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A magnetic sorbent for the efficient and rapid extraction of organic micropollutants from large-volume environmental water samples

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ABSTRACT

A magnetic solid-phase extraction (MSPE) method based on a novel magnetic sorbent was proposed for the extraction of target compounds from large-volume water samples. First, magnetic hypercrosslinked microspheres (NAND-1) were prepared via membrane emulsification–suspension polymerization and post crosslinking reaction. To ensure that the Fe_3O_4 nanoparticles could completely pass through the membrane without blocking the pores, oleic acid was used to modify the Fe_3O_4 nanoparticles, which enhanced lipophilicity and monodispersity of the magnetite nanoparticles. The obtained NAND-1 microspheres exhibited super paramagnetic characteristics and excellent magnetic responsiveness with a saturation magnetization of 2.53 emu/g. In addition, a uniform particle size (~8 μm) and a large average surface area (1303.59 m^2/g) were also observed, which were both beneficial for the extraction of the target compounds. Thus, NAND-1 has the potential to simultaneously exhibit good extraction efficiencies toward different types of organic micropollutants (OMPs), including triazines, carbamazepine and diethyl phthalate. The conditions of the MSPE based on NAND-1 were optimized by single factor and orthogonal design experiments. This MSPE method needed only a small amount of sorbent (50 mg/L) for the extraction of OMPs from a large-volume aquatic sample (5 L) and reached equilibrium in a short amount of time (30 min). Moreover, the solution volume, the pH, and the salinity had insignificant influences on the extraction of the eight target OMPs. Under the optimum conditions, the recoveries of the eight OMPs calculated by analyzing the spiked samples were from 91.7% to 99.4%. The NAND-1 could be recycled ten times and still achieve recoveries of the eight OMPs higher than 86%. The limits of detection of the eight OMPs ranged from 1.76 to 27.56 ng/L, and the limits of quantification were from 5.71 to 92.05 ng/L. These results indicated that the proposed method, based on the use of NAND-1 as a magnetic sorbent, has the advantages of convenience and high efficiency and can be successfully applied to analyze the OMPs in real water samples.

1. Introduction

Organic micropollutants (OMPs), which includes pesticides, endocrine-disrupting compounds, pharmaceutical products and personal care products, are ubiquitous in aquatic environment wastewater. Low concentrations of these organic contaminants (ng/L to μg/L) have been shown to cause significant effects on the health of vertebrate species and the ecosystem [1–5]. Thus, the sensitive determination of OMPs in the environment is needed to assess their ecological risks.

Due to the low concentration and varied composition of OMPs in water samples, their separation and preconcentration before instrumental analysis are very important for enhancing the selectivity and reducing a potential source of error. Recently, solid-phase extraction (SPE), which requires smaller volumes of reagents and can improve the analyte enrichment efficiency, has gradually replaced the classic liquid–liquid extraction (LLE) method to become the most common sample preparation technique in environmental water analysis [6–8].

However, some unavoidable difficulties are encountered when SPE is applied to extract trace target compounds from large-volume water samples. A large amount of time is consumed when an SPE column is used for the extraction because of the high backpressure [9]. New magnetic sorbents have been developed for SPE applications, and these sorbents provide a possible method to overcome the problems associated with the SPE columns. The magnetic sorbents can be evenly dispersed in a water sample and can be quickly separated from the bulk of the sample by a magnet after extraction [10]. This process greatly shortens the extraction time and improves the extraction efficiency, thereby enhancing the application of SPE sorbents when rapid detection is needed.

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Numerous magnetic solid-phase extraction (MSPE) materials have been developed through the incorporation of carbon, octadecyltrichlorosilane, aluminum isopropoxide, methacrylic acid, or polypyrrole with magnetic particles. The resulting MSPE sorbents have been applied for the determination of polycyclic aromatic hydrocarbons, linuron, antibiotics, triazines and phthalates in complex matrices [9,11–15]. However, these studies have been primarily focused on the selectivity of the detection using molecularly imprinted polymers (MIPs), which could enrich a specific compound but could not enrich all of the OMPs in water samples simultaneously.

Polymer sorbents with large specific surface areas are widely used for SPE packing materials because of their excellent absorption capacities for both hydrophilic and hydrophobic organic compounds. The most popular SPE column packings using polymer sorbents, such as Oasis HLB and LiChrolut EN, were shown to be useful in the extraction of OMPs [16–18]. Our laboratory was the first to synthesize magnetic polymers with high surface areas using suspension polymerization, and we found that they can effectively remove OMPs from aquatic environments. Our previous results indicated the possibility that the magnetic polymers could be used as an extraction material [19]. To improve the feasibility of using magnetic polymers for SPE, smaller particle sizes and more monodisperse size distributions are needed.

Membrane emulsification–suspension polymerization (MESP) is a modified suspension polymerization method that has been used for the preparation of monodisperse microspheres [20]. However, few studies on the use of this method to prepare the magnetic spheres directly from monomers have been reported [21]. Overcoming the viscosity of monomer solutions using ordinary magnetic particles and transporting them through the membrane is difficult.

The aim of this investigation was to prepare a novel magnetic polymer for the extraction of different types of OMPs from aquatic environmental samples. The magnetic microspheres (NAND-1) were obtained via membrane emulsification-suspension polymerization and a post crosslinking reaction. Eight target compounds were used to evaluate the potential application of these magnetic microspheres for the preconcentration of OMPs from large-volume aquatic environmental samples. Extraction conditions, including the elution method, the volume of the eluting solution, the amount of magnetic hypercrosslinked microspheres, the equilibrium time, the solution pH, and the salinity, were optimized by single factor experiments and orthogonal design experiments.

2. Experimental

2.1. Chemicals

DVB (80 wt%) was purchased from J&K Scientific (Shanghai, China) and was extracted with sodium hydroxide solution (10 wt%) to remove the inhibitors before being used. Benzoyl peroxide (BPO; ≥98%) and polyvinyl alcohol (PVA) were purchased from Sinopharm Chemical Reagent (China). Oleic acid (OA), 1,2-dichloroethane (DCE), acetone, and toluene were obtained from Nanjing Wanqing Chemical (Nanjing, China). Ferric chloride ($FeCl_3{\cdot}6H_2O$), ferrous chloride ($FeCl_2{\cdot}4H_2O$), and other inorganic salts were all analytical grade reagents and were purchased from Shenyang Chemical Industry (Shenyang, China). Simazine (SMZ), simetryn (SMT), atrazine (ATZ), prometon (PMT), ametryn (AMT), propazine (PPZ), carbamazepine (CBZ), and diethyl phthalate (DEP) standard samples as well as alfa humic acid (HA) were provided by J&K Scientific (Shanghai, China). The individual standard agents (100 mg/L) were prepared in methanol and stored at 255 K in the dark. The methanol (TEDIA, USA) and ethyl acetate (JT Baker, Phillipsburg, USA) were HPLC grade and were purchased from Nanjing Jukang (Nanjing, China).

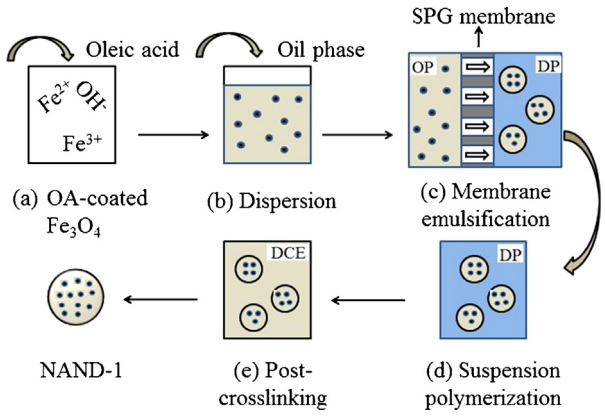

Fig. 1. Steps in the preparation of magnetic hypercrosslinked microspheres (NAND-1).

2.2. Preparation of modified Fe_3O_4 particles

The Fe_3O_4 particles were prepared via coprecipitation. Ferric chloride ($FeCl_3{\cdot}6H_2O$, 7.05 g) and $FeCl_2{\cdot}4H_2O$ (2.58 g) were dissolved in 300 mL of deoxygenated water (nitrogen purged), and the solution was transferred into a 500 mL three-necked round-bottom flask with a nitrogen inlet. The solution was heated for 30 min at 353 K with vigorous agitation under a stream of nitrogen. As 3.00 g of oleic acid dissolved in 20 mL acetone was charged into the solution, 30 mL of $NH_3{\cdot}H_2O$ (25–28 wt%) was added to the flask. Ten minutes later, another 3.00 g of oleic acid was added dropwise to the solution over a period of 30 min. After the solution was bubbled with nitrogen and heated for 30 min, the OA-coated Fe_3O_4 nanoparticles were separated from the solution using a strong magnet. The magnetic nanoparticles were stored under a nitrogen atmosphere after being washed five times with acetone.

2.3. Synthesis of magnetic hypercrosslinked microspheres

As shown in Fig. 1, the NAND-1 were synthesized via membrane emulsification–suspension polymerization and then post-crosslinking. For the membrane emulsification, the oil phase (OP) was passed through a Shirasu porous glass (SPG, SPG Technology Co., Japan) membrane with pore diameter of 2 μm and was mixed with the dispersed phase (DP) to form the homogeneous emulsion. The oil phase was composed of DVB (40.0 g), BPO (0.8 g), toluene (80.0 g), and OA-coated Fe_3O_4 nanoparticles (3.0 g). PVA (2.0 g), sodium sulphate (0.1 g), and *p*-dihydroxybenzene (0.15 g) were dissolved in 500 mL of deionized water to be used as the dispersed phase. The emulsion was subsequently heated, with stirring under a stream of nitrogen, to 353 K for 12 h for the suspension polymerization process, which resulted in the formation of the polydivinylbenzene microspheres. After being rinsed with distilled water and methanol, the microspheres were dried at 353 K for 12 h.

In the post-crosslinking process, the polydivinylbenzene microspheres were fully swelled by using 200 mL of DCE under a nitrogen atmosphere. Then, 8.0 g of $FeCl_3$ was charged into the system and dissolved by stirring for 1 h. The mixture was subsequently heated to 353 K for 12 h. The obtained microspheres were isolated from the mixture using a permanent magnet and were washed five times with methanol. Finally, the magnetic microspheres were dried at 383 K for 12 h.