Journal of the Taiwan Institute of Chemical Engineers 000 (2018) 1–10

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

High-stability polyamine/amide-functionalized magnetic nanoparticles for enhanced extraction of uranium from aqueous solutions

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ARTICLE INFO

Article history:
Received 26 November 2017
Revised 24 February 2018
Accepted 1 March 2018
Available online xxx

Keywords:
Magnetic nanoparticles
Carbon coating
Polyethyleneimine
Adsorption
Uranium

ABSTRACT

In this work, carbon-coated magnetic iron oxide nanoparticles (CCM) functionalized with polyethyleneimine/amide (PEIA) were successfully prepared. The prepared nanocomposite (CCMNPs-PEIA) was characterized by XRD, TEM, FT–IR, TGA and VSM techniques. The stability of CCM was tested in both acidic and basic media and they showed a high stability with good magnetic properties. CCMNPs-PEIA were used for separation of U (VI) from aqueous solutions. Several process parameters were tested to investigate the removal efficiency, adsorption capacity and reusability of the CCMNPs-PEIA including, pH, initial concentration of uranium, and desorption and activation media. The CCMNPs-PEIA nanocomposite was found to have excellent affinity toward U over a wide pH range. Surface oxidation of CCM was found to be of major effect of the adsorption capacity of CCMNPs-PEIA due it carboxylation which enhanced PEIA attachment to the carbon surface. The experimental uptake of the prepared nanocomposite was found to be 127.5 mg (U/g (nanocomposite), while the one calculated according to Langmuir model was found to be 123.45 mg/g with a correlation coefficient (R^2) of 0.991. The kinetics analysis of the adsorption process suggests that the kinetics can be described well by the pseudo-second order model suggesting that the rate limiting step is chemisorption.

1. Introduction

Adsorption techniques have been found to be superior for water treatment due to their simplicity of design, selectivity, low cost, flexibility, ease of operation, efficient technology, and wider applicability for the removal various types of pollutants.

Natural adsorbents, under ambient conditions, exhibit either low adsorption capacity or weak affinity for sorbate. The use of chemical modification to produce nanocomposite material increase their adsorption capacity and selectivity toward heavy metal ions, which have functional groups such as amine, amide, carbonyl, amidoxime, chitosan etc.

Adsorbents with nanoscale have better efficiency in removing contaminants from wastewater, due to their high surface to volume ratio and better dispersion in aqueous solutions. Further research is needed to improve firstly stability, capacity, selectivity, and kinetics rate, secondly, the adsorbent reusability for multicycle use, and finally, the ease of separating NP from water after desorption process.

Numerous sources release U(VI) into the environment such as nuclear power industries, fertilizers mine tailings, natural deposits and other processing of uranium application [1]. It is also the most predominant fuel in nuclear reactors and can pose serious risk to the environment during mining operations and treatment of spent nuclear fuel [2]. On the other hand, due the expected shortage of its resources, great attention was paid to uranium recovery from secondary resources, including sea water, ground water, wastewater and other sources. Therefore, significant research work is being carried out to develop highly effective extraction methods for uranium from the point view of environmental protection, resource conservation and energy security [3]. Several approaches are being considered for uranium removal from water streams including membrane separation [4], ion exchange [5], solvent extraction and adsorption techniques [6].

Magnetic nanoparticles (MNPs) have received great attention of researchers in recent years due to their magnetic properties and the possibility to manipulate selective functionalization on their surface [7]. Therefore, they have found applications including, but not limited to, medicine [8] and biomedical engineering, information storage, biosensing applications, and water treatment [9], green energy storage [10].

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https://doi.org/10.1016/j.jtice.2018.03.005
1876-1070/

Among MNPs, magnetite is considered as one of the most attractive materials in terms of low toxicity, acceptable chemical stability, easiness of preparation and possibility for production scale up. In recent years, MNPs have been extensively used in many environmental applications including water purification and wastewater treatment [3,11-14]. To increase the chemical stability of MNPs against aggressive acidic or alkaline environment, surface coating with a nano layer of inert materials were used such as carbon [15] and silica coating [16]. With such coating, the chemical stability increases, with still good magnetic properties suitable for magnetic separation.

In order for the surface-coated iron oxide nanoparticles to function as an effective adsorbent material for heavy metals, various functional materials were attached to its surface. Among these are amidoxime [3,16], chitosan [17], thiols [18], cellulose [9] polydopamine [19], phenanthrolineamide [20], and polyethyleneimine (PEI) [21]. The MNPs-based ion exchangers have a great potential in the ion-exchange processes, and it can afford many benefits over other existing ion exchange resins. They not only have high surface area, but they also can be well-dispersed, collected, manipulated and agitated by mean of an external magnetic field, making existing operations faster, easier, efficient and more sustainable.

Despite immense developments in the MNPs synthesis approaches, their application in the hydrometallurgical extraction of metals remains limited due to the difficulty of synthesizing coated MNPs with reasonable stability in corrosive environments. Most of other previously reported coated MNPs were studied at limited conditions, and most importantly, their reusability was not reported.

In the current work, we have synthesized double-coated MNPs; first coated with carbon which primarily functions as a protective layer and provides carboxyl group for further functionalization. The second layer was a branched PEI polymer network which provides further protection and, when combined with carboxyl group, results in amide functional group that is believed to be suitable for uranyl ions extraction at a wide pH range. The resulting MNPs showed a very high stability when tested in acidic and alkaline media, and interestingly exhibited a cationic/anionic exchange characteristics with unpreceded extraction efficiency and capacity toward uranyl ions.

2. Experimental work

2.1. Materials

Ferric and ferrous chlorides (97% purity) used for magnetic nanoparticles (MNPs) were obtained from Sigma Aldrich. Branched (25000 mw) polyethyleneimine (PEI), N,N-dimethylformamide (DMF) used for MNPs functionalization were also obtained from Sigma Aldrich,

Uranium standard solution of a concentration of 1000 ppm, prepared in 2–5% nitric acid, was obtained from Accustandard.

2.2. Synthesis of magnetic nanoparticles

MNPs were synthesized using the co-precipitation method [22], whereby a mixture containing both ferric and ferrous chlorides (2:1 mol ratio), prepared in deoxygenated deionized (DI) water, was added dropwise to a 0.15 M NaOH solution under vigorous agitation and nitrogen purging. The pH was maintained at about 11. The magnetic nanoparticles were then separated using a strong magnet and washed several times with DI water and ethanol and then dried at 60 °C in a vacuum oven for 6 h.

2.3. Carbon coating of MNPs

Carbon-coated iron oxide nanoparticles (CCM) were synthesized by hydrothermal synthetic process [23]. Initially, 0.5 g of MNPs were dispersed in 20 mL of DI water, and then 2.0 g glucose, 0.5 g polyethylene glycol (PEG,: 1400–1500 mw) were added to the solution. The mixture was then sonicated for 45 min. After that, the mixture was transferred to a teflon autoclave and placed inside an oven at 180 °C for 12 h. The product was then separated from the solution using a strong magnet, washed several times with DI water and ethanol and dried in a vacuum oven at 60 °C for 6 h.

2.4. Preparation of PEI carbon coated MNPs

Firstly, CCM were treated with (1 M) nitric acid for 24 h to produce carboxyl group (COOH) on their surface. The particles were then separated from the acid solution by strong magnet followed by thorough washing using DI water and drying in a vacuum oven for 24 h at 60 °C. About 1.5 g of acid treated CCM (CCMAT) was dispersed in 100 mL of DMF using an ultrasonic bath for 1 h [24,25]. Concurrently 3 g of PEI was completely dissolved in 100 mL DMF. After dispersion, the PEI solution was poured onto the CCM/DMF slurry, and sonicated for 1 h, then vigorously stirred for 48 h. After synthesis, the resulting material was separated by magnetic field, and then dried in a vacuum oven at 60 °C to evaporate all DMF. The resulting product was then washed with DI water twice to remove any unreacted PEI and byproduct. Ultimately, the CCMAT functionalized by PEI (CCMNPs-PEIA) were dried at 60 °C in an oven.

2.5. Characterization of the produced nanocomposite

Samples were characterized using XRD analysis technique employing a computer controlled Hiltonbrooks® XRD system with a Philips® PW 1050 diffractometer with Cu-$K_{\alpha 1}$ radiation ($\lambda = 1.54056$ Å). The analysis was conducted with a step size of 0.02° over a 5-80° 2θ range. Fourier Transform Infrared (FT–IR) analysis was also carried out using Bruker FTIR, model Tensor II. The magnetic properties of MNPs were performed using a vibrating sample magnetometer (MicroMag 3900, Princeton Measurements Corporation). The magnetic measurement was performed at room temperature in an applied field up to 10 kOe. The thermogravimetric analysis (Netzsch TG 209 F1 instrument) was used to study the thermal decomposition of the nano composites.

Zeta Potential of CCMNPs-PEIA nanocomposite was measured employing Malvern Zetasizer Nano (ZS90) with an auto titration kit over a pH range from 2 to 10. The particles were dispersed in type I DI water with a concentration of about 50 mg/L and the pH was adjusted using 0.1 M NaOH and 0.1 M HCl solutions. Uranium concentration was measured using iCAP Q Thermo Scientific ICP–MS; the calibration solution contained concentrations in the range from 1 to 1000 ppb. Bismuth (Bi) was used as an internal standard during ICP–MS analysis to correct for any possible instrument drift. Additionally, a quality control sample containing 50 ppb U was also analyzed every 30 min to ensure the quality of the analysis.

2.6. Adsorption tests

The batch adsorption tests of U(VI) on the CCMNPs-PEIA nanocomposite was carried out in a 100 mL conical flask; 50 mL U solution of known concentration was prepared at a specified pH (2–9) and was added to a 0.05 g of the CCMNPs-PEIA. The initial concentration of U was varied from 50 to 200 ppm. The temperature of the adsorption test was maintained using a thermostated water bath at 20 °C. During adsorption, periodic samples aliquots (0.5 mL) were withdrawn from the solution over 2 h contact time;

Please cite this article as: M. Al-Harahsheh et al., High-stability polyamine/amide-functionalized magnetic nanoparticles for enhanced extraction of uranium from aqueous solutions, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.03.005