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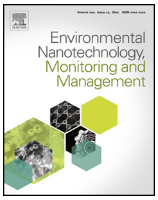

Effective removal of mercury from aqueous solution using thiol-functionalized magnetic nanoparticles

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ABSTRACT

The present investigation demonstrates the effective removal of Hg(II) ions from aqueous solution by means of thiol-functionalized magnetic nanoparticles (TF-MNPs). After preparation, TF-MNPs have been characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Fourier transform-infrared spectroscopy (FT-IR), Thermogravimetric (TG) and vibrating sample magnetometer (VSM). The XRD and FESEM analyses revealed the presence of magnetic nanoparticles with an average particle size of 15–30 nm. The result of FT-IR analysis confirmed that the magnetite nanoparticles have been successfully functionalized by thiol groups. The particles illustrated enough response to a magnetic field, hence they could be easily separated from the aqueous solutions. The amount of the grafted functional groups on the surface was assessed using the TG analysis and was observed to be 34.15%. The adsorption capacity was also investigated as a function of both pH in a range of 2–9 and initial concentration. Pseudo-second-order equation as well as both the Langmuir and Freundlich isotherm models could describe the kinetic data and adsorption equilibrium, respectively. The maximum adsorption capacity of the TF-MNPs was found to be 344.82 mg g^{-1}, which is relatively high. The Hg(II) ions were removed effectively from the surface of TF-MNPs utilizing thiourea in HCl solution. The results also indicated that TF-MNPs could provide improved adsorption capacities for removal of Hg(II) from contaminated water, by means of magnetic separation.

1. Introduction

Due to toxicity of heavy metal ions and their tendency to bioaccumulate (Benavente et al., 2011) strict environmental regulations have been implemented on the release of heavy metals. In order to meet the standard levels, purification methods, such as ion exchange, chemical precipitation, membrane filtration, electro-dialysis, coagulation, biosorption and adsorption have been applied to eliminate heavy metals present in contaminated water (Bessbousse et al., 2008; Chaudhary et al., 2001; Fu and Wang, 2011; Gasser et al., 2008; Khoramzadeh et al., 2013; Kurniawan et al., 2006; Lee et al., 2009; Navarro et al., 2005; Pang et al., 2011; Razzaghi et al., 2014; Shaidan et al., 2012; Song et al., 2007; Wang et al., 2003). Compared to other heavy metal ions, mercury is one of the most toxic ones and it seems that adsorption is one of the most efficient and widely used methods, in treatment processes for heavy metal removal from wastewater, even in low concentrations (Xu et al., 2012). Nanosized metal oxides and particularly magnetic nanoparticles have tremendous potential for providing high surface area-to-volume ratio, quick extraction dynamics, high extraction capacity and also specific affinity for heavy metal adsorption from aqueous systems. Adsorption procedure combined with magnetic separation makes magnetite a potential candidate (Xu et al., 2012), so that the adsorbent and adsorbate can be readily and simply separated from the aqueous phase by utilization of an external magnetic field. Magnetic nanoparticles as the solid phase adsorbent also possess the surface modification ability due to the presence of hydroxyl groups on the iron oxide nanoparticles surface which provides a versatile synthetic handle allowing the attachment of different functionalities (Boyer et al., 2010). Whenever certain functional ligands are bounded with these magnetic nanoparticles, these ligands could enhance their capacity and affinity for target metals from con-

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taminated water. Recent research has indicated that functionalized magnetic nanoparticles have been widely common, because of the possibility of them being applied as adsorbents for the removal of heavy metals from contaminated water (Chang and Chen, 2005; Ge et al., 2012; Girginova et al., 2010; Hao et al., 2010; Hu et al., 2010; Jeon et al., 2007; Mahdavian and Mirrahimi, 2010; Yuwei and Jianlong, 2011). Among the functional groups studied, thiol-functionalized magnetite was observed to be the most efficient one which forms a strong complex with Hg(II) species. Couple of investigations have been carried out utilizing thiol-functionalized and sulfur functionalized adsorbents, which were then applied to Hg(II) binding (Asasian et al., 2014; Hakami et al., 2012; Pan et al., 2012; Parham et al., 2012; Song et al., 2011; Walcarius and Delacôte, 2005). Although numerous efforts were made regarding this issue, a comparison of the sorption capacities of adsorbents for Hg(II) removal reported previously (Asasian et al., 2014; Hakami et al., 2012; Pan et al., 2012; Parham et al., 2012; Song et al., 2011; Walcarius and Delacôte, 2005), reveals that these adsorption capacities are not effective or the adsorbents do not possess the advantage of magnetite as a separable adsorbent. However, the present work introduces an efficient approach to remove Hg(II) ions from aqueous solution using functionalized magnetic nanoparticles with thioglycolic acid (TGA) that can form complexes with Hg(II) ions. This impressive advantage has also been combined with rapid separation by using magnetite as separable adsorbent. Moreover, the present adsorbent demonstrates high adsorption capacity in comparison with other thiol-functionalized and sulfur functionalized adsorbents (Asasian et al., 2014; Hakami et al., 2012; Pan et al., 2012; Parham et al., 2012; Song et al., 2011; Walcarius and Delacôte, 2005).

According to HSAB concept, there is a great affinity between mercury species as a soft acid and sulfur functionalities which are considered soft bases (Pearson, 1963). This is exactly the reason for selecting TGA as the functional group in this work. TGA is a potential candidate which could play a key role as a modifier to make efficient adsorption of Hg(II) possible, as it contains thiol group atoms in its structure. Thus, thiol-functionalized magnetic nanoparticles (TF-MNPs) with TGA are being examined in the recent study, with respect to their efficiency in adsorption of Hg(II) from aqueous media.

The adsorbate may compete with other hydrogen or hydroxide ions, so it is clearly expected that the adsorption amount of Hg(II) is significantly influenced by the initial pH of the medium.

Regeneration of the utilized adsorbent and the possibility of reusing it, is so important from a commercial point of view and that is the reason why, maintaining an adequate performance of the adsorbent in multi-cycle operations is one of the key factors in industrial scales(Hakami et al., 2012). The separation of Hg(II) from the loaded adsorbent is normally accomplished using hydrochloric acid (Walcarius and Delacôte, 2005), but for the removal of Hg(II) from the thiol-functionalized adsorbent, acid alone is not sufficient and the addition of thiourea is also required (Hakami et al., 2012).

In the present investigation, we have mainly focused on the preparation of modified magnetic iron oxide nanoparticles utilizing TGA to improve the adsorption capacity and then the prepared adsorbents were characterized using a variety of physicochemical techniques. Afterwards, They were utilized in the removal process of Hg(II) ions to study the results. The adsorption process demonstrated high potentials for effective removal of Hg(II) ions from contaminated water in a short time period. Several controlling parameters have been found to affect the sorption effectiveness, such as initial pH, concentration, and contact time which were also analyzed, after the experiments were carried out in a batch mood. In addition the experimental studies were performed to investigate the possibility of regeneration of the adsorbents.

2. Materials and methods

2.1. Reagents

All chemicals used are of the analytical grade and were used without any further purification and all the solutions were prepared using de-ionized water.

Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), ferrous chloride tetrahydrate ($FeCl_2{\cdot}6H_2O$), $HgCl_2$, and toluene were purchased from Merck (Darmstadt, Germany). Thioglycolic acid was from Fluka (Switzerland) and was used as a modifier for MNPs, and thiourea was obtained from Sigma-Aldrich.

Nitric acid, hydrochloric acid (37%, w/w) and sodium hydroxide were also bought from Aldrich for the pH adjustment.

2.2. Synthesis of TF-MNPs

The preparation of magnetic nanoparticles (MNPs) was performed through a co-precipitation method according to the previous reports (Mahdavian and Mirrahimi, 2010). Briefly, a solution of ferric and ferrous chlorides (2:1 molar ratio) was mixed mechanically under argon purging at 85 °C. Then the ammonia solution was added dropwise. After 2 h, the precipitated product was separated by a magnet, washed with the deionized water and ethanol, and finally dried in a vacuum oven. In this method, pH of the solution is one of the key factors in controlling the particle size distribution of MNPs (An et al., 2011).

In order to thiolate the magnetite nanoparticles with TGA, 1 g of the prepared MNPs was dispersed in 50 mL of toluene. Then 2 mL of TGA was added to the above dispersion and stirred for 1 h using a glass rod at 25 °C. After complete mixing, the product was separated by a magnetic field and then washed with ethanol several times and dried at ambient conditions.

2.3. Characterization of TF-MNPs

The structure analyses of the MNPs and TF-MNPs were obtained using an X-ray Diffractometer (X'PERT MPD, Philips) which was equipped with a Co-anode (Kα ray, $\lambda = 1.78891$ A°). The XRD pattern obtained was step-scanned from 15.0100 to 79.9900 (2θ) at 0.02°/S. For FESEM, MIRA TESCAN was utilized to identify the morphology and microscopic size of the MNPs. The functional groups and chemical bonding of the MNPs and TF-MNPs were determined by a Fourier Transform-Infrared Spectrometer (FT-IR, Bruker, Tensor27, Germany) with a resolution of 4 cm^{-1}. The amount of TGA bound on the MNPs was estimated using the weight loss percentages obtained from a thermogravimetric analysis (TG) utilizing a heating rate of 20 ° C min^{-1} under nitrogen atmosphere on the Pyris TG/DTA (PerkinElmer, USA). The magnetic behaviors of the MNPs and TF-MNPs were characterized using a VSM, PAR-155 (USA)) with hysteresis measurements being performed at 300 K with applied magnetic fields, in order to conduct demagnetisation corrections. The residual concentrations of the mercury ion in sample solutions were measured by an atomic absorption spectrophotometer (Varian AA240) equipped with a mercury hallow cathode lamp (Varian, Australia) at a wavelength of 253.7 nm after the adsorbent being recovered from the solution by an external magnetic field.

An Elmetron pH meter model Cpc-502 and a magnet (1T) were used during the experiments.

2.4. Batch adsorption procedure

The mercury adsorption/desorption runs were carried out in a batch mode at room temperature.

In general, 0.07 g of TF-MNPs was added to a 50 mL solution of Hg(II) ions (300 mg L^{-1}) adjusted to a desired pH value of 6.0 by