

Removal Mechanism of As(III) by Ferrihydrite using Co-precipitation or Adsorption process

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Abstract

Many researchers have been investigated many kinds of treatment methods for arsenic wastewater and reported As(III) is more difficult to be removed than As(V). We have investigated the arsenic removal using ferrihydrite co-precipitation process and already reported the removal mechanism of As(V) during the process. On the other hand, the removal mechanism of As(III) has not yet been revealed. Therefore, objective of this study is to reveal the removal mechanism of As(III) from wastewater during ferrihydrite co-precipitation process.

This study discussed the removal mechanism of As(III) from simulated wastewater with Fe(III) in co-precipitation process. To investigate the removal mechanism in co-precipitation process, all experimental results were compared with simple adsorption process. Arsenic and ferric concentration in filtrate after experiments were analyzed by ICP and precipitates were characterized by XRD analysis. From sorption isotherm, it was revealed that a more efficient removal of As(III) was achieved with co-precipitation process than adsorption one and removal mechanism involved not only surface complexation of As(III) to ferrihydrite but also surface precipitation or surface complexation of multiple complexes. These results suggested that removal mechanism changed depending on the initial As/Fe molar ratio and pH change during the removal process.

Keywords: arsenite, co-precipitation, adsorption, surface complexation, surface precipitation

1. INTRODUCTION

Arsenic is 20th most abundant element on earth. Contamination of groundwater is widespread and affecting many areas of the world such as Bangladesh, India, Vietnam, Thailand and Chile (Nordstrom, 2002). Arsenic often contents in water by the natural process of weathering and dissolution of minerals such as arsenopyrite. Arsenic is present at potentially toxic concentrations in environment due to mining and industries if not carefully monitored and controlled.

Exposure to arsenic via drinking water initially causes skin diseases such as pigmentation and arsenicosis. It has been stated that arsenic concentration should not exceed 10 µg/l in drinking water by the U.S Environmental Protection Agency and the World Health Organization (WHO) (U.S Environmental Protection Agency, 1999). But in many areas of the world populations are exposed to concentrations several orders of magnitude greater than limited amount

(Nordstrom, 2002).

Among the many oxidation states of arsenic (-3, 0, +3, +5), As(III) and As(V) dominate in water environments (McCleskey, et al, 2004). As(III) exhibits greater mobility and toxicity than As(V) (Yang, et al, 2005).

Ferrihydrite, one of the common forms of iron in aqueous systems, is known as an ideal adsorbent for the treatment of wastewater containing dilute anions, especially for arsenic. The As(V) removal mechanisms in treatments using ferrihydrite were experimentally investigated by comparing co-precipitation and adsorption processes (C. Tokoro, 2015).

The removal mechanism of As(III) has not yet been revealed. The objective of this study was to provide a fundamental assessment of the surface precipitation because that occurs during As(V) co-precipitation and adsorption of with ferrihydrite.

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2. EXPERIMENTS

2.1. Standards and reagents

All chemicals and solution used in this study were of analytical grade and were purchased from Kanto Chemicals, Inc., Japan. The As(III) and Fe(III) solution were prepared from As_2O_3 and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, respectively. The pH and ionic strength were adjusted by the addition of 0.1M HNO_3 and KOH . For all experiments conducted in this study, the pH was fixed at 5 or 7 and the ionic strength was fixed at 0.1. All experiments were conducted at 25°C.

2.2. Co-precipitation experiments

Co-precipitation experiments involved the formation of ferrihydrite particles in the presence of As(III) ions. The $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and As(III) solutions were initially combined in deionized water, after which the pH and ionic strength were adjusted by HNO_3 and KOH to the target levels. The suspension was then agitated using a magnetic stirrer under pH control for one hour, which is known to be enough time for the initial rapid co-precipitation reactions. The suspension was filtered through a 0.1 μm membrane filter. Next, the As(III) concentration was analyzed by ICP-AES using a SPS-7800 atomic emission spectrometer (Seiko Instruments, Japan). Flow chart of co-precipitation experiment is shown in Figure 1.

In addition, the filter residue was freeze-dried at -45 °C for 24 h.

2.3. Adsorption experiments

In this study, simple adsorption experiments using prepared ferrihydrite were conducted, and the results were then compared with those of the co-precipitation experiments. The adsorption experiments involved the formation of ferrihydrite particles and the separate adsorption of As(III). To accomplish this, the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and As(III) solutions were initially prepared separately in deionized (DI) water to give twice the target concentration of Fe(III) and As(III). The pH and ionic strength were then adjusted to the target levels by the addition of HNO_3 and KOH . Next, equal amounts of the Fe(III) solution and As(III) solution were combined and agitated using a magnetic stirrer under pH control for one hour, which was accomplished by adding a few drops of KOH . The solid/liquid separation of the solutions and analysis of the concentration of As(III) in the supernatant

were then conducted as described in the co-precipitation experiment section. Flow chart of adsorption experiment is shown in Figure 2.

2.4. XRD analysis

The powder XRD patterns were obtained using a copper target($\text{CuK}\alpha$), a crystal graphite monochromator and a scintillation detector. The XRD machine that we used was RINT-2200 which was made by Rigaku Co. in Japan. The equipment was run at 40 kV and 30 mA by stepscanning from 2° to 80° 2θ at increments of 0.02° 2θ and a scan speed of 2°/min. The filter residue was freeze dried at -45°C for 24 h prior to analysis.

3. RESULTS AND DISCUSSIONS

3.1. Comparison of co-precipitation and adsorption characteristics

Figures 3 and 4 show that a comparison of the residual ratios of As(III) in the co-precipitation and adsorption experiments conducted at pH 5 and 7. In these experiments, the initial concentration of As(III) was 10 mg/dm³. As shown in these figures, more As(III) was removed during the co-precipitation experiment than the adsorption experiments regardless of the pH. The higher removal ratios observed during the co-precipitation experiments indicate that the co-precipitation of As(III) with ferrihydrite involves more than adsorption. It should be noted that the As(III) can be removed larger amount in co-precipitation experiment than in adsorption one. However, this difference between them was smaller than it observed in As(V) removal.

3.2. XRD analysis

Figures 5 and 6 show a comparison of the XRD patterns of the co-precipitated As(III) with ferrihydrite as a function of the initial molar ratio of As/Fe at pH 7. In these experiments, the initial concentration of Fe(III) was fixed at 20 mg/dm³ and the concentration of As(III) was changed to attain the target As/Fe molar ratio of 0.125 to 10.

In these figures, XRD patterns for ferrihydrite and poorly crystalline ferric arsenate were also shown as reference materials. The poorly crystalline ferric arsenate showed two broad XRD bands, one at 28° 2θ ($d \approx 3.2 \text{ \AA}$) and a second small peak at 58° 2θ ($d \approx 1.6 \text{ \AA}$). On the other hand, ferrihydrite had two broad bands at 34° 2θ ($d \approx 2.6$

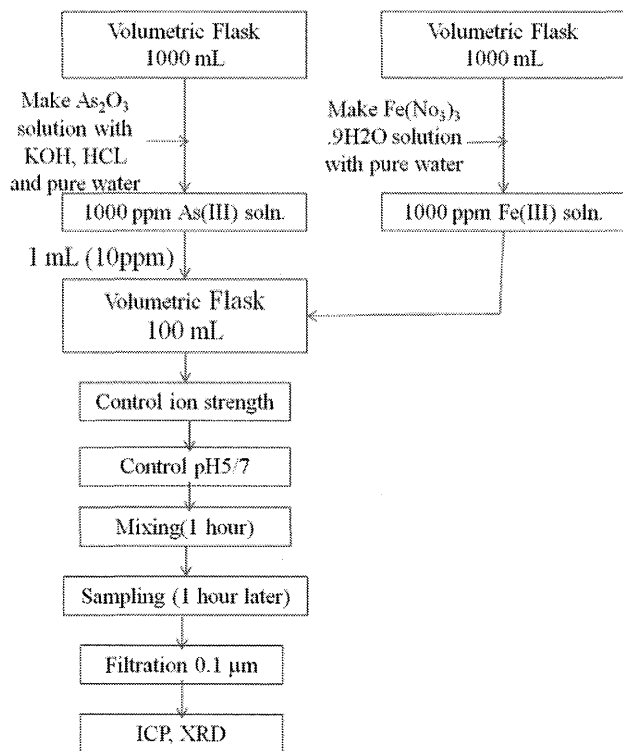


Fig. 1. Flow chart of Co-precipitation process

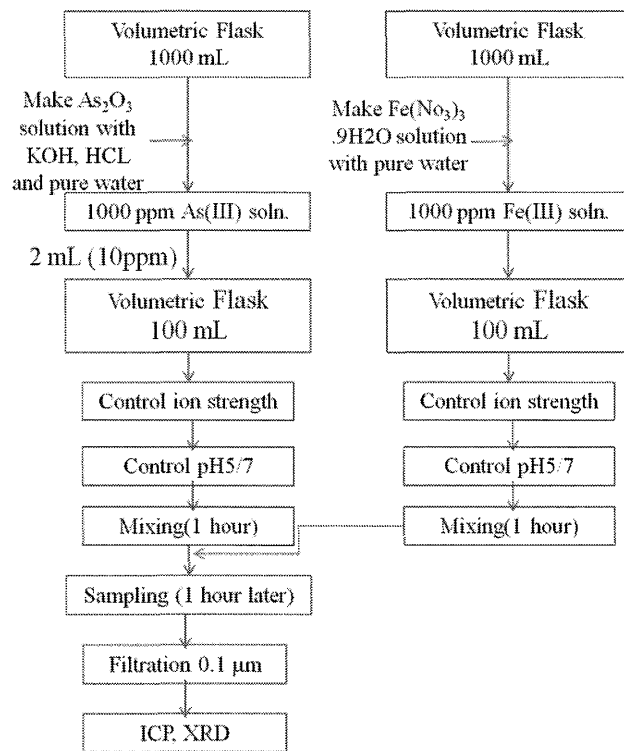


Fig. 2. Flow chart of Adsorption process

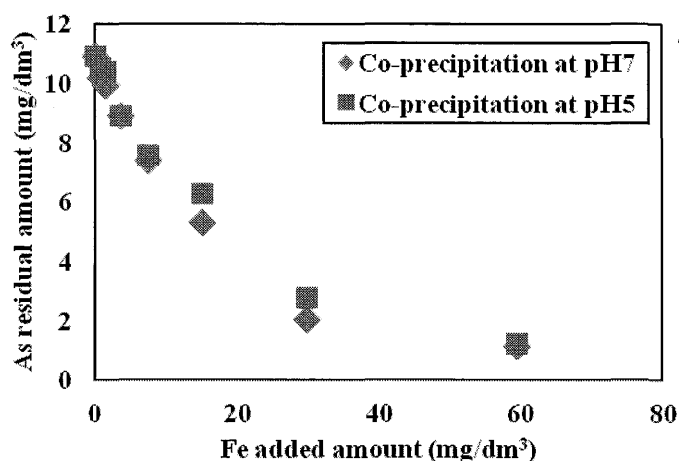


Fig. 3. As residual amount by Co-precipitation process at pH5 and 7

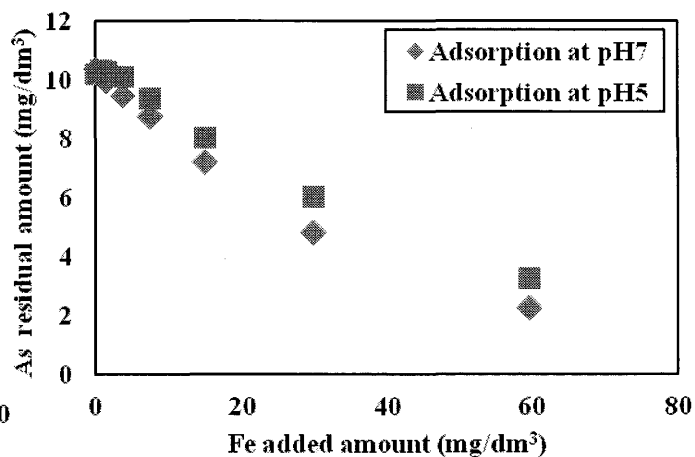


Fig. 4. As residual amount by Adsorption process at pH5 and 7

Å) and $61^\circ 2\theta$ ($d \approx 1.5$ Å).

As shown in Figure 5, when the co-precipitated products were generated using an initial As/Fe ratio of 0.125 to 1, the XRD patterns were almost identical to those of ferrihydrite. In these cases, the mechanism of co-precipitation of As(III) is predominantly adsorption to the surface of ferrihydrite. We also evaluated the XRD spectrum of As(III) adsorbed ferrihydrite at different pH values and initial As/Fe molar ratios and found that they were all the same as the spectrum of ferrihydrite, as shown in Figure 6. Conversely, when the initial As/Fe ratio was 5, the first peak of ferrihydrite became broader and shifted toward that of poorly crystalline ferric arsenate, whereas the XRD peaks formed when the initial As/Fe ratio was > 5 were located at the same positions as those of poorly crystalline ferric arsenate. In these cases, the mechanism of co-precipitation of As(III) is predominantly precipitation of ferric arsenate, which would involve partial oxidation of As(III) to As(V) at the surface of ferrihydrite and ferric arsenate surface precipitation that occurs beyond the thermodynamic bulk precipitation range.

4. CONCLUSIONS

As(III) removal mechanism in ferrihydrite co-precipitation and adsorption was investigated to determine the suitable treatment of acid mine drainage (AMD) containing As(III). More As(III) could be removed in co-precipitation process than in adsorption process. XRD patterns of precipitates suggested that removal mechanism was mainly surface complexation of As(III) to ferrihydrite in adsorption process, whereas it changed depending on the initial As/Fe molar ratio in co-precipitation process. Especially when the initial molar ratio of As/Fe was more than 5, As(III) was partially oxidized to As(V) and surface precipitation of poorly crystalline ferric arsenate was precipitated beyond the thermodynamic bulk precipitation range. This mechanism should be one of the reason why more As(III) could be removed in co-precipitation process than in adsorption process.

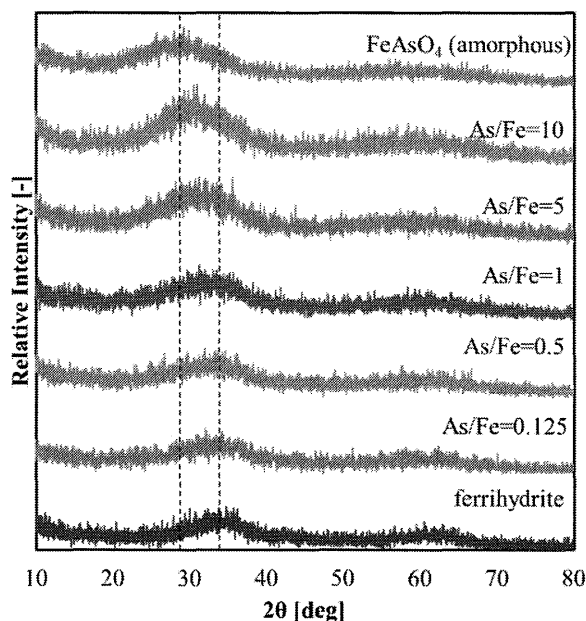


Fig. 5. XRD results by Co-precipitation process at pH7

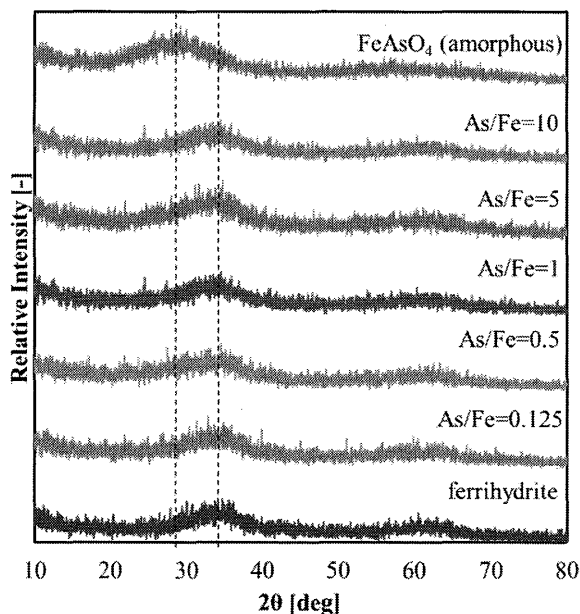


Fig. 6. XRD results by Adsorption process at pH7

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