Research article

Removal of mercury from contaminated saline wasters using dithiocarbamate functionalized-magnetic nanocomposite

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A B S T R A C T

In this study, an efficient adsorbent was proposed for the removal of mercury from saline water contaminated with mercury ions. Fe_3O_4 nanoparticles were modified using tetraethylenepentamine and carbon disulfide to incorporate dithiocarbamate functional group on the surface of the adsorbent. CHNS analysis confirmed successful modification of magnetic nanoparticles. The XRD pattern of adsorbent indicated a proper match with the standard XRD pattern of cubic Fe_3O_4. The saturation magnetization of final adsorbent was 27 emu g^{-1}. The morphology of bare and silica-coated Fe_3O_4 and final product were investigated using FE-SEM analysis. For optimizing the adsorption process, response surface methodology was applied, which was resulted in a significant quadratic model. The effect of adsorbent dosage and initial concentration of Hg (II) was much more significant than that of pH. Different concentrations of dissolved solids up to 2000 mg L^{-1} had no adverse effect on the adsorption process due to the strong interaction between dithiocarbamate functional group of adsorbent and Hg (II). The least values of RMSE (0.0950) and $\chi2$ (0.0009) were observed for Radke-Prausnitz, Redlich-Peterson, and UT isotherms. Maximum adsorption capacities calculated using Langmuir and UT models were 109.5 and 95.07 mg g^{-1}, respectively. The investigation of adsorption isotherm was conducted at the pH range of 2.0–6.5. The results showed an increase in the adsorption capacity by increasing pH. Thermodynamic studies demonstrated that the nature of the adsorption process was spontaneous and endothermic. Recovery of adsorbent was successfully carried out using HCl 0.5 mol L^{-1}. The prepared adsorbent was successfully applied for mercury removal from a real groundwater.

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1. Introduction

The elements with atomic densities over $6.0 \, g \, cm^{-1}$ are known as heavy metals. High concentrations of heavy metals may cause serious damage to human health, posing threats to the aquatic systems, and toxic impact on soil and plants systems, including growth retardation, changes in the activities of enzymes and photosynthesis (Hadavifar et al., 2016). Due to fast development in industrialization, the presence of heavy metals in wastewaters has become one of the basic worldwide problems (Anantha and Kota, 2016; Xiang et al., 2016). Heavy metals, which are non-degradable, have been increasingly discharged into the surface waters (Rahimi et al., 2015; Soleimani and Siahpoosh, 2015). One of the most hazardous toxic heavy metal ions known to man is

mercury (Parham et al., 2012). Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) has listed mercury in the third place on the "Priority List of Hazardous Substances." European Water Framework Directive (2000/60/EG) has also classified mercury as one of the thirty "dangerous pollutants" (R. Zhang et al., 2016). The toxicity of mercury results from the strong interaction between mercury and thiol functional group in proteins and enzymes, which causes malfunction of cells (Shi et al., 2015). Industrial processes like chloralkali, paint, pulp, fertilizer production, oil refineries, etc. are releasing a large amount of mercury into the environment (Choi et al., 2015). Mercury is a bioaccumulative element, which is seriously dangerous for human health even at low concentrations (AlOmar et al., 2017). Problems like brain damage, chronic diseases, severe harm to kidneys, nervous system, and other organs have been observed after exposure to mercury (Awual et al., 2016; Shen et al., 2014). It can also increase the cancer risk in humans (Shirkhanloo et al., 2016); as a consequence, mercury contamination has aroused worldwide concern and subsequently has attracted the attention of the scientific

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communities (X. Zhang et al., 2016). Environmental protection agency (EPA) has reported the maximum contaminant level of $0.001 \, mg \, L^{-1}$ for mercury, whereas World Health Organization (WHO) reported the guideline value of $0.006 \, mg \, L^{-1}$.

Many different methods have been investigated in order to remove mercury from water and wastewater, including ion exchange, precipitation, solvent extraction, ultrafiltration, reverse osmosis, flotation, etc.(Liu et al., 2017; Saleh et al., 2017b), which most of them have unavoidable drawbacks such as high cost, low efficiency, sensitivity to environmental conditions, formation of by-products, etc.(Bao et al., 2017). Among all these processes, adsorption is considered as the most promising technique ( ) for mercury removal from water due to its simplicity, high effectiveness, low cost (Duan et al., 2016; Nasirimoghaddam et al., 2015). In the past few years, many researches have been conducted for achieving new adsorbents to remove heavy metals (Saleh et al., 2017a), including mercury from water. Among the adsorbents, nanoparticles are one of the most effective adsorbents due to their unique features, including small size, which results in the high surface area (AlOmar et al., 2017; Adio et al., 2017). Not only the surface area but also functional groups on the surface of adsorbent are necessary for adsorbing the pollutants. Therefore, many researches have been reported regarding surface modification of materials to prepare an efficient adsorbent (Jabli et al., 2017). Magnetic iron oxide nanoparticles have become one of the most effective adsorbents in adsorption processes due to their unique physical and chemical properties (Golosovsky and Vasilakaki, 2013; Jagadeesh et al., 2013; Kaittanis et al., 2014). However, the adsorption capacity of magnetic iron oxide nanoparticles is low for adsorption of mercury ions, and also they are extremely susceptible to oxidation (Zia et al., 2016). Another problem of some modified magnetic nanoparticles reported in previous studies is an inefficient performance in samples with high solid content which can lead to low efficiency for real water treatment applications. Hence, it seems necessary to seek for a novel adsorbent with high adsorption capacity, facile separation after treatment, high performance in saline aquatic samples, and high recyclability.

Response surface methodology (RSM), a well-known method, applies statistical and mathematical approaches to design the experiments for the establishment a relationship between responses and independent parameters and optimization of independent variables based on a combination of experimental design techniques (Entezari et al., 2005; Iqbal et al., 2016). The purpose of using RSM in adsorption studies is to optimize the levels of effective parameters on the adsorption simultaneously in order to obtain the best adsorption performance (Dastkhoon et al., 2016; Roosta et al., 2014). In this research, the Box-Behnken Design (BBD), one of the useful response surface methodologies, was employed (Das and Mishra, 2017).

The purposes of this study were (1) introduction of new adsorbent prepared using dithiocarbamate functionalization of magnetic iron oxide nanoparticles for mercury removal from aquatic solutions, (2) characterization of the adsorbent using FTIR, CHNS, FE-SEM, VSM, and XRD analysis, (3) optimization of the adsorbent synthesis process, (4) optimization of levels of different factors using RSM, (5) investigation of the effects of various parameters on the adsorption of mercury ions from aqueous samples (6), the investigation of adsorption isotherm and thermodynamic of the adsorption process, and (7) recovery of adsorbent.

2. Materials and methods

2.1. Materials and instruments

All materials were purchased from Merck and used without any purification. Sodium hydroxide (NaOH), Iron (II) chloride (FeCl$_2 \cdot$4H$_2$O) and Iron (III) chloride (FeCl$_3 \cdot$6H$_2$O) were used for the preparation of magnetite nanoparticles. For silica coating of magnetite nanoparticles, ethanol, ammonium, and tetraethyl orthosilicate (TEOS) were used. (3-chloropropyl) trimethoxysilane (3-CPTS), tetraethylenepentamine (TEP), and carbon disulfide (CS$_2$) were utilized for functionalization. A stock solution of TDS was prepared using MgSO$_4$, CaCl$_2$, NaHCO$_3$, and KNO$_3$. Also, mercury (II) nitrate was used for the preparation of a stock solution of mercury ($1000 \, mg \, L^{-1}$), from which working solutions with different concentrations were provided for batch experiments. The pH value of each solution was adjusted with hydrochloric acid and sodium hydroxide, and a pH-meter (model B2000, Behine) was used for controlling pH. The concentration of mercury was determined using inductively coupled plasma spectroscopy (ICP, Spectro, Arcos EOP, Germany) and an atomic absorption spectrometry equipped with a cold vapor generation (CVG) system (Varian VGA 77).

2.2. Preparation of adsorbent

The preparation of adsorbent was conducted through three steps illustrated in Fig. 1. First of all, magnetic nanoparticles were coated with silica. After that, it was amine functionalized using tetraethylenepentamine (TEP). Finally, the amine functionalized nanoparticles were reacted with carbon disulfide to incorporate dithiocarbamate functional group on the surface of the adsorbent.

The magnetic iron oxide nanoparticles (MIO) were prepared using co-precipitation method previously reported (Feng et al., 2010). For silica coating, 3 g of MIO was added to the mixture of ethanol (500 mL) and water (125 mL). After 5 min of ultrasonication, 8 mL of tetraethyl orthosilicate (TEOS) and 10 mL of ammonia solution (25 %w/w) were added to the solution while mixing on a magnetic stirrer. The suspension was stirred at 25 °C for 14 h. To the magnetic iron oxide-silica coated nanoparticles (SCMIO), 5 mL of (3-chloropropyl) trimethoxysilane (3-CPTS) was added. Afterward, the resultant solution was sonicated for 15 min, and next refluxed at 40 °C for 24 h. Subsequently, the obtained core-shell nanoparticles modified with 3-CPTS were collected using a magnet. As mentioned above, 8 mL of TEOS (d: $0.94 \, g \, mL^{-1}$) and 5 mL of CPTS (d: $1.09 \, g \, mL^{-1}$) were the required amount of each component for 3 g of MIO. Therefore, the mass ratios of TEOS/MIO and 3-CPTS/MIO were 2.5 and 1.82, respectively.

Three different methods were used for immobilization of TEP on the surface of SCMIO: **(1) Immobilization of TEP on SCMIO in ethanol:** 200 mL ethanol and 25 mL water were added to the collected SCMIO and dispersed by ultrasonic waves. Next, while the solution was mixing on a magnetic stirrer, 5 mL of the TEP was added and refluxed at 40 °C for 24 h. The resulting amine functionalized magnetic iron oxide (AFMIO) was collected using a magnet. **(II) Immobilization of TEP on SCMIO in toluene:** In this procedure, 0.5 g of the collected SCMIO was refluxed with 2 mL of TEP in toluene at 110 °C for 48 h **(III) Immobilization of TEP on SCMIO directly in TEP:** In this method, 0.5 g of SCMIO was added directly into 10 mL of TEP. Then the solution was refluxed at 80 °C for 3.5 h. Different conditions for functionalization of SCMIO have been presented in Table 1.

To incorporate dithiocarbamate functional group, 0.5 g of AFMIO prepared in toluene and directly in TEP were added to an excess amount of carbon disulfide (5 mL) separately and stirred for 1 h at 25 °C. The resulting product (DFMIO) was separated by a magnet and finally dried at room temperature.

2.3. Characterization of adsorbent

The Fourier transform infrared (FTIR) spectra were recorded using Burker spectrometer. Elemental composition and