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# Oxidative removal of arsenite by Fe(II)- and polyoxometalate (POM)-amended zero-valent aluminum (ZVAL) under oxic conditions

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## ABSTRACT

Abiotic transformation of As(III) to As(V) is possible which would decrease As toxicity. This study investigated the potential applications of zero-valent Al (ZVAL) or Al wastes, such as Al beverage cans, for converting As(III) to As(V) in an acidic solution under aerobic conditions. Results showed that As(III) could not be oxidized by ZVAL within 150 min reaction at pH 1 because of the presence of an oxide layer on ZVAL. However, 85  $\mu$ M As(III) could be completely oxidized with the addition of Fe(II) or POM due to the generation of a Fenton reaction or the enhancement of H<sub>2</sub>O<sub>2</sub> production, respectively, on the ZVAL surfaces. Because Fe(II) or polyoxometalate (POM) exhibited more stable at low pH and scavenged rapidly the H<sub>2</sub>O<sub>2</sub> produced on the aerated ZVAL surfaces, OH radical productions were more efficient and As(III) was rapidly oxidized in the ZVAL/O<sub>2</sub> system with these two catalysts. The catalytic oxidation kinetics of As(III) in the presence of Fe(II) or POM were best described by zero-order reaction, and the rate constants increased with a decrease of pH from 2 to 1. Following the oxidative conversion of As(III) to As(V) in the ZVAL/Fe/O<sub>2</sub> system, As(V) was removed by the newly formed hydrous Al/Fe precipitates by increasing the solution pH to 6. Nonetheless, the As(V) removal was incomplete in the ZVAL/POM/O<sub>2</sub> system because the hydrolyzed products of POM, e.g., PO<sub>4</sub><sup>3-</sup>, inhibited As(V) removal due to the competitive adsorption of the oxyanion on Al precipitates. Discarded Al-based beverage cans exhibit a higher efficiency for As(III) oxidation and final As removal compared with that of ZVAL, and thus, the potential application of Al beverage cans to scavenge As in solutions is feasible.

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## 1. Introduction

Arsenic (As) is a ubiquitous element commonly found in the atmosphere, natural waters, soils, rocks, and organisms.

Natural processes, such as weathering reactions, biological activities, and volcanic emissions, will lead to As mobilization in the environment. Anthropogenic activities, such as mining, fossil fuel combustion, and agricultural activities, also have an

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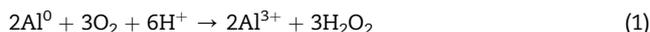
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important impact on the release and accumulation of As in ecosystems. For instance, the mining of sulfide-bearing rocks, pyrite oxidation, the disturbance of sulfidic peat soils, and the transformation of amorphous As-Iron (Fe) phases into crystalline phases could release more than  $1000 \mu\text{g L}^{-1}$  As into surface and ground waters with an extremely low pH (i.e., pH 1–3.1) in many parts of the United States, Korea, Australia, and other countries (Ahn et al., 2005; Appleyard et al., 2004; Moore et al., 1994; Schreiber et al., 2000; Smedley and Kinniburgh, 2002).

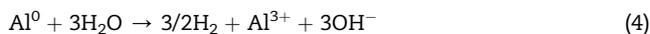
In most natural waters, As consists of two major oxyanions, As(III) and As(V) (Smedley and Kinniburgh, 2002). These two As species exhibit very different affinities to the mineral surfaces, and the retention of both As(V) and As(III) is strongly pH dependent (Jain et al., 1999). In general, low pH favors As(V) adsorption onto mineral oxides, whereas the maximum As(III) adsorption occurs at circumneutral pH and decreases with an increase or decrease in pH (Arai et al., 2001; Dixit and Hering, 2003; Jain et al., 1999; Raven et al., 1998). Arsenic behavior in the environment is also determined by its redox chemistry. Both biotic and abiotic As transformations, along with changes in the redox potentials, are possible and are toxic to organisms nearby because As(III) is more toxic than As(V). The biotic oxidation of As(III) may occur through microbial respiratory and non-respiratory enzymatic systems (Oremland and Stolz, 2003). The abiotic oxidation of As(III) by Mn(III)/Mn(IV)-containing minerals is considered an important pathway that controls As species in natural systems (Amirbahman et al., 2006). In addition, the advancement of the non-selective oxidation of organic and inorganic pollutants by zero-valent metals has gained scientific attention and has become an important environmental issue (Antia, 2010, 2011). For instance, in an aerated solution, the Fenton reaction could be created in the zero-valent iron (ZVI) system for catalytic oxidization of As(III), and the redox product of As(V) was removed by newly formed hydrous ferric oxides (Katsoyiannis et al., 2008). Nonetheless, in an anaerobic solution, Farrell et al. (2001) and Lackovic (2000) found that ZVI could also scavenge As(III)/As(V) with an initial pH 6.1–7 through the surface complexes of iron corrosion products or a surface precipitation. Due to the unique reaction properties of iron, the SONO filters containing composite iron matrix had been developed as an excellent material for treating As-containing waters (Hussam and Munir, 2007; Hussam, 2009).

Although As(III) treatment by ZVI is a promising technique, the choice of alternative zero-valent metals is still needed because ZVI may not be readily obtained by people currently struggling with As related problems, particularly in the areas containing pyrite or sulfide (Williams, 2001). For instance, groundwater of pH 1.9 with high As concentrations (up to  $7 \text{ mg L}^{-1}$ ) has been measured in the disturbed urban area of sulfidic peat soils in Western Australia (Appleyard et al., 2004). Waters discharged from the newly constructed domestic well in Minnesota (Minnesota Department of Health, 2001) and eastern Wisconsin (Schreiber et al., 2000) with high concentrations of As (up to  $5.1 \text{ mg L}^{-1}$ ) and extreme acidity (i.e., pH < 2) has also been detected. In addition, Moore et al. (1994) reported that As concentrations in groundwater and sediment can be affected for hundreds of kilometers downstream from mined areas which may potentially threaten the water supply and safety, and risk to the public health. In this regard, aluminum

alloys/foils, such as aluminum beverage cans (consisting of more than 95% aluminum, AlFsfar and Bdeir, 2008) or zero-valent aluminum (ZVAL), may be the choice of alternative metals because these materials can be recycled and because Al metal exhibits higher redox potential than that of Fe or Fe(II). A previous study found that in an aerated environment, ZVAL was capable of degrading organic pollutants through the production of OH radicals (Reactions (1) and (2)) with a concurrent oxidation corrosion of ZVAL surfaces (Bokare and Choi, 2009).



Considering its preferential oxidative ability and availability, ZVAL can be considered as a reliable source to trigger non-selective oxidation reactions. In addition, in an anaerobic condition, ZVAL or Al-based composites were also capable of removing contaminants, such as Cr(VI),  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , through a reduction coagulation process, leading to pH increase and  $\text{H}_2$  emission (Reaction (4), Bojic et al., 2004, 2009).



Despite these available works on the ZVAL-based systems, there is still a research need because the conversions of As(III) on ZVAL are unclear under ambient environments. Due to  $\text{O}_2$  dissolution, it is likely that an oxidative condition is created when Al-based materials are used to treat As-containing waters exposed to the air. Therefore, in this study, the oxidative conversions of As(III) using ZVAL as a model material were investigated to evaluate precisely the role of ZVAL in scavenging As in an aerated solution. Polyoxometalate (POM,  $\text{HNa}_2\text{PW}_{12}\text{O}_{40}$ ), a catalyst with a high Brønsted acidity, was used as a bridge for the rapid electron transfer among these reactants (Lin et al., 2009). Because excess  $\text{H}_2\text{O}_2$  was accumulated in an aerated ZVAL system (Reaction (1)) (Bokare and Choi, 2009; Lin et al., 2009), ferrous ions were also applied to accelerate the consumption of  $\text{H}_2\text{O}_2$  through the Fenton reaction, leading to the OH radical productions for As(III) oxidation. Upon finishing the redox reactions, the products of As(V), Fe(III), and Al(III) were simultaneously removed by adjusting the solution pH to 6 to co-precipitate or incorporate As(V) in the structures of the Fe/Al hydroxides.

The objectives of this study are to examine the reaction mechanisms of As(III) oxidation on ZVAL as catalyzed by POM or Fe(II) in the presence of oxygen. The applications of Al beverage cans as substitutes for ZVAL were also investigated to evaluate the potential application of these materials for As(III) oxidation and As removal.

## 2. Materials and methods

### 2.1. Materials

Each chemical and reagent used in this study was of analytical grade. The ZVAL was obtained from Merck KGaA (Darmstadt,

Germany). Prior to proceeding with the redox reaction experiments, the ZVAL was cut into small pieces with average dimensions of 5 mm × 5 mm × 0.3 mm, and a total surface area of ca.  $3.4 \times 10^{-3} \text{ m}^2 \text{ g}^{-1}$  was used in a single batch (Lin et al., 2009). All solutions were prepared with 18 MΩ Millipore water, and all glassware was cleaned with 6 M hydrogen chloride (HCl) and rinsed thoroughly with Millipore water.

## 2.2. Methods

### 2.2.1. As(III) oxidation in the aerated ZVAL system

To evaluate the oxidation of As(III) in the presence of ZVAL, approximately 1 g of ZVAL was reacted with 85 μM As(III) at a pH of 1–2 in a 250 mL reaction vessel. The solutions were not buffered and were sparged continuously with air at a rate of 50 mL min<sup>-1</sup>. The pH did not need to be adjusted afterward because there were no discernible changes in the pH during the experiments. In the absence of As(III), the production of H<sub>2</sub>O<sub>2</sub> in the air-equilibrated vessels was determined by the photometric method (Bader et al., 1988). To determine the kinetics of As(III) oxidation and Al(III) production, aliquots were withdrawn from the reaction at specific time intervals. As(III) was measured with an atomic absorption spectrometer (AAS, Hitachi) with hydride generation (please see below). The Al(III) concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin–Elmer).

### 2.2.2. Enhancement of As(III) oxidation with Fe(II) addition

Our preliminary studies found that H<sub>2</sub>O<sub>2</sub> accumulated in the aerated ZVAL system, suggesting that the efficiency of OH radical formations via Reaction (2) was low. To utilize the extra H<sub>2</sub>O<sub>2</sub>, 0.025 mM Fe(II) was added to a 250 mL reaction vessel with 4 g L<sup>-1</sup> ZVAL at a pH of 1 or 2 to obtain a final Fe(II) concentration of 0.1 mM. This procedure created a Fenton reaction in the aerated ZVAL systems to accelerate As(III) oxidation. The other benefit of using ferrous ions is to efficiently co-remove the redox product of As(V) and Fe(III) when the solution pH is increased to form hydrous ferric oxides with large sorption capacities of As(V) (Joo et al., 2004). The procedures of extracting the samples and determining the metal concentrations were the same as described previously. The As(III) analyzes using a hydride generation technique are described in detail below. Each experiment was carried out in triplicate for a given set of conditions.

### 2.2.3. Catalytic oxidation of As(III) by POM in the aerated ZVAL system

Similar to ZVI, the presence of an oxide layer on the surfaces of ZVAL is typically a major factor in decreasing the reactivities of ZVAL (Lin et al., 2009). To enhance As(III) oxidation, a specific volume of 1 mM POM stock solution (HNa<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>, Sigma) was added simultaneously with As(III) to 1 g of ZVAL in a 250 mL reaction vessel, and the final concentrations of As(III) and POM were 85 μM and 0.1 mM, respectively. The solution pH was maintained at a pH of 1 or 2 with constant stirring and sparged with air at a rate of 50 mL min<sup>-1</sup>. Sample aliquots of 1 mL were withdrawn from the reaction vessel at regular time intervals using a syringe, and the As(III) concentrations of the aliquots were measured using hydride generation. Each experiment was carried out in triplicate for a given set of conditions.

### 2.2.4. As removal by pH adjustment to 6

After the As(III) was completely oxidized to As(V), the pH in each solution, derived from the ZVAL/Fe(II)/As(III) and ZVAL/POM/As(III) system, was adjusted to 6 to form Al(III)/Fe(III) hydroxide precipitates. The suspensions were then passed through a 0.2 μm membrane filter. The concentrations of Al/Fe and As in the filtrates were analyzed by ICP-AES and AAS coupled with hydride generation system, respectively, to check the removal efficiency of As(V) on newly formed hydrous Al/Fe oxide.

### 2.2.5. Applications of Al-containing wastes for As(III) treatment

To evaluate the possible oxidation of As(III) by low-cost and readily obtained Al-containing wastes, Al beverage cans were selected to treat As(III)-containing waters. The Al-containing wastes were first polished using sandpaper to remove surface coatings and cut into pieces with dimensions of 5 mm × 5 mm. The Al pieces were dipped into a solution with 6 M HCl for 10 min and transferred immediately to an As(III)-containing solution with or without 0.1 mM Fe(II). As(III) oxidation was analyzed and recorded, and the adjustments in the pH when simultaneously removing Al/Fe and As were also investigated.

### 2.2.6. As(III) analysis and As speciation

As(III) was measured by an AAS with hydride generation by continuous-flow mixing of the 1 M HCl acidified samples using 0.7% NaBH<sub>4</sub> in a Teflon valve and liquid–gas separator. The total amount of As was determined by adding ascorbic acid (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>) or potassium iodide (KI) into the reaction vessel to reduce all As to As(III) for the subsequent hydride generation process. The selective determination of As(III) was performed by adding 0.5 M citrate buffer (pH 5) solution instead of 1 M HCl to convert only As(III) to AsH<sub>3</sub> for detection (Yamamoto et al., 1981).

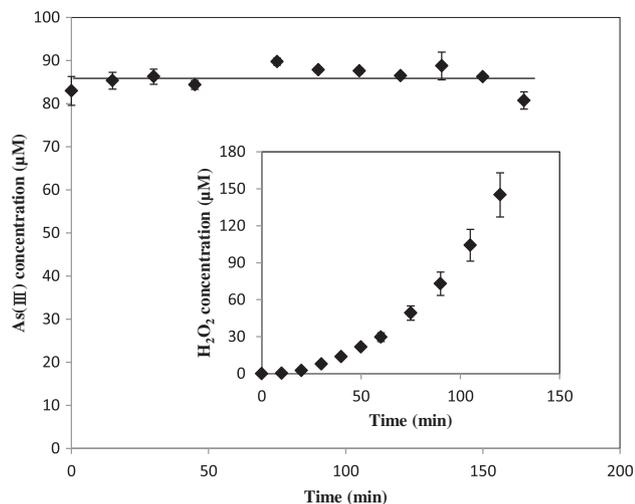
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## 3. Results and discussion

### 3.1. Variations in the As(III) concentrations in the presence of ZVAL

#### 3.1.1. Presence of oxide layers on ZVAL

No significant decreases in the As(III) concentrations were observed when 85 μM As(III) was reacted with ZVAL (4 g L<sup>-1</sup>) under aerobic conditions (Fig. 1). This observation indicates that As(III) oxidation through the redox reactions in the aerated ZVAL systems (i.e., Reactions (1) and(2)) was greatly inhibited. The adsorption/complexation of As(III) on the oxide layer of ZVAL or on the exposed Al<sup>0</sup> surface sites was ruled out because the total As(III) concentrations remained nearly constant during the reactions (Fig. 1). While examining the aerated ZVAL/As(III) system, an increase in the H<sub>2</sub>O<sub>2</sub> concentrations was observed over the course of the reaction time (Fig. 1, inset). The result indicated that upon dissolutions of a small portion of the oxide layers on the surfaces of ZVAL in an acidic solution, the dissolved oxygen was capable of interacting with exposed Al<sup>0</sup> sites, leading to H<sub>2</sub>O<sub>2</sub> production (Reaction (1)). In other words, the oxide layer on the ZVAL did not inhibit H<sub>2</sub>O<sub>2</sub> production but became a complete obstacle to As(III) oxidation within 150 min (Fig. 1, inset).



**Fig. 1** – Changes in the As(III) concentration after interactions with ZVAL ( $4 \text{ g L}^{-1}$ ) at a pH of 1 sparged with air at a rate of  $50 \text{ mL min}^{-1}$ . The production of  $\text{H}_2\text{O}_2$  during the reaction is shown in the inset of figure.

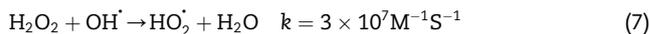
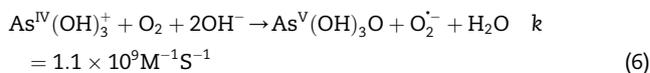
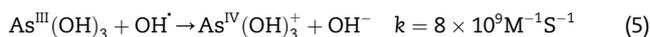
This results differed from those obtained by Bokare and Choi (2009), who noted that chlorophenol oxidation by powder ZVAL occurred when the oxide layer of ZVAL was dissolved at approximately 120 min. Compared to the powder form of ZVAL, the formation of a thin and consistent oxide (passivation) layer (ca. several nm thick) on ZVAL scraps may delay the exposure of sufficiently activated  $\text{Al}^0$  surfaces to the reactants. The inhibition of As(III) oxidation in the current study may be due to the low productivity of  $\text{H}_2\text{O}_2$  (Reaction (1)), and thus, subsequent OH radical productions through Reaction (2) were greatly inhibited on the chemical inertness surfaces of ZVAL with irremovable oxide layers. The oxidative corrosion of ZVAL (Reaction (3)) on the limited  $\text{Al}^0$  sites of ZVAL may also inhibit  $\text{H}_2\text{O}_2$  productions. Besides, no discernible changes in pH were observed during the experiments, indicating the overall stoichiometric Reactions of 1–3 in the ZVAL/ $\text{O}_2$  system were slight due to the presence of oxide layers on ZVAL.

### 3.1.2. Absence of oxide layers on ZVAL

To justify that the oxide layer on ZVAL would impede As(III) oxidation, the ZVAL was treated with 6 M HCl for 15 min because this treatment was capable of removing the oxide layer from ZVAL surfaces. With the same experimental conditions, the As(III) was completely oxidized within 10 min after being added into the acid-treated ZVAL (data not shown). This observation demonstrates that in an aerobic environment, systems with clean ZVAL surfaces can create an overall oxidative capability, which is attributed to a significant accumulation of  $\text{H}_2\text{O}_2$  concentrations (more than  $500 \text{ }\mu\text{M}$ ) that enhances subsequently OH radical productions on the clean ZVAL surfaces (Reaction (2)).

Although the production of an excess  $\text{H}_2\text{O}_2$  may serve as a scavenger of OH radicals, the reaction rate of OH radicals with As(III) (Reaction (5)) and subsequent As(IV) oxidation to As(V) (Reaction (6)) is 2 order greater than that with  $\text{H}_2\text{O}_2$  (Reaction (7)) (Hug and Leupin, 2003). Therefore, the excess  $\text{H}_2\text{O}_2$  may not influence As(III) oxidation by OH radicals, and a tendency

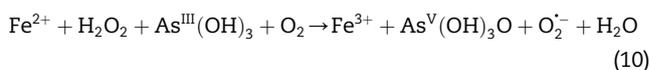
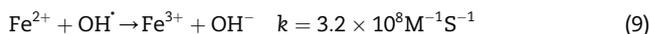
to convert As(III) to As(V) could be observed on the clean ZVAL surfaces, i.e., in the absence of the oxide layer.



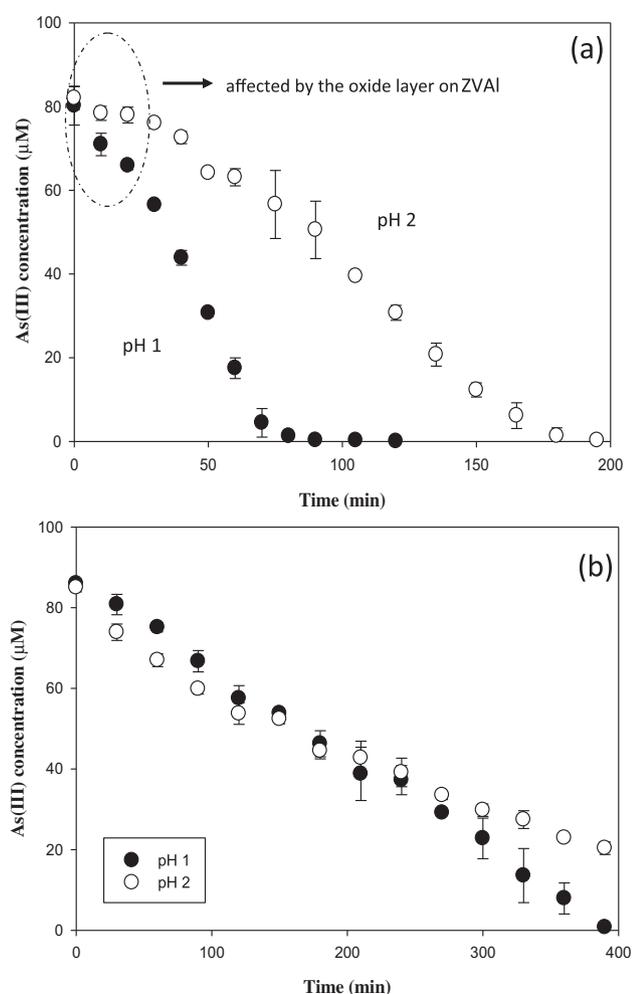
### 3.2. As(III) oxidation by ZVAL in the presence of Fe(II)

Based on the previous studies, an oxide layer-bearing ZVAL tended to create an unfavorable condition for As(III) oxidation even if  $\text{H}_2\text{O}_2$ , a precursor of the Fenton reaction, was continuously produced (Fig. 1, inset). To utilize the production of  $\text{H}_2\text{O}_2$  more efficiently in the aerated ZVAL system,  $0.1 \text{ mM}$  Fe(II) was added to adjust the system toward an oxidative environment. The results showed that at a pH of 1,  $85 \text{ }\mu\text{M}$  As(III) was rapidly oxidized within 90 min; however, a significant delay in As(III) oxidation in the aerated ZVAL system was observed at a pH of 2 (Fig. 2a). Even though the addition of Fe(II) could accelerate As(III) oxidation, the oxide layer on ZVAL delayed As(III) oxidation within 20 min reaction (Fig. 2a), leading to a slight deviation from zero-order kinetics. Exclusion of the kinetic data obtained under the influence of oxide layer, the zero-order model could describe more precisely As(III) oxidation (Table S1, Supplementary Information). As(III) oxidation rate was shown to be dependent on the pH, and it increased significantly from  $0.522$  to  $1.16 \text{ }\mu\text{M min}^{-1}$  at the pH decreased from 2 to 1. The values were slightly lower than those obtained from direct oxidation of As(III) by OH radicals generated via nitrate photolysis (Dutta et al., 2005).

After oxidation of As(III) to As(V), no reductions in As(V) were observed with a prolonged reaction time of 120 min, and the adsorption/complexation of As(V) on ZVAL was less possible because As(V) concentrations (i.e.,  $85 \text{ }\mu\text{M}$ ) remained constantly in solutions. This finding demonstrates that the efficiency of As(III) oxidation in the aerated ZVAL system was greatly promoted with the addition of Fe(II) due to the rapid production of the OH radicals (confirmed by the production of 2-propanone with the addition of 2-propanol, a radical scavenger, in the ZVAL/Fe(II) system without As(III)) through the Fenton reaction (Reaction (8), Barreiro et al., 2007). Extra Fe(II) may not impede As(III) oxidation because Fe(II) oxidation by OH radicals (Reaction (9)) was 1 order lower than that by As(III) (Reaction (5)). Combination of the Reactions of 5, 6 and 8, As(III) oxidation through the Fenton reaction in the current system could be expressed as the Reaction (10).

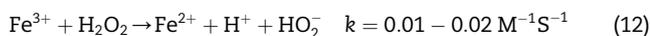


Upon Fe(II) oxidation, Fe(III) could be reduced by ZVAL, peroxide radicals (Reaction (11), Hug and Leupin, 2003), or  $\text{H}_2\text{O}_2$  (Reaction (12), Dutta et al., 2005) back to Fe(II). Thus, the

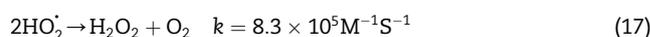
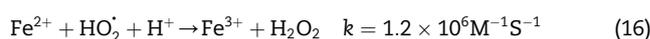
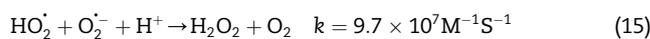
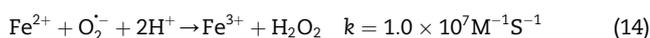
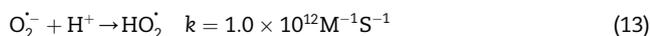


**Fig. 2** – Oxidation of 85  $\mu\text{M}$  As(III) on ZVAL ( $4 \text{ g L}^{-1}$ ) in the presence of (a) 0.10 mM Fe(II) and (b) 0.1 mM POM at a pH of 1 and 2 sparged with air at a rate of  $50 \text{ mL min}^{-1}$ .

redox products of As(V) remained in the solutions as long as the ZVAL continuously served electron donors for the production of  $\text{H}_2\text{O}_2$  (Reaction (1)) and Fe(II).



As mentioned previously, 85  $\mu\text{M}$  As(III) could be completely oxidized at 90 min, and based on Reaction (10), oxidation of 85  $\mu\text{M}$  As(III) required the same amount of  $\text{H}_2\text{O}_2$  consumption. However, only 78  $\mu\text{M}$   $\text{H}_2\text{O}_2$  was produced at 90 min, measured in the ZVAL/ $\text{O}_2$  system in the absence of Fe(II) and As(III), and the shortage of 7  $\mu\text{M}$   $\text{H}_2\text{O}_2$  could be compensated by the concurrent Reactions of 13–17 (Hug and Leupin, 2003). Because the reaction rate of peroxide radicals, produced from Reaction (10), with  $\text{H}^+$  (Reaction (13)) is 4 order larger than that with  $\text{Fe}^{3+}$  (Reaction (11)), the consumption of peroxide radical lead mainly to the  $\text{HO}_2^\cdot$  and subsequent  $\text{H}_2\text{O}_2$  production (Reactions (15)–(17)).

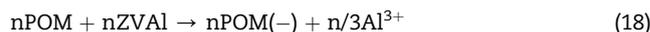


However, the amounts of  $\text{H}_2\text{O}_2$  productions from these pathways are still much lower than from the direct interactions of dissolved oxygen with ZVAL (Reaction (1)). That is, the production of Fenton reagent, i.e.,  $\text{H}_2\text{O}_2$ , was controlled mainly by the reactive efficiency of ZVAL with  $\text{O}_2$ , and thus, the ZVAL should play a key role in the determination of the zero-order kinetic behavior of As(III) oxidation in the Fe(II)/ZVAL/ $\text{O}_2$  system. Because  $\text{H}_2\text{O}_2$  production consumes protons (Reactions (1) and (13)–(16)), a relatively higher pH was unfavorable for  $\text{H}_2\text{O}_2$  production, leading to the inhibition of a Fenton-like reaction and subsequent As(III) oxidation.

### 3.3. As(III) oxidation by ZVAL/ $\text{O}_2$ in the presence of POM

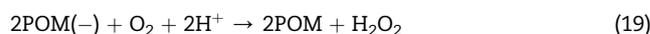
Similar to Fe(II), POM was capable of enhancing As(III) oxidation in the aerated ZVAL system, but the reaction rate was slower compared to that of the Fe(II)/ZVAL system (compared with the same counterparts in Fig. 2a and b). This observation may suggest that both Fe(II) and POM could act as catalysts, but they performed as different functions or pathways in the acceleration of As(III) oxidation in the aerated ZVAL system. Total As concentrations remained constantly during the experiments which indicated that the adsorption/complexation and precipitation of As on ZVAL/POM were excluded. The oxidation rate of As(III) in the POM/ZVAL/ $\text{O}_2$  system depended on the solution pH, and the rate constant slightly increased from 0.16 to 0.22  $\mu\text{M min}^{-1}$  with a decrease of pH from 2 to 1. These values were three to five times less than their counterparts in the Fe(II)/ZVAL/ $\text{O}_2$  system (Table S1, Supplementary Information). Several factors, such as  $\text{H}_2\text{O}_2$  concentrations and the production rate of OH radicals, other than the presence of oxide layer may impede As(III) oxidation in the POM/ZVAL/ $\text{O}_2$  system because no initial delays of As(III) oxidation were observed in the presence of POM (Fig. 2b).

POM, a strong Brønst acid, dissolved the oxide layer on the ZVAL, leading to the exposure of the more activated site on the ZVAL and the release of more Al(III) (Fig. 3a). Upon the dissolution, POM rapidly obtained electrons from the ZVAL and was converted to a reduced form with a blue color (Reaction (18), Lin et al., 2009).

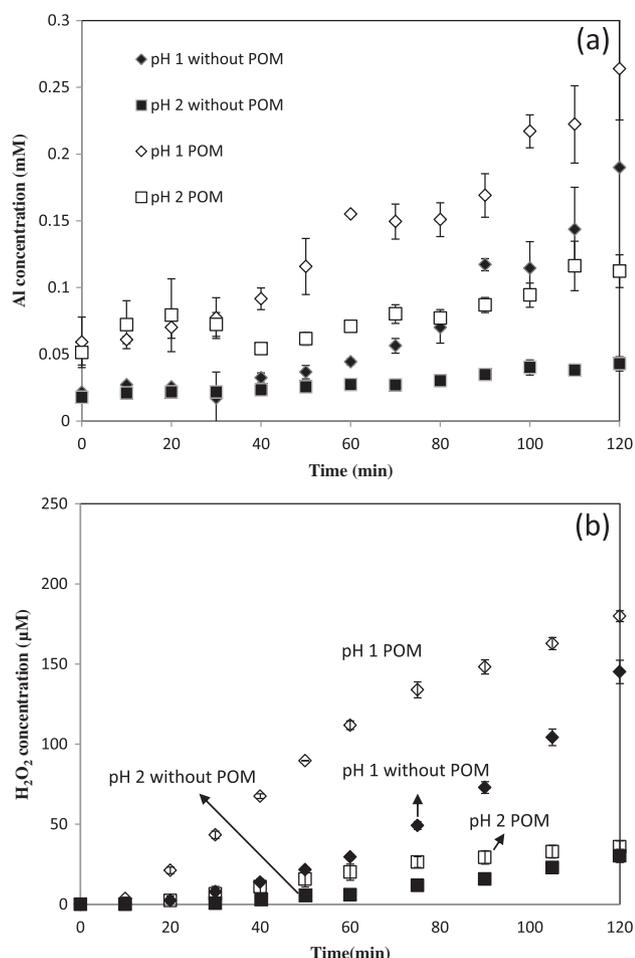


where  $n = 1, 2, \text{ or } 3$  depending on the reaction time of POM with ZVAL.

In the presence of  $\text{O}_2$ , the reduced POM (i.e.,  $\text{POM}(-)$ ) was oxidized back to its original form, simultaneously producing  $\text{H}_2\text{O}_2$  (Reaction (19), Fig. 3b) (Hiskia et al., 2001).



In other words, aside from the production of  $\text{H}_2\text{O}_2$  on the ZVAL surface with  $\text{O}_2$  (Reaction (1)), the addition of POM into the



**Fig. 3 – (a) Al dissolution and (b) H<sub>2</sub>O<sub>2</sub> production in an aerated condition with 4 g L<sup>-1</sup> ZVAL in the presence and absence of 0.1 mM POM at a pH of 1 and 2.**

aerated ZVAL system also led to the production of H<sub>2</sub>O<sub>2</sub> through the interaction of dissolved oxygen with the redox couple of POM/POM(-) (Reaction (19)). Because of the production of extra H<sub>2</sub>O<sub>2</sub> in the presence of POM (Fig. 3b), more OH radicals were expected to be produced through Reaction (2). Therefore, an increase in As(III) oxidation by the ZVAL was observed with the addition of POM. However, as mentioned previously, the efficiencies of catalytic oxidation of As(III) by POM was lower than Fe(II) in the aerated ZVAL system. This results suggests that an increase in the H<sub>2</sub>O<sub>2</sub> concentrations with the addition of POM was not as efficient as the direct production of OH radicals by Fe(II) in the ZVAL/O<sub>2</sub> system, although both systems exhibited the same zero-order reaction ( $R^2 > 0.94$ ) with respect to As(III) oxidation (Table S1, Supplementary Information).

As shown in Fig. 3b, H<sub>2</sub>O<sub>2</sub> production tended to be slower after 80 min of reaction, particularly at pH 1. The simultaneous oxidation of the reduced POM by H<sub>2</sub>O<sub>2</sub> (Reaction (20), Hiskia et al., 2006) may lead to a retardation of H<sub>2</sub>O<sub>2</sub> production. However, the catalytic oxidation of As(III) on the ZVAL with POM did not decline within the time span (Fig. 2b) which suggested that the H<sub>2</sub>O<sub>2</sub> concentrations was not a limit factor in the influence of As(III) oxidation.



Diffusion of the H<sub>2</sub>O<sub>2</sub>, produced from Reactions (1) and (19), onto the ZVAL surfaces was necessary prior to the productions of OH radicals (Reaction (2)). Although the reaction rate of H<sub>2</sub>O<sub>2</sub> on ZVAL is unclear at this stage, OH radical productions through the heterogenous reaction of H<sub>2</sub>O<sub>2(aq)</sub> on the ZVAL surfaces (Reaction (2)) may proceed slower than the homogenous reaction of H<sub>2</sub>O<sub>2(aq)</sub> and Fe(II)<sub>(aq)</sub> (Reaction (8)), having a reaction rate of 63 M<sup>-1</sup> s<sup>-1</sup> at pH ≤ 3 (Barreiro et al., 2007). Therefore, the reaction of H<sub>2</sub>O<sub>2</sub> with the ZVAL (Reaction (2)) may be a rate-determination step for As(III) oxidation in the POM/ZVAL system, leading to overall the lower catalytic efficiency of POM as compared to that of Fe(II).

The major reactions and corresponding results of the four systems investigated in the study are summarized in Table 1. System 1 demonstrated that the oxidation and removal of As(III) by ZVAL was inhibited due to the presence of the oxide layer; however, washing with acids would eliminate the passive oxide film on ZVAL, and thus, a rapid conversion of As(III) to As(V) was observed (System II). Systems III and IV showed that the reactive mechanisms of As(III) oxidation in both systems are different. With the addition of Fe(II), a Fenton reaction was created to accelerate As(III) oxidation in System III; nonetheless, enhancement of the oxide layer removal and H<sub>2</sub>O<sub>2</sub> productions facilitated As(III) oxidation in the presence of POM (System IV).

#### 3.4. Efficient removal of As from ZVAL systems

Previous results have confirmed that the addition of both Fe(II) and POM accelerated the As(III) oxidation on ZVAL. To further evaluate the removal efficiency of the redox products, i.e., metal cations (e.g., Al<sup>3+</sup> and/or Fe<sup>3+</sup>) and As(V), in the POM/ZVAL and Fe(II)/ZVAL systems, the solution pH was increased to 6 to co-precipitate metal ions and As(V) after the residual ZVAL scraps were removed. The results showed that more than 50 µg L<sup>-1</sup> As(V) (approximately 3.3% of the original As concentrations, or 20 µM) still existed in the POM/ZVAL system, indicating that the Al hydroxides could not completely scavenge As(V) from the solution. We presumed that upon pH increase, a portion of the hydrolyzed products of POM, such as PO<sub>4</sub><sup>3-</sup> and WO<sub>4</sub><sup>3-</sup>, were formed (Zhu et al., 2003). These anions competed with As(V) on the surface sites of Al hydroxides, and thus, As(V) removal was incomplete in the presence of POM. The associations of hydrolyzed productions of POM with As(V), leading to As loss with an increase of pH to 6, were ruled out because As loss was not observed when the POM/As(III)-containing solution was adjust to pH 6 in the absence of ZVAL.

Unlike the system with POM, As(V) removal was complete in the ZVAL/Fe(II) system when the solution pH was increased to 6 after the residual ZVAL scraps were removed (Table 2). Except for a trace amount of Al ion that was detected, no Fe was present in the filtrate (Table 2), which demonstrated that the formation of Fe/Al hydroxides acted as an efficient adsorbent for As(V). The results were consistent with the reports by Farrell et al. (2001) that Al and Fe salts were most commonly used materials for removing As in water treatment systems involving chemical precipitation. Our preliminary experiments found that the precipitation of 264 ± 13 µM Al(III),

**Table 1 – Summarizations of the systems settings, major reactions, and corresponding results of As(III) oxidation.**

Systems	Pre-treatment oxide layer	Major reactions	Results
I ZVAL/As(III)	No	$2Al^0 + 3O_2 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O_2$ $2Al^0 + 3/2O_2 + 2H_2O \rightarrow 2Al^{3+} + 6OH^-$	No As(III) oxidation No As(III) removal <sup>a</sup>
II ZVAL/As(III)	Yes <sup>b</sup>	$2Al^0 + 3O_2 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O_2$ $2Al^0 + 3/2O_2 + 2H_2O \rightarrow 2Al^{3+} + 6OH^-$ $Al^0 + 3H_2O_2 \rightarrow Al^{3+} + 3HO^{\cdot} + 3OH^-$ $HO^{\cdot} + As(III) + 1/2O_2 \rightarrow As(V) + HO_2$	As(III) was completely oxidized within 10 min No As(V) removal <sup>a</sup>
III Fe(II)/ZVAL/As(III)	No	$2Al^0 + 3O_2 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O_2$ $Fe^{2+} + H_2O_2 + As(III) + O_2 \rightarrow Fe^{3+} + As(V) + O_2^- + H_2O$	As(III) was completely oxidized within 90 min at pH 1 No As(V) removal <sup>a</sup>
IV POM/ZVAL/As(III)	No	$2Al^0 + 3O_2 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O_2$ $nPOM + nZVAL \rightarrow nPOM(-) + n/3Al^{3+}$ $2POM(-) + O_2 + 2H^+ \rightarrow 2POM + H_2O_2$ $Al^0 + 3H_2O_2 \rightarrow Al^{3+} + 3HO^{\cdot} + 3OH^-$ $HO^{\cdot} + As(III) + 1/2O_2 \rightarrow As(V) + HO_2$	As(III) was completely oxidized within 400 min at pH 1 No As(V) removal <sup>a</sup>

a As was not adsorbed/complexed on ZVAL during the reactions.  
b ZVAL was pre-treated with 6 M HCl for 15 min to remove the oxide layer.

dissolved from 4 g L<sup>-1</sup> ZVAL at pH 1 after 120 min reaction, could not remove completely 85 μM As(V). With the addition of Fe(II), As(V) could be scavenged efficiently due to an increase in the amount of precipitating agent and high affinity of Fe to As(V) as compared with Al. As(V) removal may be attributed to the adsorption/complexation on the surfaces of Fe/Al coprecipitates, most likely on the Fe sites, or the incorporation into the structures during the productions of Fe/Al precipitates. Based on the current experimental conditions, Fe(II) is a preferential material over POM when considering either As(III) oxidation or As(V) removal in the presence of ZVAL.

**3.5. Practical applications of Al beverage cans for As(III) oxidation**

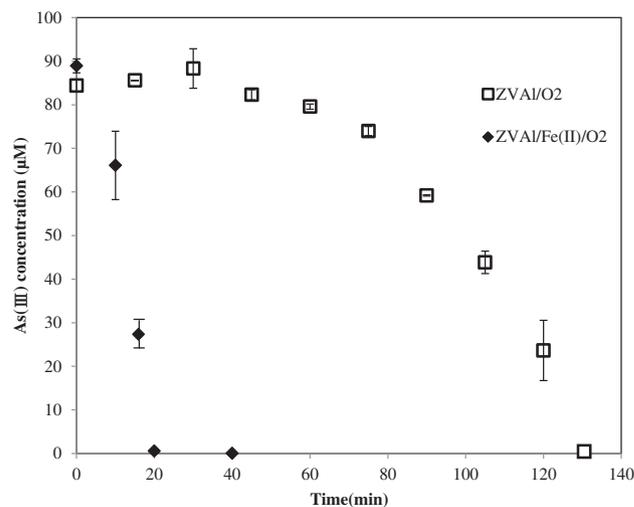
To evaluate the potential applications of disposed Al metals/alloys for the conversions of As(III) to As(V) and its final removal, an Al-based beverage can was selected as a model material. With the addition of 0.1 mM Fe(II), 85 μM As(III) was

oxidized to As(V) within 20 min in the presence of the Al beverage can; however, it took approximately 130 min to convert the same amount of As(III) to As(V) in the absence of Fe(II) (Fig. 4). Regardless of the amount of Fe(II) added, the Al beverage can exhibited a higher oxidative ability compared to its counterparts in the ZVAL system, possibly due to a combination of high surface areas and the lack of an oxide layer of ZVAL after the Al can was polished with sandpaper. Even if different performances of the oxidative conversions of As(III) existed in the Al beverage can system with or without Fe(II), at the end of the redox reactions (i.e., converting all As(III) to As(V)), both systems could remove As completely when the solution pH was increased to 6 (Table 2). The results demonstrate that the utilization of a disposed Al beverage can to treat As(III)-containing waters is a feasible method because the materials are readily obtained and the treatment of 85 μM As requires a short period of time, particularly in the presence of Fe(II).

**Table 2 – Changes of Fe, Al, As concentrations upon increasing solution pH to 6 after 85 μM As(III) was converted completely to As(V) at pH 1 or 2 in the presence of 4 g L<sup>-1</sup> ZVAL or Al beverage can with 0.1 mM Fe(III).**

Sample	pH 1			pH 2		
	Fe	Al	As	Fe	Al	As
	-μM-					
ZVAL						
Initial <sup>a</sup>	100	264 ± 13	85	100	112 ± 7	85
Final <sup>b</sup>	0	3	0	0	0.3	0
Al can						
Initial <sup>a</sup>	100	296 ± 32	85	100	166 ± 14	85
Final <sup>b</sup>	0	0	0	0	0	0

a Fe and As concentrations expressed as the amounts of initial addition; Al concentrations were measured after 120 and 60 min reaction for ZVAL and Al can, respectively.  
b Metal concentrations measured after solution pH was increased to 6 and passed through a 0.2 μm membrane filter.



**Fig. 4 – Oxidation of 85 μM As(III) by an Al beverage can with an area of 5 mm × 5 mm (4 g L<sup>-1</sup>) in the presence or absence of 0.1 mM Fe(II) at a pH of 1.**

#### 4. Conclusions

This study suggests that ZVAL can be an alternative material for treating As(III)-containing waters because Al metals exhibit a higher redox potential compared to that of ZVI. Both POM and Fe(II) can accelerate As(III) oxidation by ZVAL in an acidic solution but through different pathways. POM served as a dissolving agent for removing the oxide layer on ZVAL surfaces and an electron shuttle for transferring electrons from the ZVAL to the dissolved  $O_2$ , forming  $H_2O_2$ . As(III) was then oxidized by the OH radicals, which were produced after  $H_2O_2$  interacted with ZVAL. Fe(II) exhibited a better ability to convert As(III) to As(V) than POM in the ZVAL/ $O_2$  system. Because Fe(II) could not dissolve the oxide layer on the ZVAL, its promotion of As(III) oxidation was due to the rapid consumption of  $H_2O_2$ , produced from the surfaces of the aerated ZVAL system, through a Fenton-like reaction. The Al beverage can waste was proven to be an excellent substitute to ZVAL for oxidizing As(III) to As(V) in an aerobic environment. The As-contaminated acid mine waters may contain Fe(II). By adding Al beverage cans into the groundwater sparged with air, Fe(II) can promote the conversion of  $H_2O_2$ , produced from the interactions of the Al beverage can with dissolved  $O_2$ , to OH radicals for As(III) oxidation. Upon the oxidation of As(III) to As(V), the redox products of metal ions, such as  $Al^{3+}$  and  $Fe^{3+}$ , could be co-precipitated or could serve as adsorbents for As(V), and thus, As could be completely removed in a cost-effective manner.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2013.02.024>.

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