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Functionalized CMK-3 mesoporous carbon with 2-amino-5-mercapto-1,3,4-thiadiazole for Hg(II) removal from aqueous media

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ABSTRACT

Ordered mesoporous carbon (CMK-3) was synthesized and functionalized with 2-amino-5-mercapto-1,3,4-thiadiazole groups (AMT-OCMK-3) for Hg(II) removal from aqueous solution. The modified CMK-3 was characterized by X-ray diffraction, N₂ adsorption–desorption isotherm, scanning electron microscopy and Fourier transform infrared spectroscopy. The effects of solution pH, contact time, initial Hg(II) concentration and matrix effect were studied. The adsorption data were successfully fitted with the Langmuir model, exhibiting high adsorption capacity of 450.45 mg/g of AMT-OCMK-3. In the solid-phase extraction system a series of experimental parameters such as sample flow rate, sample volume, eluent volume and concentration of the eluent solution have been investigated and established for preconcentration of Hg(II) in aqueous solution. The results showed that the enrichment factor for Hg(II) was 250, the precision (relative standard deviation (RSD), %) for six replicate measurements was 2.05% and the limit of detection for Hg(II) was achieved at 0.17 µg/L.

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Introduction

Removal of toxic heavy metal ions from wastewater has received significant attention due to their harmful impact on the environment and public health (Rostamian et al., 2011; Teng et al., 2011). There is a great concern about mercury pollution, which is due to its toxicity, mobility, volatility, methylation and persistent character in the environment (Zolfaghari et al., 2011; Wang et al., 2012a). In recent years extensive studies have been made to find a more effective way for the removal of mercuric ions from wastewater (Najafi et al., 2012). For the removal of hazardous ions present in the wastewater, adsorption process has received more attention due to its efficiency and satisfactory environmental friendliness. Numerous typical adsorbents such as activated carbons, clay, minerals, zeolite, fibers, biosorbents and resins (Liu et al., 2011) are used. Although these materials are now playing

important roles in the fields of metal ion adsorption, separation and wastewater treatment (Zhao et al., 2010; Afkhami et al., 2010; Phuengprasop et al., 2011). The search for novel adsorbents for metal ion removal from wastewaters has been, and still, is a challenge and has constituted in an important area of contemporary research (Pacheco et al., 2011). The development of porous materials such as ordered mesoporous carbons (CMKx) that are prepared from mesoporous silica templates such as MCM-48, SBA-1 and SBA-15 (Tamai et al., 1999; Jun et al., 2000; Ryoo et al., 1999, 2001; Joo et al., 2001) with high surface area, high pore volume, regular framework and narrow pore size distribution is currently an area of extensive research, particularly with regard to potential applications as adsorbent for environmental remediation (He et al., 2009; Baniamerian et al., 2009). CMKx can be prepared from a wide variety of low-cost precursors; it is typically biocompatible and quite chemically stable under nonoxidizing

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conditions, exhibits mechanical stability and is easily handled (Stein et al., 2009). The hydrophobic and inert nature of mesoporous carbons can be unfavorable for several applications. Surface modification or functionalization of porous carbon materials is crucial not only for the development and application of hybrid mesoporous materials but also for changing the hydrophobicity and hydrophilicity character of the surface of the materials in order to make them available as good adsorbents for the selective removal of heavy toxic and contaminants (Baniamerian et al., 2009).

Most of the heavy metals are present at very low levels. Thus, the most important step in heavy metal determination is based on preconcentration procedures (Abdel-Fattah et al., 2011). Solid-phase extraction (SPE) has emerged as the most effective extraction and preconcentration technique due to it being a high selectivity and a high enrichment factor (Duran et al., 2009).

In this work, 2-amino-5-mercapto-1,3,4-thiadiazole modified mesoporous carbon molecular sieves (AMT-OCMK-3) were prepared and used to remove Hg(II) ions from aqueous solution in batch and SPE systems. The adsorption behaviors of Hg(II) on AMT-OCMK-3 were evaluated. The effects of optimum operational conditions such as sample flow rate, sample volume, eluent volume and concentration of the eluent solution were also determined for the preconcentration of Hg(II) in aqueous solutions.

1. Experimental

1.1. Materials

Reagents used in this study were tetraethylorthosilicate (98%) and EO20PO70EO20 (PluronicP123) from Aldrich. HCl (37%), sucrose, H₂SO₄ (98%), (NH₄)₂S₂O₈, 2-amino-5-mercapto-1,3,4-thiadiazole (AMT), N,N-dimethylmethanamide and HgCl₂ were purchased from E. Merck (Germany).

1.2. Preparation of adsorbents

Mesoporous carbon was synthesized using ordered mesoporous silica SBA-15 as hard template and then it was oxidized according to the previously reported procedure (He et al., 2009; Shahbazi et al., 2011). Four grams of P123 was dissolved in 90 mL solution of 2 mol/L HCl and 21 mL distilled water by stirring for 5 hr at room temperature. Then, 6.4 g tetraethylorthosilicate was slowly added. This gel was stirred for 24 hr at 40°C, and then crystallized at 100°C for 24 hr under static condition. The mixture was then allowed to cool at room temperature, and the resulting solid was filtered, washed and dried overnight at 100°C and calcined at 600°C for 6 hr. Thus, white powder (SBA-15) was obtained. The calcined SBA-15 sample was used as template for the synthesis of mesoporous carbon and sucrose as carbon recourse was introduced and polymerized inside SBA-15 with H₂SO₄ as catalyst and carbonization in N₂ atmosphere by heating up to 900°C at a rate of 2°C/min. The template SBA-15 was removed by washing with 1 mol/L NaOH solution in 1:1 EtOH–H₂O mixture (twice) at 90°C to dissolve the silica template completely. After the removal of the silica, the carbon samples were filtered, washed with ethanol and dried at 120°C for 4 hr. The O-CMK-3 was obtained by a simple chemical wet oxidation of CMK-3. Three hundred milligrams of CMK-3 was immersed into 15 mL solution of 1.75 mol/L ammonium persulfate ((NH₄)₂S₂O₈) and 2 mol/L H₂SO₄ and the

mixture was stirred at 40°C for 24 hr. Then the oxidized mesoporous carbon was filtered and washed to be neutral with the deionized water for several times. Carboxylated CMK-3 carbon is denoted as O-CMK-3.

O-CMK-3 was dispersed in SOCl₂ solution and stirred at 70°C for 24 hr. The superfluous SOCl₂ was removed by being evaporated at 50°C and dried under vacuum. Then the obtained CMK-3-COCl was mixed with 2-amino-5-mercapto-1,3,4-thiadiazole in N,N-dimethylmethanamide. After being stirred under Ar atmosphere at ambient temperature for 48 hr, the solid product was separated and succulated with N,N-dimethylmethanamide and washed with deionized water three times, then dried at room temperature under vacuum (Fig. 1).

1.3. Characterization of adsorbent

The textural properties of CMK-3, O-CMK-3 and AMT-OCMK-3 were characterized by X-ray diffraction (XRD), N₂ adsorption–desorption, Fourier transform infrared spectra (FT-IR) and scanning electron microscopy (SEM). The XRD spectra were recorded by an XRD diffractometer (X'Pert MPD, Philips, Holland) equipped with a liquid nitrogen-cooled germanium solid-state detector using Cu K_α radiation over a range of 1° < 2θ < 5°. The specific surface area was evaluated by nitrogen adsorption–desorption using the Brunauer–Emmett Teller (BET) method (Belsorp mini II, Bel, Japan). The surface morphology of adsorbents were observed using SEM (Tescan s.r.o, Czech). The FT-IR spectra were measured with KBr pellet with a model 883 spectrometer (Perkin-Elmer, USA) within the wavelength range of 400–4000 cm⁻¹.

1.4. Adsorption and isotherm tests

In order to measure the adsorption capacities, the adsorption isotherm studies were performed under equilibrium conditions. Different Hg(II) samples were prepared with concentrations of 10, 100, 200, 300 and 400 mg/L at pH 6 and in ambient temperature with a dose of 0.5 g/L AMT-OCMK-3. The samples were stirred mechanically (200 r/min) for 40 min to reach the equilibrium. The amounts of analyte adsorbed (*q_e*, mg/g) by the AMT-CMK-3 were calculated using Eq. (1).

$$\left(q_e = \frac{(C_0 - C_e)}{m} V \right) \quad (1)$$

where *C₀* (mg/L) is the initial concentration of metal ions, *C_e* (mg/L) is equilibrium concentration of Hg(II), *V* (L) is the volume of metal ion solution, and *m* (g) is the weight of the adsorbent.

The equilibrium data were fitted with the Langmuir and Freundlich isotherm models. Langmuir model occurs on localized sites with no interaction between adsorbate molecules. Maximum adsorption occurs when the surface is covered by a monolayer of adsorbate and is represented by Eq. (2) (Khazaeli et al., 2013).

$$q_e = \frac{q_m \times b \times c_e}{1 + b \times c_e} \quad (2)$$

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