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Well-defined nanostructured core–shell magnetic surface imprinted polymers ($\text{Fe}_3\text{O}_4@SiO_2@MIPs$) for effective extraction of trace tetrabromobisphenol A from water

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ABSTRACT

Magnetic molecular imprinted polymers (MIPs) with well-defined core–shell nanostructure for extracting tetrabromobisphenol A (TBBPA) have been fabricated by surface molecular imprinting method. $\text{Fe}_3\text{O}_4@SiO_2@MIPs$ exhibit the good adsorption capacity, high recognition ability and fast kinetics to TBBPA. The maximum adsorption capacity of $\text{Fe}_3\text{O}_4@SiO_2@MIPs$ towards TBBPA is 88.3 mg g^{-1} , which is 2.3 times as high as that of $\text{Fe}_3\text{O}_4@SiO_2@NIPs$. Besides, the material has the short equilibrium time (40 min), the rapid magnetic separation (15.6 emu g^{-1} , 20 s) and the high stability (the adsorption efficiency is at least 85% after seven cycles).

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Introduction

The techniques of fast enrichment and effective separation of trace chemicals show the enormous commercial value in the fields of drug separation, biological molecule purification, water treatment, and so forth [1]. Bisphenol-type chemicals, which consist of two hydroxyphenyl functionalities and several analogues, are potential endocrine disrupting chemicals extensively utilized in synthesizing epoxy resins and polycarbonate plastic [2]. Taking environmental pollutant TBBPA for instance, it may cause serious consequences like water pollution, immune toxicity and other toxicological effects as it is used in industry annually. In addition, TBBPA is used extensively as a kind of brominated flame retardant (BFR) [3], an important chemical extensively applied to be covalently bound to the resins [4,5]. It is estimated that the global consumption of TBBPA varies from 120,000 to 150,000 tons

per year, including TBBPA derivatives [6]. TBBPA has been detected in sewage, landfill leachate, sediments, wildlife and human serum [6]. Owing to its dispersive application and damages to human and animals [3,7], monitoring the content of TBBPA has been giving rise to international concern [8].

Various approaches have been used to monitor TBBPA, such as gas chromatography tandem mass spectrometry (GC–MS) [9,10], solid-phase extraction with gas chromatography tandem mass spectrometry (SPE–GC–MS) [11], high-performance liquid chromatography tandem mass spectrometry tandem mass spectrometry (HPLC–MS–MS) [12] and other complicated techniques [3,13]. However, applications of these methods are limited by the expensive instrument, high cost and complicated pretreatment procedures. Electrochemical sensor, because of its low cost, rapid response, excellent sensitivity, simplicity and in vivo detection, has been applied to detect TBBPA [14]. Trace amounts of TBBPA in real water samples are more difficult to detect. Thus a suitable sample pretreatment method is needed [15], which should be simple, cheap, efficient, rapid and compatible with various determination techniques in order to extract target substance and fully realize the benefits of reuse [16].

For some insurmountable problems, molecular imprinting techniques on practical applications were limited since being arisen in 1972 [17,18]. More efforts have been done to attempt to

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optimize the reaction conditions and develop the imprinted techniques to the preparation of MIPs [19]. Furthermore, bulk polymerization and precipitation polymerization, which are the conventional methods to synthesize MIPs, always have disadvantages of leakage of the template molecule as well as poor site accessibility because of recognition sites embedded in the matrix and residual template molecules [20].

Thanks to the imprinted sites embedded on the surface, the surface imprinted technique has been developing to one of the most available methods to prepare MIPs. The thin MIPs shell on the surface of nanoparticles contributes to the easy removal of template molecule, high binding capacity and fast binding kinetics owing to the easier accessibility and uniform distribution of recognition sites [21,22]. Nano/micro solid supports such as SiO₂ [23], carbon nanotubes [24] and porous materials [25], which could greatly improve the adsorption capacity and reduce the equilibrium time because of their surface recognition sites, have been used in surface imprinted techniques [26]. In addition, the MIP materials with magnetic property are easy to manufacture and can be separated quickly with a magnet [27].

In recent years, magnetic MIP composites are getting increasing attention because of its fast separation and the bifunctional performance of the high affinity to the target molecule. Lu et al. [28] manufactured the core-shell Fe₃O₄@MIP nanoparticles for selective extraction of environmental contaminant BPA. Shi et al. [26] used a magnetic molecularly imprinted polymers to selectively extract and determinate hydroxybenzoic acids in aqueous solution. He et al. [29] fabricated magnetic nanostructured surface MIPs for selective separation of fluoroquinolones in human urine. Because the surface of MIP shell is significant to the template binding property, the formation of the MIP layers with well-defined, uniform morphology and homogeneously distributed binding sites is still urgently needed. Surface imprinted sol-gel materials are manufactured by a traditional sol-gel procedure and involve the template into rigid inorganic or inorganic/organic networks [30]. Generally, methacrylic acid (MAA) and 4-vinylpyridine (4-VP) are usually used as functional monomers, meanwhile, ethylene glycol dimethacrylate (EGDMA) is served as cross-linker [31]. Besides, the imprinted recognition sites on the surface make the particles possessing satisfactory adsorption capacity in water phase.

There have been few reports about MIPs for extracting TBBPA. Shen et al. reported that TBBPA was utilized as the dummy template to fabricate imprinted polymer [32]. Yin et al. [33] synthesized the surface molecular imprinted polymers for extracting TBBPA in water samples. However, little literature has reported about molecularly imprinted polymers with rapid magnetic response for separating and enriching TBBPA in water sample.

In this paper, the main goal is to develop a feasible and cheap method combining the selectivity to the target molecule TBBPA and the rapid magnetic response that can be easy to separate the material from water sample. Therefore, the novel superparamagnetic TBBPA-imprinted nanoparticles with uniform MIPs shell have been prepared to extract TBBPA by the surface imprinting technique. The material selects Fe₃O₄ and SiO₂ as the core and shell respectively, which not only contributes to the functionalization of vinyl group but also protects Fe₃O₄ nanoparticles from aggregating. The growth of well-defined MIP layer on the surface of silica can be accomplished via free radical polymerization. Besides, the resultant Fe₃O₄@SiO₂@MIPs have been characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), vibrating sample magnetometer (VSM), Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The adsorption and separation properties of the nanoparticles are further evaluated

by equilibrium and kinetic analysis, binding capacity and selective adsorption. The results show that the prepared Fe₃O₄@SiO₂@MIPs have the excellent absorption ability, fast kinetics and quick separation ability and can be helpful to extract TBBPA effectively from water sample.

Experimental

Materials

Tetracetylorthosilicate (TEOS) was purchased from Xilong Chemical Plant (Shantou, China). Ethylene glycol dimethacrylate (EGDMA), tetrabromobisphenol A (TBBPA), bisphenol A (BPA), *p*-tertbutylphenol (BP), γ -methacryloxypropyltrimethoxy-silane (MPS), 4,4'-dihydroxybiphenyl (DDBP) and 4-vinylpyridine (4-VP) were purchased from Sigma-Aldrich. 2,2'-Azobis (2-methylpropanitrile) (AIBN) was purchased from Xiya Reagent (Chengdu, China) Co. Ltd. AIBN and 4-VP were purified before use. Other chemicals applied in this work were analytical grade. Water used in the work was doubly distilled.

Synthesis of Fe₃O₄ nanoparticles

Enlightened by the one-pot solvothermal method, Fe₃O₄ nanoparticles were manufactured successfully. Briefly, trisodium citrate dihydrate (1.0 g) and FeCl₃ (2.6 g) were first mixed in (CH₂OH)₂ (80 mL). Then, NaAc (4.0 g) was added with stirring. The uniform dispersible solution was transferred into the Muffle furnace and controlled the temperature at 200 °C. After reaction for 10 h, the nanoparticles were separated with a magnet and washed with water and ethanol for several times, then dried in vacuum at 50 °C.

Synthesis of Fe₃O₄@SiO₂ nanoparticles

The as-prepared Fe₃O₄ NPs (200 mg) were dissolved in the mixed solvent (ethanol:water=4:1, v/v) under ultrasonication. Next, TEOS (2.0 mL) and ammonium hydroxide (4.0 mL) were added and stirred for 8 h at room temperature. The material collected was washed and dried in accordance with the above method.

Synthesis of vinyl-modified Fe₃O₄@SiO₂ nanoparticles

Vinyl-functionalized Fe₃O₄@SiO₂ nanoparticles (Fe₃O₄@SiO₂/MPS) were prepared according to the following process. Fe₃O₄@SiO₂ (200 mg) was dispersed in the mixed solvent (ethanol:water=4:1, v/v), followed by adding ammonium hydroxide (6.0 mL) and MPS (1.2 mL), executed at 60 °C for one day. The collected product was washed and dried in accordance with the above method.

Preparation of the core-shell Fe₃O₄@SiO₂@MIPs and Fe₃O₄@SiO₂@NIPs

Fe₃O₄@SiO₂/MPS (200 mg), TBBPA (0.240 mg, 0.42 mmol) and 4-VP (0.100 mL, 1.68 mmol) were mixed in 60 mL of toluene by ultrasonication. Then the mixture was stirred under nitrogen atmosphere, subsequently adding AIBN (80 mg) and EGDMA (0.160 mL, 1.68 mmol). The solution was heated to reflux, with first prepolymerized at 50 °C for 6 h, polymerized at 60 °C for 24 h, and further aged at 80 °C for 24 h under nitrogen atmosphere. The polymer was separated and then washed with the solvent (methanol:acetic acid=9:1, v/v) to remove TBBPA. UV spectrometer was then employed to confirm whether TBBPA (229 nm) was removed. The product was washed using methanol finally.

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