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Short Communication

High performance microwave-enforced solid phase extraction of heavy metals from aqueous solutions using magnetic iron oxide nanoparticles-protected-nanosilica

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ABSTRACT

A novel technique is presented to explore and investigate the solid phase extraction of heavy metal ions from aqueous solutions using a microwave-enforced sorption heating system. A microwave-assisted surface protected and coated nano-magnetic iron oxide with nano-silica layer [Nano-Fe_3O_4@Nano-SiO_2] was used as the sorbent. The metal sorption characteristics of Nano-Fe_3O_4@Nano-SiO_2 toward Pb(II), Cu(II), Cd (II) and Hg(II) were evaluated and the sorption capacity values were found as 1100, 300, 150 and 100 μmol g^{-1}, respectively upon microwave heating for 5.0 s. These values were slightly changed to 1150, 500, 400 and 100 upon heating to 20.0 s, respectively.

1. Introduction

The importance of extraction techniques is directly based on the required speed and time to accomplish the objective of analysis. Recently, strong emphasis is mainly focused on finding out the most efficient and suitable extraction technique to isolate the compound of interest from its matrix [1]. On the other hand, isolation, extraction and removal procedures of the target species from their samples are mainly based on several important parameters including the type of extraction technique, solvent and sample as well as the time and efficiency of the selected process [2]. The extraction techniques may include liquid–liquid extraction (LLE), solid phase extraction (SPE) and microwave-assisted extraction (MAE) as well as other approaches [3–7]. Each of these techniques has its own advantages and disadvantages [8,9]. However, the MAE is the most recently reported one which is based on heating the sample under microwave energy for a short period of time to transfer the analyte (s) of interest from its solution to the extracting and partitioning solvent [10]. This technology affords reduction of the amount of solvent by a factor $\geqslant$100 and thus decreases the amount of waste hazard materials due to generation of waste solvent [11,12].

The present study is aimed to explore and investigate the solid phase extraction of some selected heavy metal ions from aqueous solutions using a microwave-enforced sorption system as a high performance methodology. The employed solid phase is a surface protected and coated nano-magnetic iron oxide with nano-silica layer which is also synthesized using microwave-assisted technique. The effects of microwave heating time and temperature on the metal capacity values of Pb(II), Cu(II), Cd(II) and Hg(II) by Nano-Fe_3O_4@Nano-SiO_2 sorbent were evaluated in this study.

2. Experimental

2.1. Materials

Anhydrous ferric chloride ($FeCl_3$) with 98.8% was purchased from BDH, UK. Ferrous chloride ($FeCl_2$) with 98.0% purity and sodium silicate were purchased from Oxford, India. Sodium hydroxide (99.0%) and hydrochloric acid (37.0%) were purchased from BDH Chemicals Ltd., Poole, England. Copper acetate monohydrate (98.0%) and mercuric chloride (99.0%) were purchased from Riedel-de Haën, AG, Seelz-Hannover, Germany. Cadmium nitrate (99.1%) and lead nitrate (99.0%) were purchased from BDH Chemicals Ltd., Poole, England.

2.2. Microwave-assisted synthesis of Nano-Fe_3O_4@Nano-SiO_2 sorbent

Nano-Fe_3O_4 was prepared in a microwave oven according to the following procedure. A 0.04 mol of $FeCl_3$ (0.324 g) and 0.02 mol of

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Table 1
Metal capacity values using microwave-assisted high performance removal of heavy metal.

Time (s)	Metal capacity (μmol g^{-1})[a]			
	Pb(II)	Cu(II)	Cd(II)	Hg(II)
5	1100	300	150	100
10	1100	350	200	100
15	1150	400	300	100
20	1150	500	350	100
25	1150	500	350	100
30	1150	500	350	100

[a] The metal capacity values are the average of triplicate analysis with ±10–25 μmol g^{-1}.

$FeCl_2$ (0.199 g) were dissolved in 50 mL of 0.5 mol L^{-1} HCl solution. This mixture was heated in a microwave oven to 80 °C for one minute. 400 mL of 2.0 mol L^{-1} sodium hydroxide solution was added to the above solution in four successive additions. Each addition was followed by heating in the microwave oven for one minute at 80 °C. After the final addition of sodium hydroxide, the iron solution was heated by the microwave oven for two more minutes. The resulting Nano-Fe_3O_4 sorbent was collected using an external magnet, washed several times with distilled water and dried at 50 °C.

The surface protection of Nano-Fe_3O_4 sorbent by Nano-silica layer was also accomplished using the microwave heating method. 1.0 g of Nano-Fe_3O_4 was suspended in 100.0 mL distilled water and heated at 80 °C by microwave irradiation for 2 min. 20.0 mL of 1.0 mol L^{-1} sodium silicate solution was added drop wise in ten successive additions with stirring and heating in the microwave oven for 30 s. The pH of this mixture was adjusted to 6.0 and the reaction mixture was further heated in the microwave oven for five minutes. The resulting Nano-Fe_3O_4@Nano-SiO_2 sorbent was collected using an external magnet, washed several times with distilled water and finally dried at 50 °C.

2.3. Microwave-assisted high performance solid phase extraction of heavy metals

A 1.0 mL of the selected metal ion, viz. Pb(II), Cu(II), Cd(II) and Hg(II) was mixed with 9.0 mL of distilled water in a test tube to obtain 0.01 mol L^{-1} of the metal ion concentration. 10.0 ± 1.0 mg of Nano-Fe_3O_4@Nano-SiO_2 sorbent was then added and heated for the selected time period (5.0–30.0 s) inside a microwave oven at 1400 W output. The reaction mixture was filtered and washed with 50 mL of distilled water (DW). The unextracted metal ion in the filtrate was titrated with a 0.01 mol L^{-1} of EDTA solution using the proper buffer and indicator for each metal ion. This procedure was repeated three times and the average value was calculated. The metal capacity values (q) of the examined metal ion is defined as the sorbed amount of metal ion and expressed in μmol per gram of dry sorbent (μmol g^{-1}) and it is calculated from Eq. (1).

$$q = \frac{(C_i - C_r)V_{(L)}}{M_{(g)}} \times 10^3 \quad (1)$$

where C_i and C_r are the initial and the residual metal ion concentration (mol L^{-1}), respectively. $V_{(L)}$ is the aqueous volume of the sorption reaction and the mass of dry sorbent used in the test was exemplified as $M_{(g)}$.

2.4. Instrumentations

A household microwave oven was used to synthesize the magnetite nano-sorbents. The microwave apparatus is (KOG-1B5H, Korea) with 1400-W output power and operates at a frequency of 2.45 GHz. Fourier transform infrared (FT-IR) of Nano-

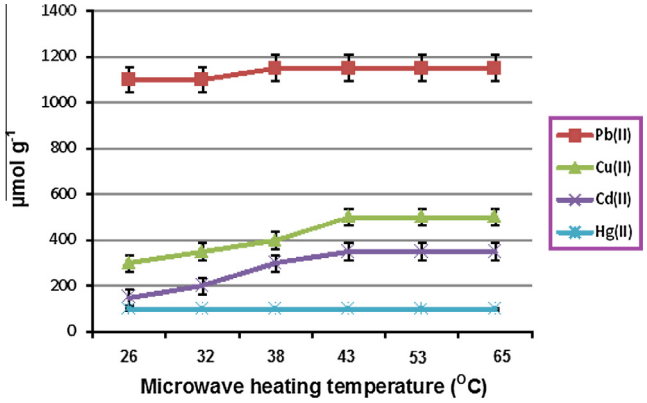

Fig. 1. Effect of microwave heating temperature (°C) on the metal capacity values of metal ions (μmol g^{-1}).

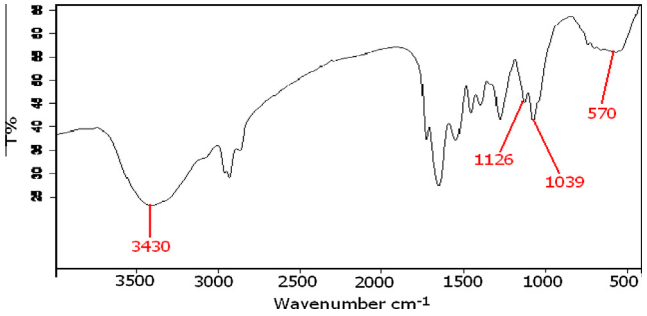

Fig. 2. FT-IR spectrum of Nano-Fe_3O_4@Nano-SiO_2 sorbent.

Fe_3O_4@Nano-SiO_2 sorbent was recorded from KBr pellets using a BRUKER Tensor 37 Fourier transform infrared spectrophotometer in the range of 400–4500 cm^{-1}. The crystalline structure and phase purity of Nano-Fe_3O_4@Nano-SiO_2 sorbent was identified using X-ray diffraction (XRD) analysis by Adrukru D8 ADUANCE, X-ray diffractmeter using target Cu Kα. The scanning electron microscope (JSM-6360LA, JEOL Ltd.), (JSM-5300, JEOL Ltd.) and an ion sputtering coating device (JEOL-JFC-1100E) were used to image the surface morphology of Nano-Fe_3O_4@Nano-SiO_2 sorbent. High resolution-transmission electron microscopy (HR-TEM) model JEM-2100 was used to image the Nano-Fe_3O_4@Nano-SiO_2 sorbent. The HR-TEM technique includes scanning image observation device to give bright and dark-field STEM images at 200 kV. Thermal gravimetric analysis (TGA) and thermoanalytical curves of magnetic nano-sorbent were measured by using a Perkin-Elmer TGA7 Thermobalance. Surface area analysis was determined using the BET method using Nova 3200 Nitrogen physisorbtion Apparatus, USA.

3. Results and discussion

3.1. Microwave-assisted high performance solid phase extraction of heavy metals

The proposed microwave-assisted high performance solid phase extraction technique of heavy metals is mainly based on heating the metal ion solution in contact with the sorbent for a short time. Under this condition, the dissolved metal ion in solution is allowed to contact the sorbent for a short period of time under the microwave heating energy. The metal ions are thus forced to bind and sorb on the surface of solid material. This process is dependent on the characteristics of the solid phase as well as the interacting metal ion. A fast equilibrium condition is attained in few seconds to allow and enforce the transfer of the