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Arsenic removal from water by iron-sulphide minerals

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Abstract In bench-scaled experiments, iron-sulphide minerals, pyrite and pyrrhotite are used as adsorbents for arsenic removal from As-spiked water of As^{5+} and As^{3+} species. The adsorption rate, efficiency, As-adsorption stability and the associated pH conditions have been examined. Observations indicate that these iron-sulphide minerals are very efficient to adsorb arsenic from water for both As^{5+} and As^{3+} species. Similar to other studies, As^{3+}-adsorption shows a slower rate than As^{3+}. The stability of the adsorbed arsenic seems closely related to the pH values of the solution. A lower pH level commonly less than 4.0 is required to protect the adsorbed arsenic from serious oxidation and backward release. Fining of the mineral powders and shaking of the solution during adsorption enhance the adsorption efficiency and adsorption rate. For practical use of the method presented in this study, the waste produced should be managed with great care to keep it from redistribution over water system. A further study of the protection for the waste from oxidation on real water systems will greatly enhance the application of the strong ability of arsenic adsorption by these minerals, which is observed from this study.

Keywords: arsenic contamination, arsenic removal, iron-sulphide minerals.

Arsenic contamination of drinking water has been reported from many parts of the world including Asia, Europe and America along the belt of low latitudes. It causes a variety of diseases particularly skin cancer[1,2]. Detailed studies of arsenic contamination of water system and the associated arsenism in the areas of Xinjiang, China have been carried out for years[3]. Arsenic poisoning in Bengal and western India occurred in recent years, where millions of people are poisoned or in the risk of arsenic poisoning, is claimed as “the worst hydrogeological problem in the world”, or “the world’s biggest environmental health disaster”[4]. The recent literature is flooded with such reports[4—8]. The World Health Organization suggests to lower the limits of 0.05 mg/L arsenic of the old standard to be less than 0.01 mg/L[9], and the US Environmental Protection Agency proposes a further lower limit of 0.002 mg/L[5]. The World Bank has recently announced a US$32.4 million, zero-interest loan to Bangladesh for work to reduce the problem[10]. With increase in coal consumption and mining of gold and other metal ores in China, which are the major sources of arsenic pollution, arsenic contamination of the environment will certainly be a big potential problem, and thus studies of arsenic pollution and treatment of removal are in great importance for human health and economic development of the entire nation.

Numerous studies of arsenic removal from drinking water and waste waters use methods involving chemical precipitation such as alum and iron precipitation[11—13], lime softening[14,15], membranes[16], colloidal flotation[17], adsorption by activated iron and alumina[13], and ion exchange resin[16]. However, all the available treatments have some defects either in their efficiency or waste disposal problems they produced[16], or expensive equipments required, which poses the difficulties for their application for areas under poor economic conditions. This study try to search for some geologic materials practical in use to remove arsenic from water, which has the potential in large scales of treatment of arsenic removal from water systems.

Arsenic is frequently associated with sulphide minerals and typically forms its own minerals like arsenopyrite (FeAsS)[18], so that arsenic commonly concentrated in many types of sulphide mineral deposits with gold. Some extreme examples of pollution are associated with careless management of mine waste as in the Mediterranean[19]. On the other hand, such affinity of arsenic with sulphide minerals raises a potential use of sulphide minerals for arsenic removal from water. In this study, we show the possibility of these minerals in practice to adsorb arsenic from arsenic-spiked waters through bench-scaled experiments.

1 Materials and methods

As^{5+}-spiked water was prepared from sodium hydroarsenate ($Na_2HAsO_4 \cdot 7H_2O$) with deionized water. Pyrite (FeS_2) and pyrrhotite were put into the solution as arsenic adsorbents. Before quantitative experiments, the crystals of pyrite and pyrrhotite were used to test their ability in arsenic adsorption. After a few hours of exposure with the water containing arsenic and then rinsed with deionized water and dried up, the minerals were examined using Auger and X-ray photoelectron spectroscopy. It was found that the surface of the minerals was coated with a layer of arsenic. For quantitative analysis, pyrite and pyrrhotite powder with size-controls was used in the subsequent experiments.

Pyrite and pyrrhotite powder less than 300 mesh, and pyrite powder plus iron filings made three consecutive measurement lines; each line consists of 25 samples. Each individual sample contains 100 mL of 10 mg/L As-spiked water with addition of the powder adsorbent, 0.4g pyrite, or 0.4g pyrrhotite, or 0.3g pyrite plus 0.2g iron. During the first 5 days, all samples were shaken for 5 min for every 8 h. Afterwards, shaking was made once a day. One sample of each line was measured each day. For measurement of arsenic concentration, the supernatants were separated using a centrifuge (20 000 r/min for 20 min) and analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) with a low detection limit of 0.005 mg/L.

To examine the adsorption ability of these minerals to As^{3+}, the As^{3+}-spiked water was made using sodium arsenite ($NaAsO_2$) and deionized water. The initial arsenic concentration was 10 mg/L. The adsorbents, methods and procedures were the same as used in the above experiments. The pH measurement was made using hydrogen-electrode pH meter with a precision less than 0.2. All chemicals were purchased from VWR Inc. The standard solutions of arsenic and sulfer were provided by the ICP-OES Instrument Company, and checked with the standards made by the authors.

2 Results and discussion

The consecutive measurements of As^{5+} concentration for the water samples treated with pyrite, pyrrhotite and pyrite plus iron filings are plotted in fig. 1 and listed in table 1. Obviously, pyrite adsorbs arsenic faster than pyrrhotite; after 5 days all the arsenic is removed from the water (at least the arsenic

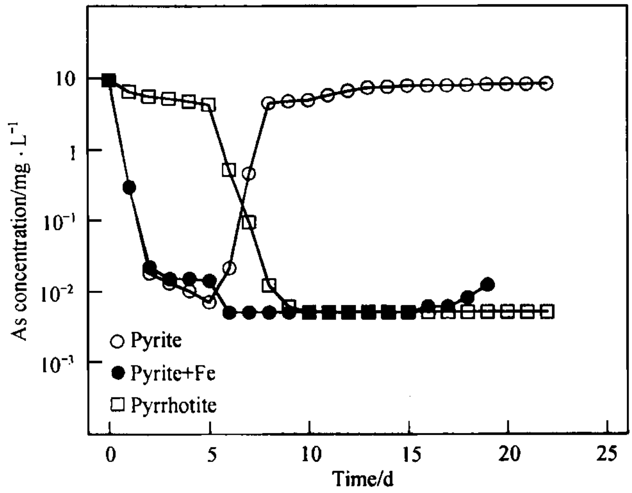

Fig. 1. Changes of arsenic concentrations in spiked waters with time after adding iron-sulphide minerals. The arsenic concentrations of 0.005 mg/L are in fact equal to or lower than the ICP-OES detection limit.

concentration is lower than the lower detection limit of the instrument). At the 8th day, however, the adsorbed arsenic begins serious release to the water. About 20 days later, the arsenic in the solution rises to a level close to the initial concentration. From the line of pyrite with addition of iron filings, the backward release of the adsorbed arsenic is significantly reduced. With the lapse of time more and more rust is produced. In another experiment, however, we found that iron filings virtually have no ability to adsorb arsenic. These could suggest that the backward release of adsorbed arsenic by pyrite be subjected to oxidation. Iron filings provide some help for maintaining a reducing condition for the solution.

Table 1 Arsenic concentrations (mg/L) in spiked waters after As^{5+} removal by three powder adsorbents

Time/d	Pyrite	Pyrrhotite	Pyrite + Fe
0	10	10	10
1	0.303	6.74	0.297
2	0.018	5.78	0.022
3	0.013	5.36	0.015
4	0.010	4.86	0.015
5	0.007	4.39	0.014
6	0.021	0.52	$\leqslant$0.005
7	0.46	0.094	$\leqslant$0.005
8	4.58	0.012	$\leqslant$0.005
9	4.86	0.006	$\leqslant$0.005
10	5.05	$\leqslant$0.005	$\leqslant$0.005
11	5.92	$\leqslant$0.005	$\leqslant$0.005
12	6.81	$\leqslant$0.005	$\leqslant$0.005
13	7.54	$\leqslant$0.005	$\leqslant$0.005
14	7.72	$\leqslant$0.005	$\leqslant$0.005
15	8.01	$\leqslant$0.005	$\leqslant$0.005
16	8.01	$\leqslant$0.005	0.006
17	8.01	$\leqslant$0.005	0.006
18	8.15	$\leqslant$0.005	0.008
19	8.31	$\leqslant$0.005	0.012
20	8.37	$\leqslant$0.005	
21	8.44	$\leqslant$0.005	
22	8.52	$\leqslant$0.005	

The As concentrations less than $\leqslant$0.005 mg/L are in fact lower than the ICP-OES detection limit.

Compared with pyrite, pyrrhotite adsorbs arsenic at a low rate (fig. 1 and table 1) but the adsorption is much stable. Only a very slight backward release of the adsorbed arsenic is detected (rose to 0.01 mg/L) after 6 months. It has been observed that the arsenic concentration of the spiked water decreased proportionally with the increase in sulfer (data not shown). This suggests that arsenic adsorption results from replacement of sulfer on the mineral surface by arsenic and formation of arsenopyrite. During the arsenic adsorption by pyrrhotite, the formation of each arsenopyrite molecule also produces a free iron, which changes the mineral surface structure and allows arsenic to penetrate into the depth of the mineral. By this mechanism, the adsorption process could continue until all available arsenic is consumed provided that the amount of the mineral suffices. We also observed that the pyrrhotite powder in all the samples forms a solid layer coating on the bottom of the beakers after a period of time. In contrast, pyrite powder always remains loose, indicating that the arsenic adsorption is mainly restricted on the surface. The free iron produced during arsenic adsorption by pyrrhotite effectively maintains a reducing condition for the water and thus protects the adsorbed arsenic from oxidation and backward release. Because pyrite is enriched in sulfer than pyrrhotite, it could provide more sulfer for substitution by arsenic during the surface adsorption process, given the same amount and the same grain size of these minerals. Therefore, pyrite shows a higher adsorption rate than pyrrhotite.

Comparative studies of As^{5+} and As^{3+} adsorption by both minerals (the data are listed in table 2)

Table 2 Comparison of adsorption rate of As^{3+} with As^{5+} by pyrite+Fe and pyrrhotite powders

Time/day	Pyrite+Fe As (III)	Pyrite+Fe As (V)	Pyrrhotite As (III)	Pyrrhotite As (V)
0	10	10	10	10
2	5.49	0.052	4.98	2.78
4	0.439	0.007	0.192	0.010
6	0.221	$\sim$0.005	0.082	$\sim$0.005
8	0.007	$\sim$0.005	0.013	$\leqslant$0.005
9	0.007	$\sim$0.005	0.009	$\leqslant$0.005

The As concentrations less than $\leqslant$0.005 mg/L are in fact lower than the ICP-OES detection limit.

are illustrated in fig. 2. As concluded from many studies[11—13,16], the adsorption rates of As^{3+} are significantly slower than those of As^{5+} at the first stage. Nevertheless, both arsenic species can be completely removed by pyrite and pyrrhotite after about 10 days. Therefore, As^{3+} may not be necessarily oxidized into As^{5+} first and then to be cleaned up if a natural water system is treated and the adsorption efficiency is pursued most.

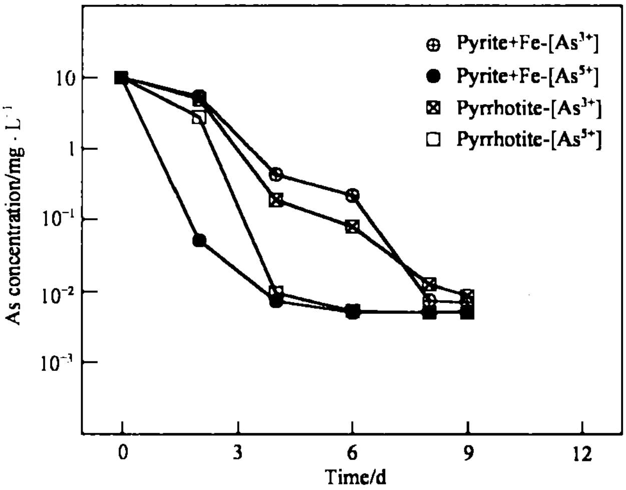

Fig. 2. Comparison of adsorption rate of As^{3+} with As^{5+} by pyrite+Fe and pyrrhotite. The arsenic concentrations of 0.005 mg/L are in fact equal to or lower than the ICP-OES detection limit.

During the experiments for construction of fig. 1, we also observed dramatic changes in the pH value of the As-spiked water samples. In the early stage when the adsorbed arsenic remains stable, i.e. the arsenic concentration of the solution falls down and stays at the lowest level, the pH values of all the samples are less than 4.0. During the period of backward release of the adsorbed arsenic, the pH value rises to a level higher than 7.0. This change occurs prior to serious backward release. Therefore, the pH value is an important factor for arsenic removal by both pyrite and pyrrhotite and for the stability of the adsorbed arsenic.

Shaking can significantly affect the adsorption rate. For samples prepared as described in fig. 1, 24 h of shaking is sufficient for pyrite to adsorb all the arsenic or for the arsenic concentration to fall down to a level lower than the low detection limit. Fining of the adsorbent powder enhances their adsorption efficiency, but also increases difficulty for separation of the solids from water. Both factors should be considered in order to optimize the treatment using this method.

Compared with other geologic materials like hematite, feldspar, and clay as adsorbents to remove arsenic from water[20], we found that pyrite and pyrrhotite have much higher efficiency, at least two orders greater in magnitude. Arsenic speciation study[21] indicates that arsenic in the natural fresh water systems is dominated by As^{5+}. However, arsenic contamination occurring in Bengal and western India contains a considerably higher portion of As^{3+}[22]. For arsenic removal from a real water system, the arsenic species involved in the system should be specified and be well understood. There are some available methods that can be used to convert As^{3+} to As^{5+}[13], for example, the chloride oxidation method, if such a treatment is necessary. When using adsorption method presented in this study to remove arsenic from drinking water, the solid waste produced must be managed with great care, because oxidation of the sulphide minerals containing arsenic is a main path for arsenic mobilization and redistribution in natural systems[23].

3 Conclusions

Iron sulphide minerals like pyrite and pyrrhotite are effective adsorbents for arsenic removal from water, thus have great potential in future practical treatment of arsenic polluted water. Compared with other adsorption materials, for example, lime, ferric chloride[24], and other minerals examined previously, iron sulphide minerals produce less waste and the waste is more easily separated from water. In practice, however, the waste disposal should be safe enough to protect the adsorbed arsenic from mobilization and redistribution over the environment. The strong ability of iron sulphide minerals in arsenic adsorption provides a new way for arsenic removal. Once a proper management for these wastes is achieved on a large scale, practical use of these minerals for arsenic removal will be enhanced greatly.

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(*To be continued on page* 1434)

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