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# Carbon quantum dots-modified ferrofluid for dispersive solid-phase extraction of phenolic compounds in water and milk samples

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ABSTRACT

In this study, novel carbon quantum dots/oleic acid-coated $Fe_3O_4$ composites ($Fe_3O_4$-OA/CQDs) were successfully synthesized via a simple synthesis strategy and used to prepare the ferrofluid for the extraction and determination of phenolic compounds from water and pretreated milk samples followed by HPLC. The ferrofluid was composed of ionic liquids (ILs) and $Fe_3O_4$-OA/CQDs. With the introduction of CQDs, the ferrofluid showed good dispersing capability in aqueous samples, and the method exhibited lower relative standard deviations (RSDs) (1.1–2.1%), which indicated its good reproducibility. In addition, a proper carbon chain length for ILs might maintain the integrity of the ferrofluid during the extraction process and increase the extraction efficiency of the method. Under the optimum conditions, the limits of detection were in the range of 0.09–0.17 μg $L^{-1}$. And the intra-day and inter-day precision (RSD%) for the analytes at 20 and 100 μg $L^{-1}$ were in the range of 1.5–2.6% and 1.6–2.8%, respectively. The recoveries of bisphenols and 4-tert-octylphenol in water and milk samples were between 94.5 and 102.1%, and the RSDs were all in range of 1.7 to 4.1%.

## 1. Introduction

Bisphenol-A (BPA), bisphenol-AF (BPAF), tetrabromobisphenol-A (TBBPA) and 4-tert-octylphenol (4-TOP) are the main ingredients used for the production of synthetic plastic materials, adhesives, epoxy resins, drink and food packaging [1,2]. These phenolic compounds are considered as the endocrine disrupting compounds and have a serious impact on the humans and animals at low concentrations [3]. Due to the low concentrations of phenolic compounds existing in real samples, a sensitive, effective and rapid preconcentration method is necessary for the determination of BPs and 4-TOP prior to chromatographic analysis. Liquid phase microextraction (LPME), using a water-immiscible solvent as the extractant, is often employed for extraction and determination of phenolic compounds from complex matrices and can be selected as an alternative to traditional preparation techniques. Very recently, several extraction solvents, such as supercritical fluids, ionic liquids and supramolecular solvents, have been employed for the separation and preconcentration of trace levels of organic compounds [4–6]. ILs, as the eco-friendly extraction solvents, can be promising as they both have unique chemical and physical properties [7]. It has been widely used in dispersive liquid-liquid microextraction (DLLME) as an extraction solvent [7].

To facilitate the retrieval of the extracting solvent, researchers have combined extraction solvents with magnetic nanoparticles (MNPs) [8–10]. The ferrofluid based on the combination of MNPs and carrier liquid can be used to overcome some inconveniences in retrieving extractant. Ferrofluids, as a colloidal system, are stable suspensions of MNPs suspended in a carrier liquid such as ester, water and hydrocarbons [11]. The main interesting features of ferrofluids are the combination of fluid behavior and magnetic properties [12,13]. The stability of ferrofluids can be achieved through a number of different interactions (e.g. Vander Waals forces, magnetostatic interactions or dipolar attractive interactions) [9,12]. Because of their unusual magnetic, optical and electronic properties, the ferrofluid has been applied in nanotechnology and biomedicine [14,15].

Moreover, the magnetic nanoparticles for the ferrofluid should have a narrowly distributed particle size and nearly spherical shape [16]. Carbon quantum dots (CQDs), as the new class of carbon nanomaterials, are receiving increasing attention because of their high water solubility, small sizes, neglectable toxicity, environmental friendliness, favorable compatibility, high photostability and excellent photocatalytic activities [17–19]. And the tunable surface functionalization of CQDs was widely used in photocatalysis, optoelectronics, chemical and electronic sensor [20–23]. In addition, the presence of many polar moieties (e.g. —COOH and —OH) is also a hot research point, which can be used to improve the dispersion and hydrophilicity of materials, and meant to broaden their applications [24]. The possibility of carry-over occurred in the process of extraction can be also eliminated under the presence of CQDs.

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Hence, CQDs have been regarded as promising new materials in separation science, and have been widely applied in different materials and techniques [25–27].

In this study, a novel $Fe_3O_4$-OA/CQDs composite was synthesized through a simple one-pot method. The ferrofluid prepared by $Fe_3O_4$-OA/CQDs composite was then applied for the determination of phenolic compounds in water and pretreated milk samples. To the best of our knowledge, there is no report on using magnetically CQDs for the preparation of ferrofluids. In addition, the synthesized $Fe_3O_4$-OA/CQDs composites were characterized, and various factors affecting performance of the ferrofluid were also investigated in details. The feasibility of the ferrofluid for determination of phenolic compounds in real samples was further studied.

## 2. Experimental

### 2.1. Chemicals and standard solutions

All chemicals were analytical regent-grade and used as received. Bisphenol-A (BPA), bisphenol-AF (BPAF), tetrabromobisphenol-A (TBBPA) and 4-tert-octylphenol (4-TOP), iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and ammonium iron (II) sulfate hexahydrate ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$) were provided by Aladdin Industrial Corporation (Shanghai, China). 1-Butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIm]PF_6$), 1-pentyl-3-methylimidazolium hexafluorophosphate ($[C_5MIm]PF_6$), 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6MIm]PF_6$), 1-heptyl-3-methylimidazolium hexafluorophosphate ($[C_7MIm]PF_6$), 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8MIm]PF_6$) and 1-decyl-3-methylimidazolium hexafluorophosphate ($[C_{10}MIm]PF_6$) were all purchased from Center for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences (Lanzhou, China). The ILs were diluted twice with methanol before use. Ammonia solution ($NH_3 \cdot H_2O$) (25% w/w), sodium chloride (NaCl), sodium acetate (NaAc), citric acid, urea, magnesium sulfate ($MgSO_4$), acetonitrile (ACN), methanol (MeOH), ethanol and oleic acid (OA) were obtained from Tianjin chemical reagent Technology Co., Ltd. (Tianjin, China). Fig. S1 shows the structures of OA, 4-TOP, BPs and ILs. HPLC-grade acetonitrile and methanol were obtained from Merck (Darmstadt, Germany). Standards stock solutions (200 $\mu g\ mL^{-1}$) of BPs and 4-TOP were prepared in methanol and stored in the refrigerator at 4–8 °C. More diluted working solutions were prepared daily by appropriate dilution of the stock solutions with methanol. Ultrapure water used in the experiment was prepared by using Milli-Q Water Purification System (Millipore Corporation, Bedford, MA, U.S.A.).

### 2.2. Instrumentation

Fourier transform infrared (FTIR) spectra of prepared materials (4000–400 $cm^{-1}$) were recorded on the infrared spectrometer Tensor 27 (Germany, Bruker). Transmission electron microscopy (TEM) images of the sorbents were obtained with a Tecnai G2 F20 (FEI) electron microscope (200 kV, point-to point resolution 0.24 nm) (FEI, Holland). X-ray photoelectron spectroscopy (XPS) analysis were obtained using a Thermo Scientific K-Alpha (Thermo Fisher Scientific Inc., U.S.A.) X-ray powder diffraction (XRD) data were recorded on D/Max 2200 with Cu Kα radiation ($\gamma = 1.5405$ A) ranging from $2\theta = 5°$ to $90°$ (Rigaku, America). All pH values were detected by a pH-meter Sartorious PB20 (Göttingen, Germany). A vortex agitator (Jintan Guo Wang experimental instrument factory, Jingsu, China), ultrasonic cleaner (KMH1-120W, Shenzhen, China) and a vacuum drying oven (BPZ-5300, Shanghai, China) were used in the experiment.

The concentrations of BPs and 4-TOP were determined with an Agilent 1260 series HPLC system equipped with a UV–vis diode array detector (Agilent Technologies, America). The HPLC separation was performed on a reversed-phase system (Agilent TC-C18 column, 150 mm × 4.6 mm i.d., 5 μm) at column temperature of 25 °C. The mobile phase was performed as follows: 42% acetonitrile (0–8.0 min), 85% acetonitrile (8.0–11.0 min). The flow rate was set at 1 $mL\ min^{-1}$, and the detector was set to a wavelength of 280 nm.

### 2.3. Synthesis of $Fe_3O_4$-OA/CQDs

CQDs prepared through hydrothermal method were carried out as followings: 3.0 g citric acid and 1.0 g urea were dissolved into 20 mL water. Then the clear solution was transferred into a Teflon-lined stainless steel autoclave (50 mL) and maintained at 200 °C for 6 h. After it had cooled down, the solution was centrifuged at 12,000 rpm for 15 min to remove the insoluble substances. Finally, the yellow solution was filtered with a 0.22 μm membrane and dried overnight at 65 °C to obtain CQDs power.

A one-pot synthesis method was employed for the preparation of $Fe_3O_4$-OA/CQDs. In brief, CQDs (0.15 g) (the optimum amount of CQDs was obtained experimentally) and $FeCl_3 \cdot 6H_2O$ (4.10 g) were dissolved in 80 mL of deionized water under $N_2$ atmosphere with vigorous stirring. Then, the mixture was heated to 80 °C, and $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (2.82 g) was added. After stirred for 5 min, $NH_3 \cdot H_2O$ (10 mL) and OA (2 mL) were added drop-wise into the mixture containing $Fe^{3+}$/CQDs. The reaction was stirred at 80 °C for an additional time of 2 h. After cooling down to room temperature, the obtained $Fe_3O_4$-OA/CQDs were magnetically separated and washed repeatedly with ethanol for three times to remove the excess OA and CQDs, and vacuum-dried at 60 °C for 8 h. Finally, the $Fe_3O_4$-OA/CQDs were redispersed in deionized water via sonication and then used in the following experiments. The concentration of the prepared $Fe_3O_4$-OA/CQDs suspension was set to 24.5 $mg\ mL^{-1}$.

### 2.4. Preparation of ferrofluids

A range of ILs ($C_4$-$C_{10}$) (100 μL) and $Fe_3O_4$-OA/CQDs NPs (300 μL) were mixed in a screw cap polyethylene centrifuge tube by sonication for 3 min. After $Fe_3O_4$-OA/CQDs NPs were dispersed in IL, the obtained ferrofluid was magnetically collected and used for the following extraction process.

### 2.5. Extraction procedure

The extraction of BPs and 4-TOP by using prepared ferrofluid allowed rapid separation through an external supermagnet. First, a 20 mL aliquot of aqueous samples was placed in a 50 mL screw cap polyethylene centrifuge tube containing the ferrofluid. Then, the mixture was vortex-shaken immediately for 2 min. The solution pH was adjusted to 6.0 with 0.1 $mol\ L^{-1}$ HCl and NaOH. After 5 min, the ferrofluid were magnetically separated from the solution with an external magnet. Finally, 1 mL of MeOH containing 1% NaOH was used to elute the enriched BPs and 4-TOP from the isolated ferrofluid and 20 μL of the extract was injected into HPLC system for analysis.

### 2.6. Sample preparation

Milk samples were purchased from the local supermarket (Kunming, China). Lake water samples were collected from the LaoYu River (Kunming, China). Waste water samples were collected from the Chenggong wastewater treatment plant (Kunming, China). Water samples were filtered through a nylon membrane (0.45 μm) to remove insoluble substances and acidified to 6 with 0.1 $mol\ L^{-1}$ HCl and NaOH. The water and milk samples were stored at 4 °C before analysis and analyzed within 3 days.

Milk samples were pretreated to induce protein precipitation before the analysis of the milk samples. For this purpose, NaAc (0.2 g), $MgSO_4$ (0.8 g) and acetonitrile (4 mL) were added in to 10 mL of samples and then vortex-shaken for 1 min. After that, the mixture was centrifuged