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Short communication

Ion-imprinted magnetic nanoparticles for specific separation and concentration of ultra-trace methyl mercury from aqueous sample

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ABSTRACT

For rapidly and sensitively determining ultra-trace methyl mercury (MeHg) in aqueous environment, we herein synthesized a MeHg ion-imprinted magnetic nanoparticle (MeHg IIMN) to simply and specifically extract/concentrate ultra-trace MeHg from water samples. The MeHg IIMN employed core-shell $Fe_3O_4@SiO_2$ nanoparticles ($Fe_3O_4@SiO_2$ NPs) as supporting structure, the complex ion of 1-pyrrolidinecarbodithioic acid and MeHg (PDC-CH_3Hg^+) as template, methacrylic acid (MAA) as functional monomer and trimethylolpropane trimethacrylate (TMPTM) as cross linker. The MeHg IIMN offered obvious advantages such as low cost, easy manipulation, better specificity and stability, and recycling characteristics. It can be used to separate/concentrate ultra-trace MeHg from natural water sample within 30 min with a recovery >95%, an enrichment factor of 250, a relative standard deviation (RSD, n = 5) <7%, a 25 mg MeHg/g of maximum adsorption capacity, 50 times of recycling, and without obvious interference of other ions. Combining with capillary electrophoresis-inductively coupled plasma mass spectrometry (CE-ICP-MS), it can be used for the accurate detection of ultra-trace methyl mercury in natural water samples with a limit of detection of 0.084 pg/mL, a recovery of 92–99% and a RSD (n = 5) <8%. The success of this study promises a valuable technique for relatively simple detection of ultra-trace methyl mercury in aqueous environment.

1. Introduction

The utilization of mercury always caused tremendous environmental concern due to its high toxicity. Many studies have demonstrated that mercury released into the environment could be easily transformed to diverse chemical forms (mainly organic mercury) via biogeochemical processes [1], and the diverse chemical forms of mercury give rise to distinguishing bioavailability, mobility and toxicity, which poses a threat to human health as well as to the ecosystem [2]. Among a wide range of mercury species, organic mercury especially methyl mercury (MeHg), exhibits much higher toxicity than inorganic one (Hg^{2+}). As well as, the organic mercury is easier to enter and accumulate in organism to form bioamplification [3–5], and therefore it is inevitable to bring potential risks to human health through biological chain [6]. Hence, a strict restriction on the intake of MeHg (1.6 μg/kg/week) was established by the World Health Organization (WHO) [1]. In China, the limitation of MeHg in natural water was set as 1 pg/mL by the national environmental quality standards (GB 3838-2002). To ensure the effectiveness of these legal provisions and further protect human health, it is highly desirable to establish a sensitive and simple technique for rapidly and simply determining ultra-trace MeHg in natural water.

It was well known, all element-selective techniques, such as atomic fluorescence spectrometry (AFS) and inductively coupled plasma mass spectrometry (ICP-MS) etc, can not be used to specifically detect MeHg in water sample directly since these techniques can not distinguish different mercury species. To date, the techniques used for the speciation analysis of MeHg are mainly on the basis of the combination of separation technology and element-selective detectors, such as high performance liquid chromatography (HPLC) hyphenated with AFS or ICP-MS, gas chromatography (GC) hyphenated with AFS or ICP-MS and capillary electrophoresis (CE) hyphenated with ICP-MS [7–15]. However, all above techniques can not be used to directly determine ultra-trace MeHg in aqueous environment due to the insufficient sensitivity and the interference of matrix. To resolve the limitations of these techniques, usually, an "on-line" or "off-line" pre-concentration

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step was employed. For example, all species of mercury including inorganic and organic mercury were previously pre-concentrated by solid phase extraction/solid phase micro-extraction (SPE/SPME) [16,17], or cloud point extraction (CPE) [18], or liquid–liquid micro-extraction [19], and then the speciation analysis of MeHg was performed by HPLC-ICP-MS or CE-ICP-MS.

Lately, we reported a MeHg ion-imprinted silica microsphere, which was used as sorbent for the extraction/pre-concentration of ultra-trace MeHg from natural water [20]. The proposed MeHg ion-imprinted silica microsphere has good stability, better specificity and larger adsorption capacity. However, the extraction and enrichment of ultra-trace MeHg from natural water with MeHg ion-imprinted silica microspheres needs a relatively long time and a complicated procedure since the MeHg ion-imprinted silica microspheres dispersed in water are difficult to be isolated and collected [20]. Mono-dispersed magnetic Fe_3O_4 nanoparticles (Fe_3O_4 NPs) have good water solubility, and are easy to functionalize and collect. The magnetic sorbents may largely simplify manipulation and shorten the pre-concentrating time in dispersive solid phase extraction [21–23]. Especially, the combination of Fe_3O_4 NPs and ion-imprinted polymers may provide a more efficient technique for the specific and rapid extraction/enrichment of target ions from complicated matrix [24,25]. So far, the ion-imprinted magnetic materials used for the selective extraction/enrichment of MeHg have not been reported, although some ion-imprinted magnetic materials have been developed for the selective separation of other metallic ions such as Co^{2+}, Cu^{2+} and Pb^{2+} [26–29] and several other magnetic sorbents have also been developed for the non-selective extraction/enrichment of both Hg^{2+} and MeHg [30–32]. In this study, a MeHg ion-imprinted magnetic nanoparticle (MeHg IIMN) was synthesized, aiming to provide a more convenient, effective and specific sorbent for the selective and rapid extraction/pre-concentration of ultra-trace MeHg from water sample to resolve the problem of speciation analysis of ultra-trace MeHg.

2. Materials and methods

2.1. Preparation of MeHg ion-imprinted magnetic nanoparticles (MeHg IIMN)

For preparing MeHg IIMN, firstly, the Fe_3O_4 NPs was prepared with solvothermal method, which uses $FeCl_3{\cdot}6H_2O$ and $CH_3COONa{\cdot}3H_2O$ as raw materials. Then, the obtained Fe_3O_4 NPs were coated by SiO_2 to form core-shell Fe_3O_4@SiO_2 NPs, and the obtained Fe_3O_4@SiO_2 NPs were further modified with 3-methacryloxypropyltrimethoxyl silane (γ-MAPS) to form Fe_3O_4@SiO_2-γ-MAPS NPs via self-assembling method. Finally, the MeHg ion-imprinted polymer was synthetized on the surface of Fe_3O_4@SiO_2-γ-MAPS NPs via thermally polymerization, which uses methylmercury chloride, pyrrolidinecarbodithioic acid (PDC), methacrylic acid (MAA), azodiisobutyronitrile (AIBN) and trimethylolpropane trimethacrylate (TMPTM) as raw materials, to obtain MeHg ion-imprinted polymer-coated Fe_3O_4@SiO_2 NPs. Subsequently, the template ion (CH_3Hg^+) in the MeHg ion-imprinted polymer-coated Fe_3O_4@SiO_2 NPs was removed to obtain MeHg IIMN. The resulting MeHg IIMN, which possesses three-dimensional cavities of MeHg on the surface, was employed for extracting/concentrating ultra-trace MeHg from water sample. The detailed procedure of preparing MeHg IIMN was provided in Supplementary information, and the non-imprinted Fe_3O_4 NPs were also prepared with the same procedure but without PDC-CH_3Hg^+ template ion.

2.2. The extraction/enrichment of ultra-trace MeHg from water sample with MeHg IIMN

For extracting/concentrating ultra-trace MeHg from water samples with MeHg IIMN, 500 mL water sample was firstly filtrated through a 0.45 μm filter to remove any sediment, and then was adjusted to pH 5.0 with diluted HCl or NaOH solution. Subsequently, 50 mg MeHg IIMN was added into water sample solution and the whole was amply stirred for 20 min under room temperature. Then, the MeHg IIMN was separated/collected from water sample with a magnet (see Fig. S1 in Supplementary information). The MeHg adsorbed on the MeHg IIMN was then eluted by soaking the MeHg IIMN with 1 mL mixture of 0.1 M thiourea and 2 M HCl for twice under moderately agitation, with each time for 5 min. The eluent was used for the detection of MeHg with CE-ICP-MS. The MeHg IIMN was recycling used for next samples with a 50 times of recycling.

3. Results and discussions

3.1. Characterization of MeHg IIMN

As shown in Fig. 1, in this study, the MeHg IIMN was prepared by using a cross-linking dispersion copolymerization method, which uses core-shell Fe_3O_4@SiO_2 NPs as supporting structure, PDC-CH_3Hg^+ as template, AIBN as an initiator, MAA as functional monomer, TMPTMA as cross-linking agent and ethanol as a solvent. In order to confirm whether the MeHg IIMN was successfully prepared as Fig. 1, various techniques have been used to characterize the as prepared MeHg IIMN.

Firstly, the surface morphology of Fe_3O_4 NPs, Fe_3O_4@SiO_2-γ-MAPS NPs and MeHg IIMN was examined by transmission electron microscope (TEM), respectively. As the TEM images shown in Fig. 2, the Fe_3O_4 NPs has a spherical shape with a diameter of 200–300 nm (Fig. 2A). Compare to Fe_3O_4 NPs, a several nano-meters of coating layer can be observed in the TEM images of Fe_3O_4@SiO_2-γ-MAPS NPs and MeHg IIMN (Fig. 2B and C), revealing that Fe_3O_4 NPs seem have been converted to Fe_3O_4@SiO_2-γ-MAPS NPs and the MeHg ion-imprinted polymer seem has been fabricated on the surface of Fe_3O_4@SiO_2-γ-MAPS NPs successfully.

The infrared spectroscopy (IR) experiments further demonstrated above deduction. As the IR spectra shown in Fig. 3A, the pure Fe_3O_4 NPs showed a typical characteristic peak of Fe-O at 585 cm^{-1} (curve a). Whereas, the Fe_3O_4@SiO_2-γ-MAPS NPs not only showed a typical characteristic peak of Fe—O at 585 cm^{-1} but also showed typical characteristic peaks of Si—O—Si at 1100 cm^{-1} and Si—O at 800 cm^{-1} and 470 cm^{-1}, indicating that Fe_3O_4 NPs have been successfully modified as Fe_3O_4@SiO_2-γ-MAPS NPs (curve b). Compared to Fe_3O_4 NPs and Fe_3O_4@SiO_2-γ-MAPS NPs, the MeHg ion-imprinted polymer-coated Fe_3O_4@SiO_2 NPs (CH_3Hg^+ has not been removed, curve c) and MeHg IIMN (CH_3Hg^+ has been removed from the MeHg ion-imprinted polymer-coated Fe_3O_4@SiO_2 NPs, curve d) exhibited an obvious characteristic peak of C=O at 1728 cm^{-1} besides characteristic peak of Fe—O at 585 cm^{-1}, characteristic peaks of Si-O-Si at 1100 cm^{-1} and Si—O at 800 cm^{-1} and 470 cm^{-1}, suggesting that MAA and TMPTM were successfully polymerized on the surface of Fe_3O_4@SiO_2 NPs.

The X-ray photoelectron spectroscopy (XPS) results, which reflect the chemical composition and surface electronic states of material, also demonstrated that the MeHg IIMN was successfully prepared as Fig. 1. The XPS spectra shown in Fig. 3(B-1,B-2) and Fig. S2 (see Supplementary information) clearly disclosed that the prepared MeHg IIMN contained C, O, S, Si and Hg. From Fig. 3(B-1,B-2) and Fig. S2, we observed that both of the MeHg ion-imprinted polymer-coated Fe_3O_4@SiO_2 NPs and MeHg IIMN exhibited O 1s