



Enhanced reductive removal of bromate using Acid-Washed Zero-Valent iron in the presence of oxalic acid



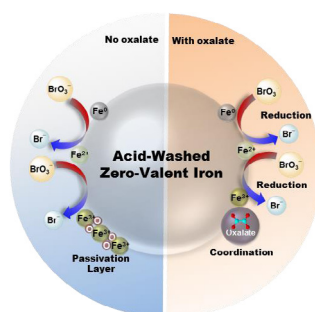
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HIGHLIGHTS

- Oxalic acid (OA) is used to mediate bromate reduction using acid-washed ZVI.
- Bromate reduction is remarkably enhanced by AZVI in the presence of OA = 250 μM .
- Addition of OA prevents the formation of passivation layer of iron oxides/hydroxides.
- The presence of OA enables AZVI to be recycled efficiently even without regeneration.

GRAPHICAL ABSTRACT



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ABSTRACT

While zero-valent iron (ZVI) has been demonstrated to reduce bromate to bromide, ZVI rapidly loses its reductive power because it is oxidized and a passivation layer forms on its surface. In this study, oxalic acid (OA) is introduced to prevent the formation of passivation layer and maintain reductive reactivity of acid-washed ZVI (AZVI). Despite the fact that AZVI is able to remove bromate, bromate reduction by AZVI is remarkably enhanced in the presence of a very small amount of OA (250 μM). OA can coordinate with oxidized iron species (Fe^{3+}) and thus prohibit the formation of passivation layer of iron oxides and hydroxides, allowing AZVI to remain highly reactive for reducing bromate to bromide completely. AZVI + OA also exhibits much lower activation energy than AZVI, indicating that AZVI + OA is much preferred for bromate reduction over AZVI. While bromate reduction by AZVI is considerably hindered under alkaline conditions, the presence of OA lessens the adverse effect and especially retains the reductive reactivity of ZVAI under weakly alkaline conditions. OA is also proven to make AZVI highly reactive even in the presence of co-existing anions without efficiency loss. More importantly, the presence of OA enables AZVI to be reused for bromate reduction quite efficiently even without acid-washing regeneration. These findings reveal that OA-mediated AZVI can enhance bromate reduction, enable AZVI to be highly reactive even under unfavorable conditions, and improve recyclability of AZVI for bromate reduction. These features validate that introduction of OA into bromate reduction by AZVI is advantageous and promising.

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1. Introduction

While advanced oxidation processes (AOPs) are extensively employed for wastewater treatments and water purification,

by-products generated from AOPs, especially toxic ones, pose serious threats to ecology and human being. Recently one of the toxic by-products, bromate (BrO_3^-), which results from oxidation of bromide (Br^-), has received increasing attention because it has been listed as a 2B substance by International Agency for Research on Cancer [1]. Traditionally, the occurrence of bromate is attributed to ozonation of bromide-containing water [2]. Lately, a number

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of recent reports also indicate that bromate can be also produced by widely-used sulfate radical-based AOPs [3,4]. Since these AOPs are intensively and increasingly implemented [5], the occurrence of bromate should be controlled and mitigated in order to prevent its adverse effects.

While various approaches have been developed for removing bromate from water, such as adsorption [6], ion exchange [7], as well as filtration [8], these approaches merely move bromate from aqueous solutions to solid materials and its toxicity still remains. Consequently, several alternative approaches are proposed to reduce bromate to bromide by catalytic hydrogenation [9–12] and zero-valent metals [13–17]. Even though catalytic hydrogenation can reduce bromate to bromide, excessive consumption of hydrogen and borohydrides is demanded. In addition, preparation of heterogeneous catalysts for hydrogenation is relatively complicated and involved with precious metals [18–22].

On the other hand, bromate reduction using zero-valent metals is relatively simple; thus, many zero-valent metals (ZVMs) have been employed for bromate reduction, including zero-valent iron (ZVI) and zero-valent aluminum [13–17]. While these zero-valent metals have been successfully demonstrated for bromate reduction, these ZVMs rapidly lose their reductive power as they donate electrons and become oxidized during reductive reactions. These oxidized metals may precipitate and build up on the surface of ZVMs, forming so-called “passivation layer”, which prevents reactions between target pollutants and ZVMs. Even though some regeneration treatments (e.g., acid-washing) can rejuvenate reductive power of ZVMs, these regeneration treatments are time-consuming and intensive acids are required [13,14].

Recently, a number of studies indicate that addition of organic acids and polycarboxylates, which exhibit high affinities towards oxidized metals, prevent the formation of passivation layer and improve efficiencies of reductive reaction [23–25]. While this concept has been demonstrated in reduction of Cr(VI) using ZVMs [23,25], few studies have been conducted to examine whether the introduction of small amounts of organic acids can enhance bromate reduction using ZVMs. Thus, this study aims to investigate bromate reduction using ZVMs in the presence of organic acids. In particular, ZVI is selected as a representative ZVM because it has extensively studied for reducing bromate because ZVI is easily accessible [15–17] and several studies have demonstrated effective bromate reduction using ZVI [26], nanoscale ZVI (nZVI) [17] and nZVI composites [16]. Oxalic acid is adopted as a model organic acid for evaluating its effect on bromate reduction using ZVI as oxalates can be also found in natural water bodies and various industrial wastewaters [27,28].

To obtain ZVI conveniently, commercially available fine iron powder is used. Since iron powder is easily oxidized, forming an oxide layer on its surface, an acid-wash pretreatment is adopted to prepare acid-washed ZVI (AZVI). The influence of OA on bromate reduction using AZVI under various conditions is investigated, such as change in temperature and initial pH (pH_{in}), and effect of co-existing ions. Recyclability of AZVI for bromate reduction with and without OA is also evaluated.

2. Experimental

2.1. Materials

Chemicals involved in this study were received from major reagent suppliers and used directly without purification. Iron powder (spherical, $<10 \mu\text{m}$), sodium nitrate, sodium sulfate and sodium phosphate were purchased from Alfa Aesar (USA). Sodium bromate, sodium bromide and oxalic acid were received from Sigma-Aldrich (USA). Hydrochloric acid (HCl) (37%) was acquired from Union Fine Chemicals (Taiwan). Deionized (DI) water was prepared to exhibit conductivity less than $18 \text{ MOhm}\cdot\text{cm}$.

2.2. Reduction of bromate using acid-washed iron

The as-received spherical iron powder required acid-washing treatments to remove the passivation layer as illustrated in Fig. 1. Since HCl is considered as the most effective acid to remove the oxide layer [13,14,29], HCl was selected and employed in the pre-treatment. The typical acid-washing pretreatment started by adding 1.2 g of iron powder to 10 mL of HCl solution and the resulting mixture was instantly placed on an orbital shaker and stirred vigorously for 2 min at room temperature. The acid-washed ZVI (AZVI) was then washed with oxygen-free DI water repeatedly and then used for bromate reduction immediately.

Bromate reduction by AZVI was implemented by batch-type experiments. In a typical experiment of bromate reduction, 1 g of AZVI (dry basis) was added to a glass beaker containing 200 mL of bromate solution with an initial concentration (C_0) of 10 mg L^{-1} (i.e., $78.1 \mu\text{mol g}^{-1}$). The dry basis of AZVI mass was determined by measuring the weight of AZVI using an electronic balance after being dried in a conventional oven at 65°C for 6 h. The beaker was then placed on a stirring hot plate (300 rpm) for continuous stirring at a fixed temperature. After pre-set intervals, sample aliquots were withdrawn from the container and filtered through syringe filter ($0.22 \mu\text{m}$). The filtrate was then analyzed using an ion chromatography system (Dionex ICS-1100, USA) to measure concentrations of the residual bromate (C_t) and the resulting bromide (C_r) at a given time t . The reduction efficiency (q_t) of AZVI for reducing bromate and generating bromide was quantified via the following formula (Eq. (1)):

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

where v is the solution volume and W is the mass of AZVI. Since reaction time was set up to 60 min, q_t at 60 min was denoted as q_e , representing the reduction efficiency at the end. Experimental procedures for bromate reduction in the presence of oxalic acid were similar to the aforementioned procedures except addition of a given amount of oxalic acid (e.g., $250 \mu\text{M}$ or $500 \mu\text{M}$) to bromate solutions before introducing AZVI.

The effect of temperature was examined by changing the solution temperature to 20, 40 and 60°C , whereas the effect of pH_{in} was investigated by adjusting pH_{in} of solution to 3, 4.5, 5, 7, 9



Fig. 1. Schematic illustration of acid-washed zero valent iron for reductive removal of bromate.

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