Chemical Engineering Journal 223 (2013) 318–327

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Design of novel nano-sorbents based on nano-magnetic iron oxide–bound-nano-silicon oxide–immobilized-triethylenetetramine for implementation in water treatment of heavy metals

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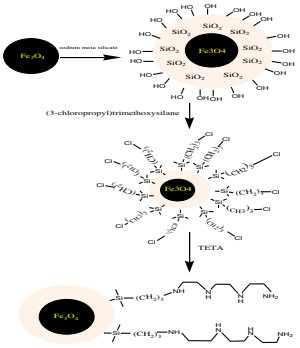
HIGHLIGHTS

- A novel nano-sorbent was designed.
- Magnetic nano-iron oxide–nano-silicon oxide-triethylenetetramine sorbent.
- Comparison of the metal sorption properties was reported.
- Evaluation of the selectivity for some heavy metals.
- Implementation in water treatment.

GRAPHICAL ABSTRACT

A novel nano-sorbent (Nano-Fe_3O_4–SiO_2–TETA) was designed for implementation in water treatment and this sorbent was produced by the direct surface impregnation of magnetic nano-iron oxide with nano-silicon oxide followed by covalent surface binding and immobilization of triethylenetetramine.



ARTICLE INFO

Article history:
Received 9 January 2013
Received in revised form 20 February 2013
Accepted 22 February 2013
Available online 4 March 2013

Keywords:
Nano-Fe_3O_4
Nano-SiO_2
Functionalization
Sorption
Heavy metals

ABSTRACT

Novel nano-sorbents were synthesized from the direct surface impregnation of magnetic nano-iron oxide (Nano-Fe_3O_4) with nano-silicon oxide (Nano-SiO_2) for the formation of (Nano-Fe_3O_4–SiO_2) sorbent. The product material was further functionalized with target nitrogen donor atoms via covalent surface binding and immobilization of triethylenetetramine (TETA) for the formation of (Nano-Fe_3O_4–SiO_2–TETA) sorbent. Functionalized magnetic nano-sorbents were collected by facile separation under the influence of an external magnetic field. The magnetic nano-sorbents were identified by using FT-IR, SEM technique and TGA. The average particle size was found in the range of 14–40 nm based on the SEM analysis. All synthesized nano-sorbents were examined to evaluate their selectivity and efficiency in removal of some heavy metal ions such as Cu(II) and Pb(II) from water samples by the batch equilibrium and micro-column techniques. (Nano-Fe_3O_4–SiO_2–TETA) sorbent was identified by a high Cu(II) sorption capacity (480 μmol g^{-1}) in pH 7.0, while (Nano-Fe_3O_4) and (Nano-Fe_3O_4–SiO_2) sorbents were characterized by high affinity to Pb(II). The contributions of various controlling factors such as solution pH, contact time and sorbent dosage on the extraction and sorption processes of metal ions were also studied and optimized.

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http://dx.doi.org/10.1016/j.cej.2013.02.097

1. Introduction

Recent advances have been devoted to the progressively growing field of nano-technology and nano-science in the last two decades. Design of novel nano-materials is also a subject of research interest in recent years. Magnetic nano-materials are representing an important class of compounds that are known by their unusual characteristics as well as multidiscipline applications [1–3]. The high interests in magnetic nano-materials are mainly related to their direct and simple separation from their matrices by the action of an external magnetic field. Magnetic nano-materials are also considered as potential adsorbents due to their high surface area and excellent chemical selectivity [4–6]. In addition, the particle shape, core size and surface functional groups are also important controlling factors that generally affect their magnetic properties. However, free magnetic nano-materials such as nano-magnetic iron oxide particles are characterized by some limitations such as hydrophobic surface properties which limit their dispersion into aqueous solutions and matrices. This behavior will also affect the chemical and physical reactivity toward interaction with other contacted species [7]. In order to overcome such limitations along with the maintenance of the magnetic properties of such nano-particles, various selected approached are generally used to modify the surface via loading of other target chemicals or biological materials [1–3].

The literature survey refers to a good number of newly developed chemically and biologically modified magnetic nano-materials with the direct implementation in heavy metal removal as well as organic compounds extraction. Adsorption of arsenate on iron(III) oxide coated ethylenediamine functionalized multi-wall carbon nano-tubes was recently reported [8]. Magnetic binary oxide particles (MBOPs) synthesized by using chitosan template was investigated and reported for the uptake of arsenic (III) [9]. A newly synthesized effective adsorbent for cadmium removal from aqueous solution by coating a shellac layer, a natural biodegradable and renewable resin with abundant hydroxyl and carboxylic groups, on the surface of iron oxide magnetic nano-particles was recently reported [10]. Removal of cobalt from aqueous solution was studied and reported by magnetic multi-walled carbon nano-tube/iron oxide composites [11]. Copper (II) removal by pectin–iron oxide magnetic nano-composite adsorbent was also studied and evaluated [12]. The effective removal of mercury (II) ions from contaminated surface waters by modified magnetic iron oxide nano-particles (M-MIONPs) with 2-mercaptobenzothiazole as an efficient adsorbent was recently reported [13]. The potential adsorption of the Se oxoanions, selenite and selenate, from aqueous solutions onto nano-synthesized $MnFe_2O_4$ was investigated using batch techniques and DRC-ICP-MS spectroscopy [14]. Fabrication of β-cyclodextrin conjugated magnetic HNT/iron oxide composite for high-efficient decontamination of U(VI) was studied [15]. On the other hand, various modified iron oxide magnetic nano-sorbents were also reported for removal of some dyes [16,17] and other organic compounds [18–22].

The magnetic sorbents are generally unstable in strong acidic solutions and undergoes leaching. It strongly limits the reusability and reduces the lifetime of such materials. Further limitations are also based on the large ratio of surface area to volume. This behavior leads to aggregation of particles and thus a minimization in their surface energy is produced due to strong magnetic attractions between particles [23]. The encapsulation of magnetic iron oxide nano-materials with silica shells is a promising technique to overcome the limitation encountered by these sorbents.

This approach prevents the agglomeration of particles as well as providing an environment for the transferring of hydrophobic iron oxide nano-particles into a hydrophilic system [24]. Surface modification via immobilization and derivatization with silica particles can afford additional applications via attached surface functionalized groups [25,26].

The aim of this paper was directed toward surface modification of magnetic nano-particles with nano-silicon oxide for the formation of new combined nano-magnetic sorbent. Silicon oxide was chosen because of its high stability under acidic conditions and inertness to redox reactions. Therefore, it is considered as an ideal shell to protect the inner magnetic core [27,28]. The surface of modified nano-sorbent was also used as a substrate for further surface chemical immobilization of nitrogen donor functional groups incorporated into triethylenetetramine. The product is a novel nano-sorbent that combines the magnetic characters due to the existence of magnetic nano-particles with the high surface area of nano-silicon oxide as well as surface incorporated selectivity based on the loaded nitrogen donor atoms. The resulting nano-sorbents were characterized by scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), and FT-IR infrared spectroscopy. The ultimate objective of this study was to compare and explore the potential applications of this novel sorbent in water treatment of heavy metals.

2. Experimental

2.1. Materials

Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) with 98% purity and Ferrous chloride ($FeCl_2$) with 98% purity were purchased from Oxford, India. Sodium metasilicate was purchased from Alpha, India. Sodium hydroxide (NaOH), sodium acetate anhydrous (CH_3COONa), 3-chloropropyltrimethoxysilane with 97% purity and triethylenetetramine was purchased from BDH, UK. Lead nitrate was purchased from Oxford, India and copper(II) acetate was obtained from Lab Chemical Trading.

2.2. Synthesis

2.2.1. Synthesis of Nano-Fe_3O_4

The magnetic nano-particles were prepared by using the coprecipitation method [27,29]. 0.04 mol of $FeCl_3.6H_2O$ and 0.02 mol of $FeCl_2$ were dissolved in 50 mL of 0.5 M HCl solution. This mixture was added to 500 mL solution of 1.5 mol L^{-1} of sodium hydroxide drop wise at 80 °C under vigorous stirring for 30 min. The obtained Nano-Fe_3O_4 particles were separated by a magnetic field and repeatedly washed with distilled water followed by drying at 50 °C until complete dryness.

2.2.2. Synthesis of Nano-Fe_3O_4–SiO_2

To prepare Nano-Fe_3O_4-coated-silicon oxide [27], 2.0 g of Nano-Fe_3O_4 was suspended in 400.0 mL distilled water at 80 °C. 40.0 mL of 1.0 mol L^{-1} sodium silicate solution was added drop wise to this suspension under vigorous stirring for 2.0 h. The pH of this mixture was adjusted at 6.0 and the reaction mixture was further stirred for 3 h. The Nano-Fe_3O_4–SiO_2 was washed with distilled water and dried at 50 °C.

2.2.3. Synthesis of Nano-Fe_3O_4–SiO_2–Cl

Nano-Fe_3O_4–SiO_2–functionalized-Cl was synthesized via surface reaction of Nano-Fe_3O_4–SiO_2 by using 3-chloropropyltrimethoxysilane as the silylation agent. 2.0 g of Nano-Fe_3O_4–SiO_2 and 50.0 mL of toluene were mixed into a 250-mL round flask. 4.0 mL of 3-chloropropyltrimethoxysilane was then added and the mixture was refluxed at 110 °C with continuous stirring for 6 h. The resulting functionalized Nano-Fe_3O_4–SiO_2–Cl was collected and