

Phosphorus recovery by mesoporous structure material from wastewater

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Abstract This study was designed to investigate the fundamental aspects of a possible removal of phosphorus from wastewater by using the mesoporous structure materials for wastewater reuse. The zirconium sulphate with mesoporous structure as a new type of ion exchangers was synthesised by hydrothermal reaction. From the results of X-ray diffraction and transmission electron microscope, it was discovered that the synthesised material had hexagonal mesoporous structure with a pore size of approximately 40–50Å. Experimental results showed that the zirconium sulphate with mesoporous structure had very high sorption capacity for the phosphorus. The novel ion exchange occurred between PO_4^{3-} and SO_4^{2-} , OH^- . The amount of phosphate ions exchanged into the solid was as great as 3.4 mmol/g-ZS. Furthermore, it is possible to obtain a higher removal efficiency than other ion exchange media and adsorbents.

Keywords Adsorption; ion exchange; mesoporous structure material; phosphorus; zirconium sulphate

Introduction

Due to population explosion, uncontrolled use, inefficient management and pollution of water, the shortage in available water becomes a severe problem in Korea. The demand of clean water for urban consumption has been continuously increasing. In Korea, 184 sewage treatment plants have been discharging 20 million tons of treated effluent annually and only 2.4% of the effluent was used for water reuse. According to the Ministry of Korea, increasing the reuse percent of secondary effluent by 5% could show the same result of having a dam holding 360 million tons of water (MOE, 2002). The secondary effluent reclamation of wastewater treatment could be produced more extensively and used for many purposes. Therefore, water reclamation and reuse has the potential to be a key process to save water resources and protect environments.

Phosphorus in wastewater is usually considered to be the limiting nutrient with respect to the eutrophication of water bodies. Removal of phosphorus from wastewater might be an essential process for the control of eutrophication caused by reclaimed water in lakes and similar water bodies. Tertiary chemical treatment has been widely used for the removal of phosphate. Lime, aluminium sulphate (alum), and ferric chloride are the common precipitants used for phosphate removal. However, the sludge generated after reaction has been considered a potential problem.

In recent years, usage of adsorbents and ion-exchangers has drawn most attention as a removal and recycling technology for phosphorus in wastewater. Among them, the metal-loaded ligand exchangers have been highly recommended as a promising sorbent with their selectivity for phosphate ion, particularly in secondary wastewater (Chubar *et al.*, 2005).

Mesoporous structure materials have recently been synthesised by using surfactant micelle as the template, since the mesoporous structure material could be used as a very effective absorbent or ion exchanger. Mesoporous structure materials possess a regular pore diameter ranging from 20 to 500 nm depending on the kinds of templates and the reaction conditions. As base materials, the zirconium has the highest affinity to phosphorous and novel anion exchange reaction between SO_4^{2-} in the precursor and PO_4^{3-} in the solution is occurred. Iwamoto *et al.* (2002) reported that ion exchange can effectively occur in the mesoporous structure of zirconium sulphate. Furthermore, the hexagonal mesoporous structure material has a great potential to remove and recover heavy metal from wastewater (Tanaka *et al.*, 2004).

Thus, this study was designed to investigate the fundamental aspects of a possible remediation strategy for phosphorous removal, using the mesoporous structure material as a new type of ion exchanger. Furthermore, the adsorption characteristics of phosphate onto as-synthesised mesoporous structure material were investigated for wastewater reuse, including estimation of the adsorption isotherms of phosphate and comparison of other adsorbents.

Material and methods

Synthesis of zirconium mesoporous structure

Zirconium mesoporous structure (ZS) was synthesised by the same process reported by Ciesla *et al.* (1996) and Reddy and Sayari, 1996) previously described as in the following. The 2.5 g of zirconium sulphate tetrahydrate ($\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) was dissolved in 85 ml deionised water. The 4.55 g of hexadecyltrimethyl ammonium bromide ($\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Br}$) was dissolved in 15 ml deionised water at the same time. When two reagents were mixed, a white precipitate was formed immediately. The mixture was stirred vigorously for 2 h at room temperature. A mass of the precipitate suspended in the mixture when stirring was stopped. The hydrothermal reaction for zirconium sulphate synthesis was carried out for 48 h at 100°C in autoclave. After hydrothermal reaction, the precipitate was filtered, washed with deionised water several times to get rid of remained surfactant. In parallel, the synthesised materials were dried in an oven for 5 h at 80°C . The as-synthesised materials of zirconium mesoporous structure material were designated as ZS and passed through 300 mesh sieve for further use.

Characterisation of synthesised materials

To characterise hexagonal mesostructure, X-ray diffraction (XRD: Rigaku DMAX-2500) measurements were performed. Transmission electron microscope (TEM: CM 30 Philips) images were obtained. Ion exchanges between PO_4^{3-} and SO_4^{2-} were characterised by Fourier transform infrared (FT-IR: Thermomattson Infinity Gold FT-IR 60AR) spectra. FT-IR spectra were measured on a Thermomattson Infinity Gold FT-IR 60AR. In this method, potassium bromide (KBr) was used as a support and a pure KBr pellet was used to correct the background. The measurement limit ranged from 400 to $4,000\text{ cm}^{-1}$.

Ion exchange of phosphate

Phosphate ion exchange capacity of ZS was studied and typical sorbents or ion exchangers such as zirconium oxide (ZrO_2), lanthanum carbonate hydrate (99.9%, $\text{La}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$), and lanthanum hydroxide (99.9%, $\text{La}(\text{OH})_3$) were compared. Batch conditions were as follows: 400 mg of the sorbent was introduced in Erlenmeyer flasks, various amounts of phosphate stock solution and distilled water were added to obtain the determined initial phosphate concentration in a total volume of 60 mL. The initial pH was 4.7 and was not adjusted. The flasks were stirred in a temperature controlled room for 2 h at $25 \pm 2^\circ\text{C}$. Then, flasks were removed, filtrated with a $0.45\text{ }\mu\text{m}$ membrane filter and the

filtrate was analysed for phosphate and sulphate ions by single column ion chromatography with low conductivity mobile phase.

Results and discussion

Mesoporous structure material of zirconium sulphate

X-ray diffraction patterns of materials are shown in Figure 1. The XRD results confirmed the ordered hexagonal structure. Diffraction from [100], [110], and [200] planes appeared at 2.14, 3.68 and 4.16° of low-angle diffraction, respectively. This XRD results implied that synthesised ZS had the ordered hexagonal structure. At low-angle diffraction, [100] plane shows the highest intensity which reduced with increase of diffraction peaks. Hexagonal arrangement can be characterised by [100] peak with d -spacing (d_{100}). Spacing in hexagonal unit cell was compared with experimental data using following calculation:

$$d_{100} = a_0 \times \sin 60^\circ = \sqrt{3}/2 a_0$$

$$d_{110} = a_0 \times \sin 30^\circ = 0.5 a_0$$

$$d_{200} = 0.5 d_{100} = \sqrt{3}/4 a_0$$

where, d_n is d -spacing of n peak and a_0 is centre interval (Å).

A distance between centres in a two-dimensional hexagonal arrangement was obtained as $2/\sqrt{3} \times d_{100}$. Size of pores could be given as a_0 , except pore wall. Therefore, pore diameter can be compared with d -spacing because pore walls are not so different in the same materials. Centre interval (a_0) distribution with a mean value of 47.6 Å is obtained from above method.

TEM was generally applied to confirm mesoporous structure (Beck *et al.*, 1992; Ciesla *et al.*, 1999). The TEM pictures of some of the prepared mesoporous structure material of zirconium sulphate after hydrothermal treatment are shown in Figure 2. A regular and well ordered array of mesopores is observed. Figure 2 also reveals that crystallisation occurred vertically to pores. The hexagonal arrays of the cylindrical pores are viewed from the side, resulting in long channel-like images as described by Kim *et al.* (2003) (Figure 2). The two-dimensional hexagonal structure is therefore confirmed.

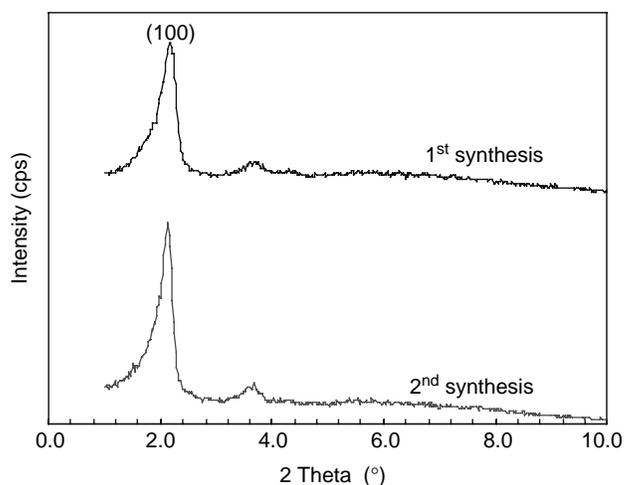


Figure 1 Typical X-ray diffraction patterns of ZS synthesised; $2\theta = 2.18^\circ(100)$, $2\theta = 3.60^\circ(110)$, $2\theta = 4.24^\circ(200)$

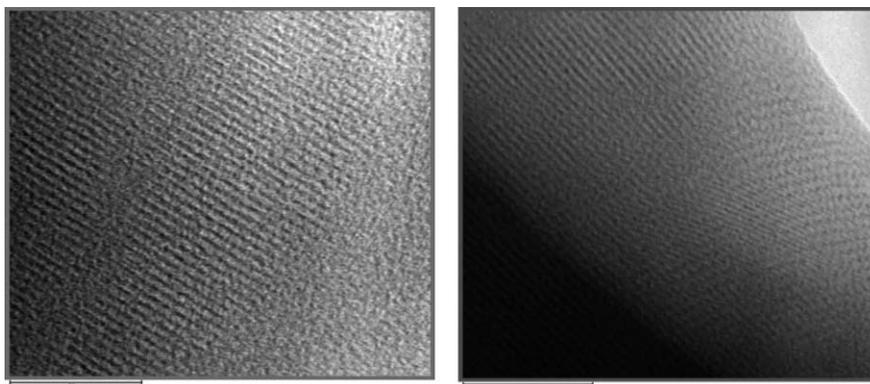


Figure 2 Transmission electron micrograph of ZS

Ion exchange on mesoporous structure material

The entrapment of PO_4^{3-} ions with concentration range from 0 to 40 mmol/L in the mesoporous structure material was carried out by contacting the sample of as-synthesised ZS. **Figure 3** depicts the FT-IR spectra of ZS before and after exchanging with phosphate solution for varying initial concentration of phosphate (curves (a)–(d)). From the measurements of absorption spectra, the higher initial concentration of phosphate in aqueous solutions represented the lower peak of SO_4^{2-} and the higher HPO_4^{2-} in spectra curve. It is also confirmed that OH^- ion is reduced to be associated with ion exchange. The results of exchange of HPO_4^{2-} with OH^- is similar to the phenomenon in the case of zirconium ferrite ($\text{ZrFe}_2(\text{OH})_8$) (Takai and Murasawa, 2001)

Shown in **Figure 4** are the powder XRD patterns of as-synthesised ZS and after exchange of PO_4^{3-} . The XRD results showed that the peak intensity was significantly reduced. This phenomenon might be caused by contraction of the structure because the bonding strength of PO_4^{3-} is higher than that of SO_4^{2-} . Using the previous equation, pore size was calculated as a_0 of 44.7 Å ($d_{100} = 38.71$) which is smaller than the original a_0 of 46.7 Å ($d_{100} = 40.49$).

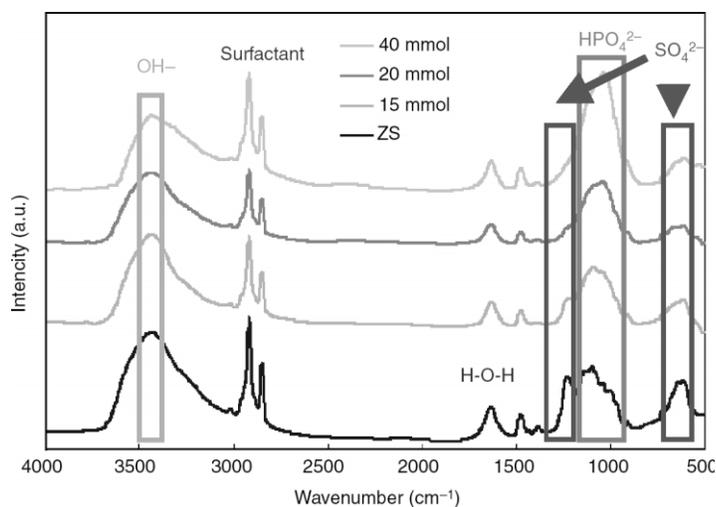


Figure 3 FT-IR spectra of ZS(a) and treated with phosphate solution of 15 mmol/L(b), 20 mmol/L(c) and 40 mmol/L (d)

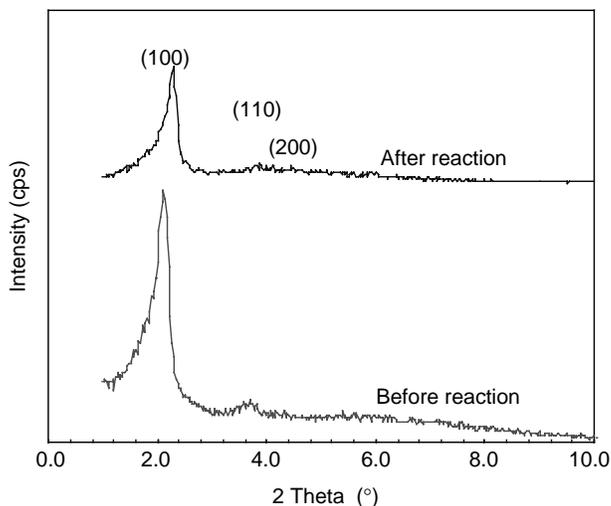


Figure 4 X-ray diffraction patterns of ZS after and before ion exchange reaction in phosphorous solution of 40 mmol/L

The TEM pictures after 24 h of reaction in 40 mmol/L solution of PO_4^{3-} are shown in Figure 5. The ZS represents various layered shapes due to reaction with phosphate solution. ZS crystal, however, formed distinct hexagonal array rather than changed. Wu and Iwamoto (1998) reported that the hexagonal structure was enhanced after treatment with 0.01 to 2 mol of phosphate solution at room temperature. Furthermore, the Brunauer–Emmett–Teller (BET) specific surface area increased after calcination at 500 C.

The release of SO_4^{2-} ions as a result of PO_4^{3-} exchange was investigated during ion exchange reaction as shown in Figure 6. The release profiles showed that SO_4^{2-} ion was released from the mesoporous material almost 1:1 until introduced P (mmol/g-ZS) was 1.2, since unstable SO_4^{2-} ion reacts with PO_4^{3-} ion first. With over 1.2 of introduced P

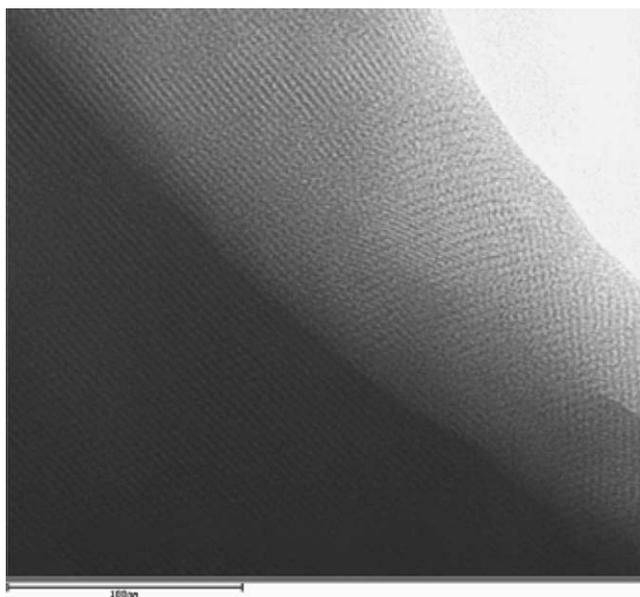


Figure 5 Transmission electron micrograph of ZS treated with phosphate solution of 40 mmol/L

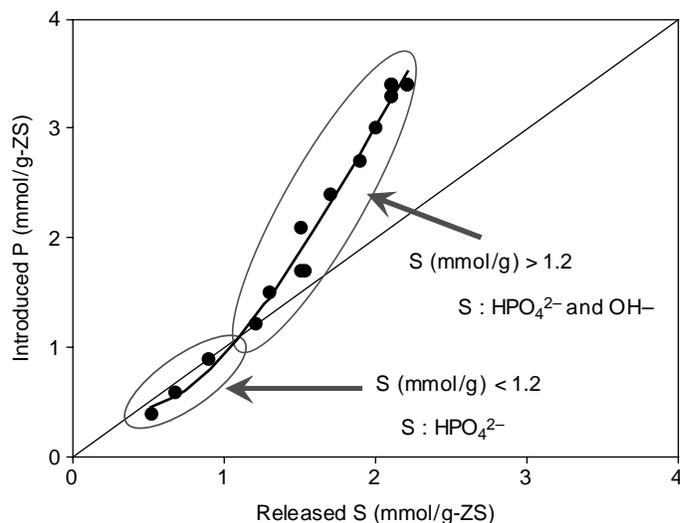


Figure 6 Correlation between the amount of S released and that of P introduced

(mmol/g-ZS), no significant release or a very slow release was observed. These findings can be explained by the different ionic compositions of the media. It was indicated that PO_4^{3-} ion exchanged with OH^- ion, although it was very stable on mesoporous structure due to lack of exchangeable SO_4^{2-} in the matrix. In Figure 3, OH^- reduction could be confirmed with ion exchange.

Phosphate removal by zirconium sulphate with mesoporous structure

The adsorption isotherm of the powdered ZS for phosphate at 25 C is shown in Figure 7. The equilibrium phosphate concentration (C_e) and the adsorbed amount (q_e) were plotted. The adsorption isotherm was approximated by the modified Langmuir equation (Chubar *et al.*, 2005). The anions uptake was determined according to the following equation (Svarovsky, 1990).

$$q_e = (C_0 - C_{eq}) \cdot V/M \quad (1)$$

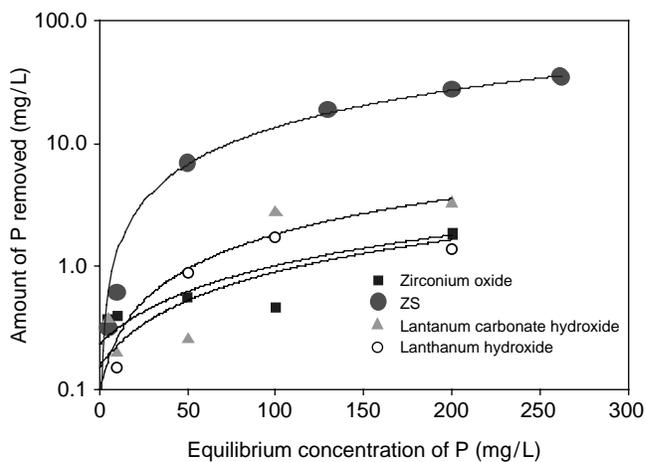


Figure 7 Phosphate adsorption isotherm on various adsorbents

where q_e (mg/g) is the amount of phosphate adsorbed per gram of the mesoporous structured material, C_0 (mg/L) the initial concentration of the phosphate ion, C (mg/L) the final (or equilibrium) concentration of the phosphate ion, V (L) the volume of the solution and M (g) the mass of the adsorbent.

The maximum adsorption capacity (3.4 mmol-P/g-ZS) of the powdered ZS was obtained. It indicates that ZS is a very effective adsorbent. The plots in Figure 7 graphically show isotherms, as well as fitting of the experimental results to the curves of adsorption models approached using zirconium oxide for comparison of the capacity of phosphate removal. The results indicated that zirconium sulphate was more effective than zirconium oxide and other adsorbents.

Conclusion

Zirconium sulphate with mesoporous structure (ZS) was synthesised using $Zr(SO_4)_2 \cdot 4H_2O$ and surfactant, hexadecyltrimethyl-ammonium bromide ($CH_3(CH_2)_{15}N(CH_3)_3Br$). Hexagonally-packed cylindrical pores were confirmed by using XRD and TEM. The sizes of mesopores synthesised were calculated to be around 47 Å. The ion exchange reaction was confirmed using FT-IR spectra.

Phosphate ion in water was removed through ion exchange with sulphate and hydroxyl ion contained in the mesoporous structure material. The maximum capacity of adsorption was 3.4 mmol/g-ZS at equilibrium isotherm. This value indicates that ZS has a significantly high capacity for phosphate ion-exchange compared to other adsorbents. In conclusion, the ZS has been revealed to be an excellent ion exchanger for removal of phosphate ion in wastewater.

Acknowledgements

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