



Use of microwave irradiation for modification of mesoporous silica nanoparticles by thioglycolic acid for removal of cadmium and mercury



I.M.M. Kenawy^a, Y.G. Abou El-Reash^a, M.M. Hassanien^b, N.R. Alnagar^a, W.I. Mortada^{c,*}

^a Chemistry Department, Faculty of Science, Mansoura University, Mansoura 35516, Egypt

^b Chemistry Department, Beni-Suef University, Beni-Suef 62511, Egypt

^c Urology and Nephrology Center, Mansoura University, Mansoura 35516, Egypt

ARTICLE INFO

Article history:

Received 15 July 2017

Received in revised form

7 September 2017

Accepted 18 September 2017

Available online 21 September 2017

Keywords:

Functionalized silica nanoparticles

Thioglycolic acid

MCM-41

Adsorption

Cadmium

Mercury

ABSTRACT

Herein, we report the organized investigation on adsorption of Cd(II) and Hg(II) by thioglycolic acid modified mesoporous silica nanoparticles prepared by the sol-gel procedure. The modification process is enhanced by microwave irradiation. The morphological behavior of the prepared sorbent (MCM-41-TgA) was identified by SEM and TEM imaging as well as BET surface area analysis. The proposed chemical properties were confirmed by elemental analysis, FT-IR, XRD, and zeta potential. EDX and FT-IR spectra were used to confirm the adsorption process. Both ions could be quantitatively recovered from aqueous samples at pH 6 after shaking for 30 min at room temperature. The solid phase has relatively high adsorption capacity 91.3 and 42.8 mg g⁻¹ for Cd(II) and Hg(II), respectively. *Langmuir* isotherm model fitted well with the experimental data confirming the formation of a mono layer with homogeneous adsorption sites. The thermodynamic studies concluded spontaneity and exothermic behavior of the adsorption process. MCM-41-TgA could be regenerated using 0.5 mol L⁻¹ thiourea or EDTA for at least 10 adsorption/desorption cycles, and it was applied to preconcentrate Cd(II) and Hg(II) from real samples before their determination using ICP-OES.

© 2017 Elsevier Inc. All rights reserved.

1. Introduction

Contamination by heavy metals is considered to be a critical problem for human life and environment. Some of metal ions are toxic for living cells and they have no biological functions. So, excessive exposure to these metal ions may cause health problems. For example, chronic exposure to cadmium (Cd) may lead to osteoporosis and tubular kidney diseases [1]. Human exposure to mercury (Hg) compounds may cause cardiovascular, hematological, pulmonary and renal effects [2].

Atomic spectroscopic instruments such as graphite furnace atomic absorption spectrometry (GFAAS), flame atomic absorption spectrometry (FAAS), and inductively coupled plasma optical emission spectrometry (ICP-OES) are the most common techniques used for the determination of metal ion concentration. However, a preconcentration step is usually needed prior to the instrumental

detection to remove any expected matrix effects and to improve the sensitivity of the instrument by decreasing the detection limit. Several separation and preconcentration procedures like ionic liquid extraction [3], cloud point extraction [4–6], electrochemical deposition [7], ion exchange [8], coprecipitation [9], and solid phase extraction (SPE) [10–15] are used for this purpose. Mostly, SPE is preferred to other procedure due to its simplicity, selectivity and applicability.

One of the main goal of SPE is to use an inexpensive substance as a support material such as active carbon [16], cellulose [11], chitosan [17] and silica [18]. Recently, several studies have explored the utilization of nano-particles (NPs) as sorbents for SPE of metal ions [19]. Compared with other sorbents, NPs have a considerably higher surface area that offers much greater adsorption capacity [20].

Since its preparation for the first time in 1992 [21], Mobil Crystalline of Materials 41 (MCM-41) has become the most common type of mesoporous adsorptive substances due to its uniform pore channels, pore size, and high surface area [22]. MCM-41 has many applications in catalysis [23], biosensors development [24],

* Corresponding author.

E-mail address: w.mortada@yahoo.com (W.I. Mortada).

removal of dyes and metal ions [25,26] and drug delivery systems [27].

To enhance the adsorption efficiency of MCM-41 towards metal ions, several organic groups were added to the structure such as amine and nitrilotriacetic acid anhydride [28], sodium dodecylsulphate [29], 2-(3-(2-aminoethylthio)propylthio) ethanamine [30], and 5-mercapto-1-methyltetrazole [31]. Generally, the modification process consumes time and energy and result in relatively low yield. The microwave heating system has proved to be a suitable alternative to reflux heating method. It has the advantages of limiting the time and temperature of reaction. Moreover; the use of microwave radiation in organic modification reactions is a cleaner, simpler, faster and a much more efficient procedure than classical refluxing systems. This method has other advantages like applying a uniform heating system, producing good quality materials, finer particles with higher adsorption capacity, at the same time, providing a good cost-benefit ratio and energy saving [11,32].

According to our knowledge, none of the published papers reported the modification of MCM-41 with thioglycolic acid. Therefore, this work presents the modification of MCM-41 by thioglycolic acid using the microwave irradiation. The new sorbent (MCM-41-TGA) was characterized by FT-IR, XRD, SEM, TEM, EDX and zeta potential. The removal of Cd(II) and Hg(II) by MCM-41-TGA from aqueous solutions was investigated and optimized. The procedure was utilized for separation of Cd(II) and Hg(II) from real samples prior to ICP-OES measurements.

2. Experimental

2.1. Chemicals

Double distilled water (DDW) and analytical grade chemicals were used through the study. All glassware were soaked overnight in 10% v/v HNO₃, then washed with DDW and dried before the use. Stock solutions (1000 mg L⁻¹) of Cd(II) and Hg(II) were prepared using the appropriate amounts of CdCl₂·H₂O and HgCl₂ (Merck, Darmstadt, Germany), dissolved in DDW. For each experiment; the needed working solutions were daily prepared by the dilution from stock solutions.

2.2. Preparation and functionalization of MCM-41

MCM-41 was synthesized by applying the procedure described previously by Sepehrian et al. [33]. In 460 mL of DDW, 12 g CTAB was dissolved and then stirred for 15 min. Thereafter, 80.38 g of sodium silicate nonhydrate was added with vigorous stirring for 4 h at pH 9 adjusted by adding HCl (2 mol L⁻¹). A bulk white gelatinous substance was formed then separated and left into a Teflon vessel at room temperature for 24 h. The product was filtered, washed with DDW and then dried at 50 °C for 6 h. The sample was calcined at 550 °C for 6 h.

Two grams of the calcinated silica and 2.2 mL of (3-aminopropyl)trimethoxysilane (APTMS) and 50 mL xylene were added then the mixture was heated under refluxing for 24 h at 120–140 °C. The mixture was filtered and the amino-MCM-41 was rinsed several times with ethanol (EtOH) then dried for 24 h at 50 °C. One gram of amino-MCM-41 were mixed with 1 mL of thioglycolic acid in the presence of 30 mL of xylene and the mixture was heated in a round bottom flask for 5 min in a domestic microwave oven (Sharp® Carrousel II, 600 W). The product (MCM-41-TGA) was filtered, washed by EtOH and then dried under vacuum at 60 °C for 2 h. The steps of MCM-41-TGA preparation are summarized in Scheme 1.

2.3. Instrumentation

A Nicolet *i10* spectrometer (Nicolet Instrument Technologies, Madison, WI, USA) was used in recording the FT-IR spectra in the range of 4000 to 400 cm⁻¹. Bruker D8 advance diffractometer (Bruker AXS, Karlsruhe, Germany) was utilized to perform XRD analysis using copper target, wavelength = 1.54 Å under working conditions of 45 kV and 40 mA. N₂ adsorption/desorption isotherm was carried out at -196 °C using a Quantachrome NOVA touch LX4 instrument (Quantachrome Instruments, South San Francisco, CA, USA). BET-method was used to measure the specific surface area [34]. The pore size distribution of the prepared sorbents was calculated using the adsorption branch of the isotherm and the Barrett-Joyner-Halenda (BJH) formula [35].

The size and morphology of MCM-41-TGA were obtained by TEM (JEOL TEM-1230, JEOL Ltd., Tokyo, Japan) with a CCD camera at an accelerating voltage of 120 kV. EDX spectrometer (Model X-Max 20, Oxford Instruments, UK) was employed to record EDX spectra. The zeta potential of MCM-41-TGA was measured using a Malvern ZEN 2600 Zetasizer Nano ZS (Malvern Instruments Ltd, Malvern, UK). The concentrations of Cd(II) and Hg(II) were measured by Agilent's 5100 ICP-OES (Agilent Technologies, Melbourne, Australia). The analysis of Hg(II) was performed by coupling the ICP-OES with a VGA-77 Hydride Generator (Varian, Palo Alto, CA, USA). The instrumental parameters of ICP-OES were given in Table 1. A microwave digestion system (Speed wave four, Berghof Products, Germany) equipped with 12 TFMTM-poly tetrafluoro ethylene vessels was used for digestion of real samples.

2.4. The general procedure for removal of Cd(II) and Hg(II)

In a polypropylene centrifuge tube, 25 mg of MCM-41-TGA was added to 25 mL of 10 mg L⁻¹ metal ion solution. The pH of solutions was adjusted during the experiments to 6.0 using 1 mol L⁻¹ HNO₃ and the mixtures were stirred using a mechanical shaker with a fixed 250 rpm speed (Burrell Corporation, Pittsburgh, Pennsylvania) at room temperature (25 ± 1 °C) for 30 min. The samples were filtered to determine the concentration of Cd(II) and Hg(II) remained in the supernatant by ICP-OES. The adsorption capacity (q_e, mg g⁻¹) and the removal % of the sorbent were calculated as:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

$$\text{Removal (\%)} = \frac{(C_i - C_e)100}{C_i} \quad (2)$$

where C_i and C_e are the initial and equilibrium concentration (mg L⁻¹) of Cd(II) and Hg(II) in solution, respectively. V is the volume of solution (L) and m is the mass (g) of MCM-41-TGA.

2.5. Desorption and reusability experiments

25 mg of MCM-41-TGA was stirred with 25 mL solution containing metal ion (10 mg L⁻¹, pH 6.0) for 30 min at room temperature. Then the solid phase was filtered and washed three times with DDW, to eliminate the non-adsorbed metal ion. The loaded MCM-41-TGA was then stirred for 5 min with 3 mL of different concentrations of some eluting agents (HCl, HNO₃, thiourea or EDTA). The mixture was filtrated again and the concentrations of Cd(II) and Hg(II) in the supernatant were analyzed. The desorption ratio (D%) was defined as:

Download English Version:

<https://daneshyari.com/en/article/4757970>

Download Persian Version:

<https://daneshyari.com/article/4757970>

[Daneshyari.com](https://daneshyari.com)