Arsenic Removal by Nanoiron in the Gas-bubbled Aqueous Solution

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Abstract - **Nano-scale zero-valent iron (NZVI) was used for the removal of both As(III) and As(V) in aqueous solution. Firstly, batch experiments were conducted to investigate the effects of initial pH and dissolved oxygen (DO). Arsenic removal rates were found higher in the system with lower initial pH and higher DO. Secondly, the gas bubbling of solution was the focus to improve arsenic removal by NZVI. The CO_2 bubbling resulted in not only acidification of solution but also stripping of DO; consequently, the arsenic removal was observed to decrease significantly. Thus, with the gas bubbling scenario of pretreatment of CO_2 and the subsequent air bubbling, it was demonstrated that the As(V) was removed remarkably, and the As(III) to a lesser degree.**

Keywords-Arsenic; arsenate; nanoscale iron; gas bubbling
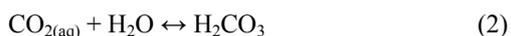
I.   Introduction

The contamination of arsenic in groundwater has become an issue of worldwide concern because of its toxicity and health hazards. Arsenic exists in natural waters mostly in the forms of arsenite (As(III)) and arsenate (As(V)) in reducing and oxidizing environments, respectively [1]. Arsenic is typically associated with iron oxide under oxic condition, and pyrite minerals under anoxic one [2]. Arsenic may be released to the environment from natural sources (e.g., the oxidative weathering and geochemical reaction) as well as from anthropogenic activities (e.g., industrial waste discharge containing arsenic, mining, and arsenical pesticides) [3-5]. Consuming water with high level of arsenic will cause skin, lung, bladder, kidney cancer and black foot diseases [1]. As was reported, the countries affected by high arsenic concentration in groundwater include Bangladesh, Cambodia, Canada, China, India, Nepal, Taiwan, Thailand, the United States, and Vietnam [6, 7]. To mitigate health impact by arsenic, the standard of maximum contamination level of arsenic in drinking water was set at 10 µg/L, according to USEPA [8].

There are many technologies for removing arsenic from groundwater such as precipitation, coagulation and filtration, reverse osmosis, electrodialysis, and ion exchange [9], but these are only effective for As(V), and require a preoxidation step for As(III) removal [10]. Thus, the adsorption process of zero-valent iron (ZVI) is a promising alternative for arsenic removal because this adsorptive media can remove both As(V) and As(III) simultaneously, without the need of pre-oxidation [11], and such a process does not require the use of additional chemical reagent. The ZVI was first used for arsenic removal by Lackovic et al. (2000) [10]; they reported that the ZVI has a high capacity for arsenic remediation, both As(III) and As(V). Afterwards, there were many other researchers reporting arsenic removal by the ZVI. Bang et al. (2005) [12] used iron filings for arsenic removal in a batch system, with iron filings pretreated by acid to remove the oxide layer on the iron surface. They revealed that the removal rate of As(V) under oxic condition was faster than under anoxic condition and the removal rate was higher at pH 4 than at pH 7. Sun et al. (2006) [11] performed experiments by using packed column of iron chippings. Their results show that As(III) was removed more rapidly than As(V) under deoxygenated condition, but the reverse phenomenon was observed under oxic condition. Melitas et al. (2002) [8] reported the effectiveness of packed column of iron fillings for As(V) removal. They concluded that the performance of As(V) removal was dependent on the adsorptive sites of iron oxide generated from reaction, and on the ability of As(V) reaching to those adsorptive sites. However, the problem associated with the use of ZVI is that the reaction time required for the complete removal of arsenic is in days [13]. However, based on the method of nano-scale ZVI (NZVI) synthesis developed by Lehigh university research group in 1995 [14], Kanel et al. (2005) investigated the As(III) and As(V) removal by NZVI [15, 16] and they found that the arsenic was rapidly removed in minutes, and a pseudo-first order reaction was observed.

Based on the above, it appears that the arsenic can be better removed under acidic condition than under base

condition. However, to adjust solution pH by using acidic species results in undesirable species, which will affect the treated water quality. According to the study earlier [17], the above issue of concern can be resolved by CO_2 bubbling, which can adjust the solution pH to acidic condition due to the hydrogen ions generated from carbonated water, as described in Reactions (1)-(4):

$$CO_{2(g)} \leftrightarrow CO_{2(aq)} \tag{1}$$

$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3 \tag{2}$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \tag{3}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \tag{4}$$

In addition, it was reported that high amount of NZVI was required for arsenic removal in field groundwater [16], due to the competition between arsenic species and the background species of groundwater, or due to the inadequate amount of dissolved oxygen (DO) required for iron oxidation to enhance the process performance. With such understanding in mind, the air bubbling was employed and tested in the studied process. Thus, this paper focuses on the effect of gases bubbling on the arsenic removal rate by the NZVI, including CO_2 and air. In addition, characterization of the NZVI behavior in solution was also performed for the treatment system design purpose.

II. MATERIALS AND METHOD

A. Materials

The chemicals of reagent grade used in this study include $FeCl_3 \cdot 6H_2O$ (99%, Merck), and $NaBH_4$ (> 96%; Merck). Both the As(III) and As(V) stock solution were prepared from $NaAsO_2$ (Fluka) and $Na_2HAsO_4 \cdot 7H_2O$ (J.T. Baker), respectively. The H_2SO_4 and NaOH were used for adjusting the initial solution pH. All chemical solutions were prepared with deionized water (18.2 MΩ Mill-Q). Gases of CO_2 (99.5%), Air (O_2 21%, N_2 79%), and N_2 (99.99%) used in this study were purchased from a local supplier (Tainan, Taiwan).

B. NZVI synthesis

The NZVI was synthesized according to Glavee et al. (1995) [14]. A liquid volume of 40 mL of 0.25 M $NaBH_4$ were added into 40 mL of 0.045 M $FeCl_3$ aqueous solution to form nanoiron particles. The mixture was agitated by a revolving propeller. The reaction for NZVI formation is shown in Reaction (5).

$$Fe(H_2O)_6^{3+} + 3BH_4^- + 3H_2O \rightarrow Fe^0 + 3B(OH)_3 + 10.5H_2 \tag{5}$$
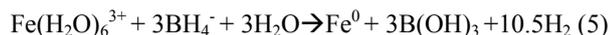
The NZVI particles formed were separated from the liquid solution using a magnet. Immediately, it was then used in the treatment system.

C. Reaction system

The NZVI was used in the arsenic treatment system right after it was synthesized. A dosage of 0.023 g/L of NZVI was applied throughout all experiments. As described in earlier study [18], the reactor with liquid volume of 4.4 L was designed to combine the two chambers for both reactants reaction and particles settling in one unit. The external-circulating pump was installed at outlet of the reactor to form a recirculation mode for arsenic removal (see Figure 1). The solution pH was measured by pH meter (Suntex TS1), while the DO was measured by DO meter (Oxi 330i). The total arsenic, (As(V) and As(III)), was determined by inductively coupled argon plasma (ICP) using Thermo Scientific Model iCAP 6000 series (Thermo Scientific, USA).
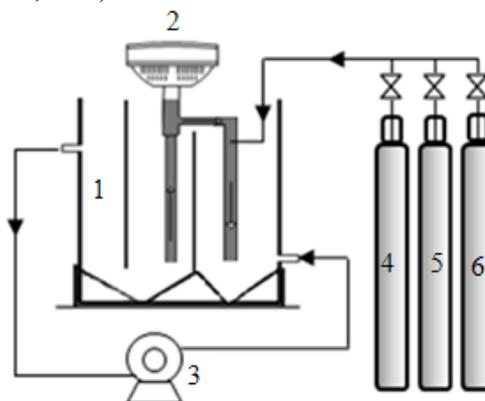

Figure 1. Experimental setup for arsenate treatment: 1. Reactor; 2. Internal recirculated pump; 3. External recirculated pump; 4. CO_2 tank; 5. Air tank; 6. N_2 tank

D. Batch experiments

The initial arsenic concentration applied was 1000 µg/L for all experiments studied, while the initial solution pH's were 4.0, 7.0 and 9.0. To reveal the role of DO in the reaction solution, experiments were designed to explore arsenic removal under deoxygenated and oxygenated conditions. Prior to reaction, the solution was bubbled with N_2 gas for 30 min to strip out dissolved oxygen from the solution until the DO level was less than 0.5 mg/L, a deoxygenated condition.

In the part of gas bubbling, several sets of experiments were designed to optimize the process performance for arsenic removal. Three various gas-bubbled scenarios were proposed and tested. The details were further explained in Table 1. In Scenario 1, the initial solution pH was controlled within neutral range, and the system was then treated by continuous CO_2 bubbling to create a favorable acidic condition. In Scenario 2, the solution was initially acidified by CO_2 bubbling, and then followed by its treatment without any gas bubbling. In Scenario 3, the solution was bubbled in sequence by CO_2 gas and by air to create a low pH and high DO condition, and it was then treated by continuous air aeration.

TABLE I. GAS BUBBLING SCENARIOS IN THE ARSENIC TREATMENT SYSTEM

Scenario	Pre-treatment	Treatment
1	pH adjusted to 7 by H_2SO_4 or NaOH	CO_2 gas bubbling at 300 mL/min
2	pH adjusted to around 4 by CO_2 bubbling of 300 mL/min for 30 min	No gas bubbling
3	pH adjusted to around 4 by CO_2 bubbling of 300 mL/min for 5 min; oxygen supply by air bubbling of 300 mL/min for 10 min	Air bubbling of 300 mL/min

III. RESULTS AND DISCUSSION

A. Effect of initial pH and DO

As shown in Figure 2, the removal performance of arsenic was highly influenced by the initial pH: the arsenic was removed more under acidic condition than under base condition. Such phenomenon can be elucidated from speciation of arsenic in solution. Arsenic exists in solution by different forms, depending on the pH condition. According to the available literature data, the pH of zero point charge (pH_{pzc}) for iron oxides was 8.0 [19]. Also, the pK_a values reported for As(III) are listed as follows: $pK_1 = 9.22$, $pK_2 = 12.13$, and $pK_3 = 12.7$; as for the As(V), they are: $pK_1 = 2.2$, $pK_2 = 6.97$, and $pK_3 = 11.53$ [20]. In the range of pH 2-7, the dominant form of As(V) is $H_2AsO_4^-$,

whereas the adsorbent surface shows a positive charge. The opposite charges of the ion and the adsorbent surface led to the enhancement of the arsenic removal through electrostatic attraction force. For the basic pH condition (7-12), the dominant form of As(V) is $HAsO_4^{2-}$, whereas the adsorbent surface became negatively charged. Thus the electrostatic repulsion force resulted in the decrease of As(V) adsorption. Similarly, under conditions of pH 4-7, the dominant form for As(III) is H_3AsO_3 which is with the form of neutral charge. Still this can result in attraction with the positively charged adsorbent, however, with a lesser degree of attraction tendency. However, for the basic pH condition, the dominant forms of As(III) are with the negative charges, $H_2AsO_3^-$ and $HAsO_3^{2-}$, while the adsorbent surface is also negatively charged. Therefore, the As(III) removal decreased.

Concerning the effect of DO on arsenic removal, Figure 2 shows that arsenic removal was enhanced in the presence of oxygen because arsenic can form inner- and/or outer-sphere complexes with the oxygen-induced iron corrosion products such as iron (hydr)oxides, according to several recent spectroscopic studies [21-24]. In other words, the presence of DO promotes the rate of iron corrosion, and indirectly improves the arsenic adsorption as well.
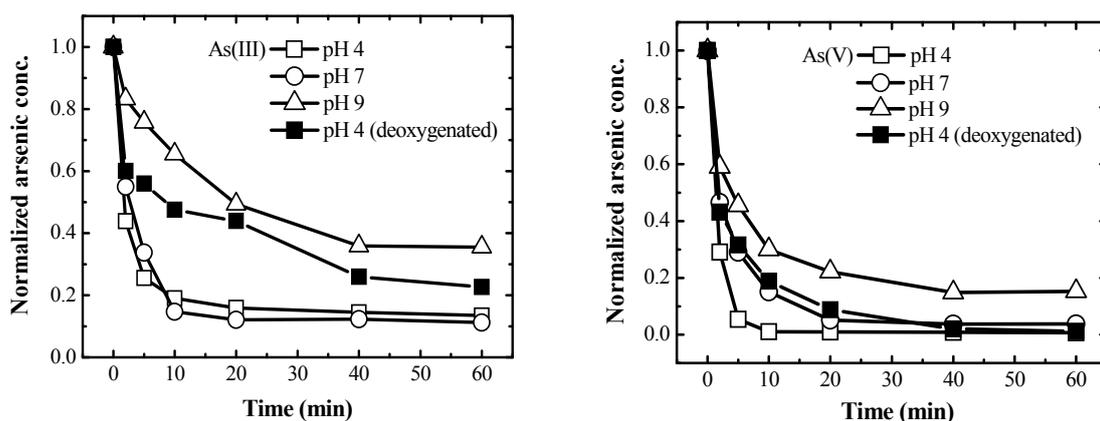

Figure 2. Effect of initial solution pH and DO on As(III) and As(V) removal: NZVI dosage = 0.023 g/L, initial As concentration = 1000 µg/L.

B. Effect of gas bubbling

For Scenario 1, as shown in Figure 3, the arsenic concentrations of both As(III) and As(V) decreased for the first 5 min and then increased gradually. As can be seen from the two DO profiles, because of the DO consumed by NZVI and stripped out by CO_2 gas bubbling, the DO level decreased rapidly in the initial period of reaction, and after 5 min, the system became anoxic condition. In addition, the supply of CO_2 gas can result in the increase of bicarbonate (HCO_3^-) species. As reported in the literature, the release of arsenic from sandstone aquifer was found to be strongly and positively related to the HCO_3^- concentration in the leaching solution [25]. Another report describes that the HCO_3^- can promote iron dissolution from hematite (α-Fe_2O_3) surface

[26], leading to the increase of the dissolved arsenic in solution. The evidence of this study exists in the DO profiles of the later reaction period, which show a gradual increase with the increasing arsenic concentration due to the oxygen release from dissolution reaction of arsenic-adsorbed iron oxides.

As was concluded from the previous results of this study, the initial pH is an important parameter to affect the performance of arsenic removal. Thus, Scenario 2 was designed to create acidic environment through bubbling of CO_2 gas. According to Figure 3, the percentage of equilibrium concentration was around 50% of the initial arsenic concentration for As(III), and it was around 40% for As(V). If compared to the two arsenic profiles of solution pH 4 in Figure 2, where the pH was adjusted by H_2SO_4,

Scenario 2 shows a lower performance of arsenic removal. The key reason behind such difference was its lack of dissolved oxygen, due to the stripping by CO_2 gas bubbling. As can be seen from Figure 3, the initial DO (1-2 mg/L) was low for Scenario 2, after CO_2 bubbling. A low DO level will slow the rate of iron oxidation, resulting in the decrease of arsenic removal.

Based on the above results, Scenario 3 was further proposed to verify the most favorable condition for arsenic removal, i.e., lower pH and higher DO condition. As shown in Figure 3, the pH and DO profiles for Scenario 3 demonstrate that both acidic environment and high initial

DO has been obtained. In addition, the removal efficiency of As(V) was higher than that of As(III). The As(III) concentration decreased gradually over the later reaction period, with the final concentration around 20% of the initial arsenic concentration, whereas the As(V) was rapidly removed and reached to its equilibrium concentration at 10 min. Such results indicate that Scenario 3 is recommended to achieve a satisfactory removal of As(V), without addition of any acidic species. On the other hand, it will take much more reaction time to remove As(III) to achieve the same degree of removal as As(V). Preoxidation of As(III) can be considered when Scenario 3 is applied.
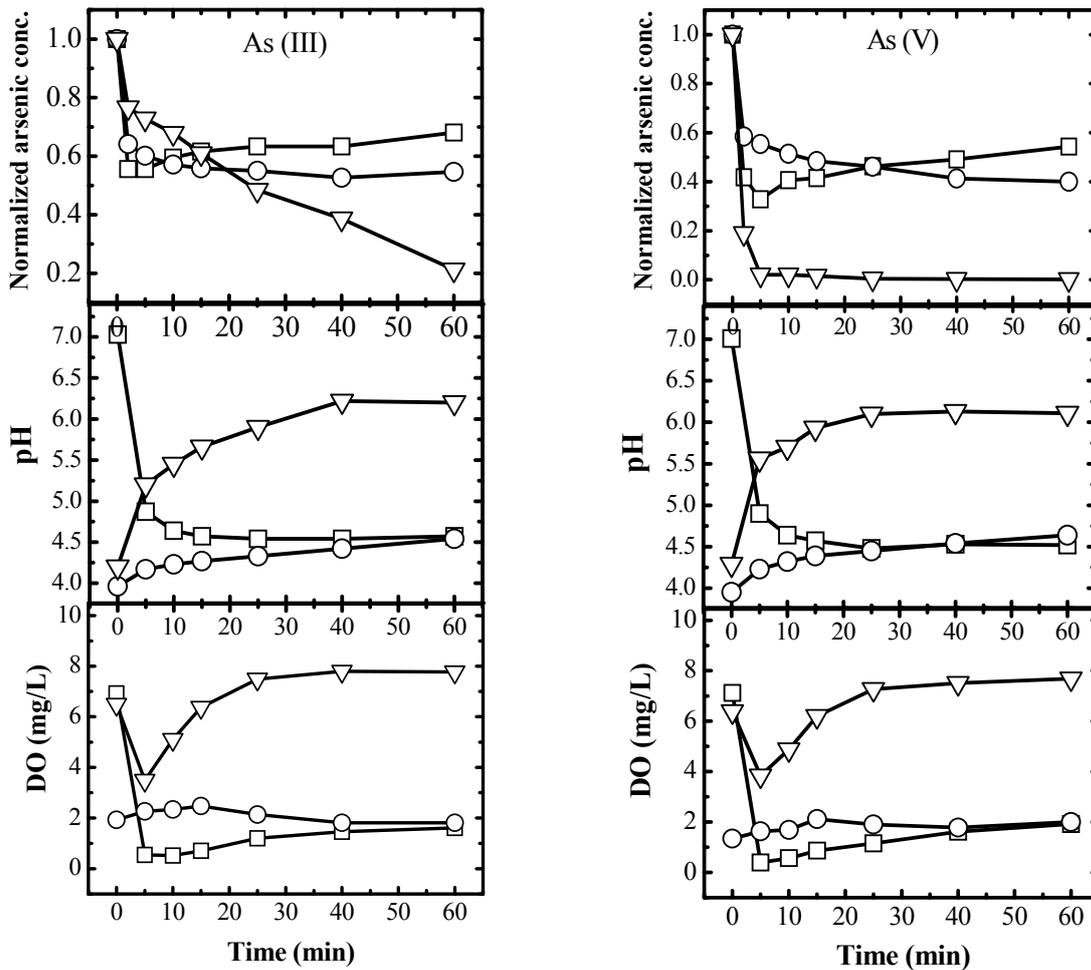

Figure 3. Behavior of As(III) and As(V) removal by NZVI under various gas-bubbling conditions: Scenario 1(-□-), Scenario 2(-○-), Scenario 3 (-▽-); arsenic concentration = 1000 ppb; NZVI dosage = 0.023 g/L.

IV.   CONCLUSIONS

This study was conducted to investigate performance of NZVI in removing arsenic from aqueous solutions. Different parameters such as initial solution pH and DO were studied for their effects on arsenic removal. It was observed that arsenic can be removed favorably under acid condition and high DO level. To avoid the use of acidic

species, which may deteriorate the water quality, different gas bubbling scenarios was investigated. Consequently, pretreatment by CO_2 and air bubbling in sequence is recommended for satisfactory performance of As(V) removal. The advantage of CO_2 bubbling is to create favorable acidic environment for arsenate removal, without sacrificing the treated water quality. As for air bubbling, it will help generate iron corrosion products such as iron

(hydr)oxides, providing reactive sites for arsenic adsorption. To remove As(III) by following the gas bubbling scenario proposed in this study, a preoxidation process needs to be considered to achieve a desired performance of its removal.

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