Preparation of Highly Selective Phosphorus Adsorbent from Zircon Sand (ZrSiO₄) by Mechanochemical Treatment

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Abstract

In this study, it is attempted to prepare the adsorbent with highly selective phosphorus adsorption material from zircon sand by a simple mechanochemical treatment. The phosphorus adsorption property of the products obtained under various mechanochemical treatment conditions were investigated by various phosphorus adsorption experiments. With increasing the time of mechanochemical treatment, the phosphorus adsorption amount of the product increased within 10 min, regardless the ball diameter. The phosphorus adsorption amount of the product was about 2.5 times larger than that of the raw zircon sand. The adsorption amount of phosphorus increased with decreasing the pH value at the equilibrium, and was about 3.5 times larger at pH 1 than at pH 7. The product showed the same adsorption amount in Imari bay seawater as that in the aqueous solution at pH 7, which means that phosphorus can be selectively adsorbed on the product in the solution with high salt concentration. The adsorption isotherm at pH 1 was found to applicable to Langmuir model rather than Freundlich model. The maximum calculated adsorption amount was 0.034 mmol g⁻¹. XRD and FT-IR analyses of the product did not change greatly by mechanochemical treatment, except the Zr-O binding of zircon sand.

Keywords: Zircon sand, Mechanochemical treatment, Highly selective removal, Phosphorus adsorption

1. Introduction

Phosphorus (P) is discharged from agriculture soil and industrial wastewater to the surface water and the increase of phosphorus concentration in the surface water strongly contributes to eutrophication. Therefore, phosphorus removal from wastewater has received considerable attention. Several methods have been used to remove phosphorus from water, such as crystallization, coagulation precipitation, biological dephosphorization and adsorption. Among them, zirconium-based adsorbent is known to have high selectivity to phosphorus from wastewater, because of the high chemical affinity of Zr-OH to phosphorus. It is reported that as the adsorption mechanism in the aqueous solution, OH group bonded to zirconium on the adsorbent surface can be exchanged for phosphate ion (H₂PO₄⁻, HPO₄²⁻ and PO₄³⁻) to adsorb phosphorous. Typical adsorbents include materials based on zirconium ferrite, Zr-immobilized ion exchange resin, and zirconia (ZrO₂). Zirconium-based adsorbent, mainly zirconia, is prepared from zircon sand (ZrSiO₄) using wet-refining method. This method needs a lot of energy to produce zirconium-based materials expensively.
Mechanochemistry is the phenomenon of giving mechanical energy to pulverize materials\(^a\). When pulverizing materials, a part of mechanical energy is consumed in irreversible work such as lattice defect formation and amorphization of the pulverized material\(^b\). As a result, the pulverized material is activated and the reactivity increases\(^c\). Therefore, mechanochemical treatment is used for the complexation by surface coating of different materials, the development of adsorbent materials by surface modification of particles and the preparation of amorphous alloy\(^d\). For example, there are reports for preparation of magnesium oxide as a high performance lithium adsorbent by mechanochemical treatment\(^e\) and development of phosphorus adsorbent using mechanochemical treated calcium silicate\(^f\).

In this study, the adsorbent with high selectivity phosphorus adsorption ability was prepared from inexpensive zircon sand by a simple mechanochemical treatment. The phosphorus adsorption properties of the products, such as pH dependency, selectivity and adsorption capacity, are evaluated.

2. Experimental

2.1 Sample

Raw zircon (zirconium silicate) used in this study was purchased from Wako Pure Chemical Industries, Ltd., Japan. Seawater used in this study was collected from the surface layer of Imari bay, Saga prefecture, Japan. The chemical composition of seawater is shown Table 1, and the pH of seawater is about 7.

| Ion   | Concentration / (mmol L\(^{-1}\)) |
|-------|----------------------------------|
| SO\(_4^{2-}\) | 40.8 |
| Cl\(^-\) | 827 |
| Na\(^+\) | 482 |
| K\(^+\)  | 11.6 |
| Mg\(^2+\) | 75.3 |
| Ca\(^{2+}\) | 13.0 |

2.2 Mechanochemical treatment and phosphorus adsorption amount

A planetary ball mill (P-6, Fritsch) was used for mechanochemical treatment. Pots and balls were made of silicon nitride with high wear resistance. Treatment was carried out at the rotation speed of 400 rpm for 1 to 60 min using three different diameter balls (\(\phi 5\), 10, 15 mm). The volume filling ratio of ball into pot was about 30 %, and the number of balls with \(\phi 5\) mm, \(\phi 10\) mm and \(\phi 15\) mm in diameter were 180, 18 and 7, respectively. The products after mechanochemical treatment were analyzed using a powder X-ray diffractometer (XRD, MiniFlex 600, Rigaku) and a Fourier transform infrared spectrophotometer (FT-IR, NICOLET iS5, Thermo Fisher), respectively.

The amounts of phosphorus adsorption of products obtained under each mechanochemical treatment condition were calculated as follows. The product of 0.1 g after mechanochemical treatment was added into 0.5 mmol L\(^{-1}\) KH\(_2\)PO\(_4\) aqueous solution of 10 mL in a 50 mL centrifugal tube and was shaken with a reciprocal shaker at room temperature for 12 h. After shaking, the tube was centrifuged and a part of the supernatant was collected. The pH of the collected solution was measured with a pH meter (C-37, AS ONE) and their phosphorus concentration was determined by the molybdenum blue method. The adsorption amount and the ratio were calculated from the measured phosphorus concentration by following equations;

\[
q = \frac{(C_0 - C)L}{W} \quad (1)
\]

\[
\%\text{removal} = \frac{(C_0 - C)}{C_0} \times 100 \quad (2)
\]

where \(q\), \(C_0\), \(C\), \(W\) and \(L\) are the adsorption amount, the initial phosphorus concentration, the concentration after shaking, the weight of sample and the volume of solution, respectively.

2.3 Phosphorus adsorption capacity

Phosphorus adsorption capacities of the product obtained by mechanochemical treatment for 10 min using \(\phi 5\) mm balls in diameter were investigated.

\(\text{pH}\) dependence of the phosphorus adsorption amount of the product was investigated and was compared with that of zircon (the raw material). The \(\text{pH}\) of 0.5 mmol L\(^{-1}\) KH\(_2\)PO\(_4\) solution was adjusted to 1 - 12 using hydrochloric acid and NaOH (aq). The product of 0.1 g was added into KH\(_2\)PO\(_4\) solution with different \(\text{pH}\) values and was shaken for 12 h at room temperature. After shaking, the mixture was centrifuged. The \(\text{pH}\) of supernatant was measured with the \(\text{pH}\) meter. The phosphorus concentration in the supernatant was determined by the molybdenum blue method to calculate the phosphorus adsorption amount using equations (1) and (2).

The amount of phosphorus adsorption in Imari bay seawater as a high salt concentrations solution was examined for phosphorus-selective adsorption of the product and was compared with that in aqueous solution of \(\text{pH}\) 7. The product of 0.1 g was added into 10 mL Imari bay seawater or distilled water with 0.05 - 0.5 mmol L\(^{-1}\) KH\(_2\)PO\(_4\), and was shaken for 12 h. After shaking, the mixture was centrifuged. The \(\text{pH}\) (i.e. the equilibrium \(\text{pH}\)) of supernatant was measured with the \(\text{pH}\) meter. The phosphorus concentration in the supernatant was determined by the molybdenum blue method to calculate the phosphorus adsorption amount using equations (1) and (2).
Phosphorus adsorption isotherm was examined using KH$_2$PO$_4$ aqueous solution with pH 1. Hydrochloric acid was added dropwise to 0.05 - 0.5 mmol L$^{-1}$ KH$_2$PO$_4$ solution of 10 mL to adjust pH to 1. The product of 0.1 g was added into KH$_2$PO$_4$ solution, and was shaken for 12 h. After shaking that, the mixture was centrifuged. The pH (i.e. the equilibrium pH) of supernatant was measured with a pH meter. The phosphorus concentration in the supernatant was determined by the molybdenum blue method to calculate the phosphorus adsorption amount using equations (1) and (2).

3. Results and discussion

3.1 Phosphorus adsorption amount and capacity

The amounts of phosphorus adsorption of the product obtained by mechanochemical treatment are shown in Fig. 1. With increasing the mechanochemical treatment time, the amounts of phosphorus adsorption of the product increase until 10 min, and then become almost constant regardless of the ball diameter. The amount after 10 min mechanochemical treatment is 0.01 mmol g$^{-1}$, which is almost 2.5 times larger than that of the raw zircon (0.004 mmol g$^{-1}$). It is noted that the amount the product was about 1/2 to that of zirconia (0.03 mmol g$^{-1}$), and 1/10 to that of commercially available Orlite F (0.2 mmol g$^{-1}$). It is also noted that the adsorption ratio of phosphorus was about 20%.

pH dependence of the phosphorus adsorption of the product is shown in Fig. 2. The phosphorus adsorption amounts of the product increase with decreasing pH. The amount in the solution with pH 1 is 0.025 mmol g$^{-1}$, which is about 3.5 times larger than with pH 7, while adsorption of the raw zircon was almost constant. It is reported that the adsorption amount of zirconium adsorbent increased as pH decreased$^{6}$. It is considered that Zr-O-H is generated on the surface of the product by mechanochemical treatment.

Figure 4 shows the adsorption isotherms of the product in phosphorus solution at pH 1. As the equilibrium concentration increases, the phosphorus adsorption increased sharply until the equilibrium concentration of 0.1 mmol L$^{-1}$ and then gradually increased.
The experimental results obtained in Fig. 4 were analyzed by Langmuir and Freundlich adsorption model to estimate the phosphorus adsorption behavior of the product. The linearized equations of Langmuir and Freundlich adsorption models are as follows;

\[
\frac{C}{q} = \frac{1}{q_{\text{max}}K_L} + \frac{C}{q_{\text{max}}} \quad (3)
\]
\[
\ln q = \ln K_F + \frac{1}{n} \ln C \quad (4)
\]

where \( q_{\text{max}} \), \( K_L \), \( K_F \) and \( n \) are the maximum adsorption amount, adsorption equilibrium constant of Langmuir model, and adsorption equilibrium constant of Freundlich model, respectively.

The results analyzed are shown in Table 2. According to the correlation coefficient \( R^2 \), Langmuir equation can be more suitable than Freundlich equation. The calculated maximum adsorption capacity of the product can be obtained from Langmuir equation and is 0.034 mmol L\(^{-1}\).

| Model     | Parameter | Value |
|-----------|-----------|-------|
| Langmuir  | \( q_{\text{max}} \) | 0.034 |
|           | \( K_L \) | 15.3  |
|           | \( R^2 \) | 0.919 |
| Freundlich| \( K_F \) | 0.063 |
|           | \( R^2 \) | 0.710 |

### 3.2 Structure of the product by mechanochemical treatment

XRD patterns of the products after mechanochemical treatment using ø 5 mm ball are shown in Fig. 5. XRD patterns of the product were almost same regardless of the ball diameter. New peaks are not observed by mechanochemical treatment. The ratio of the peak intensity at each diffraction angle to the intensity at the face of (1 0 1) is shown in Fig. 6. As the mechanochemical treatment time increases, peak intensities at the face of (2 0 0) and (3 0 1) decrease, while other faces and almost constant. Lattice planes for the two diffraction angles in zircon are shown in Fig. 7 and intersection of two faces of zircon sand unit cell are in Fig. 8. It was found that the bond between Zr and O was changed. From this result, the Zr-OH bond appears on the surface by destroying the Zr-O bond present in the zircon sand structure by mechanochemical treatment.

Fig. 5 XRD patterns of the product after mechanochemical treatment using ø 5 mm balls.

Fig. 6 The ratio of the peak intensity at each diffraction angle of the product after mechanochemical treatment using ø 5 mm balls.

Fig. 7 Lattice planes for the two diffraction angles of zircon sand unit cell.

Fig. 8 Intersection of two faces of zircon sand unit cell (yellow point).
FT-IR spectra of the products after mechanochemical treatment are shown in Fig. 9. FT-IR spectra of the product were almost same regardless of the ball diameter. The ratio of the peak intensity at each wave number to the peak intensity at 795 cm\(^{-1}\) is shown in Fig. 10. The peak of 896 cm\(^{-1}\) of Zr-O after mechanochemical treatment showed an increase as the mechanochemical treatment time increased\(^7\). This suggests that the change in Zr-O may cause an increase in adsorption amount. From this result, there is a possibility that the bond of Zr and O existing in the zircon sand changed to other bonds, such as Zr-OH, to adsorb phosphorus. It is noted that no significant increase for other peaks was observed after mechanochemical treatment.

![Fig. 9](image1.png)

**Fig. 9** FT-IR spectra of the product after mechanochemical treatment using \(\Phi 5\) mm ball.

![Fig. 10](image2.png)

**Fig. 10** The ratio of the peak intensity at each wave number of the product after mechanochemical treatment using \(\Phi 5\) mm balls.

4. Conclusion

It was attempted to prepare highly selective phosphorus adsorbent from zircon sand by mechanochemical treatment using a planetary ball mill. The phosphorus adsorption properties of the product, such as phosphorus adsorption amount, pH dependence and phosphorus selectivity, were investigated. The results are as follows;

1. The amount of phosphorus adsorption of zircon could increase rapidly within 10 min of mechanochemical treatment.
2. The amount of phosphorus adsorption of the product increased with decreasing pH.
3. The phosphorus adsorption of the product in Imari bay seawater was the same as in distilled water solution.
4. The adsorption isotherm at pH 1 was expressed by Langmuir model better than Freundlich model. The calculated maximum adsorption amount was 0.034 mmol g\(^{-1}\).
5. By XRD and FT-IR analysis, the bond between Zr and O in the zircon was changed by mechanochemical treatment.

From these results, highly selective phosphorus adsorbent could be prepared from zircon sand by simple mechanochemical treatment.

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