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## ADSORPTION OF TRIVALENT IRON IN THE IONIC AND COLLOIDAL STATES ON SILICA GEL IMPREGNATED WITH MANGANESE DIOXIDE

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### SUMMARY

The sorption of trivalent iron in the ionic and colloidal states on silica gel impregnated with manganese dioxide from aqueous solution has been studied by batch equilibrations. Adsorption isotherms, for the given range of sorbent loading, can be expressed by the Langmuir adsorption equation.

The behaviour of  $\text{Fe}^{3+}$  and colloidal  $\text{Fe(III)}$  on the sorbent column has also been investigated. Conditions for the sorption of  $\text{Fe}^{3+}$  from nitric acid and colloidal  $\text{Fe(III)}$  from aqueous solution at different pH values are given.

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### INTRODUCTION

The adsorption of different ions on hydrated manganese dioxide has been studied by many workers<sup>1-5</sup>. A series of separations on a column of manganese dioxide have been performed successfully, such as the following: the separation of Ba and Ra (ref. 6);  $\text{UO}_2^{2+}$  and  $\text{PuO}_2^{2+}$  from Zr, Nb, Ru and Cs, which remained on the column after eluting uranium and plutonium<sup>7</sup>;  $^{51}\text{Cr}$  adsorption and  $^{60}\text{Co}$ - $^{59}\text{Fe}$  separation<sup>4</sup>; the separation of Tc from Mo for obtaining  $^{99m}\text{Tc}$  of high purity<sup>4</sup>; and the elimination of Ra from liquid wastes in the uranium industry<sup>8</sup>. Manganese dioxide in a mixture with hydrated  $\text{Fe}_2\text{O}_3$  is a very suitable scavenger for various radionuclides from aqueous solutions<sup>9</sup> and for  $^{60}\text{Co}$ ,  $^{65}\text{Zn}$  and  $^{106}\text{Ru}$  from sea water<sup>10</sup>.

Owing to its good adsorption properties, hydrated manganese dioxide could be suitable for larger scale adsorption, especially for the removal of various radionuclides from aqueous solutions. However, owing to difficulties in the preparation of manganese dioxide with a definite grain size and low stability of grains, *i.e.*, formation of smaller  $\text{MnO}_2$  particles during long equilibration times in batch experiments, it is less suitable for studying the adsorption of ions from aqueous solutions.

For this reason, manganese dioxide was prepared by precipitation on granular silica gel used as a carrier. The sorbent thus prepared has been used in investigations of the adsorption of trivalent iron in the ionic and colloidal states from aqueous solutions.

## EXPERIMENTAL

*Preparation of the sorbent*

Silica gel "for column chromatography", 0.2–0.5 mm (Merck, Darmstadt, G.F.R.) was used as a support. The silica gel was separated from powder by several decantations with water, treated with 1:1 hydrochloric acid, washed with distilled water and dried for 4 h at 110°. Impregnation was performed by pouring 150 ml of 0.23 *M* manganese sulphate solution over 100 g of dried silica gel in a beaker. The silica gel thus prepared was then dried at 60°. The sorbent, manganese dioxide on granular silica gel, was prepared by gradual addition of the above silica gel to 1200 ml of a solution of 0.019 *M* potassium permanganate in 1 *M* nitric acid with constant stirring. The sorbent was separated from supernatant liquid and from manganese dioxide powder by repeated decantation, and was then washed with 500 ml of 3 *M* nitric acid and with water until it was free from acid. After drying at 110° for about 3 h, the sorbent was treated with boiling 3 *M* nitric acid for 5 min, washed with distilled water and again dried at 110° for 3 h. The amount of manganese dioxide on the silica gel was 29.05 mg per gram of the sorbent or 29.97 mg per gram of silica.

The procedure described above for the preparation of manganese dioxide on granular silica gel as a carrier has been used earlier<sup>7</sup> for the preparation of manganese dioxide identified as  $\gamma$ -MnO<sub>2</sub>.

*Preparation of the solutions*

Experiments with Fe<sup>3+</sup> were carried out in nitric acid solution with practically carrier-free <sup>59</sup>Fe and with different concentrations of iron(III) nitrate labelled with <sup>59</sup>Fe. The original solution of <sup>59</sup>Fe in the chloride form (Radiochemical Centre, Amersham, Great Britain) was converted into the nitrate form by treating with 1 *M* nitric acid and by repeated evaporation under an infrared lamp.

Solutions of colloidal Fe(III), *i.e.*, iron(III) oxide sols, were prepared by hydrolysis of iron(III) acetate by boiling. Fe<sup>3+</sup> (20 ml of 0.38 *M* Fe<sup>3+</sup>) was precipitated as the hydroxide with ammonia solution from 0.5 *M* nitric acid solution. The iron(III) hydroxide was washed with water (to pH *ca.* 6) and dissolved in glacial acetic acid (10 mole of acid per mole of iron). Complete dissolution was achieved after 20 h. The solution was then diluted to about 600 ml (Fe < 1 mg/ml) with distilled water and boiled for 1–2 h. Colloid formation was indicated by a change in the colour of solutions from reddish to reddish brown. The colloidal solution was then evaporated on a water-bath almost to dryness, and the residue was dissolved in about 10 ml of distilled water. After several days, the colloidal solution of Fe(III) was centrifuged at 4200 *g* for 2 h. An intensely coloured solution was then separated from the isolated gel and stored in a hermetically sealed glass vessel. This colloidal solution of iron is clear in transmitted light and turbid in reflected light (showing the Tyndall effect). The final Fe(III) colloidal solution did not contain ionic iron and was stable for several months.

Solutions of colloidal Fe(III) used in batch and column experiments were prepared under the same conditions starting from Fe<sup>3+</sup> solutions (0.5 ml of 0.38 *M* Fe) labelled with <sup>59</sup>Fe.

Part of the colloidal solution was lyophilized. The solids, which were stored in a vacuum desiccator over phosphorus pentoxide, were analyzed together with the colloidal solutions for iron and acetate content.

### *Batch equilibration experiments*

Each time 100 mg of the sorbent was weighed into 6-ml glass test-tubes with stoppers and 2 ml of Fe solution in the ionic or colloidal state were added. The mixture was shaken for 24 h in a thermostat at a given temperature, then centrifuged and samples of 50–500  $\mu\text{l}$  were taken for measurement. The liquid phase of sample equilibrated at 50° and 70° was transferred into other test-tubes and then centrifuged.

To avoid sorption on glass, all laboratory glassware used for storing and handling the labelled iron solutions was rinsed with a 5% solution of dichlorodimethylsilane (BDH, Poole, Great Britain) in carbon tetrachloride, then dried and heated at 250° for 2.5 h to form a water-repellent silicone layer.

### *Column experiments*

The column used was 0.42 cm in diameter with a bed height of 15 cm, and was thermostated by means of a water-jacket. A given amount of iron in the ionic or colloidal state was transferred to the top of the column, pre-treated with the solution from which sorption was being investigated.  $\text{Fe}^{3+}$  was eluted at 25° and 60° using nitric acid of an appropriate concentration. Colloidal iron was eluted at 25° using water, dilute nitric acid and sodium nitrate solution of desired pH.

### *Analytical methods*

After dissolution and separation from silica, the content of manganese in the sorbent was determined by EDTA titration using pyrocatechol violet as indicator<sup>11</sup>. The density of the colloid was calculated from the weights of samples of colloidal solution and colloid-free solvent in a 10-ml pycnometer. After separation from iron, by precipitation and filtration of iron(III) hydroxide, acetate ion was determined by pH titration<sup>12</sup> and the iron content was determined by EDTA titration<sup>13</sup>. The colloidal iron was converted into the ionic state by treating the solution with concentrated hydrochloric acid. The lyophilized material was dissolved in concentrated hydrochloric acid. The charge sign of the colloidal trivalent iron was determined by electrophoretic measurements in the usual manner. The particle size of the colloid were determined by electron microscopy (JEOL JEM-7). The structure of the samples of the colloid was identified by X-ray diffraction (Simens-Kristalloflex 4 X-ray diffractometer with a Geiger-Müller counter and a recorder).

The activity of the  $^{59}\text{Fe}$  was measured on a Nuclear Chicago Geiger-Müller counter with a thin window (*ca.* 2 mg/cm<sup>2</sup>). The activity of the experimental solutions varied from about  $10^4$  to  $10^5$  counts·min<sup>-1</sup>·ml<sup>-1</sup>.

## RESULTS AND DISCUSSION

From the dependence of the distribution coefficients ( $K_d$ ) of  $\text{Fe}^{3+}$  ( $2.7 \cdot 10^{-7}$  M) on the nitric acid concentration (Fig. 1) it can be concluded that the sorption of  $\text{Fe}^{3+}$  depends strongly on the acidity of the aqueous solution, as would be expected for a real ion-exchange process. The  $K_d$  values are independent of the  $\text{Fe}^{3+}$  concentration (Henry's law) below  $7 \cdot 10^{-6}$  M.

The adsorption isotherms for  $\text{Fe}^{3+}$  (Fig. 2) were also determined. The results

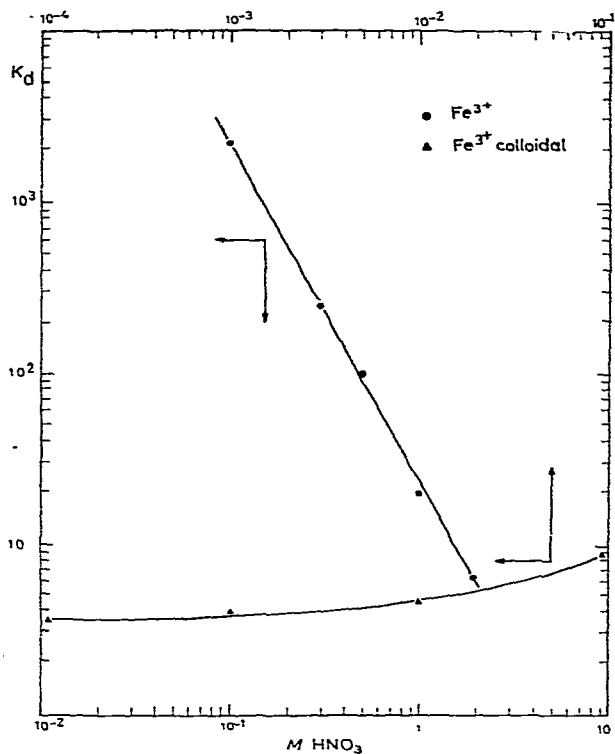


Fig. 1. Dependence of the distribution coefficients,  $K_d$ , of  $\text{Fe}^{3+}$  (trace amounts) and colloidal trivalent iron ( $3.5 \cdot 10^{-5}$  g Fe/ml) on the  $\text{HNO}_3$  concentration.

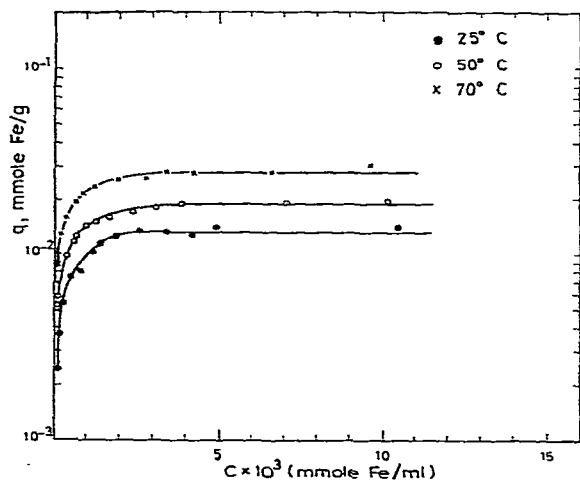


Fig. 2. Adsorption isotherms for  $\text{Fe}^{3+}$  at  $25 \pm 0.2^\circ$ ,  $50 \pm 0.5^\circ$  and  $70 \pm 0.5^\circ$ . Liquid phase:  $0.2 M \text{ HNO}_3$ .

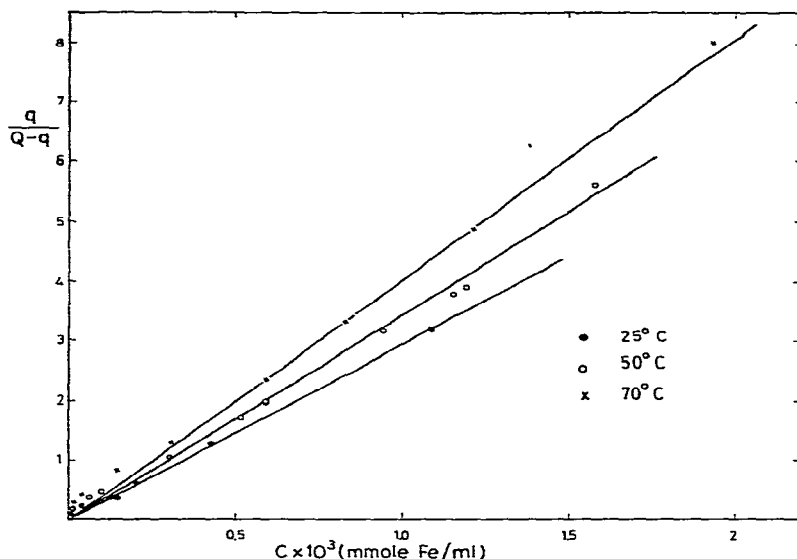


Fig. 3. Dependence of  $q/(Q-q)$  on the equilibrium concentration of  $\text{Fe}^{3+}$  in the liquid phase.

obtained, in the range 30–100% saturation, can be expressed by the Langmuir equation:

$$q = Q \cdot \frac{Kc}{1 + Kc} \quad (1)$$

where  $q$  (mmole/g) is the amount of the element adsorbed per gram of the adsorbent,  $Q$  is the same quantity at saturation,  $c$  (mmole/ml) is the equilibrium concentration of the element in the solution and  $K$  is the equilibrium constant.

The equilibrium constant ( $K$ ) is obtained from the slope of the curve  $q/(Q-q)$  versus  $c$  (Fig. 3).

The  $K$  and  $Q$  values obtained are given in Table I. The equilibrium constant and the adsorption capacity increase with increasing equilibration temperature. The capacity for  $\text{Na}^+$  is 18  $\mu\text{equiv./g}$  at pH ca. 6 and 25°.

It has been reported that isotherms for the adsorption of  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Sc}^{3+}$  on  $\rho\text{-MnO}_2$  fit the Langmuir adsorption equation<sup>4</sup>. Large differences in the adsorption capacities of these ions were explained by the assumption that the number of adsorbing sites varies for the different ions<sup>4</sup>. From the results for  $\text{Fe}^{3+}$  adsorption given in

TABLE I

COEFFICIENTS OF THE LANGMUIR ADSORPTION EQUATION FOR  $\text{Fe}^{3+}$  ADSORBED ON  $\text{SiO}_2\text{-MnO}_2$  FROM 0.2 M  $\text{HNO}_3$

Temperature (°C)	$Q$ ( $\mu\text{equiv./g}$ )	$K$
25	39.7	$3.0 \cdot 10^3$
50	57.1	$3.5 \cdot 10^3$
70	84.7	$4.0 \cdot 10^3$

this paper, it can be concluded that active sites on manganese dioxide, on a granular silica gel carrier, differ in their properties.

As iron belongs to the group of metals (aluminium, tin, iron) which, depending on the manner of preparation, may form colloids or polymers during hydrolysis<sup>14</sup>, it was necessary to characterize the iron solution that we obtained in this way.

The  $\text{CH}_3\text{COO}^-:\text{Fe}^{3+}$  molar ratios in colloidal solution and in solid material obtained by lyophilization are identical (0.32) and the composition of the lyophilized material is  $\text{FeO}_{1.5}\text{CH}_3\text{COO}_{0.32}$ . The specific gravity of the colloid (at 18–22°) varies from 4.6 to 5.2. X-ray analysis of samples prepared as a solid film by evaporation or by drying colloidal solutions at room temperature showed that our product is  $\alpha\text{-Fe}_2\text{O}_3$ . The structure of colloidal particles, as determined by X-ray analysis, should therefore be taken as strictly referring to gels. However, from the data given for the specific gravity of the colloid in solution and from the composition of the lyophilized product, it can be concluded that evaporation was not followed by significant changes, so that the product obtained is  $\text{Fe}_2\text{O}_3$ . However, the presence of some other species (amorphous hydroxide or hydrated oxides) in small amounts is not excluded. Colloidal particles are roughly spherical, 60–300 Å in diameter, *ca.* 50% of the particles being 120 Å in diameter and *ca.* 84% being 60–120 Å in diameter. The average molecular weight, calculated from the given data for particle size and specific gravity of  $\text{Fe}_2\text{O}_3$  (5.3), is  $3.3 \cdot 10^6$ . It was reported<sup>15</sup> that the iron sol obtained by hydrolysis of  $\text{Fe}^{3+}$  with hexamethylenetetramine at 100° is a hydrated oxide (structure rhombohedral, particle size *ca.* 250 Å).

The polymeric hydrolysis products of iron were isolated by gel filtration on a Sephadex G-25<sup>16–18</sup>. It is interesting that our colloidal solution of iron on a Sephadex G-25 column behaves in a similar manner to the polymer. About 93% of colloidal Fe(III) was excluded by the gel.

Adsorption of the colloidal trivalent iron on the sorbent increases very slowly on increasing the nitric acid concentration from  $10^{-4}$  to  $10^{-1}$  M (Fig. 1). The dependence of the sorption of colloidal trivalent iron on pH is characterized by a sorption maximum in the region of weakly acidic to neutral solutions. The sorption decreases in weakly basic solutions and at pH 9.5 it is negligible (Fig. 4). A similar dependence of the sorption of radionuclides (at extremely low concentrations, below  $10^{-6}$  M) on pH was reported earlier<sup>19</sup>.

The colloidal particles of trivalent iron are positively charged in weakly acidic and negatively charged in weakly basic solutions, as has been determined by electrophoretic measurements. The surface charge of inorganic sorbents (of the type of hydrated oxides) also depends on the pH and concentration of the electrolytes<sup>19,20</sup>. In alkaline solution, the sorbent surface acquires a negative charge or changes to more negative values. Therefore, the results obtained support the assumption that the sorption of colloidal particles proceeds via a physical mechanism.

The increase in sorption on increasing the inert electrolyte concentration (Table II) can be explained by the electrolyte coagulation effect<sup>19</sup>.

The adsorption isotherm for colloidal trivalent iron, determined in weakly acidic solution at pH 2.90 (Fig. 5), fits the Langmuir adsorption equation in the range 50–100% saturation. The adsorption capacity for colloidal trivalent iron is  $5.8 \cdot 10^{-3}$  mmole of Fe per gram of sorbent.

The results obtained in the column runs are given in Tables III and IV.

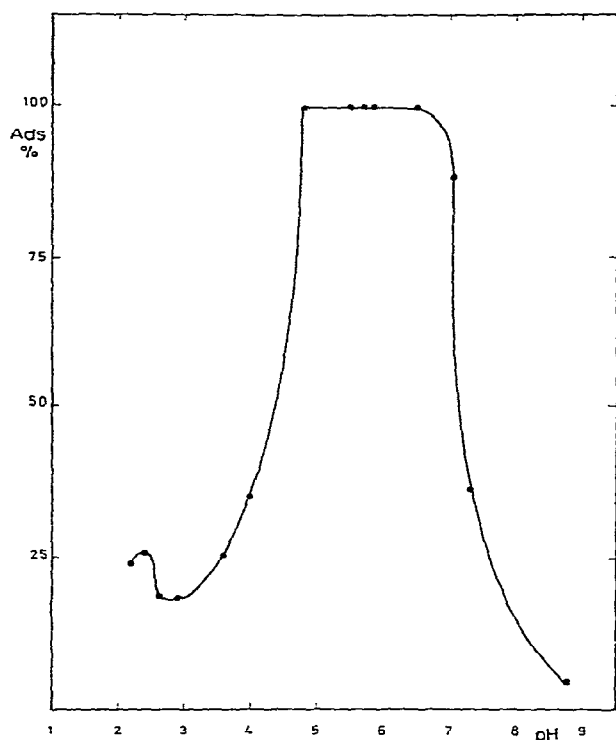


Fig. 4. Dependence of the sorption of colloidal trivalent iron ( $3.5 \cdot 10^{-5}$  g Fe/ml) on pH. Solution ionic strength  $\mu = 0.01$  ( $\text{NO}_3^-$ ).

From the sorption and desorption behaviour of  $\text{Fe}^{3+}$  one can conclude that  $\text{Fe}^{3+}$  is adsorbed on the sorbent at very low acidity at room temperature. At higher temperatures,  $\text{Fe}^{3+}$  is quantitatively sorbed at higher nitric acid concentrations. It is difficult to desorb  $\text{Fe}^{3+}$  from the column, especially when desorption follows adsorption after a longer period ( $> 24$  h). This behaviour indicates that, in addition to the ion-exchange process, some other kind of retention may also occur. It was reported that hydrolysed iron ions sorbed on organic cationic (weakly acidic) exchangers from dilute acid solutions ( $\text{pH} > 1$ ) form complexes with functional (carboxylic) groups of the exchanger<sup>21</sup>. Modification of  $\text{FeOOH}$  occurs in the exchanger phase as a result of ageing, which causes a low solubility of the complex<sup>21</sup>. From the sorption-desorption behaviour of  $\text{Fe}^{3+}$  in our sorbent we consider that complexes of hydrolysed iron ions with functional OH groups of the sorbent are formed in a similar manner.

TABLE II

DEPENDENCE OF THE PERCENTAGE OF COLLOIDAL TRIVALENT IRON SORPTION ON  $\text{NaNO}_3$  CONCENTRATION

Colloidal  $\text{Fe(III)}$ :  $11.4 \cdot 10^{-6}$  g Fe/ml; 0.01 M  $\text{HNO}_3$ .

$\text{NaNO}_3$ (mole/l)	0.005	0.01	0.02	0.04
Sorption (%)	44.3	48.3	54.5	61.1

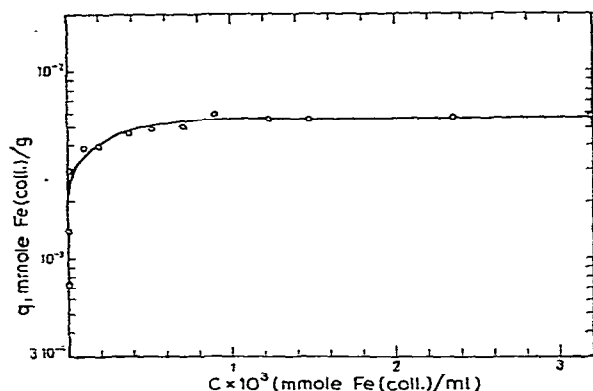


Fig. 5. Adsorption isotherm for colloidal trivalent iron at  $25 \pm 0.2^\circ$ . Liquid phase:  $0.01 M \text{NaNO}_3$ , pH 2.90.

The results obtained for the colloid on the column are not in agreement with those obtained by batch equilibration. On the column the colloid was adsorbed from weakly basic solutions, which was not the case in batch experiments. No satisfactory explanation for this phenomenon has been given so far. However, the results demonstrate good sorption properties of the sorbent for both the ionic and colloidal forms of iron.

TABLE III

ADSORPTION OF  $\text{Fe}^{3+}$  ON  $\text{SiO}_2\text{-MnO}_2$  COLUMN

Column,  $15 \text{ cm} \times 0.14 \text{ cm}^2$ ; elution flow-rate,  $1 \text{ ml/cm}^2 \cdot \text{min}$ .

$\text{Fe}^{3+}$ sorbed from $\text{HNO}_3$ (M)	Temperature ( $^\circ\text{C}$ )	Percent of $\text{Fe}^{3+}$ eluted in fractions			
		$0.01 M \text{HNO}_3$ (20 ml)	$0.1 M \text{HNO}_3$ (20 ml)	$0.5 M \text{HNO}_3$ (20 ml)	$4 M \text{HNO}_3$ (20 ml)
0.01	25	—*	—	42.7	32.0
0.10	25	—	53.7	21.8	15.9
0.10	60	—	—	—	99.8
0.10	60	—	—	41.2	48.7

\* — = not eluted.

TABLE IV

ADSORPTION OF COLLOIDAL TRIVALENT IRON ON  $\text{SiO}_2\text{-MnO}_2$  COLUMN

Column,  $15 \text{ cm} \times 0.14 \text{ cm}^2$ ; elution flow-rate,  $1 \text{ ml/cm}^2 \cdot \text{min}$ ; temperature,  $25^\circ$ .

Colloidal $\text{Fe(III)}$ sorbed from solutions	Sorbent in the form	Percent of colloidal $\text{Fe(III)}$ eluted in fractions				
		Water dist. (20 ml)	$0.01 M \text{NaNO}_3$ pH 9.8	$0.01 M \text{HNO}_3$ (10 ml)	$0.1 M \text{HNO}_3$ (10 ml)	$4 M \text{HNO}_3$ (20 ml)
Water dist.	$\text{Na}^+$	—*	—	—	—	21.0
$0.01 M \text{NaNO}_3$ (pH 9.8)	$\text{Na}^+$	—	—	—	—	76.0
$0.01 M \text{HNO}_3$	$\text{H}^+$	—	—	77.3	1.5	9.1

\* — = not eluted.



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