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Adsorption of Europium onto Manganese Dioxide from Acid Solutions

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Abstract

Adsorption of europium on manganese dioxide from nitric and perchloric acid solutions has been studied as a function of shaking time, concentration of electrolytes, adsorbent, and adsorbate. The influence of different anions and cations on adsorption has been examined. The adsorption of other metal ions on the oxide has been measured, under specified conditions, to check its selectivity. Adsorption of europium decreases with an increase in electrolyte or its own concentration. Zr(IV), Cr(III), La(III), Ce(III), EDTA, and citrate reduce adsorption appreciably in both acids. More than 99% europium adsorbed on the oxide column can be eluted with 40 cm^3 of 3 mol/dm^3 nitric acid solution. Europium obeys the Freundlich adsorption isotherm in both media over concentrations ranging from 10^{-7} to 10^{-4} g/cm^3.

INTRODUCTION

Preconcentration/separation procedures based on adsorption phenomena are important in the analytical and radiochemistry of trace elements because of their simplicity, efficiency, and selectivity. Various metal oxides and hydroxides have been used successfully for this purpose. (*1, 2*). Manganese dioxide, stable to high temperature and radiation, has been explored in several investigations as an adsorbent (*3*–

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7). In our laboratory this oxide has been studied to evaluate its potentials for the preconcentration or separation of different elements at micro levels. Our results about the adsorption of cobalt (*8*), strontium (*9*), cesium (*10*), cadmium (*11*) and mercury (*12*) on manganese dioxide have been reported. Earlier, adsorption of europium on manganese dioxide was mentioned briefly for analytical separation (*13*). Moreover, adsorption of europium on antimony pentoxide (*14*), silica gel (*15, 16*), iron oxide (*17*), and alumina (*18*) was also reported from different points of view. This communication deals with our findings about the adsorption of europium on manganese dioxide from acid solutions.

EXPERIMENTAL

Reagents and Radiotracers

Manganese dioxide (product No. 11015), B.D.H. microanalytical reagent, black in color, 10-20 mesh, was used. All solutions were prepared from doubly distilled deionized water and analytical reagents. $^{152+154}$Eu tracer was produced by irradiating specpure Eu_2O_3 in a PARR-I research reactor of this Institute at a thermal flux of 2×10^{13} neutrons cm^{-2} s^{-1}. Most of the radiotracers used in this work were produced locally, and a few more procured commercially from Radiochemical Centre, Amersham, England.

Procedure

Adsorption was measured radiometrically. The procedure for adsorption measurement, computation of distribution coefficient (K_D), and percent adsorption (%) are given in detail elsewhere (*12*). The instruments used for radioassay were mentioned earlier (*9*). All measurements were carried out at room temperature (23 ± 2°C) at least in duplicate. The concentration of total europium in aqueous solution (4.5 cm^3) was (1.2–1.46) $\times$ 10^{-5} mol/dm^3, and the amount of manganese dioxide used was 50 or 100 mg except where specified otherwise.

RESULTS AND DISCUSSION

Preliminary experiments were conducted to establish the time required for the adsorption equilibrium of europium between solid and liquid

phases. For this study, 50 mg of manganese dioxide was shaken with a 4.5-cm^3 solution of europium in 0.01 mol/dm^3 nitric acid and 0.0125 mol/dm^3 perchloric acid separately for different intervals of time ranging from 1 to 435 min. The results are recorded in Fig. 1. Adsorption variation with time is similar in both the acids and is fast in the initial stages but then proceeds slowly and attains equilibrium after about 1 h. In 1 h of shaking, >93% adsorption of europium was achieved. However, beyond 40 min the adsorption from nitric acid solutions is somewhat greater than from perchloric acid solutions. The results are shown up to 240 min, but no change in adsorption was noticed even in 435 min. One hour of shaking time was employed in further experiments.

Adsorption of europium on 50 mg manganese dioxide was studied as a function of nitric acid (0.001–9 mol/dm^3) and perchloric acid (0.005–3 mol/dm^3) concentration in solution. The results are given (Fig. 2) both in terms of distribution coefficient (K_D) and percent adsorption (%). In general, from both the acids, the adsorption decreases with an increase in electrolyte concentration. From 0.001 mol/dm^3 nitric acid solution, ~98%

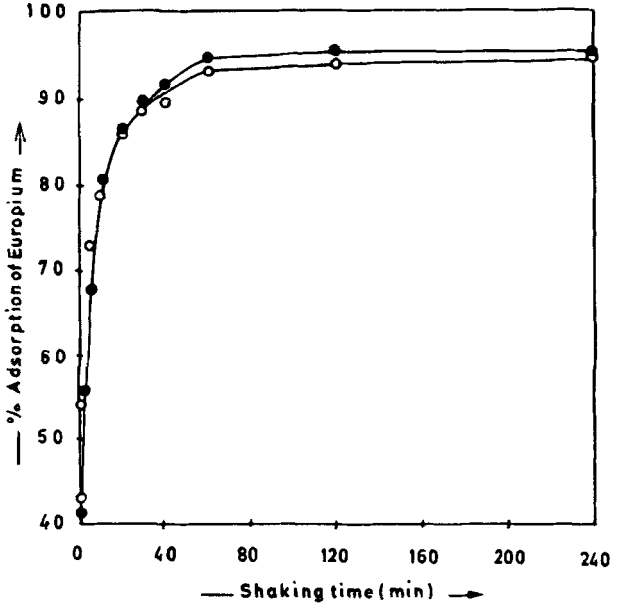

FIG. 1. Percent adsorption of europium as a function of shaking time. (●) From 0.01 mol/dm^3 nitric acid on 50 mg of manganese dioxide: [Eu] = 1.35×10^{-5} mol/dm^3. (○) From 0.0125 mol/dm^3 perchloric acid on 50 mg of manganese dioxide: [Eu] = 1.20×10^{-5} mol/dm^3.

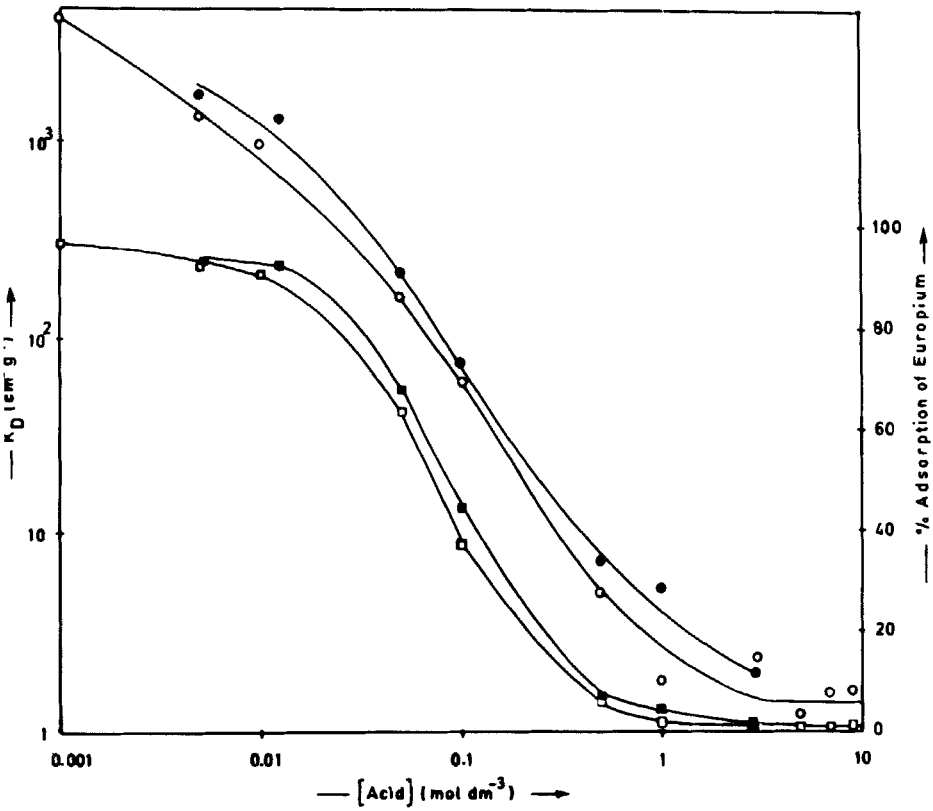

FIG. 2. Adsorption variation with the concentration of electrolyte. (○) K_D and (□) % adsorption from nitric acid solutions on 50 mg of manganese dioxide: [Eu] = 1.20×10^{-5} mol/dm^3. (●) K_D and (■) % adsorption from perchloric acid solutions on 50 mg manganese dioxide: [Eu] = 1.34×10^{-5} mol/dm^3.

europium is adsorbed which reduces to 2% from 1 mol/dm^3 nitric acid solution. The high percentage of adsorption indicates the possibility of manganese dioxide being used as an efficient bed for preconcentration or removal of europium from its very dilute solutions. The extent of adsorption from perchloric acid is somewhat greater than from nitric acid solutions throughout the entire range of acid concentration investigated. The pH during this acid range would be between 2.3 to −0.95. According to stability constants reported (*19*), in this pH range no hydrolysis of europium is expected and the entire europium present in the acid solutions would be in the form of Eu^{3+} ions. It can be concluded from Fig. 2 that europium can be very well adsorbed on the oxide surface from very dilute acid solutions and can be subsequently removed from the surface with somewhat concentrated acid solution (>1 mol/dm^3). Therefore, in our elution studies, europium was adsorbed from dilute nitric acid solution and then removed from the oxide column with 3 mol/dm^3 nitric acid solution. For further experiments, 0.01 mol/dm^3 nitric acid and 0.005 mol/dm^3 perchloric acid solutions were used as electrolytes.

The amount of adsorbent sometime affects the adsorption of adsorbate. Adsorption was, therefore, determined as a function of the amount of manganese dioxide in the range from 10 to 500 mg. The dependence of adsorption on the amount of adsorbent from both electrolytes is shown in Fig. 3. A marked increase in the percent adsorption is observed with an increasing amount of manganese dioxide, but at higher amounts the adsorption is not influenced. The extent of adsorption increases rapidly between 10 and 50 mg and attains a constant value at >100 mg. The adsorption behavior of europium in relation to the mass of adsorbent is almost identical in both media. A similar trend in adsorption has been noticed in our results about the adsorption of cesium (*10*) and mercury (*12*) on this oxide. Figure 3 reveals that more than 99% europium is adsorbed on 350 mg or more of the oxide. However, for further investigations, 50 and 100 mg of manganese dioxide were employed in perchloric acid and nitric acid solutions, respectively.

Another parameter that influences adsorption is the concentration of europium itself in the solution. The adsorption of europium on the oxide was measured in the range of 10,000-fold of its concentration from 1.26×10^{-6} to 1×10^{-2} mol/dm^3. Figure 4 represents the effect of europium concentration on its adsorption from both media. Figure 4 shows that the distribution coefficient (K_D) of europium increases with the dilution of its bulk concentration. Comparing the K_D values from both acids, adsorption is higher in the moderate concentration range in nitric acid solutions and at low and higher concentrations in perchloric

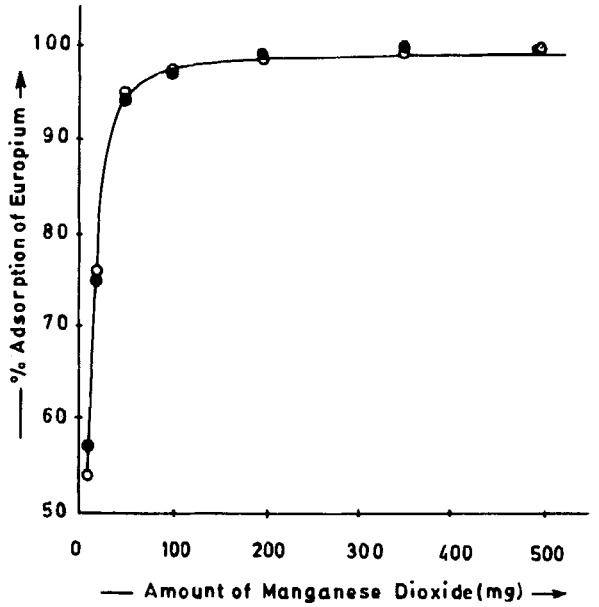

FIG. 3. The influence of the amount of manganese dioxide on the adsorption of europium from (○) 0.01 mol/dm^3 nitric acid, [Eu] = 1.46×10^{-5} mol/dm^3, and (●) from 0.005 mol/dm^3 perchloric acid solution, [Eu] = 1.20×10^{-5} mol/dm^3.

acid solutions. Similar observations were noticed for strontium (*8*) and cadmium (*11*) adsorption variation with their concentrations in solution. The increase in K_D values with an increase in dilution is likely due to the fact that a larger surface area is available for a relatively lesser number of europium ions at higher dilution. This conclusion is supported by Fig. 5 where our data have been tested by the Freundlich adsorption isotherm in the following form (*20*):

$$\log C_{\text{Adsorbed}} = \log A + \frac{1}{n} \log C_{\text{Bulk}} \tag{1}$$

where C_{Adsorbed} is the adsorbed concentration in g/g of manganese dioxide, C_{Bulk} is the bulk concentration of europium in g/cm^3, and A and n are characteristic constants for a particular adsorption system. A linear log-log plot of the adsorbed and bulk concentration of europium (Fig. 5), with slopes of 0.91 and 0.98, respectively, from perchloric acid and nitric acid medium, describes the validity of the Freundlich adsorption isotherm up to 10^{-4} g/cm^3 bulk concentration whereas at higher concentration ($>10^{-4}$

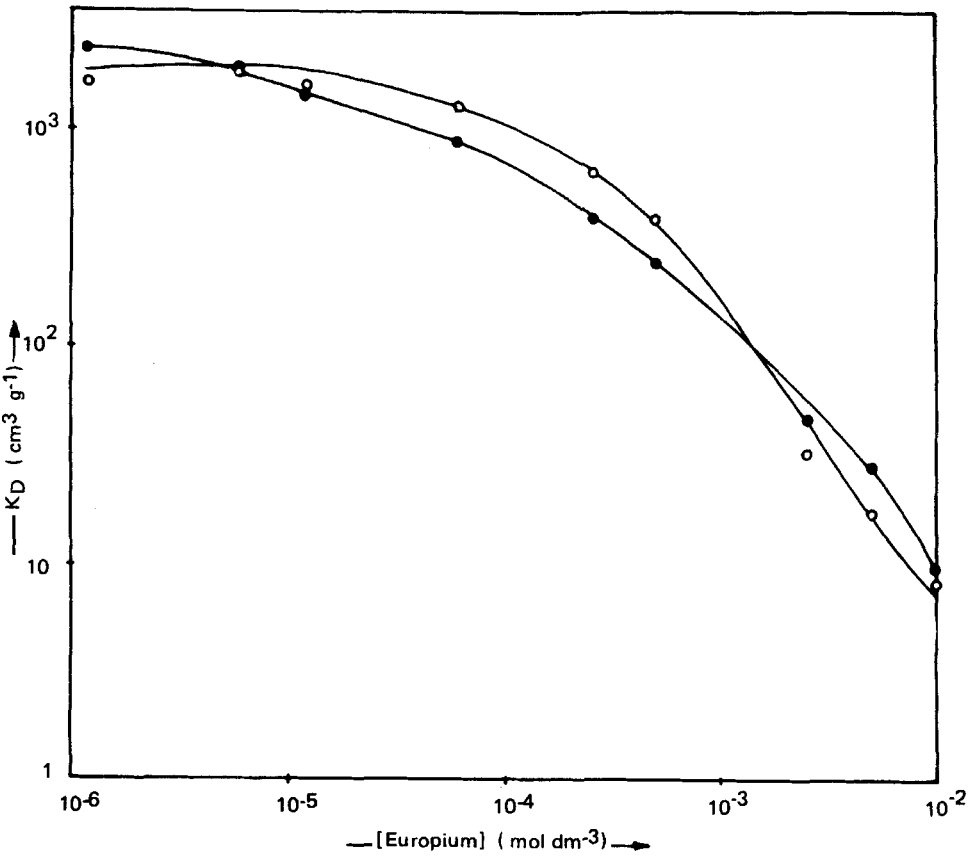

FIG. 4. The relationship between the distribution coefficient of europium and its concentration in aqueous solution. (O) From 0.01 mol/dm^3 nitric acid on 100 mg manganese dioxide. (●) From 0.005 mol/dm^3 perchloric acid on 50 mg manganese dioxide.

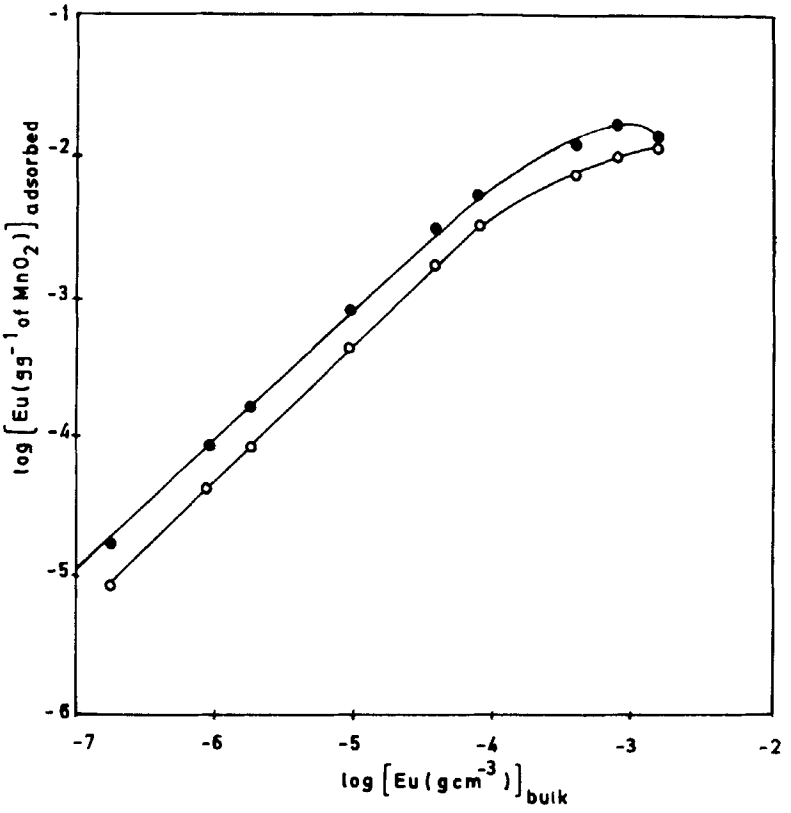

FIG. 5. Freundlich adsorption isotherm of europium. (○) From 0.01 mol/dm^3 nitric acid solution. (●) from 0.005 mol/dm^3 perchloric acid solution.

g/cm^3) europium does not obey the Freundlich adsorption isotherm. It is interesting to note that this isotherm is valid throughout the entire bulk concentration investigated in the adsorption of cobalt (*8*), strontium (*9*), cesium (*10*), and mercury (*12*) on manganese dioxide. The same data were also subjected to the Langmuir adsorption isotherm (*7*):

$$\frac{C_{\text{Bulk}}}{C_{\text{Adsorbed}}} = \frac{C_{\text{Bulk}}}{C_{\text{Saturation}}} + \frac{1}{B} C_{\text{Saturation}} \qquad (2)$$

where $C_{\text{Saturation}}$ is the limiting concentration of the adsorbate (g/g of MnO_2) and B is a constant related to the intensity of adsorption. The ratio of bulk and adsorbed concentrations was plotted against the bulk

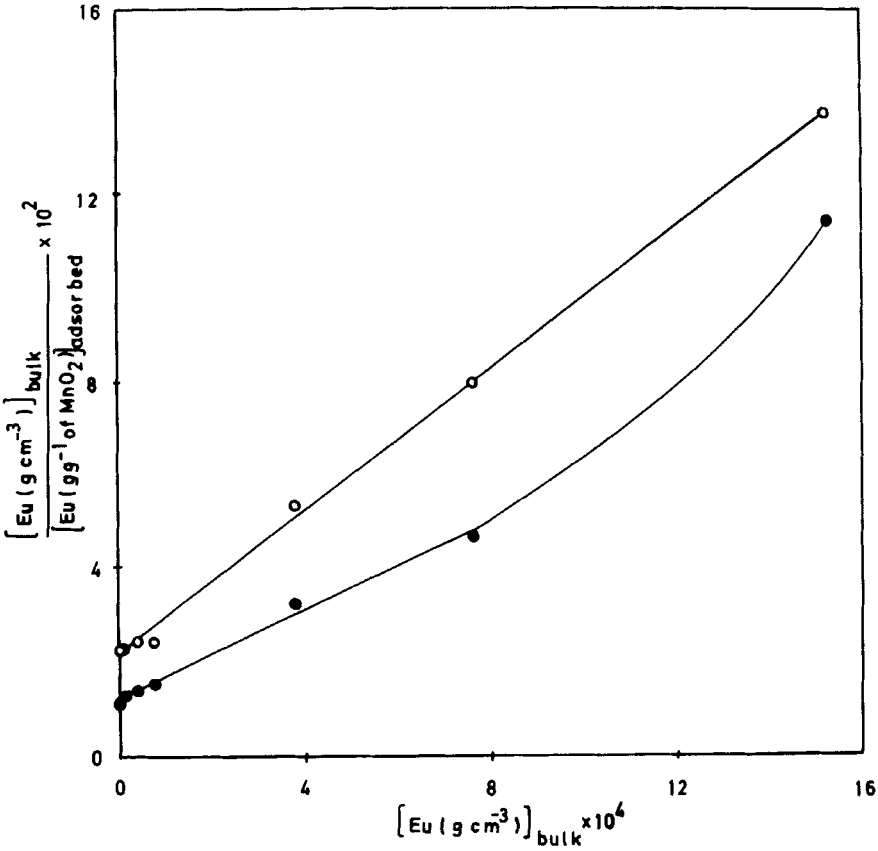

FIG. 6. Langmuir adsorption isotherm of europium. (○) From 0.01 mol/dm^3 nitric acid solution. (●) From 0.005 mol/dm^3 perchloric acid solution.

concentration (Fig. 6). Europium follows the Langmuir adsorption isotherm from nitric acid solutions over the entire bulk concentration; however, deviation from linearity is observed from perchloric acid solutions at a bulk concentration of 1.52×10^{-3} g/cm^3. It is concluded that adsorption of europium from nitric acid and perchloric acid solutions follows the Langmuir adsorption isotherm over the entire range of europium bulk concentrations examined, except at the highest bulk concentration used in perchloric acid solution. It was reported earlier that europium follows the Langmuir adsorption isotherm in its adsorption from nitric acid solutions on manganese dioxide (*13*).

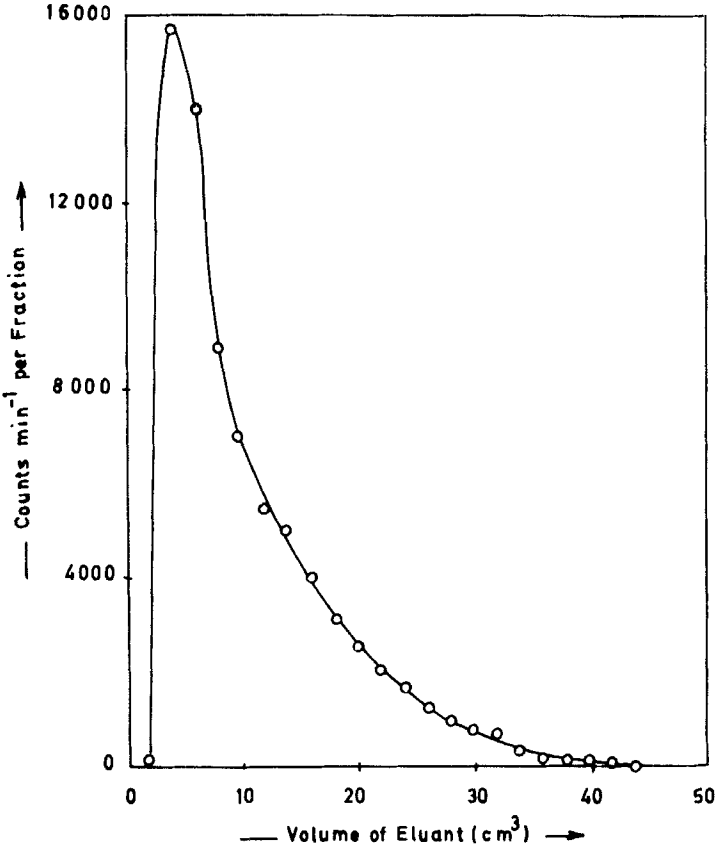

FIG 7. Elution curve of europium with 3 mol/dm^3 nitric acid solution from 3 cm × 1 cm i.d. manganese dioxide column at a flow rate of 0.5–0.67 cm^3/min.

The influence of certain additional anions on the adsorption of europium was also examined under specified conditions. The concentration of anion was of the order of 10^{-2} mol/dm^3, a thousandfold europium concentration in aqueous solutions. All the anions were added in the form of their sodium or potassium salts. The results, recorded in Table 1, indicate that the adsorption is appreciably suppressed by the addition of ascorbate, citrate, EDTA, and tartrate ions whereas the presence of acetate, cyanide, oxalate, thiocyanate, and thiosulfate enhance the adsorption from both acids. However, the presence of fluoride and iodide substantially increases the adsorption in perchloric acid medium. Complexes of EDTA (*19, 21*), oxalate (*19*), tartrate (*19, 21*), citrate (*21*), acetate (*19*), and fluoride (*22*) with europium have been reported in the literature. It may be inferred that the affinity of the complexes of anions which suppress europium adsorption is low toward the oxide whereas the complexes of europium with anions which enhance adsorption are more strongly adsorbed on the oxide surface than the metal ions themselves.

TABLE 1
The Influence of Additional Anions on the Adsorption of Europium (1.2×10^{-5} mol/dm^3) from Aqueous Nitric and Perchloric Acid Solutions

Additional anion ($\sim 10^{-2}$ mol/dm^3)	0.01 mol/dm^3 Nitric acid solution (100 mg manganese dioxide)		0.005 mol/dm^3 Perchloric acid (50 mg manganese dioxide)	
	% Adsorption	K_D (cm^3/g)	% Adsorption	K_D (cm^3/g)
Nil	97.3	1,649	94.3	1,495
Acetate	97.8	1,981	99.4	14,028
Ascorbate	94.0	711	89.8	793
Chloride	95.6	1,007	93.9	1,388
Citrate	79.7	177	40.2	61.9
Cyanide	99.7	13,553	99.3	12,440
EDTA	53.4	51.5	25.6	30.9
Fluoride	97.0	1,492	96.5	2,538
Iodide	97.0	1,502	99.3	12,178
Oxalate	99.3	7,331	94.8	1,648
Tartrate	93.7	676	85.6	537.2
Thiocyanate	97.8	1,970	96.4	2,397
Thiosulfate	99.5	9,554	99.5	17,784
Vanadate	96.6	1,292	86.4	575

The effect of certain cations of different valence states on adsorption has also been studied. The cations were added as nitrates, and their concentration (10^{-2} mol/dm^3) was a thousand times greater than the concentration of europium in the bulk solution. In general, all the added cations show an inhibition effect on adsorption (Table 2), but this effect is well pronounced in the case of Cr(III), La(III), Ce(III), and Zr(IV) in both electrolyte solutions. The substantial decrease in the adsorption of europium due to the presence of trivalent Cr, La, and Ce indicates an inhibiting role by such cations. It is likely that because of the identical charge and comparable ionic radii of La, Ce, and Eu (1.061, 1.034, and 0.95 Å (*23*)), these cations can fit into a lattice and act as potential-determining ions and consequently give rise to an electric double layer necessary for adsorption (*24*).

The adsorption of other metal ions was measured under specific conditions to check the selectivity of the oxide. The results, presented in Table 3, indicate that the adsorption of Fe(III), Ru(III)-Rh(III), Nd(III), and Ta(V) is rather low in both electrolytes except for the fairly high adsorption noticed for Nd(III) in perchloric acid solution. However, Hg(II), Sm(III), Gd(III), Yb(III), and Hf(IV) in nitric acid and Hg(II), Nd(III), Sm(III), Lu(III), and Hf(IV) in perchloric acid have fairly high distribution coefficients on the oxide surface. Therefore, these metal ions can be coadsorbed on the oxide column along with europium. Their high

TABLE 2
The Effect of Additional Cations on the Adsorption of Europium (1.2×10^{-5} mol/dm^3) from Aqueous Nitric and Perchloric Acid Solutions on Manganese Dioxide

Additional cation ($\sim 10^{-2}$ mol/dm^3)	0.01 mol/dm^3 Nitric acid solution (100 mg manganese dioxide)		0.005 mol/dm^3 Perchloric acid solution (50 mg manganese dioxide)	
	% Adsorption	K_D (cm^3/g^1)	% Adsorption	K_D (cm^3/g^1)
Nil	97.3	1649	94.3	1495
Li(I)	95.7	988	93.5	1308
Na(I)	94.8	828	92.2	1058
Ag(I)	87.4	314	75.4	277
Co(II)	90.3	420	85.3	527
Ni(II)	90.4	434	88.0	663
Zn(II)	93.3	628	84.3	485
Cr(III)	6.1	2.9	4.7	4.5
La(III)	25.8	15.7	9.3	9.3
Ce(III)	19.5	10.9	4.4	4.2
Zr(IV)	47.4	40.6	20.1	22.7

adsorption from a suitable medium can be exploited for their preconcentration or removal in a group from very dilute solutions. The elements showing low adsorption affinity for the oxide can be separated from those metal ions having fairly large distribution coefficients in appropriate aqueous solutions. The data can be utilized for separation/preconcentration either for analytical purposes or for liquid radioactive waste disposal.

The adsorption data obtained by the batch technique was applied to investigating suitable conditions for the adsorption of europium on an oxide column and its subsequent removal from the column. For elution, a solution of radioeuropium in 0.01 mol/dm^3 nitric acid solution (3 × 0.5 cm^3) was loaded into a 3 cm × 1 cm i.d. column of manganese dioxide (738 mg) so that the entire column length was in contact with the radioeuropium solution for 1 h. More than 99% europium was adsorbed on the oxide. It is evident from our results that desorption can be achieved with moderate nitric acid solutions because of the low K_D values found for these concentrations. Therefore, adsorbed europium was eluted from the oxide with 3 mol/dm^3 nitric acid solution at a flow rate of 0.5–0.67 cm^3/min, and 2 cm^3 fractions were collected each time for radioassay.

TABLE 3
The Adsorption of Other Metal Ions from Nitric and Perchloric Acid Solutions on Manganese Dioxide

	0.01 mol/dm^3 Nitric acid solution (100 mg manganese dioxide)		0.005 mol/dm^3 Perchloric acid solution (50 mg manganese dioxide)	
Metal ion	% Adsorption	K_D (cm^3/g)	% Adsorption	K_D (cm^3/g)
Ag(I)	—	—	95.2	1848
Cs(I)	72.1	116	67.2	184
Co(II)	74.7	133	73.7	253
Hg(II)	97.7	1951	96.4	2396
Fe(III)	31.4	20.7	24.3	29.3
Ru(III)-Rh(III)	40.0	30.3	33.1	44.6
Nd(III)	41.9	32.4	94.5	1550
Sm(III)	98.0	2250	92.9	1187
Gd(III)	96.7	1318	—	—
Tm(III)	84.2	248	81.1	389
Yb(III)	96.8	1349	84.4	496
Lu(III)	94.8	826	93.9	1415
Zr(IV)	—	—	55.0	112
Hf(IV)	97.4	1687	98.4	5641
Ta(V)	58.1	62.8	60.7	140

It was found that more than 99% of adsorbed europium was flushed into 40 cm^3 nitric acid solution. A typical elution curve obtained is shown in Fig. 7.

The rapid and high degree of adsorption of europium on manganese dioxide indicates the possibility of its use as a good adsorbent in chromatography and as an efficient bed for its preconcentration from dilute solutions or to remove $^{152+154}Eu$ from radioactive liquid waste along with other radionuclides which show comparable adsorption properties on this oxide.

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