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Arsenate Removal by Nano Zero-valent Iron in the Gas Bubbling System

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***Abstract*—**This study focused on arsenate removal by nano zero-valent iron (NZVI) in the gas-bubbled aqueous solution. It appears that solution acidified by H_2SO_4 is far more favorable than by CO_2-bubbled acidification. In addition, as dissolved oxygen was stripped out of solution by N_2 gas bubbling, the arsenate removal dropped significantly. To take advantages of common practice of carbonation and oxic condition, pretreatment of CO_2 and air bubbling in sequence are recommended for a better removal of arsenate.

***Keywords*—** Arsenic, arsenate, zero-valent iron.

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I. Introduction

ARSENIC is hazardous material. Consuming water with high level of arsenic will cause skin, lung, bladder, and kidney cancers [1]. The standard of maximum contamination level (MCL) of arsenic in drinking water is 10 μg/L according to U.S. Environmental Protection Agency [2]. Arsenic is stable in several oxidation states, of which the arsenite (As(III)) and arsenate (As(V)) are the most common forms in natural waters. The dominant arsenic species depend greatly on condition of water environment. The As(V) is stable in oxidizing environment, whereas the As(III) is mainly found in reducing one [1]. The adsorption process by using ZVI is a promising alternative for arsenic removal because of its capability of removing both As(V) and As(III) simultaneously [3]. Lackovic et al. (2000) first reported arsenic removal by using ZVI in 2000 for remediation purpose [4]; On the other hand, based on the method of nano-scale zero valent (NZVI) synthesis developed by Lehigh university research group in 1995 [5]; it was found that NZVI possesses higher capacity for arsenic removal than micro-scale zero valent (MZVI) [6, 7]. According to the literature [6], the As(V) can be better removed in acidic condition than in base condition. But, to adjust solution pH by using acidic species H_2SO_4, HCl, or acetic acid may produce undesirable alien species such as sulfate, chloride, and acetate, which will affect the treated water quality. Based on the earlier report [8], the above issue of concern can be resolved by CO_2 bubbling, which can adjust the solution pH to acidic condition due to the increased hydrogen ions from carbonated water, as described below:

$$CO_2\ (g) \leftrightarrow CO_{2(aq)} \quad (1)$$
$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3 \quad (2)$$
$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \quad (3)$$
$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \quad (4)$$

Thus, attempt was made to investigate the effects of gases bubbling, including CO_2, air, and N_2 on the rates of arsenate removal by NZVI. In addition, characterization of NZVI behavior in solution was also performed for the treatment system design purpose

II. Materials and Methods

The chemicals of reagent grade used in this study include $FeCl_3 \cdot 6H_2O$ (99%) and $NaBH_4$ (> 96%) (Merck). The As (V) stock solution was prepared from $Na_2HAsO_4 \cdot 7H_2O$ (J.T. Baker). The CO_2 gas with high purity (99.5%), Air, and N_2 were purchased from a local supplier. All chemical solutions were prepared with deionized water (18.2 MΩ Mill-Q). The NZVI was synthesized according to Glavee et al.(1995) [5]. 0.25 M of $NaBH_4$ was added into 0.045 M of $FeCl_3$ aqueous solution. The mixture was agitated by a revolving propeller. The ferric iron is reduced by the borohydride, as shown in Reaction (5):

$$Fe(H_2O)_6^{3+} + 3BH_4^- + 3H_2O \rightarrow Fe^0 + 3B(OH)_3 + 10.5H_2 \quad (5)$$

Right after the synthesis of NZVI, it was applied immediately in the arsenic treatment system (Figure 1), in which the arsenate concentration (C_0) and NZVI dosage were 1000 μg/L and 0.023 g/L, respectively. As for the gas bubbling system, four scenarios were designed to evaluate each individual performance of arsenate removal. As depicted in Table 1, the solution pH was adjusted either by H_2SO_4 or CO_2 bubbling. To obtain the oxic and anoxic environment, with and without N_2 gas bubbling were applied to control the level of dissolved oxygen in the solution.

As shown in Figure 1, the total bed volume of reactor used in this study was 4.4 L. In addition, the treated liquid samples were filtrated by using a 0.45 μm membrane filter and the solution pH and ORP were measured by pH and ORP meter (Suntex TS1), while the dissolved oxygen was measured by DO meter (Oxi 330i). The residual arsenic (C) was determined by Inductively Coupled argon Plasma (ICP) using Thermo Scientific Model iCAP 6000 series.

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TABLE I
GAS BUBBLING SCENARIOS IN
THE ARSENATE TREATMENT SYSTEM

Scenario	pH adjustment and gas bubbling
1	The pH was adjusted to 4 by H_2SO_4.
2	The pH was adjusted to 4 by CO_2 gas bubbling at 300 mL/min for 30 min.
3	The pH was adjusted to 4 by H_2SO_4, and immediately this was then followed by N_2 gas bubbling to strip out dissolved oxygen from solution.
4	The pH was adjusted to 4 by CO_2 gas bubbling at 300 mL/min for 5 min, and immediately this was then followed by air bubbling until the end of reaction at 300 mL/min

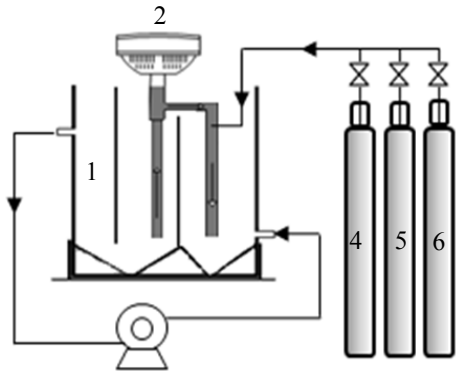


Fig. 1 Experimental setup for arsenate treatment: 1. Reactor; 2. Internal recirculated pump; 3. External recirculated pump; 4. CO_2 tank; 5. Air tank; 6. N_2 tank

III. RESULTS AND DISCUSSION

A. Effect of gas bubbling scenario

Effect of DO on arsenate removal performance comparison can be made between Scenario 1: oxic condition and Scenario 3: anoxic condition. As shown in Figure 2, the arsenate was removed under oxic condition more than anoxic condition. The reason is due to enhanced adsorption through oxygen-induced corrosion iron (hydr)oxide products [4, 9, 10].

Effect of pH adjusted either by acid or by CO_2 gas bubbling was investigated through Scenario 1 (H_2SO_4 addition) and Scenario 2 (CO_2 bubbling). As shown in Figure 2, the one with H_2SO_4 adjustment has higher removal of arsenate than the one with CO_2 bubbling. The key reason is the stripping of oxygen because of CO_2 bubbling. In Scenario 2, the resulted DO was near to zero (anoxic), while the DO remained relatively high in Scenario 1. As mentioned earlier, dissolved oxygen can promote the adsorption of arsenate. Without DO, Scenario 2 exhibits lower removal of arsenate though it's in favorable acidic condition.

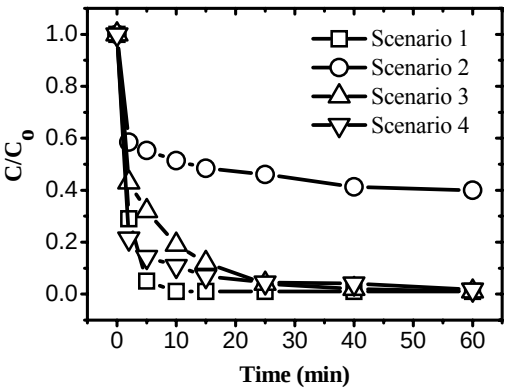


Fig. 2 Comparison of arsenate removal under various gas bubbling conditions

In summary, the following conditions are desired to remove arsenate effectively: lower pH and higher DO. Based on this principle, Scenario 4 was designed to achieve the best removal of arsenate: CO_2 bubbling plus air bubbling. The first bubbling is to ensure a favorable acidic environment, while the second bubbling is for increasing DO content in the solution to be treated. In so doing, the adverse water quality effect by acidic species H_2SO_4 can be prevented. As a result, Figure 2 shows a profile for the Scenario 4 comparable to that for Scenario 1. The removal efficiency for Scenario 4 is more than 95% at time of 25 min.

B. Treated water characterization

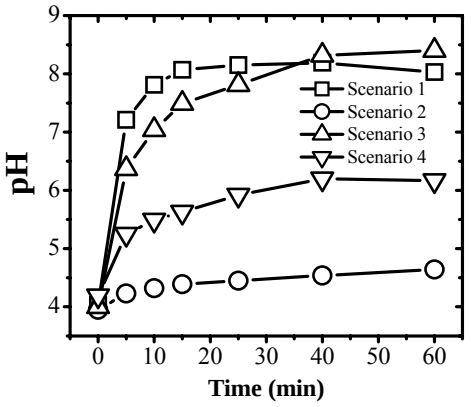
Based on the four mentioned scenarios, Figure 3 shows the three important profiles of pH, DO, and ORP. From Figure 3(a), the initial pH of all scenarios were around 4; the pH's with Scenarios 1 and 3 were adjusted by H_2SO_4 and Scenarios 2 and 4 by CO_2 gas bubbling. All solution pH profiles were observed rise continuously throughout reaction period, due to the build-up of OH^- as presented in Reactions (6) and (7) [11].

$$Fe^0 + 2H_2O \leftrightarrow Fe^{2+} + H_2 + 2OH^- \quad (6)$$
$$2Fe^0 + 2H_2O + O_2 \leftrightarrow 2Fe^{2+} + 4OH^- \quad (7)$$

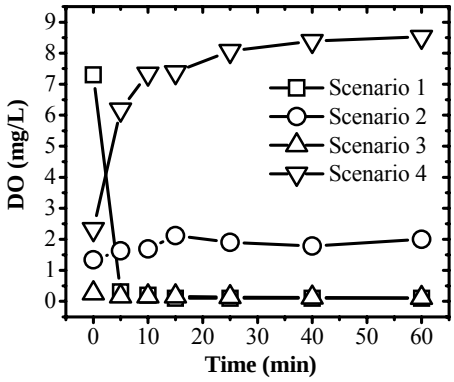
In Figure 3(b), the DO profile for Scenario 1 was seen to decrease rapidly according to Equation (7). Whereas the profiles for Scenarios 2 and 3 remain rather unchanged since the solution has been pretreated by bubbling of CO_2 and N_2, respectively, resulting in low DO value.

On the other hand, for Scenario 4, the air bubbling was supplied continuously throughout all reaction period, and this resulted in increasing DO value. In Figure 3(c), as the NZVI was added into arsenic-contaminated solution, the ORP value decreased rapidly from the positive values to the negative ones. Such situation occurs due to the electrons being released from the NZVI. At time of around 5 min, the ORP for all scenarios, except Scenario 4, were negative values, indicating that the reducing environment of solution has been created [11].

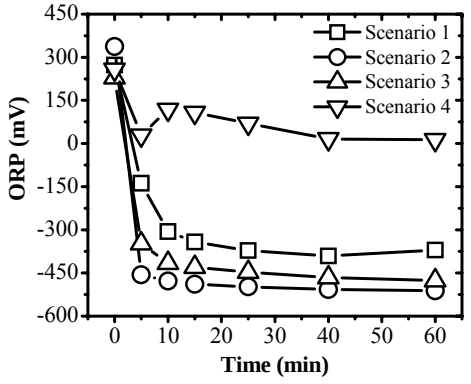
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(a)



(b)



(c)

Fig. 3 Treated water characterization in terms of (a) pH, (b) DO, and (c) ORP variation

Furthermore, the ORP profiles for Scenarios 2 and 3 were lower than the one for Scenario 1. This suggests that the ORP strongly relates with the DO in solution; the higher the DO, the higher the ORP. Thus, the ORP for Scenario 4 was observed to maintain in positive value because of air bubbling and thus higher DO in the solution

IV. CONCLUSIONS

This study was conducted to investigate performance of arsenic removal by using NZVI under different gas bubbling conditions. It was found that As(V) can be removed favorably in acid condition and high DO. Adjusting solution pH to acidic condition by CO_2 bubbling alone could not improve performance of arsenate removal because DO had been stripped out of solution. To avoid the use of acidic species H_2SO_4, which may deteriorate the water quality because of sulfate, a scenario was recommend by bubbling CO_2 and air in sequence, and this thus resulted in satisfactory removal of arsenate.

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