



Fabrication, characterization and physical properties of a novel magnetite graphene oxide/Lauric acid nanoparticles modified by ethylenediaminetetraacetic acid and its applications as an adsorbent for the removal of Pb(II) ions



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ABSTRACT

Nanocomposite of magnetite graphene oxide/Lauric acid containing ethylenediaminetetraacetic acid nanoparticles (GO/Fe₃O₄/LA/EDTA) was synthesized in aqueous media by chemical co-precipitation method. Morphology, particle size, structure and physical properties of GO/Fe₃O₄/LA/EDTA nanocomposites were characterized using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Raman spectroscopy, Energy dispersive X-ray (EDX) spectroscopy, Thermal gravimetric analysis (TGA), Vibrating sample magnetometer (VSM), Scanning electron microscopy (SEM), Atomic force microscopy (AFM), Transmission electron microscopy (TEM) and Brunauer–Emmett–Teller analysis (BET). The effects of independent variables including pH of solution, concentration of Pb(II) ions, contact time and temperature were coded as x_1 , x_2 , x_3 and x_4 at five levels (−2, −1, 0, 1 and 2), in these calculations Y was considered as the response (the secondary concentration of Pb(II) ions in mg L^{−1}). The optimum condition was achieved at secondary concentration of 120.18 mg L^{−1} at pH = 3, the initial concentration of 280 mg L^{−1}, time of 105 min at 20 °C. In addition, GO/Fe₃O₄/LA/EDTA nanocomposite can be recovered easily using magnetic separation technology. The experimental equilibrium data was fitted well with the Freundlich model while adsorption kinetics had the highest consistency with the pseudo second-order kinetic model. Thermodynamics parameters including ΔG° , ΔS° and ΔH° showed that the adsorption reaction of Pb(II) onto GO/Fe₃O₄/LA/EDTA was spontaneous and endothermic in nature.

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1. Introduction

Recently, contamination of wastewaters with toxic heavy metal ions has been one of the most challenging environmental problems [1]. In this regard, Heavy metals with densities higher than 5000 g/L are considered toxic to the environment [2,3]. Industrial discharges and particulates in the atmosphere are the two main sources of imported heavy metals in waterway [4]. The major heavy metals which can cause serious damages to the environment, animals and public health are Hg, Cu, Th, Cd, Pb, Cr, As and Ni [3,5]. Among these toxic heavy metal ions, lead is one of the most toxic elements even at low concentrations which has serious health risks for young children under the age of six, including reduced IQ, learning disabilities, attention deficit disorders,

behavioral problems, stunted growth and impaired hearing [6]. According to the World Health Organization (WHO), the maximum allowable limit (MPL) of lead in drinking water is 0.05 mg L^{−1}. Moreover, the permitted limit for Pb (II) in sewage, given by Environmental Protection Agency (EPA), is 0.05 mg L^{−1} while in industrial sewage, the concentration of lead-ion approaches 200–500 mg L^{−1} which is extremely higher compared to water quality standards [7].

The main techniques for the removal of Pb(II) ions from waste water are chemical precipitation, ion exchange, membrane filtration, electrochemical treatment, reverse osmosis, solvent extraction, bio-removal, coagulation and adsorption processes [2,6]. Among these methods, adsorption process has become one of the most commonly used removal technique due to low cost, ease of operational conditions and the availability of adsorbents [2,3]. In this sense, application of nanocomposite adsorbents in removal systems have become of raising importance in recent years. These adsorbents include Fe₃O₄-EDTA [8], EDTA-graphene oxide [9,10],

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magnetic EDTA-modified chitosan/SiO₂/Fe₃O₄ [2], magnetic PS-EDTA resin [11], sulfonated magnetic graphene oxide [12], EDTA-modified chitosan–silica hybrid [13], EDTA/or DTPA cross-linked chitosan [14] and silica gel functionalized with EDTA/or DTPA [15].

Graphene, the new member of carbonaceous materials, with an atomic-layer-thickness and two-dimensional honeycomb crystal structure has triggered considerable research interest in nanoscience and nanotechnology [14,16,17]. After the discovery of graphene, many endeavors had been performed to synthesize graphene oxide (GO) [18]. The surface of graphene oxide contains units of oxygen functional groups (carboxyl, hydroxyl, epoxy group, and so on) which render graphene strongly hydrophilic with good dispersion in aqueous media [19,20]. These unique functional groups and large surface area of GO makes it a promising candidate for loading magnetic and ferromagnetic nanoparticles, such as Ni, Co and Fe [19–21]. In the last few years, several approaches reported the preparation of GO/Fe₃O₄ using high temperature decomposition with Fe(acac)₃ precursor on GO, ion exchange and subsequent calcinations, attachment of Fe₃O₄ nanoparticles to GO through covalent bonding, hydrothermal technique, microwave irradiation, and chemical precipitation [19,22]. The interaction between iron oxide particles and GO sheets leads to the formation of nano GO/Fe₃O₄ which can further be used in solid–liquid separation systems. Research has shown that the sorption capability of graphene oxide is reduced due to the interactions with magnetic nanoparticles. In order to refine this drawback, a great number of new functional groups such as sulfonic acid, EDTA and ethylenediamine could be attached to the surface of the magnetic GO [21].

The aim of this study were to (1) synthesis of a novel GO/Fe₃O₄/LA/EDTA nanocomposite, (2) characterizations of particle size, chemical structure, morphology and physical properties of the prepared nanocomposite. (3) investigation of GO/Fe₃O₄/LA/EDTA nanocomposite efficiency for the removal of Pb(II) ions from aqueous solution in a batch system; (4) modelling and optimization of the adsorption process with RSM technique; (5) analysis of process parameters effects on Pb (II) ions adsorption; (6) investigation of the adsorption mechanism with kinetic, isotherm and thermodynamic models.

2. Materials and methods

2.1. Chemicals

All the chemical reagents used in this work including graphite powder (<50 μm, d = 2.2 g/cm³), hydrogen peroxide (H₂O₂, 30 wt. %), sulfuric acid (H₂SO₄, 98 wt.%), potassium permanganate (KMnO₄, 99.9%), hydrochloric acid (HCl, 37 wt.%), ferric chloride hexahydrate (FeCl₃·6H₂O, 98%), ferrous chloride tetrahydrate (FeCl₂·4H₂O, 98%), ammonium hydroxide (NH₄OH, 25%), Lauric acid (CH₃(CH₂)₁₀COOH, 99%), ethylenediaminetetraacetic acid (C₁₀H₁₄K₂N₂O₈·2H₂O, 99.9%) and Lead(II) nitrate (Pb(NO₃)₂, 99.5%) were purchased from Merck. Stock solution of 1000 mg L⁻¹ was prepared by dissolving appropriate amounts of Pb(NO₃)₂ in deionized water (DI).

Working solutions ranging from 60 to 500 mg L⁻¹ of Pb(II) was prepared by diluting the stock solution. Adjustment of pH was performed using 0.1 M HCl and 0.1 M NaOH.

2.2. Preparation of graphene oxide

Graphene oxide (GO) was synthesized by a modified Hummers method, in which graphite powders (1 g) was added to concentrated H₂SO₄ (23 mL) in an ice bath at 0 °C followed by addition of potassium permanganate (2 g) under vigorous stirring at a temperature below 15 °C for 2 h. Then the temperature was raised

to 35 °C and 80 mL of deionized water was slowly added to the mixture and stirred for 30 min 30 mL of 5% H₂O₂ was added to the solution which changed its color from dark brown to yellow. The resulting slurry was centrifuged and washed five times with 5% HCl and deionized water until pH of the supernatant becomes neutral. The fabricated graphene oxide was dried in a vacuum at 60 °C for 12 h where a brown powder, was achieved [16].

2.3. Preparation of GO/Fe₃O₄/LA nanocomposite

The GO/Fe₃O₄/LA nanocomposite was prepared by chemical coprecipitation of FeCl₃·6H₂O and FeCl₂·4H₂O, in the presence of GO and Lauric acid. In detail, 40 mg of GO in 40 mL of deionized water was ultrasonicated for 30 min, into which a 50 mL solution of Fe³⁺ and Fe²⁺ (molar ratio 2:1) in deionized water was added at room temperature under N₂ flow. The mixture was then stirred for 30 min in order to remove any dissolved oxygen. The temperature of the mixture was adjusted at 85–90 °C when 30% ammonia aqueous solution was added for raising the pH to 10. Then, 0.18 mg of Lauric acid was dispersed in a solvent mixture of GO/Fe₃O₄ and deionized water by sonication at a constant temperature of 90 °C for 40 min. After cooling to room temperature, the resulting sample was collected by a permanent magnet. Finally, GO/Fe₃O₄/LA was washed three times with deionized water and dried in vacuum at 60 °C for 12 h.

2.4. Preparation of GO/Fe₃O₄/LA/EDTA nanocomposite

To prepare nano GO/Fe₃O₄/LA/EDTA, 20 mg of GO/Fe₃O₄/LA was dissolved in toluene (4 mL) and further mixed with the EDTA ligand (50 mg) suspended in methanol (10 mL). The mixture was vigorously stirred overnight (18 h to 24 h) [8] and subsequently rinsed two times with ethanol, acetone, and deionized water to remove excess ligand and finally dried in vacuum at 60 °C for 12 h. The schematic diagram of sequential co-precipitation process for preparation of nano GO/Fe₃O₄/LA/EDTA composite was shown in Fig. 1

2.5. Characterization techniques

The chemical structure of samples was revealed using a Fourier transform infrared spectrometer (FTIR, Bruker, TENSOR 27, and Germany). X-ray diffraction was collected on a Philips X'Pert MPD X-ray system with Co Kα (λ = 1.78901 Å) (Holland) at room temperature. The microscopic morphology of samples was characterized using Scanning electron microscopy (SEM, VEGA3 TESCAN) equipped with an Energy Dispersive X-ray analysis (EDX, Sirius SD). Structural and size distribution of samples was characterized with Transmission electron microscopy (TEM, Zeiss, EM10C, 80KV). AFM images was recorded on a Dimension Icon System (Easyscan2 Flex) using a tapping mode through Nanosurf Easy Scan software at a scan area of 5 μm × 5 μm. Thermal analysis of GO/Fe₃O₄/LA/EDTA was carried out on a thermal gravimetric analysis (TGA) (TG209F1, Netzsch, Germany). Raman spectrum was measured by using a Raman spectrometer (BRUKER, SENTERRA, Germany). The BET specific surface area of the as-synthesized sample was determined using nitrogen adsorption–desorption measurements at 77 K (Bel, Belsorp mini II Instruments, Japan). The magnetic property measurement was performed using a Vibrating sample magnetometer (VSM) at room temperature (300 K) (Lake Shore 7410, USA). A 1.2 KW power, 40 MHz frequency generator-Vista-PRO CCD Simultaneous ICP-OES (Varian Technologies, Inc.) with a cross flow nebulizer and a cyclonic model spray chamber was used for the determination of Pb(II) concentrations. The auxiliary gas (Ar) flow rate, carrier gas (Ar) flow rate and plasma gas (Ar) flow rate were 1.5, 1.5 and 15 L min⁻¹, respectively, and the

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