Synthesis of β -type Strontium Hydrogen Phosphate Nanosheets and Its Immobilization of Pb^{2+} in Acidic Aqueous Solution

Fu-Qiang Zhuang · Rui-Qin Tan · Wen-Feng Shen · Xian-Peng Zhang · Wei Xu · Wei-Jie Song

Received: 30 May 2014/Revised: 31 July 2014/Published online: 21 January 2015
© The Chinese Society for Metals and Springer-Verlag Berlin Heidelberg 2015

Abstract Highly crystalline β -type strontium hydrogen phosphate (β -SrHPO₄) nanosheets were prepared by a hydrothermal method and used for the immobilization of lead ions (Pb^{2+}) from acidic aqueous solution. The effects of various parameters on the immobilization process, including solution pH value, contact time, initial ion concentrations, and coexistent competing cations, were studied to optimize the conditions for maximum immobilization. The β -SrHPO₄ nanosheets exhibited a capacity of $(1,120 \pm 22)$ mg/g toward Pb^{2+} in acidic solution (pH value is 3.0), and the equilibrium was achieved within 8 min. The competing cations such as Cu^{2+} , Zn^{2+} , Cd^{2+} , and Co^{2+} affected slightly on the selective immobilization of Pb^{2+} . The results revealed that the removal mechanism of Pb^{2+} by the β -SrHPO₄ nanosheets was the dissolution/precipitation process in the acidic solution.

KEY WORDS: Strontium hydrogen phosphate; Nanosheets; Immobilization; Lead ions; Dissolution/precipitation

1 Introduction

Water quality control is one of the major challenges that humanity is facing in the twenty-first century. Toxic heavy metal ions are mainly released from mining operations and lead acid battery production industry. It is well known that heavy metal ion pollution will cause severe health problems in animals and human beings even at a low concentration because of its degradation and bioaccumulation in the food chain [1, 2]. The removal of heavy metal ions from aqueous solution has attracted much attention

during the past decades. A lot of materials have been developed to remove heavy metal ions from the wastewater such as mesoporous materials [3], activated carbon [4], chitosan [5], and iron-based hybrid materials [6]. However, the capacity and selectivity for the removal of Pb^{2+} need to be further improved, especially in a highly acidic wastewater with large amount of competing cations.

Strontium hydrogen phosphate (SrHPO₄), an important inorganic and biomaterial, has been claimed as a catalyst, proton conductor, and surface conditioner as well as for application in batteries, fuel cells, flame proofing, and thermal cathodes [7, 8]. In the clinical application, Sr^{2+} could stimulate bone formation effectively and inhibit bone resorption [9]. Guo et al. [10] synthesized Sr^{2+} -substituted calcium phosphate bone cements by substitution of calcium hydrogen phosphate by strontium. Knowledge of the crystal structures of the dibasic phosphates of calcium and strontium is in a similar state [11]. Recently, Minh et al. [12] reported that monetite with higher solubility and solids with HPO_4^{2-} surface groups were more active than dehydrated calcium hydroxyapatite for the fixation of Pb^{2+} .

Available online at <http://link.springer.com/journal/40195>

F.-Q. Zhuang · R.-Q. Tan (✉)
Faculty of Electrical Engineering and Computer Science, Ningbo University, Ningbo 315211, China
e-mail: tanruiqin@nbu.edu.cn

W.-F. Shen · X.-P. Zhang · W. Xu · W.-J. Song
Ningbo Institute of Material Technology and Engineering,
Chinese Academy of Sciences, Ningbo 315201, China

However, no works have been reported on the immobilization of Pb^{2+} using SrHPO_4 .

In this work, the synthesis of β - SrHPO_4 nanosheets and their applications in the immobilization of Pb^{2+} in highly acidic aqueous solution were reported. The effects of various parameters on the immobilization process such as the solution pH, the contact time, the initial ion concentrations, and coexisting cations have been investigated. The removal mechanism of Pb^{2+} by the β - SrHPO_4 nanosheets was also discussed.

2 Experimental Methods

2.1 Reagents

Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$), hexadecyl trimethyl ammonium bromide (CTAB), diammonium phosphate ($(\text{NH}_4)_2\text{HPO}_4$), and other reagents ($\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. (China) with analytical grade. All chemicals were used as received without further purification, and all solutions were prepared with deionized water.

2.2 Materials Preparation

The SrHPO_4 nanosheets were prepared by a hydrothermal method. Firstly, solution A was prepared by dissolving $\text{Sr}(\text{NO}_3)_2$ (6.3 g) and CTAB (0.036 g) in 40 mL deionized water under mechanical stirring for 20 min. Secondly, solution B was prepared by dissolving $(\text{NH}_4)_2\text{HPO}_4$ (3.3 g) in 20 mL deionized water. Solution B was added into solution A under vigorous mechanical stirring for 20 min. The mixture was then kept in a stainless steel autoclave at 90 °C for 6 h. After then, it was kept in the room temperature for 12 h. Finally, the obtained white powders were filtered, washed three times with deionized water and two times with ethanol, and dried in a vacuum oven at 60 °C for 8 h.

2.3 Characterization

The structure of the samples was characterized by an X-ray diffractometer (Bruker AXS D8) using monochromatized CuK_α radiation ($\lambda = 1.5406$ nm) with a step rate of 0.02°/s over the range of 2θ from 10° to 70°. The morphology of samples was characterized by field emission transmission electron microscope (FE-TEM, Model Tecnai F20, FEI) and field emission scanning electron microscope (FE-SEM, Hitachi S-4800). Batch experiments of Pb^{2+} immobilization were analyzed using an inductively coupled plasma

atomic emission spectrometry (ICP-AES, Optima 2100, PerkinElmer) at room temperature.

2.4 Immobilization Experiments

In order to investigate the immobilization behavior and capacity of the prepared SrHPO_4 nanosheets toward Pb^{2+} , batch experiments of Pb^{2+} immobilization were carried out. Standard 0.1 mol/L HNO_3 and 0.1 mol/L NaOH solutions were used to adjust the desired pH value. The effect of pH value (2.0–6.0) on the Pb^{2+} immobilization was investigated by adding 50 mg SrHPO_4 into 50 mL Pb^{2+} solution with an initial stock concentration of 2,000 mg/L under stirring for 1 h. The immobilization kinetics (time ranging from 0 to 60 min, initial concentration of 2,000 mg/L) and isotherms were studied by adding the same amount of SrHPO_4 into the Pb^{2+} solutions with different concentrations at pH value of 3.0. The supernatant of the suspension was analyzed by an ICP-AES at room temperature. Furthermore, we obtained the Pb^{2+} solutions containing the possible interferential ions (Cu^{2+} , Zn^{2+} , Cd^{2+} and Co^{2+}) by dissolving the corresponding nitrates (1 mmol/L for all ions) at pH value of 3.0 to investigate the effects of coexisting cations on Pb^{2+} immobilization. The removal rate was calculated as follows.

$$R_{\text{cr}} = \frac{C_0 - C_e}{C_0} \times 100\%, \quad (1)$$

where R_{cr} is the immobilization ratio of Pb^{2+} by the prepared nanosheets, C_0 (mg/L) is the initial concentrations of Pb^{2+} in solution, C_e (mg/L) is the equilibrium concentrations Pb^{2+} after immobilization.

3 Results and Discussion

3.1 Microstructure of β - SrHPO_4 Nanosheets

Figure 1a shows the XRD pattern of the as-synthesized powders. All the peaks were consistent with the standard data of β -type SrHPO_4 (JCPDS card No. 12-0368), indicating that the obtained sample had a pure hexagonal crystal structure [7]. The SEM images (Fig. 1b, c) show that the obtained sample was composed of nanosheets, which self-assembled as flower-like spherical particles with an average size of 20 μm . Figure 1d shows the TEM image of the obtained square nanosheets with a non-uniform size over 100 nm.

3.2 Effects of pH Value on Pb^{2+} Immobilization

Heavy metal ions in wastewater are normally concentrated in a strongly acidic region. In this work, the solution pH value was chosen from 2.0 to 6.0 with an increment of 1.0.

Fig. 1 Characterization of the pristine β -SrHPO₄ nanosheets: **a** XRD pattern; **b**, **c** SEM images; **d** TEM image

The effects of pH value on the removal of Pb²⁺ were studied when the dosage of β -SrHPO₄ (50 mg), the concentration of Pb²⁺ (9.66 mmol/L), and the reaction time (60 min) were kept constant. Figure 2 shows the effect of initial pH on the uptake capacity of Pb²⁺ and the amount of released Sr²⁺ by β -SrHPO₄ nanosheets. When the solution pH value was 2.0, the amount of released Sr²⁺ was much higher than the amount of Pb²⁺ fixed because of the dissolution of the β -SrHPO₄. The metal uptake capacity increased sharply when the pH value varied from 2.0 to 3.0. The capacity changed slowly followed by the amount of released Sr²⁺ remaining relatively stable when the pH increased gradually from 3.0 to 6.0. We proposed that the dissolution of β -SrHPO₄ and precipitation of lead hydrogen phosphate is the primary mechanism for Pb²⁺ removal [13]. The capacity reached about 5.92 mmol/g [(1,225 ± 20) mg/g] at pH value of 6.0. It was demonstrated that the optimum pH value for Pb²⁺ immobilization by the β -SrHPO₄ was 3.0. The pH value of 3.0 was thus selected for further studies.

Fig. 2 Effect of pH value on the uptake of Pb²⁺ by β -SrHPO₄ nanosheets

3.2.1 Kinetics and Isotherm of Pb²⁺ Immobilization by the β -SrHPO₄ Nanosheets

The effect of contact time on Pb²⁺ immobilization was studied using the solution with a concentration of 2,000 mg/L. Figure 3a shows the kinetics immobilization

Fig. 3 Immobilization curves of Pb^{2+} immobilized on 50 mg $\beta\text{-SrHPO}_4$ nanosheets in 50 mL Pb^{2+} solution at 30 °C and pH value of 3.0: **a** kinetics curve, start concentration of Pb^{2+} is 2,000 mg/L; **b** isotherm curve, time is 60 min

Table 1 Comparison of Pb^{2+} removal capacity using $\beta\text{-SrHPO}_4$ nanosheets with that of other materials

Materials	q_{max} (mg/g)	pH value	Ref.
Carbonate hydroxyapatite	101	5.0	[14]
Natural phosphate/activated phosphate	115.34/ 155.04	3.0	[15]
Low-crystallinity hydroxyapatite	506	5.8	[16]
Ca-HA	750	5.0–6.0	[17]
Calcium hydroxyapatite (HAp)	450	3.0–5.0	[18]
Keratin colloidal solution,	43.3	5.0	[19]
Hydroxyapatite	357.14	6.0	[20]
$\beta\text{-SrHPO}_4$	1,120	3.0	This work

curves of Pb^{2+} immobilized on 50 mg $\beta\text{-SrHPO}_4$ nanosheets in 50 mL Pb^{2+} solution at 30 °C and pH value of 3.0. It is found that the equilibrium reached within 8 min, which is more expeditious than other reference materials [14, 15]. Figure 3b shows the isotherm curve of Pb^{2+} immobilized on 50 mg $\beta\text{-SrHPO}_4$ nanosheets for 60 min in 50 mL Pb^{2+} solution at 30 °C and pH value of 3.0. From Fig. 3b, it can be obtained that the maximum immobilization capacity of $\beta\text{-SrHPO}_4$ nanosheets for Pb^{2+} is $(1,120 \pm 22)$ mg/g at pH value of 3.0. Table 1 shows the comparison of the maximum capacity (q_{max}) of the synthesized $\beta\text{-SrHPO}_4$ nanosheets together with the results that are reported in Refs. [14–20], which reveals that the $\beta\text{-SrHPO}_4$ nanosheets has the advantage over other materials in term of metal uptake capacity. From the results of Pb^{2+} removal, we observe that SrHPO_4 was more active than hydroxyapatite (HAp). The reaction of SrHPO_4 nanosheets with Pb^{2+} in the solution to form precipitation and release free Sr^{2+} was considered as a biphasic liquid–solid reaction. This reaction is favorable when acidic orthophosphate species are more available in the reaction medium [12]. Thus, SrHPO_4 with higher solubility and solids with

HPO_4^{2-} surface groups compared with HAp are more active for the immobilization of Pb^{2+} .

3.3 Effect of Coexisting Cations on Pb^{2+} Removal

The effects of cations such as Cu^{2+} , Zn^{2+} , Cd^{2+} , and Co^{2+} on the immobilization of Pb^{2+} were studied, which may deteriorate the uptake capability of Pb^{2+} , as shown in Fig. 4. When only Pb^{2+} was contained in the solution, obviously, the removal percentage of Pb^{2+} was nearly up to 100% without any coexisting cations. By contrast, the $\beta\text{-SrHPO}_4$ nanosheets had small immobilization capacities towards other coexisting ions. In the bi-systems of $\text{Pb}^{2+} + \text{Cu}^{2+}$, $\text{Pb}^{2+} + \text{Zn}^{2+}$, $\text{Pb}^{2+} + \text{Cd}^{2+}$, and $\text{Pb}^{2+} + \text{Co}^{2+}$, little difference of the uptake capacity towards Pb^{2+} was observed.

It is suggested that the high removal efficiency and selectivity towards Pb^{2+} by $\beta\text{-SrHPO}_4$ are resulted from the similar ionic radii of Pb^{2+} (0.149 nm) and Sr^{2+} (0.145 nm) [21]. On the other hand, the electronegativity of Pb^{2+} (1.8) is much larger than that of Sr^{2+} (1.0), which leads to the preferential uptake towards Pb^{2+} [22]. It was also reported that the stability of the final product played an important role in the selectivity of immobilization. The lead phosphate precipitate after immobilization is more stable than other metal phosphates, which in turn leads to the reasonable selectivity of $\beta\text{-SrHPO}_4$ towards Pb^{2+} [23, 24].

3.4 Mechanism of Immobilization of Pb^{2+} Ions

SEM images and EDX results of the solids after the treatment of the acidic solutions (Fig. 5a, b) show that the precipitation is consisted of rhombic crystals (about 15 μm in diagonal) and bright needles (about 3–5 μm in length). The EDX analysis revealed that the ratio of lead in the needles was about 13.57%, larger than that of rhombic crystals (10.45%). Figure 5c shows the XRD results of the final solids after treating the solution with a Pb^{2+}

Fig. 4 Effects of coexisting ions on the uptake of Pb²⁺ by β -SrHPO₄ nanosheets

concentration of 2,000 mg/L using the synthesized β -SrHPO₄. It revealed that the precipitation was a mixture of lead hydrogen phosphate (PbHPO₄) and PbHAp.

Most researchers proposed that the dissolution of apatite [25–27] can release phosphate anions for the subsequent precipitation of the new solid phases which present lower solubility and hence increase the stability of the immobilization process. For the same principle, the dissolution of β -SrHPO₄ also provides the phosphate anions, which are available for the subsequent precipitation of Pb²⁺ from aqueous solution. Aia *et al.* [28] reported that the theoretical solubility (K_{sp} , i.e. $-\log K_{sp}$) of crystalline β -SrHPO₄ was about 7.14 at pH value of 3.0. In this study, when the β -SrHPO₄ nanosheets were added into the solution with pH value of 3.0, some amount of β -SrHPO₄ dissolved and converted to PbHPO₄. The process of dissolution of β -SrHPO₄ and precipitation of PbHPO₄ can be described as

$$\text{SrHPO}_4(\text{solid}) + \text{aq} \rightleftharpoons \text{Sr}^{2+}(\text{aq}) + \text{HPO}_4^{2-}(\text{aq}), \quad (2)$$

On the other hand, H₂PO₄[−] phosphate species also exist in the acidic condition. The immobilization process with

Fig. 6 Evolution of pH value during Pb²⁺ immobilization by β -SrHPO₄ nanosheets

H₂PO₄[−] species could be expressed as the following chemical reactions of Eq. (4) and Eq. (5).

The above hypothesis is supported by the continuous monitoring of pH during the adsorption process (Fig. 6). The pH value of solution slightly increased to 3.1 at the first few seconds of immobilization process, which resulted from the dissolution of the as-synthesized β -SrHPO₄ nanosheets. After 5–6 min, the pH value decreased and kept constant at about 2.76 after the lead precipitation reached the equilibrium.

In view of the similar theoretical solubility of β -SrHPO₄ in the solution with pH value of 3.0–6.0 at 25 °C [28], it is supposed that the precipitation of Pb²⁺ followed the same mechanisms as mentioned above. This hypothesis was confirmed by the fact that the amount of Sr²⁺ released was almost the same as that of Pb²⁺ immobilized when pH

Fig. 5 Characterization of the precipitation after Pb²⁺ immobilization experiments: **a** SEM images; **b** EDX result; **c** XRD pattern

value is 3.0–6.0 (Fig. 2). The shift of pH value to more acidic conditions is favorable to the formation of PbHPO_4 while the precipitation of PbHAp is suppressed [29]. This resulted in a dramatic decrease in the Pb^{2+} removal when the pH value of the solution was as low as 2.0.

In the present study, the mechanism of lead immobilization by $\beta\text{-SrHPO}_4$ was made up of two co-current processes including: (I) the dissolution of phosphate in the acidic conditions; (II) the formation of new solid phases (PbHPO_4 , PbHAp) and subsequent precipitation.

4 Conclusions

In summary, the environmental-friendly $\beta\text{-SrHPO}_4$ nanosheets were successfully synthesized by a hydrothermal method, which could effectively remove Pb^{2+} from acidic aqueous solution. The immobilization capacity towards Pb^{2+} reached $(1,120 \pm 22)$ mg/g at pH value of 3.0. Coexistent cations such as Cu^{2+} , Zn^{2+} , Cd^{2+} and Co^{2+} had little effect on the immobilization of Pb^{2+} . The immobilization of Pb^{2+} ions by the $\beta\text{-SrHPO}_4$ nanosheets was due to dissolution/precipitation process in acidic solution. It suggested that the $\beta\text{-SrHPO}_4$ is a promising material for Pb^{2+} purification in the actual wastewater.

Acknowledgments This work was financially supported by the National Natural Science Foundation of China (No. 21377063) and K.C. Wong Magna Fund in Ningbo University.

References

- [1] R.P. Schwarzenbach, T. Egli, T.B. Hofstetter, U. Von Gunten, B. Wehrli, *Annu. Rev. Environ. Resour.* **35**, 109 (2010)
- [2] Y.Z. Lan, S. Zhang, J.K. Wang, R.W. Smith, *Acta Metall. Sin. (Engl. Lett.)* **19**, 449 (2006)
- [3] H. Javadian, M. Ghaemy, M. Taghavi, *J. Mater. Sci.* **49**, 232 (2014)
- [4] K. Pyrzyńska, M. Bystrzejewski, *Colloids Surf. A* **362**, 102 (2010)
- [5] S. Chatterjee, S. Chatterjee, B.P. Chatterjee, A.K. Guha, *Colloids Surf. A* **299**, 146 (2007)
- [6] D. Kołodziejka, M. Kowalczyk, Z. Hubicki, *J. Mater. Sci.* **49**, 2483 (2014)
- [7] M. Roming, C. Feldmann, *J. Mater. Sci.* **43**, 5504 (2008)
- [8] M. Dinamani, P.V. Kamath, *Mater. Res. Bull.* **36**, 2043 (2001)
- [9] M. Schumacher, A. Henss, M. Rohnke, M. Gelinsky, *Acta Biomater.* **9**, 7536 (2013)
- [10] D. Guo, M. Mao, W. Qi, H. Li, P. Ni, G. Gao, K. Xu, *J. Mater. Sci. Mater. Med.* **22**, 2631 (2011)
- [11] R.W. Mooney, M.A. Aia, C.W.W. Hoffman, R.C. Ropp, *J. Am. Chem. Soc.* **81**, 826 (1959)
- [12] D.P. Minh, N.D. Tran, A. Nzihou, P. Sharrock, *Chem. Eng. J.* **243**, 280 (2014)
- [13] Q.Y. Ma, T.J. Logan, S.J. Traina, *Environ. Sci. Technol.* **29**, 1118 (1995)
- [14] D. Liao, W. Zheng, X. Li, Q. Yang, X. Yue, L. Guo, G. Zeng, *J. Hazard. Mater.* **177**, 126 (2010)
- [15] M. Mouflih, A. Aklil, S. Sebt, *J. Hazard. Mater.* **119**, 183 (2005)
- [16] T. Sasaki, Y. Sakai, A. Iizuka, T. Nakae, S. Kato, T. Kojima, A. Yamasaki, *Ind. Eng. Chem. Res.* **50**, 9564 (2011)
- [17] D.P. Minh, N.D. Tran, A. Nzihou, P. Sharrock, *Chem. Eng. J.* **232**, 128 (2013)
- [18] B. Sandrine, N. Ange, B.A. Didier, C. Eric, S. Patrick, *J. Hazard. Mater.* **139**, 443 (2007)
- [19] Y. Sekimoto, T. Okiharu, H. Nakajima, T. Fujii, K. Shirai, H. Moriwaki, *Environ. Sci. Pollut. Res.* **20**, 6531 (2013)
- [20] S. Ramesh, N. Rameshbabu, R. Gandhimathi, M.S. Kumar, P.V. Nidheesh, *Appl. Water. Sci.* **3**, 105 (2013)
- [21] R.D. Shannon, *Acta Crystallogr. Sect. A* **32**, 751 (1976)
- [22] K. Zhu, K. Yanagisawa, R. Shimanouchi, A. Onda, K. Kajiyo-shi, J. Qiu, *Mater. Res. Bull.* **44**, 1392 (2009)
- [23] B.C. Pan, Q.R. Zhang, W. Du, W. Zhang, B. Pan, Q. Zhang, Q. Zhang, *Water Res.* **41**, 3103 (2007)
- [24] Z.Z. Zhang, M.Y. Li, W. Chen, S. Zhu, N. Liu, L. Zhu, *Environ. Pollut.* **158**, 514 (2010)
- [25] Q.Y. Ma, S.J. Traina, T.J. Logan, J.A. Ryan, *Sci. Technol.* **27**, 1803 (1993)
- [26] H.Y. Xu, L. Yang, P. Wang, Y. Liu, M. Peng, *J. Environ. Manag.* **86**, 319 (2008)
- [27] X.Y. Zhao, Y.J. Zhu, J. Zhao, B.Q. Lu, F. Chen, C. Qi, J. Wu, *J. Colloid Interface Sci.* **416**, 11 (2014)
- [28] M. Aia, J. Mathers, R. Mooney, *J. Chem. Eng. Data* **9**, 335 (1964)
- [29] S. Sugiyama, T. Ichii, M. Fujii, M. Fujisawa, K. Kawashiro, H. Hayashi, *Inorg. Chem. Commun.* **5**, 606 (2002)