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Europium Removal at Trace Concentrations by Manganese Dioxide from Slightly Acidic Mixtures of Water and Tetrahydrofuran

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ABSTRACT

Adsorption of europium on manganese dioxide from binary mixture of tetrahydrofuran and sulfuric acid has been studied in detail. Various parameters like contact time, composition of the binary mixture and foreign ions are also studied. Adsorption of other metal ions under the same conditions was also monitored. From the observed data, separation of europium from silver and especially from mercury can be achieved in good fashion.

INTRODUCTION

The importance of inorganic adsorbents of various types in various fields of application, including nuclear waste disposal, is well known (1–5). These adsorbents are quite selective toward certain metal ions and can be used for separation/preconcentration of various elements. Europium is one of the important radionuclides in a fission process, and demands attention for its removal from nuclear fuel. The process of adsorption of europium on various surfaces in different solvents has been cited in the literature (6–8), whereas limited data are available on this type of study

from binary mixtures (9–11). This paper describes the adsorption behavior of europium ions on manganese dioxide from slightly acidic solutions in the presence of tetrahydrofuran. The conditions of maximum adsorption and the effect of additives are reported.

EXPERIMENTAL

Manganese dioxide (Product No. 11015), a BDH microanalytical reagent black in color and of 10–20 mesh, was used as such. The BET surface area determined by adsorbing nitrogen was found to be 113 m^2/g. The porosity was 2.17 cm^3/g, and 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 specpure 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}·s^{-}. All other isotopes used in this work were prepared locally by irradiating metals or their appropriate compounds in the same manner. The radiochemical purity of these radiotracers was checked by gamma spectroscopy.

INSTRUMENTS

The activity measurements were carried out by counter model from Canberra Inc., USA. Shaking the tubes required a wrist-action shaker (Griffin and George). Gamma-ray spectroscopy was done with the help of a semiplanar 30 cm^3 Ge(Li) detector (Canberra Inc.) coupled with a Nuclear Data 4410 computerized multichannel analyzer having a 8K memory. Gross gamma measurements were carried out with a Nuclear Chicago Model 8725 well-type scintillation counter using a 58 cm^2 NaI(Tl) crystal. The surface area of manganese dioxide was measured with a BET Quantosorb sorption system Model No. QS-11. The pore size analysis and density measurements were done with a mercury porosimeter, micromeritic Auto Pore 9200 model.

PROCEDURE

The adsorption measurements were made by a batch method using a radiotracer technique at room temperature (27 ± 2°C). The results were computed for K_D values in the usual manner (12). All measurements were the average of at least triplicate runs.

RESULTS AND DISCUSSION

Since adsorption, in general, depends upon the contact time between the adsorbate and adsorbent, experiments were conducted to determine the optimum contact time to establish equilibrium between the adsorbent and adsorbate. For this study, 50 mg of manganese dioxide was shaken with 4.5 cm^3 of the binary mixture having europium concentration of 2×10^{-5} mol·dm^{-3} for different intervals of time ranging from 1 to 120 minutes. Variation in percent adsorption with respect to shaking time is shown in Fig. 1. These results show that equilibrium is established at 20 minutes and there is no change in adsorption beyond this limit. Therefore, 20 minutes shaking time was selected for further experiments. The adsorption of europium on manganese dioxide was studied at room temperature from various combinations of the binary mixtures having different concentrations of their components. During this study, the concentration of adsorbate (2×10^{-5} mol·dm^{-3}) and the amount of adsorbent (50 mg) was kept constant. The shaking time was 20 minutes. The results are shown in Table 1. From these results it is clear that the distribution coefficient of europium on manganese dioxide decreases with an increase of THF concentration up to 50%, keeping the acid concentration constant. Distribution coefficient values then increase with a further increase in THF concentration, and K_D values are maximum at 99% THF with a few exceptions. Since the maximum K_D of europium on manganese dioxide is obtained from the binary mixture having the acid concentration at 5×10^{-4} mol·dm^{-3} and 99% THF (binary mixture A) and the minimum K_D is shown

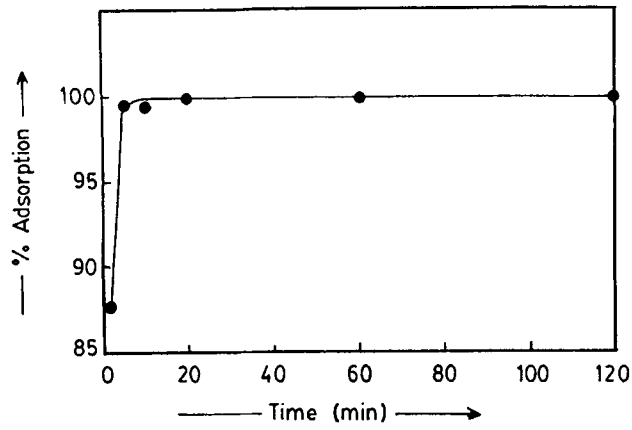

FIG. 1 Percent adsorption of Eu from binary mixture of 5×10^{-4} mol·dm^{-3} H_2SO_4 and 99% THF as a function of time.

TABLE 1
Adsorption of Europium on MnO_2 from Binary Mixtures of THF and H_2SO_4

THF, % by volume	2.0×10^{-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 [a]	% Ads[b]	K_D [a]	% Ads[b]	K_D [a]	% Ads[b]	K_D [a]	% Ads[b]
0	7.0×10^3	98.8	3.9×10^3	97.8	8.3×10^2	90.2	9.5×10^1	51.4
10	6.9×10^3	98.7	2.5×10^3	96.6	7.4×10^2	89.2	9.0×10^1	50.3
20	2.4×10^3	96.4	3.0×10^3	97.1	5.8×10^2	86.6	1.0×10^2	53.8
30	2.2×10^3	96.1	2.7×10^3	96.8	6.2×10^2	87.3	8.0×10^1	46.7
40	2.2×10^3	96.1	1.7×10^3	95.0	3.6×10^2	79.9	8.9×10^1	49.7
50	1.8×10^3	95.3	1.7×10^3	95.2	7.6×10^2	89.4	1.5×10^2	62.7
60	2.3×10^3	96.3	1.9×10^3	95.6	6.0×10^2	87.1	1.6×10^2	63.7
70	3.4×10^3	97.5	2.5×10^3	96.6	1.5×10^3	94.4	3.8×10^2	80.9
80	6.6×10^3	98.7	4.8×10^3	98.2	2.2×10^3	96.1	6.9×10^2	88.5
90	1.4×10^4	99.3	8.5×10^4	99.9	7.2×10^3	98.8	1.7×10^3	95.0
99	1.7×10^4	99.5	1.5×10^5	99.9	1.1×10^4	99.2	1.2×10^4	99.0

[a] Distribution coefficient ($cm^3 \cdot g^{-1}$).
[b] Percent adsorption.

by the mixture with the composition of 30% THF and 5×10^{-2} mol·dm^{-3} acid (binary mixture B), these two mixtures have been selected for further studies.

The effect of various anions on the adsorption of europium from the above binary mixtures A and B were also examined under optimum conditions. All the anions were added as their sodium salts except for thiocyanate for which the potassium compound was added. The concentration of the anions was 0.01 mol·dm^{-3}. The results are shown in Table 2. From the results, the K_D value of europium on manganese dioxide from the binary mixture A is increased only in the presence of thiosulfate. This means that the complex of europium with thiosulfate is more strongly adsorbed than the europium ions themselves from this mixture. An increase in the adsorption of europium on MnO_2 from perchloric and nitric acid solutions in the presence of thiosulfate has been reported (13). Other anions (thiocyanate, bromide, citrate, oxalate, iodide, molybdate, chromate, acetate, fluoride, and EDTA) exert a small depressive effect on adsorption from mixture A. The decrease in K_D in their presence may be attributed to low adsorption of their complexes with europium on the oxide surface. Complexes of europium with these anions have been identified (14, 15). Slow adsorption of sulfate on manganese dioxide has also been cited (16), leading to less adsorption.

In mixture B, anions like molybdate and fluoride enhance the adsorption to some extent, whereas EDTA, chromate, and thiocyanate suppress ad-

TABLE 2
The Influence of Added Anions on the Adsorption of Europium on Maganese Dioxide from Binary Mixtures A and B

Added anion	Binary mixture A		Binary mixture B	
	K_D [a]	% Ads[b]	K_D [a]	% Ads[b]
None	1.5×10^5	99.9	7.9×10^1	46.7
Thiosulfate	3.3×10^5	100.0	8.0×10^1	47.4
Thiocyanate	4.7×10^4	99.8	1.6×10^1	15.1
Bromide	1.8×10^4	99.5	5.2×10^1	36.6
Citrate	1.8×10^4	99.5	1.0×10^2	52.6
Oxalate	1.7×10^4	99.5	4.6×10^1	33.8
Iodide	1.6×10^4	99.4	5.5×10^1	37.9
Molybdate	1.6×10^4	99.4	3.4×10^2	79.1
Chromate	1.5×10^4	99.4	3.4×10^1	27.4
Acetate	8.7×10^3	99.0	8.0×10^1	47.4
Fluoride	8.5×10^3	99.0	1.4×10^2	61.6
EDTA	8.2×10^3	98.9	1.3×10^1	12.6

[a] Distribution coefficient ($cm^3 \cdot g^{-1}$).
[b] Percent adsorption.

sorption. This shows that anionic complexes of molybdate and fluoride with europium are more strongly adsorbed on the oxide surface in this mixture, whereas the oxide shows less affinity for the complexes of europium with EDTA, chromate, and thiocyanate. Strong complexes of europium with these anions are reported in the literature (14, 15). These complexes are stabilized in solution by hydrogen bonding, leading to their descreased adsorption. The presence of such hydrogen bonds for EDTA has been identified (15). For better results with the separation or preconcentration of europium from mixture A, it seems essential that anions like EDTA, fluoride, or acetate should not be present in the europium solutions to be adsorbed on the oxide surface.

Likewise, experiments were performed in order to measure the adsorption of europium on MnO_2 from binary mixtures A and B in the presence of foreign cations of different valence states. All the cations were added in the form of their nitrates, and the concentration added was 0.01 $mol \cdot dm^{-3}$. The results are shown in Table 3. One can see from the table that the K_D of europium does not increase in the presence of any cation tested from the binary mixture A. The effect of Bi(III), K(I), Ce(III), and Ca(II) on percent adsorption is minimum. However, the presence of Ag(I) and Al(III) strongly suppresses the adsorption of europium, and $<1\%$ of europium could be adsorbed in the presence of Al(III). Adsorption of

europium on manganese dioxide from binary mixture B is increased only in the presence of Ca(II) and to some extent in the presence of Li(I). The remainder of the cations added show no significant effect on the percent adsorption from the mixture. Hasany et al. (13) reported a similar depressive effect of Cr(III) on the adsorption of europium on MnO_2 from 0.01 mol·dm^{-3} nitric acid and 0.005 mol·dm^{-3} perchloric acid solutions. A similar depressive effect of Cr(III) was also observed (17) on the adsorption of traces of zirconium on MnO_2 from 0.1 mol·dm^{-3} nitric acid and 0.1 mol·dm^{-3} perchloric acid solutions.

Adsorption behavior of other metal ions on manganese dioxide was also checked from mixtures A and B under the same conditions as were used for the adsorption study of europium. The results are shown in Table 4. The study shows that adsorption of silver on the oxide surface is 97% from both binary mixtures A and B. The elements cesium, samarium, scandium, and terbium are very well adsorbed on manganese dioxide from mixture A, whereas their adsorption is poor from binary mixture B. Thus, they can be adsorbed from mixture A and eluted from mixture B. Since their adsorption is high from mixture A, they can adsorb equally on manganese dioxide along with europium from this solution; thus, their separation from europium is not possible from mixture A. Silver can be adsorbed up to 97% on manganese dioxide from mixture B, whereas the adsorption

TABLE 3
Effect of Additional Cations on the Adsorption of Europium on Manganese Dioxide from Binary Mixtures A and B

Added cations	Binary mixture A		Binary mixture B	
	K_D [a]	% Ads[b]	K_D [a]	% Ads[b]
None	1.5×10^5	99.9	8.0×10^1	46.7
Bi(III)	1.3×10^4	99.3	1.0×10^2	53.4
K(I)	1.0×10^3	99.1	6.1×10^1	40.4
Ce(III)	3.9×10^3	97.8	7	7.2
Ca(II)	3.0×10^3	97.1	5.0×10^2	84.5
Li(I)	1.1×10^3	92.5	1.0×10^2	64.5
Mg(II)	8.5×10^2	90.5	8.0×10^1	47.7
Ni(II)	2.8×10^2	76.0	6.0×10^1	40.0
Zn(II)	7.0×10^1	43.8	4.0×10^1	30.8
Cr(III)	6.5×10^1	41.9	2.5×10^1	21.7
Ag(I)	8	8.2	1.0×10^1	11.8
Al(III)	<1	<1.0	2.0×10^1	18.9

[a] Distribution coefficient ($cm^3 \cdot g^{-1}$).
[b] Percent adsorption.

TABLE 4
Adsorption of Other Metal Ions on Manganese Dioxide from Binary Mixtures A and B

	Binary mixture A		Binary mixture B	
Metal[a]	K_D [b]	Separation factor[c]	K_D [b]	Separation factor[c]
Eu(III)	1.5×10^5	—	8.0×10^1	—
Ag(I)	3.7×10^3	40.5	3.0×10^3	0.02
Cs(I)	2.6×10^3	57.7	1.8×10^2	0.44
Sm(III)	2.0×10^3	75	7.0×10^1	1.1
Sc(III)	1.4×10^3	101.1	1.8×10^2	0.44
Tb(III)	1.0×10^3	150	1.0×10^2	0.8
Co(II)	6.0×10^2	250	1.1×10^1	7.3
Lu(III)	1.6×10^2	937	2.2×10^1	3.63
Zn(II)	1.0×10^2	1500	6	13.3
Hg(II)	<2	7.4×10^4	<1	>79

[a] Added as radiotracers.
[b] Distribution coefficient ($cm^3 \cdot g^{-1}$).
[c] Separation factor = K_D(Eu)/K_D(other metal ion).

of europium is only 47%. Silver and europium can be separated from this solution up to about 50%. All the metal ions tested show very low adsorption on manganese dioxide from binary mixture B except silver, which shows 97% adsorption. Mercury is very poorly adsorbed on manganese dioxide from solutions A and B, thus it can be separated from europium by either mixture.

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