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

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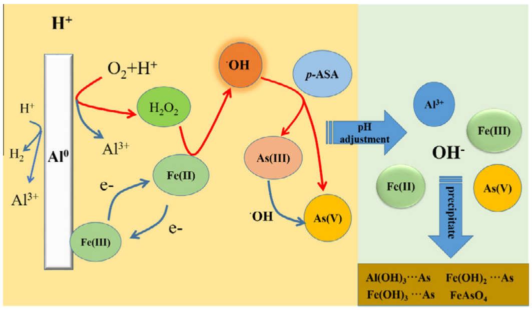
HIGHLIGHTS

- A strategy of "waste control by waste" for treating organic arsenic was proposed.
- Fe(II) significantly enhances the yield of $^{\cdot}OH$ 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 (AlBCs) 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 $\leqslant$ 2.0 in the aerobic AlBCs/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 H_2O_2 by the absence of oxygen. In the AlBCs/Fe(II) system, Fe(II) did not only catalytically transform H_2O_2 to $^{\cdot}OH$ 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.

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

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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_2 [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/$S_2O_8^{2-}$ [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_2O_2, $O_2^{\cdot -}$, 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 (AlBCs) contains several impurities, including Fe, Cu, Mn, Mg, etc. (see Table S1), metal aluminum is the main component of the AlBCs (see Fig. S1), thus the AlBCs 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 AlBCs 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 AlBCs/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 ($FeSO_4{\cdot}7H_2O$, >99%), coumarin ($C_9H_6O_2$, 97%), H_2SO_4 (73.0–75.0%), HCl (36–38%), eriochrome cyanine S ($C_{23}H_{15}Na_3O_9S$, >99%), hexadecyltrimethyl ammonium bromide ($C_{19}H_{42}BrN$), antimony potassium tartrate ($K(SbO)$-$C_4H_4O_6{\cdot}0.5H_2O$, >99%), L-ascorbic acid ($C_6H_8O_6$, >99.7%), 1,10-phenanthroline monohydrate ($C_{12}H_8N_2{\cdot}H_2O$, 99%) and hydroxylamine hydrochloride ($HONH_3Cl$, 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 $FeSO_4{\cdot}7H_2O$ in 1 mM H_2SO_4 with adding a small amount of reduced iron powder. The AlBCs were cleaned with fine emery paper to remove the paint and the organic film. Then, the AlBCs 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 AlBCs loading was fixed at 10 g/L and previously treated with 3% v/v HCl for 30 min to remove the Al_2O_3 layer. All of the working solutions were prepared by diluting the stock solution with deionized water. Solution pH was adjusted with concentrated H_2SO_4 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 AlBCs 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 $mmolL^{-1}$ KIO_3 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_2O_2 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].

$$\text{coumarin} + HO^{\cdot} \rightarrow 7 - \text{hydroxycoumarin} \quad k_1 = 2 \times 10^9\ M^{-1}\ s^{-1} \tag{1}$$

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