Research Article

Synthesis of Pure Micro- and Nanopyrite and Their Application for As (III) Removal from Aqueous Solution

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Arsenic is one of the materials that has a worldwide concern because of its high toxicity and chronic effects on human health. The existence of arsenic as As (III) is about 56 times poisonous as As (V) and more difficult to process. The investigation takes the pyrite as an adsorbent to remove As (III) from waste water. Different morphology and granularity of pyrite were synthesized by hydrothermal and liquid-phase precipitation methods, respectively. The findings show that the addition of pyrite nanoparticles to the solution provided highest As (III) removal efficiency of 88.53%. 1 gL^{-1} pyrite nanoparticles can reduce the concentration of arsenite in the waste water from an initial As content of 30 mgL^{-1} to 3.4 mgL^{-1} at pH 11. Under the similar operating conditions, the synthetic micropyrrite and natural pyrite have a lower As (III) removal; both were less than 70%. In addition, the synthetic pyrite nanowires obtained 86.70% removal efficiency of arsenite. The results confirmed that the morphology and granularity of pyrite can significantly influence the adsorption of arsenite removal from aqueous solution.

1. Introduction

Arsenic can widely exist in the earth's soil, sediment, crust, and several kinds of rock. With geologic function, it is easily transferred to groundwater and air. Besides, a lot of industrial wastewater also contains arsenic. It is considered as one of the most toxic inorganic pollutants and exposure to arsenic through drinking water is a great threat to human health. Arsenic can cause stomach-intestine, liver, kidney, and heart disorders as well as neurological, dermal haematopoietic, reproductive, and carcinogenic diseases [1].

In natural waters, arsenic exists in two different states, arsenate [As (V)] and arsenite [As (III)]. The As (V) species (H_2AsO_4^- or HAsO_4^{2-}) is the predominant form at oxidation environment, and the pH can range from 2 to 12. When the pH value was below 9.2, the existent form of As (III) species was mainly H_3AsO_3^0 [2]. The arsenite and arsenate species are both widespread in surface waters, but they were different in soil according to the environmental conditions. In an oxidation atmosphere, arsenate is the primary form, whereas under reducing conditions arsenic is main form [3]. Numerous studies have covered recently the remediation of

inorganic arsenic, including adsorption [4], ion exchange [5], reverse osmosis [6], and coagulation [7].

Adsorption is considered as a low cost and reliable technique [8] and much more efficient choice for removal of inorganic compounds than the conventional treatment [9]. The various adsorbents have been applied to remove arsenic, such as natural iron containing minerals [10], titanium dioxide [11], zero-valent iron [12], red mud [13], and magnetic nanoparticles [14].

In reducing environments, such as sulfide-rich soils, a large amount of trace metals can form insoluble sulfides. However, arsenic is quite different and when the pH was not lower than 5.5, it is comparatively soluble. And this mobility can exist over a very wide range of redox conditions [15]. In order to reduce the release of arsenic in the reduction environment, adsorbents that have high adsorptive capacity of arsenic and very strong stability during long geological periods are ideal materials for treating water or soils contaminated with arsenic.

Pyrite (FeS_2) is one kind of such materials and very appropriate to apply under the reducing atmosphere [16]. Pyrite is basically produced as a by-product in typical mineral

processing plants. Since it is the most abundant sulphide mineral in the earth's crust, it has a very low economic significance. The most common treatment of pyrite is to produce sulphuric acid, and it is generally stored as waste minerals. Secondly, pyrite is thermodynamically stable in many reducing conditions. Arsenic can be present in pyrite with a strong affinity. The adsorption of arsenic on the pyrite would maintain being stable as arsenopyrite, arsenian pyrite, or some other sulfide solid phase in an anoxic landfill environments. This is the most primary merit of pyrite-based removal technologies. Thirdly, As (III) do not need to be oxidized to As (V) by using pyrite adsorption. It makes the arsenic removal process more simple and cost-effective.

In the previous report, the arsenic sorption onto natural and synthetic pyrite mineral has already been conducted by some researchers [16]. However, the different morphology and sizes of synthetic pyrite will have significantly different adsorption results of arsenic. Unfortunately, up to now, there is still lack of evidence about how the morphology and size of synthetic pyrite influence the arsenic from solutions.

In this study, the uptake of As (III) species from aqueous solutions by adsorbing onto different morphology and size of pyrite samples was investigated. The objectives of this study includes (1) to make pure micro- and nanopyrite crystals; (2) to investigate the effect of morphology and size of pyrite on As (III) removal; (3) to determine the sorption envelopes of As (III) as factors such as pH value, arsenic concentration, and contact time are changed. The study can be expected to contribute to the design of processes for removal of arsenic from water and processes that stabilize residuals produced by other removal processes.

2. Materials and Methods

2.1. Pyrite Synthesis. All chemicals used in this study were of analytical grade. All experiments were carried out with distilled water. For the synthesis of micropyrte, a solvothermal method was applied. Thiourea and ferric nitrate were used as the source of sulfur and iron, respectively. A 100 mL Teflon-lined stainless steel autoclave was equipped with a temperature controller. The synthesis process was performed at stirring speed 200 rpm. In a typical process, an appropriate amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and NH_2CSNH_2 was dissolved in 40 mL of solvent ethylene glycol. The mixture was then put into the reactor. The autoclave was controlled at 200°C for 48 h. After that, the reactor was cooled down to the room temperature. The black precipitates were firstly filtered off and sequentially washed for three times with distilled water and ethanol, respectively. The final synthetic products were dried at 60°C for 5 h to get the black powder.

For the synthesis of nanopyrite, a liquid phase precipitation process was used. Sodium thiosulfate and ferrous chloride were served as the source of sulfur and iron, respectively [17]. In a typical synthesis, 0.259 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and the appropriate amount of stabilizer thioglycolic acid (TGA) were mixed in 90 mL of dimethyl sulfoxide (DMSO). The solution was placed in a three-necked flask under vigorously magnetic stirring and nitrogen gas was bubbled through for 30 min. After that, 1.45 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ was dissolved in

10 mL deionized water in a beaker to form sodium thiosulfate solution and was then dropwise added into the ferrous chloride solution with continuously stirring and purging N_2 for half an hour. The pyrite nanoparticles were formed and grown up under the reflux conditions at 139°C for 4 h. After the reaction was completed, the pyrite products were separated from the solution by centrifugation. The precipitate was then washed with ethanol and deionized water for three times, respectively. Finally, the obtained pyrite was dried in a vacuum at 60°C for four hours. Two different morphologies of nanopyrite were prepared based on the process above. For pyrite nanoparticles, the molar ratios of $[\text{Fe}^{2+}]/[\text{TGA}]$ were 1:4. While, for pyrite nanowires, ethylenediamine (EDA) partially replaced thioglycolic acid and served as a cosolvent and costabilizer, the molar ratios of $[\text{Fe}^{2+}]/[\text{EDA}]/[\text{TGA}]$ were 1:4:2. EDA was added in the three-necked flask before the reaction temperature was raised.

2.2. Adsorption Experiments. The synthetic micro- and nanopyrite materials were applied to remove As (III). A pure natural pyrite mineral after ultrafine grinding was conducted to compare the removal ability of As (III) with the synthetic pyrite materials. The amount of pyrite was set at 1 g L^{-1} . And the desired adsorption conditions, such as contact time, initial arsenic concentration, and pH value, were investigated. The contact times of pyrite in the solution were 10, 20, 30, 40, 50, and 60 min, respectively. The desired initial concentrations of As (III) were performed at 10, 20, 30, 40, and 50 mg L^{-1} , respectively. The desired pH was adjusted using 0.5 M HCl or 0.5 M NaOH. The desired pH values were changed from 3.0 to 11.0. After adsorption finished, the pyrite were removed from the solution by centrifugal separation. The remaining solution was collected to analyze the residual content of As (III).

2.3. Characterization and Analytical Methods. The X-ray diffraction (XRD) analysis was conducted to confirm that the mineral synthesized was pyrite. The XRD patterns of pyrite were operated at 40 kV and 20 mA, between 20 and 90° (2θ) with a step size of 0.05° . A scanning electron microscopy (SEM) (Zeiss Ultra Plus, Germany) equipped with energy dispersive X-ray spectroscopy (EDS) system was utilized to study the morphology and chemical composition of synthesized micropyrte. A transmission electron microscopy (TEM) (Tecnai G20, FEI) was also used to study the morphologies of pyrite nanoparticles and nanowires. The concentration of As (III) in the solution was determined using a UV/visible spectrophotometer.

3. Results and Discussion

3.1. Characterization of Synthetic Pyrite. XRD patterns of different pyrite materials are displayed in Figure 1. All the diffraction peaks observed for the pyrite samples can be assigned to the pure cubic pyrite phase of FeS_2 (JCPDS Card no. 42-1340). No other peaks from impurities are observed, such as marcasite (FeS_2), greigite (Fe_3S_4), pyrrhotite (Fe_{1-x}S), troilite (FeS), or Fe-O compounds, which usually appear simultaneously in cubic pyrite phase of FeS_2 . From Figure 1,

FIGURE 1: XRD patterns of different pyrite samples.

the natural pyrite material has the strong and sharp diffraction peaks, indicating the high crystalline nature of mineral powder. The micropyrte has sharper diffraction peaks than nanopyrite material, suggesting the higher crystallinity of micropyrte. The pyrite nanowires obtained different peak intensities than the others. The peak (421) is the sharpest for pyrite nanowires while (200) peak is the sharpest for the other samples. This can be attributed to the different morphology for the pyrite nanowires.

Though there are different pathways to synthesize pure pyrite materials, they are both involved with the formation of FeS. For the synthesis of micropyrte, thiourea experienced the thermal decomposition first in the autoclave as follows:

Then ferric nitrate was reduced by the pyrolysis products of hydrogen sulfide and sulfur compounds and finally produced micropyrte in an appropriate time as follows:

For the synthesis of nanopyrite, at first, sodium thiosulfate was transferred into sodium sulphate, sodium sulfide, and sulfur after heating. Then the sodium sulfide reacted with ferrous chloride and yielded FeS. At last, nanoscale pyrite materials were prepared by the reaction of FeS and sulfur at 139°C as follows:

The morphology and particle size are an important factor that will affect pyrite performance in a treatment system. The

SEM and TEM images and particle size distribution of various pyrite samples are shown in Figure 2.

Figure 2(a) presents an SEM image of the micro-FeS₂ sample prepared with a solvothermal method, showing general morphologies of nearly monodisperse microspheres with diameters of 2–16 μm. The pyrite material seems to be formed by the agglomeration of the particles, and the mean particle size is 10.6 μm, calculated from Figure 2(b). The TEM images of the synthetic pyrite nanoparticles were shown in Figure 2(c). The particles is uniform, and the average grain diameter is 13.5 nm from Figure 2(d), confirming that the pyrite nanoparticles were successfully prepared. The morphology of the pyrite nanowires can be seen from Figure 2(e), and there is no doubt that the pyrite nanowires were well produced by the liquid phase precipitation method. The ratio of length to width ranges is from 7 to 10. The mean length of the pyrite nanowires is 176 nm from Figure 2(f). Comparing to the synthetic pyrite microparticles, the natural pyrite has been ground very fine, and its surface was more smooth (Figure 2(g)). After calculating from Figure 2(h), the average particle size of the natural pyrite is 1.05 μm. From the morphology characterization above, it can be learnt that the four typical pyrite samples were obtained.

3.2. Arsenic Removal Results. Figure 3 shows the effect of contact time on sorption of with various pyrite samples. It is easy to find that the adsorption reactions of As (III) for all pyrite samples are fast. Mass transport of arsenic can rapidly occur within 10 min. The pyrite nanomaterials obtained a larger arsenic removal than micropyrte and natural pyrite. 65% of As (III) was removed by pyrite nanoparticles after 10 min, while only 34% and 24% were removed using micropyrte and natural pyrite, respectively. The pyrite nanowires have a similar rate as pyrite nanoparticles. The difference in removal kinetics must be attributed to the morphology and particle size of pyrite. The smaller the pyrite material, the larger the specific surface area, which may induce faster reaction rates on the surface. It also can be learnt that with the contact time was prolonged from 10 min to 60 min, and the arsenic removal has some minor updates all the time. 79.3% of As (III) was removed by pyrite nanoparticles when it came to 60 min. Though the particle size of natural pyrite is less than that of synthetic micropyrte; however, from Figure 2, the synthetic micropyrte was shown more porous than the natural pyrite, and the high specific area is beneficial to the arsenic adsorption, which may be the cause of higher arsenic removal of synthetic micropyrte.

The effects of the initial arsenic concentration on sorption of arsenic are shown in Figure 4. In general, nanoscale pyrite presented better removal effect of As (III) than microscale pyrite samples for the whole arsenic concentration region (10–50 mgL⁻¹). The difference of removal rate for the two scales can range from 15% to 40%. Pyrite nanoparticles have the highest arsenic removal when the initial concentration of As (III) was controlled at 30 mgL⁻¹. It is also found that the pyrite microparticles and nanowires also obtained their best removal effects at this concentration. Furthermore, the pyrite nanowires exhibit excellent stability in terms of arsenic removal. It is worth noting that pyrite nanowires achieved the

FIGURE 2: Morphology and particle size distribution of different pyrite samples: (a) and (b) for synthetic pyrite microparticles; (c) and (d) for synthetic pyrite nanoparticles; (e) and (f) for synthetic pyrite nanowires; (g) and (h) for natural pyrite material.

FIGURE 3: Effect of contact time on sorption of arsenic (pH = 7, initial arsenic concentration of 30 mgL⁻¹).

FIGURE 4: Effect of initial arsenic concentration on sorption of arsenic (pH = 7, contact time = 60 min).

best removal of As (III) at other initial arsenic concentrations. The natural pyrite gained a low arsenic removal overall and it may be due to its small surface area. As can be seen in Figure 2, the natural pyrite has a large particle size and smooth surface, which reduces the reactive areas. The results confirm that the particle size and the morphology have a significant effect on the adsorption reaction of As (III).

Figure 5 shows the results of experiments using various pyrite samples at different pH values to remove As (III), respectively. There is obviously the fact that arsenic removal for all pyrite materials enhanced with increasing pH value. The addition of nanopyrite particles to the solution provided highest As (III) removal efficiency of 88.53% at pH 11; that is, the concentration of As (III) in the waste water can reduce

FIGURE 5: Effect of pH on sorption of arsenic (contact time = 60 min, initial arsenic concentration = 30 mgL⁻¹).

from an initial value of 30 mgL⁻¹ to 3.4 mgL⁻¹. The low pH is not beneficial to the arsenic adsorption.

Ferric ions are stable at pH levels below 2.5 and relatively higher potentials, while Fe(OH)₂⁺ complexes are more stable in the pH range of 4.8–5.8. On the other hand, H₂AsO₄⁻ species (As (V)) exist in this pH range. Therefore Fe(OH)₂⁺ reacts with H₂AsO₄⁻ forming a scorodite-like mineral, FeAsO₄·2H₂O, which has the minimum solubility at pH 5. However, the existent form of As (III) species was mainly H₃AsO₃⁰ when the pH value was below 9.2, and it is not easy to react with other species unless As (III) exists as ionic species at high pH values. This may be the different optimum pH for As (V) and As (III).

Previous report has also used X-ray absorption spectroscopy (XAS) to identify reaction products and reaction stoichiometry. It has been proposed that As (III) reacts with FeS₂ to form longer chain polysulfides such as iron tetrasulfide (FeS₄) [18]. The equation is shown as follows:

The surface precipitates containing FeAsS were observed for FeS₂ after contact with As (III). FeAsS has a very high environmental stability and field evidence demonstrates that arsenopyrite does not readily decompose under water-saturated near-surface conditions [19, 20]. As(OH)₃ binds As more weakly than FeAsS, and the reaction makes As less released to solution. The high pH will contribute to the stability of FeAsS and Fe(OH)₃. Besides, the colloidal Fe(OH)₃ also has some adsorption effect of arsenic at high pH:

From the above researches, the morphology and granularity of pyrite were confirmed to affect the above reactions speed on the surface of pyrite.

4. Conclusions

It was concluded that pure pyrite micro- and nanomaterials were successfully prepared by solvothermal and liquid phase precipitation methods, respectively. The morphology and particle size affect pyrite removal performance a lot in a treatment system of As (III). Arsenic removal by pyrite materials also depends on the contact time, initial arsenic concentration, and pH value. It is found that the nanoscale pyrite had better removal of As (III) than the microscale pyrite. Pyrite nanoparticles obtained a highest As (III) removal efficiency of 88.53% at pH 11 when the contact time was 60 min. Pyrite nanowires and the natural pyrite achieved a similar removal effect as pyrite nanoparticles and micro-particles, respectively. The optimized initial arsenic concentration was 30 mgL^{-1} , and it is also observed that, with increasing contact time and pH value, the removal of As (III) by the pyrite materials can significantly improve.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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