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Removal of mercury from aqueous solution using mesoporous silica nanoparticles modified with polyamide receptor

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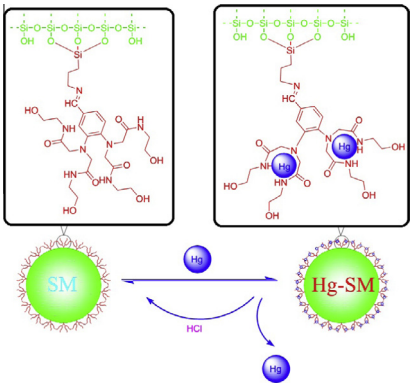
HIGHLIGHTS

- The **SM** was designed based on the principle of fluorescent chemical sensor.
- The polyamide receptor was grafted to the mesoporous silica nanoparticles.
- The **SM** adsorbed trace Hg^{2+} from water within 3 min and a wide range of pH 3–11.
- The **SM** could extract trace Hg^{2+} from **TCM** and has no influence on the ingredients.

GRAPHICAL ABSTRACT

A novel material for toxic metal ions extraction was designed and prepared by grafting poly-amide derivative. This kind of separation material showed the lowest extraction concentration of Hg^{2+} from aqueous solution and it was the first example for extracting trace mercury from Traditional Chinese Medicine but had no influence on their effective ingredients.



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ABSTRACT

Based on the principle of supramolecular recognition and fluorescent chemical sensors, a novel kind of material for the separation of toxic heavy metal ions was designed and synthesized. Mesoporous silica nanoparticles MCM-41 with high surface areas and large ordered pores were used as the supporting matrix. Poly-amide derivative, was grafted to the mesoporous silica nanoparticles for extracting and separating trace Hg^{2+} from aqueous solution, with a short adsorption time (t = 3 min) and a wide range of pH application (pH 3–11). The separation material could also extract trace mercury from Traditional Chinese Medicine, and has no influence on their effective components.

1. Introductions

Currently, a number of techniques such as chemical precipitation, oxidation/reduction sedimentation, ion exchange, membrane filtration and solid phase extraction are available for removing

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heavy metal ions from liquid effluents [1–6]. Some of these processes require high capital investment and reoccurring expenses, and generate huge volumes of sludge or waste products that require safe disposal. Especially, it is difficult to extract and separate some toxic metal ions such as mercury when their concentrations are very low coexisting within higher concentration of other metal ions.

Nanomaterials with engineered features such as size, shape, composition and function, play a leading role for their emerging applications in diverse areas [7–11]. Mesoporous silica materials have been investigated extensively in recent years for use in chemical probes, preconcentrators, heavy metal ions adsorbent, and hard templates for the preparation of other related materials [12–15]. Small mesopores limit ions and molecules which can be admitted to the interior of mesoporous materials. Controlling the pore size could also offer the possibility of molecular sieving or molecular selectivity. Mesoporosity can also endow a material with a high surface area exceeding 1000 m^2/g and pore volume greater than 1.0 cm^3/g, which expands their potentials for application to adsorption and as a support carrier for immobilized catalytic or sensing moieties [16].

Based on the principle of molecular recognition, we have been focusing on the discovery of novel highly selective or specific binding receptors for the metallic ions [17]. More importantly, with the combination of supporting matrix and the as-synthesized receptors with fluorophores, novel "catchers" for metallic ions, with dual detection and separation properties, will be further developed. We previously reported a reusable inorganic–organic hybrid bifunctional fluorescent material for simultaneous detection and separation of trace Hg^{2+} in water and serum, which contained a naphthalimide derivative of 2,6-bis(aminomethyl)pyridine grafted to the surface of silica particles [18]. The hybrid material could be reused to detect toxic mercuric ions with high selectivity and sensitivity. It can also be used as an adsorbent for the removal of mercuric ions from the contaminated aqueous solution. In addition, it can be regenerated and reused by simple pH adjustment.

The above results demonstrated that the non-cyclic nitrogen-containing receptors can be used in the separation and recovery of metal ions, but it might be difficult for the cyclic receptors containing little nitrogen or neither. This is contributed to the much bigger differences of the former's configuration before and after the binding with metal ions and being protonated. Furthermore, such kind of non-cyclic nitrogen-containing receptors are easier to be synthesized and much cheaper than the crown ethers.

Therefore, the principle of supramolecular recognition and fluorescent chemical sensor can be applied in toxic metal ions separation/extraction. Firstly, we can use fluorescent sensor to discover new highly selective ion recognition receptor, as a basic part for separation materials; Secondly, fluorescent sensors with high selectivity and sensitivity, will be combined with different supporting materials to develop hybrid materials with bifunctions for sensing and detecting metal ions, which could be used to evaluate the different types of templates materials. Further we can simplify the fluorescent sensor structure by retaining the ion recognition receptor but weakening the fluorophore units. With the assistance of optimum supporting materials, novel types of separation/extraction materials for trace metal ions were designed and developed.

In the present study, MCM-41 with high surface areas and large ordered pores were used as supporting matrix. Poly-amide derivative, developed by our group as receptor (Scheme. 1) [19–22], was grafted to the mesoporous silica nanoparticles for the extraction and separation of trace heavy metals such as Hg^{2+}, Pb^{2+}, Cd^{2+} from aqueous solution and Traditional Chinese Medicine, with a short adsorption time (t = 3 min) and a wide range pH application (pH 3–12).

2. Experimental

2.1. General procedures

All the solvents were of analytical grades without further purification unless otherwise noted. All pH measurements were made with a Sartorius basic pH-Meter PB-20. Fluorescence spectra were determined using a Varian Cary Eclipse fluorescence spectrometer. Concentration of metal ions was analyzed by a Varian 710ES Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

Dynamic light scattering (DLS) measurements were performed using Malvern Zetasizer Nano ZS (Worcestershire, UK). The nanoparticles were dispersed to 0.5 mg/mL using DDIW (distilled de-ionized water) and each measurement was taken in triplicate and the averages ± standard deviations are reported.

SEM images of the particles were taken by Hitachi S-520 scanning electron microscopy to assess the particle size and shape. To prepare the samples for SEM studies, nanoparticles were dispersed in water, and the resulting suspension was vortexed and sonicated for 2 min. A drop (1–10 mL) of the nanoparticles suspension was then placed on a piece of a microglass slide and dried overnight in a desiccator.

TEM images of the particles were obtained with a JEM-2100 transmission electron microscope operating at 200 keV. Samples for TEM were prepared by spreading a drop of the nanoparticle solution in ethanol onto standard carbon coated copper grids (200 mesh). Dimensional analysis of nanoparticles from TEM images were performed with the Digital Micrograph software.

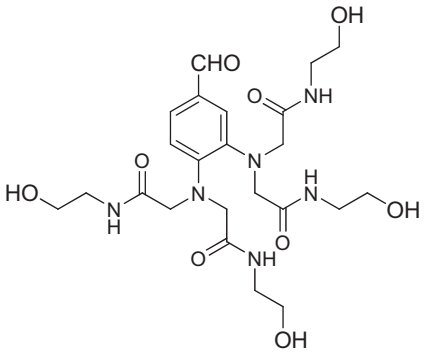
FT-IR spectra (4000–500 cm^{-1}) in KBr were collected on a Nicolet NEXUS 470 FT-IR spectrometer. The receptor (or nanoparticles) were mixed with KBr and pressed to a thin disc for FT-IR detection.

XRD experiments were carried out on a Rigaku D/Max-RB diffractometer with Cu Kα radiation (λ = 0.15418 nm), and it was operated in the range of 0.6–10° (2θ) with the 2θ length.

N_2 adsorption–desorption isotherms were measured at 77 K using a Quantachrome Nova 4000e analyzer. The samples were measured after being outgassed at 423 K overnight. Pore size distributions were calculated using the BJH model. The specific surface areas (BET) of samples were determined from the linear parts of BET plots (p/p_0 = 0.05–0.25).

2.2. Synthesis of Aminopropyl MCM-41 (MCM-NH_2)

The synthesis method was adapted from *Victor S.-Y. Lin* et al. [23–25]. Briefly, Sodium hydroxide (0.83 g, 20.75 mmol) was dissolved in 80.0 mL of deionized water, and CTAB (1.52 g, 4.2 mmol) was added while stirring continuously to get a clear solution, then (3-Aminopropyl) triethoxysilane (1.24 g, 5.6 mmol) was added.



Scheme 1. Poly-amide Derivative Receptor.