Hydrometallurgy 161 (2016) 117–126

Contents lists available at ScienceDirect

Hydrometallurgy

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

A new nanostructured material amino functionalized mesoporous silica synthesized via co-condensation method for Pb(II) and Ni(II) ion sorption from aqueous solution

Masoomeh Ghorbani [a], Seyyed Mostafa Nowee [a], Navid Ramezanian [b], Foad Raji [a],*

[a] *Department of Chemical Engineering, Ferdowsi University of Mashhad, Mashhad, Iran*
[b] *Department of Chemistry, Ferdowsi University of Mashhad, Mashhad, Iran*

ARTICLE INFO

Article history:
Received 4 October 2015
Received in revised form 2 February 2016
Accepted 4 February 2016
Available online 17 February 2016

Keywords:
Amino-functionalized MCM-41
Pb(II)
Ni(II)
Sorption isotherm
Kinetic parameters

ABSTRACT

In this investigation, MCM-41/*N*-(3-trimethoxysilyl)-propyl)diethylenetriamine (MCM-41/TMSPDETA) adsorbent was prepared via co-condensation method and characterized by FTIR, BET, XRD, TEM, SEM and DLS analytical techniques. Experiments were carried out to investigate the influence of different sorption parameters, such as pH, adsorbent dosage, contact time, initial concentration of heavy metal ions and solution temperature in a batch system. Optimum conditions of sorption experiments were obtained at 20 °C with the pH of 6.0 and contact time of 60 min for Pb(II) and 120 min for Ni(II). The pseudo-first-order, the pseudo-second-order and intraparticle diffusion models have been used to analyze the sorption kinetic results. The sorption process was found to be well described by the pseudo-second-order rate model. The Langmuir and Freundlich isotherms have been used to describe the equilibrium sorption; the adsorption data obeyed the Langmuir isotherm. The maximum capacity of the nanosorbent was 77.52 and 58.47 mg g^{-1} for Pb (II) and Ni (II) ions, respectively. In order to verify the nature of sorption processes as physical or chemical, the equilibrium data were also fitted to the Dubinin–Radushkevitch (D–R) model. Based on D–R isotherm results, the values of mean free energy were 13.36 and 9.13 kJ mol^{-1} for Pb(II) and Ni(II) sorption, respectively. These values of E (kJ mol^{-1}) indicating chemical sorption for both metal ions. The selectivity order of lead and nickel sorption onto the adsorbent was Pb(II) > Ni(II).

1. Introduction

A wide range of heavy metal contamination that can become a risk to human health are produced by industries such as battery manufacturing, electroplating, mining, tanneries, metal processing, petroleum refining, textile, pesticides, printing, paint and pigment manufacturing and photography (Gupta and Ali, 2004). Even at very low concentrations, heavy metals like lead and nickel, are toxic because of their persistent nature. Chronic exposure to Pb(II) and Ni(II) can lead to bone degeneration, liver and lung damage; therefore, they must be removed before discharge (Sheng et al., 2004). coagulation (Goncharuk et al., 2001), chemical precipitation (Mellah et al., 2007), ion exchange (Shoushtari et al., 2006), sorption process (Abbasizadeh et al., 2013; de Pablo et al., 2011) and etc. Among these technologies, sorption is considered to be very suitable due to simplicity, high efficiency and low cost (Babel and Kurniawan, 2003). In recent years, a number of investigations have been reported to test the higher efficiency and low cost effective adsorbents for heavy metal removal from aqueous solutions (Engates and Shipley, 2011). For this purpose, mesoporous silica materials have been lately proposed as suitable adsorbents for heavy metals because of their unique surface area, well-defined pore shape and pore size (Beck et al., 1992; Kresge et al., 1992). Since their initial synthesis in 1992, M41S family of mesoporous silica materials has been used in many fields. M41S family such as MCM-41 has hexagonal regular arrays of uniform-sized pore, large surface areas, mild acidic property and thermal stability (Kumar et al., 2002; Morin et al., 1997). These properties of MCM-41, propose opportunities of application in chemical separation (Thomas, 1994), composite materials (Huber et al., 1994) and sorption process (Rathousky et al., 1994).

Pure Si–MCM-41 cannot be directly applied to remove toxic heavy metals from wastewater because it does not have enough capability for sorption process (Walcarius and Delacôte, 2003). Therefore, surface of MCM-41 must be functionalized by organic groups to change and achieve specific characteristics (Vinu et al., 2005). In general, functionalization of these materials can be carried out by two independent methods (Stein et al., 2000). The first method is carried out by grafting the surface of the preformed silica by means of silanol group with an organoalkoxysilane compound supporting the active functional group. The second method consists of simultaneous co-condensation within the synthesis medium of the alkoxysilane precursor of the silica mesostructure and a selected organoalkoxysilane to obtain the

---

* Corresponding author.
E-mail address: Foad.raji@gmail.com (F. Raji).

http://dx.doi.org/10.1016/j.hydromet.2016.02.002
0304-386X/© 2016 Elsevier B.V. All rights reserved.

functionalized material after one step. Amine groups can improve the sorption of heavy metals if bonded to adsorbents (Feng et al., 1997). For instance, Lam et al. (2006) investigated the selectivity of gold for an amine functionalized adsorbent from MCM-41 family. Algarra et al. (2005) used functionalized MCM-41 with aminopropyl groups for the removal of copper and nickel from electroplating waste. Yoshitake et al. (2003) evaluated the potential of the amino functionalized MCM-41 for arsenate removal. Little attention has been paid to the sorption of Pb(II) and Ni(II) ions onto the functionalized mesoporous silica. According to our knowledge, sorption of Pb(II) and Ni(II) ions by MCM-41/TMSPDETA has not yet reported. In this study, synthesis and surface modification of MCM-41 mesoporous silica with amino group via co-condensation method were investigated. The adsorbent was prepared under basic conditions by using methanol as solvent, hexadecyltrimethylammoniumbromide as template and fumed silica as the silica source by means of sol–gel method. Specific surface area of MCM-41/TMSPDETA nano adsorbent was measured by the Brunauer–Emmett–Teller (BET). The structure of the prepared nano adsorbents was characterized using Fourier Transform Infrared (FTIR), X-ray diffraction (XRD), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM) and Dynamic Light Scattering (DLS) analytical techniques. The goal of the present paper was the sorption of Pb (II) and Ni (II) on MCM-41/TMSPDETA nanosorbent. The influences of various parameters including pH, contact time, initial concentration, temperature and adsorbent dosage on the sorption process were investigated in a batch system. The pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models were tested to interpret the experimental kinetic data. Three well-known sorption isotherms namely Langmuir, Freundlich and Dubinin–Radushkevich (D–R) are used to analyze the equilibrium data of Pb (II) and Ni (II) ions.

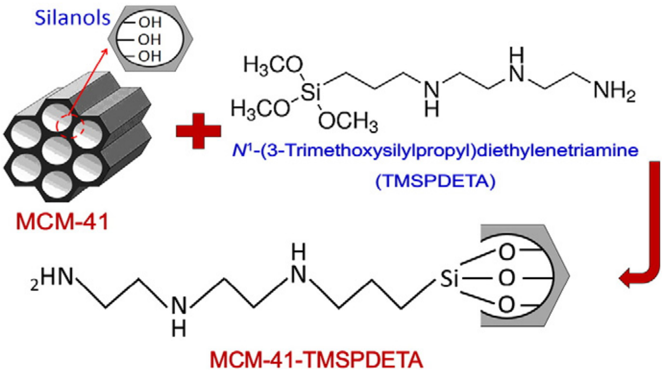
2. Experimental

2.1. Materials

Materials deployed in this study were analytical grade from either Aldrich or Merck Companies and were used without further purification. Hexadecyltrimethylammoniumbromide (CTAB) was used as structure directing agent; Tetraethoxysilane (TEOS) and *N*-(3-trimethoxysilyl)-propyl) diethylenetriamine (TMSPDETA) were used as silica and propylamine precursors, respectively. $Pb(NO_3)_2$ and $Ni(NO_3)_2$ of synthesis grade were the sources of Pb(II) and Ni(II) heavy metal ions during the sorption experiments. The aqueous solutions were prepared by dissolving weighed amounts of lead and nickel nitrates in deionized water. It should be mentioned that deionized water was utilized throughout this experiment.

2.2. Amino-functionalized MCM-41 via direct co-condensation method

The synthesis of amino-functionalized MCM-41 via the co-condensation method was conducted as follows. CTAB (500 mg) and NaOH (1.75 ml, 2 M) were dissolved in deionized water (240 ml) while heating and stirring for 15 min. Afterwards the Si sources (2.5 ml TEOS) were added to the above mixture drop wise and stirred for 15 min. Then 2 mmol *N*-(3-trimethoxysilyl)-propyl) diethylenetriamine (TMSPDETA) was added to the mixture and the solution was stirred 300 rpm for 4 h at 80 °C, and the precipitated white particles were filtered, washed with methanol and dried at 25 °C. The surfactant in the as-synthesized sample was removed by a solvent extraction method. Where 1.0 g of the as-synthesized sample was added to the HCl/MtOH solution (100 ml of methanol containing 5 ml HCl aq. Concentration ca. 35 wt.%) under the magnetic stirring at 25 °C for 24 h. The obtained amino-functionalized MCM-41 with *N*-(3-trimethoxysilyl)-propyl)diethylenetriamine (TMSPDETA) silanes (MCM-41/TMSPDETA) was selected for sorption experiments as the adsorbent. The structure of MCM-41/TMSPDETA is shown in Scheme 1.



Scheme 1. Structure of MCM-41/TMSPDETA.

2.3. Characterization

Fourier transform infrared (FT-IR) spectra were recorded using a spectrometer (Shimadzo, FTIR4300 spectrophotometer) in the range of 400–4000 cm^{-1} by spectroscopic quality KBr technique (sample/KBr $=$ 1/100). Surface area of adsorbents was determined by the Brunauer–Emmett–Teller (BET) method, total pore size and pore volume distribution were measured by the Brrett–Joyner–Halenda (BJH) method on a Micrometrics ASAP 2010 at 77 K. X-ray diffraction (XRD) patterns were recorded by Low-angle X-Ray diffraction in the 2θ range of 1.5–10° at 0.02° steps. Patterns of the samples were obtained on a powder diffractometer (X'pert, Philips, Holland) with Cu Kα ray ($\lambda =$ 1.54056 A°) as the incident radiation source. Scanning electron microscopy (SEM) was recorded using a Hitachi S-4160 scanning electron microscope. Transmission electron microscopy (TEM) was carried out on a Leo 912 AB electron microscope working at 200 kV. Dynamic Light Scattering (DLS) was obtained by SALD-2101 Shimadzu Japan. The concentrations of the metal ions in the solutions were determined using an Atomic Absorption Spectrophotometer (Shimadzu AA-670).

2.4. Batch sorption studies

Batch sorption experiments of Pb (II) and Ni (II) ions were investigated by placing specific amount of nanosorbent of MCM-41/TMSPDETA in 50 ml of the heavy metal solutions under various operating conditions. The initial pH of the solutions was adjusted with 0.1 M HCl and/or 0.1 M NaOH solutions by varying the pH of heavy metal solution from 2 to 6.

- The effect of *pH* varied between 2 to 6 at a temperature of 25 °C and contact time of 120 min.
- The effect of temperature was studied in the range of 20–50 °C at the contact time of 120 min, and with an optimum pH.
- The effect of contact time was investigated by varying the time from 0 to 120 min at a temperature of 25 °C and with an optimum pH.
- The *adsorbent dose* values were varied between 1 and 5 g L^{-1} at the contact time of 120 min, a temperature of 25 °C and with an optimum pH.

The sorption isotherms were studied in various concentrations of heavy metal ion solutions from 10 to 70 mg L^{-1} and at same temperatures (20 °C). The residual concentration of Pb(II) and Ni (II) ions was determined by a coupled plasma atomic emission spectrophotometer (Shimadzu AA-670). The sorption capacity for heavy metal ions was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where q_e (mg g^{-1}) is the sorption capacity, C_0 and C_e (mg L^{-1}) are the initial and equilibrium liquid-phase concentrations of metal ions,