Application of Fe$_3$O$_4$@MIL-100 (Fe) core-shell magnetic microspheres for evaluating the sorption of organophosphate esters to dissolved organic matter (DOM)

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HIGHLIGHTS

- Fe$_3$O$_4$@MIL-100 (Fe) core-shell magnetic microspheres were used for evaluating the sorption of OPEs to DOM.
- Freely dissolved OPEs can be selectively extracted by MIL-100 (Fe) due to the volume exclusion effect.
- The equilibration time can be reached within a short time because of large contact area of microspheres.
- The sorption coefficients (logK_{DOC}) of OPEs to DOM were highly consistent with the previous study using nd-SPME.

GRAPHICAL ABSTRACT
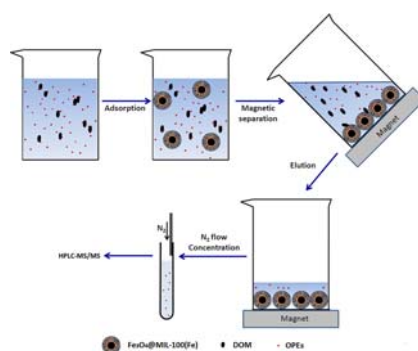
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ABSTRACT

Organophosphate esters (OPEs) are widely used as flame retardants and plasticizers in many products and materials. Because of the potential biologic toxicity on human beings, OPEs are regarded as a class of emerging pollutants. Dissolved organic matters (DOM) have significant effects on the bioavailability and toxicity of the pollutants in the environment. Negligible-depletion solid-phase microextraction (nd-SPME) is an efficient way for measuring the freely dissolved pollutants but suffers from long equilibrium time. Metal-organic frameworks (MOFs) are a class of porous crystalline materials with unique properties such as high pore volume, regular porosity, and tunable pore size, being widely used for the extraction of various organic compounds. Here we developed a novel method for quick determination the sorption coefficients of OPEs to DOM in aquatic phase using Fe$_3$O$_4$@MIL-100 (Fe) core-shell magnetic microspheres. The mesoporous structures of the as-synthesized microspheres hindered the extraction of OPEs which associated with humic acid due to the volume exclusion effect. However, the freely dissolved OPEs can access into the mesoporous and then were extracted by MIL-100 (Fe). Due to the small pore size (4.81 nm), large surface area (141 m^2 g^{-1}), high pore volume (0.17 g^3 g^{-1}), and ultra-thin MOFs layers, Fe$_3$O$_4$@MIL-100 (Fe) core-shell magnetic microspheres have large contact area for the analytes in aqueous phase and therefore the diffusion distance was largely shortened. Besides, the microspheres can be collected conveniently after the extraction process by applying a magnetic field. Compared to the nd-SPME method with 35 h equilibration time ($t_{90\%}$), the proposed method for these studied OPEs only need 24 min to achieve equilibrium. The sorption coefficients (logK_{DOC}) of the OPEs to humic acid were ranged from 3.84–5.28, which were highly consistent with the results by using polyacrylate-coated fiber and polydimethylsiloxane-coated fiber with nd-SPME.

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1. Introduction

Organophosphate esters (OPEs) are widely used as flame retardants and plasticizers in many products and materials. Chlorinated OPEs are commonly employed as flame retardants, including tri(2-chloroethyl) phosphate (TCEP), tri(chloropropyl) phosphate (TCPP), and tri (dichloropropyl) phosphate (TDCP). While, nonhalogenated OPEs such as tris-(2-butoxyethyl) phosphate (TBEP), tributyl phosphate (TnBP), and triphenyl phosphate (TPhP) are mainly used as plasticizers (van der Veen and de Boer, 2012). Most of the OPE compounds are regarded as a class of high-production chemicals with commercial production > 1000 tons per year in Western Europe. As the important substitutes of polybrominated diphenyl ethers (PBDEs), OPEs have already been widely used as flame retardants nowadays with their production surging from 204,000 tons in 2005 to 370,000 tons in 2013 (http://www.cefic-efra.com). Generally, OPE compounds are physically mixed into the appliances and therefore inducing the release into the environment through abrasion, dissolution, and volatilization (Lai et al., 2015). Hitherto, OPEs have been found in the surface water, sewage sludge, terrestrial and atmospheric environments. The potential adverse effects of OPEs on ecosystems and human health have aroused wide concerns by many researchers (Quintana et al., 2008; Wei et al., 2015).

Dissolved organic matters (DOM) are ubiquitous throughout the environment and exhibit important effects on the bioavailability and toxicity of pollutants (Chen et al., 2015; Graham et al., 2017; Shi et al., 2017). It has been reported that high hydrophobic-OPEs exhibited strong sorption with terrestrial humic acid and thus affect the transportation and bioavailability (Pang et al., 2013). Therefore, it would be of great significance to evaluate the sorption of OPEs to DOM for further investigating their accumulation, metabolism, and potential risks for ecosystem and human health.

Solid-phase microextraction (SPME) was introduced by Arthur and Pawliszyn for the extraction of analytes (Kataoka et al., 2000). Negligible-depletion solid-phase microextraction (nd-SPME) was then developed to measure dissolved rather than total concentrations based on the distribution between the sample and the polymer coating of the SPME fiber. Nowadays, nd-SPME has already been widely used for studying the sorption of analytes to humic acid (Mayer et al., 2000; Pang et al., 2013), protein (Broeders et al., 2011; Peltenburg et al., 2015), and other matrix (Hu et al., 2010; Hu et al., 2014). However, the thickness of the fiber coating is usually ranged from few to several ten microns and thus the extraction time for reaching equilibration is long. Especially for high hydrophobic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), the equilibration time was even more than ten days (Endo et al., 2013; Jonker et al., 2007; Yang et al., 2008). Metal-organic frameworks (MOFs) are a class of porous crystalline materials resulted from the combination of metal ions and polyfunctional organic ligands with unique properties such as high pore volume, regular porosity, and tunable pore size by using different organic groups within the framework (Farha and Hupp, 2010). Thus, it would provide an opportunity for measuring the freely dissolved concentration of target analytes with such advantages: (1) the adjustable pore size of MOFs could be used for the selective extraction of freely dissolved analytes through volume exclusion effect; (2) high specific surface area could increase the contact area between target analytes and sorbent materials, and thus significantly shorten the equilibrium time; (3) the synthesis of MOFs possessing magnetism would be benefit for the collection after the extraction process.

The aim of this present study is to develop a novel method for quick evaluating the sorption of OPEs to DOM in aqueous phase using Fe$_3$O$_4$@ MIL-100 (Fe) core-shell magnetic microspheres. OPEs associated with DOM would be hindered due to the volume exclusion effect, but the freely dissolved OPEs could be enriched into the MOFs. The as-synthesized microspheres had a large contact area and largely shortened the diffusion distance of OPEs from aqueous phase to the MOFs layers. Therefore, the extraction equilibrium could be reached within a short time.

2. Materials and methods

2.1. Reagents and materials

Trimethyl phosphate (TMP, 99.5%), triethyl phosphate (TEP, 99.5%), tris-(2-butoxyethyl) phosphate (TBEP, 95.8%), 2-ethylhexyl diphenyl phosphate (EHDPP, 89.0%), and tricresyl phosphate (TCrP, 99.0%) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The physico-chemical parameters of the OPEs were listed in Table 1. Iron chloride hexahydrate (97%), ethylene glycol, polyethylene glycol 4000, sodium acetate (99%) and 1,3,5-Benzenetricarboxylic acid (99%) were obtained from J & K (Beijing, China). Mercaptoacetic acid (MAA, >98.0%) was purchased from TCI (Shanghai, China). HPLC-grade methanol and acetonitrile (ACN) were supplied by Fisher (Shanghai, China). The humic acid, a representative of DOM used in this study, was purchased from Acros Organics. Ultrapure water (18.25 MΩ) was prepared by a Milli-Q gradient system.

2.2. Preparation of Fe$_3$O$_4$@MIL-100 (Fe) microspheres

The Fe$_3$O$_4$@MIL-100 (Fe) core-shell magnetic microspheres were synthesized as described in the literature with minor modifications (Huo and Yan, 2012). In brief, Fe$_3$O$_4$ nanoparticles were synthesized by using solvothermal method and then the products were functionalized with MAA. In this step, Fe$_3$O$_4$ (1 g) was added into ethanol solution (100 mL) containing MAA (0.29 mM). After shaking around 24 h at room temperature, the products were recovered and then washed several times with ethanol and ultrapure water. The synthesized MAA-functionalized Fe$_3$O$_4$ core was then dispersed into FeCl$_3$ ethanol solution (40 mL, 10 mM). Fifteen minutes later, 40 mL of benzenetricarboxylic acid ethanol solution (10 mM) was slowly added under ultrasonic conditions for 30 min at 70 °C. This step was repeated 10 cycles and the final products were dried under vacuum at 70 °C until constant weight.

2.3. Characterization of materials

Powder X-ray diffraction (XRD) measurements were recorded on a Rigaku D/Max-2500 X-ray diffractometer using Cu Kα as a radiation. Field emission scanning electron microscope (FE-SEM) was conducted using a JSM-6490LV scanning electron microscope. Transmission electron microscopy (TEM) micrographs were taken on a JEOL JSM-6490LV system. The N$_2$ adsorption–desorption isotherms were conducted using a Micromeritics ASAP 2010 instrument with a liquid nitrogen at the temperature of 77 K. The specific surface area and pore size distribution data were performed by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method, respectively.

2.4. Ultra-high performance liquid chromatography-tandem mass spectrometric (UPLC-MS/MS) analysis

The determination and identification of OPEs were conducted using a UPLC system (Ultimate 3000, Thermo Scientific, USA) equipped with a triple quadrupole mass spectrometer (TSQ Endura, Thermo Scientific, USA). A Hypersil GOLD C18 (2.1 mm × 10 mm, 1.9 μm) column was chosen for separation. The gradient elution was performed using a binary mobile phase of an aqueous solution of 0.01% formic acid (A) and ACN containing 0.01% formic acid (B) with a flow rate of 0.25 mL min^{-1}. The gradient was set as follows: 0 min (40% B), 2.5 min (40% B), 4.5 min (50% B), 6 min (70% B), 7 min (80% B), 9 min (100% B), 10.5 min (100% B), and 15 min (40% B). An electrospray ionization (ESI) was operated in the positive ion mode with peak width resolution of 0.7 *m/z*. The spray voltage was set at 3500 V. Sheath gas pressure and