



Adsorbents based on crown ether functionalized composite mesoporous silica for selective extraction of trace silver



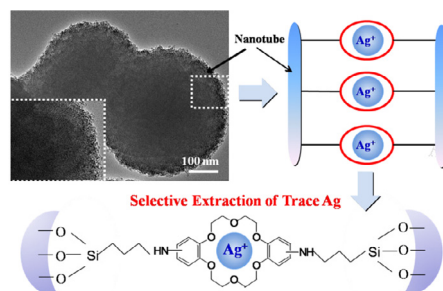
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HIGHLIGHTS

- MS-C-D is an efficient Ag(I) adsorbent to overcome concentrated interfering ions.
- Trace levels of Ag(I) can be selectively adsorbed by MS-C-D adsorbent.
- MS-C-D shows higher adsorption affinity and selectivity coefficient of Ag(I).
- MS-C-D maintains high capacity and selectivity for Ag(I) after 3 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

The selective extraction of trace-level metal ions from unconventional sources such as wastewaters is a long-standing challenge, due to the large concentration difference between the target metal ions and the interfering ions in the matrix. We show here that an adsorbent based on crown ether functionalized mesoporous silica (MS-C-D) overcomes this limitation for selective sequestration of Ag(I) ion. This new adsorbent has hierarchical structure with large specific area and pore framework, which is conducive to the selective adsorption of trace levels of Ag(I) from a complex solution containing concentrated interfered ions such as Cu(II), Zn(II) and Pb(II) ions. The adsorption affinity (b value of 1.45) and selectivity coefficient (distribution coefficient K_D of 1.50×10^5 mL/g) of Ag(I) by using MS-C-D were dramatically higher than many other reported adsorbents (e.g. an Ag(I)-ion-imprinted materials with K_D of 392 mL/g) in literatures. Furthermore, the lower ion concentration corresponded to higher selectivity for Ag(I). The hierarchically structure of MS-C-D and the rigid cavity of dibenzo-18-crown-6 contributed to the selective adsorption of Ag(I). The adsorbent keeps high capacity (about 39.8 mg/g) and selectivity for Ag(I) adsorption after three regeneration cycles. This new composite adsorbent is promising in extracting trace levels of Ag(I) from unconventional wastewaters containing high concentrations of interfered ions.

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1. Introduction

The selective extraction of metal ions from unconventional sources such as industrial/mining waters and seawaters is a long-standing goal for environmental remediation, metallurgical extraction and water purification [1–4]. Current strategies for metal ions removal include liquid-liquid extraction [5], adsorption [6], and chemical/biochemical reduction and precipitation [7]. Among

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these, the effective methods usually involve the use of organic reagents to chelate the target metal ions [6]. In particular, the organic extractants [8] or metal-ion-imprinted materials [9] with a hydrophobic coating and/or rigid ligand can achieve the selective extraction of metal ions. Nevertheless, the disadvantages of these techniques are the high cost of fabrication, relatively low thermal stability of materials, and/or poor reproducibility of synthesis [2,10].

In comparison, adsorbents based on inorganic nanomaterials (e.g. carbons, TiO₂, Fe₂O₃ and Mn₂O₃) are readily available [11–14]. In this class, nano-adsorbents with hierarchical structures usually provide large surface area and thus show high adsorption capacity (>hundreds of mg/g) for heavy metal ions [15]. However, to the best of our knowledge, there are only a few reports of nano-materials that achieve the selective extraction of trace-level metal pollutants. Worse still, the adsorption capacity of the adsorbents frequently decrease dramatically in a dilute system to several mg/g or even µg/g [16]. This phenomenon may be explained by the steric hindrance and electric repulsion of the adsorbed metal ion imposed upon additional ions [17]. Another challenge is the significantly lower level of target metal ions (several mg/L) as compared to the background ions (over hundred mg/L) in a mixed solution [18]. Adsorption driven by electrostatic interaction alone is insufficient for selective adsorption of target metal ions [19,20].

Mesoporous silica (MS) materials such as MCM-41 have shown great potential in environment remediation thanks to their large specific surface area, good chemical stability, and low cost [21]. Nevertheless, the pristine MS materials have low capacity and weak selectivity as adsorbents for metals [22]. On the other hand, macrocyclic crown ethers have excellent ability as a selective neutral host for charged metal ions in its narrow cavity [23]. For instance, Extraction and recycling of Ag(I) have received considerable attention due to its high toxicity, high economic value, and extensive usage in chemical, electronic, and medical fields [2–4]. Dibenzo-18-crown-6 with cavity size slightly greater than the ion radius of Ag(I) exhibits favorable adsorption ability and selectivity toward Ag(I) [24]. A composite of MS and crown ethers may create a selective, efficient, and economical adsorbent for extracting Ag(I) from dilute systems.

In this work, we report a Ag(I) adsorbent based on the composite of MS with dibenzo-18-crown-6 (denoted as MS-C-D) prepared by a facile hydrothermal method. The adsorption affinity (b value) and selectivity (distribution coefficient K_D) for Ag(I) were studied in a mixed solution containing varied concentrations of Ag(I), Cu(II), Zn(II) and Pb(II). High capacity and good selectivity for Ag(I) were observed and the underlying mechanism studied.

2. Experimental sections

2.1. Materials

Tetraethoxysilane (TEOS), cetyltrimethylammonium bromide (CTAB), ethanol (99.8%), ammonia solution (NH₃·H₂O, 29%), acetic acid, nitric acid (HNO₃, 65–68%), toluene, chloroform (CHCl₃), hydrazine hydrate (N₂H₄·H₂O), triethylamine, hydrochloric acid (HCl, 37%), silver nitrate (AgNO₃), copper nitrate (Cu(NO₃)₂), zinc nitrate (Zn(NO₃)₂), and lead nitrate (Pb(NO₃)₂) were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). 3-Chloropropyltrimethoxysilane (CPTMS, 97%), dibenzo-18-crown-6 (DB18C6, >98%), and palladium on carbon (Pd/C) catalyst (5% Pd) were obtained from Aladin. All the reactants were of analytical grade and used as received without further purification. Deionized water in all experiments was obtained from a Milli-Q water purification system (Millipore SAS-67120 Molsheim, France).

2.2. Synthesis of MS-C-D sorbent

2.2.1. Syntheses of MS and MS-CPTMS

The synthetic route for MS was optimized as follows [21]. CTAB (2.5 g) was dissolved in a mixed solution containing 50 mL deionized water and 72 mL ethanol. After that, NH₃·H₂O (13.2 g) was added slowly into the mixture, and the reaction was kept under stirring for 15 min. Then TEOS (4.7 g) was added into the solution dropwise at room temperature under vigorous stirring for 2 h, which generated a white gel. The gel was then transferred into a Teflon-lined autoclave and heated at 398 K for 24 h. After that, the autoclave was cooled to room temperature. The white precipitate was filtered and dried at 363 K. The dried powder (MS) was calcined at 823 K for 6 h. In aforementioned procedure, the molar ratio of TEOS: CTAB: NH₃: H₂O: EtOH was 1:0.3:11:14:58.

Before the modification of CPTMS on MS, the pristine MS was activated at 353 K overnight. Then activated MS (1.0 g), CPTMS (5 mL), and 60 mL toluene were mixed and heated at 363 K under vigorous stirring and refluxing for 24 h using nitrogen protection (Fig. 1). The resulting solid (denoted as MS-C) was filtered, washed with toluene and ethanol successively, and then dried at 363 K for 12 h [22].

2.2.2. Synthesis of DAB18C6

Di(aminobenz)-18-crown-6 (DAB18C6) was synthesized (Fig. 1) by an oxidation reaction of DAB18C6 followed by a reduction reaction [25]. DB18C6 (1 g), acetic acid (10 mL) and chloroform (25 mL) was mixed in a 250 mL round-bottom flask. Following is the slow injection of an aqueous solution containing nitric acid (1 mL) and acetic acid (4 mL), which lasted for approximately 30 min. The obtained mixture was vigorously stirred at 333 K for 5 h. After that, it was cooled down to the room temperature, filtrated and washed by water and ethanol successively, and finally dried at 333 K overnight to obtain a yellow powder di(nitrobenzo)-18-crown-6, denoted as DNB18C6.

DNB18C6 was reduced by hydrazine hydrate using Pd/C as the catalyst. In a typical procedure, DNB18C6 (0.8 g), deionized water (15 mL), and 0.05 g (Pd/C) catalyst were mixed in a 250 mL round-bottom flask and heated to 353 K. Then hydrazine hydrate (20 mL) was added dropwise into the flask in 30 min. The reduction reaction was carried out at 393 K under reflux for 1 h with agitation. After that, the Pd/C catalyst was removed by filtration at 393 K and the filtrate was cooled for crystallization. Yellow crystals of DAB18C6 were formed, which were filtrated, washed with ethanol, and dried at 353 K overnight.

2.2.3. Immobilization of DAB18C6 on MS-C

After activation at 353 K for 2 h, MS-C (2.5 g), DAB18C6 (0.5 g), and triethylamine (1 mL) were mixed in 50 mL toluene, which was heated at 393 K under vigorous stirring, and refluxed for 2 h under nitrogen protection (Fig. 1). After that, the solid product (i.e. MS-C-D) was filtered, washed with toluene and ethanol successively, and dried at 353 K.

2.3. Characterization

The concentrations of the metal ions were determined by SHIMADZU AA-6880 atomic absorption spectrophotometer (AAS). The XRD patterns of the samples were recorded on a Philips X'pert-MPDX-ray diffractometer using Cu K_α radiation. Fourier transform infrared spectra (FTIR) were recorded on Tj270-30A spectrophotometer in the range of 400–4000 cm⁻¹. Thermogravimetric analysis (TGA) of samples were conducted using a TGA-Q600 (Switzerland) at a heating rate of 5 °C min⁻¹ from 25 to 800 °C. The morphologies of the MS and MS-C-D were investigated by scanning electron microscope (SEM, Philips XL30). TEM images

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