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Studies on the Selective Adsorption of Anion by Metal-Ion Loaded Ion-Exchange Resin. V. Adsorption of Phosphate Ion on Ion-Exchange Resin Loaded with Zirconium(IV), IRC 50-Zr(IV)

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Abstract

The adsorption behavior of phosphate ion from aqueous solution on a zirconium-loaded cation exchange resin (Amberlite IRC 50) was investigated by batch and column operations. The adsorption capacity increased with increasing concentration of zirconium loaded on the resin, and with increasing temperature up to 45°C. The optimum pH range for phosphate adsorption was 2 to 4. Two parameters (K and $1/n$) in Freundrich's equation $Q = KC^{1/n}$, (where Q and C represent phosphate ion concentrations on adsorbent and aqueous phase, respectively) were determined by analyzing the adsorption behavior in the column experiment. These are $K = 6.5$ mg-P/g and $1/n = 0.15$. Phosphate ion adsorbed on the resin can be eluted readily by treating with 1 *M* sodium hydroxide, and the resin can be regenerated for the next adsorption cycle by treating the desorbed resin with 0.1 *M* hydrochloric acid. The adsorption capacity remained almost unchanged during five adsorption-desorption regeneration cycles.

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Phosphorous, in its form of phosphate ion, has been known to be one of the elements which are responsible for the eutrophication of environmental water. Various approaches have been reported to remove phosphate from the wastewater of sewage treatment plants and industrial plants. Phosphate ion can be precipitated as coagulated sedimentations by treating with lime, magnesium salt, or ferric salt. However, the sedimentation process needs a large plant area and suffers from solid waste disposal. Another approach is the use of the column adsorption process in which phosphate-selective adsorbents are employed. While various adsorbents such as activated alumina (*1*), soil (*2, 3*), and gelatinous particles (*4–6*) have been proposed, few are of practical value with respect to their selectivity and recycling capabilities.

We have been investigating the adsorption behavior of anions to a cation-exchange resin which is loaded with a specific metal ion. In previous papers we reported the selective adsorption of phosphate ion on iron(III)-loaded cation-exchange resins (*7, 8*). While these adsorbents are highly selective for phosphate ion and have a high adsorption capacity, the adsorption capacity decreased gradually after repeated adsorption–desorption cycles.

This paper reports on an improved type of phosphate adsorbent in which zirconium(IV) is loaded on a weakly acidic cation-exchange resin (Amberlite IRC-50). The new adsorbent is not only highly selective for phosphate, but also the adsorption capacity remains almost unchanged during the recycling process. The result of an investigation on the adsorption isotherm indicated that the adsorption activity is higher with the zirconium-loaded resin than with the iron(III)-loaded resin.

EXPERIMENTAL

Materials

Preparation of Adsorbent

About 40 g of Amberlite IRC 50 (30–50 mesh) was washed three times with 100 mL portions of 2 *M* hydrochloric acid and 2 *M* sodium hydroxide, alternatively, and finally equilibrated with 2 *M* sodium hydroxide. After the resin was filtered under suction, it was mixed with 150 mL of an aqueous solution containing 25.8 g of zirconium(IV) oxychloride octahydrate. During the mixing, the pH of the solution was kept at 3 by the occasional addition of 3 *M* hydrochloric acid. After standing for 24 h, the zirconium loaded resin was collected by suction filtration, then centrifuged for use in an adsorption study. The adsorbent thus prepared contained 1.20 mmol of zirconium per gram of dry adsorbent. Other batches of adsorbent with lower zirconium contents (0.403 and 0.125 mmol Zr/g) were prepared in similar fashion by using smaller amounts of zirconium.

Determination of Zirconium Content in Adsorbent

An exactly weighed amount (0.5 g) of adsorbent was mixed with 20 mL of 4 *M* hydrochloric acid. After standing for 10 h, the aqueous phase was transferred into a 50-mL volumetric flask. Another 10 mL portion of 4 *M* hydrochloric acid was added to the adsorbent and the mixture was allowed to stand for 8 h. The aqueous phase was again transferred to the volumetric flask. This treatment was repeated once more and the combined acid eluate in the volumetric flask was diluted to volume. By this procedure the recovery of zirconium was found to be quantitative, because even an trace of zirconium could not be detected in the wet-acid decomposition product of residual resin after acid treatment. Zirconium concentration in the acid eluant was determined by absorption photometry using xylenol orange (*9*).

The water content of the adsorbent was determined on a separate sample from the same batch of adsorbent, according to the procedure previously reported (*8*). The zirconium content of the adsorbent was expressed as $C_Z(r)$ (mmol of Zr/g of dry adsorbent).

Procedure for Adsorption Study

Determination of Distribution Ratio between Adsorbent and Aqueous Phase

The distribution ratio was determined by batchwise operation using the adsorbents of three different zirconium content in a pH range of 1 to 13. To 0.5 g of adsorbent, 10 mL of 0.5 *M* sodium chloride and 3 mL of sodium dihydrogen phosphate solution (1000 ppm as P) were added and the pH of the solution was adjusted to the desired value by adding a predetermined amount of 0.1 *M* hydrochloric acid or 0.5 *M* sodium hydroxide, then the mixture was diluted to 50 mL. The mixture was incubated at 35°C for 48 h in a water bath with occasional shaking. Finally, phosphate concentrations were determined on the aqueous phase (C_P mg/mL) and on the adsorbent ($C_P(r)$ mg/g). The distribution ratio is expressed as D (mL/g) = $C_P(r)/C_P$, and the pH dependencies of log D are illustrated in Fig. 1.

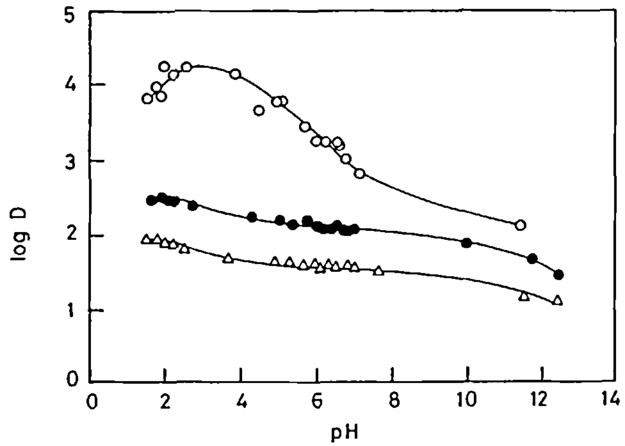

FIG. 1. pH profiles of distribution ratio, D, of phosphate ion by zirconium loaded resins, IRC 50-Zr(IV), at 35°C. $\mu = 0.10$ with NaCl. $C_Z(r) = 1.20$ mmol/g (○), 0.403 mmol/g (●), and 0.125 mmol/g (△).

The phosphate ion concentration in the aqueous phase was determined by the standard molybdenum blue method (*10*). That in the adsorbent was determined similarly after eluting phosphate by treating the adsorbent with 13 mL of 2 *M* sodium hydroxide for 10 h for three times.

Temperature dependencies of the distribution ratio were investigated in a similar procedure by carrying out the experiment using an adsorbent of $C_Z(r) = 1.20$ at pH 4.6 (0.1 *M* acetate buffer) and different temperatures from 5 to 45°C. The result is illustrated in Fig. 2.

Column Operation

A weighed amount of adsorbent [3.8 g of $C_Z(r) = 1.06$ mmol/g] was packed in a glass column of 0.55 cm i.d. and 30 cm in length. This made a bed volume of 5 mL and a column hight of 20.8 cm. The sample solution containing phosphate was passed through the column downward at flow rates of 10 to 20 mL/h, the pH of the solution being adjusted to 2.0 with sodium hydroxide–sulfuric acid. The effluent was collected in 10 mL fractions, and phosphate ion concentration was determined in each fraction. The breakthrough curves are illustrated in Fig. 3.

Phosphate ion adsorbed on the column was recovered by eluting it with 40 mL of 1 *M* sodium hydroxide solution at a flow rate of 12 mL/h.

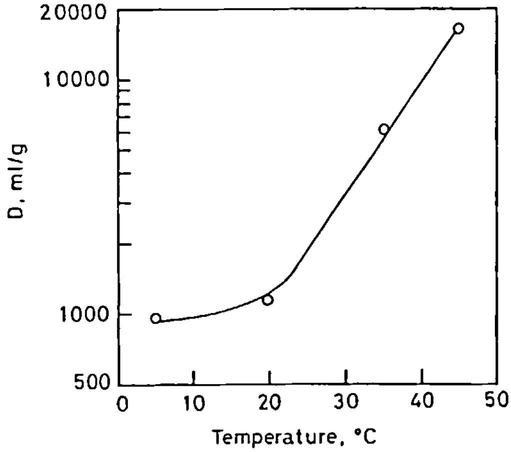

FIG. 2. Temperature effect on the distribution ratio, D, of phosphate ion. $\mu = 0.20$ with NaCl and CH_3COONa. Adsorbent: $C_Z(r) = 1.20$ mmol/g. pH: 4.6 with 0.1 M CH_3COOH-CH_3COONa.

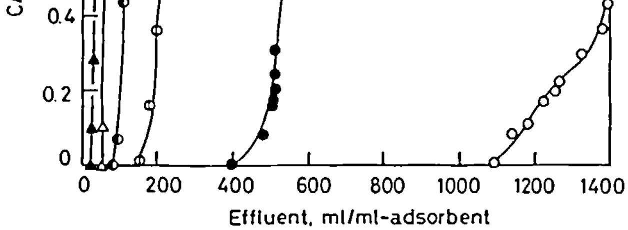

FIG. 3. Breakthrough curves for the adsorption of phosphate ion on a column of zirconium-loaded resin. Adsorbent: $C_Z(r) = 1.06$ mmol/g. Column: 5.0 mL in volume, 20.8 cm in height. Flow rate: 10 to 20 mL/h. pH of influent solution: 2.0 with 0.1 M H_2SO_4-Na_2SO_4. Temperature: 20°C. ppm as P: (▲) 250, (△) 100, (◐) 50, (⦶) 30, (●) 10, and (○) 3.

For the recycling use of the column for the adsorption of phosphate ion, the column was regenerated for the next adsorption cycle by treating with 100 mL of 0.1 *M* hydrochloric acid at flow rates of 10 to 20 mL/h.

Instruments

A Toa model HM-10B was used for pH measurements. Adsorption photometries for phosphate and zirconium were carried out with a Shimadzu model 140 spectrophotometer.

RESULTS AND DISCUSSION

Distribution Ratio of Phosphate Ion between Water and Adsorbents

It is seen from Fig. 1 that the distribution ratio increases with an increase of zirconium content in the adsorbent, suggesting that resin-bound zirconium is the site for the adsorption of phosphate ion as in the case of phosphate ion adsorption on the iron(III)-loaded chelating resin (*7*).

Figure 1 also shows that the value of the distribution ratio is larger in the acidic range than in neutral or alkaline range. The maximum value is observed near pH 3–4 on the adsorbent of highest zirconium concentration. While phosphate ion is expected to be adsorbed more favorably from the solution of higher pH, this result indicates that the competitive adsorption of hydroxide ion prevails in the weakly acidic range and is more pronounced in the neutral and alkaline ranges. The result can be understood if one remembers the remarkable high value of the hydrolysis constant of zirconium [$Zr^{4+} + OH^- \rightleftharpoons Zr(OH)^{3+}$, $\log K = 13.8$] (*11*). The appearance of a maximum on the pH profile of the distribution ratio may result from the offset of both effects. For the adsorbents of lower zirconium load, the proton dissociation of free carboxyl groups of the cation-exchange resin at higher pH regions also prevents the adsorption of phosphate, resulting in a pH profile which is slightly different from that of the adsorbent with a higher zirconium load.

The temperature dependence of the distribution ratio is illustrated in Fig. 2, which indicates that the adsorption of phosphate ion is an endothermic reaction and the higher temperature is favorable for adsorption within the temperature range investigated in this study.

Adsorption of Phosphate in Column Operation

Breakthrough curves for phosphate adsorption in column operation are illustrated in Fig. 3. As expected, the breakthrough point shifted to the higher elution volume with a decrease of phosphate ion concentration in the influent.

The amount of phosphate ion adsorbed on the column, Q_C, can be approximately given by

$$Q_C = C_0 \times V_{BP} \tag{1}$$

where C_0 is the phosphate ion concentration in the influent and V_{BP} is the volume of effluent passed through the column until the breakthrough point is reached. If we combine this relationship with the well-known Freundlich's equation, $Q = KC^{1/n}$, the following equation can be derived:

$$(C_0 \times V_{BP})/w = KC_0^{1/n} \tag{2}$$

where K and n are constants and w is the weight of adsorbent packed in the column on a dry basis. By rearranging Eq. (2), we obtain

$$\log V_{BP} = \log(wK) + \frac{1-n}{n} \log C_0 \tag{3}$$

A plot of log V_{BP} against log C_0 should give a straight line whose slop and intercept are $(1 - n)/n$ and log (wK), respectively. As illustrated in Fig. 4, the experimental results are in good agreement with theoretical treatment. The constants $1/n$ and K were evaluated as 0.15 and 6.5 mg P/g of adsorbent, respectively. These values indicate that the zirconium-loaded Amberlite IRC 50 is superior as an adsorbent for phosphate ion to the various kinds of iron(III)-loaded ion-exchange resins.

Recovery of Phosphate Ion

Phosphate ion on the adsorbent can readily be desorbed by treating the column with 40 mL of 1 *M* sodium hydroxide solution at a flow rate of 12 mL/h. As summarized in Table 1, the recovery of phosphate ion ranged from 82 to 93%, with an average of 89.0 ± 4.2%. The lower the phosphate ion concentration in the influent, the lower is the recovery of phosphate. In the

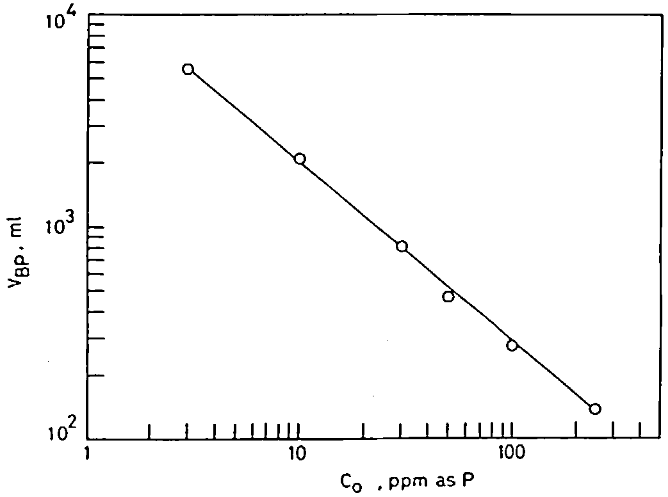

FIG. 4. Relationship between V_{BP} and initial phosphate ion concentration C_0. Adsorbent: $C_Z(r)$ = 1.06 mmol/g. Column: 5.0 mL in volume, 20.8 cm in height. Flow rate: 10 to 20 mL/h. Temperature: 20°C. pH: 2.0 with 0.1 *M* H_2SO_4-Na_2SO_4.

case of an influent which contained such diverse anions as chloride, cyanide, and fluoride, the recovery was also slightly lower.

However, these levels of recovery may be of practical value for using this adsorbent as a means of selective preconcentration for the determination of trace phosphate in environmental waters. Such examples are also shown in Table 1. A river water and a lake water from our urban area were analyzed for phosphate after preconcentration on this adsorbent.

Regeneration and Repeated Use of the Column

The adsorbent after the desorption of phosphate by treating with aqueous sodium hydroxide is not ready to be used for the next adsorption cycle, but has to be regenerated by treating with 100 mL of 0.1 *M* hydrochloric acid at flow rates of 10 to 20 mL/h. The regeneration process is necessary to replace hydroxide ions on the resin-bound zirconium with aquo ions for the subsequent adsorption of phosphate ion.

Five repeated cycles were carried out by passing 1000 mL of sample solution containing 10 ppm of phosphate which is 0.1 *M* in sulfuric acid and is adjusted to pH 2 with sodium hydroxide at flow rates of 10 to 20 mL/h.

TABLE 1

Adsorption and Recovery of Phosphate Ion by IRC 50-Zr(IV) [$C_Z(r) = 1.06$ mmol/g] Column at Room Temperature[a]

No.	C_0 (ppm)	Influent[b] volume passed (mL)	Phosphate ion recovered[c] (μg as P)	Percent recovery or original concentration (ppm as P)
1	0.01	2000	16.5	82.5%
2	0.05	2000	89.0	89.0%
3	0.10	1000	94.3	94.3%
4[d]	1.00	1000	901.8	90.2%
5[e]		500	40.0	0.090 ppm
6[f]		500	57.7	0.13 ppm

[a] Column: 5.0 mL in volume and 20.8 cm in height, about 20°C.

[b] pH 2.0 with 0.1 *M* H_2SO_4-Na_2SO_4, Flow rate = 10–20 mL/h.

[c] Eluent: 40 mL of 1 *M* NaOH, Flow rate = 12 mL/h.

[d] Influent contained 1000 ppm CH_3COOH, 1000 ppm Cl^-, 100 ppm CN^-, and 10 ppm F^- in addition to phosphate.

[e] Iseri river in Kumamoto-shi, acidified to pH 2.0 with 0.1 *M* H_2SO_4-Na_2SO_4.

[f] Lake Ezu in Kumamoto-shi, acidified to pH 2.0 with 0.1 *M* H_2SO_4-Na_2SO_4.

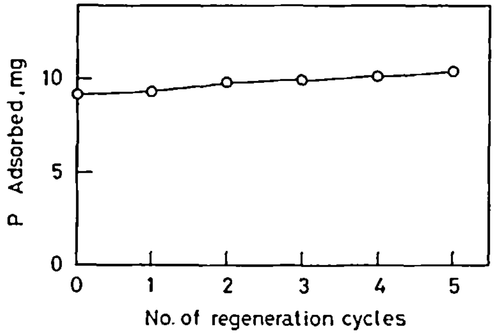

FIG. 5. Change in adsorption capacity after repeated use of column. Adsorbent: $C_Z(r) = 1.06$ mmol/g. Column: 5.0 mL in volume, 20.8 cm in height. Influent solution: pH 2.0 with 0.1 *M* H_2SO_4-Na_2SO_4 and 10 ppm as P. Volume passed and flow rate: 1000 mL at 10 to 20 mL/h. Eluate solution: 40 mL of 1 *M* NaOH.

After each adsorption cycle the column was washed with water, then eluted and regenerated as described in the experimental part.

The result, as summarized in Fig. 5, indicates that the adsorption capacity of the column did not decrease after repeated adsorption–desorption cycles, but increased slightly. No leaking of zirconium was observed during the cycles. The reason for the slight increase in the adsorption capacity after repeated use is not clear, but may be partly attributed to the gradual elution of phosphate which remained on the adsorbent in the earlier desorption cycle.

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