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Adsorption of Europium on Manganese Dioxide from Binary Mixtures of Aqueous Sulfuric Acid and Methanol

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ABSTRACT

The adsorption of europium on manganese dioxide from a binary mixture of aqueous sulfuric acid and methanol has been studied in relation to the concentration of adsorbate. The influence of contact time, composition of binary mixture, and foreign ions was also investigated. Citrate, chromate, molybdate, EDTA, Cr(III), Fe(III), and Al(III) drastically reduce adsorption. Adsorption of other metal ions under the same conditions was also investigated. Based on the observed data, separation of europium from mercury can be achieved.

INTRODUCTION

Adsorption behavior of a variety of elements has been examined based upon their importance in industry, the agricultural environment, or waste management processes, including waste disposal (1–10). Europium, as one of the important radionuclides in a fission process, demands attention to its removal from the fuel. The adsorption of europium on various surfaces in aqueous or neat solvents has been cited in the literature (11–16). However, such experimental work in mixed solvents is rarely available for ready reference (17–19). Our present work is aimed in this direction, and we here report the adsorption of europium on manganese dioxide

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from the binary mixture of methanol and sulfuric acid. The conditions of maximum adsorption are evaluated. The adsorption behavior of other metal ions [e.g., Hg(II), Ag(I), Sc(III), Cs(I), Co(II), etc.] was also studied and compared to Eu(III) adsorption.

EXPERIMENTAL

Manganese dioxide (Product 11015), BDH microanalytical reagent, black in color, of 10–20 mesh, was used as received. The BET surface area, determined by adsorbing nitrogen, was found to be 113 m^2/g. The porosity was found to be 2.17 cm^3/g, and the average pore diameter was 0.17 μm. The solid phase density was determined to be 6.63 g/cm^3.

Radiotracer $^{152+154}Eu$ was prepared by irradiating spec-pure europium oxide (Eu_2O_3) in the PARR-1 research reactor of PINSTECH at Islamabad. The oxide was irradiated at a thermal flux of 2×10^{13} neutrons $cm^{-2} \cdot s^{-1}$. All other isotopes used in this work were prepared locally by irradiating metals or their appropriate compounds in the same reactor. The radiochemical purity of these radiotracers was checked by gamma spectroscopy.

All the chemicals used in this study were of analytical grade except the commercial grade sulfuric acid. Doubly distilled deionized water was used for dilutions wherever necessary.

INSTRUMENTS

The surface area of manganese dioxide was measured with a BET Quantasorb sorption system model No. QS-11. The pore size analysis was done with a mercury porosimeter Micromeritics Auto Pore 9200 model. Gross gamma measurements were carried out with the help of a Nuclear Chicago model 8725 well-type scintillation counter using a 58 cm^2 NaI(Tl) crystal. Gamma ray spectroscopy was done with the help of a semiplaner 30 cm^2 Ge(Li) detector (Canberra Inc.) coupled with a Nuclear Data 4410 computerized multichannel analyzer having an 8K memory. The activity measurements were carried out with a counter model MB-1 Canberra Inc. Tennelec (USA). A wrist action shaker (Griffen and George) was used for the shaking of tubes. Centrifugation was performed with the help of a Fisher Scientific Inc. centrifuge.

PROCEDURE

Adsorption measurements were carried out radiometrically by the batch technique at room temperature (27 ± 2°C). Fifty microliters of europium tracer solution was added to a vial containing 5 cm^3 of the appropriate binary mixture of methanol and sulfuric acid which was mixed uniformly. The resultant europium concentration was 2×10^{-5} mol·dm^{-3}. An aliquot (0.5 cm^3) was withdrawn, and its activity was noted with the help of a counter. This activity was assayed for an initial activity. A known amount of the adsorbent (0.05 g manganese dioxide) was added to the remaining 4.5 cm^3 of the binary mixture. The vial was then shaken for a fixed interval of time (usually 20 minutes, except where specified). After shaking, the solution was centrifuged for 5 minutes for phase separation. The activity of 0.5 cm^3 of the supernatant solution was observed with the counter and labeled as the final activity. The results are presented as the distribution coefficient (K_D), defined as

$$K_D = \frac{A_i - A_f}{A_f}\frac{V}{M}\ (\mathrm{cm^3 \cdot g^{-1}})$$

where A_i and A_f are the initial and final activities, V is the volume of the remaining solution, and M is the mass of the adsorbent.

RESULTS AND DISCUSSION

Since adsorption, in general, depends upon the contact time between the adsorbate and adsorbent, the initial investigations were carried to determine the time for equilibrium. For this study, 50 mg of manganese dioxide was shaken with 4.5 cm^3 of a binary mixture of methanol and sulfuric acid in various mole fractions having a europium concentration of 2×10^{-5} mol·dm^{-3}. The composition of the binary mixture was shown to have a strong effect on the adsorption behavior. The distribution coefficient generally increases as the concentration of the organic component of the binary mixture is increased. The results of variation in percent adsorption of Eu with respect to shaking time is shown in Fig. 1. From this figure it is seen that equilibrium is achieved at 20 minutes, therefore this time was employed for all further studies. In the binary mixtures selected for adsorption studies, it was seen that the maximum distribution coefficient was achieved from the mixture containing 99% methanol and 2.5×10^{-4} mol·dm^{-3} of sulfuric acid (hereafter called Mixture A). The binary mixture with a composition of 10% methanol and 5×10^{-2} mol·dm^{-3} sulfuric acid (hereafter called Mixture B) showed a minimum distribution coefficient. The effect of the composition of the binary mixture on the K_D value is shown in Table 1. The two extreme cases (i.e., Mixture A and Mixture B) were used for all further studies. Since maximum adsorption (>99%) has been obtained from Mixture A, it can be

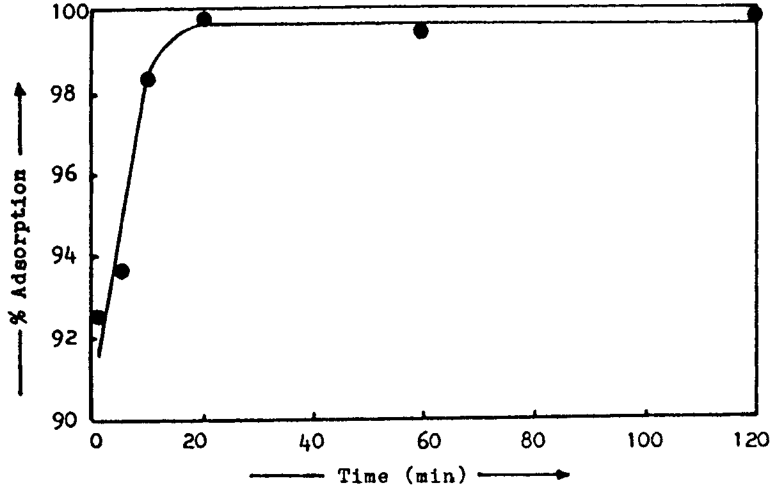

FIG. 1 Percent adsorption of Eu on MnO_2 from the Binary Mixture A as a function of shaking time.

effectively used for the preconcentration of europium from dilute solution or for its removal with the help of manganese dioxide.

Since the electrolyte concentration has a strong effect on the compact layer and diffuse layer potential (20), the adsorption of europium on manganese dioxide can be discussed in terms of the effect of the binary mixture composition. Chemisorption of matter on manganese dioxide has already been reported (21). An increase in europium adsorption on manganese dioxide with an increase in the organic component of the binary mixture may be due to the decreased amount of water, which in turn leads to increased availability of adsorption sites for europium. It is also known that the adsorption of europium is strongly pH dependent (22) and increases with an increase in pH. This effect is directly reflected in our studies.

Foreign anions present in the solution have a marked effect on the adsorption of trace elements. The adsorption of europium on manganese dioxide was studied in the presence of various anions under optimum conditions of shaking time, amount of MnO_2 and concentration of europium trace solution from the Binary Mixtures A and B. All the anions were added as their sodium salts except for thiocyanate, where the potassium compound was added. The concentration of each anion was 10^{-2} mol·dm^{-3}. The results are shown in Table 2. It is clear from the results that none of the anions tested have increased the K_D value from Binary Mixture A. EDTA, citrate, chromate, and molybdate interfere with the

TABLE 1
Adsorption of Europium on MnO_2 from Binary Mixtures of MeOH and H_2SO_4[a]

MeOH (% by volume)	2.5×10^{-4} mol·dm^{-3} H_2SO_4		5×10^{-4} mol·dm^{-3} H_2SO_4		5×10^{-3} mol·dm^{-3} H_2SO_4		5×10^{-2} mol·dm^{-3} H_2SO_4	
	K_D	% Ads	K_D	% Ads	K_D	% Ads	K_D	% Ads
0	7,659	98.8	3,974	97.8	827	90.2	95	51.4
10	4,126	97.9	2,958	97.0	509	85.0	37	29.1
20	4,380	98.0	1,926	95.5	504	84.8	50	35.7
30	3,529	97.5	2,109	95.9	318	77.9	89	49.7
40	3,875	97.7	3,195	97.3	440	83.0	183	67.0
50	5,953	98.5	1,237	93.2	709	88.7	262	74.4
60	5,411	98.4	1,213	93.1	794	89.8	203	69.3
70	14,684	99.4	2,833	96.9	798	89.9	286	76.1
80	34,262	99.7	8,458	98.9	1,688	94.9	427	82.6
90	97,440	99.9	11,650	99.2	3,576	97.5	2,166	96.0
99	127,216	99.9	21,109	99.6	8,131	95.9	3,012	97.1

[a] K_D (distribution coefficient) in cm^3·g^{-1}. % Ads = percent adsorption.

TABLE 2
Effect of Added Anions on the Adsorption of Europium on Manganese Dioxide[a]

Added anions[b]	Binary Mixture A		Binary Mixture B	
	K_D	% Adsorption	K_D	% Adsorption
No anion	127,216	99.9	37	29.1
Fluoride	44,750	99.8	70	43.8
Thiocyanate	13,552	99.3	25	21.7
Acetate	4,512	98.0	37	29.1
Thiosulfate	4,384	98.0	38	29.7
Sulfate	3,736	97.6	42	31.8
Iodide	3,362	97.4	24	21.1
Cyanide	1,088	92.4	53	37.1
Oxalate	1,004	91.8	43	32.3
Chromate	671	88.2	6	6.3
Molybdate	619	87.3	588	88.7
Citrate	280	75.7	41	31.3
EDTA	100	52.6	9	9.1

[a] K_D (distribution coefficient) in cm^3·g^{-1}.

[b] Anions were usually added in the form of sodium salts except for thiocyanate for which potassium salt was added. Their concentrations were 10^{-2} mol·dm^{-3}.

adsorption of europium at trace levels, causing a drastic reduction in the K_D values. This is probably due to complexation of these anions with europium which has a low affinity toward the oxide surface. Very strong complexes of europium with these anions have been reported (23–25). These complexes are stabilized in solution due to hydrogen bonding which results in decreased adsorption of the metal ion. Such evidence of hydrogen bond formation in solution by EDTA complexes is known (26). The influence of fluoride, thiocyanate, acetate, and thiosulfate on the percent adsorption of europium is less pronounced.

The effect of anions from Binary Mixture B on the adsorption of europium on manganese dioxide is negligible in all anions tested except for chromate, EDTA, and molybdate. The K_D value in the presence of molybdate is significantly increased whereas a reduction in the distribution coefficient is observed in the presence of chromate and EDTA. It is concluded from these results that nearly 100% europium can be adsorbed on MnO_2 from Binary Mixture A as a loading solution in the absence of any additional anions and remains unadsorbed up to 94% when using Mixture B in the presence of chromate or EDTA.

The influence of various cations of different valence states on adsorption has also been investigated under optimum conditions in Binary Mixtures A and B. The cations were added as nitrates, and their concentrations were kept at 10^{-2} mol·dm^{-3}. From the results shown in Table 3 it

TABLE 3
Influence of Added Cations on the Adsorption of Europium on Manganese Dioxide[a]

Added cations[b]	Binary Mixture A		Binary Mixture B	
	K_D	% Adsorption	K_D	% Adsorption
Nil	127,216	99.9	37	29.1
Bi(III)	12,376	99.3	37	29.1
Cr(III)	10	10.0	7	7.2
Fe(III)	9	9.1	4	4.3
Al(III)	5	5.3	18	16.7
Mg(II)	34,272	99.7	43	32.3
Co(II)	14,316	99.4	35	28.0
Ni(II)	5,248	98.3	39	30.2
Pb(II)	1,122	92.6	52	36.6
Sr(II)	438	83.0	—	—
Zn(II)	167	65.0	22	19.6
Ba(II)	94	51.1	—	—
Ag(I)	306	77.3	14	13.5

[a] K_D (distribution coefficient) in cm^3·g^{-1}.

[b] All cations were added as their nitrates, and their concentrations were 10^{-2} mol·dm^{-3}.

is clear that none of the cations has increased the K_D value from Binary Mixture A. This value, however, is drastically reduced in the presence of Cr(III), Fe(III), and Al(III), and largely suppressed in the presence of Pb(II), Sr(II), Zn(II), Ba(II), and Ag(I). The percent adsorption in the presence of Bi(III), Mg(II), Co(II), and Ni(II) is not significantly decreased, but there is a sufficient decrease in the K_D value of europium in the presence of these cations.

The results from Binary Mixture B show that cations like Bi(III), Mg(II), Co(II), Ni(II), and Zn(II) have no effect on adsorption. Since Ag(I) did have some effect on the Eu adsorption, it appears to have lowered the percent of Eu adsorbed by one-half. The distribution coefficient is significantly decreased in the presence of Cr(III) and Fe(III).

The suppression in adsorption of europium in the presence of trivalent Cr, Fe, and Al from both binary mixtures may be due to their preferred adsorption on the oxide surface than Eu(III), due to which the active sites of the oxide are blocked. The selective adsorption of Fe(III) by MnO_2 has been reported (27). In another study, a significant decrease in the adsorption of europium on manganese dioxide in the presence of Cr(III) from nitric acid and perchloric acid solution was described (28). Thus it can be seen that europium is adsorbed on manganese dioxide from Binary Mixture A and remains unadsorbed by the addition of cations like Cr(III), Fe(III), or Al(III).

Under the same optimum conditions of the amount of adsorbent, electrolyte, and shaking time described previously, the adsorption of other metal ions was investigated from Binary Mixtures A and B. The procedure for the adsorption measurement of these metal ions (as radiotracers) was the same as for europium. The results are shown in Table 4. From the table it is clear that the distribution coefficients of these metal ions are generally very low in Binary Mixture B compared to that from Binary Mixture A. The affinity for adsorption on the oxide is fairly low for divalent mercury in both mixtures, and for cobalt and zinc in Mixture B. Another notable feature is that the K_D values obtained for Sc(III), Cs(I), Tb(III), Sm(III), Co(II), Lu(III), and Zn(II) are fairly different in both binary mixtures.

Since metal ions like Ag(I), Sc(III), Cs(I), Tb(III), and Sm(III) have sufficiently higher K_D values and their adsorption is >90%, they can be considered to be coadsorbed on manganese dioxide along with europium from the Binary Mixture A. However, europium can be very well separated from mercury in Mixture A since its adsorption on MnO_2 in this mixture is less than 2%. Low separation factors have been obtained between europium and Co(II), Lu(III), and Zn(II). Adsorption of Ag(I) is high from both binary mixtures, so it can be separated from

TABLE 4
Distribution Coefficients (K_D) of Other Metal Ions from Binary Mixtures A and B on Manganese Dioxide[a]

Metal ions[b]	Binary Mixture A K_D	Binary Mixture A % Adsorption	Binary Mixture B K_D	Binary Mixture B % Adsorption
Eu(III)	127,216	99.9	37	29.1
Ag(I)	9,192	99.0	1,886	95.4
Sc(III)	2,553	96.6	34	27.4
Cs(I)	1,069	92.2	80	47.1
Tb(III)	1,018	91.9	43	32.3
Sm(III)	843	90.4	30	25.0
Co(II)	142	61.2	3	3.2
Lu(III)	123	57.7	12	11.8
Zn(II)	25	21.7	2	2.2
Hg(II)	>2	>2.0	7	7.2

[a] K_D (distribution coefficient) in $cm^3 \cdot g^{-1}$.
[b] Added as radiotracers.

Co(II), Lu(III), Zn(II), and Hg(II) by selective adsorption on MnO_2 from Mixture B.

CONCLUSIONS

In the present study of the adsorption of europium on manganese dioxide from binary mixtures of aqueous sulfuric acid and methanol, it is concluded that since very high adsorption (>99%) of europium is achieved from Binary Mixture A, manganese dioxide can be used for the preconcentration of europium. The oxide may also be employed for the removal of europium from very dilute solutions or to eliminate its radionuclides from radioactive waste solutions. Since anions and cations strongly interfere with the adsorption of europium, they should be removed prior to the preconcentration process.

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