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Magnetic porous carbon as an adsorbent for the enrichment of chlorophenols from water and peach juice samples

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ABSTRACT

In this paper, porous carbon with a highly ordered structure was synthesized using zeolite ZSM-5 as a template and sucrose as a carbon source. Through the in situ reduction of Fe^{3+}, magnetic property was successfully introduced into the ordered porous carbon, resulting in a magnetic porous carbon (MPC). MPC was used as an adsorbent for the extraction of some chlorophenols (2-chlorophenol, 3-chlorophenol, 2,3-dichlorophenol and 3,4-dichlorophenol) from water and peach juice samples followed by high performance liquid chromatography-ultraviolet detection. Good linearity was observed in the range 1.0–100.0 ng mL^{-1} and 2.0–100.0 ng mL^{-1} for water and peach juice sample, respectively. The limits of detection ($S/N = 3$) were between 0.10 and 0.30 ng mL^{-1}. The relative standard deviations were less than 5.3% and the recoveries of the method for the compounds were in the range from 87.8% to 102.3%. The results demonstrated that the MPC had a high adsorptive capability toward the four chlorophenols from water and peach juice samples.

1. Introduction

In recent years, the pollutions from chemical contaminants in environment have become a major public concern. Currently, chlorophenols have been widely used in the production of dyes, papers, pesticides (including fungicides, biocides and herbicides), preservatives, and in many other industrial processes [1]. However, due to their toxicities, chlorophenols have been classified by the International Agency for Research on Cancer as possible carcinogenic agents to humans and also have been included in the priority pollution list of the European Union and US Environmental Protection Agency [2,3]. Therefore, it is necessary to develop sensitive, convenient and reliable analytical methods for the effective determination of these compounds in environmental samples.

Because chlorophenol contaminations often exist at very low concentrations in food and environmental samples, sample pretreatment is often required to preconcentrate the analytes prior to their instrumental analysis. For the preconcentration of chlorophenols from different samples, several approaches have been reported, such as Soxhlet extraction [4], solid phase extraction (SPE) [5,6], solid phase microextraction (SPME) [7,8], single-drop microextraction (SDME) [9], stir bar sorptive extraction (SBSE) [10], dispersive liquid–liquid microextraction (DLLME) [11,12], hollow fiber liquid phase microextraction (HF-LPME) [13,14], molecularly imprinted solid-phase extraction (MISPE) [15,16] and magnetic solid-phase extraction (MSPE) [17,18]. Among them, the sorbent-based techniques, mainly SPE, SPME and MSPE, have become widely accepted and increasingly used for the pre-concentration and purification of chlorophenols from aqueous samples due to the variety of the adsorbent materials and the different extraction formats in these techniques [19]. Compared with traditional adsorbents, magnetic adsorbents used in MSPE can be easily separated from sample solutions by an external magnetic field without the need of additional centrifugation or filtration. Moreover, since the adsorbent can be dispersed in sample solution in MSPE, the contact area between analytes and adsorbents is very large, which results in a rapid mass transfer and rapid extraction equilibrium. For the above reasons, MSPE has found wide applications in the field of sample preparation. Since adsorbent plays a key role in MSPE, the development of new magnetic adsorbent materials with high adsorption capacities has been a significant research field. Up to now, various MSPE adsorbents, such as polymer materials [17], C18 microspheres [18], activated carbon [20], carbon nanotubes [21] and graphene [22] have been developed.

Recently, porous carbon materials have sparked remarkable interest from researchers. Owing to the presence of pores, ordered porous carbon materials could interact with some kinds of

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molecules and ions not only at their surfaces, but also throughout the bulk of the materials. Porous carbon materials have unique physical and chemical properties, such as high surface area, large pore volume, regular pore size, interconnected frameworks, as well as good chemical and physical stabilities [23]. Thus far, porous carbon materials have been explored as the efficient adsorbents not only for the removal of dyes [24–26] and bisphenol A [27] from aqueous solutions, but also for the adsorption of sulfur compound [28], alkaloids [29], etc. The results demonstrated that porous carbon materials were efficient and promising adsorbents with high adsorption rate and adsorption capacities. However, porous carbon materials were difficult to be separated and recovered from the sample solution because of their small sizes, which could hinder their practical applications. The incorporation of magnetic components into porous carbon materials could be an effective approach to address the above problem [30]. Up to date, the applications of porous carbon-based magnetic nanocomposite as the adsorbent have been very few in the literature. In this regard, Amini synthesized magnetic mesoporous carbon as an adsorbent for removal of sulfur from model oil [31]. A highly ordered mesoporous carbon functionalized with carboxylate groups and magnetic nanoparticles exhibited a good performance for the removal of toxic organic compounds from waster-water [32]. Mesoporous magnetic Co/carbon nanocomposite was used for the adsorption of methyl orange from aqueous solution and showed a good adsorption capacity [33]. However, thus far, the application of magnetic porous carbon for the enrichment of trace pollutants from real samples has still remained untouched.

In this study, a porous carbon was synthesized by using zeolite ZSM-5 as a template and sucrose as a carbon source. Then, the as-prepared material was further integrated with magnetic property to produce a magnetic porous carbon (MPC) with high surface area and sufficient magnetism. To evaluate the performance of the MPC as an alternative, low-cost and non-toxic MSPE adsorption material, some chlorophenols (2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 2,3-dichlorophenol (2,3-DCP), and 3,4-dichlorophenol (3,4-DCP)) were selected as model compounds. After the MSPE with the MPC, the analytes were determined by high-performance liquid chromatography with ultraviolet detection (HPLC-UV). To the best of our knowledge, this is the first report about the application of such MPC for the pre-enrichment of chlorophenols from water and beverage samples.

2. Experimental

2.1. Chemicals and materials

The standards of 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 2,3-dichlorophenol (2,3-DCP) and 3,4-dichlorophenol (3,4-DCP) were purchased from Aladdin-reagent (Shanghai, China). Methanol (HPLC-grade) was obtained from Kermel Chemical Reagents Company (Tianjin, China). Acetonitrile, acetone, hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride (NaCl) and all other reagents were purchased from Beijing Chemical Reagents Company (Beijing, China). The water used throughout the work was double-distilled on a SZ-93 automatic double-distiller purchased from Shanghai Yarong Biochemistry Instrumental Factory (Shanghai, China). Mineral water and peach juice samples were purchased from the local supermarket (Baoding, China), and both the water and juice samples were directly used for MSPE without further treatment.

A mixture stock solution containing 2-CP, 3-CP, 2,3-DCP and 3,4-DCP each at 20.0 μg mL^{-1} was prepared in methanol. A series of standard solutions were prepared by mixing an appropriate amount of the stock solution with methanol in a 10-mL volumetric flask. All the standard solutions were stored at 4 °C and protected from light.

2.2. Apparatus

The HPLC system was a Model LC-20AT (Shimadzu, Japan) which consists of two pumps and a Model SPD-20A UV/vis 104 detector. Chromatographic separations were performed on a Century SIL C18 column (250 mm × 4.6 mm I.D., 5.0 μm) from Dalian Johnsson Separation Science Technology Corporation (Dalian, China). The mobile phase was a mixture of methanol–water (65:35, v/v) at a flow rate of 1 mL min^{-1}. The UV monitoring wavelength was chosen at 280 nm.

The size and morphology of the magnetic nanoparticles were observed by transmission electron microscopy (TEM) using a JEOL model JEM-2011 (HR) (Tokyo, Japan) at 5 kV and scanning electron microscopy (SEM) using S-3000 N microscope (Hitachi, Japan). X-ray diffraction (XRD) patterns of the samples were recorded with a X-ray diffractometer (XRD-6000 Shimadzu). The Brunauer–Emmett–Teller (BET) surface areas were determined from the N_2 adsorption at 77 K using TristarII3020 (USA). The magnetic property was analyzed using a JDM-13 vibrating sample magnetometer (VSM, Jilin University, Changchun, China) at room temperature.

2.3. Synthesis of MPC

Porous carbon material was synthesized using ZSM-5 zeolite as a template and sucrose as a carbon source according to the reported methods [34,35,26] with some modifications. The typical synthetic procedures are as follows. Typically, 1 g ZSM-5 was mixed homogeneously with an aqueous solution composed of 5 mL of distilled water and 1.5 g sucrose under stirring for 50 min at room temperature. Then, 0.19 g H_2SO_4 (98 wt%) was added. After being stirred for 10 min, the mixture was heated in an oven at 100 °C for 6 h and at 160 °C for 6 h. The mixture was then cooled to room temperature and the resultant black precipitate was ground to a fine powder. After the addition of 1 g of sucrose, 0.1 g of H_2SO_4 (98 wt%) and 5 mL of distilled water, the mixture was treated again at 100 °C for 6 h and at 160 °C for 6 h. The obtained ZSM-5/sucrose composite was carbonized in a conventional furnace at 900 °C for 2 h in nitrogen flow. Subsequently, the ZSM-5 template was removed by mixing the composite with 20 mL of HF (25%, wt%) for 10 h and the obtained porous carbon was rinsed with ethanol and distilled water, respectively, to neutralize the material surface. Finally, the ordered porous carbon (OPC) material was air-dried.

MPC was synthesized by the in situ chemical coprecipitation of Fe^{2+} and Fe^{3+} in alkaline solution in the presence of OPC [22]. The magnetic composite was prepared by suspending 1.0 g OPC in 500 mL of solution containing 0.85 g (4.33 mmol) $FeCl_2{\cdot}4H_2O$ and 2.34 g (8.66 mmol) $FeCl_3{\cdot}6H_2O$ at 50 °C under N_2 atmosphere. After the solution was sonicated (200 W, 40 kHz) for 10 min, 40 mL 14% $NH_3{\cdot}H_2O$ aqueous solution was added dropwise to precipitate the iron oxides and the reaction was carried out at 50 °C for 1 h under constant mechanical stirring. The resultant precipitate was separated from the aqueous dispersion by an external magnetic field and washed with double-distilled water until the pH was 7. Finally, the MPC composite was dried under vacuum.

2.4. MSPE procedures

For the MSPE, 15 mg of MPC was placed in a 150 mL conical flask containing 100 mL of sample solution. After the pH of the mixture was adjusted to 5.0 with 0.1 mol L^{-1} HCl, the mixture was shaken on a slow-moving platform shaker for 25 min. Subsequently, the MPC adsorbent was separated from the sample solution by placing a magnet at the bottom of the conical flask. The supernatant