Removal and recovery of thallium from aqueous solutions via a magnetite-mediated reversible adsorption-desorption process

Huosheng Li [a, b], Xiuwan Li [c, e], Yongheng Chen [a, *], Jianyou Long [d], Gaosheng Zhang [a], Tangfu Xiao [d], Ping Zhang [b, c], Changlin Li [d], Lingzhi Zhuang [d], Wenyu Huang [d]

[a] Collaborative Innovation Center of Water Quality Safety and Protection in Pearl River Delta, Guangzhou University, Guangzhou, 510006, China
[b] Key Laboratory for Water Quality and Conservation of the Pearl River Delta, Ministry of Education, Guangzhou University, Guangzhou, 510006, China
[c] School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou, 510006, China
[d] School of Environmental Science and Engineering, Guangzhou University, Guangzhou, 510006, China
[e] Research Institute of Environmental Studies at Greater Bay, Guangzhou University, Guangzhou 510006, China

A B S T R A C T

Thallium (Tl), an extremely toxic heavy metal, has received much less attention than other toxic heavy metals such as Hg, Cd, and Pb. To date, Tl pollution control studies have usually focused on its removal only, while very few studies have explored its recovery from wastewater. In this study, a magnetite (Fe_3O_4)-mediated reversible adsorption-desorption process for the removal and recovery of Tl(I) from wastewater was investigated. Fast and efficient removal of Tl(I) was achieved via adsorption under alkaline conditions at pH > 11.0, while rapid and effective enrichment of Tl(I) was achieved via desorption under acidic conditions at pH < 3.0. The Tl adsorption was effective under high ionic strength even when multiple cations were present. Furthermore, efficient removal of Tl was also observed when magnetite was applied to the treatment of real industrial wastewater. Fourier transform infrared and X-ray photoelectron spectroscopic studies reveal that surface complexation and electrostatic attraction are the main mechanisms of Tl(I) removal. The removal and recovery of Tl(I) could be effectively and stably repeated without obvious loss of magnetite, indicating that the magnetite-based reversible adsorption-desorption process is a promising technique that can be developed further.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Thallium (Tl) is one of the most toxic and dangerous metals owing to its extremely high toxicity and mobility (Huangfu et al., 2017; Kersten et al., 2014; Vaněk et al., 2016). However, Tl has received much less attention than other toxic metals (such as Cd, Cu, Hg, and Pb) and metalloids (such as As), despite its high risk to human health and ecosystem (Li et al., 2017a, 2017b; Vaněk et al., 2013, 2015). Recent studies have revealed that Tl pollution is found in aquatic environments near industrial plants (Liu et al., 2016). With new and increasing applications of Tl in different industrial fields (Brininstool, 2015), Tl pollution poses a growing threat to human health and environment.

In aqueous media, Tl has two oxidation states: Tl(I) and Tl(III). Theoretical calculation and experimental results have indicated that Tl(I) is the dominant Tl species in water (Li et al., 2017a; Vink, 1993). Tl(I) is stable and mobile and its properties are similar to those of potassium; in contrast, Tl(III) is reactive and tends to be hydrolyzed under neutral or alkaline conditions, its properties are similar to those of aluminum (Blasco et al., 1999; Coetzee et al., 2004; Peter and Viraraghavan, 2005). Further, it is much more difficult to remove Tl(I) than Tl(III), and therefore, Tl(I) is much more undesirable and its removal is gaining more attention (Zhang et al., 2018).

Several techniques, including chemical oxidation and precipitation (Twidwell and Williams-Beam, 2002), ion exchange (Li et al., 2017a), microbial oxidation (Wang et al., 2018), coagulation (Huangfu et al., 2017; Liu et al., 2017), and adsorption (Birungi and Chirwa, 2015; Chen et al., 2017) have been proposed for Tl(I) removal from wastewater. Among these, adsorption is widely recognized as an efficient technique, given its simplicity, effectiveness, and capacity (Hua et al., 2012). Different absorbents have

been tested for adsorption of Tl(I) from wastewater, for example, MnO_2 (Wan et al., 2014), TiO_2 (Zhang et al., 2009), polyacrylamide (Senol and Ulusoy, 2010), multi-walled carbon nanotubes (Pu et al., 2013), powdered eucalyptus leaves (Dashti Khavidaki and Aghaie, 2013), and sawdust (Memon et al., 2008). Despite intensive studies on the removal of Tl(I) by these methods, the reuse of these adsorbents and the recovery of Tl(I) are usually neglected. Further, the adsorbents that have captured a high amount of Tl(I) are hazardous materials that should be treated appropriately. From the perspective of sustainability, the adsorbents should be repeatedly reusable, and the desorption process should be simple and effective. By employing a small volume of an appropriate eluent for the desorption of Tl(I) from the used adsorbent and thus its enrichment in the eluent, it is possible to simultaneously reuse the adsorbent and concentrate the Tl(I) to a high level, rendering the recovery of Tl possible while minimizing the hazardous materials.

The magnetic adsorbent has a unique separation property that renders it an excellent adsorbent for heavy metals and it can be readily removed/recovered from solutions (Gomez-Pastora et al., 2017; Zhou et al., 2016). Bare Fe_3O_4 was shown to be potentially useful to remove heavy metals at a capacity of 73 mg/g (Mahdavi et al., 2012). Fe_3O_4 as magnetic core coated with a variety of composites has been demonstrated to be useful for the removal of heavy metals (Hua et al., 2012; Su, 2017). However, so far, there have been very limited studies on the use of magnetic adsorbents for Tl(I) removal/recovery (Fu and Wang, 2011; Gomez-Pastora et al., 2017; Su, 2017). Yantasee et al. (2007) reported that magnetic Fe_3O_4 nanoparticles modified by dimercaptosuccinic acid could bind Tl(I) via the dimercaptosuccinic acid ligands and thus to remove Tl(I), pointing out the feasibility of using magnetic adsorbents for Tl(I) removal. However, little information is available on the various influencing factors, adsorption isotherms, kinetics, and desorption methodologies for Tl(I) removal and recovery using magnetite.

In this study, a magnetite-based adsorption/desorption process was investigated for the removal and recovery of Tl(I) from wastewater samples. The influencing factors, adsorption isotherms, kinetics, thermodynamics, and recovery methodologies were investigated. The treatment of real industrial wastewater using this magnetite-based technique was also performed. In addition, various techniques including X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) spectroscopy were used to uncover the unique pH-responsive reversible adsorption/desorption mechanisms.

2. Materials and methods

2.1. Reagents, chemicals, and synthesis of magnetite

Analytical grade chemicals and reagents were used as received from the supplier (Aldrich, USA). A Tl(I) stock solution (1000 mg/L) was prepared by dissolving $TlNO_3$ (99.9%) in deionized water. Standard working solutions were prepared from the stock solution by serial dilution with deionized water. Aqueous solutions of $NaNO_3$, $CaCl_2$, and $MgSO_4$ were added as co-existing ions when needed. Further, aqueous solutions of ethylene diamine tetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DTPA), and humic acid sodium salt (HA, $C_9H_8Na_2O_4$) were added as co-existing organics when required.

Preparation of the magnetite powder was carried out according to a method proposed by Liu et al. (2008) with some modification. Briefly, 24.4 g of $FeCl_3 \cdot 6H_2O$ and 16.8 g of $FeSO_4 \cdot 7H_2O$ were dissolved in 400 mL water under vigorous stirring (600 rpm) and heated to 90 °C. Then, 40 mL of ammonium hydroxide (25%) was rapidly added to the iron solution. The resultant mixture was

stirred at 90 °C for 30 min and then cooled to room temperature. The suspensions were washed thrice with deionized water and then isolated using a magnet. The obtained magnetite particles were dried at 40 °C for 24 h, ground into a powder in an agate mortar, filtered through a 100-mesh sieve, and finally stored in a desiccator for future use.

2.2. Adsorption tests

Adsorption/desorption tests were conducted in centrifuge tubes in a temperature-controlled shaker at 200 rpm unless otherwise specified. The dosage tests and kinetics tests for adsorption were conducted on the same batch in beakers with temperature-controlled stirrers. Unless otherwise specified, the reaction temperature was maintained at 298 K. All adsorption tests were performed in triplicates. Detailed experimental conditions are described in the following section.

2.2.1. Adsorbent dosage and kinetics analysis

The tests were performed in a 250-mL beaker containing a synthetic Tl(I) solution at an initial volume of 200 mL, an initial Tl(I) concentration of 10 mg/L, and an initial pH of 12.0. Mixing was performed on a temperature-controlled stirrer at 200 rpm. Dosages of 0.50, 1.25, and 2.5 g/L magnetite were used to determine the appropriate dosage. After the dosing of the adsorbent, 2.5 mL aliquots of the suspension were withdrawn with a syringe and filtered through 0.22 µm disposable filters after different intervals: 15 s, 30 s, 45 s, 60 s, 2 min, 3 min, 5 min, 10 min, 20 min, 40 min, 60 min, 2.0 h, 4.0 h, 8.0 h, 12 h, and 24 h. For the control experiment without the adsorbent, the same synthetic Tl(I) solution maintained at pH 12.0 was sampled after 1, 2, 12, and 24 h. Owing to the presence of nano-magnetic particles, the first filtrate was centrifuged at 10000 rpm followed by a second filtration of the supernatant through a 0.22 µm filter. Finally, a 50 µL aliquot of the HNO_3 solution (50%, v/v) was added to each filtrate to preserve the sample.

For modeling the kinetics, the dynamic data profiles were fitted to pseudo-first order, pseudo-second order, and intraparticle diffusion equations according to previous reports (Blanchard et al., 1984; Ho, 1995; Tran et al., 2017). In brief, the related kinetic equations are expressed in Eq. (1) to Eq. (3).

$$Q_t = q_e \left(1 - e^{-k_1 t} \right) \tag{1}$$

$$Q_t = \frac{k_2 \, q_e^2 \, t}{1 + q_e \, k_2 \, t} \tag{2}$$

$$Q_t = k_p t^{\frac{1}{2}} + C \tag{3}$$

where, t, Q_t and q_e are the reaction time (h), the calculated adsorption capacity (mg/g) at time t, and at equilibrium, respectively; k_1 (h^{-1}), k_2 (g·mg^{-1}·h^{-1}), and k_p (mg·g^{-1}·h$^{-1/2}$) are the rate constants of the pseudo-first order, pseudo-second order, and intraparticle diffusion processes, respectively.

2.2.2. Influencing factors

The influence of various factors including the reaction pH, reaction temperature, ionic strength, co-existing ions, and organic complexes was investigated by changing each variable with the other conditions fixed. A 25-mL volume of the synthetic Tl(I) solution with an initial concentration of 10 mg/L was used for adsorption. Mixing was performed on a temperature-controlled shaker at 200 rpm and the reaction time was 20 min. The sampling was carried out in a manner similar to that described in