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Synthesis of Large Porous Particles of Iron Oxide and Their Arsenic Adsorption Characteristics in Aqueous Solution

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Abstract. A novel method has been developed for the synthesis of large porous particles of iron oxide. In this synthesis, large particles of phosphosiderite ($FePO_4{\cdot}2H_2O$)were first prepared by coprecipitation from an Fe(II) and P(V) aqueous solution by oxygen injection at about 368 K. Porous particles of iron oxide were then obtained by removing the phosphorus in the particles in an alkaline solution. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to characterize formation of the porous particles of iron oxide. The extended X-ray absorption fine structure (EXAFS) in the range of the Fe K absorption edge was investigated to characterize the local structure of the porous particles. The characteristics of As adsorption onto the porous particles of iron oxide were examined by analyzing the As concentration in aqueous solution. For comparison, the As adsorption characteristics of γ-Fe_2O_3 particles, which were prepared from γ-FeOOH, were also studied. The results showed that the porous particles of iron oxide prepared from large phosphosiderite particles had superior As adsorption characteristics compared to those of γ-Fe_2O_3 particles prepared from γ-FeOOH. It was shown that large porous particles of iron oxide with high filterability in water are promising for use as As adsorbents in aqueous solution.

Keywords. Porous iron oxides, iron oxides, water.

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1 Introduction

Arsenic (As) pollution in water, mainly groundwater, is a worldwide problem, so there is a strong need for methods of immobilizing As species. Processes using adsorption and coprecipitation with iron oxides, including oxyhydroxides, are effective for As immobilization in contaminated water and these processes are relatively economical compared with other methods such as ion exchange and electrolysis. Thus, a large number of studies of As adsorption onto different iron oxides in water have been reported to date [1–10]. The results showed that As in water is effectively adsorbed onto different iron oxides, but the adsorption depends on the water conditions.

In order to immobilize high concentrations of As, a number of studies have also been performed on the coprecipitation, solubility, and stability of ferric arsenate compounds in water [11–18]. This knowledge is indispensable for non-ferrous metal processes because high concentrations of As are emitted in these processes. Elements such as As, antimony (Sb), selenium (Se), and tellurium (Te), which are present as impurities in non-ferrous metal ores, are produced as byproducts in copper smelting processes. In particular, toxic As needs to be immobilized as stable compounds, such as ferric sulfate compounds containing arsenate, e.g. jarosite [$MFe_3(SO_4)_2(OH)_6$, $M = H_3O^+$, Na^+, K^+, NH_4^+, etc.], and ferric arsenate compounds, e.g. scorodite ($FeAsO_4{\cdot}2H_2O$). The results obtained in previous studies showed that the chemical properties of As, such as solubility and adsorption depend on the morphology and structure of the ferric arsenate compounds [11, 14, 18].

In order to immobilize high concentrations of As in aqueous solution, a process in which large scorodite particles are coprecipitated by oxidation of aqueous Fe(II) and As(V) solutions has recently been developed [19–21]. In this process, coprecipitation of scorodite occurs when oxygen or air is injected into Fe(II) and As(V) aqueous solutions. Scorodite particles with diameters over 10 μm were synthesized under specific conditions; these particles are considerably larger than the fine scorodite particles prepared from Fe(III) and As(V) solutions. The concentration of As dissolved from these large particles in aqueous solution is much less than that dissolved from fine particles obtained from Fe(III) and As(V) solutions. The properties of the large scorodite particles are adequate for immobilization or storage of As

However, methods for As adsorption onto adsorbents are still required for immobilization of low concentrations of As in aqueous solution. Iron oxide particles are effective As adsorbents [1–10]. Although fine iron oxide particles of large surface area may be effective as adsorbents, the filterability in aqueous solution of such fine iron oxide par-

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ticles is obviously low. Thus, as a high particle porosity increases the surface area of the particles, the synthesis of large porous iron particles for use as As adsorbents is needed

The above background prompted us to synthesize precursors of large particles of iron compounds and then to prepare porous iron oxide particles from the precursors by appropriate treatment. In this study, large particles of phosphosiderite ($FePO_4{\cdot}2H_2O$) were prepared as the precursor by oxidation of a mixture of Fe(II) and P(V), as the preparation of large scorodite particles from Fe(II) and As(V) solutions is already known [19–21]. In order to obtain large porous particles of iron oxide, phosphorus was removed from the phosphosiderite particles in alkaline solution Scanning electron microscopy (SEM), X-ray diffractometry (XRD), and extended X-ray absorption fine structure (EXAFS) measurements were used to characterize the morphology, crystallographic structure, and local structure of the solid particles prepared by these processes. Inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis was used to determine the concentration of residual As in the contaminated aqueous solution. The adsorption characteristics of As onto large porous iron oxide particles are compared with those of γ-Fe_2O_3 prepared from γ-FeOOH.

2 Experimental

2.1 Sample Preparation

Large solid particles, which were later identified as being mainly phosphosiderite, were synthesized by injecting oxygen into an aqueous solution containing P(V) and Fe(II) ions at approximately 368 K. The synthetic method is similar to the method used to synthesize large scorodite particles [19] The procedure is briefly as follows. A reaction solution in which the concentration of P(V) was 21 g/L and the Fe/P molar ratio was 1.5, was prepared in a beaker by adding Fe(II) sulfate hexahydrate to a P(V) solution. The reaction solution was heated up to approximately 368 K with stirring at 300 rpm. Oxygen gas was then injected into the solution which was stirred at 300 rpm by a propeller. A suspension containing solid particles coprecipitated in the solution was obtained. The suspension was filtered through a membrane to separate the solid particles, and then the solid particles were rinsed with distilled water, filtered and dried.

In order to remove the phosphorus from the solid particles, which were identified as being mainly phosphosiderite the particles were treated with a 1 M NaOH solution. The resulting solid particles, which were porous iron oxide, were characterized using SEM, XRD and EXAFS. Maghemite (γ-Fe_2O_3) particles were also prepared by heating commercial γ-FeOOH particles at about 523 K [22]. These particles which will be referred to as γ-Fe_2O_3, were used as reference samples

2.2 Measurements

SEM observations were performed using a Hitachi SU6600 electron microscope (Hitachi, Japan) to characterize the morphology of the solid particles prepared by the above method. The crystallographic structure of the solid particles was identified by powder XRD. The apparatus used in this study was a Rigaku RINT2000 (Rigaku, Japan), in which Cu Kα radiation was used. Extended X-ray absorption fine structure (EXAFS) spectra at the Fe K absorption edge were measured to characterize the local structure of the iron in the solid particles. The EXAFS measurements were carried out using the high brilliant synchrotron radiation in BL01B1 of SPring-8 at the Japan Synchrotron Radiation Research Institute, Hyogo, Japan. The sample powders for EXAFS measurements were diluted with powdered boron nitrate and compressed to form a disk 10 mm in diameter. The intensity of the incident beam was monitored using an ion chamber. The intensity of the transmitted X-rays was measured for the Fe K absorption edge EXAFS spectra. The measured spectra were treated using a Rigaku REX2000. In order to examine the chemical state of the iron, preliminary measurements of the X-ray absorption near edge structure (XANES) spectra at the Fe K absorption edge were also carried out using a Rigaku R-XAS Looper [21]. The results confirmed that the iron oxide consisted of ferric species.

3 Results and Discussion

3.1 Morphology and Structure of Solid Particles Formed From P(V) and Fe(II) Solutions

Figure 1 shows SEM images, at different magnifications, of solid particles coprecipitated from P(V) and Fe(II) solutions by injection of oxygen gas for 180 min. The solid particles coprecipitated by oxidation were cauliflower-like in shape, and approximately 20 µm in diameter. The fact that the solid particles consist of small round particles suggests that micrometer-sized particles aggregated to form large particles. The water filterability of the solid particles was sufficiently high compared with that of iron oxide particles formed in water since the pore size of conventional filters is sub-micrometer. It should be noted that the shape of the present solid particles formed from P(V) and Fe(II) solutions is different to the characteristic polyhedral shape of large scorodite particles [19–21]. Although the reason for the difference between the shape of the present particles and that of scorodite particles is unclear, the large size of these particles may be due to coprecipitation of particles from the Fe(II) and anion solutions.

XRD measurements were carried out to identify the crystallographic structure of the solid particles obtained from P(V) and Fe(II) solutions by the above method. The XRD pattern of the solid particles formed by oxidation for 180 min is shown in Figure 2; the diffraction data

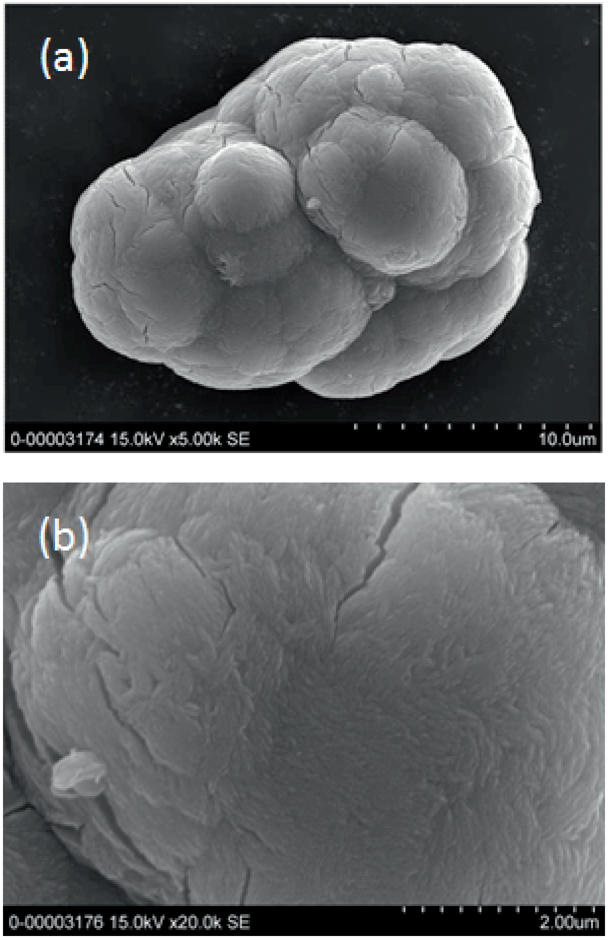

Figure 1. SEM images of solid particles coprecipitated by oxygen injection, observed at (a) low magnification and (b) high magnification.

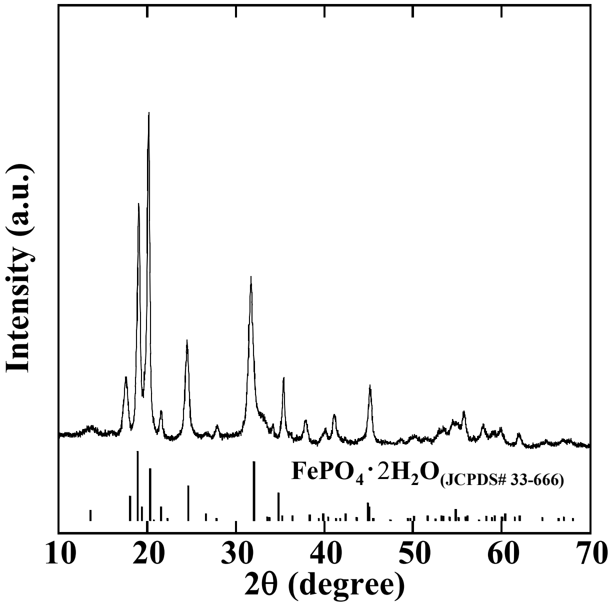

Figure 2. XRD pattern of solid particles synthesized by coprecipitation from a solution containing P(V) and Fe(III), with reference phosphosiderite data.

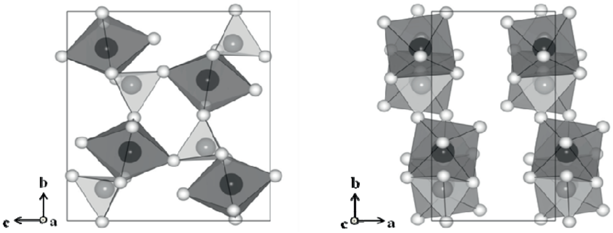

Figure 3. Packing of FeO_6 octahedra and PO_4 tetrahedra in the phosphosiderite unit cell.

of phosphosiderite are also given for reference These results indicate that the solid particles were phosphosiderite ($FePO_4{\cdot}2H_2O$) particles, although small unidentified peaks were sometimes observed.

The crystallographic structure of phosphosiderite is composed of structural units of cations and anions like the scorodite structure [21] Phosphosiderite contains ferric cations, phosphate anions, and water molecules; as shown in Figure 3, phosphosiderite consists of FeO_6 octahedral and PO_4 tetrahedral units. The Fe in the FeO_6 unit is coordinated to O atoms shared by four PO_4 tetrahedra and two water molecules. All the O atoms coordinated to Fe form bridges between Fe and P, producing four Fe-O-P linkages. As several stable crystallographic planes are observed in the structure, the flat facets of the phosphosiderite particles seem to reveal stable planes, the same as in the case of scorodite [21]. However, such flat planes were not observed in the morphology of the phosphosiderite particles.

4 Morphology and Structure of Solid Particles Obtained by Alkaline Treatment

Since phosphate compounds are unstable in alkaline solution, the large phosphosiderite particles obtained by the above method were treated with 1 M NaOH aqueous solution (alkaline treatment) to obtain porous iron oxide. Figure 4 shows SEM images of the solid particles obtained by the alkaline treatment, along with a cross-sectional image. The solid particles were washed sufficiently with water after alkaline treatment. SEM observations indicated that the shape of the solid particles was basically similar to that of the precursor phosphosiderite particles. However, ICP-AES analysis of the particles showed that there was no phosphorus in the solid particles obtained by the alkaline treatment. It is concluded from these facts that the solid particles have very fine pores, although the pores are not observed in conventional SEM images. The alkaline treatment induces formation of porous iron oxides, which were also prepared from scorodite by a similar alkaline treatment [23].

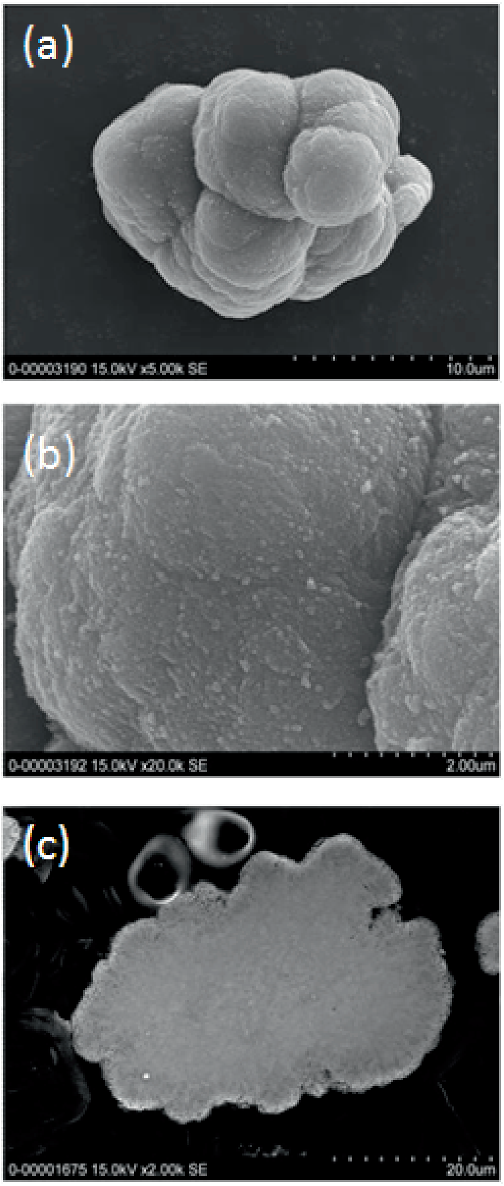

Figure 4. SEM images of solid particles obtained by alkaline treatment, observed at (a) low magnification and (b) high magnification; (c) particles cross-section.

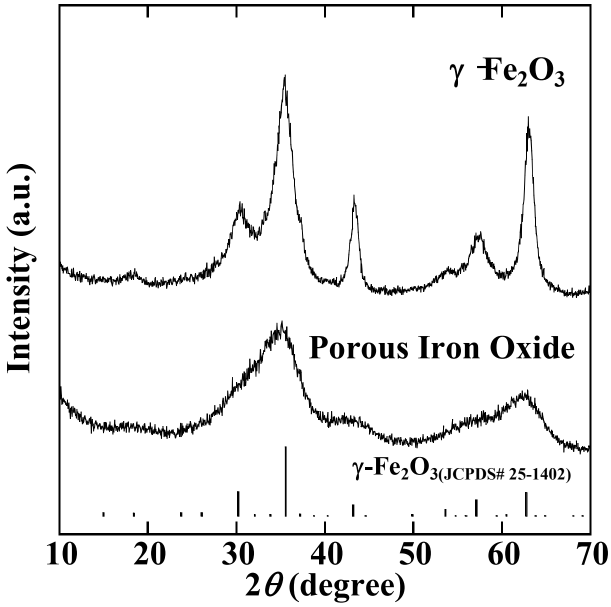

Figure 5. XRD patterns of solid particles obtained by alkaline treatment and of γ-Fe_2O_3 particles obtained by heating γ-FeOOH particles at 523 K.

Figure 5 shows the XRD pattern of the porous iron oxide particles obtained by alkaline treatment, together with the XRD pattern of the γ-Fe_2O_3 particles obtained by heating γ-FeOOH particles. The diffraction peaks of the γ-Fe_2O_3 particles are fairly consistent with the γ-Fe_2O_3 reference data. The broad XRD peaks of the porous iron oxide particles suggest that these particles have a similar structure to that of γ-Fe_2O_3, but the crystallite size is very small. The broadening of the XRD peaks may be caused by formation of pores, induced by the alkaline treatment. The ideal γ-Fe_2O_3 structure is the spinel structure (AB_2O_4: A is a tetrahedral site, B is an octahedral site, and O is an oxygen site), so the broad XRD peaks of the present porous iron oxides indicate that the structure contains a lot of defects. Therefore, the local structure of the porous iron oxide particles prepared by alkaline treatment was characterized using EXAFS measurements.

4.1 Local Structure of Solid Particles Obtained by Alkaline Treatment

Figure 6 shows the k^3-weighted EXAFS spectra, $k^3\chi(k)$, at the Fe K absorption edge for the porous iron oxide particles obtained by alkaline treatment, γ-Fe_2O_3 particles prepared from γ-FeOOH, and reference α-Fe_2O_3 particles. The shape of the EXAFS spectrum for the porous iron oxide particles is quite similar to that of γ-Fe_2O_3, but it is quite different from that of α-Fe_2O_3, which has a different structure. These EXAFS spectra and broad XRD peaks suggest that the local structure of the resulting porous iron oxide particles is fairy analogous to that of γ-Fe_2O_3, but that the structure contains a lot of defects. Such a defective porous iron oxide particles structure may be formed by the removal of phosphorus atoms in the phosphosiderite structure (Figure 4) during the alkaline treatment, although the pore-formation processes in the iron oxide particles are still unclear. In order to investigate the porosity of the present iron oxides and the adsorption characteristics of As onto the porous iron oxide, As adsorption tests were conducted.

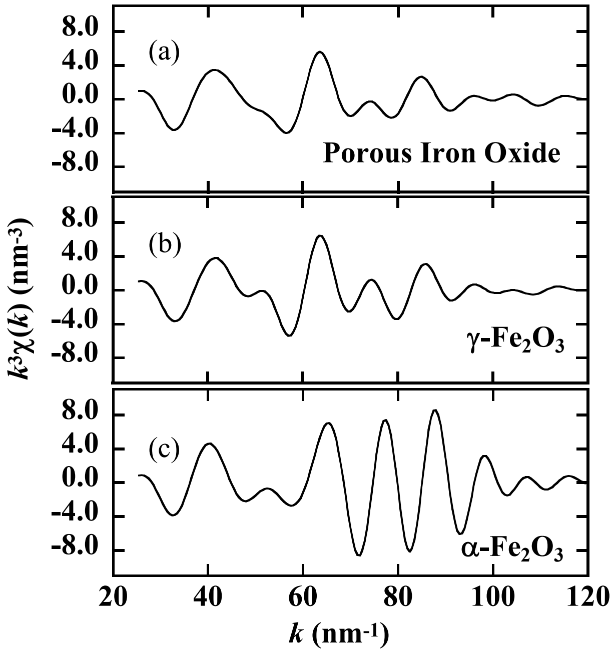

Figure 6. EXAFS spectra at Fe K absorption edge of (a) large porous iron oxide particles obtained from phosphosiderite by alkaline treatment, (b) γ-Fe_2O_3 particles prepared from γ-FeOOH, and (c) reference α-Fe_2O_3 particles.

4.2 Characteristics of As Adsorption Onto Porous Iron Oxide Obtained by Alkaline Treatment

A small amount of the porous iron oxide particles or of γ-Fe_2O_3 prepared from γ-FeOOH was immersed in an aqueous solution containing As. The amount of immersed iron oxide was 1 g/L-H_2O. The As concentration in the solution was 100 mg/L-H_2O, and the pH was three. Figure 7 shows the residual As concentration in the solution versus time after immersion of the porous iron oxide particles and γ-Fe_2O_3 particles in the stirred aqueous solution. The As concentration in the solution decreases with time, indicating that As in the solution was adsorbed onto the surface of these iron oxides. The decrease in the As concentration is larger for the porous iron oxide particles than for γ-Fe_2O_3 particles. The As adsorption capacity of the porous iron oxide particles is about three times higher than that of the γ-Fe_2O_3 particles. The filterability was also high for the porous iron oxides particles, although a quantitative evaluation needs to be performed.

The present results for As adsorption characteristics indicate that the large porous iron oxide particles prepared in the present study are useful as an As adsorbent, although many process parameters should be evaluated to clarify the adsorption characteristics of As under different conditions. It has been shown so far that parameters such as the pH, the As concentration in the water, and the surface area of the adsorbent are important in characterizing the adsorption of As onto iron oxides [3,9]. The results showed that the chemical state of As is important in adsorption onto iron oxide in water. The adsorption of As(III) as well as of As(V) onto iron oxides has been studied using As K EXAFS measurements [9], and the As(III) and As(V) adsorption sites on different iron oxides have been considered. In future studies, these parameters of the particles and aqueous solution should be investigated for the porous iron oxide particles prepared by the present method.

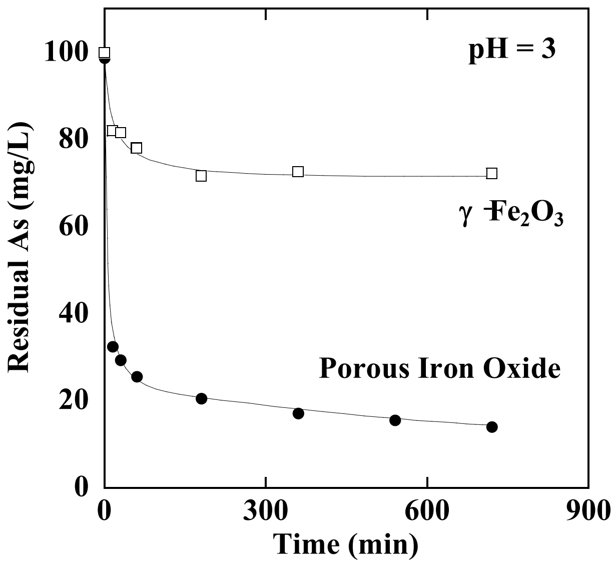

Figure 7. The As concentration in an aqueous solution of pH 3 versus time after immersion of porous iron oxide particles or γ-Fe_2O_3 particles in the solution. The As concentration decreases as a result of As adsorption onto the particles.

5 Concluding Remarks

A novel method has been developed for the synthesis of large porous particles of iron oxide. SEM observations and XRD and EXAFS measurements were used to characterize the large particles coprecipitated from Fe(II) and P(V) aqueous solutions, and the iron oxide particles prepared from these large particles by alkaline treatment were also characterized. The main results are as follows:

(i) SEM and XRD results showed that large particles of phosphosiderite ($FePO_4 \cdot 2H_2O$) were prepared by coprecipitation from Fe(II) and P(V) aqueous solutions by oxygen injection at about 368 K. The porous particles of iron oxide were large enough to exhibit high filterability from water.

(ii) XRD patterns showed that large porous particles of iron oxide were obtained by removing phosphorus in the phosphosiderite particles in an alkaline solution. EXAFS spectra in the range of the Fe K absorption edge indicated that the porous particles had a local structure similar to that of γ-Fe_2O_3.

(iii) The amount of As adsorbed onto the porous particles of iron oxide in aqueous solution was higher than the amount of As adsorbed onto γ-Fe_2O_3 particles prepared from γ-FeOOH. The results showed that the porous particles of iron oxide prepared from large phosphosiderite particles had superior As adsorption characteristics in water compared to those of γ-Fe_2O_3 particles.

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