Journal of Industrial and Engineering Chemistry 23 (2015) 93–99

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Synthesis and characterization of porous magnetic silica composite for the removal of heavy metals from aqueous solution

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ARTICLE INFO

Article history:
Received 17 April 2014
Received in revised form 28 July 2014
Accepted 31 July 2014
Available online 7 August 2014

Keywords:
Adsorption
Magnetic composite
Heavy metals
Kinetics
Isotherm

ABSTRACT

Magnetic core and porous silica shell (Fe_3O_4@nSiO_2@mSiO_2) composite has been synthesized using surfactant assisted template approach. The composite was characterized by scanning electron microscopy, transmission electron microscopy, N_2 adsorption-desorption isotherm, X-ray photoelectron spectroscopy, Fourier transform-infrared spectroscopy. The efficiency of Fe_3O_4@nSiO_2@mSiO_2 for Pb(II) and Cd(II) adsorption was studied under the influence of solution pH, contact time and initial solution concentration. Kinetic study illustrated that the pseudo-second-order equation was well correlated with the kinetic data, and the intra-particle diffusion model indicated the multi step adsorption process. In single metal adsorption system, the adsorption affinity of Fe_3O_4@nSiO_2@mSiO_2 for Pb(II) was 1.52 times greater than Cd(II) while in binary system, it was 2.59 times higher at pH 5.5.

Introduction

The heavy metals in effluents are highly fatal and carcinogenic to human beings, animals and plants [1]. Heavy metals must be removed from wastewater before released in environment. Several effective techniques such as chemical precipitation, membrane filtration, ion-exchange, adsorption, and reverse osmosis etc. can be applied to remove the heavy metals. Among them, removal of heavy metals by adsorption is most efficient and frequently used technique because of its simplicity and low operation cost [2]. Therefore, development of new eco-friendly low cost materials with high adsorption capacity is always in need. The applications of mesoporous silicas, functionalized silica based adsorbents have been extensively investigated for the removal of heavy metals [3–6]. The sorption efficiency of silica based adsorbents for the removal of heavy metals is greatly affected by the porosity and surface area which is vice versa [7]. Recently, few researchers synthesized functionalized magnetic core silica adsorption, investigated its metal ions uptake capacity and reported that efficient adsorption of heavy metals by these materials [1,3,4]. However, largely these composites are prepared by using a variety of chemicals, in N_2 atmosphere and other experimental conditions which might be costly. Thus, a simple economically feasible synthetic route is always preferred where less number of chemicals is used in easy experimental conditions.

Since the discovery in 1992, mesoporous silicas such as MCM-42, KIT, SBA etc., have been consistently explored in a variety of fields in separation, catalysis, sensors, drug delivery, and control release applications [8]. In last decade, mesoporous silica has been widely used as adsorption for wastewater purification due to their high surface area, well defined pores, nontoxicity, biocompatibility as well as presence of silanol groups which add to its functionality and thus it can easily bind with the adsorbate having compatible functionality [9]. However, being a good adsorbent, mesoporous silica shows separation limitations from aqueous solution. To overcome this problem, recently several reports have been published using magnetic core-mesoporous silica shell structures which could be used as adsorbent without the above mentioned limitations of mesoporous silica [8,9]. Magnetic separation technique for wastewater purification solves the issue of filtration, centrifugation, and gravitational separation as magnetic particles can be easily removed by applying an appropriate magnetic field [1,3,10].

In this work, we have synthesized Fe_3O_4@nSiO_2@mSiO_2 microspheres using Cetyltrimethylammonium bromide template approach by a simple facile route. The adsorption efficiency of

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http://dx.doi.org/10.1016/j.jiec.2014.07.046
1226-086X/

Fe_3O_4@nSiO_2@mSiO_2 for Pb(II) and Cd(II) was investigated as a function of solution pH, contact time and initial concentration. The kinetics and isotherm modeling of the adsorption process have also been performed.

Materials and methods

Materials

Tetraethyorthosilicate (98%) and cetyltrimethylammonium bromide (CTAB) were purchased from Fluke chemical and Merck, Germany. Lead nitrate and cadmium nitrate were purchased from Panreac Quimica SAU and BDH chemicals Ltd. Sodium dodecyl sulfate (SDS) was obtained from Scharlab S.L. Spain.

Preparation of Fe_3O_4

Chemical precipitation method was used for the synthesis of magnetic nanoparticles [11]. For the synthesis of Fe_3O_4, 3.47 g $FeSO_4 \cdot 7H_2O$ and 12.24 g $Fe_2(SO_4)_3 \cdot 5H_2O$ was dissolved in de-ionized water and stirred at 80 °C. Thereafter, 2.15 g SDS was added to the solution under stirring condition. Subsequently, 25 ml ammonium hydroxide (28%) was added to the solution and vigorously stirred at 80 °C for 3 h. The obtained black precipitate was collected and washed thoroughly with hot de-ionize water and ethanol.

Preparation of Fe_3O_4@nSiO_2@mSiO_2

The synthesis of Fe_3O_4@nSiO_2@mSiO_2 was according to the procedure reported by Deng et al. [12] with slight modification using sol–gel approach. Initially, a thin silica layer was coated over Fe_3O_4. In a typical process, 2.0 g Fe_3O_4 particles were ultrasonicated in the mixture of 100 mL ethanol–water (each 50 mL) for 25 min at 40 °C. Thereafter, 15 mL of ammonia solution (28 wt%) was added to the mixture and ultrasonicated for 1 h. To this solution, 2.0 mL of TEOS was added drop wise and shaked for 4.5 h. The resulting Fe_3O_4@nSiO_2 was filtered, washed with hot deionized water and ethanol and later dried at 60 °C for 16 h.

For the synthesis of Fe_3O_4@nSiO_2@mSiO_2, surfactant template approach was used to deposit SiO_2 on the Fe_3O_4@nSiO_2 using CTAB as a template. Briefly, 0.5 g of CTAB was dissolved in 150 mL ethanol and then 2.0 g of Fe_3O_4@nSiO_2 was added under ultrasonication at 30 °C for 5.5 h. Thereafter, 25 mL of ammonia solution (28 wt%) was added to the mixture followed by addition of 5 mL of TEOS drop wise to the solution under constant stirring. After 18 h, the product was filtered and washed thoroughly with hot de-ionized water and ethanol. The resulting CTAB/SiO_2 coated on the Fe_3O_4@nSiO_2 was re-dispersed in 60 mL acetone and ultrasonicated for 1 h. This procedure was carried out three times for the complete removal of CTAB template.

Characterization

The morphology (SEM and TEM) of Fe_3O_4@nSiO_2@mSiO_2 was investigated by FEI—Quanta 450 FEG SEM and Tecnai G2 F20 Super Twin (TEM analysis) at 200 kV with LaB_6 emitter. X-ray diffraction analysis of composite was done by EQUINOX1000 INEL-diffractometer with a linear curved detector (CPS120 INEL). The X-ray source used was Co$K\alpha$ with a wavelength of 1.79 Å. The XPS measurements were recorded on SPECS GmbH, (Germany) spectrometer operated at a base pressure of 10^{-10} mbar. A non-monochromatic Mg-$K\alpha$(1253.6 eV0X-ray source was used to irradiate the sample surface with 13.5 kV, 100 W X-ray power. The nitrogen adsorption–desorption isotherm analysis was performed at 77 K Quantachrome Nova Win 2 (Quantachrome instruments) equipment by degassing the sample at 200 °C. FTIR spectra of Fe_3O_4@nSiO_2@mSiO_2 was recorded using a Perkin Elmer Spectrum 100 FTIR Spectrometer over a range of 500–4000 cm^{-1}.

Adsorption studies

The adsorption kinetics and isotherm studies of Pb(II) and Cd(II) removal were carried out by taking 0.02 g of Fe_3O_4@nSiO_2@mSiO_2 in 20 mL of metal ion solution with concentration ranging from 10 to 100 mg L^{-1} at fixed pH and temperature. The effect of pH on the removal of Pb(II) and Cd(II) from aqueous solution was studied in the pH range from 2 to 5.5 for Pb(II) and 2 to 6.5 for Cd(II) by adding 0.1 M HCl or 0.1 M NaOH. The kinetic study was performed with the initial concentration of 100 mg L^{-1} and after a fixed time interval, the sample was withdrawn from the water bath shaker and the concentration of metal ions remaining in the supernatant solution was determined using HACH LANGES LCK 308 for Cd(II) and using LCK 306 for Pb(II) with HACH LANGES DR-6000 UV–visible spectrophotomer. The equilibrium adsorption capacity was calculated from:

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

where q_e is the adsorption capacity (mg g^{-1}), C_0 and C_e are the initial and equilibrium metal ion concentration (mg L^{-1}), respectively, V is the volume (L) of solution and m is the mass (g) of adsorbent.

Binary component adsorption of Pb(II)–Cd(II) onto Fe_3O_4@nSiO_2@mSiO_2 was performed by taking 20 mL of solution with concentration of each metal in the range of 5 to 50 mg L^{-1}. The solution pH was adjusted to pH 5.5 using 0.1 M HCl or 0.1 M NaOH, followed by addition of 0.02 g Fe_3O_4@nSiO_2@mSiO_2. The solutions were kept in a water bath shaker at 200 rpm at 30 °C until equilibrium was established.

Results and discussion

Characterization

The architectural porosity of Fe_3O_4@nSiO_2@mSiO_2 was determined by N_2 adsorption desorption analysis, which shows type–IV isotherm (Fig. 1a). The amount of N_2 sorption increases gradually with the increases in the relative pressure (P/P_0) upto 0.1, which indicates the monolayer adsorption at the porous surface of Fe_3O_4@nSiO_2@mSiO_2 [13]. The BET and DFT surface area for Fe_3O_4@nSiO_2@mSiO_2 was found to be 96.786 and 66 $m^2\,g^{-1}$, respectively. Non-local density functional theory (NLDFT) was used to estimate the pore size distribution as shown in Fig. 1b. The pore volume and pore width were found to be 0.083 $m^3\,g^{-1}$ and 1.348 nm, respectively, with 0.083 $cm^3\,g^{-1}$ micropores and 0.021 $cm^3\,g^{-1}$ mesopores in Fe_3O_4@nSiO_2@mSiO_2.

The wide angle XRD pattern of Fe_3O_4@nSiO_2@mSiO_2 is presented in Fig. 2, showing various diffraction peaks. The broad peaks at 2θ between 20 and 30° corresponding to the amorphous silica. A sharp peak at $2\theta = 41.5°$ can be indexed as the (1 3 1) reflection corresponding to the d spacing of 2.532 Å of the magnetite (Fe_3O_4) [14]. The diffraction peaks with d spacing 2.429, 2.10, 1.616, and 1.489 Å are in the accordance with the (2 0 2), (0 4 0), (1 5 1) and (4 0 4) diffraction of Fe_3O_4, confirming the synthesis and presence of magnetite in Fe_3O_4@nSiO_2@mSiO_2. A 2D diffractogram (Fig. 3d) of core shell particle shows that the structure is corresponding to (1 3 1) system. The SEM and TEM images (Fig. 3) show that the spherical particle agglomerates with each other having dimension of 174–202 nm for Fe_3O_4@nSiO_2@mSiO_2.

The oxidation sate and elements analysis of Fe_3O_4@nSiO_2@mSiO_2 was investigated using XPS. Fig. 4a illustrates the wide scan