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Synthesis of a unique nanostructured magnesium oxide coated magnetite cluster composite and its application for the removal of selected heavy metals

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ABSTRACT

The removal of heavy metal such as lead (Pb), cadmium (Cd), and copper (Cu) was assessed using magnesium oxide cores with silica coated nano-magnetite (MTM) prepared by a simple method using chemicals such as iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), magnesium (II) nitrate hexahydrate [$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], tetraethyl orthosilicate (TEOS), and urea. The MTM was characterized using X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDS), and alternating gradient magnetometer (AGM) analyses. The isotherm, kinetic, and intra-particle diffusion studies indicated that the MTM had excellent removal capacities towards heavy metals (Pb, Cd, Cu) and the adsorption capacities were as high as 238 mg g^{-1} (1.15 mmol g^{-1}) for Pb, 85.1 mg g^{-1} (0.75 mmol g^{-1}) for Cd, and 33.5 mg g^{-1} (0.5 mmol g^{-1}) for Cu. The intra-particle diffusion, FE-SEM, XPS, and XRD results indicated that the mechanism of heavy metal removal was mainly substitution, followed by precipitation. A leaching test revealed that MTM showed no leaching of Fe ions at $\text{pH} > 2$. This material is cheap, simple, and can be produced in massive amounts. MTM can be used for the large-scale remediation of waste water containing heavy metals via applying a simple and fast magnetic separation.

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1. Introduction

In the environment, heavy metals are not only more persistent than organic contaminants, such as pesticides or petroleum by-products, but can also become mobile in soils depending on soil pH and their speciation so that a fraction of the total mass can leach to the hydrosphere and can become bioavailable to living organisms [1,2]. The most toxic forms of metals are the ionic species (e.g., Cd^{2+} , Pb^{2+} , Hg^{2+} , Ag^+), which can react with biomolecules to form stable biotoxic compounds that are difficult to dissociate [3]. Thus, exposure to heavy metals, even at trace levels, is believed to be a significant risk for ecosystems and human beings [4–6]. Nowadays, numerous methods, including chemical precipitation, coagulation, ion exchange, filtration, and electrochemical technologies, have been proposed for remediating heavy metals from

water [7–10]. However, their applications have been restricted by limitations; for example, precipitation or coagulation requires various chemicals and involves high sludge volumes while filtration or electrochemical technologies require relatively large capital investments and electricity supplies [11].

Adsorption is an effective and economical method for heavy metal waste water treatment. Especially, when adsorbents have high sorption capacities and speeds, adsorption is considered to be one of the most promising technologies due to its simple and economical set-up and facile operation [12]. As promising sorbents, nanomaterials have been suggested as efficient, cost-effective, and environmental friendly alternatives. To date, nanomaterials with various morphologies have been studied and their potential applications include catalysis, energy conversion and storage, sensors, and biological applications. Through self-assembly processes, the developed nanomaterials are nanoparticles, nanofibers, and nanofilms, which may have flower-like and rod-like shapes [13]. Among nanomaterials, nano-sized metal oxides (NMOs), including ferric oxides, manganese oxides, aluminum oxides, titanium oxides, magnesium oxides, and cerium oxides,

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provide high removal capacities of heavy metals due to their high surface areas and specific affinities [14–16]. Especially, magnetic NMOs have received much attention in terms of their potential applications because of their unique properties, such as extremely small size, high surface area to volume ratio, surface modifiability, excellent magnetic properties, and high biocompatibility [17–20]. Because magnetic NMOs allow easy separation from the aqueous phase for recycling or regeneration [21], operational efficiency can be improved, reducing overall operational costs in water treatment. However, due to their nano-sizes, magnetic NMOs may not be suitable for actual wastewater treatment due to blocking and fouling problems in subsequent filtration steps. Moreover, if such nanoparticles are not fully recovered, secondary contamination could occur, eventually affecting the ecosystem [22].

To solve the problems above, in this study, we synthesized magnetic NMOs with a unique morphology. The designed morphology of the magnetite was octahedral magnetite, which has a high magnetic saturation and coercivity force, which enhances the magnetic separation strength. This magnetically separable clustered adsorbent was prepared through synthesizing nano-magnetite (NM) and clustering NMs via coating with TEOS (designated as MT), and then further incorporating nano-structured magnesium oxide (MgO, designated as MTM). The prepared cluster material resulted in a micron-sized material that has a high surface area and does not cause secondary pollution due to its high recoverability, versus a nano-sized material.

The objectives of this study were (i) to synthesize NM, MT, and MTM using environmentally friendly and economically viable precursors via a simple synthesis route, (ii) to determine the lead (Pb), cadmium (Cd), and copper (Cu) sorption capacities and rates of the prepared media, and (iii) to examine the removal mechanism of heavy metals through conducting a series of tests of various physicochemical characteristics, such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscopy (FE-SEM), vibrating sample magnetometer (VSM), and transmission electron microscopy (TEM).

2. Materials and methods

2.1. Materials

Iron (II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), potassium nitrate (KNO_3), tetraethyl orthosilicate (TEOS), ammonia, ethanol, magnesium (II) nitrate hexahydrate [$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], and urea were of analytical grade and obtained from Aldrich and R&M products.

2.2. Method

2.2.1. Preparation of nano-magnetite (NM)

The method of preparation was according to Schwertmann and Cornell [23]. First, 40 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 500 mL distilled water. Then, the solution was heated to 80 °C. Meantime, another solution of KNO_3 (3.3 g) and NaOH (22.4 g) was prepared in 415 mL distilled water through dissolving KNO_3 and NaOH. This solution was then added drop-wise into $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution while maintaining it at 80 °C. A color change from yellow to black was observed after the addition. It was then left stirring overnight at 25 °C. The precipitate was later separated, washed with distilled water, and dried in an oven at 60 °C.

2.2.2. Preparation of nano-magnetite coated TEOS (MT)

The magnetite nanoparticles coated with silica were prepared by a modified method of Chang et al. [24]. First, a mixture of ethanol (100 mL) and distilled water (20 mL) was added to magnetite

nanoparticles (1 g), and the resulting dispersion was sonicated at 37 kHz for 10 min. After ammonia solution (2.5 mL) was added into the suspension, TEOS (2 mL) was injected into the solution. The resulting dispersion was stirred mechanically and continuously at 25 °C. The magnetic MT nanoparticles were collected by magnetic separation and washed with ethanol and deionized water in sequence. MT was then dried at 70 °C overnight.

2.2.3. Preparation of MgO-coated MT (MTM)

The $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and urea used were of analytical grade. In the procedure, a solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (60 g) and urea (30 g) was added in 25 mL of distilled water. The prepared solution was then used to coat 4.5 g of MT in a Teflon-lined autoclave bottle. The Teflon-lined autoclave bottle was then sonicated for about 5 min to disperse the solution over the MT surface. The autoclave was then sealed and placed in a microwave oven and heated to 150 °C for 30 min. After cooling to room temperature, the precipitate was collected by centrifugation and washed with distilled water. Then, as MTM, the precipitate was further calcined at 400 °C for 2 h.

2.3. Characterization

XRD patterns were obtained using an X-ray diffractometer (PANalytical Empyrean) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54443 \text{ \AA}$) at 40 kV and 40 mA. The microscopic features of the materials were characterized by FE-SEM (Hitachi SU 8000), while energy-dispersive X-ray spectroscopy (EDS) was conducted using a Bruker XFlash Detector 6/30 and TEM (Tecnai TF30). The nitrogen adsorption and desorption isotherms were measured using a Micromeritics TriStar II 3020 system. Magnetization tests were conducted using VSM (Lake Shore, 7400 series VSM system). FTIR analysis were performed using a Perkin Elmer FTIR-Spectrum 400 while the XPS analysis was conducted using an ULVAC-PHI Quantera II.

2.4. Adsorption isotherms and kinetics

Batch adsorption tests were conducted to determine the adsorption kinetics and capacities for heavy metals of the prepared material. Each stock solution containing 3 mmol L^{-1} of heavy metal was prepared through dissolving $\text{Pb}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, or $\text{Cu}(\text{NO}_3)_2$ in distilled water. To conduct isotherm tests, the stock solution was diluted to be various concentrations ranging from 0.3 to 3 mmol L^{-1} . For all prepared solution, the ionic strength was kept to 0.1 M using NaCl. Solid samples (0.05 g) were put into 50 mL centrifuge tubes, and then 25 mL of metal solution containing various initial concentrations (0.3–3.0 mmol L^{-1}) was added. The centrifuge tubes were then shaken at 150 rpm at 25 °C for 20 h in a bench shaker. Then, the suspensions were separated using an external magnet bar and the solutions were filtered through a 0.45- μm syringe filter to determine the equilibrium concentrations of each heavy metal by inductively coupled plasma-optical emission spectroscopy (ICP-OES; PerkinElmer OPTIMA 8300). The adsorption capacities were calculated with the following Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where q_e is the adsorbed amount of heavy metal on the adsorbent, C_0 and C_e are the initial and final concentrations of the metal ions, V is the volume of metal containing solution, and W is the weight (g) of adsorbent used. The adsorption data were fitted to the Langmuir isotherms as follows.

The linear form of the Langmuir model can be depicted as follows. When adsorption is held with an uniform binding energy across adsorption sites, the Langmuir model (2) fits the isotherm

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