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Valorization of aluminum scrap via an acid-washing treatment for reductive removal of toxic bromate from water

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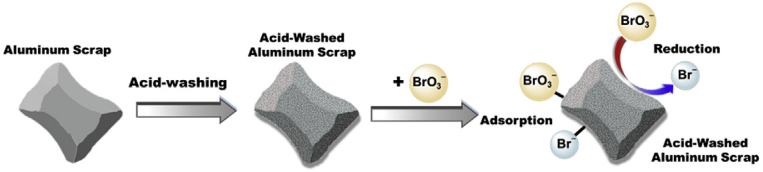
HIGHLIGHTS

- Aluminum scrap (AS) is utilized as an aluminum source to prepare zero-valent Al.
- HCl is the most effective acid to prepare acid-washed AS (AWAS) for bromate removal.
- Bromate removal from water by AWAS can be attributed to reduction and adsorption.
- Effects of temperature, pH, co-existing anions, particle size are investigated.
- Recyclability of AWAS is improved by acid-washing regeneration to reduce bromate.

GRAPHICAL ABSTRACT



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ABSTRACT

Aluminum scrap (AS) is adopted for the first time as a readily available aluminum source to prepare zero-valent aluminum (ZVAl) for removing bromate from water via a reductive reaction. Since aluminum is easily oxidized to aluminum oxide (Al_2O_3) on exposure to air, an acid-washing pretreatment on AS is developed to remove the layer of Al_2O_3. HCl is found as the most effective acid to pretreat AS and the HCl-pretreated or acid-washed AS (AWAS) is able to remove bromate from water and convert it to bromide. Factors, such as temperature, pH, co-existing anions, and particle size, which influence the bromate removal using AWAS are also investigated. The mechanism of bromate removal by AWAS can be attributed to both reduction and adsorption. The elevated temperature also significantly improves bromate removal capacity of AWAS as well as the reaction kinetics. The bromate removal capacity of AWAS is substantially improved under acidic conditions. However, the basic conditions and co-existing anions suppress or interfere with the interaction between bromate and AWAS, leading to much lower removal capacities. The recyclability of AWAS is also evaluated and the acid-washing regeneration is necessary to restore its capacity. However, the mass of AWAS can gradually decrease due to multi-cycle acid-washing regeneration. Through this study, the valorization of AS via acid-washing is demonstrated and optimization of acid-washing parameters is presented. Our findings reveal that the acid-washing is a useful technique to utilize AS as an inexpensive and efficient material for removing bromate from water.

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1. Introduction

Chemical oxidation treatments are widely recognized as the most effective method for disinfection and degradation of organic pollutants. However, by-products are inevitably produced during disinfection (*i.e.*, disinfection by-products (DBPs)), and advanced oxidation processes (AOPs). Among these by-products, bromate has drawn increasing attention because it is categorized as a Group 2B substance by the International Agency for Research on Cancer (Pinkernell and von Gunten, 2001). The USEPA and the WHO have restricted its contaminant level to 10 $\mu g\ L^{-1}$ in drinking water due to its carcinogenicity (Pinkernell and von Gunten, 2001). Although ozonation of bromide is considered as the most typical situation where bromide is oxidized to hypobromous, then hypobromite and finally bromate, recent studies have reported that oxidation of bromide-containing water by Oxone (*i.e.*, potassium peroxymonosulfate) can also produce bromate (Li et al., 2015; Liu et al., 2015). As these chemical oxidation processes are extensively employed in wastewater treatment, development of practical and efficient methods to eliminate bromate from water is urged.

To date, several methods have been proposed to control bromate in water. One of them is to remove the bromate precursor, bromide, from water before oxidation; nevertheless it is extremely difficult to completely eliminate bromide (Amy et al., 1999). Another method is to inhibit the formation of bromate during oxidation, but it has been proven to diminish oxidation efficiency simultaneously (Song et al., 1996). The third method is to remove the resulting bromate, including ion exchange (Wiśniewski and Kabsch-Korbutowicz, 2010), adsorption (Bhatnagar et al., 2009), as well as filtration (Listiarini et al., 2010). While these methods are capable of removing bromate from water, bromate is simply transferred from one phase to another phase, and its toxicity also remains. Therefore, several studies propose to reduce bromate to its original precursor, bromide (Chen et al., 2010; Marco et al., 2013; Sun et al., 2013; Lin and Chen, 2015a, b; Restivo et al., 2015; Chen et al., 2016; Lin et al., 2016). One of the most common approaches for converting bromate to bromide is catalytic hydrogenation of bromate using hydrogen gas (Chen et al., 2010; Marco et al., 2013; Sun et al., 2013; Restivo et al., 2015) or borohydrides as reductants (Lin and Chen, 2015a, b); however these techniques require continuous consumption of these reductants. Instead of using reductants during the hydrogenation, another approach is reducing metal species to become zero-valent metals (*e.g.*, iron and aluminum), which can directly act as reducing agents to reduce bromate without usage of other reductants (Lien et al., 2010; Fu et al., 2016; Lin and Lin, 2016). While zero-valent iron (ZVI) is extensively applied as a reducing agent in wastewater treatment, zero valent aluminum (ZVAl) can be more advantageous as it exhibits a relatively high thermodynamic driving force for electron transfer ($E^o = -1.662$ V) than ZVI (*i.e.*, -0.43 V) (Lien et al., 2010; Fu et al., 2016). In addition, aluminum is also one of the most abundant elements on the earth (Fu et al., 2016); it has been adopted as an useful reducing agent for reduction of toxicants in wastewater treatment (Cheng et al., 2006; Chen et al., 2008; Lien et al., 2010).

Even though aluminum seems a promising metal for treating bromate-contaminated water, existing studies are conducted using the chemical reagent-grade aluminum (Lin and Lin, 2016) which is primarily derived from bauxite ores. As aluminum is the third abundant element on earth, many aluminum wastes are produced, including aluminum scrap (AS), aluminum packages, and used aluminum products. These aluminum wastes can be recycled to manufacture aluminum as 18 million tons of aluminum is produced from aluminum wastes in 2010 (Tenorio and Espinosa, 2002). These aluminum wastes in fact represent a readily available aluminum source, which can be instantly used to prepare ZVAl for wastewater treatment. Direct usage of aluminum wastes can save energy and offer ecological benefits (Macaskie et al., 2010) because much less mining and processing is required to prepare aluminum (Barrera-Díaz et al., 2015). However, to our knowledge, no relevant studies have been conducted by using aluminum wastes for reducing bromate in water. Therefore, the present study aims to utilize aluminum scrap (AS) for treating bromate-containing water. Since aluminum is easily oxidized on exposure to air, the surface of aluminum becomes aluminum oxide (*i.e.*, Al_2O_3), which should be removed in order to utilize ZVAl of AS. To do so, an acid-washing treatment is proposed and the corresponding parameters are optimized to prepare this acid-washed AS (AWAS). The AWAS was characterized for its morphology, chemical composition, and crystallinity as well as surface charges. Factors influencing bromate removal by AWAS were investigated, including acid species, acid-washing duration, temperature, pH, co-existing anions, and particle size. Recyclability tests of AWAS with and without acid-washing regeneration were also conducted to examine whether AWAS can be re-used for multiple times.

2. Experimental

2.1. Materials

Shredded AS was obtained from an aluminum processing factory located in Kaohsiung City, Taiwan. Although it is possible to use shredded AS chips directly to remove bromate in wastewater treatment, these AS chips are quite different in shape and size. Powdered AS with a certain range of sizes can offer more consistent and accurate results for further investigation; therefore, shredded AS was ground into fine powders by an electronic grinder (650 W, 25,000 rpm, 50 Hz). The AS powders were then sieved using standard sieving meshes (ASTM No. 20, 40 and 70) to afford three groups of powders with different size ranges. The first size range was 425–850 μm, the second size range was 212–425 μm and the third range was below 212 μm. The resulting powders were cleaned by washing it repeatedly with ethanol/water, and dried at 333 K for 12 h before use. Chemical reagents used in this study were all commercially available and used without purification. Deionized (DI) water was prepared to less than 18 MOhm-cm.

2.2. Preparation and characterization of acid-washed AS (AWAS)

The acid-washing treatment started from adding 0.7 g of AS powder to a glass vial which contained 10 ml of pure acid. Acids selected in this study were hydrochloric acid (HCl, 37% in water), sulfuric acid (H_2SO_4, 98%), nitric acid (HNO_3, 90%) and phosphoric acid (H_3PO_4, 99%). The vial was then placed on an orbital shaker for a pre-set time (*e.g.*, 30–120 s) to facilitate the acid-washing process. In the end of the acid-washing treatment, AWAS powder was washed thoroughly with DI water before use. The morphological variation of AS before and after the acid-washing was monitored by scanning electronic microscopy (JEOL JSM-6700, Japan) equipped with energy dispersive X-ray spectrometer (EDS) (Oxford Instruments, UK). XRD analysis of the acid-washed AS (AWAS) powder was conducted using an X-ray diffractometer (Bruker D8 Discover, USA), whereas the zeta potential of AWAS was measured by a zetasizer (Nano-ZS, Malvern Instruments Ltd, Malvern, UK). Surface areas of AS powders were determined using a volumetric gas sorption analyzer (Quantachrome AutoSorb IQ, USA).

2.3. Removal of bromate from water using AWAS

To evaluate removal of bromate from water by AWAS, batch-type experiments were conducted. After AS was pre-treated by an