



# Utilization of spent aluminum for *p*-arsanilic acid degradation and arsenic immobilization mediated by Fe(II) under aerobic condition



Yukun Liu<sup>a</sup>, Ping Hu<sup>a</sup>, Jingtang Zheng<sup>a,\*</sup>, Mingbo Wu<sup>a,\*</sup>, Bo Jiang<sup>a,b,\*</sup>

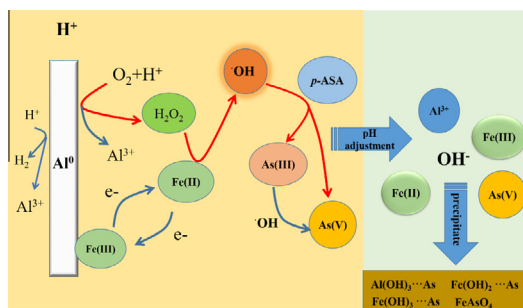
<sup>a</sup> State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao 266580, Shandong, PR China

<sup>b</sup> School of Environmental and Municipal Engineering, Qingdao University of Technology, Qingdao 266033, PR China

## HIGHLIGHTS

- A strategy of “waste control by waste” for treating organic arsenic was proposed.
- Fe(II) significantly enhances the yield of  $\cdot\text{OH}$  in aerobic Al beverage cans system.
- Arsenic can be immobilized at pH = 6.0 with Fe(III)/Al(III) as flocculating agents.
- The corrosion of metal aluminum would not cause Al(III) pollution in effluent.

## GRAPHICAL ABSTRACT



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## ABSTRACT

As a typical feed additive, *p*-arsanilic acid (*p*-ASA) potentially brings about the risks of toxic inorganic arsenic contamination in natural environments. In this study, the potential utilization of the spent aluminum beverage cans (AIBCs) for the degradation of *p*-ASA and immobilization of the produced inorganic arsenic was unprecedentedly evaluated. The results show that the degradation efficiency of *p*-ASA increased with decreasing solution pH, and *p*-ASA can be completely degraded to inorganic arsenic species within 180 min at pH  $\leq$  2.0 in the aerobic AIBCs/Fe(II) system. The optimal performance for *p*-ASA degradation was obtained at Fe(II) concentration of 0.2 mM. But under anaerobic condition, the degradation of *p*-ASA was significantly retarded due to the inhibited production of  $\text{H}_2\text{O}_2$  by the absence of oxygen. In the AIBCs/Fe(II) system, Fe(II) did not only catalytically transform  $\text{H}_2\text{O}_2$  to  $\cdot\text{OH}$  via Fenton reaction, but also, combining with Al(III) ion, acts as preferable flocculant for inorganic arsenic removal. Thus, the produced As(V) species can be completely removed via the formation of As(V)-bearing amorphous hydrous Al/Fe precipitates by simple adjusting solution pH to 6.0. Generally, the present study provides a cost-effective and environmentally friendly strategy for degrading organic arsenic pollutants and immobilizing the hypertoxic inorganic arsenic species.

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## 1. Introduction

The contamination of carcinogenic arsenic species in natural water poses serious health risks to humans in many regions of the world, which is caused by both natural processes and/or anthropogenic activities [1–3]. The inorganic/organic arsenic species are the common chemical pollutants in natural environments, including arsenate (As(V)), arsenite (As(III)), and some organic

\* Corresponding authors at: State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao 266580, Shandong, PR China (J. Zheng); School of Environmental and Municipal Engineering, Qingdao University of Technology, Qingdao 266033, PR China (B. Jiang).

E-mail addresses: jtzheng03@163.com (J. Zheng), wumb@upc.edu.cn (M. Wu), bjiang86upc@163.com (B. Jiang).

arsenic compounds, etc. [4]. In natural waters, inorganic arsenic is commonly encountered in two oxidation states, namely arsenite (As(III)) and arsenate (As(V)) [2]. In contrast to As(III), As(V) is less toxic and can be more easily removed by absorbents and coagulants due to its lower mobility. Thus, till now, many approaches, e.g., Fenton reaction [5], UV photolysis [6], UV/iron [7], UV/TiO<sub>2</sub> [8,9], have been successfully and effectively applied for the oxidative conversion of As(III) to As(V).

Although, contrast to inorganic arsenic species, the organic arsenic compounds often exhibit non-toxicity, they can potentially transform to more toxic and mobile counterpart inorganic species (i.e., As(III) and As(V)) via biotic and abiotic reactions when they are released into aquatic/soil environment [10–12]. Thus, the organic arsenic pollutants contaminated wastewaters produced by factory farms and industries pose a serious threat to environment. In view of this, it is an important and urgent task to develop environmentally benign and more effective technologies toward the treatment of the organic arsenic pollutants [12–14]. In recent decades, a number of studies have investigated the degradation process (e.g., UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> [15], chemical oxidation [16], photocatalysis [17]) for the degradation of organic arsenic pollutants. However, the toxic species of the inorganic arsenic are still remaining in solution, and require subsequent immobilization processes (e.g., adsorption or flocculation), which are of high cost and complicated.

Zero-valent aluminum (ZVAL) is a strong reducing agent ( $E^0 = -1.662$  V) and demonstrates to be able to activate molecular oxygen to produce reactive oxygen species in situ, e.g., H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub><sup>-</sup>, and ·OH, which are capable of oxidizing organic contaminants [15,18–20]. Consequently, the electrons releasing of ZVAL through the corrosion of metal aluminum have already been exploited for the treatment of wastewater. Bokare et al. [21] demonstrated that ZVAL was capable of degrading organic pollutants (e.g., nitrobenzene, 4-chlorophenol, and phenol) in an aerated environment, through the production of ·OH. However, few studies have paid attention to the utilization of ZVAL for degradation of organic arsenic and immobilization of the inorganic arsenic species produced in-situ.

Although the aluminum beverage cans (AIBCs) contains several impurities, including Fe, Cu, Mn, Mg, etc. (see Table S1), metal aluminum is the main component of the AIBCs (see Fig. S1), thus the AIBCs can be utilized as substitutes for ZVAL to degrade the organic contaminants. In view of this, this study examined the flexibility of an environmentally favorable and cost-effective strategy to degrade organic arsenic pollutants using the spent AIBCs mediated by Fenton reaction and immobilize the inorganic arsenic produced via simple adjusting the solution pH. Here, a typical organic arsenic pollutant, namely *p*-arsanilic acid (*p*-ASA), was selected as a probe contaminant to investigate the oxidation capacity of AIBCs/Fe(II) system with considering its widespread use. The influences of various operating parameters including solution pH, initial Fe(II) concentration and gas atmosphere, etc., were studied to inspect the reaction mechanisms. Generally, the results are expected to offer an excellent example of a “waste control by waste” strategy for the treatment of organic pollutants.

## 2. Experimental section

### 2.1. Materials

Chemicals that were used in this study include *p*-arsanilic acid (*p*-ASA, 98%), ferrous sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O, >99%), coumarin (C<sub>9</sub>H<sub>6</sub>O<sub>2</sub>, 97%), H<sub>2</sub>SO<sub>4</sub> (73.0–75.0%), HCl (36–38%), eriochrome cyanine S (C<sub>23</sub>H<sub>15</sub>Na<sub>3</sub>O<sub>9</sub>S, >99%), hexadecyltrimethyl ammonium bromide (C<sub>19</sub>H<sub>42</sub>BrN), antimony potassium tartrate

(K(SbO)–C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·0.5H<sub>2</sub>O, >99%), L-ascorbic acid (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>, >99.7%), 1,10-phenanthroline monohydrate (C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>·H<sub>2</sub>O, 99%) and hydroxylamine hydrochloride (HONH<sub>2</sub>Cl, 98.5%) which were supplied by Xiya Reagent and Sinopharm Chemical Reagent Co. Ltd., respectively. The aluminum beverage cans were used by Coca Cola®.

All chemical reagents used were all of analytical grade. Deionized water was used for all experiments. The stock solutions of *p*-ASA (0.5 mM) was prepared by dissolving appropriate amounts of *p*-ASA with deionized water. Fe(II) solution (10 mM) was prepared by dissolving FeSO<sub>4</sub>·7H<sub>2</sub>O in 1 mM H<sub>2</sub>SO<sub>4</sub> with adding a small amount of reduced iron powder. The AIBCs were cleaned with fine emery paper to remove the paint and the organic film. Then, the AIBCs were cut into 3 mm × 3 mm pieces.

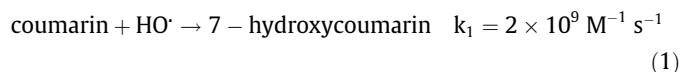
### 2.2. Experimental procedure

All of the experiments were conducted in an open condition, 200 mL, cylindrical glass tube, magnetically stirred and at the room temperature. Unless otherwise mentioned, the AIBCs loading was fixed at 10 g/L and previously treated with 3% v/v HCl for 30 min to remove the Al<sub>2</sub>O<sub>3</sub> layer. All of the working solutions were prepared by diluting the stock solution with deionized water. Solution pH was adjusted with concentrated H<sub>2</sub>SO<sub>4</sub> or NaOH solution. The reaction solution was bubbled continuously with 100 mL/min air. To create an anaerobic atmosphere, the working solution was bubbled continuously with argon for 20 min prior to initiating the reaction.

In the cases of adding Fe(II) and the insoluble substance of AIBCs releasing to the solution, the reaction samples were withdrawn at the given specific time intervals and immediately filtrated through 0.45 μm PTFE microporous filtering film, and then the concentrations of residual As and Fe in the filtrate were analyzed. All experiments were carried out induplicate for a given set of conditions to make the relative error less than 5%.

### 2.3. Analysis

Solution pH value of the working solution was measured by pH meter (PHS-3C). The degradation efficiency of *p*-ASA was reflected by monitoring the concentration of inorganic arsenic, As(V) and As (tol) (As(V) + As(III)). The concentration of As(V) was determined by the modified ammonium molybdate spectrophotometry, with a detection limit of 0.03 μM [22]. Briefly, for each 1 mL of sample and 1.8 mL of the color reagent (1 mL of methanol, 0.5 mL of the 2% HCl acidifying solution and 0.3 mL of the color reagent) were mixed sequentially. For As(tol) determination, the 2% HCl containing 2 mmol L<sup>-1</sup> KIO<sub>3</sub> was used instead of 2% HCl solution [22]. The ferrous ion concentration was determined by the developed 1,10-phenanthroline spectrophotometry at the wavelength of 510 nm [23]. The concentration of H<sub>2</sub>O<sub>2</sub> was detected by using titanium potassium oxalate through spectrophotometry [24]. The concentration of Al(III) ion was determined by the developed eriochrome cyanine S spectrophotometry at the wavelength of 612 nm [25]. The quantitative analysis of metal ions was conducted on an inductively coupled plasma spectrometer (ICP). Based on Eq. (1), ·OH concentration was measured by using 1.0 mM coumarin to scavenge ·OH. The fluorescence intensity of 7-hydroxycoumarin was detected by fluorescence spectrophotometer (F97PRO, Lengguang Tech.) [26].



The precipitate was separated from solution through vacuum suction filtration with 0.45 μm PTFE membrane, washed

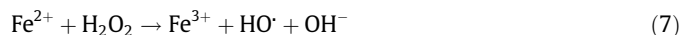
repeatedly with pure water and dried in a vacuum oven for 40 h. Then, the solid powder was collected to analyze its mineral compositions using XPS (PHI5000 Versa Probe, ULVAC-PHI, Japan).

### 3. Results and discussion

#### 3.1. Degradation of *p*-ASA in different processes

According to the previous literature [13,27–30], the oxidation capacity of ZVAL/O<sub>2</sub> depend on the production of active species. The reactions in the ZVAL/O<sub>2</sub> system should start with the corrosive dissolution of aluminum and the concurrent reduction of dioxygen (Eqs. (2) and (3)), which competes with proton for reactive electron (Eq. (6)). The disproportionation of HO<sub>2</sub> with rate of  $9.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  leads to the formation of H<sub>2</sub>O<sub>2</sub>, which subsequently generate ·OH, a highly oxidative species ( $E_{(\text{HO}^\cdot/\text{H}_2\text{O}_2)}^0 = 2.8 \text{ V}$ ), via Fenton like reactions (Eqs. (4) and (5)) [Zero-Valent Aluminum for Oxidative Degradation of Aqueous Organic Pollutants]. As shown in Fig. 1 (a), in AIBCs/O<sub>2</sub> reaction system, a great amount of H<sub>2</sub>O<sub>2</sub> (approximately 50 mg/L) were generated within 180 min, accompanying with the formation of ·OH, which can be qualitatively determined using coumarin as a scavenger (Fig. 1(b)). Thus, in AIBCs/O<sub>2</sub>/*p*-ASA reaction system, approximately 23 μM inorganic arsenic can be produced after the reaction time of 180 min, which mainly consists of As(V) (approximately 20 μM). The OH radical was probably the primary species for the degradation of *p*-ASA, which is consistent with previous studies [2,31]. However, this degradation process was sluggish, which is probably ascribed to the inferior rate

of heterogeneous Fenton-like reaction with metal aluminum as the catalyst (Eq. (5)).



As a homogeneous catalyst, Fe(II) ion can effectively transform mild oxidant H<sub>2</sub>O<sub>2</sub> to ·OH (Eq. (7)) [38]. To sufficiently utilize H<sub>2</sub>O<sub>2</sub> produced via the electron transfer reaction between AIBCs and oxygen (Eqs. (2)–(4)), 0.2 mM Fe(II) was added to improve the oxidative environment of AIBCs system. It can be seen in Fig. 1(c) that in the case of AIBCs/Fe(II)/O<sub>2</sub>/*p*-ASA, 100 μM *p*-ASA can be rapidly and completely transformed to inorganic arsenic within 180 min, which almost entirely existed as As(V). The interaction between Fe(II) ion and oxygen molecule may induce the generation of ·OH, but a control reaction carried out in Fe(II) containing solution without the presence of AIBCs showed little sign of *p*-ASA degradation.

As presented in Fig. 1(a), when Fe(II) ion was added into AIBCs system, negligible concentration of H<sub>2</sub>O<sub>2</sub> was detected, suggesting that H<sub>2</sub>O<sub>2</sub> was probably transformed to ·OH via Fenton reaction.

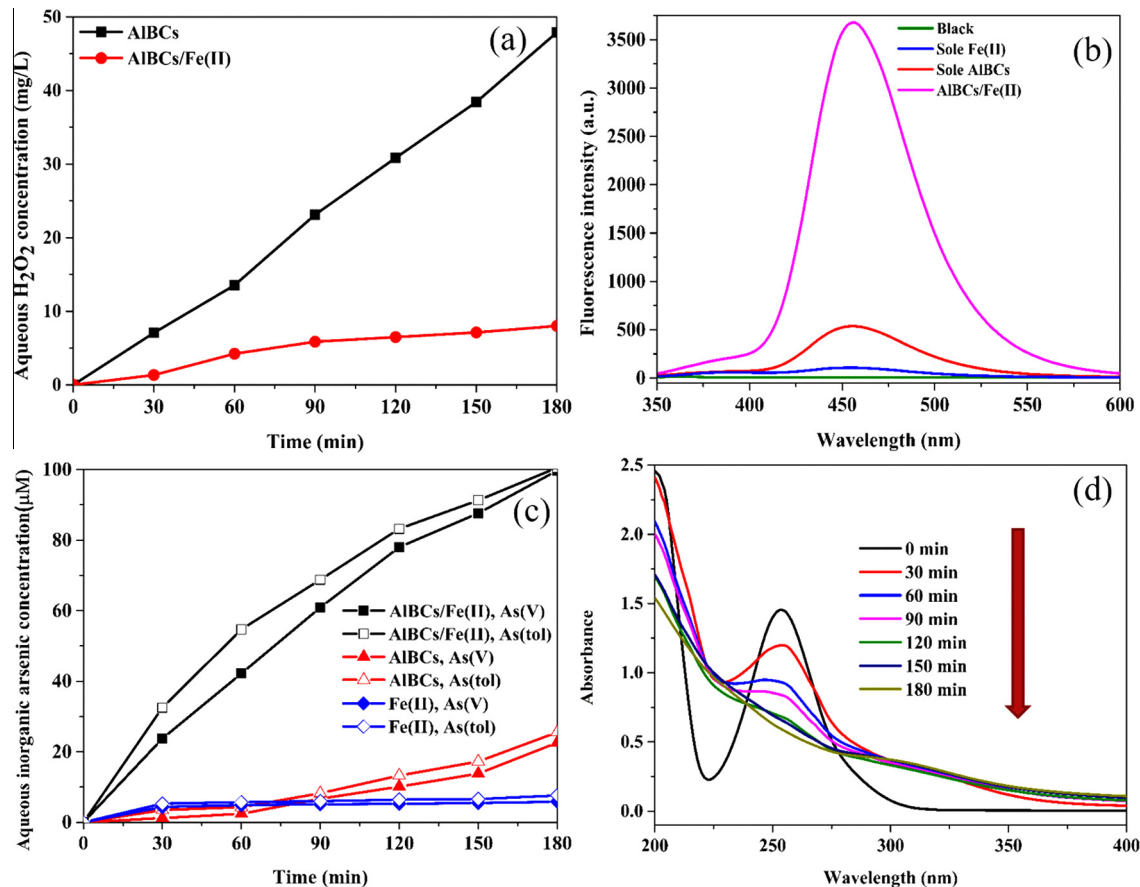


Fig. 1. The production of the H<sub>2</sub>O<sub>2</sub> in AIBCs and AIBCs/Fe(II) systems (a); the fluorescence intensity of 7-hydroxycoumarin at 90 min in different reaction systems (b); the oxidation of *p*-ASA in different reaction systems (c); changes of UV-vis spectra in AIBCs/Fe(II) system (d) ( $[\textit{p}\text{-ASA}]_0 = 100 \mu\text{M}$ ,  $[\text{Fe(II)}]_0 = 200 \mu\text{M}$ ,  $[\text{AIBCs}]_0 = 10 \text{ g/L}$ ,  $\text{pH}_0 = 2.0$ ).

And this can be validated by the significantly enhanced production of  $\cdot\text{OH}$  in AIBCs/Fe(II) system in comparison with these in the case of sole AIBCs and sole Fe(II) systems (see Fig. 1(b)). This powerfully proves that there was a synergistic effect in the oxidation capacity of AIBCs system mediated by Fe(II).

It is known that UV–vis spectra can reflect the structures of some organic molecule [32]. Therefore, to inspect the oxidation of *p*-ASA in AIBCs/Fe(II) system, the UV–vis spectra changes of *p*-ASA were monitored with the reaction time. As shown in Fig. 1(a), the absorption band of initial *p*-ASA solution at 256 nm, which mainly originates from the aromatic ring in *p*-ASA molecule [32,33]. In AIBCs/Fe(II)/O<sub>2</sub>/*p*-ASA system, the intensity of the absorption band at 256 nm gradually decreased with the degradation time and until the peak was disappeared. In this reaction process, TOC reduced from 9.15 mg L<sup>-1</sup> to 4.41 mg L<sup>-1</sup>. Hence, the structure of *p*-ASA molecule would be effectively destroyed during the degradation process by the oxidative species (i.e.,  $\cdot\text{OH}$ ).

According to the mechanisms involved in Fenton process [31,34,35], the main mechanism for *p*-ASA degradation induced by  $\cdot\text{OH}$  can be mainly differentiated into three different pathways: dehydrogenation, electrophilic addition to unsaturated bond, and electron transfer [34]. Because of the property of electron-rich in the molecule of *p*-ASA, the As–C bond is easily cleaved by  $\cdot\text{OH}$  through electrophilic addition [1,36]. In this process, As(IV), an intermediate of the As–C bond breaking, can easily disproportionate to As(III) and As(V) with the ratio of 1:1 [34]. Then, As(III) can be rapidly oxidized to As(V) by  $\cdot\text{OH}$  [37]. Thus, As(V), as the final degradation product of *p*-ASA, is the dominant species of inorganic arsenic products in solution. As mentioned above, the degradation of organic arsenic can convert arsenic from organic arsenic form to inorganic arsenic form and thus the concentration of inorganic arsenic species can be used as a reliable index to reflect the oxidation of *p*-ASA in the system.

### 3.2. Effect of initial *p*-ASA concentration

Fig. 2 illustrates that increasing initial concentration of *p*-ASA reduced the efficiency of inorganic arsenic formation, but the concentration of inorganic arsenic increased. Specifically, when the *p*-ASA initial concentration was 200  $\mu\text{M}$ , only approximately 70% inorganic arsenic (approximately 140  $\mu\text{M}$ ) were generated within 180 min. It can be attributed to the fact that the higher initial concentration of organic arsenic has stronger competition

between the initial reactant and the intermediate products with the reactive oxygen species.

### 3.3. Effect of different gas atmosphere

It has been demonstrated that oxygen is an indispensable substrate for the production of reactive oxygen species in ZVAI-bearing system [38,39]. As shown in Fig. 3(a), the formation of inorganic arsenic is significantly retarded in the an aerobic conditions, while significant concentrations of As(V) and As(tol) were produced in the air-equilibrated condition. The small quantity of As(III) oxidized in an argon atmosphere may be attributed to remnants of oxygen dissolved in the reaction mixture. Due to lack of the electron acceptor (O<sub>2</sub>) in the working solution, the generation of H<sub>2</sub>O<sub>2</sub> via the electron transferring from Al<sup>0</sup> to oxygen molecule was interrupted (Eq. (5)). As depicted in Fig. 3(b) and (c), in an aerated environment, the concentration of H<sub>2</sub>O<sub>2</sub> and the fluorescence intensity of 7-hydroxycoumarin continued to accumulate with the reaction time; however, they were greatly inhibited in an argon atmosphere due to the absence of oxygen. These results are consistent with the aforementioned formation efficiency of inorganic arsenic species, and validate that the oxygen is the prerequisite reactant for *p*-ASA degradation in the AIBCs/Fe(II) system.

### 3.4. Effect of initial concentration of Fe(II)

Since the oxidation capacity of Fenton reaction system is closely related with the concentration of iron, the effect of adding Fe(II) with the ranges of 0–1.0 mM was studied in this section. As presented in Figs. 4(a) and S2(a), Fe(II) ion as the catalyst could significantly enhance the *p*-ASA transform to inorganic arsenic via Fenton reaction (Eq. (7)). For example, in comparison with the case of sole AIBCs, when 0.05 mM Fe(II) concentration was added, the rate of *p*-ASA degradation from 20% raised to 80%. After 180 min reaction, the optimal degradation efficiency of *p*-ASA was achieved at initial Fe(II) concentration of 0.2 mM. However, when further increasing initial Fe(II) concentration above 0.2 mM, the formation efficiency of As(V) unexpectedly decreased. As for 1.0 mM Fe(II), the rate of *p*-ASA degradation reduced to 80%. It can be validated by the fluorescence spectra of 7-hydroxycoumarin Figs. 4(b) and S2(b), increased production of  $\cdot\text{OH}$  can be further improved by increasing the concentration of Fe(II) from 0.05 to 0.2 mM.

In fact, in AIBCs/Fe(II) system, the dissolution of aluminum depleted H<sup>+</sup> (Eq. (6)), which led to an increase in pH value over time (Fig. S4). This can be partially confirmed by the fact that solution pH gradually increases from 2.0 to 2.15, 2.3, 2.5, 2.6, 2.8 after 180 min in AIBCs system with the presence of 0.05, 0.1, 0.2, 0.5, 1.0 mM Fe(II), respectively. The increased solution pH possibly led to the formation of insoluble precipitates of iron hydroxide (see Figs. S2(c), S2(d) and S4), which blocked active sites on the surface of AIBCs and therefore reduced the formation of H<sub>2</sub>O<sub>2</sub>. This phenomenon was aggravated in AIBCs/Fe(II) system with high concentration of Fe(II). Besides, the presence of Fe(II) would compete with O<sub>2</sub> for the electrons derived from the corrosion of metal aluminum ( $E_{(\text{O}_2/\text{H}_2\text{O}_2)}^0 = 0.695\text{V}_{\text{NHE}}$  vs  $E_{(\text{Fe(III)/Fe(II)}}^0 = 0.771\text{V}_{\text{NHE}}$ ) [38]. Therefore, it is thermodynamically feasible that the redox reaction occurred between Al<sup>0</sup> and Fe(III) for Fe(II) regeneration. It can be verified by the result that in the presence of AIBCs the concentration of Fe(II) decreased first and then increased after 90 min, which is significantly different from the variation of Fe(II) concentration in Fe(II)/H<sub>2</sub>O<sub>2</sub> and Fe(II)/O<sub>2</sub> system (Fig. S6).

As shown in Fig. 4(c), with the initial concentration of Fe(II) increasing, the amount of Al(III)–Fe(II) demonstrates dome-shaped correlation with maximum at 0.2 mM of Fe(II). When the Fe(II) concentration was relatively small, the Fe(II) devoting to

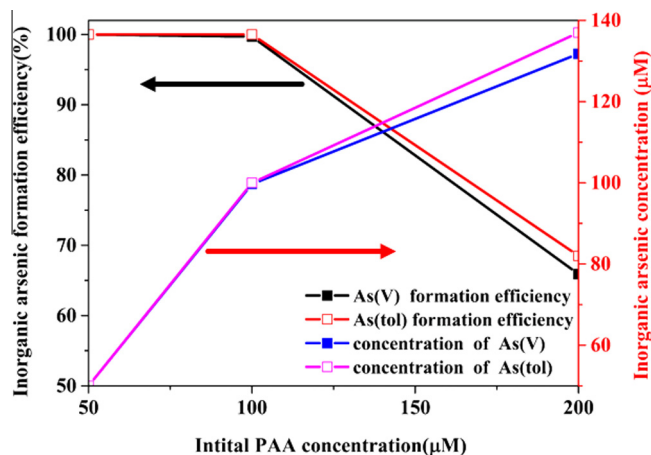
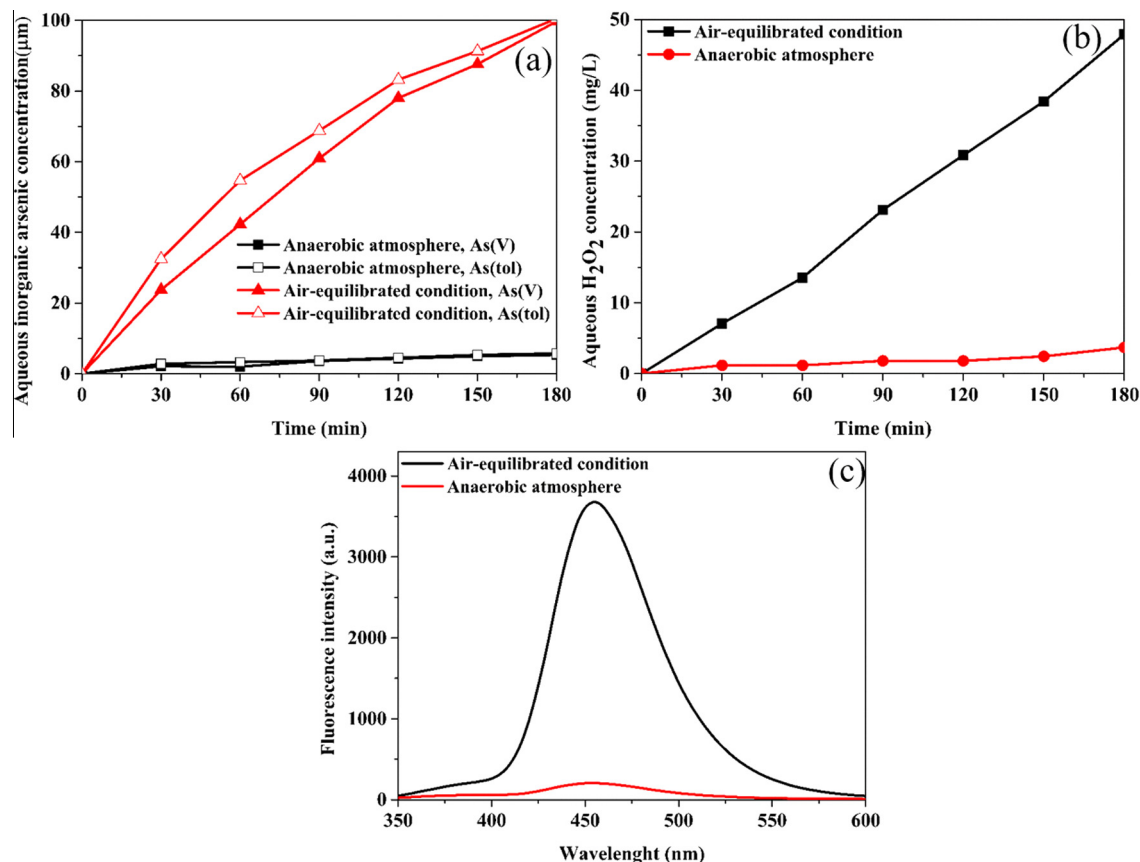


Fig. 2. Effect of initial *p*-ASA concentration (50, 100, 200  $\mu\text{M}$ ) on the final formations of inorganic arsenic species within 180 min ( $[\text{Fe(II)}]_0 = 200 \mu\text{M}$ ,  $[\text{AIBCs}]_0 = 10 \text{ g/L}$ ,  $\text{pH}_0 = 2.0$ ).





**Fig. 3.** Effect of various gas atmosphere on the formation of inorganic arsenic species (a), the production of H<sub>2</sub>O<sub>2</sub> (b) and the fluorescence intensity of 7-hydroxycoumarin (c) ( $[p\text{-ASA}]_0 = 100 \mu\text{M}$ ,  $[\text{AIBC}]_0 = 10 \text{ g/L}$ ,  $[\text{Fe(II)}]_0 = 200 \mu\text{M}$ ,  $\text{pH}_0 = 2.0$ ).

Fenton reaction. But increasing the concentration of Fe(II), the excessive Fe(II) would capture the strong oxidizing substances and transform to Fe(III). The formed Fe(III) can compete with dissolved O<sub>2</sub> for reactive electrons, which impeded the generation of H<sub>2</sub>O<sub>2</sub>. Consequently, the efficiency of the degradation of *p*-ASA was retarded in a high concentration of Fe(II) solution. Besides, the higher concentration of Fe(II) was added, the more ferric hydroxide precipitate can be formed, which can adhere to the surface of AIBCs and retard the corrosion of metal Al. Therefore, with increasing the concentration of Fe(II), the aluminum ions decreased.

### 3.5. Effect of initial pH

Solution pH is a critical factor on the corrosion of metal aluminum, Fenton reaction and hydrolytic reaction, thus the effect of different initial pH of solution on the degradation rate of *p*-ASA was investigated in the pH range of 1.5–3.5. As described in the Fig. 5(a) and Fig. S6(a), the rate of *p*-ASA degradation increased with the reducing initial pH value, illustrating that higher acidic condition is much more suitable for the degradation of *p*-ASA. For example, 100 μM *p*-ASA can be completely degraded within 180 min at pH = 1.5 and 2.0. But the degradation efficiency of *p*-ASA was only 58% and 24% at pH 2.5 and 3.5, respectively, which are considerably inferior to that obtained at pH 2.0. The main reason accounts for the experimental results with the following aspects. For one thing, under the stronger acidic condition, more activated site of the AIBCs was exposed to the dissolved oxygen for more H<sub>2</sub>O<sub>2</sub> production due to the corrosive dissolution of inert aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) layer. For another, the formation and

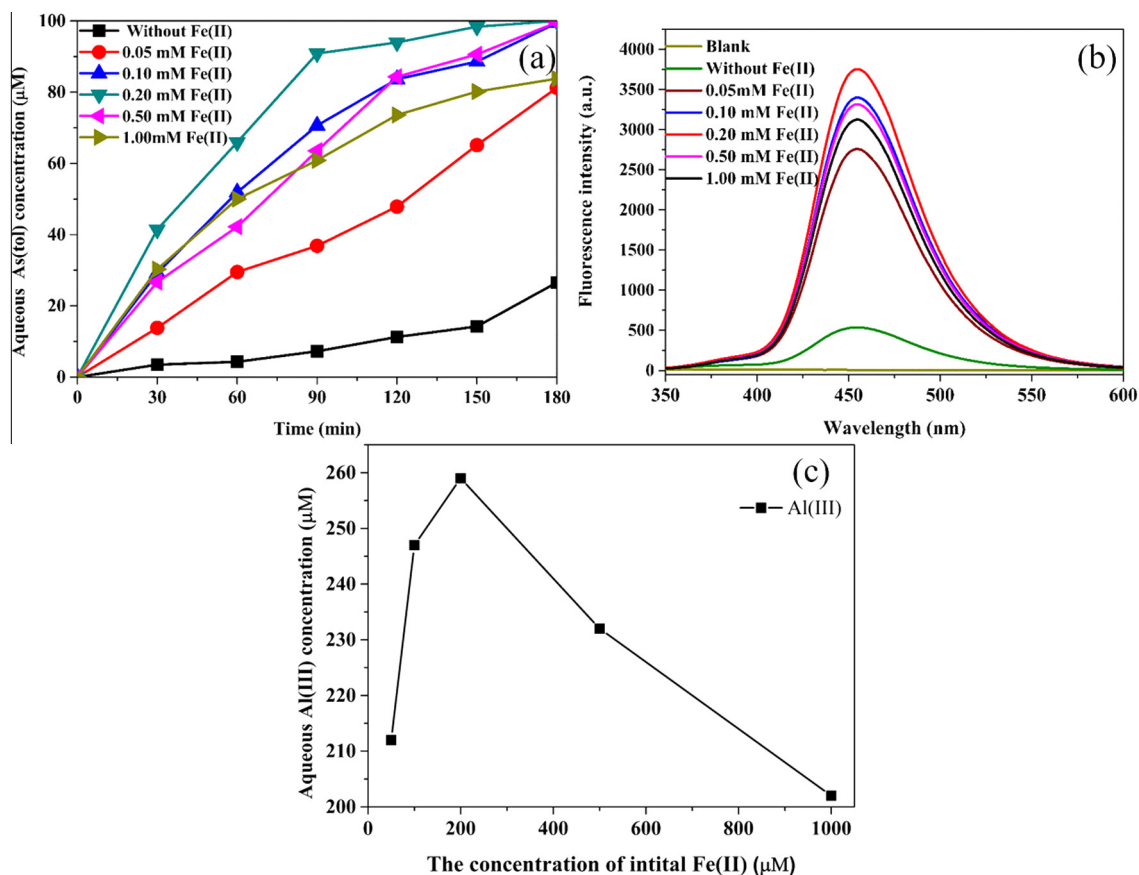
accumulation of ·OH in the solution produced from Fenton reaction is highly favored under higher acidic condition [40].

As shown in Figs. 5(c) and S4(b), when pH value is above 3.0, Fe(III) easily forms insoluble ferric hydroxide precipitates. With decreasing of the Fe(III) concentration, the Fe(II) which consumed via Fenton reaction could not be completely regenerated, and some of the Fe(II) could be adsorbed by the ferric hydroxide precipitates. Consequently, the concentration of the Fe(II) was decreased in a weak acidic solution (Fig. S6(b)). And the formed ferric hydroxide adhered to the surface of AIBCs and thus interrupted the reaction between metal aluminum and oxygen molecules, which impeded the generation of H<sub>2</sub>O<sub>2</sub> (Fig. 5(b)).

As seen in Figs. 5(d) and S7, the concentration of Al(III) ion was positively related to the concentration of proton. With the corrosion of the oxide layer (Al<sub>2</sub>O<sub>3</sub>) and metal aluminum, the Al(III) ion continued to accumulate at the front stage. But with the formation of the ferric hydroxide precipitates, the formed Al(III) ion could be adsorbed onto the ferric hydroxide. Besides, the ferric hydroxide adhered to the surface of AIBCs and thus inhibited the corrosion of the metal Al.

### 3.6. Inorganic arsenic immobilization

It has been widely demonstrated that Al and Fe salts can be effectively used for the immobilization of inorganic arsenic in water remediation systems via coprecipitation process [41,42]. Iron salts are more widely used than aluminum salts because they are more effective for immobilization of As(III) compounds [43]. Thus, the inorganic arsenic species can be immobilized via the formation of the hydroxides of aluminum and iron. Robins et al. [43]



**Fig. 4.** Effect of initial Fe(II) concentration on the formation of inorganic arsenic species (a); and the fluorescence intensity of 7-hydroxycoumarin produced at 90 min in AIBCs/Fe(II) system with various Fe(II) concentration (b); the amount of the Al(III)-Fe(II) content for 120 min at the initial Fe(II) concentrations of 50, 100, 200, 500, 1000  $\mu\text{M}$  (c). ( $[p\text{-ASA}]_0 = 100 \mu\text{M}$ ,  $[\text{AIBCs}]_0 = 10 \text{ g/L}$ ,  $\text{pH}_0 = 2.0$ ).

investigated the roles of aluminum and ferric hydroxides in removal As(III) and As(V) from aqueous environment. It was reported that  $\text{pH} = 6.0$  was an optimum for As(V) adsorption on ferric hydroxide, and the optimum pH for aluminum hydroxide was  $\sim 7.5$ . In addition, the adsorbent capacity of ferric hydroxide for As(V) is better than that in aluminum hydroxide [44]. As described in above section, after the degradation of *p*-ASA to inorganic arsenic, externally added iron ion and internally generated aluminum ion were remaining in strongly acidic solution, in which these flocculation ions can not be utilized for the immobilization of inorganic arsenic. Therefore, the AIBCs system may not provide the best of both worlds at a same pH with an effective degradation of *p*-ASA and preferable immobilization of the produced inorganic arsenic. Thus, to obtain the best of both worlds, an effective strategy was proposed that the degradation of *p*-ASA proceeds under strongly acidic solution, then the solution pH was simply adjusted for inorganic arsenic immobilization with the complete precipitation of Al(III) and Fe(III) ions. Here, for the complete precipitation of the products (i.e., Fe(III), Al(III) and inorganic arsenic), the pH value of the solution treatment was adjusted to 6.0.

Table 1 shows that the inorganic arsenic produced in the AIBCs/Fe(II) system can be completely immobilized after adjusting solution pH to 6.0. Meanwhile, a trace amount of Fe(III) ion was detected in above reaction systems. The mechanism of inorganic arsenic immobilization may be attributed to the fact that the ionic As(V) immediately coprecipitated with ferric ions as ferric arsenate or was adsorbed on the surface or incorporated into the structures during the formation of the Fe/Al hydroxides, which was produced

via the hydrolysis reactions of aqueous Fe(III) and Al(III) ion ions (see Figs. S4 and S7) [26]. It is widely known that the solubility of ferric arsenate is lower than that of Fe/Al hydroxide in a mildly acidic condition [45–47]. Therefore, in the formation of precipitation process, the ferric arsenate should be formed preferentially, after which Fe/Al hydroxide would be gradually formed. Consequently, it proves that the mixture of Al/Fe ions can act as an efficient flocculating agent for the inorganic arsenic species immobilization.

The residual Al(III) ion concentration in solution is an important factor in evaluating the application of the ZVAI-based treatment process, due to the toxicity of Al(III) ion towards humans and natural environments [21,48]. In the present study, the residual concentration of the Al(III) ion in the working solution was 6.75 mg/L. While, by adjusting the working solution pH to 6.0, the Al(III) ion concentration level was reduced to 0.006 mg/L (detected by ICP technique), which was far below the maximum contaminant level in drinking water (0.2 mg/L) [40]. Thus the simple way adjusting solution pH to neutral values can simultaneously prevent the secondary contamination of aluminum species.

In spite of the good stabilization of inorganic arsenic in the precipitate, the inorganic arsenic are easily released due to the reduction of ferric hydroxide in the an aerobic environment and thus do great damage to the environment [31]. So the sludge produced by the immobilization process should be transferred to the professional solid waste treatment company, in which cement solidification/stabilization are the most common method for the safe disposal of the sludge [49,50].

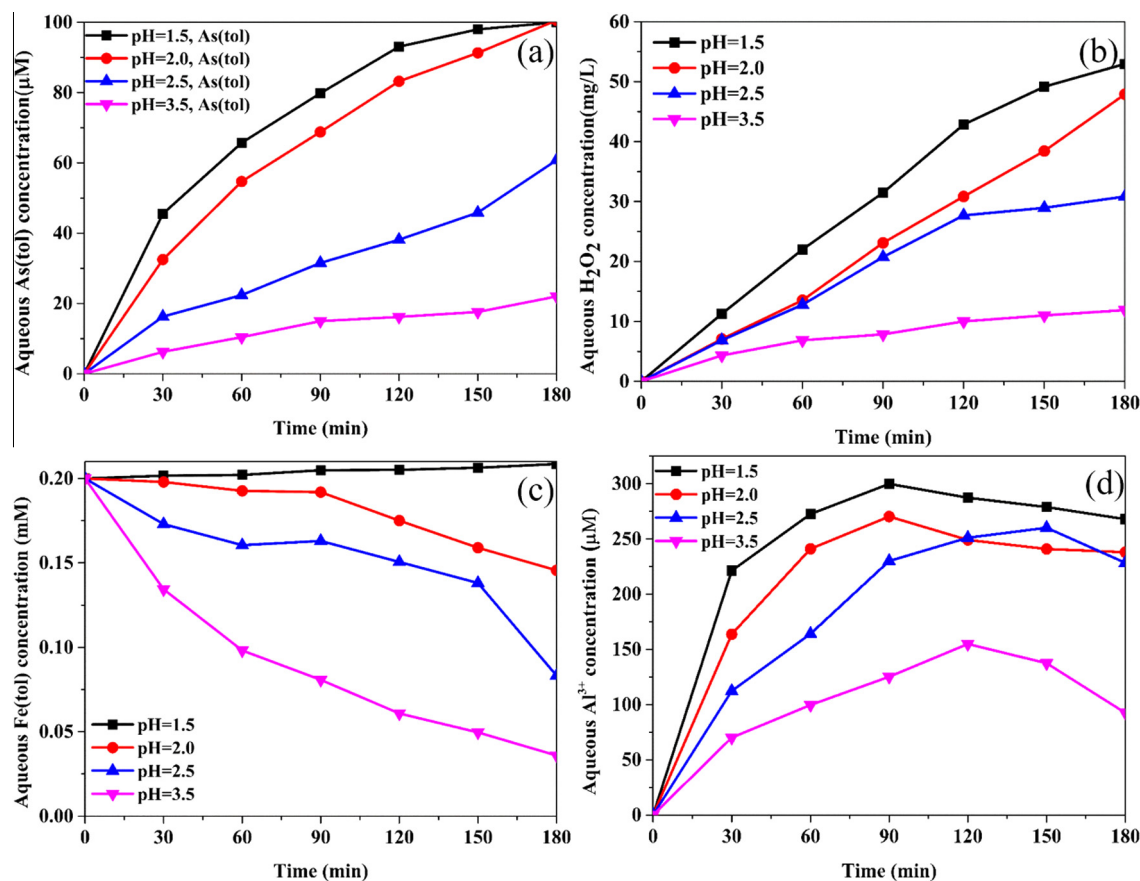


Fig. 5. Effect of initial solution pH on the formation of aqueous As(tol) (a), the concentration of iron ion (b), the generation of  $\text{H}_2\text{O}_2$  (c) and the production of Al(III) ion (d) in AIBCs/Fe(II) reaction system ( $[p\text{-ASA}]_0 = 100 \mu\text{M}$ ,  $[\text{AIBCs}]_0 = 10 \text{ g/L}$ ,  $[\text{Fe(II)}]_0 = 200 \mu\text{M}$ ).

Table 1

Changes of iron and arsenic concentrations upon increasing solution pH to 6.0 after 180 min reaction at  $\text{pH}_0 = 2.0$  in 10 g/L AIBCs system mediated by various Fe(II) in aerobic condition.

Fe(II) initial <sup>a</sup>	As(V)		As(tol)		Fe(II)		Fe(tol)		Al(III)	
	End <sup>b</sup>	Final <sup>c</sup>	End <sup>b</sup>	Final <sup>c</sup>	End <sup>b</sup>	Final <sup>c</sup>	End <sup>b</sup>	Final <sup>c</sup>	End <sup>b</sup>	Final <sup>c</sup>
	Sample concentration ( $\mu\text{M}$ )									
100	97.3	N.D. <sup>d</sup>	99.5	N.D.	34	N.D.	92	N.D.	253	N.D.
200	100	N.D.	100	N.D.	91	25	145	26	235	N.D.
500	96.1	N.D.	99.6	N.D.	340	38	490	40	247	N.D.

<sup>a</sup> The concentrations of Fe(II) were added in the system before the start of the reaction.

<sup>b</sup> The concentrations of As and Fe ions were measured after 180 min reaction in AIBCs/Fe(II) system.

<sup>c</sup> The concentrations of As and Fe ions were measured after solution pH increased to 6.0.

<sup>d</sup> Not detected.

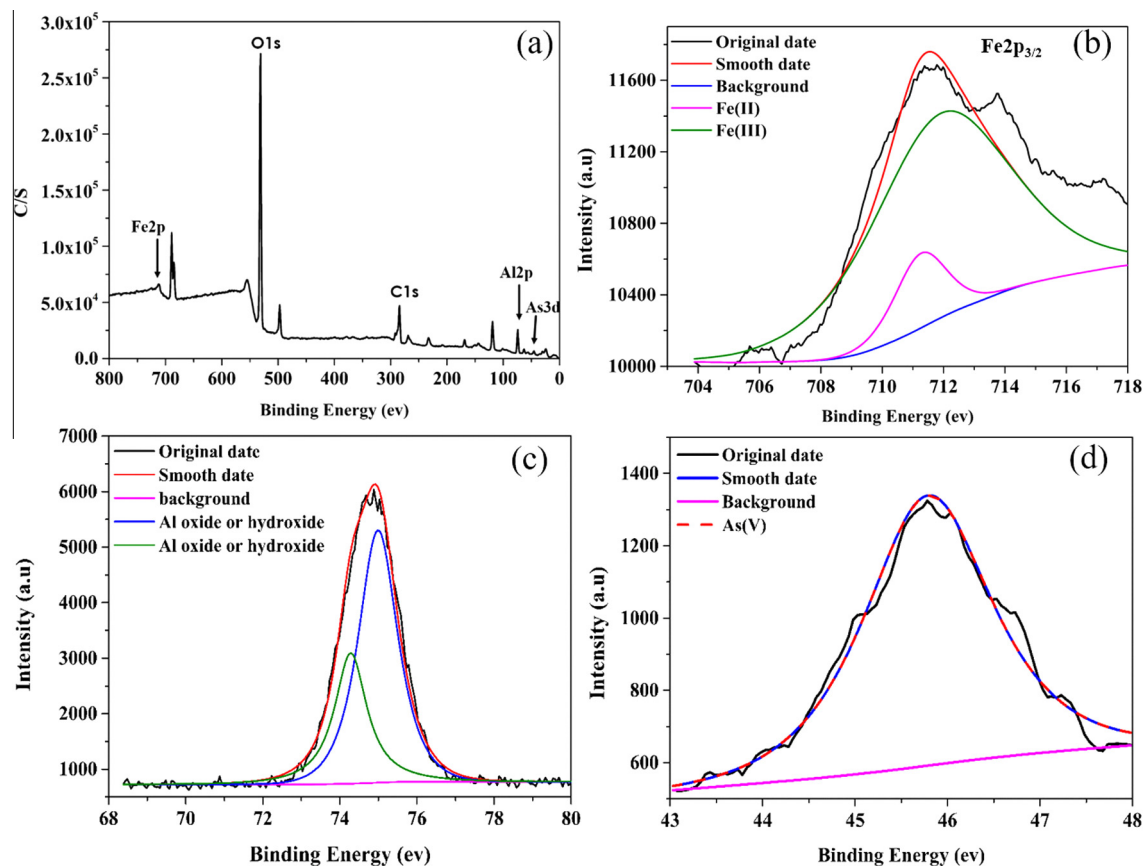
### 3.7. Characterization of the precipitate

The precipitate was analyzed by XPS to identify its composition and the chemical state present. Fig. 6(a) presents the wide-scan XPS spectrum containing surface composition of precipitate. Fe, O, Al, As and C were detected in the precipitate. The binding energies at 711.2 eV and 711.9 eV in the characteristic peak of Fe  $2p_{3/2}$  represented Fe(II) and Fe(III) in iron hydroxides. Furthermore, the iron signal appears at  $\sim 711.5$  eV, which is indicating the formation of iron hydroxides [45]. As shown in Fig. 6(c), the spectra of Al $2p$ , photoelectron peaks at 74.3 eV and 74.9 eV both correspond to the binding energies of Al-oxide or hydroxide [51]. The spectra of As occurred in the precipitate, providing direct evidence for inorganic arsenic immobilization by formation of ferric arsenate and coprecipitation with Fe/Al hydroxide. As reported in previous

literature [2], the binding energy of As3d for As(III) and As(V) in arsenic oxides are  $44.6 \pm 0.13$  eV and  $46.0 \pm 0.17$  eV when arsenic species is adsorbed by iron oxide or hydroxide. In Fig. 6(d), As3d spectra can be fitted with one component of binding energies 45.8 eV. These results indicated that inorganic arsenic species in the precipitation mainly existed as As(V), which is consistent with the results in Table 1.

### 3.8. Application of AIBCs in organic contamination treatment

Till now, many methods (e.g., UV/ $\text{S}_2\text{O}_8^{2-}$  [15], and glow discharge plasma [47], photocatalysis [2]) have been applied for organic arsenic pollutants degradation. As shown in Table 2,  $\text{TiO}_2$ -based photocatalysis and UV degradation processes exhibit preferable treatment performance. For example, 38  $\mu\text{M}$  phenylar-



**Fig. 6.** The survey scan XPS spectra (a); the curve-fitted narrow of Fe 2p<sub>3/2</sub> (b); Al2p (c); and As3d (d) of precipitate generated in AIBCs/Fe(II)/*p*-ASA reaction system ([AIBCs]<sub>0</sub> = 10 g/L, [*p*-ASA]<sub>0</sub> = 100 μM, [Fe(II)]<sub>0</sub> = 200 μM, pH<sub>0</sub> = 2.0).

**Table 2**

Summary of previous studies on the degradation of various organic arsenic compounds.

Target compound	Treatment method	Other parameters	Treatment efficiency	Arsenic species removal efficiency
ROX	Glow discharge plasma/Fenton	[ROX] <sub>0</sub> = 100 mM; Input energy 58 W; [Fe(II)] <sub>0</sub> = 500 μM; pH = 4.0 Time = 17 min	100%	87%
<i>p</i> -ASA	Fenton	[ <i>p</i> -ASA] <sub>0</sub> = 10 mg/L; pH = 3.0 [H <sub>2</sub> O <sub>2</sub> ] <sub>0</sub> = 2.12 mM; Time = 32 min [Fe(II)] <sub>0</sub> = 0.53 mM;	98%	100%
Phenylarsonic acid	UV/TiO <sub>2</sub> photocatalysis	[Phenylarsonic acid] <sub>0</sub> = 38 μM λ = 350 nm; [TiO <sub>2</sub> ] <sub>0</sub> = 0.1 g/L Time = 20 min;	90%	15%
<i>p</i> -ASA	UV photodegradation	[ <i>p</i> -ASA] <sub>0</sub> = 20 mg/L; UVA 500 W pH = 4.3; Time = 180 min	87%	–
<i>p</i> -ASA, Phenylarsonic acid	UV/ TiO <sub>2</sub> photocatalysis	[ <i>p</i> -ASA] <sub>0</sub> = 38 μM; [TiO <sub>2</sub> ] <sub>0</sub> = 0.1 g/L; Time = 30 min; λ = 350 nm.	100%	16.5
Phenylarsonic acid	UV/O <sub>3</sub>	[Phenylarsonic acid] <sub>0</sub> = 13.4 mM UVC 15 W, [O <sub>3</sub> ] <sub>0</sub> = 9 g/h; pH = 7 Time = 180 min	99.6%	–
Monomethylarsonic acid (MMA); Dimethylarsonic acid (DMA)	UV/S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	[MMA] <sub>0</sub> = 100 μM; [DMA] <sub>0</sub> = 100 μM UVC 6 W; λ = 254 nm; pH = 3.0 [S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ] <sub>0</sub> = 1.0 mM Time <sub>(MMA)</sub> = 21 min Time <sub>(DMA)</sub> = 35 min	MMA: 99.4% DMA: 96.7%	–

sonic acid can be readily degraded to form As(V) and As(III), and the degradation efficiency was 90% after 20 min with the load of 0.1 g/L TiO<sub>2</sub> [8]. However, this treatment process led to approximately 55% of produced As(V) remaining in the solution, which still required subsequent treatment technology to completely relieve the toxicity of the produced inorganic arsenic species. Although Fenton reaction process can completely degrade *p*-ASA (10 mg/L)

adding excess dosage of Fenton's reagent ([Fe(II)]<sub>0</sub> = 1.0 mM, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 4.0 mM) and near complete removal of the As(V) released from *p*-ASA degradation was observed over the final pH ranges of 3.0–8.0. However, this process consumed a large number of chemical reagents and the industrial utilization of H<sub>2</sub>O<sub>2</sub> was restrained by its hazardousness, inconvenient storage and requirement for large quantities. Compared with these processes, present



study involving AIBCs/Fe(II) system possessed remarkable advantages, which is more cost-effective and environmentally friendly. In addition, the Al beverage cans are abundantly available spent aluminum in daily life, and the spent AIBCs was demonstrated effectively in degrading organic arsenic pollutant and immobilizing the produced inorganic arsenic species. Consequently, the AIBCs/O<sub>2</sub> system can be a good candidate for an ex situ oxidation treatment method and be recognized as an excellent model of a “waste control by waste” strategy for pollutant removal.

#### 4. Conclusions

In this study, the spent Al beverage cans was proven to be an excellent alternative to ZVAL for the degradation of organic arsenic pollutant under acidic and oxic condition. The addition of ferrous ion can rapidly consume H<sub>2</sub>O<sub>2</sub> to generate ·OH via Fenton reaction and significantly improve the degradation of *p*-ASA and the production of inorganic As(V) in AIBCs-bearing system. Both oxygen and strong acidic condition are critical variables for *p*-ASA degradation. In this reaction system, the produced highly toxic inorganic arsenic species can be completely removed via the formation of As(V)-bearing amorphous hydrous Al/Fe precipitates via simple adjusting solution pH to 6.0. As such, the spent AIBCs coupled with the Fenton process is an efficient strategy for degradation of organic arsenic and immobilization of inorganic arsenic, and exhibits a broad prospects for the remediation of organic pollution wastewater.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2016.03.092>.

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