



Research Paper

Enhanced bromate reduction using zero-valent aluminum mediated by oxalic acid

Kun-Yi Andrew Lin^{a,*}, Chu-Hong Lin^a, Hongta Yang^{b,*}^a Department of Environmental Engineering, National Chung Hsing University, 250 Kuo-Kuang Road, Taichung, Taiwan^b Department of Chemical Engineering, National Chung Hsing University, 250 Kuo-Kuang Road, Taichung, Taiwan

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ABSTRACT

Although zero-valent aluminum (ZVAL) has been proposed to reduce bromate to bromide, ZVAL quickly loses its reductive power because of a passivation layer formed on its surface, leading to very low reduction efficiencies. In this study, oxalic acid (OX) is added to prohibit the formation of passivation layer. As ZVAL exhibits a quite low removal efficiency (q_e) ($< 5 \mu\text{mol g}^{-1}$), an introduction of a very low amount of OX ($50 \mu\text{M}$) substantially improves q_e to $9 \mu\text{mol g}^{-1}$. When the dose of OX increases to $500 \mu\text{M}$, q_e of ZVAL also increases to $22 \mu\text{mol g}^{-1}$, demonstrating that the presence of OX certainly leads to a positive effect on bromate reduction. OX can coordinate with oxidized Al species (Al^{3+}) and thus suppress the formation of passivation layer of $\text{Al}(\text{OH})_3$. The activation energy (E_a) for bromate reduction by ZVAL + OX is then determined as 25 kJ mol^{-1} . The presence of OX also makes ZVAL exhibit a considerably higher removal efficiency than ZVAL alone even under unfavorable situations, such as alkaline conditions. ZVAL + OX remains highly reactive for reducing bromate even in the presence of various anions. In addition, the presence of OX effectively improves the reusability of ZVAL for bromate reduction even without acid-washing regeneration. These results indicate that ZVAL mediated by OX can enhance bromate reduction, enable ZVAL to be highly reactive even under unfavorable conditions, and improve recyclability of ZVAL for bromate reduction. These features demonstrate that the mediation of OX in bromate reduction using ZVAL is promising and useful.

1. Introduction

Bromate (BrO_3^-), a product derived from oxidation of bromide, attracts increasing attention in view of its potential carcinogenicity according to International Agency for Research on Cancer [1]. To date, many techniques have been proposed for eliminating bromate from water, including filtration [2], adsorption [3], and ion exchange [4]. These techniques, even though are able to remove bromate, just transfer bromate from aqueous phases to solid phases, and its toxicity still exists. Therefore, recently another strategy is developed by reducing bromate to bromide via catalytic hydrogenation [5–8], reduction by zero-valent metals (ZVMs) [9–13] and electrochemical reduction [14,15]. While catalytic hydrogenation can reduce bromate to bromide, hydrogen and noble metallic catalysts are usually required [16–20]. The continuous consumption of hydrogen/borohydrides makes catalytic hydrogenation of bromate costly and complicated. For electrochemical reduction of bromate, even though this method can successfully reduce bromate to bromide, its operational capacity is significantly low [14,15]. In addition, fabrication of electrodes is

relatively complicated and electrodes still require dopants of noble metals to enhance efficiency of bromate reduction.

In contrast, bromate reduction by ZVMs is relatively straightforward and controllable [9–13]. Therefore, several ZVMs have been used for reducing bromate, such as zero-valent iron (ZVI), zero-valent zinc (ZVZ) and zero-valent aluminum (ZVAL) [9–13]. Although bromate reduction by ZVI is widely studied as ZVI is a versatile material, ZVAL ($E^\circ = -1.662 \text{ V}$) can exhibit a much higher reductive power than ZVI ($E^\circ = -0.43 \text{ V}$) and ZVZ ($E^\circ = -0.76 \text{ V}$) [21,22]. Aluminum (Al) is also one of the most abundant element on earth [21], making ZVAL an attractive material for bromate reduction.

While a few previous studies had demonstrated the usage of ZVAL for bromate reduction, the reduction efficiency was significantly low. This was possibly because ZVAL is highly reactive and prone to form aluminum oxides or hydroxides on its surface, forming the so-called “passivation layer (or passive oxide layer)”, which blocks access of bromate to the surface of ZVAL [22–24]. Recently, some alternative methods are proposed to prevent the formation of passivation layer and improve efficiency of reductive reaction by adding organic acids which

* Corresponding authors.

E-mail addresses: linky@nchu.edu.tw (K.-Y.A. Lin), hyang@nchu.edu.tw (H. Yang).

exhibit high affinities towards metal species [25–27]. Even though this approach has been proven to improve reduction of Cr(VI) [25,27], almost no studies have been implemented for evaluating whether ZVAL mediated by organic acids can enhance bromate reduction. Thus, this study aims to investigate behaviors of bromate reduction by ZVAL in the presence of organic acids. Oxalic acid (OX) is particularly selected as a model organic acid because it can be easily detected in natural water and wastewaters [28,29].

In this study, commercially available Al powder is used to obtain ZVAL via an acid-wash pretreatment. Efficiencies of bromate reduction by ZVAL and ZVAL with OX (ZVAL + OX) are compared. Factors influencing bromate reduction by ZVAL + OX are investigated, including temperature, pH, and co-existing anions. Recyclability of ZVAL + OX with and without acid-washing regeneration is also studied.

2. Experimental

Chemicals involved in this study were commercially available and used directly without purification. The detailed information of reagents can be found in the Supporting information. The as-received aluminum powder required acid-washing treatments to remove the passivation layer as illustrated in Fig. 1(a). As HCl is proven as the most effective acid to remove the oxide layer [9,10,21], HCl was adopted in the pretreatment. The preparation of acid-washed ZVAL can be found in the Supporting information. The morphology of ZVAL was characterized using scanning electronic microscopy (JEOL JSM-6700, Japan). ZVAL powder was placed on an SEM specimen holder on which a piece of carbon tape (2 mm × 2 mm) was adhered. The as-prepared specimen was coated with platinum using a platinum sputter coater and then placed inside the chamber of SEM which was evacuated. After the pressure of chamber reached the desired pressure, morphological

observation of specimen was started. Bromate reduction by ZVAL was evaluated via batch-type experiments and the detailed procedure of bromate reduction experiments and analytical methods of bromate and bromide can be seen in the Supporting information.

The concentration of resulting bromide at t is denoted as (C_R , mol L⁻¹). The efficiency (q_t) of ZVAL ($\mu\text{mol g}^{-1}$) for reducing bromate was calculated using the following equation (Eq. (1)):

$$q_t = \frac{(C_0 - C_t) \times v}{W} \quad (1)$$

where v is the volume of bromate solution (mL) and W represents the mass of ZVAL (g). The amount of resulting bromide (q_R) was determined by the following equation (Eq. (2)):

$$q_R = \frac{(C_R - C_0) \times v}{W} \quad (2)$$

The experimental reaction time was set to 120 min, and q_t at 120 min was denoted as q_e ($\mu\text{mol g}^{-1}$), representing the reduction efficiency at equilibrium.

3. Results and discussion

3.1. Bromate removal by ZVAL in the presence of OX

Since the as-received Al powder was easily oxidized, forming a layer of Al₂O₃ on its surface, HCl-washing was adopted to remove this layer for obtaining ZVAL. Fig. 1(b) and (c) shows that the as-received Al exhibited very smooth surface and no obvious pores were observed. However, after the acid-washing, the morphology of Al powder had changed significantly (Fig. 1(d), (e)) as the resulting ZVAL surface became highly roughened and pores of different sizes appeared, validating

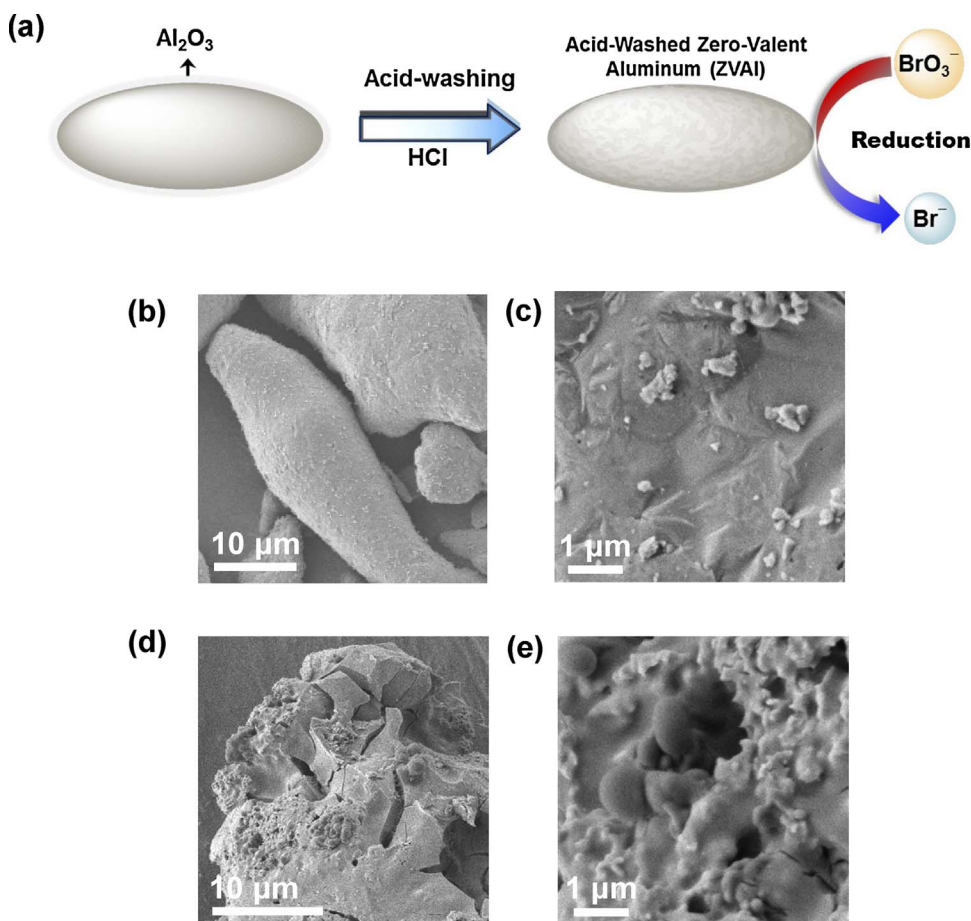


Fig. 1. Acid-washed zero valent aluminum (ZVAL): (a) a schematic illustration; (b), (c) SEM images of Al powder; and (d), (e) SEM images of ZVAL.

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