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One-pot preparation of magnetic carbon adsorbent derived from pomelo peel for magnetic solid-phase extraction of pollutants in environmental waters

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ABSTRACT

In this work, magnetic carbon material derived from pomelo peels (MCMPs) was conveniently fabricated utilizing one-pot synthesis method and employed as adsorbent of magnetic solid-phase extraction (MSPE). Several characterized measures including infrared spectroscopy, scanning electron microscopy, transmission electron microscopy and vibrating sample magnetometer were used to investigate the morphology, spectroscopic and magnetic properties of prepared adsorbent. Apolar parabens and polar fluoroquinolones (FQs) were used to investigate the extraction performance of MCMPs. Under the optimized extraction conditions, the MCMPs displayed satisfactory extraction performance for target analytes. At the same time, the MCMPs/MSPE was combined with HPLC-DAD for the sensitive determination of parabens and FQs in real-life water samples. Results showed that the limits of detection (S/N = 3) for parabens and FQs were in the ranges of 0.011–0.053 μg/L and 0.012–0.46 μg/L, respectively. The spiked recoveries were in the range of 76.6–116% for parabens and 80.2–114% for FQs with good repeatability (relative standard deviations less than 10%). In comparison to reported methods, the developed MCMPs/MSPE-HPLC-DAD showed some merits including low-cost, simplicity, satisfactory sensitivity and green non-pollution.

1. Introduction

Sample preparation is an indispensable step in the whole analytical procedure. Typically, solvent-based extraction (SBE) and adsorbent-based extraction (ABE) are the two main approaches in sample pretreatment [1]. Because of low consumption of organic solvent, ABE is more popular than SBE. So far, various ABE formats such as solid-phase extraction (SPE) [2], magnetic solid-phase extraction (MSPE) [3], stir bar sorptive extraction (SBSE) [4], solid-phase microextraction (SPME) [5], multiply monolithic fibers SPME (MMF-SPME) [6] have been developed and applied to extract pollutants in multifarious samples.

In ABE, the core is extraction medium (adsorbent) which decides the extraction performance and analytical results. Till now, all kinds of adsorbents have sprung up and parts of them have been commercialized. Porous monoliths [6], silica-based carbonaceous [7], carbon materials [8], polymeric ionic liquids (PIL) [9] and metal-organic frameworks (MOFs) [10] et al. have been widely exploited to extract a great variety of compounds from complex matrices. Among the various adsorbents, carbon materials including carbon nanotubes, graphene, fullerene, carbon fibers etc., have raised concern because they have a large specific surface area, chemical stability and outstanding adsorption characteristics [11]. Hence, carbon materials have been successfully used to remove pollutants from wastewaters [12]. However, the preparation and regeneration of carbon nanotubes, graphene and fullerene are relatively difficult and costly, thus, their popularization is limited. Therefore, fabricating carbon materials with simple preparation procedure and low-cost is highly desired.

Recently, biochar derived from natural biomass have received great attention because of their high porosity, low price, wide source and eco-friendliness [13]. Hence, biochar has been applied to adsorb different various pollutants [14]. Pomelo is a characteristic fruit of South China. Typically, the pomelo peels (PPs) made up one half of the total weight of the pomelo. However, the PPs

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are inedible to humans and discarded in landfills, which pollutant the environment. Recent studies indicated that PPs contained rich plant fiber and various functional groups such as carboxyl, amino and hydroxyl groups [15]. Carbon materials derived from PPs (CMPs) have been prepared and utilized to wastewater treatment and satisfactory results were achieved [14]. However, the CMPs are difficult to be recovered fully from a treated solution, resulting in poor cyclic utilization. To overcome this dilemma, magnetic CMPs (MCMPs) were synthesized and conveniently realized the separation of MCMPs from treated solution by an external magnetic field. According to hydrothermal method, Su et al. [16] used PPs, $Fe(NO_3)_3{\cdot}9H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ to synthesize a magnetic composite material of $CoFe_2O_4$/graphene-like carbons (LGC). The LGC displayed satisfactory adsorption performance for methylene blue (MB) in water. At the same time, the LGC could be easily recovered by an external magnetic field. However, the synthesized temperature of LGC was 200 °C and the preparation time was as long as 20 h. Wang [8] ever utilized hydrochloric acid pickling water as chemical activation agent and iron oxide precursor to fabricate MCMPs. The prepared MCMPs had a relative high surface area of 760 m^2/g and could be fast separated from water under a moderate magnetic field. The MCMPs was successfully used to remove phenol in aqueous solution. However, the total synthesized time of MCMPs was as long as 36 h. At the same time, the components of hydrochloric acid pickling water were varied, which would affect the preparation repeatability of MCMPs. The previous studies well demonstrate that the MCMPs combine the advantages of magnetic separation and biochar, displaying obvious application prospect in sample preparation. However, to the best of knowledge that there are only a few studies reported the preparation and application of MCMPs. At the same time, milder reaction conditions and shorter preparation time for MCMPs are worthy of being expected.

In the present work, a simple, mild and quick one-pot synthesized method for the fabrication of MCMPs was developed. Its morphology, spectroscopic and magnetic properties were characterized by infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM). Parabens and fluoroquinolones (FQs) were selected as target analytes to evaluate the extraction performance of MCMPs for apolar and polar compounds under MSPE format, respectively. At the same time, sensitive and robust method for the determination of parabens and FQs in real-life waters were developed by the combination of MCMPs/MSPE and high-performance liquid chromatography with diode array detection (HPLC-DAD).

2. Experimental

2.1. Chemicals and materials

PPs were collected as raw material from local market. The pretreatment of PPs and the preparation of CMPs were processed according to previous studies with suitable modification [15,16]. The detailed preparation procedure, diagrammatic sketch (Fig. S1), specific surface area and SEM (Fig. S2) of CMPs can be found in Supplementary data. The $FeCl_3{\cdot}6H_2O$ (99%), $FeCl_2{\cdot}4H_2O$ (98%), ethanediamine (96%) and formic acid (FA, 98%) were purchased from Xilong Chemical Co. (Guangzhou, China). HPLC-grade acetonitrile (ACN), methanol and ethanol were bought from Tedia (Fairfield, USA). Water used throughout the study was purified with a Milli-Q water-purification system (Millipore, USA).

The parabens including methylparaben (MHB), ethylparaben (EHB), propylparaben (PHB), isopropylparaben (IPHB), butylparaben (BHB), isobutylparaben (IBHB), heptyl 4-hydroxybenzoate (HHB), 2-ethylhexyl4-hydroxybenzoate (OHB), and FQs containing marbofloxacin (MAR), norfloxacin (NOR), ciprofloxacin(CIP), lomefloxacin (LOM), enrofloxacin (ENR), sarafloxacin (SAR), sparfloxacin (SPA) were purchased from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). The basic properties of the target parabens and FQs are listed Table S1 and Table S2, respectively. The individual stock solutions of target parabens (or FQs) were prepared at a concentration of 1000 mg/L in methanol. The mixed solution of parabens (or FQs) containing 10.0 mg/L of each compound was prepared by diluting individual stock solutions in methanol. All solutions were stored at 4 °C and diluted with ultrapure water to give the required concentration.

2.2. Apparatus

HPLC analyses of parabens and FQs were carried on Thermo Scientific Dionex UltiMate 3000 Series (Thermo Fisher Scientific, USA) equipped with a quaternary pump (LPG-3400SDN), a diode array detector (DAD-3000), WPS-3000 auto samplers (WPS-300SL) and column compartment (TCC-3000RS). All chromatographic separation was performed at room temperature. The Kromasil C18 column (5 μm particle size, 250 mm × 4.6 mm I. D.) was utilized to separate parabens and FQs. The optimum separation of parabens was obtained with a binary mobile phase composed of ultrapure water (solvent A) and ACN (solvent B). The gradient elution program was as follows: 0.0–11.0 min = 45% B, 11.0–17.0 min = 50% B, 17.0–22.0 min = 95% B, 22.0–24.0 min = 45% B and kept to 27.0 min. The detection wavelength, flow rate and injection volume were 254 nm, 1.0 mL/min and 20 μL, respectively. The mobile phase used for the separation of FQs was composed of FA aqueous (0.5%, v/v) (solvent A) and ACN (solvent B). The gradient elution program was as follows: 0–9.5 min = 18% B, 9.5–15.0 min = 17% B, 15.0–16.0 min = 18% B and kept to 18.0 min. The detection wavelength was set at 300 nm for MAR and SPA, 279 nm for other FQs. Other conditions were the same as the separation conditions of parabens.

The oscillator (SHZ-82) was purchased from Guohua Electrical Equipment Co. (Jiangshu, China). The prepared MCMPs were characterized with elemental analysis (EA), Fourier transform infrared spectrum (FT-IR), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM). The detailed information about these instruments was listed in the Supplementary data.

2.3. One-pot preparation of MCMPs

Typically, 5.4 g $FeCl_3{\cdot}6H_2O$ and 2.0 g $FeCl_2{\cdot}4H_2O$ were dissolved in 100 mL ultrapure water, then 1.0 g CMPs were added and mixed ultrasonically to form a homogeneous solution. After that, the solution was put into a three-necked flask equipped with a mechanical stirrer, a reflux condenser and a thermometer. The flask was then placed in a thermostat water bath with mechanical stirring (300 rpm) at 80 °C. Subsequently, 10 mL of ethanediamine was added dropwise into the above solution under nitrogen gas protection and vigorous mechanical stirring (500 rpm) for 2 h. After the reaction, the resulting products were separated from the reaction medium by an external magnetic field. The particles were washed with water and methanol repeatedly with the aid of a magnet. Finally, the products were dried in a vacuum oven at 60 °C for 6 h to obtain the final MCMPs. Compared with reported methods for the preparation of MCMPs [8,16], the proposed one-pot preparation method is quite simple, mild and quick. The schematic of the one-pot preparation method of MCMPs is showed in Fig. 1.

2.4. MCMPs/MSPE procedure

Methanol and ultrapure water were utilized to activate the MCMPs. After the activation, the MCMPs were placed in a 100 mL