



Reusability of zero-valent iron particles for zinc ion separation

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ABSTRACT

Zero-valent iron (ZVI) is known to be effective in separating heavy metals from aqueous solution. However, used ZVI particles are usually discarded in heavy metal-containing sludge. Therefore, an appropriate technique for the reactivation of used ZVI for reuse is discussed in this work. A series of zinc desorption tests from zinc-adsorbed ZVI revealed that zinc desorption required both acidic conditions to dissolve zinc-containing iron hydroxide layers on ZVI and reductants to remove insoluble iron oxide layers from the ZVI surface. Organic acid reductants, such as citric acid, satisfy both these requirements. The ZVI particles that were reactivated by the desorption of zinc using 10.0-mM citric acid were applied repeatedly for zinc removal. Reusing the ZVI particles four times did not affect their zinc removal performance relative to that of virgin ZVI. Furthermore, the used 10.0-mM citric acid could be reused to desorb zinc from the used ZVI particles after separating the zinc and iron ions by hydroxide precipitation at pH 12 and re-acidifying the solution to pH 2.5 by the addition of sulfuric acid. Thus, both the ZVI particles and the 10.0-mM citric acid cleansing liquid were found to be reusable for zinc separation from aqueous solution.

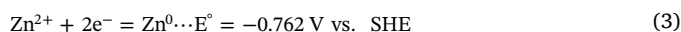
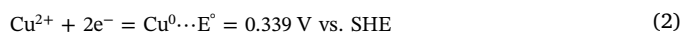
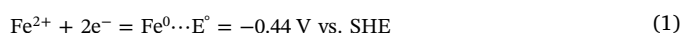
1. Introduction

Zinc is widely used in applications such as die casting, metal plating, and zinc alloy manufacturing. The use of zinc has increased rapidly over the last century and a half [1]. However, in 2011, the recycling rate of zinc was only 29.5% relative to the apparent supply in the United States, which is much lower than those of lead (74.3%), aluminum (51.9%), iron (50.1%), magnesium (46.0%), and nickel (44.6%) [2]. Because of this low recycling rate, a substantial amount of zinc has been discharged into aqueous environments from point sources, such as mining facilities, chemical plants, metal manufactures, and sewers, and non-point sources, such as abrasion of tires, corrosion of galvanized metals, and usage of zinc-containing pesticides [3].

The toxicity of zinc to humans is relatively low, particularly upon oral consumption [4]. However, many reports have addressed the toxicity of zinc to aquatic organisms and ecosystems [5–7], and the ecological hazard quotient (HQ_E) of zinc compounds has been estimated to be in the highest hazard class based on publicly available information in the Japanese Pollutant Release and Transfer Register (PRTR) system [8]. Therefore, the Japanese government established environmental water quality standards for zinc at 0.03 mg/L for public freshwater areas and 0.02 mg/L for public seawater areas in 2003 to protect aquatic organisms. In this context, an effective technique for the

removal and recovery of zinc ions from wastewater is required.

Recently, many researchers have reported the successful application of zero-valent iron (ZVI) to ground water remediation and wastewater treatment [9]. ZVI can remove nitrate, chlorinated organic compounds, nitroaromatic compounds, dyes, phenols, arsenic, and heavy metals via reduction, oxidation in the presence of dissolved oxygen (DO), adsorption, surface precipitation, surface complexation, and co-precipitation [9]. Zero-valent metals such as ZVI can remove heavy metals by the cementation process; this is an electrochemical process by which a noble metal ion is precipitated from solution and replaced by a metal that is higher in the ionization series [10]. However, because zinc shows a higher ionization tendency than iron, cementation does not occur when ZVI is used to remove zinc [10]. For instance, standard potentials of Fe²⁺/Fe, Cu²⁺/Cu, and Zn²⁺/Zn couples are as follows [11]:

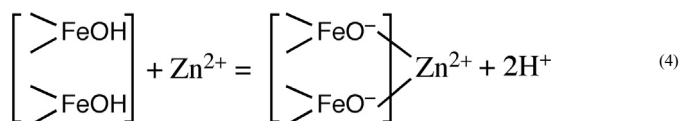


where E[°] and SHE depict the standard electrode potential and the standard hydrogen electrode, respectively. Since a higher potential is thermodynamically more favorable to the rightward reaction, Cu²⁺ can

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be reduced to Cu^0 by cementation with the oxidation of Fe^0 to Fe^{2+} , whereas Zn^{2+} cannot be done. Instead, adsorption on, surface complexation with, and co-precipitation with amorphous iron oxyhydroxide, which is produced via the oxidation of iron by DO, are thought to be the mechanisms underlying zinc removal by ZVI [12–15] as follows:



where protonated surfaces of amorphous iron oxyhydroxide act as adsorption sites. Because of the synergistic effect of multiple functions of ZVI, a nanoscale ZVI was demonstrated to exhibit advantages for lead and zinc removal over those of lime, which is the most widely used precipitant for heavy metals [16]. However, the surface of the amorphous iron oxyhydroxide layer underwent additional oxidation by DO and was transformed into a thin oxide layer comprising magnetite, maghemite, or ferrihydrite, thereby decreasing the zinc removal performance [15]. Therefore, developing methods for controlling the amorphous iron oxyhydroxide layer is a challenge for the effective application of ZVI for zinc removal. Furthermore, the repeated use of ZVI particles has not been considered in most conventional ZVI techniques. As a result, the use of ZVI generates waste sludge containing used ZVI particles. Accordingly, an appropriate technique for the reactivation of used ZVI should be established to effectively utilize ZVI for zinc removal. Sequential extraction procedures were widely used for investigating the mechanism of uranium and other heavy metals removal by ZVI [17,18]. These techniques may be applicable to desorbing zinc from and reactivating used ZVI after simplifying the extraction procedure. Such a technique is proposed in this research.

2. Experimental

2.1. Materials

Atomized iron powders provided by Wako Pure Chemical Industries (Osaka, Japan) were used as the source of ZVI; the median diameter of the powders was 82 μm , and the Brunauer-Emmett-Teller (BET) surface area was 0.048 m^2/g . A zinc solution was prepared by dissolving zinc sulfate heptahydrate (ZnSO_4) in distilled and deionized water to a final concentration of 1.0 mM (64 mg-Zn/L), which is similar to the zinc concentration in electroplating wastewater (76.3 mg/L [19]). The solution pH was not controlled but was in the range of 5–6. Citric acid, ascorbic acid, sodium citrate, and sulfuric acid were considered as cleansing liquids for refreshing the used ZVI, namely separating adsorbed zinc from the used ZVI and reactivating its surface for reuse. Citric acid, ascorbic acid, and sodium citrate can act as reducing agents, which are widely used for extracting heavy metals bound to iron (hydr) oxides [17]. Sodium hydroxide was used as a precipitant to separate iron and zinc from the cleansing liquid. Zinc chloride (ZnCl_2), zinc oxide (ZnO), and zinc iron oxide (ZnFe_2O_4 , CAS 12063-19-3, Sigma-Aldrich Japan, Tokyo, Japan) were used as reference zinc compounds for X-ray absorption near edge structure (XANES) analysis of zinc-adsorbed ZVI. All reagents except the atomized iron powder and ZnFe_2O_4 were of analytical grade, supplied by Nacalai Tesque (Kyoto, Japan), and used without further purification.

2.2. Adsorption of zinc on the surface of ZVI

A ZVI-packed column was prepared by packing 15.00 g of iron powder into an acrylic resin pipe with a diameter of 10 mm and sandwiching the powder with glass wool to prevent washout. To obtain zinc-adsorbed ZVI, 500 mL of the prepared zinc solution was treated in

the ZVI-packed column for 70 min at a circulation flow rate of 50 mL/min achieved using a peristaltic pump (RP-1000, EYELA, Tokyo, Japan) (Fig. 1(a)). Then, the treated solution was discharged from the column, and the zinc-adsorbed ZVI was utilized in a series of zinc desorption experiments. The residual zinc concentrations before and after adsorption were determined by inductively coupled plasma spectrometry. The existence of zinc on ZVI was checked with an electron probe micro analyzer (EPMA). The structure of the zinc species on zinc-adsorbed ZVI was investigated by X-ray absorption near-edge structure (XANES) analysis and X-ray diffraction (XRD) analysis. The adsorbed mass of zinc was calculated as follows:

$$M_A = (C_0 - C_f)V_A \quad (5)$$

where M_A is the adsorbed mass of zinc [mg], C_0 is the initial zinc concentration (= 64 mg/L), C_f is the zinc concentration after adsorption [mg/L], and V_A is the volume of zinc solution (= 0.50 L).

2.3. Zinc desorption from zinc-adsorbed ZVI

Zinc desorption experiments were performed to select the cleansing liquid immediately after zinc adsorption. Two flow modes—pass-through mode (Fig. 1(b)) and circulation mode (Fig. 1(a))—were used. In pass-through mode, the cleansing liquid was fed into the column containing the zinc-adsorbed ZVI at a flow rate of 40 mL/min for 20 min using the peristaltic pump. In circulation mode, 500 mL of cleansing liquid was circulated between a reservoir tank and the column at a flow rate of 40 mL/min for 60 min. The cleansing liquids investigated and the flow mode applied for each run are summarized in Table 1. The use of a combination of sodium citrate and sulfuric acid was also examined in Run 7 as follows: The zinc-adsorbed ZVI in the column was exposed to 500 mL of 10.0-mM sodium citrate solution for 30 min in circulation mode, and then, 500 mL of diluted sulfuric acid solution (pH 2.5) was substituted for the sodium citrate solution and circulated for 30 min. The desorbed mass of zinc and the desorption efficiency were calculated using the following equations.

$$M_D = C_D V_D \quad (\text{in circulation mode}) \quad (6)$$

$$M_D = \int C_{Dt} Q dt \quad (\text{in pass-through mode}) \quad (7)$$

$$E_D = M_D / M_A \quad (8)$$

where M_D is the desorbed mass of zinc [mg], C_D is the zinc concentration of the cleansing liquid after desorption [mg/L], C_{Dt} is the zinc concentration of the effluent from the column at time t [mg/L], V_D is the volume of cleansing liquid (= 0.50 L), Q is the flow rate of cleansing liquid (= 0.040 L/min), t is the time [min], and E_D is the desorption efficiency [–].

2.4. Iron and zinc separation from used cleansing liquid

Based on the zinc desorption experiments (Section 2.3), 10.0-mM citric acid (pH 2.5) was selected as the cleansing liquid. The used cleansing liquid was prepared as follows. Zinc-adsorbed ZVI prepared according to the procedure described in Section 2.2 was washed with 200 mL of 10.0-mM citric acid solution for 10 min in circulation mode at a flow rate of 40 mL/min. Then, the cleansing liquid was collected. The used cleansing liquid was adjusted to pH 2.5 by adding sulfuric acid, because its pH increased to about 3 by cleansing operation. The pH-adjusted cleansing liquid was subsequently used to wash additional zinc-adsorbed ZVI. This procedure was repeated four times to accumulate zinc in the cleansing liquid.

The used cleansing liquid contained zinc, ferrous, and ferric ions. Therefore, the solution pH was adjusted to 12 by the addition of sodium hydroxide for zinc and iron separation, resulting in zinc hydroxide and ferrous/ferric hydroxide precipitation. The obtained sludge (20 mL)

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