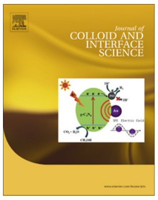
Journal of Colloid and Interface Science 468 (2016) 334–346

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis



Magnetic magnetite (Fe_3O_4) nanoparticle synthesis and applications for lead (Pb^{2+}) and chromium (Cr^{6+}) removal from water

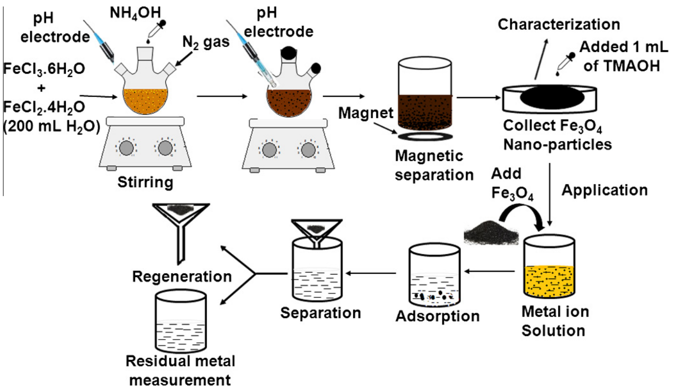
Shalini Rajput [a], Charles U. Pittman Jr. [b], Dinesh Mohan [a,*]

[a] School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110067, India
[b] Department of Chemistry, Mississippi State University, Mississippi State, MS 39762, USA

HIGHLIGHTS

- Fe_3O_4 was synthesized by coprecipitation using TMAOH and thoroughly characterized.
- Magnetite nanoparticles successfully remediated aqueous Cr^{6+} and Pb^{2+}.
- Magnetite Langmuir adsorption capacities of ~35 (Cr^{6+}) and ~53 (Pb^{2+}) mg/g were obtained.
- Likely Cr^{6+} and Pb^{2+} sorption mechanisms versus pH were described.
- Kinetics were pseudo-second order, rate dependent on the number of surface sites.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 September 2015
Revised 1 December 2015
Accepted 2 December 2015
Available online 14 December 2015

Keywords:
Adsorption
Co-precipitation method
Removal, magnetite nanoparticles
Wastewater treatment, lead and chromium removal

ABSTRACT

Magnetic magnetite (Fe_3O_4) nanoparticles synthesized by chemical co-precipitation were characterized using XRD, TEM, SEM-EDX, FT-IR, ED-XRF, PPMS, point of zero charge (pH_{pzc}) and surface area measurements. As-prepared Fe_3O_4 nanoparticles were successful for aqueous Cr^{6+} and Pb^{2+} removal. Batch adsorption experiments systematically investigated the influence of pH, temperature, contact time and adsorbate/adsorbent concentration on Cr^{6+} and Pb^{2+} adsorption. Maximum Cr^{6+} and Pb^{2+} removal occurred at pH 2.0 and 5.0, respectively. Sorption data fit pseudo-second order kinetics, indicating a chemical adsorption. The Freundlich, Langmuir, Redlich–Peterson, Toth, Radke and Sips adsorption isotherm models were applied to describe equilibrium data. The Sips and Langmuir models best described Cr^{6+} and Pb^{2+} adsorption on magnetite nanoparticles, respectively. The maximum Langmuir adsorption capacities were 34.87 (Cr^{6+}) and 53.11 (Pb^{2+}) mg/g at 45 °C, respectively. Fe_3O_4 nanoparticles are promising potential adsorbents and exhibited remarkable reusability for metal ions removal in water and wastewater treatment.

1. Introduction

Heavy metal ions in aquatic environments are a serious problem for living organisms and public health [1–3]. Heavy metals are non-biodegradable and tend to bioaccumulate [4]. Cr^{6+} and Pb^{2+} are common industrial pollutants posing serious ecosystem threats [5]. Strong Cr^{6+} oxidizing properties cause toxic effects on biological systems [6]. Chromium is released to the ecosystem from leather tanning, metal processing, electroplating, pigment synthesis, dying, wood protection, electrical and electronic equipment, etc. [7,8].

---

* Corresponding author.
E-mail address: dm_1967@hotmail.com (D. Mohan).

http://dx.doi.org/10.1016/j.jcis.2015.12.008
0021-9797/© 2015 Elsevier Inc. All rights reserved.

Severe lead poisoning causes sterility, abortions, neonatal mortality, and most serious detrimental effects to the central nervous system [5,9]. Fossil fuel combustion, sulfide ore smelting, mining, agriculture, battery manufacturing, paper, pulp industries are major lead release sources [4,10,11]. The US Environmental Protection Agency (EPA) recommended maximum drinking water levels of chromium (0.1 mg/L) and lead (0.015 mg/L) [8,12–14]. The World Health Organization (WHO) and the Bureau of Indian Standards (BIS) have set the maximum permissible drinking water limits of 0.05 mg/L and 0.01 mg/L for chromium and lead, respectively [13–16].

Chemical precipitation [17], ion exchange [18], adsorption [8,13,19], ultrafiltration [20], constructed wetland [21], membrane separation [22] have been used for metal removal. Advantages and disadvantages of chromium removal techniques were reviewed [8,17,23,24]. Adsorption is often superior since it is cost effective, easy handling, flexible and selective. The concentrated recovered adsorbate can be stripped and recycled. Many adsorbents have been used for Cr^{6+} and Pb^{2+} removal [13,25–27], but keen interest exists in improved and advanced low cost adsorbents with high surface areas and sorption capacities [28].

Nanosorbents are sought because small particle sizes and high surface areas enhance chemical reactivity and adsorbate/adsorbent interactions [29,30] and these remove contaminants over a wide concentration range (~1–1000 ppm) rapidly [1]. Natural and synthetic iron oxide was investigated to remediate heavy metals from water [31,32]. We considered nano sized Fe_3O_4 particles to remove heavy metals due to their magnetic properties, high surface area, chemical stability, easy synthesis and low toxicity [29,33]. Magnetite (Fe_3O_4) is an important member of spinel-type ferrite family, with a cubic inverse spinal structure of space group Fd3m and an edge length of 0.839 nm [34–36].

Magnetite nanoparticles have been synthesized and used for remediation previously [37–43]. Co-precipitation of aqueous Fe^{3+} and Fe^{2+} is an efficient route [44,45]. Magnetite nanoparticles have been synthesized using 3-mercaptopropionic acid [46], reactive blue-19 [47], hydroxyapatite/magnetite composite [48], polyacrylic acid (PAA) [49], chitosan [50,51], and carboxymethyl-β-cyclodextrin (CM-β-CD) polymer modified Fe_3O_4 nanoparticles (CDpoly-MNPs) [52] in order to improve the surface area and to prevent the aggregation of magnetite.

In the present study, tetramethylammonium hydroxide (TMAOH), a well known phase transfer agent with surfactant properties, was used during magnetite formation by co-precipitation to prevent nanoparticle agglomeration based on its success in that role reported by others [53–57]. The nanoparticle surface and chemical properties were characterized and they were demonstrated as promising adsorbents for aqueous Cr^{6+} and Pb^{2+} removal. Solution pH, contact time, adsorbent dose and initial metal concentration were investigated and kinetics, equilibrium adsorption parameters and reusability were evaluated. The adsorption behavior and mechanism were investigated. Adsorption capacities for Cr^{6+} and Pb^{2+} were compared with previously reported adsorbents.

2. Experimental details

2.1. Reagents and equipment

All chemicals used were either AR or GR-grade. $FeCl_2{\cdot}4H_2O$ (99.0%), $Pb(NO_3)_2$, $K_2Cr_2O_7$ were purchased from Merck, India. $FeCl_3{\cdot}6H_2O$ (97.0%) was obtained from CDH. Tetraethylammonium hydroxide (25% solution) was purchased from Qualigens, India. Stock solutions of chromium and lead (1000 ppm) were prepared in double distilled water. Solution pHs were measured using a multiparameter ion meter (model thermo Orion 5 star). HNO_3 (0.1 N) and NaOH (0.1 N) were used to adjust solution pHs. Water bath shakers (models RC51000 and MSW-275) mechanically agitated adsorbent–adsorbate mixtures at a constant temperature. Initial and equilibrium concentrations of chromium and lead were determined using atomic absorption spectrometer (model Aanalyst 400, Perkin Elmer) at 357.8 and 283.3 nm wavelengths, respectively.

2.2. Preparation of magnetite nanoparticles

Magnetite nanoparticles were prepared by a modified co-precipitation method reported earlier [58]. In brief, $FeCl_3{\cdot}6H_2O$ (10.4 g) and $FeCl_2{\cdot}4H_2O$ (4.0 g) were dissolved in a 2:1 mol ratio in 200 mL of degassed distilled water while stirring under nitrogen. Ammonium hydroxide was added drop-wise to raise the pH ~ 8.0. At this pH the solution turned from brown to black. Subsequently, black particles were magnetically separated, quickly washed three times with distilled water, further treated with 1 mL of tetramethylammonium hydroxide and dried in air. Nanoparticles were stored in airtight containers.

2.3. Physicochemical characterizations

Powder X-ray diffraction (XRD) (model PANalytical X'pert PRO) with Cu Kα ($\lambda = 1.5406$ Å) radiation at 45 kV and 40 mA probed the nanoparticle structure and phases. The sample was scanned for $2\theta = 20$–$90°$ with a step size of 0.05° and a scan rate of 3 s per step.

Functional group analyses using FTIR spectroscopy (model Varion 7000 FTIR) used pellets prepared with spectrometric grade KBr under a 10 ton hydraulic press (model Spectrachrom Instruments, CAP-15T). Spectra were recorded in transmittance mode from 4000 to 400 cm^{-1} using 8 scans at 4 cm^{-1} resolution.

Magnetic magnetite (Fe_3O_4) nanoparticles morphology was examined by scanning electron microscopy (SEM) (model Zeiss, Evo 40) at a 20,000 V accelerating voltage and working distance: 10,000–10,500 μm. The samples were coated with a thin gold layer mounted on a aluminium stab using a double stick carbon tape. Elemental compositions were determined by SEM/EDX analyses. X-ray EDX analyses were carried out on sintered pellets using the Zeiss, EVO 40 SEM employing a BRUKER EDX system. The samples were placed onto carbon tapes supported aluminum stubs. Sample images were then recorded at different magnifications. EDX and elemental mapping analysis was carried out at randomly selected areas of sample to find out the atomic distribution on the adsorbent surface. Software Quantax 200 Espirit 1.8 was used for elemental mapping analysis.

TEM analysis was carried out at 200 keV (model JEOL 2100F) and the sample was dispersed in ethanol and ultrasonicated for 10 min. A drop was placed on copper grid and excess ethanol was blotted off by filter paper.

The magnetite nanoparticle composition was analyzed by inductively coupled plasma emission spectrometry (ICP-AES) (model Perkin–Elmer Optima 5300) and reported in weight percent on an ash basis. Samples were incinerated to remove all volatiles and elements were reported as oxides.

The CHNS analysis was obtained on an elemental analyzer (model LECO CHNS-932). Ash content was measured by incineration (~1 g) at 650 °C in air for 12 h.

The point of zero charge (pH_{pzc}) was measured using 0.01 M NaCl adjusted to pH 2, 4, 6, 8, and 10 by either a 0.1 N HCl or a 0.1 N NaOH aqueous solution. Samples (0.01 g) were contacted with 5 mL of each solution followed by agitation for 48 h. The supernatant was then decanted and its pH measured. The pH_{pzc} value was determined from a plot of initial pH versus pH of the supernatant.