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# ADSORPTION OF EUROPIUM(III) IN IONIC AND COLLOIDAL STATES ON MANGANESE DIOXIDE DEPOSITED ON A SILICA GEL SURFACE

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## SUMMARY

The sorption of europium(III) in ionic and colloidal states on manganese dioxide deposited on a silica gel surface has been studied as a function of pH of aqueous solutions by batch equilibrations.

The behaviour of $Eu^{3+}$ and colloidal Eu(III) on the sorbent column has also been investigated. Conditions for the sorption of europium from aqueous solutions are given.

## INTRODUCTION

In previous papers[1,2] the adsorption of colloidal Fe(III), *i.e.* iron(III) oxides sols, on alumina and manganese dioxide from aqueous solutions was studied as a function of pH and concentration. The results obtained showed that the adsorption is determined by the sign of the surface charge of the sorbent and colloidal particles. As the sign of the surface charge of hydrated oxides depends on the pH of the solution, the adsorption of colloidal particles also depends on the pH.

The objects of the work reported in this paper were to provide information about the sorption of colloidal Eu(III) and $Eu^{3+}$ on manganese dioxide deposited on a silica gel surface and to find conditions for the sorption of europium from aqueous solutions.

## EXPERIMENTAL

The sorbent was prepared as described previously[1]. The amount of manganese dioxide on the silica gel was 29.05 mg per gram of the sorbent.

Solutions of colloidal Eu(III) were obtained by peptization of Eu(III) hydroxide (labelled with [152]Eu) as described in ref. 3. Large colloidal particles of Eu(III) hydroxide were isolated from the sol by centrifugation at 3400 g. The final Eu(III) colloidal solution is clear in transmitted and turbid in reflected light.

The chemicals used were of analytical grade.

Batch equilibrations and column experiments have been described in previous papers[1,2].

To avoid sorption on glass, all laboratory glassware used was rinsed with a solution of dichlorodimethylsilane, as described previously[1].

The isoelectric point (i.e.p.) of manganese dioxide was determined by the adsorption method, which has been used successfully for metal oxides[4]. The i.e.p. of manganese dioxide deposited on silica gel is at pH 3.3.

For pH determination a Beckman pH meter with Beckman glass and saturated calomel electrodes was used.

The $\gamma$-radioactivity of $^{152}$Eu was measured on a Nuclear Chicago DS5-5 well scintillation counter. The activity of the experimental solutions varied from *ca.* $10^4$ to $10^5$ counts $\text{min}^{-1}$ $\text{cm}^{-3}$.

RESULTS AND DISCUSSION

The dependence of sorption of colloidal Eu(III) on pH is characterized by a sorption maximum in the pH range 4–7.5 (Fig. 1). In this range the colloid is positively charged and the sorbent charge is negative. If the pH of the solution is increased from 7.5 to 9.3, the sorption of colloidal Eu(III) decreases. In this pH range the surface of the Eu(III) colloidal particles becomes negatively charged, with increasing negative values. These results indicate that the i.e.p. of colloidal Eu(III) is at pH 7–7.5.
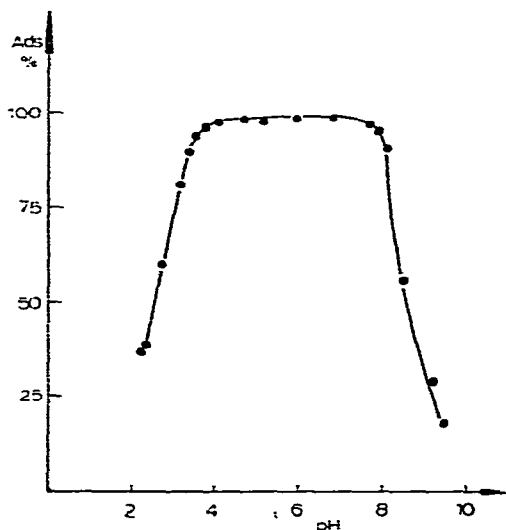


Fig. 1. Dependence of the sorption of colloidal Eu(III) (Eu $2 \cdot 10^{-4}$ *M*) on pH. Solution ionic strength $\mu = 0.01$ ($\text{NO}_3^-$).

If the pH of the solution is increased from 8 to 11, at solution ionic strength $\mu = 0.1$ ($\text{NO}_3^-$), the sorption of colloidal Eu(III) slightly decreases (Fig. 2). In this case the colloidal Eu(III) was not adsorbed at the sorbent–solution interface. The colloid was coagulated and precipitated separately.

The dependence of the sorption of $\text{Eu}^{3+}$ on pH, at solution ionic strength $\mu = 0.01$ ($\text{NO}_3^-$), is shown in Fig. 3. It can be seen that the sorption of $\text{Eu}^{3+}$ at pH 2 is very
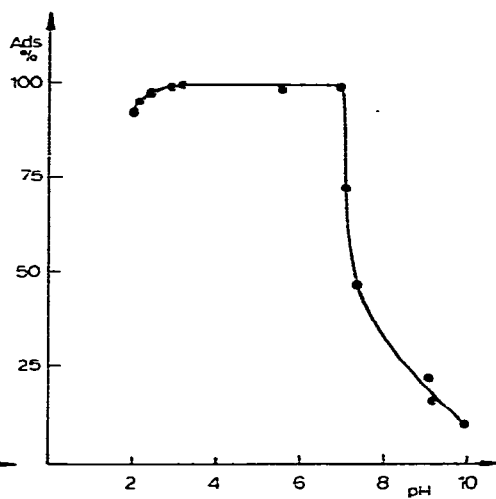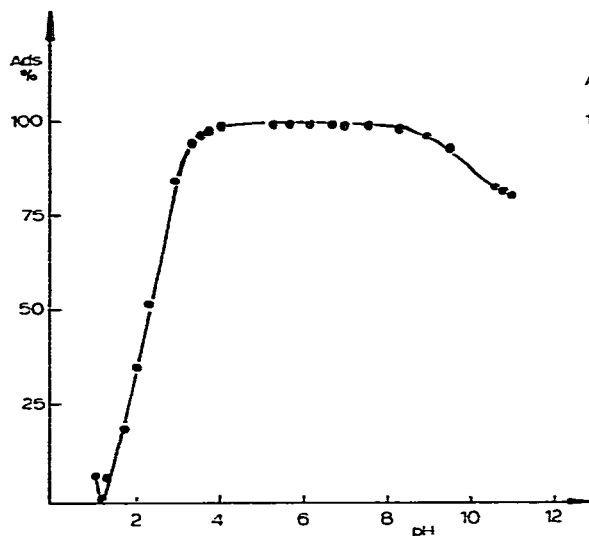
Fig. 2. Dependence of the sorption of colloidal Eu(III) (Eu $2.4 \cdot 10^{-4}$ $M$) on pH, solution ionic strength $\mu = 0.1$ ($NO_3^-$).

Fig. 3. Dependence of the sorption of $Eu^{3+}$ ($5 \cdot 10^{-7}$ $M$) on pH. Solution ionic strength $\mu = 0.01$ ($NO_3^-$).

high (92 %). The sorption of $Eu^{3+}$ increases with increasing pH in the range 2.1–3.0. The sorption maximum is in the pH range 3–7.1. If the pH of the solution is increased to 9.5 the sorption of $Eu^{3+}$ decreases. At pH > 7 the sorption behaviour of both $Eu^{3+}$ (Fig. 3) and colloidal Eu(III) (Fig. 1) is similar. The obtained results are in agreement with the reported electrophoretic data[5] for $Eu^{3+}$.

The sorption behaviour of $Eu^{3+}$ at pH < 5 can be explained by an ion-exchange process, at pH 5–7 by interaction of hydroxo complexes of $Eu^{3+}$ with a negatively charged sorbent surface, and at pH > 7 by electrostatic repulsion between the negatively charged sorbent surface and colloidal particles (or polynuclear complexes) of Eu(III). At pH > 7, the formation of pseudocolloid by adsorption of hydrolysed europium on foreign colloidal material is not excluded[5,6]. However, it is not evident whether $Eu^{3+}$ (at $10^{-7}$ $M$) forms true colloid or pseudocolloid.

If the pH of the solution is increased from 7 to 9.5, at solution ionic strength $\mu = 0.1$ ($NO_3^-$), the amount of adsorbed $Eu^{3+}$ remains constant (100 %) (Fig. 4). These results can be explained by the assumption that, under given experimental conditions, large colloidal (or pseudocolloidal) particles of Eu(III) are formed, and precipitated by centrifugation. As reported in the literature[5,7], the adsorption behaviour of $Eu^{3+}$ on glass, $Fe(OH)_3$ and $Fe_2O_3$ in the pH range 7–12, at 0.15 $M$ NaCl, is quite similar.

From the dependence of the distribution coefficients ($K_d$) of $Eu^{3+}$ ($5 \cdot 10^{-7}$ $M$) on the nitric acid concentration (Fig. 5) it can be concluded that the sorption of $Eu^{3+}$ depends strongly on the acidity of the aqueous solution, as would be expected for a real ion-exchange process. The sorption of colloidal Eu(III) also depends strongly on the acidity of the aqueous solution, (Fig. 5). This behaviour of colloidal Eu(III) is quite different from the sorption behaviour of colloidal Fe(III) under the same conditions[1].
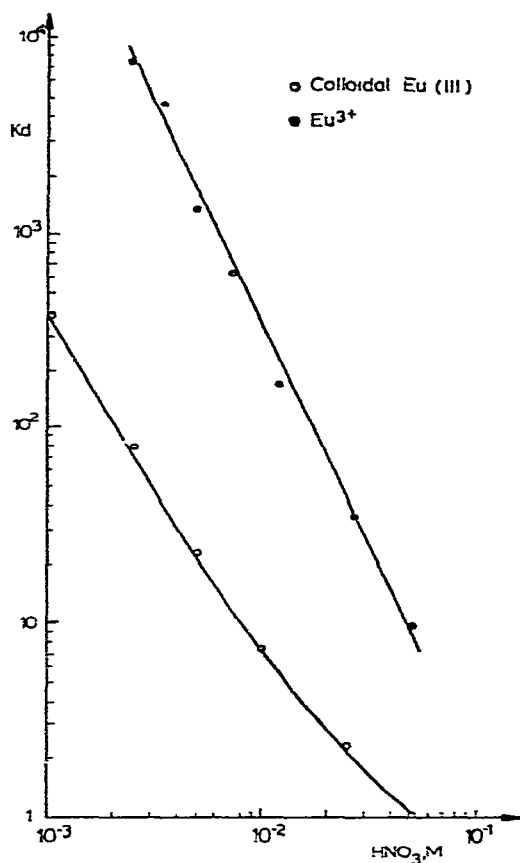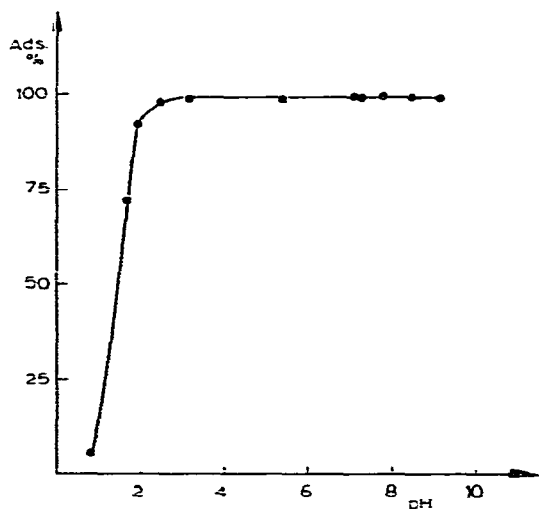
Fig. 4. Dependence of the sorption of $Eu^{3+}$ ($5 \cdot 10^{-7}$ $M$) on pH. Solution ionic strength $\mu = 0.1$ ($NO_3^-$).

Fig. 5. Dependence of the distribution coefficients, $K_d$, of $Eu^{3+}$ ($5 \cdot 10^{-7}$ $M$) and colloidal Eu(III) (Eu $2.4 \cdot 10^{-4}$ $M$) on the $HNO_3$ concentration.

TABLE I

ADSORPTION OF $Eu^{3+}$ ON $SiO_2$–$MnO_2$ COLUMN

Column. 15 cm $\times$ 0.14 cm$^2$; elution flow-rate. 2 cm$^3$/cm$^2$ min.

| $Eu^{3+}$ sorbed from $HNO_3$ ($M$) | Percentage of $Eu^{3+}$ eluted in fractions | | | |
|---|---|---|---|---|
| | 0.001 $M$ $HNO_3$ (25 cm$^3$) | 0.01 $M$ $HNO_3$ (25 cm$^3$) | 0.5 $M$ $HNO_3$ (25 cm$^3$) | 1.0 $M$ $HNO_3$ (25 cm$^3$) |
| 0.0001 | | * | 98.2 | |
| 0.001 | * | * | | 99.6 |
| 0.01 | | * | | 99.8 |
| 0.01 | | * | 98.0 | |

* Not eluted.

TABLE II

ADSORPTION OF COLLOIDAL Eu(III) ON $SiO_2$–$MnO_2$ COLUMN

Column, 15 cm × 0.14 $cm^2$; elution flow-rate. 2 $cm^3$/$cm^2$ min.

| Colloidal Eu(III) sorbed from solutions | Sorbent in the form | Percentage of colloidal Eu(III) eluted in fractions | | | |
|---|---|---|---|---|---|
| | | Water, pH 7.2 (25 $cm^3$) | Water, pH 11.9 (25 $cm^3$) | $HNO_3$ 0.01 M (25 $cm^3$) | $HNO_3$ 1.0 M (25 $cm^3$) |
| Water (pH 7.2) | $Na^+$ | * | | 51.4 | 46.2 |
| Water (pH 11.9) | $Na^+$ | | * | | 99.0 |
| 0.01 M $HNO_3$ | $H^+$ | | | 68.6 | 31.3 |

* Not eluted.

The results obtained in the column runs are given in Table I and II.

The elution curves of colloidal Eu(III) with 0.01 M $HNO_3$ and $Eu^{3+}$ with 0.5 M $HNO_3$ are given in Fig. 6.

From the sorption and desorption behaviour of $Eu^{3+}$ (Table I) one can conclude that $Eu^{3+}$ is adsorbed on to the sorbent at low acidity (less than 0.01 M $HNO_3$). It is easy to desorb $Eu^{3+}$ using 0.5–1.0 M nitric acid.

The colloidal Eu(III) is adsorbed on to the sorbent at pH > 3. The colloid can be partly (50–70 %) eluted from the column by 0.01 M $HNO_3$, and quantitatively with
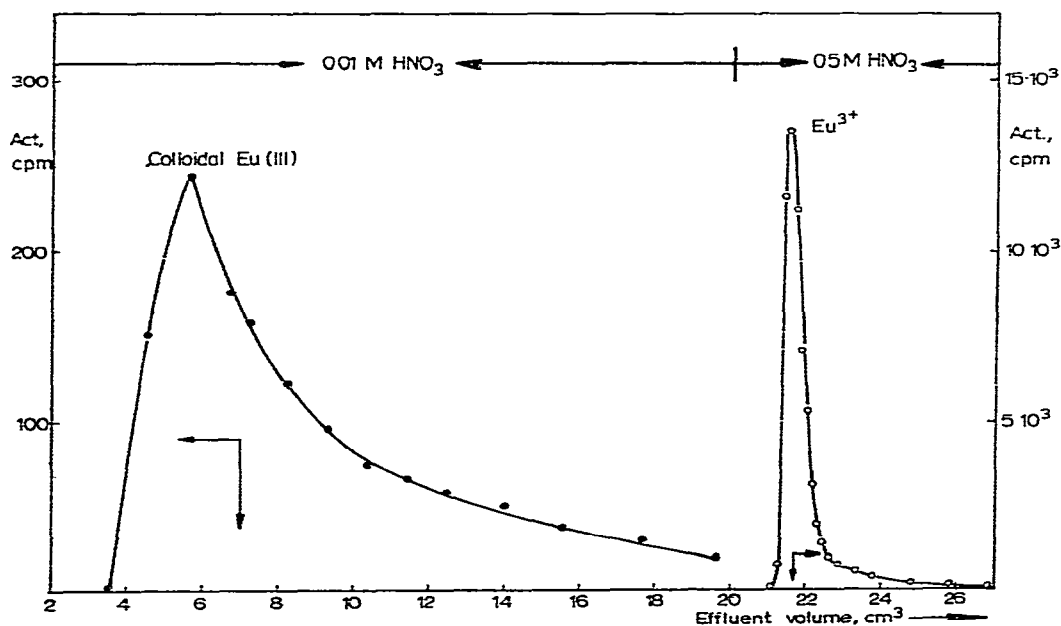


Fig. 6. The elution of colloidal Eu(III) with 0.01 M $HNO_3$ and $Eu^{3+}$ with 0.5 M $HNO_3$. Column, 8 cm × 0.2 $cm^2$; elution flow-rate 1 $cm^3$/$cm^2$ min.

0.5–1.0 $M$ HNO$_3$ (Table II). The results demonstrate good sorption and desorption properties of the sorbent for both the ionic and colloidal forms or europium.

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