

Phosphate Adsorption on Zirconium-Loaded Activated Carbon, and its Application for Phosphate Recovery from Deep Seawater

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Abstract—The adsorption of phosphate onto zirconium-loaded activated carbon (Zr-AC) was studied, and phosphate was recovered from deep seawater using the Zr-AC. The Zr-AC complex was prepared by mixing activated carbon with a zirconyl nitrate solution. The amount of phosphate that adsorbed onto the Zr-AC depended on the pH of the solution. Phosphate was adsorbed quantitatively at below pH 8.0, and the amount adsorbed decreased as the pH increased. Zr-AC was found to adsorb phosphate from seawater almost as efficiently as from an aqueous solution made with distilled water. The equilibrium adsorption capacity of the Zr-AC for phosphate in seawater was measured and extrapolated using the Langmuir and Freundlich isotherm models. The Langmuir model fitted the experimental data better than did the Freundlich model, and the calculated maximum adsorption capacity for phosphate was 0.64 mmol/g. Phosphate was recovered from deep seawater using a chromatographic selective recovery process using a packed-bed column. The results showed that phosphate was selectively adsorbed in the adsorption step, and the phosphate could be recovered and concentrated into a NaOH solution in the desorption step. The adsorbent in the column was able to be repeatedly used to recover phosphate from seawater.

Index Terms—Column test, deep seawater, phosphate recovery, Zirconium-loaded activated carbon.

I. INTRODUCTION

Phosphorus plays key roles in sustaining the production of food, animal feed, and biofuels and is used in industrial applications. Phosphorus is generally applied to agricultural soils in fertilizers that are produced from phosphate rocks. However, global supplies of phosphate rocks are limited [1]–[3]. Currently, 178.5 Mt of phosphate rock, equivalent to 23 Mt of phosphorus, is mined every year, and 90 % of the rock is used in the production of food (approximately 82 % is used as fertilizer and approximately 7 % is used in animal feed additives) [4]. Increased demand for food and animal feed mean that phosphate rock is expected to become increasingly scarce and expensive in future [1]. Phosphate rock deposits are very unequally distributed, and only three countries (China, Morocco, and the United States) control more than 85 % of deposits [5]. The control of phosphate rock deposits may cause severe geopolitical problems by affecting the availability of phosphorus fertilizers and regional food

production and food security [6]. It is important to develop new techniques and economic opportunities for recovering phosphorus to ensure the long-term sustainability of food production.

Efficiently using phosphorus fertilizers in agriculture and recovering and recycling phosphorus in wastewater, natural water, and waste materials will be key to increasing the time global phosphorus reserves will last. Releases of phosphorus to groundwater and surface water have already caused serious eutrophication problems around the world, and these problems negatively affect the abilities of many aquatic species to survive and decrease the safety of drinking water supplies [7], [8]. It has been found that phosphorus concentrations higher than 0.02 mg/L in lake water can generally accelerate eutrophication [9], [10]. Treatments to remove phosphorus from water have therefore been studied extensively [11]–[13]. A wide range of methods for treating phosphorus pollution, involving adsorption, chemical precipitation, biological processes, electro dialysis, ion exchange, and reverse osmosis, have been developed and applied [14]–[17]. Methods involving adsorption are promising because they are simple, effective, easily used in practice, appropriate for low phosphorus concentrations, and can allow the phosphorus that is removed to be recovered [8].

Adsorbents have been developed for removing phosphate, and they have been used in practical applications. The sorption of phosphate has been investigated in many studies using many sorbents, but very few studies of the influences of major electrolytes present in natural fresh water on the uptake of phosphate by sorbents have been performed [18]–[20]. Similarly, only a few studies have been performed on the influences of electrolytes in seawater on the uptake of phosphate by sorbents such as goethite [21], [22], manganese dioxide [23], aluminum oxide hydroxide [24], layered double hydroxide [25], La(III)-Chelex resin [26], and aluminum [27]. Hydrated zirconium oxide has been found to be remarkably selective for phosphoric ions [28] and to be very resistant to acids, alkalis, oxidants, and reductants [29]. In previous studies [18], [30], [31], it has been found that zirconium oxide has a high adsorption capacity for phosphorus and can be used to remove phosphorus from water. However, pure zirconium oxide is relatively expensive, so using it to remove phosphorus from water is not cost-effective. Zirconium-loaded materials with high phosphate affinities have therefore been prepared. Such materials are prepared by loading zirconium onto materials such as activated carbon (AC) [32], resin [33], wheat straw [34], orange waste gel [35], [36], and okara [37], [38].

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In this study, zirconium-loaded AC (Zr-AC) was prepared with the aim of using it to recover phosphate from deep seawater. Zr-AC was prepared because AC is a popular material for loading with metals. Deep seawater (at depths of between about 500 m and 1000 m) circulates around the world. Deep seawater is clean and rich in mineral components, especially nutrients such as nitrate, phosphate, and silicate, compared with surface seawater. Attempts to use deep seawater in many ways have been made [39]. Japan is surrounded by seas and the ocean, and developing ocean resources could bring benefits to Japan. However, to the best of our knowledge, the recovery of phosphate in deep seawater using Zr-AC has not previously been studied. An original study of the effectiveness of Zr-AC at selectively recovering phosphate from deep seawater is described here.

II. EXPERIMENTAL

A. Preparation of Zr-AC

The Zr-AC complex was prepared by adding AC to a zirconyl nitrate solution (with a zirconium concentration of 20 g/L). Two types of commercial AC, powdered AC (Wako Pure Chemical Industries, Osaka, Japan) and granular AC with a granule diameter of 0.5 mm (Kureha, Tokyo, Japan), were used. AC (10 g) was purified by adding it to 3 M aqueous hydrochloric acid and stirring the mixture at 25 °C for 1 d. The mixture was then filtered, and the AC was added to a zirconyl nitrate solution. The mixture was stirred for 3 d, washed with distilled water, then dried in a drying oven for 2 d. The crystalline phases of the Zr-AC were analyzed by X-ray diffractometry using a Mini-flex 600 instrument (Rigaku, Tokyo, Japan).

B. Phosphate Adsorption Properties of the Zr-AC

The phosphate adsorption properties of Zr-AC were investigated by performing tests using powdered Zr-AC.

The adsorption of phosphate by Zr-AC was investigated at different pH values. A series of 1 mM NaH₂PO₄ solutions were prepared at pH values between pH 3 and pH 12 (the initial pH was adjusted by adding HCl or NaOH). A 0.1 g aliquot of the Zr-AC sample was added to a 20 mL aliquot of a phosphate solution in a centrifuge tube (50 mL) at room temperature, and the tube was shaken for 12 h using a reciprocal shaker. The mixture was then centrifuged, and the aqueous phase was separated from the solid phase. The pH of the supernatant was measured using a pH meter (a LAQUA F-72 pH/ion meter; Horiba, Kyoto, Japan). The phosphate concentration in the supernatant was determined using the molybdenum blue method. The amount of phosphate that had been adsorbed, q (mmol/g), was calculated using the equation

$$q = (C_0 - C) \cdot V / w, \quad (1)$$

where C_0 and C are the concentrations (mmol/L) of phosphate ions in the initial solution and sampling solution, respectively, V is the volume (L) of the solution, and w is the mass (g) of Zr-AC added.

The adsorption capacities of Zr-AC at different initial phosphate concentrations and salinities were determined. Solutions containing NaH₂PO₄ at between 1 and 20 mM, in

distilled water or seawater were tested. Seawater was collected from the surface water layer in Imari Bay, Saga Prefecture, Japan. The chemical composition and the pH of the seawater are shown in Table I. A 0.1 g aliquot of Zr-AC was added to 20 mL of a test solution in a centrifuge tube (50 mL) at room temperature, and the tube was shaken for 12 h using a reciprocal shaker. The mixture was then centrifuged, and the aqueous phase was separated from the solid phase, then the pH of the supernatant was measured using a pH meter. The phosphate concentration in the supernatant was determined using the molybdenum blue method. The amount of phosphate that was adsorbed, q (mmol/g), was then calculated.

C. Column Test Using Deep Seawater

Chromatographic experiments were performed using deep seawater, using Zr-AC packed in a column as shown in Fig. 1. The deep seawater was purchased from Koshiki Deep Ocean Water Co. (Kagoshima, Japan). The chemical composition and pH of the deep seawater are shown in Table I. The deep seawater contained 0.0015 mmol/L phosphate, and the other elements were found at almost the same concentrations in the deep seawater as in the seawater. Granular Zr-AC (0.2 g) was packed into a column to a depth of 3 cm (the volume of the wet product was 0.07 cm³) sandwiched between layers of quartz wool. Distilled water was passed through the column to prepare it for use. Deep seawater was then passed upward through the column at a flow rate of 5.0 mL/min. The deep seawater was supplied to the column using a ceramic pump. The effluent was collected using a fraction collector, and the phosphate concentration in each fraction was determined using the molybdenum blue method.

The desorption of phosphate from Zr-AC that had been loaded with phosphate in an adsorption test using deep seawater was studied. The seawater in the loaded Zr-AC in the column was washed out by passing distilled water through the column. The phosphate was then desorbed by passing 2.5 mol/L NaOH_(aq) upward through the column at a flow rate of 5.0 mL/min. The NaOH solution was supplied to the column using a ceramic pump. The effluent was collected using a fraction collector, and the phosphate concentration in each fraction was determined using the molybdenum blue method.

The bed volume of the column, BV , was calculated using the equation

$$BV = v \cdot t / V, \quad (2)$$

where v is the flow rate of the solution (mL/min), t is the time the feed solution was supplied (min), and V is the volume of the wet product (mL).

TABLE I: CHEMICAL COMPOSITION AND PH OF THE SEAWATER (SW) AND DEEP SEAWATER (DSW)

	Chemical and concentration (mmol/L)						pH	
	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻		P
SW	468	9	52	9	472	26	N.D.	7.4
DSW	491	10	57	8	462	29	0.0015	8.0

N.D.: Not detected

D. Regeneration and Reuse of the Adsorbent

A regeneration experiment was performed using a column

packed with granular Zr-AC, using a 1 mM NaH_2PO_4 solution in seawater. Granular Zr-AC (0.5 g) was packed into a column to a depth of 5 cm (the volume of the wet product was 0.22 cm^3) sandwiched between layers of quartz wool. Distilled water was passed through the column to prepare it for use. The seawater containing 1 mmol/L NaH_2PO_4 was then passed upward through the column at a flow rate of 5.0 mL/min. The seawater was supplied to the column using a ceramic pump. The effluent was collected using a fraction collector, and the phosphate concentration in each fraction was determined using the molybdenum blue method. After equilibrium had been achieved, the seawater in the column was washed out by passing distilled water through the column. The phosphate was then desorbed by passing 0.1 mmol/L $\text{NaOH}_{(\text{aq})}$ upward through the column at a flow rate of 2.0 mL/min. The NaOH solution was supplied to the column using a ceramic pump. The effluent was collected using a fraction collector, and the phosphate concentration in each fraction was determined using the molybdenum blue method. After the phosphate had been desorbed, the column was washed by pumping distilled water through the column for 30 min until the effluent had a neutral pH. The regenerated bed was used in another sorption cycle, and five adsorption–desorption cycles were performed in total.

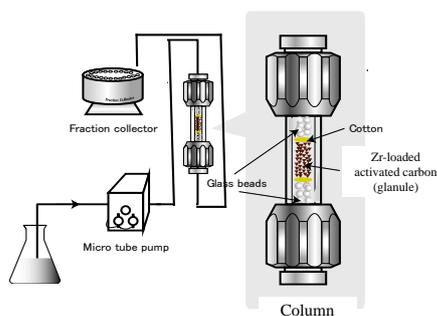


Fig. 1. Schematic of the adsorption and desorption column apparatus.

III. RESULTS AND DISCUSSION

A. Adsorption of Phosphate by Zr-AC

The X-ray diffractometry patterns of the AC and Zr-AC are shown in Fig. 2. No crystalline phases were found in the AC or Zr-AC, indicating that no crystalline structures formed when Zr was loaded onto the AC.

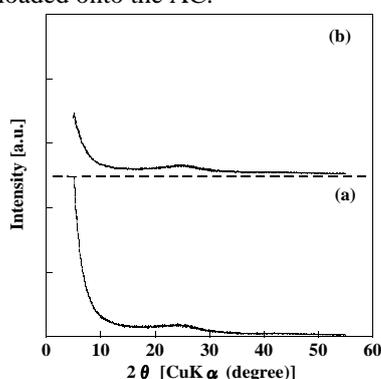


Fig. 2. X-ray diffractometry patterns of (a) the activated carbon and (b) the zirconium-loaded activated carbon.

The pH of an aqueous solution will have important effects on the processes involved in the recovery of phosphate. The

pH values when equilibrium had been reached in tests performed at different initial pH values are shown in Fig. 3. The equilibrium pH was lower than the initial pH in each test, especially when the initial pH was around 10, indicating that Zr-AC is weakly acidic. Seawater generally has a pH of around 8, so seawater from which phosphate has been removed using Zr-AC will have a pH of approximately 6.

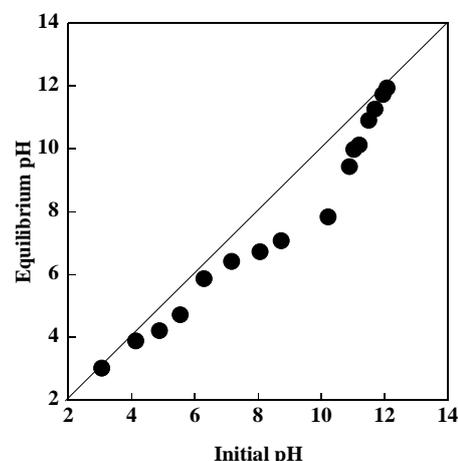


Fig. 3. Initial pH and pH after equilibrium had been reached when phosphate was removed from solutions with different initial pH values using the zirconium-loaded activated carbon.

The amounts of phosphate adsorbed onto Zr-AC in phosphate solutions at different pH values are shown in Fig. 4. It can be seen that 0.2 mmol of phosphate was removed per gram of Zr-AC at below pH 6, and the amount of phosphate adsorbed decreased as the pH increased. It was concluded that Zr-AC can adsorb phosphate from acidic and neutral solutions and release phosphate to alkali solutions.

Our results showed that Zr-AC could adsorb phosphate from seawater because the Zr-AC, being acidic, would cause the seawater pH to decrease to 6. Our results also showed that the phosphate could be desorbed from the Zr-AC using an alkaline solution.

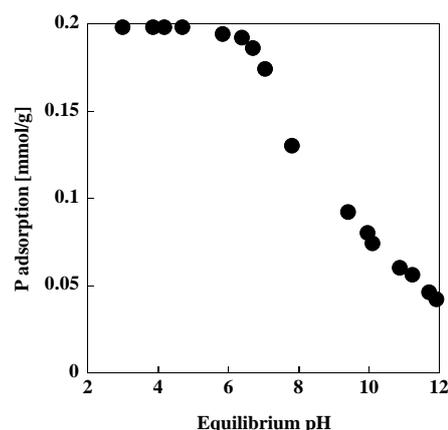


Fig. 4. Amount of phosphate adsorbed from solution per gram of zirconium-loaded activated carbon at different equilibrium pH values.

The phosphate adsorption isotherms for the AC and Zr-AC for solutions in distilled water and seawater are shown in Fig. 5. The amount of phosphate adsorbed per gram of Zr-AC increased to approximately 0.6 mmol/g and then remained almost constant as the equilibrium concentration increased, whereas almost no phosphate was adsorbed per gram of AC.

The adsorption of phosphate in distilled water and seawater followed almost the same behavior. These results indicate that the Zr-AC had a higher adsorption capacity for phosphate than did the AC, and that the Zr-AC could adsorb phosphate as effectively from seawater as from distilled water.

The adsorption data for phosphate in distilled water and seawater were assessed using isotherm models. Several isotherm models for describing equilibrium sorption distributions are available, and the Langmuir and Freundlich models are commonly fitted to experimental data. The linear form of the Langmuir model is shown in (3), and the linear form of the Freundlich model is shown in (4).

$$C_e / q_e = 1/(Q_{\max} \cdot K_L) + C_e / Q_{\max} \quad (3)$$

$$\ln(q_e) = \ln(K_F) + (1/n) \cdot \ln(C_e) \quad (4)$$

In (3) and (4), q_e is the amount of phosphate adsorbed at equilibrium (mmol/g), Q_{\max} (mmol/g) and K_L (L/mg) are Langmuir constants related to the maximum adsorption capacity (corresponding to the complete coverage of available adsorption sites) and a measure of the adsorption energy (equilibrium adsorption constant), respectively, and K_F and n are Freundlich constants.

The Langmuir and Freundlich constants and the regression coefficients for the adsorption of phosphate are given in Table II. The correlation coefficients (R^2) indicated that the Langmuir model fitted the data better than did the Freundlich model for solutions in distilled water and solutions in seawater. The maximum adsorption capacity of Zr-AC for phosphate in seawater, calculated using the Langmuir model, was found to be 0.64 mmol/g.

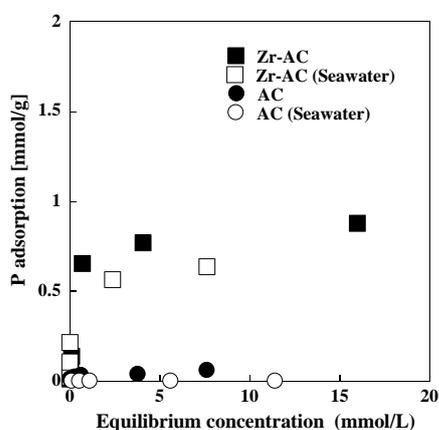


Fig. 5. Isotherms for the adsorption of phosphate from distilled water and seawater by the activated carbon and zirconium-loaded activated carbon.

TABLE II: ISOTHERM PARAMETERS FOR THE ADSORPTION OF PHOSPHATE BY THE ZIRCONIUM-LOADED ACTIVATED CARBON

	Langmuir parameters			Freundlich parameters		
	Q_{\max}	K_L	R^2	K_F	N	R^2
Distilled water	0.92	1.32	0.996	1.69	0.33	0.826
Seawater	0.64	6.72	0.998	5.95	0.47	0.996

B. Chromatographic Separation and Recovery of Phosphate

A chromatographic test was performed. First, deep seawater was used as a feed solution. The profile for the adsorption of phosphate from deep seawater is shown in Fig.

6(a). The phosphate concentration gradually increased and reached 1.5 $\mu\text{mol/L}$ at > 80000 bed volumes. The profile for the desorption of phosphate from the adsorbent (into aqueous NaOH) is shown in Fig. 6(b). The results indicate that phosphate was easily desorbed from Zr-AC and could be recovered quickly (at < 2000 bed volumes). Phosphate in deep seawater was able to be recovered using Zr-AC. In the experiment, 0.0936 μmol of phosphate was collected and the phosphate concentration was 12 times higher in the desorbed solution than in the deep seawater.

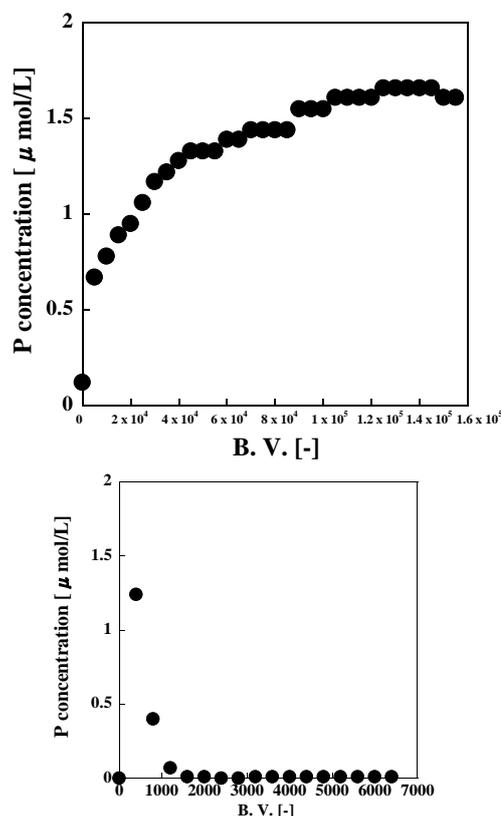


Fig. 6. Curves for the (a) adsorption and (b) desorption of phosphate in deep seawater by zirconium-loaded activated carbon (B.V. = bed volumes).

The adsorption and desorption curves for the five adsorption–desorption cycles are shown in Fig. 7. The amount adsorbed followed a similar trend in every cycle, increasing sharply at the beginning of the process and then reaching a constant value at < 100 bed volumes. The amount desorbed increased rapidly at < 50 bed volumes, then decreased gradually. The adsorption and desorption breakthrough times were almost the same. In the first cycle, 14.51 mmol of phosphate (as phosphorus) was desorbed from the Zr-AC, and in the second to fifth cycles 3.7–5.5 mmol of phosphate (as phosphorus) was desorbed. The phosphate concentration in the desorbed solution in the first cycle was 65 times higher than the phosphate concentration in the initial phosphate solution, whereas the phosphate concentrations in the desorbed solutions in the second to fifth cycles were 17–25 times higher than the phosphate concentration in the initial phosphate solution. More phosphate was recovered in the first cycle than in the later cycles. It is possible that some of the zirconium, which would have been weakly bound to the AC, was eluted in the first cycle. However, no significant losses were found after the second cycle, so the Zr-AC could

be used repeatedly to recover phosphate from seawater.

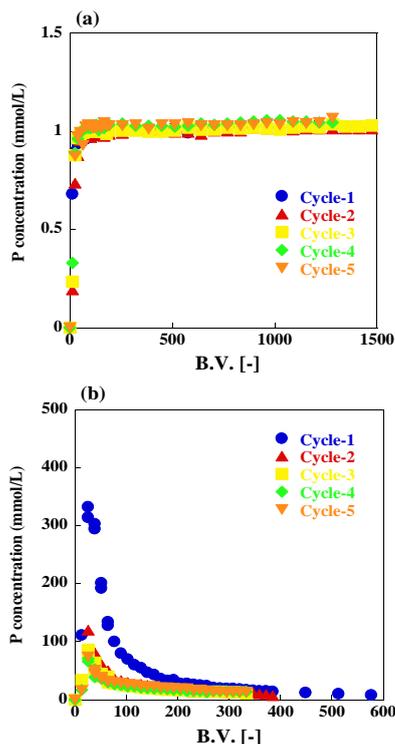


Fig. 7. Curves for the (a) adsorption and (b) desorption of phosphate from seawater containing 1 mmol/L phosphate in five adsorption-desorption cycles.

IV. CONCLUSIONS

A novel adsorbent, Zr-AC, was used to attempt to selectively adsorb phosphate from seawater. The adsorption of phosphate onto the Zr-AC was studied to determine whether phosphate could be recovered from deep seawater. Zirconium could be loaded onto AC by mixing the AC with a solution of zirconyl nitrate, and the Zr-AC produced could adsorb phosphate from seawater. Zr-AC could very selectively adsorb phosphate from seawater. The Langmuir model fitted the experimental isotherm data better than did the Freundlich model, and the calculated maximum adsorption capacity for phosphate was 0.64 mmol/g. The Zr-AC could adsorb phosphate from acidic and neutral solutions and release phosphate into alkaline solutions. The selective recovery of phosphate from deep seawater using a chromatographic technique was studied, and it was found that phosphate could be selectively adsorbed from deep seawater in the adsorption step and recovered and concentrated into aqueous NaOH in the desorption step. A column packed with Zr-AC could be used for repeated adsorption-desorption cycles.

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