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## The synthesis of calcium arsenate@iron arsenate coating materials and their application for arsenic-containing wastewater treatment†

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The current method of treating arsenic-containing wastewater is mainly to use a calcium method to synthesize stable calcium arsenate. It is easy to cause reverse dissolution by rain or other erosion, releasing arsenic into the natural world and polluting soil and groundwater. So, calcium arsenate is not an ideal material for removing and immobilizing arsenic. Iron arsenate ( $\text{FeAsO}_4$ ) is much better than calcium arsenate because of its stability and acid resistance. In this study, calcium arsenate@iron arsenate coating materials were synthesized. From the results of the XRD and SEM analyses, it was shown that calcium arsenate was coated by an iron arsenate shell which consisted of nanoparticles. The stability of the coating materials was determined using the Toxicity Characteristic Leaching Procedure (TCLP). The results showed that the concentrations of As for  $\text{CaHAsO}_4$  and  $\text{Ca}_3(\text{AsO}_4)_2$  were  $744 \text{ mg L}^{-1}$  and  $302.2 \text{ mg L}^{-1}$ , respectively. Arsenic was not detected through the TCLP tests for  $\text{CaHAsO}_4@FeAsO_4$  and  $\text{Ca}_3(\text{AsO}_4)_2@FeAsO_4$  coating materials, and the best coating condition was confirmed to be an Fe/As molar ratio of 4 : 1, pH of 4, and temperature of 50 °C. The stability of the materials showed a significant improvement. The results indicated that calcium arsenate materials could be converted to coating materials by using ferric salts. The coating materials had excellent stability in an aqueous solution. Thus, the coating was suitable for the removal and immobilization of arsenic in industrial applications. This work provided a new way to treat arsenic-containing wastewater, which was simple and economical. This method has potential for use in the field of wastewater treatment containing arsenic.

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### 1. Introduction

At present, the most common method for removing and immobilizing arsenic in industrial applications is the calcium arsenate ( $\text{Ca}_3(\text{AsO}_4)_2$ ) precipitation method.<sup>1–3</sup> The arsenic-containing wastewater is treated by using calcium oxide or calcium hydroxide to form a calcium arsenate precipitate.<sup>4</sup> However, calcium arsenate is not stable, it easily reacts with carbon dioxide in the air and cannot exist stably in nature for very long.<sup>5</sup> It is easy for reverse dissolution to occur from rain or other erosion, releasing arsenic into the natural world and polluting soil and groundwater.<sup>6</sup> So calcium arsenate is not an ideal material for removing and immobilizing arsenic. The calcium arsenate can be stabilized using a treatment to make it more stable overall and resist external erosion.<sup>7</sup> This is the best way to retain the economic advantages of calcium arsenate and avoid secondary pollution. Using iron arsenate ( $\text{FeAsO}_4$ ) is

much better than using calcium arsenate because of its stability and acid resistance.<sup>8–10</sup> It is also used to remove and immobilize arsenic.<sup>11</sup> However, the cost of the calcium salt to treat arsenic-containing wastewater is much lower than the iron salt. So most non-ferrous metal smelting companies choose the calcium arsenate method.<sup>12</sup> However, iron arsenate has obvious advantages in terms of the efficiency of arsenic removal and the safety of arsenic.<sup>13</sup> The solubility of iron arsenate ( $K_{\text{sp}} = 10^{-21}$  to  $10^{-24}$ ) is about 1 million times smaller than that of calcium arsenate ( $K_{\text{sp}} = 10^{-18}$  to  $10^{-21}$ ) in water.<sup>14,15</sup> Calcium arsenate can react with carbon dioxide to produce calcium carbonate and water-soluble arsenic acid, resulting in the re-dissolution of arsenic.<sup>16</sup> In this study, the advantages and disadvantages of these two arsenates are considered. The calcium arsenate is stabilized using treatment with ferric chloride. In this research, the iron arsenate is synthesized and then calcium arsenate is coated with the synthesized iron arsenate. The iron–arsenic ratio is studied to achieve the best stabilization of calcium arsenate. Calcium hydrogen arsenate ( $\text{CaHAsO}_4$ ) and calcium arsenate ( $\text{Ca}_3(\text{AsO}_4)_2$ ) are the two most common calcium arsenate phases. In this research, they are synthesized and coated with iron arsenate. The Fe/As ratio, reaction time and pH are studied for the stabilization of the calcium arsenate. Furthermore, the stability of the synthesized samples was measured

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using the Toxicity Characteristic Leaching Procedure (TCLP), and its application properties were also evaluated.<sup>17</sup>

## 2. Material and methods

### 2.1 Reagents

Leaching liquid of smelting dust was used as the As(v) source. The components of the dust and leaching liquid are shown in Table 1. Analytical reagent grade calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) was used as the calcium source. Analytical reagent grade ferric chloride ( $\text{FeCl}_3$ ) was used as the iron source. Analytical reagent grade nitric acid ( $\text{HNO}_3$ ), and sodium hydroxide ( $\text{NaOH}$ ) were used only for pH adjustment.

### 2.2 Calcium arsenate synthesis

A portion of arsenic-containing solution (800 mL) was taken and the pH value was adjusted to 5 using  $\text{NaOH}$ . Next, 0.75 mol of  $\text{Ca}(\text{OH})_2$  was dissolved ultrasonically in 200 mL of deionized water. To obtain a  $\text{Ca}(\text{OH})_2$  suspension, the pH value of the  $\text{Ca}(\text{OH})_2$  solution was adjusted to 5 using  $\text{HNO}_3$ . Then, the  $\text{Ca}(\text{OH})_2$  suspension was poured into the arsenic-containing solution, and the pH was adjusted to 5 with stirring. The reaction was maintained at 50 °C for 24 h. Finally, the product was washed, with suction, and dried at 60 °C. The product was named sample 1.

The synthesis process of sample 2 was same as for sample 1 except the reaction pH value was 10.

Sample 1 or sample 2 was dispersed in deionized water. A certain amount of  $\text{FeCl}_3$  was added into the solution and then dissolved. The Fe/As molar ratios were 0.5 : 1, 1 : 1, 2 : 1, 3 : 1, 4 : 1, and 5 : 1. Then the pH of solution was adjusted to 4, 6, 7, 8, 10, or 12 using  $\text{NaOH}$ , and the reaction was left to occur for 12 h at room temperature, with stirring. Finally, the precipitations were washed with deionized water and dried at 60 °C. The products obtained were stabilized calcium arsenate@iron arsenate coated samples.

### 2.3 Characterization

The morphology of the synthesized products were observed using field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan). The X-ray diffraction (XRD) patterns were collected using a diffraction instrument with  $\text{Cu K}\alpha$  radiation (Bruker D8, 40 kV, 40 mA).

### 2.4 Stability evaluation of the products

Leaching tests were conducted, to examine the leach ability of the precipitates, according to the Toxicity Characterization Leaching Procedure (TCLP) tests (EPA, 1994).<sup>17</sup> Glacial acetic acid (HAc, 5.7 mL) and  $\text{NaOH}$  solution (64.3 mL, 1 mol  $\text{L}^{-1}$ ) were

Table 1 Components of dust and leaching liquid

	As	K	Zn	Na	Pb
Dust (%)	46.8	0.9	0.7	0.4	14.7
Leaching liquid ( $\text{g L}^{-1}$ )	20.1	0.5	0.1	0.2	—

sequentially added to 500 mL of distilled water and then diluted to 1 L to give a pH of  $4.93 \pm 0.05$  to prepare the leaching agent.

The operating procedures of the leaching tests are briefly described here. The samples were each placed in PTFE bottles with extraction liquor at a liquid to solid (L/S) mass ratio of 20 : 1. The leaching tests were conducted for  $16 \pm 2$  h for the HAc solution. The temperature was maintained at 25 °C during the leaching tests. After leaching, the supernatant was collected using 0.8  $\mu\text{m}$  quantitative filter paper and the concentrations of arsenic and iron in the leaching solutions of the stability tests were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer Optima 5300 DV, USA). The determination wavelength of As was 188.98 nm, and the detection limit of As was 0.01 mg  $\text{L}^{-1}$ .

## 3. Results and discussion

### 3.1 Characterization of samples

The synthesized samples were identified by XRD. Fig. 1(a) shows that  $\text{CaHAsO}_4$  was synthesized successfully using the method of a previous report. As is known, the main peaks of scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ) are located at approximately 30.1°, 27.8°, 16.9° and 10.9°, which can be indexed as the (221), (220), (101) and (020) lattice planes of scorodite (JCPDS no. 18-0288), respectively.<sup>18</sup> The diffraction peak intensity was strong, and the  $\text{CaHAsO}_4$  had excellent crystallinity. Fig. 1(b) shows that  $\text{Ca}_3(\text{AsO}_4)_2$  was synthesized successfully by the method of the previous report. As is known, the main peaks of scorodite located at approximately 30.8° and 31.7°, can be indexed as the (020) and (021) lattice planes of  $\text{Ca}_3(\text{AsO}_4)_2$  (JCPDS no. 01-0933).<sup>19</sup> Sample 1 and sample 2 were the two most common calcium arsenate phases in the arsenic-containing wastewater treatment.

### 3.2 Analysis of calcium arsenate@iron arsenate coated samples

**3.2.1 Stability analysis of  $\text{CaHAsO}_4@\text{FeAsO}_4$ .** Fig. 2 shows the concentrations of arsenic found by TCLP test after sample 1 was treated by  $\text{FeCl}_3$  to give it stability. Because of the design of the experiment, the products should be  $\text{CaHAsO}_4@\text{FeAsO}_4$ , and the synthesized  $\text{CaHAsO}_4$  was coated by  $\text{FeAsO}_4$ . Fig. 2(a) shows the TCLP test results of the products which were reacted with different molar ratios of Fe/As at 25 °C. The concentration of arsenic was 744 mg  $\text{L}^{-1}$  without stability treatment. This indicated that  $\text{CaHAsO}_4$  was not stable in the solution. The concentrations of arsenic decreased when the Fe/As molar ratio was increased. The results indicated that the stability treatment by  $\text{FeCl}_3$  obviously increased the stability of  $\text{CaHAsO}_4$ . The concentrations of arsenic were 1.075 mg  $\text{L}^{-1}$  and 0.982 mg  $\text{L}^{-1}$  when the Fe/As molar ratios were 4 : 1 and 5 : 1, respectively. These two results were below the standard value of TCLP (1.5 mg  $\text{L}^{-1}$ ). 1.075 mg  $\text{L}^{-1}$  and 0.982 mg  $\text{L}^{-1}$  of the concentration were little difference. The reason for this was because the  $\text{CaHAsO}_4$  could be completely coated when the Fe/As molar ratio was more than 4 : 1, and then the  $\text{FeAsO}_4$  shell would prevent the continued reaction between the internal  $\text{CaHAsO}_4$  and the  $\text{FeCl}_3$  solution. However, it was more economical when



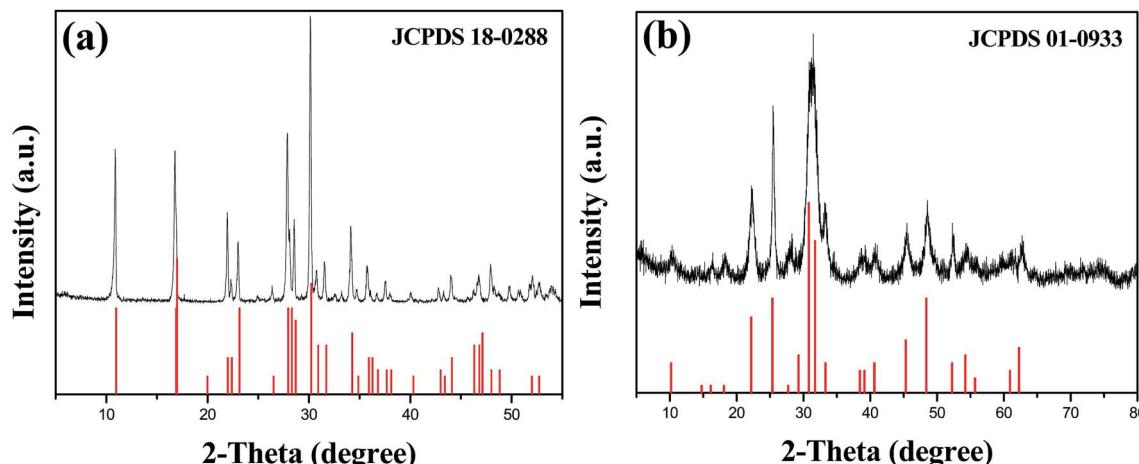


Fig. 1 The XRD patterns of (a) sample 1, (b) sample 2.

the Fe/As molar ratio was 4 : 1, so the best Fe/As molar ratio should be 4 : 1.

Fig. 2(b) shows the TCLP test results of products which were reacted at different pH values at 25 °C. The Fe/As molar ratio of the reaction was 4 : 1, and the reaction pH was 2. However, there was no precipitation because  $\text{CaHAsO}_4$  and  $\text{FeCl}_3$  were both dissolved completely when the pH was 2. The concentrations of arsenic obtained from the TCLP test increased when the pH value was 4 to 8. The reason for this was that  $\text{CaHAsO}_4$  could react with  $\text{Fe}^{3+}$  and the  $\text{FeAsO}_4$  shell formed when the solution was acidic. The concentrations of arsenic decreased when the pH value was 8 to 12. The reason for this was that  $\text{Fe}^{3+}$  would react with  $\text{OH}^-$  and form  $\text{Fe}(\text{OH})_3$  preferentially when the solution was alkaline, and so  $\text{FeAsO}_4$  could not form. So, the products were a  $\text{CaHAsO}_4/\text{Fe}(\text{OH})_3$  mixture. The solution of TCLP test was acetic acid solution ( $\text{HAc}$ ,  $\text{pH} = 4.93 \pm 0.05$ ). The  $\text{Fe}(\text{OH})_3$  reacted with  $\text{H}^+$  preferentially in the TCLP test, this caused the pH value of the TCLP solution to increase. The newly produced  $\text{Fe}^{3+}$  ions reacted with  $\text{CaHAsO}_4$  and formed  $\text{FeAsO}_4$ , and this process made the materials more stable. The best pH of the stability treatment was 4, and the concentration of arsenic was  $0.379 \text{ mg L}^{-1}$ .

Fig. 2(c) shows the TCLP test results of the products which were reacted at  $\text{pH} = 4$  at different temperatures. The Fe/As

molar ratio of the reaction was 4 : 1. The results indicated that the reaction rate increased as the temperature of the reaction increased. When the temperature was 50 °C, the  $\text{CaHAsO}_4$  could be coated perfectly by  $\text{FeAsO}_4$ . Arsenic was not detected by TCLP test.

**3.2.2 Stability analysis of  $\text{Ca}_3(\text{AsO}_4)_2@\text{FeAsO}_4$ .** Fig. 3 shows the concentrations of arsenic obtained by the TCLP test after sample 2 was stability treated with  $\text{FeCl}_3$ . Because of the design of the experiment, the products should be  $\text{Ca}_3(\text{AsO}_4)_2@\text{FeAsO}_4$ , as a result of the synthesized  $\text{Ca}_3(\text{AsO}_4)_2$  being coated by the  $\text{FeAsO}_4$ . Fig. 3(a) shows the TCLP test results of products which were reacted with different Fe/As molar ratios at 25 °C. The concentration of arsenic was  $302.2 \text{ mg L}^{-1}$  without stability treatment. This indicated that  $\text{Ca}_3(\text{AsO}_4)_2$  was not stable in the solution. This was the same as the results given in Section 3.2.1, and it indicated that the stability treatment could increase the stability of  $\text{Ca}_3(\text{AsO}_4)_2$ , and the best Fe/As molar ratio was 4 : 1.

Fig. 3(b) shows the TCLP test results of the products which were reacted at different pH values at 25 °C. The Fe/As molar ratio of reaction was 4 : 1 and the reaction pH was 2. However, there was no precipitation because  $\text{Ca}_3(\text{AsO}_4)_2$  and  $\text{FeCl}_3$  were both dissolved completely when the pH was 2. The concentrations of arsenic obtained from the TCLP test increased when the pH value was 4 to 8. The reason for this was same as for the

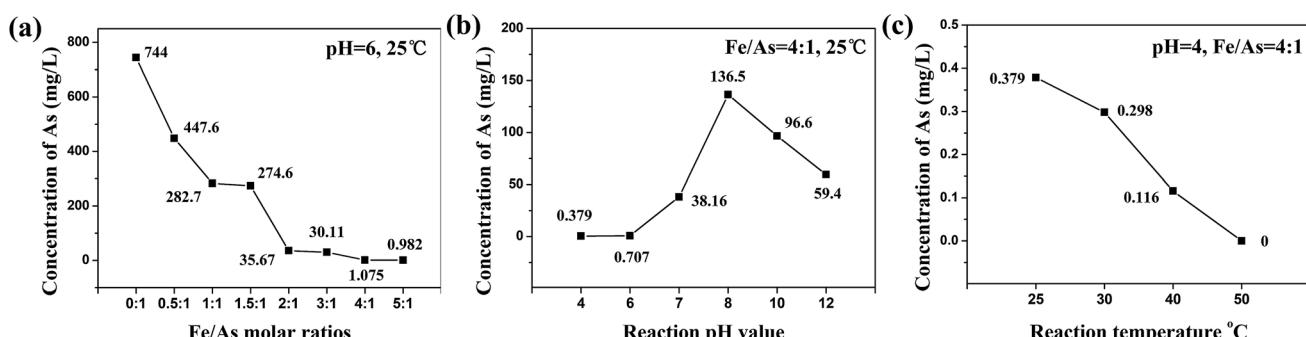


Fig. 2 Concentrations of arsenic obtained using the TCLP test after sample 1 was treated with  $\text{FeCl}_3$ . (a) Different Fe/As molar ratios, (b) different reaction pH values, (c) different reaction temperatures.



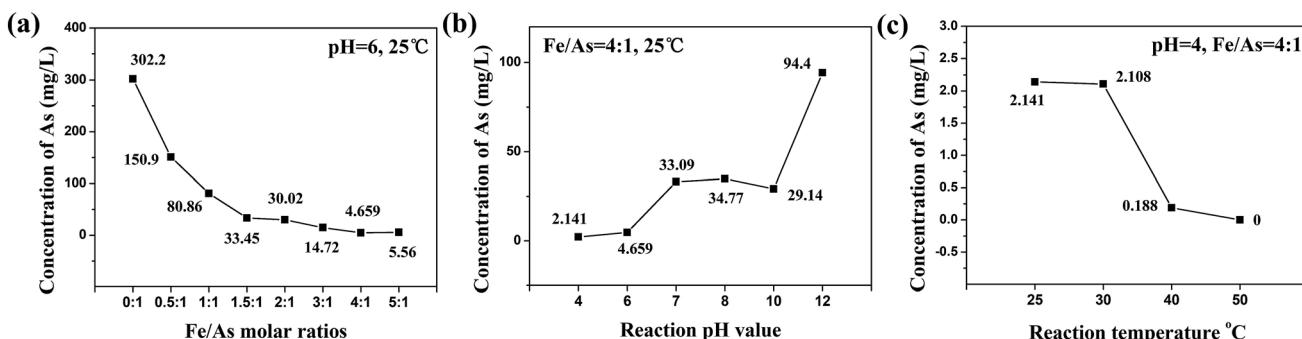


Fig. 3 Concentrations of arsenic obtained using the TCLP test after sample 2 was treated with  $\text{FeCl}_3$ . (a) Different Fe/As molar ratios, (b) different reaction pH values, (c) different reaction temperatures.

$\text{CaHAsO}_4$  system given in Section 3.2.1. The best pH for the stability treatment was 4, and the concentration of arsenic obtained from the TCLP test was  $2.141 \text{ mg L}^{-1}$ .

Fig. 2(c) shows the TCLP test results of the products which were reacted at  $\text{pH} = 4$  at different temperatures. The Fe/As molar ratio of reaction was 4 : 1. The results indicated that the reaction rate increased as the temperature of the reaction increased. When the temperature was  $50^\circ\text{C}$ , the  $\text{Ca}_3(\text{AsO}_4)_2$  could be coated perfectly by the  $\text{FeAsO}_4$ . Arsenic was not detected by the TCLP test.

### 3.3 Morphology of samples

Sample 3 was  $\text{CaHAsO}_4@\text{FeAsO}_4$  which was obtained by the  $\text{FeCl}_3$  stability treatment of sample 1 (Fe/As = 4 : 1, pH = 4,  $50^\circ\text{C}$ ). Sample 4 was  $\text{Ca}_3(\text{AsO}_4)_2@\text{FeAsO}_4$  which was obtained by the  $\text{FeCl}_3$  stability treatment of sample 2 (Fe/As = 4 : 1, pH = 4,  $50^\circ\text{C}$ ).

As shown in Fig. 4, the SEM images show the morphology of samples 1, 2, 3 and 4. Fig. 4(a) and (b) show that the synthesized  $\text{CaHAsO}_4$  and  $\text{Ca}_3(\text{AsO}_4)_2$  were both layered structures. The thickness of the layers was about 30 nm. This structure corresponded to previous reports of calcium arsenate.<sup>1</sup> The surface of the layers was smooth without particles. Sample 3 and sample 4 were the  $\text{CaHAsO}_4$  and  $\text{Ca}_3(\text{AsO}_4)_2$ , respectively, which had been stability treated with  $\text{FeCl}_3$ . As shown in Fig. 4(c) and (d), the layered structure remained, and the layer was coated by nanoparticles. According to the XRD and TCLP results, the particles were  $\text{FeAsO}_4$ . The  $\text{FeAsO}_4$  nanoparticles could prevent the internal calcium arsenate contacting with the solution, so the dissolution of calcium arsenate stopped. Fig. 4(e) shows the schematic diagram of the stability treatment process. The  $\text{CaHAsO}_4$  or  $\text{Ca}_3(\text{AsO}_4)_2$  dissolved into the aqueous solution, released  $\text{Ca}^{2+}$  and  $\text{AsO}_4^{3-}$  ions. The  $\text{AsO}_4^{3-}$  ions reacted with the  $\text{Fe}^{3+}$  ions and formed  $\text{FeAsO}_4$  particles. These particles were

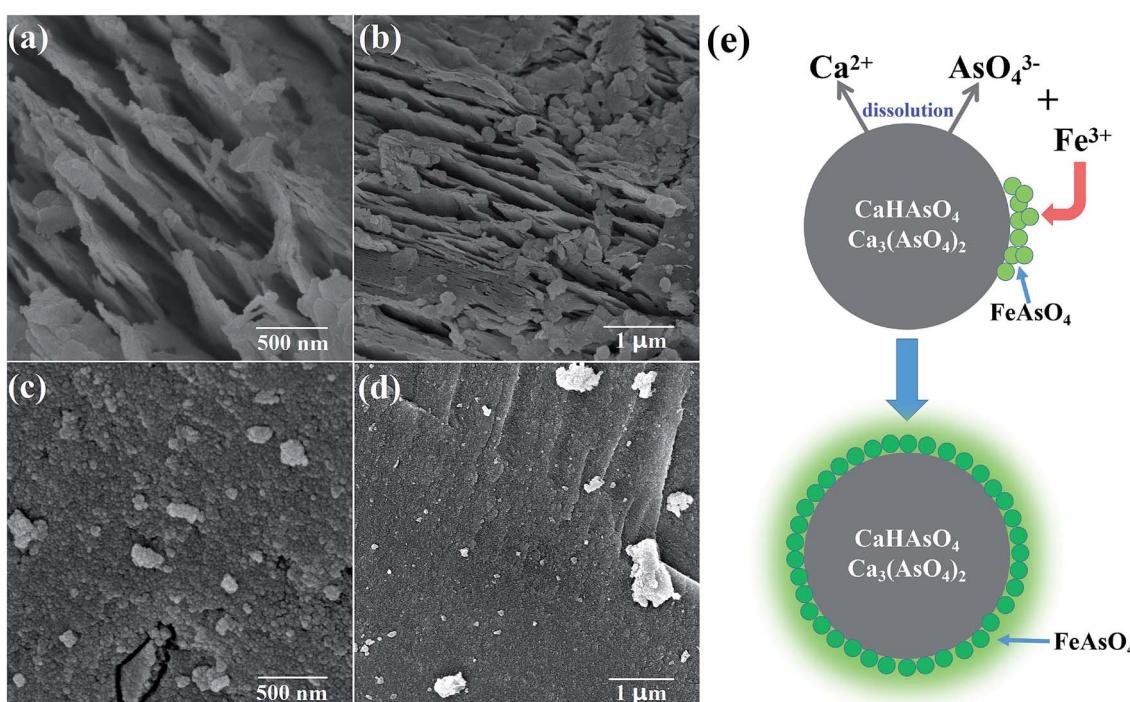


Fig. 4 The SEM images of (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4; (e) schematic diagram of the stability treatment process.



deposited on the surface of calcium arsenate until the calcium arsenate was coated completely. Because the solubility of  $\text{FeAsO}_4$  was much less than the solubility of  $\text{CaHAsO}_4$  or  $\text{Ca}_3(\text{AsO}_4)_2$ , the  $\text{FeAsO}_4$  was insoluble material and could not react with  $\text{H}^+$  and  $\text{OH}^-$ . The  $\text{FeAsO}_4$  shell could protect the internal  $\text{CaHAsO}_4$  and  $\text{Ca}_3(\text{AsO}_4)_2$ . They would not be corroded by the external solution. This structure was more stable after the stability treatment with  $\text{FeCl}_3$ .

The XRD pattern is shown in Fig. S1 (ESI).<sup>†</sup> The EDS analysis results of sample 1 and 3 are shown in Fig. S2 and S3 (ESI).<sup>†</sup>

## 4. Conclusion

The leaching liquid of smelting dust was used as the As(v) source. Layered  $\text{CaHAsO}_4$  and  $\text{Ca}_3(\text{AsO}_4)_2$  were synthesized. The  $\text{CaHAsO}_4$  and  $\text{Ca}_3(\text{AsO}_4)_2$  were stability treated with  $\text{FeCl}_3$  because the  $\text{FeAsO}_4$  formed has a lower solubility and higher stability. From the XRD and SEM analyses, it can be seen that the  $\text{CaHAsO}_4@\text{FeAsO}_4$  and  $\text{Ca}_3(\text{AsO}_4)_2@\text{FeAsO}_4$  were synthesized successfully. The layered calcium arsenate was coated by a  $\text{FeAsO}_4$  shell which consisted of nanoparticles. The stability of the coating materials was determined by the TCLP tests. The results showed that the concentrations of As for  $\text{CaHAsO}_4$  and  $\text{Ca}_3(\text{AsO}_4)_2$  were  $744 \text{ mg L}^{-1}$  and  $302.2 \text{ mg L}^{-1}$ , respectively. The concentration of As for  $\text{CaHAsO}_4@\text{FeAsO}_4$  and  $\text{Ca}_3(\text{AsO}_4)_2@-\text{FeAsO}_4$  were both  $0 \text{ mg L}^{-1}$ , and the best coating conditions were confirmed as a Fe/As molar ratio of 4 : 1, a pH of 4, and a temperature of  $50^\circ\text{C}$ . The stability of the materials showed a significant improvement. The results indicated that calcium arsenate materials could be converted to coating materials by the ferric salts. The coating materials had excellent stability in aqueous solution. It was suitable for the removal and immobilization of arsenic in industrial applications. This work provided a new way to treat the arsenic-containing wastewater, which was simple and economical. This method has potential applications in the field of arsenic-containing wastewater treatment.

## Conflicts of interest

There are no conflicts to declare.

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