Journal of the Taiwan Institute of Chemical Engineers 000 (2018) 1–10

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Zero valent iron as an electron transfer agent in a reaction system based on zero valent iron/magnetite nanocomposites for adsorption and oxidation of Sb(III)

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ARTICLE INFO

Article history:
Received 3 October 2017
Revised 31 December 2017
Accepted 23 January 2018
Available online xxx

Keywords:
$nZVI/Fe_3O_4$ nanocomposites
Sb(III)
Adsorption
Oxidation

ABSTRACT

Due to the toxicity and carcinogenicity, antimony and its compounds have been included as priority pollutants by Environmental Protection Agency of the United States (USEPA) and the European Union (EU). The removal methods of antimony need to be further studied. In this study, $nZVI/Fe_3O_4$ nanocomposites were synthesized, characterized, and applied to remove Sb(III). The $nZVI/Fe_3O_4$ nanocomposites before and after reaction with Sb(III) were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), vibrating sample magnetometry (VSM), and X-ray photoelectron spectroscopy (XPS). $nZVI/Fe_3O_4$ nanocomposites have a maximum Sb(III) adsorption capacity of 87.6 mg/g at pH 7.0. The removal of Sb(III) was a complex process including surface adsorption and oxidation. The removal of Sb(III) mainly involved three processes: (1) most Sb(III) was adsorbed on the surface of $nZVI/Fe_3O_4$ nanocomposites; (2) part of Sb(III) was rapidly oxidized to less toxic Sb(V); and (3) the generated Sb(V) was further adsorbed on the surface of $nZVI/Fe_3O_4$ nanocomposites. The $nZVI/Fe_3O_4$ nanocomposites can be separated from solution with an external magnet. The high Sb(III) removal efficiency and rapid separability of $nZVI/Fe_3O_4$ nanocomposites exhibited the great potential for the removal of Sb(III) from wastewater.

1. Introduction

Antimony (Sb) exists ubiquitously in the environment because of natural processes and human activities [1]. Antimony has been widely used in industrial products such as flame retardants, catalysts for plastics synthesis, ammunition, textiles, battery grids, and paints [2]. In recent years, antimony contamination has aroused wide public concern. Similar to arsenic, antimony and its compounds are nonessential and toxic to human health. Antimony in the environment affects the health of human through food chain of water–soil–crops–human. Antimony and its compounds can destroy enzyme activity, lead to the metabolic disorders, and damage to the nervous system and other organs [3]. What is worse, antimony can cause lethal and carcinogenic toxicities when its concentration is high enough. Therefore, antimony and its compounds have been declared as priority pollutants by Environmental Protection Agency of the United States (USEPA) and the European Union (EU). The maximum allowable concentrations of antimony established by USEPA and EU are 6 and 5 μg/L in drinking water, respectively [4].

The most common oxidation states are 5, 3, and −3 in antimony compounds. However, in the environment, Sb(III) and Sb(V) are predominant species. The toxicity and mobility of antimony depend on its oxidation states, and Sb(III) has 10 times higher toxicity than Sb(V).

A number of methods have been used for the removal of antimony, such as adsorption [5], electrochemical deposition [6], coagulation–flocculation–sedimentation [7], ion exchange [8], ultrafiltration [9], and bioremediation [10,11]. Among these methods, adsorption method is one of the most preferred techniques because of its cost effectiveness, simplicity in the design and applicability, high efficiency as well [12]. Adsorption capacity for antimony vastly depends on the adsorbents. A number of adsorbents have been used to remove Sb(III) or Sb(V), such as graphene [13], polyvinyl alcohol-Fe^0 [14], goethite [15], ferrihydrite [16], biochars [17], and Fe–Mn bimetal oxides [18]. However, the adsorbents that both adsorb Sb(III) and transform Sb(III) to less toxic Sb(V) are scarce. Therefore, there is an urgent demand to develop the multifunctional adsorbents that both efficiently adsorb Sb(III) and transform Sb(III) to less toxic Sb(V).

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https://doi.org/10.1016/j.jtice.2018.01.032
1876-1070/

In recent years, nanoscale zero valent iron (nZVI) has been widely used in environmental remediation by virtue of its strong reducibility and high surface area. However, nZVI has some defects. For example, nZVI particles are easy to agglomerate due to the high interfacial energy. In addition, nZVI particles are unstable, which can be easily oxidized by water or oxygen in surrounding environment and form a passive layer. In order to overcome these problems, some efforts have been done. For example, nZVI loaded on solid materials such as carbon, resin, kaolinite had been studied to remove contaminants [19]. Recently, nZVI loaded on Fe_3O_4 has been reported as well [20–22]. nZVI/Fe_3O_4 nanocomposites have been proved to be efficient for degradation of decabromodiphenyl ether [20], and removal of phosphate [21] and nitrite [22].

So far, nZVI/Fe_3O_4 nanocomposites were not widely applied in the removal of heavy metals ions. The tremendous potential of nZVI/Fe_3O_4 nanocomposites in heavy metals ions removal need to be further studied. In this study, nZVI/Fe_3O_4 nanocomposites were applied to remove Sb(III). The performances of nZVI/Fe_3O_4 nanocomposites with different mass ratios were observed. nZVI/Fe_3O_4 nanocomposites before and after reaction were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), vibrating sample magnetometer (VSM), energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). The aims of this paper were: (1) to study the performances of nZVI/Fe_3O_4 nanocomposites with different mass ratios at different pH values for Sb(III) removal; (2) to investigate the variation of Sb species during reaction process; and (3) to explore the reaction mechanism of Sb(III) with nZVI/Fe_3O_4 nanocomposites.

2. Materials and methods

2.1. Materials

All the chemical reagents used in this study were analytical or guaranteed reagents. Ferric sulfate ($Fe_2(SO_4)_3$), ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), ammonium hydroxide ($NH_3{\cdot}H_2O$), and sodium borohydride ($NaBH_4$) were used for the synthesis of nZVI/Fe_3O_4 nanocomposites. The stock solution of 1.0 g/L Sb(III) was prepared by dissolving $K(SbO)C_4H_4O_6{\cdot}1/2H_2O$ in deionized water containing 20% (V/V) HCl. The solution of 10.0 mg/L Sb(III) was prepared by diluting stock solution before use.

2.2. Preparation of nZVI/Fe_3O_4 nanocomposites

nZVI/Fe_3O_4 nanocomposites were prepared according to the method reported by Lv et al. [23] with some modifications. The whole production process was performed under nitrogen environment. Under stirring rapidly (150 rpm), 0.4793 g $FeSO_4{\cdot}7H_2O$ was added into a beaker with 100 mL solution containing 0.6894 g $Fe_2(SO_4)_3$. Then, 2.5 mL 8.0 M $NH_3{\cdot}H_2O$ was added drop by drop for the formation of Fe_3O_4. The whole process was kept at 60 °C in water bath for 0.5 h. Fe_3O_4 particles were produced according to the following equations [24]:

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \quad (1)$$

$$Fe(OH)_3 \rightarrow FeO(OH) + H_2O \quad (2)$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad (3)$$

$$2FeO(OH) + Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O \quad (4)$$

The generated Fe_3O_4 was washed by oxygen-free deionized water for three times. Then, the Fe_3O_4 was transferred into another beaker with 400 mL solution containing 0.4965 g $FeSO_4{\cdot}7H_2O$. With stirring rapidly (150 rpm), 150 mL 0.05 M $NaBH_4$ alkaline aqueous solution was added drop by drop (about 60 drops/min) into the mixed liquor. The generated nZVI/Fe_3O_4 nanocomposites (Eq. (5)) were washed by oxygen-free deionized water for three times. Finally, the nZVI/Fe_3O_4 nanocomposites were filtered through 0.45 μm filter membrane and dried at 60 °C in vacuum oven.

$$nFe_3O_4\text{–}Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow nFe_3O_4\text{–}Fe^0 + 2B(OH)_3 + 7H_2 \quad (5)$$

2.3. Batch experiments

Batch experiments were carried out in 500 mL glass vessels containing 200 mL Sb(III) solution. The initial concentration of Sb(III) was 10.0 mg/L, and the dosage of 1.0 g/L nZVI/Fe_3O_4 nanocomposites was used according to Fig. S1. The nZVI/Fe_3O_4 nanocomposites with different mass ratios were used for Sb(III) removal to investigate the impact of mass ratios during the reaction process. To study the impact of initial pH, the initial pH of solution was adjusted to the certain values (3.0, 5.0, 7.0, 9.0, and 11.0) with 0.1 M HCl or 0.1 M NaOH. All reactions were performed on a thermostatic shaker (130 ± 5 rpm) at 25 ± 1 °C. At the designated time, about 5 mL supernatants were taken and immediately filtered through 0.45 μm filter membrane.

2.4. Adsorption isotherm

The adsorption isotherm experiments were performed at 25 ± 1 °C and pH 7.0 ± 0.2. Initial concentration of Sb(III) varied from 20.0 to 120.0 mg/L. After adsorption for 20 h, the supernatants were filtered by 0.45 μm membrane and analyzed for the residual concentration of Sb(III). The adsorption capacity (q_e) for Sb(III) was calculated according to Eq. (6):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (6)$$

where q_e (mg/g) is the equilibrium adsorption capacity; C_0 and C_e (mg/L) are the initial and equilibrium concentration of Sb(III); V (L) is the volume of the solution; and m (g) is the mass of the nZVI/Fe_3O_4 nanocomposites used in the experiment.

The adsorption isotherm parameters were analyzed using Langmuir and Freundlich isotherm models.

Langmuir isotherm model:

$$q_e = \frac{q_m k_1 C_e}{1 + k_1 C_e} \quad (7)$$

The linearized form of Langmuir isotherm model [25]:

$$\frac{C_e}{q_e} = \frac{1}{k_1 q_m} + \frac{C_e}{q_m} \quad (8)$$

where k_1 (L/mg) is the Langmuir constant; q_m (mg/g) is the maximum adsorption capacity.

Freundlich isotherm model:

$$q_e = k_2 C_e^{1/n} \quad (9)$$

The linearized form of Freundlich isotherm model [25]:

$$\ln q_e = \ln k_2 + \frac{1}{n} \ln C_e \quad (10)$$

where k_2 and n are the Freundlich constants.

2.5. Adsorption kinetics

To express the kinetic characteristics of the adsorption process of Sb(III) on nZVI/Fe_3O_4 nanocomposites, pseudo-first-order and

Please cite this article as: W. Li et al., Zero valent iron as an electron transfer agent in a reaction system based on zero valent iron/magnetite nanocomposites for adsorption and oxidation of Sb(III), Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.01.032