Extraction of methylmercury and ethylmercury from aqueous solution using surface sulfhydryl-functionalized magnetic mesoporous silica nanoparticles

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ABSTRACT

Surface sulfhydryl-functionalized magnetic mesoporous silica nanoparticles were prepared, aiming to extract trace alkylmercury from aqueous solution. The prepared nanoparticles were characterized by TEM, ED, EDX, DLS, FTIR, and SERS. Compare with that the non-sulfhydryl-functionalized $Fe_3O_4@SiO_2$ exhibited almost no affinity for CH_3Hg^+ and $CH_3CH_2Hg^+$; the sulfhydryl-functionalized $Fe_3O_4@SiO_2$ exhibited high adsorption affinity for them, resulting from chelating interaction by surface sulfhydryl group, and the adsorption was not significantly impacted by pH within the range of 3.5–9.0 or coexisting metal ions. The monolayer adsorption on surface of $Fe_3O_4@SiO_2$–RSH could reach equilibrium in 2 min. Moreover, the CH_3Hg^+ and $CH_3CH_2Hg^+$ adsorbed on $Fe_3O_4@SiO_2$–RSH could be quickly separated from the matrix in a magnetic field and desorbed easily by acetonitrile and L-cysteine aqueous solution or HCl solution, and the recoveries were more than 80%. Findings of the present work highlight the potential for using $Fe_3O_4@SiO_2$–RSH magnetic nanoparticles as effective and reusable adsorbents for extraction of ultra trace alkylmercury from environmental water samples.

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1. Introduction

More than 2500 tons of mercury is emitted annually from global anthropogenic sources [1]. Mercury is a ubiquitous contaminant that is widely dispersed throughout the environment mostly via atmospheric deposition [2]. For different speciation of mercury, the toxicity is significantly difference. Generally, organic mercury is more toxic than inorganic mercury. The methylmercury (MeHg), CH_3Hg^+, because of the lipophilic property and biological amplification, is hundreds of times more toxic than inorganic Mercury. However, all of the mercury released in the ecosystem undergoes biogeochemical transformation processes and can be converted into MeHg by microorganisms and microalgae in aquatic environments [3]. Moreover, there have been evidence suggests that ethylation could also play an important role in the biogeochemical cycling of mercury [4]. Therefore, only monitoring the total mercury concentrations in the environment is not enough, and

speciation analysis provides more useful information to assess the toxicity and health risks of mercury and further understand biogeochemical cycling of mercury compounds [5]. But the organic Mercury concentrations of the environmental water samples are very difficult to measure precisely because they are so low and suffer from matrix effects when samples are analyzed directly. Therefore, a sample pretreatment step, which can separate the analytes from the matrix components and preconcentrate them, is exceedingly important.

Sulfhydryl-cotton fiber Solid-phase extraction (SCF-SPE) and distillation are main approaches for the extraction of trace alkylmercury from water. SCE-SPE technology was developed over 30 years ago and remains the most popular SPE method for determining alkylmercury. For offering a number of advantages such as high enrichment factor and low consumption of organic solvents [6], the method has been adopted by the national standard methods of China (GB/T 14204-1993 and GB/T 17132-1997). But, in practice, operation of the method is complex and time consumed. On the other hand, distillation, as a more effective method in terms of CH_3Hg^+ recovery [7], has been adopted by the U.S. Environmental Protection Agency as a standard method (EPA 6030). However, the sample is distilled relatively slowly such that the total

distillation time is 5–6 h. More importantly, regents are added to the sample prior to distillation, which increases the possibility for contamination or increased blank levels [2].

In recent years, modified Silica-coated core–shell magnetic nanoparticles ($Fe_3O_4@SiO_2$) have shown great potential for using as adsorbents in various fields, such as removal of heavy metal ions from aqueous solution [8–13], selective adsorption of Hg^{2+} [14], adsorption of phosphate [15], separation of phosphopeptides [16], chiral separation of recemic compounds [17], and recently magnetic solid phase extraction (MSPE) [18–23]. Moreover, the previous studies demonstrated that γ-Mercaptopropyltrimethoxy-silane (γ-MPTMS) modified $Fe_3O_4@SiO_2$ nanoparticles can rapidly and quantitatively adsorb Cd, Cu, Pb, and Hg from aqueous solution [18]. According to the theory of Hard–Soft-Acid–Base (HSAB), sulfhydryl group (soft alkali) also has high adsorption affinity for CH_3Hg^+ (soft acid). However, to the best of our knowledge, no attempt has been made to extract trace CH_3Hg^+ and ethylmercury (EtHg), $CH_3CH_2Hg^+$, from aqueous solution using surface sulfhydryl-functionalized $Fe_3O_4@SiO_2$ magnetic nanoparticles. In this study, $Fe_3O_4@SiO_2$–RSH nanoparticles were prepared as adsorbents for extraction of trace MeHg and EtHg from aqueous solution. And accompanied with high performance liquid chromatography on-line coupled with atomic fluorescence spectrometry (HPLC-AFS) technique, the extraction properties of $Fe_3O_4@SiO_2$–RSH toward CH_3Hg^+ and $CH_3CH_2Hg^+$ in aqueous solution were investigated for adsorption capacity, effect of pH and coexisting metal ions, desorption and regeneration.

2. Experiment section

2.1. Reagents

Methyl mercury (GBW08675), ethyl mercury (GBW(E)081524), Hg^{2+} (GBW08617) were obtained from National Institute of Metrology, China. K, Na, Ca(II), Mg(II), Cu(II), Pb(II), Zn(II) and Cd(II) (1 g/L) were obtained from Accustandard, USA. Tetraethoxysilane (TEOS, 95.0%) was obtained from Sigma–Aldrich, USA. 3-MPTMS (95.0%) was obtained from aladdin, China. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99.0%), Ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$, 98.0%), ammonium hydroxide ($NH_3 \cdot H_2O$, 25%), ethanol (99.7%), methanol (99.9%), acetic ammonium (98.0%), potassium hydroxide (KOH, 85.0%), sodium hydroxide (NaOH, 98.0%), potassium persulfate ($K_2S_2O_8$, 99.0%), and potassium borohydride (KBH_4, 95.0%) were obtained from Sinopharm Chemical Reagent Co., Ltd., China. Ultra pure grade hydrochloric acid (HCl, 36–38%) was obtained from Xi-Long Chemical Co., Ltd., Shantou, China. Acetonitrile (HPLC Grade, 99.9%) was obtained from Fisher, USA. L-cysteine (98.5%) was obtained from Hui-Shi Co., Ltd., Shanghai, China. Highly pure deionized water (18.25 MΩ cm) was obtained from Milli-Q Element System (Millipore France).

2.2. Adsorbents preparation and characterization

The Fe_3O_4 nanoparticles were prepared using a simple chemical coprecipitation method according to previously reported method [12]. Then, the StÖber method [24] to prepare silica-coated Fe_3O_4 nanoparticles was used. Briefly, 100 mg of Fe_3O_4 nanoparticles, 20 mL of H_2O, and 0.1 mL of TEOS were homogeneously dispersed in 80 mL of ethanol with ultrasonication. Following, 1.5 mL of $NH_3 \cdot H_2O$ was added into the above mixture to start the reaction with stirring at 25 °C for 6 h under a nitrogen atmosphere. The materials obtained are referred to as $Fe_3O_4@SiO_2$ nanoparticles.

$Fe_3O_4@SiO_2$–RSH nanoparticles was prepared by the hydrolysis of 3-MPTMS and condensed with the surface hydroxyl groups of

$Fe_3O_4@SiO_2$ subsequently. 100 mg of Fe_3O_4 nanoparticles and 2 ml of H_2O were homogeneously dispersed in 98 mL of ethanol with ultrasonication. Then 0.2 mL of 3-MPTMS added into the flask with stirring and ultrasonication for 10 min. Following, 0.5 mL of $NH_3 \cdot H_2O$ was added into the above mixture to start the reaction with stirring at 25 °C for 12 h under a nitrogen atmosphere. The obtained black precipitates were separated by a magnet and thoroughly washed with deionized water and methanol. The materials obtained are referred to as $Fe_3O_4@SiO_2$–RSH nanoparticles.

The transmission electron microscope (TEM), electron diffraction (ED), and energy dispersive X-ray (EDX) analysis of the nanoparticles were used a field emission TEM (TECNAI-F20, FEI, Netherlands) equipped with EDX (EDAX, USA) at an acceleration voltage of 200 kV. The dynamic light scattering (DLS) analysis of the nanoparticles was carried out using an eighteen angle laser light scatterometer (DAWN HELEOS II, WYATT, USA). Briefly, 0.5 mg of nanoparticles was dispersed in 5 mL of H_2O and ultrasonication for 10 min. Then the dispersion was used for DLS measurement. The functional groups of the nanoparticles were examined through a Fourier-transform infrared spectroscopy (FTIR, VERTEX-70, BRUKER, Germany) use KBr pressed disk, and a Renishaw 2000 model confocal microscopy Raman spectrometer equipped with a holographic notch filter (Renishaw Ltd., UK). Surface-enhanced Raman scattering (SERS) spectra were collected using a microscope objective (N.A. = 0.4) with 50% amplitude and laser intensity 15 mW at the sample. The acquisition time was typically 10 s.

2.3. Determination methods of MeHg and EtHg

Concentration of CH_3Hg^+ and $CH_3CH_2Hg^+$ was determined by an AFS-930 model atomic fluorescence spectrometer equipped with a SA-20 model speciation analysis pretreatment apparatus (Beijing Ji Tian Apparatus Co., Ltd., China). The process of on-line pretreatment include: Firstly, different speciation of mercury in aqueous solution was separated by Venusil MP-C18 model HPLC column (150.0 mm × 4.6 mm × 5 μm, agela, China). The mobile phase was 10 mmol/L L-cysteine 60 mmol/L acetic ammonium and 5% (v/v) acetonitrile aqueous solution. Secondly, the outflow from HPLC column, mixed with oxidants (10 g/L $K_2S_2O_8$ and 3.5 g/L KOH aqueous solution) and air, irradiated by ultraviolet lamp subsequently. Then the organic mercury was oxidized to inorganic mercury. Finally, the above mixture mixed with reducing agent (10 g/L KBH_4 and 3.5 g/L KOH aqueous solution) and 7% (v/v) HCl solution. Through hydride reaction, the inorganic mercury was reduced to Hg atom. The Hg atoms, coupled with H_2, were purged by the carrier gas (Ar 99.99%), introduced directly into the AFS detector.

Instruments operating conditions are given in Table 1. Before adsorption experiments, the methods were evaluated by analyzing 2 μg/L of standard solutions. The relative standard deviations (RSD, $n = 7$) of CH_3Hg^+ and $CH_3CH_2Hg^+$ were 3.2% and 4.8%, and the detection limits (3σ) were 0.2 μg/L and 0.3 μg/L, respectively.

2.4. Adsorption experiments

In a typical process, the adsorbents were dispersed into the high purity water to form a standard solution (2 g/L). Then 150 μL (0.3 mg) of the aqueous dispersion was added into 10 mL solution. The pH value of the mixture was adjusted by 0.1 M HCl and 0.1 M NaOH solutions. The adsorption experiments were carried out in a temperature incubator at 20 ± 1 °C and 100 rpm. After sorption reached the equilibrium, the adsorbents were separated via an external magnetic field. The equilibrium adsorbed concentration, q_e (μg/mg), was calculated according to the following equation: