in plots of the uptake percentage as a function of the pH (1.9-9.5) for Cs^{+1} and(1.9-6.5) for Eu^{+3} solutions(Figure 1). It is evident that the adsorption of Cs^{+1} on zirconium molybdate was greatly influenced by a change of pH. Very low value of adsorption was observed at pH values lower than 6 but above 6, a steady increase in the uptake percentage was observed. These indicates that zirconium molybdate behaves as cation and an-

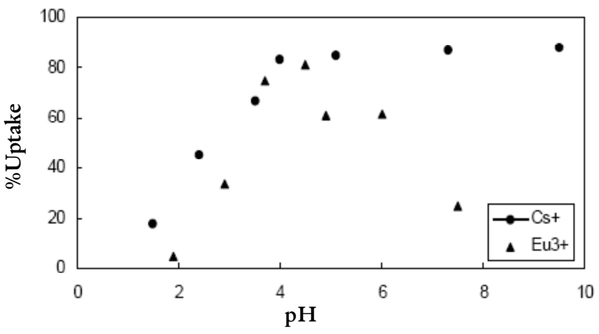

Figure 1 : Effect of pH on the percentage uptake of Cs^+ and Eu^{+3} on zirconium molybdate ion exchanger at 10^{-4} M metal ion concentration

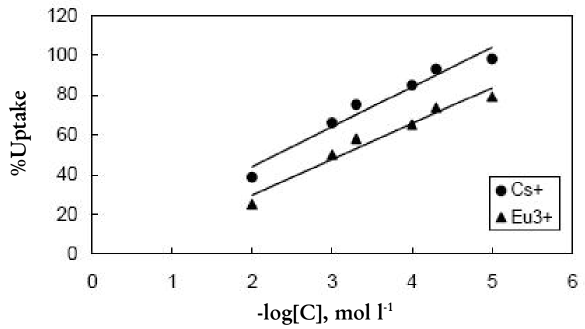

Figure 2 : Effect of Cs^+ and Eu^{+3} ion concentration on the adsorption on zirconium molybdate at pH 9.5 and 3.5, respectively

ion exchanger in alkaline and acidic media respectively[16]. On the other hand, the uptake percentage of adsorption of Eu^{+3} on Zirconium molybdate (Figure 1) increases gradually until ~pH=4. With values of pH higher than ~4, a large decrease in the uptake was observed by the increase of pH. These can be attributed to hydrolysis of Eu^{+3} after pH=5.

Effect of concentration

Figure 2 shows that the uptake percentage changes as the concentration changes. Starting from in the studied range 10^{-5}M till 10^{-2}M of Cs^{+1} and Eu^{+3} aqueous solutions. With increasing metal concentrations, the uptake percentage decreased.

Adsorption isotherm

The adsorption isotherm for zirconium molybdate exchanger was performed at different cesium or europium chloride concentrations varying from 10^{-5} till 10^{-3}mol/l at 298K.

The concentration was investigated as a function of time at constant temperature(298 K) for both cesium and europium ions at pH values of 9.5 and pH4.7 for Cs^{+1} and Eu^{+3} respectively. The results obtained are represented in(Figures 3 and 4). It could be seen that the rate of uptake of Cs^{+1} or Eu^{+3} is rapid at the beginning, becomes slower in latter stages and finally it reaches an apparent saturation for all studied con-

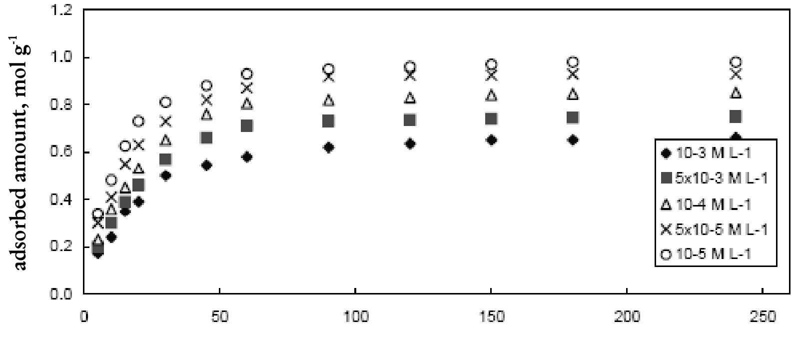

Figure 3 : Variation of the adsorbed Cs^+ ions, on hydrous zirconium molybdate, with time different cesium concentration, 298K and pH 9.5

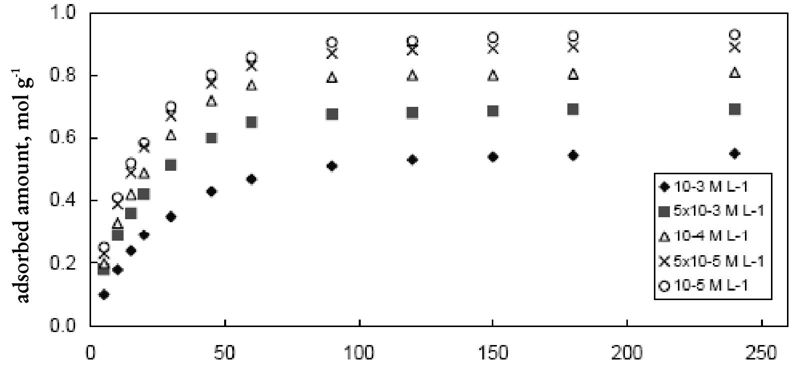

Figure 4 : Variation of the adsorbed of Eu^{3+} ions, on hydrous zirconium molybdate, with time different cesium concentration, 298K and pH 9.5

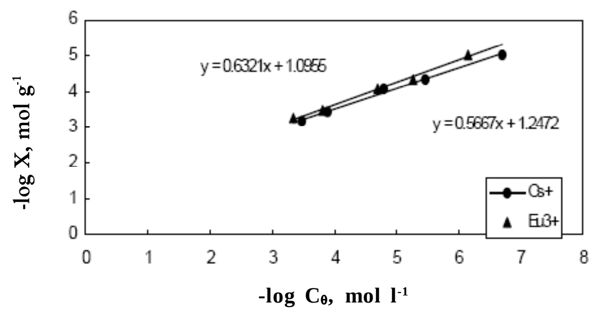

Figure 5 : Freundich sclsoption isothems of Cs^+ and Eu^{3+} on zirconiummdybdate at 298k

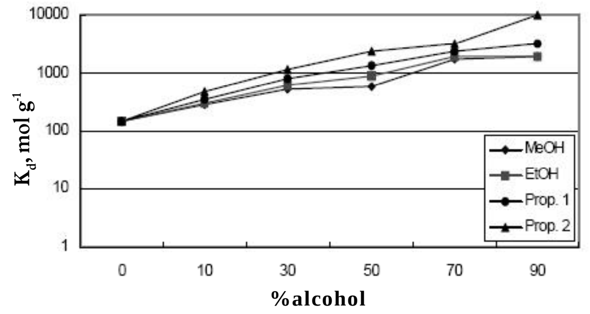

Figure 6 : Effect of alcohol concentration on the distribution ratio, k_d, of Cs^+ on zinconium molybdate ion exchanger

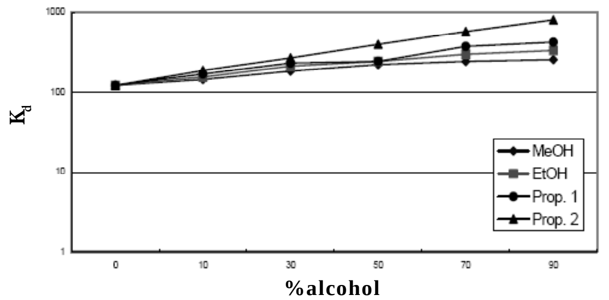

Figure 7 : Effect of alcohol on the distribution ratio, k_d, of Eu^{3+} on zirconium molybdate ion exchanger

TABLE 1: The amount adsorbed(meq/g) of Cs^{+1} and Eu^{+3} (10^{-3}M) solutions at pH 9.5 and 4.7 respectively on zirconium molybdate at 70% alcohols

Medium	Cs^{+1}(meq/g)	Eu^{+3}(meq/g)
Aqueous (without alcohol)	0.066	0.165
Methanol	0.094	0.213
Ethanol	0.095	0.225
Propanol-1	0.096	0.237
Propanol-2	0.099	0.255

centrations. The time required to reach a saturation value was found to be 60minutes for Cs^{+1} and 90 minutes for Eu^{+3}. The figures revealed that, the amount of Cs^{+1} or Eu^{+3} adsorbed at equilibrium increased from 0.98×10^{-6}meq/g to 0.66×10^{-4}meq/g and from 0.93×10^{-6} meq/g to 0.55×10^{-4} meq/g respectively, when Cs^{+1} or Eu^{+3} ion concentrations increased from 1×10^{-5} to 1×10^{-3}M. The percentage adsorption was high at high dilution of Cs^{+1} or Eu^{+3} ion solution. The maximum values obtained for Cs^{+1} and Eu^{+3} were 98% and 93% respectively, at 10^{-5}mol/l metal ion concentrations. This is explained to by due to the fact that, at high dilutions, relatively large numbers of surface sites are available for uptake of small numbers of Cs^{+1} or Eu^{+3} ions from the aqueous solution[23].

Adsorption data were further analyzed using the Freundlich adsorption isotherm. Logarithmic dependence of the amount of Cs^{+1} and Eu^{+3} adsorbed at equilibrium(a_e) versus bulk concentration of Cs^{+1} and Eu^{+3} at equilibrium(C_e) was found to be linear (Figures 5, 6) confirming the freundlich isotherm:

$$\text{Log } a_e = \log K + b \log C_e$$

where K and b are freundlich constants corresponding to adsorption capacity and adsorption intensity respectively. These constants were estimated from the intercept and slope of the straight-line plot. The freundlich constants were found to be 1.2472mol.g^{-1} and 0.5667mol.g^{-1} for Cs(I) and 1.0955 mol.g^{-1} and 0.6321 mol.g^{-1} for Eu(III), respectively.

The fractional value of b for both elements under investigation proved that the surface of the adsorbent is probably of heterogeneous nature[24]. The higher value of K(adsorption capacity) for zirconium molybdate shows once more that this material is a more efficient exchanger, at least for Cs(I) and Eu(III) removal from aqueous solutions.

Adsorption from alcoholic solutions

The effect of increasing concentrations of methanol, ethanol, propanol-1 and propanol-2 on the adsorption of Cs^{+1} and Eu^{+3} from 10^{-3}M CsCl and $EuCl_3$ at pH9.5 for Cs^{+1} and pH4.7 for Eu^{+3} is given in figures 6 and 7. The data presented in figures 6 and 7 indicate that the substitution of increasing the amounts of water by alcohols was found to increase the uptake percentage of Cs^{+1} and Eu^{+3}. For the same alcohol concentration, the magnitude of enhancement in the uptake percentage of Cs^{+1} and Eu^{+3} from one alcohol to another is according to the sequence:

Propanol-2 > Propanol-1 > Ethanol > Methanol

This sequence may be related to the decrease in the reciprocal value of the dielectric constant of the

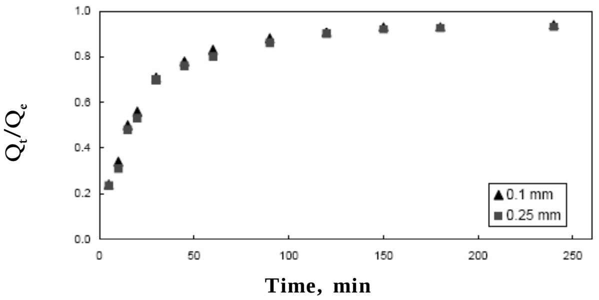

Figure 8 : Effect of particle size on the rate of adsorption of Cs^+ ions from 10^{-3}M CsCl solution on zirconium molybdate

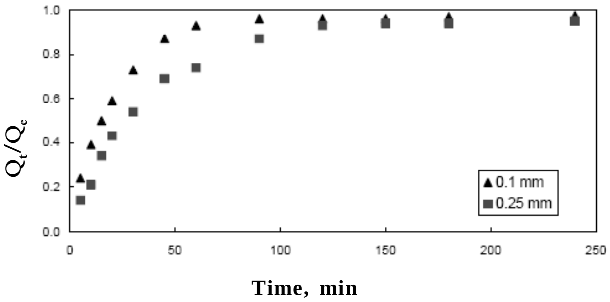

Figure 9 : Effect of particle size on the rate of Eu^{3+} ions from 10^{-4} M $EuCl_3$ solution on zirconium molybdate

alcohol and of decreasing chain length between the last three solvents.

Also the amounts adsorbed of Cs^{+1} and Eu^{+3} ions at for different alcohols are shown in TABLE 1

TABLE 1 shows that all values of the adsorbed amounts are higher in mixed solvents than in both ions of CsCl and $EuCl_3$ solutions separately. This may be due to the partial dehydration of the ions resulting from the accessibility of more exchange sites and higher affinity to these sites. Also due to the more basicity of the used mixed solvents[25,26] leading to the replacement of more weakly acidic H^+ in zirconium molybdate[27].

The data given in this figure indicates that, for a certain alcohol concentration, the adsorption of the mentioned elements decreases with increasing of the metal concentration.

Effect of particle size

The effect of particle size, on the rate of adsorption of Cs^{+1} and Eu^{+3}(10^{-3}M and 10^{-4}M) solutions on zirconium molybdate ion exchanger are shown in figures 8 and 9. The variation of Q_t/Q_e where Q_t= amount exchanged at time t and Q_e=amount exchanged at equilibrium.

From figure 8, no effect of the particle size in case of adsorption of Cs^{+1} ions, on zirconium molybdate due to the difference in particle size from 0.1mm to 0.25mm. Thus the rate of adsorption is chemically controlled and no diffusion along the particles takes place.

Adsorption of Eu^{+3} ions on zirconium molybdate at 10^{-4}M solution is given in (Figure 9). The particle size has a marked effect on the rate of exchange, indicating existence of diffusion mechanism[28].

REFERENCES

[1] Feasibility of Separation, Utilization of Cesium, Strontium from High Level Waste, Technical Report Series 356. IAEA. Vienna, **(1993)**.

[2] S.M.Rao, K.M.Kulkarni; 'Proc.Intern.Conf. on Applications of Radioisotopes and Radiation in Industrial Development (ICARID-94)', Mumbai, India, 7-9 **(1994)**.

[3] J.F.Diehl; Radiat.Phys.Chem., **63**, 211 **(2002)**.

[4] R.Sadat, A.Ross, H.Leveziel; 'Proc.Intern.Conf.on Applications of Radioisotopes and Radiation in Industrial Development (ICARID-94)', S.M.Rao, K.M.Kulkarni (Eds) Mumbai India, **177**, 7-9 **(1994)**.

[5] List of Clearance of Irradiated Foods, International Atomic Energy Agency, Vienna, **(1992)**.

[6] T.Lissel; 'Proc.Intern.Conf.on Applications of Radioisotopes and Radiation in Industrial Development (ICARID-98)', D.D.Sood, A.V.R.Reddy (Eds); Mumbai, India, **105**, 4-6 **(1998)**.

[7] D.D.Sood; 'Proc.Intern.Conf.on Applications of Radioisotopes and Radiation in Industrial Development (ICARID-98)', D.D.Sood, A.V.R.Reddy (Eds); Mumbai, India, 35 **(1998)**.

[8] G.J.Luckman; Radiat.Phys.Chem., **63**, 285 **(2002)**.

[9] A.Clearfield; Solvent Extr.Ion.Exch., **18**, 655 **(2000)**.

[10] M.Abe; 'Ion Exchanger and Solvent Extraction', J.A.Marinsky, Y.Marcus (Eds) M.Dekker; Inc., New York, **12**, 381 **(1995)**.

[11] M.Suss, G.Pfrepper; Radiochim.Acta, **29**, 33 **(1981)**.

[12] R.Harjula, J.Lehto, A.Paajanen, L.Brodkin, E.Tusa; Nucl.Sci.Eng., **137**, 206 **(2001)**.

[13] T.Moller, A.Clearfield, R.Harjula; Micropor.Mesopor. Mater, **54**, 187 **(2002)**.

[14] C.B.Amphlett; Inorganic Ion Exchangers, Elsevier, Amsterdam **(1964)**.

[15] G.Alberti, S.Allulli, V.Costantino, M.A.Massucci, E. Torraca; Society of Chemical Industry, London, 318 (1970).

[16] V.Vesely, V.Pekarek; Talanta, **19**, 219 (**1972**).

[17] A.Clearfield, G.H.Nancollas, R.Blessing; 'Ion Exchange and Solvent Extraction', Edited by J.A.Marinsky, Y.Marcus, Dekker New York, Chapter, **5**, 1 (**1973**).

[18] G.Alberti; Acc.Chem.Res., 11, 163 (**1978**).

[19] N. Souka, A.S.Abdel-Gawad, R.Shabana, K.Farah; J.Radiochim.Acta, **22**, 180-182 (**1975**).

[20] N.Tadros, E.Metwally; Russian, Radiochem., **48(4)**, 347-351 (2006).

[21] Yamagichi, Y.Morita, M.Kubota, M.Tsuji; J.Radiochim.Acta, **75**, *27* (**1996**).

[22] Mathew, S.N.Tandon; J.Radional.Chem., **27**, 315 (**1975**).

[23] S.P.Mishra, S.S.Dubey, D.Tiwari; Journal of Radioanalytical and Nuclear Chemistry, **261(2)**, 457-463 (2004).

[24] Clark; 'The Theory of Adsorption and Catalysis', Academic Press, New York, 54 (1970).

[25] D.Feakins, P.Watson; J.Chem.Soc., 4734 (**1963**).

[26] O.Popovych; Crit.Rev.Anal.Chem., **1**, 73 (1970).

[27] V.A.Bessonov, N.N.Krylova; Kolloidn-Zh., **36**, 832 (**1974**).

[28] T.N.Morcos; Ph.D thesis, Ain Shams University, Cairo, (2001).