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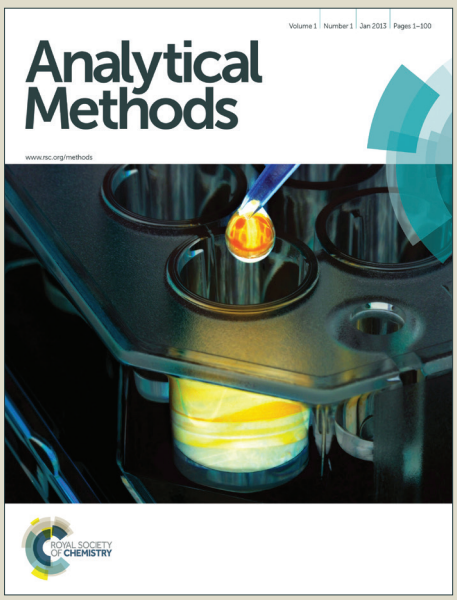





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# Mesoporous carbon reinforced hollow fiber liquid-phase microextraction for the enrichment of phenylurea herbicides followed by their determination with high performance liquid chromatography

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**Abstract:** In this paper, a new sample preparation method based on mesoporous carbon reinforced hollow fiber liquid phase microextraction (MC-HF-LPME) was developed for the extraction of some phenylurea herbicides (chlortoluron, isoproturon, monolinuron and buturon) in river water and soil samples prior to high performance liquid chromatography-diode array detection. Mesoporous carbon was synthesized using MCM-41 as a template and sucrose as a carbon precursor. The as-prepared mesoporous carbon was characterized by SEM, TEM and nitrogen adsorption. Several important parameters that affect the extraction efficiencies, such as concentration of ordered porous carbon, fiber length, extraction time, sample solution pH, salt addition and stirring rate, were investigated and optimized. Under the optimum conditions, the linearity for buturon was in the range of 0.3-100.0 ng $mL^{-1}$ and 5.0-300.0 ng $g^{-1}$ for river water and soil sample, respectively. The linearity for the other three analytes was in the range of 0.2-100.0 ng $mL^{-1}$ for river water sample, 2.0-300.0 ng $g^{-1}$ for soil sample. The limits of detection ($S/N$ = 3) of the method ranged from 0.05 to 0.1 ng $mL^{-1}$ for river water sample and 0.5 to 1.0 ng $g^{-1}$ for soil sample. The results indicated that the developed method is simple, efficient and environmentally friendly method for the extraction and determination of phenylurea herbicides in river water and soil samples.

**Keywords:** Hollow fiber liquid-phase microextraction; Mesoporous carbon; Phenylureas; High performance liquid chromatography

## Introduction

Phenylurea herbicides are commonly used in agriculture for controls of many annual and perennial weeds by inhibiting their photosynthesis pathways.[1] Because of their widespread use, they are detected in various environmental matrices, such as soil, water and crops. These compounds may produce a range of toxic side effects and can eventually pose risk to the environment and humans.[2] Some phenylureas have been included in the European "black list" and some are reported to be potential carcinogens.[3] Thus, monitoring phenylureas in different samples is of prime importance for the sake of human health and environmental pollution control. It is highly desirable to develop sensitive and efficient analytical methods to determine phenylurea herbicides at trace levels.

According to the literatures, phenylurea herbicides have been determined mostly by high-performance liquid chromatography (HPLC)[1-3] and gas chromatography (GC).[4] Nevertheless, because most phenylurea herbicides are thermally labile, they are not conducive to GC analysis without their prior derivatization.[4] So, HPLC analysis is a better choice than GC analysis and has become the most commonly used techniques for the determination of phenylurea herbicides.

Prior to chromatographic analysis, sample pretreatments are often required and are sometimes even crucial step of the whole analytical procedure to obtain accurate and sensitive results. For the determination of phenylurea herbicides, several sample preparation methods, including liquid-liquid extraction (LLE),[5] solid phase extraction (SPE),[6-7] solid-phase microextraction (SPME),[8-9] partitioned dispersive liquid–liquid microextraction (PDLLME),[1] and microwave assisted ionic liquid microextraction (MAILME),[10] and supercritical fluid extraction[11] have been developed.

Recently, a microextraction techniques called hollow fiber liquid-phase microextraction (HF-LPME), has attracted considerable research attentions since it is first introduced by Pedersen-Bjergaard and Rasmussen.[12] HF-LPME is one of the promising preconcentration techniques. It can provide a high analyte preconcentration factor for some analytes and has excellent clean-up efficiency as the hollow fiber can play a role as a filter. The large molecules can not permeate through the wall pores of the hollow fiber, which makes it very applicable to complex matrix samples. Moreover, the hollow fiber is disposable after each use due to its

cheapness, which can overcome the carry-over problems and enhance the reproducibility. However, since HF-LPME is a miniaturized extraction technique based on solvent microextraction, its sensitivity still need to be improved. To further improve the extraction efficiency of HF-LPME, carbon materials reinforced hollow fiber liquid phase microextraction has been reported. For example, carbon nanotubes (CNTs) reinforced hollow fiber solid/liquid phase microextraction have been developed for the determination of caffeic acid in medicinal plants,[13] carbamate pesticides in water and fruit samples,[14] and triazine herbicides in water and milk samples.[15] We have developed a graphene reinforced hollow fiber liquid phase microextraction method to pre-concentrate some carbamate pesticides[16] and phenylurea herbicides from different samples.[17] In these works, the CNTs or graphene were incorporated in a hollow fiber system and acted as a nanoscale solid-phase extractant with high surface area, which provide sites at which the analyte molecules can transfer from the donor to the acceptor phase and result in a higher selectivity and enrichment for the analytes.

Mesoporous carbon (MC) is a relatively new type of carbonaceous materials and has created much research interest in recent years. Due to the high surface area and large pore volume, mesoporous carbon materials could interact with targets analytes not only at their surfaces, but throughout the bulk of the materials.[18-19] Mesoporous carbon materials have been used as efficient adsorbents not only for the removal of dyes [20-23] and endocrine disrupting phenol (bisphenol A),[24] but also for the adsorption of alkaloids,[25] sulfur compound,[26] $CO_2$[27] and so on. These studies prove that porous carbon materials are efficient and promising adsorbents, which make it reasonable that MC might improve the extraction performance when it was introduced into HF-LPME. To the best of our knowledge, mesoporous carbon reinforced hollow fiber liquid phase microextraction (MC-HF-LPME) has not yet been reported.

In the present work, MC-HF-LPME was developed for the first time for the extraction of phenylurea residues in water and soil samples prior to their determination by HPLC with diode array detection. The developed method could provide both preconcentration and clean-up effect for the analytes in a single step and had a good performance in terms of linearity, selectivity, sensitivity and repeatability.

# Experimental

## Chemicals and materials

The standards of phenylurea herbicides (chlortoluron, isoproturon, monolinuron and buturon) were purchased from Aladdin-reagent (Shanghai, China). Chromatography-grade acetonitrile, methanol, and other chemicals (acetone, hydrochloric acid, sodium hydroxide, hydrofluoric acid (HF), 1-octanol, ethyl acetate, tetrahydrofuran and *n*-hexane) were purchased from Huaxin Chemical Reagent Company (Baoding, China). Sodium chloride (NaCl) was from Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). The water used throughout the work was purified by a SZ-93 automatic double-distiller purchased from Yarong Biochemistry Instrumental Factory (Shanghai, China). A 85-2B temperature-controlled magnetic stirrer was obtained from Jintan (Jiangsu, China). Accurel Q 3/2 polypropylene hollow fiber membrane (200 μm thick wall, 600 μm inner diameter and 0.2 μm average pore size) was bought from Membrana GmbH (Wuppertal, Germany). MCM-41 molecular sieve was purchased from Nanjing XFNANO Materials Tech Co., Ltd (Nanjing, China). A stock solution containing chlortoluron, isoproturon, monolinuron and buturon 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 $^{o}$C and protected from light. River water was collected from Baoding (Baoding, China). Soil samples were collected from the plough layer of the field at Xixiaozhuang (Baoding, China).

## Instruments

The HPLC system, assembled from modular components (Waters, Milford, MA, USA), consisted of an in-line degasser, a 600E pump, and a diode array detection (DAD) system. A Millennium 32 workstation (Waters) was utilized to control the system and for the acquisition and analysis of the data. The injection loop volume was 20.0 μL. A Centurysil $C_{18}$-BDS column (250 mm × 4.6 mm I.D., 5.0 μm) from Dalian Johnsson Separation Science Technology Corporation (Dalian, China) was used for separations. The mobile phase was a mixture of methanol-water (85:15, v/v) at a flow rate of 1.0 mL $min^{-1}$. DAD monitoring wavelengths were chosen at 254 nm. The identification of

the four phenylurea insecticides was made by both their retention times and ultraviolet absorption spectra by DAD detection. The peak area of each analyte was used for quantification.

The pH of the solution was measured with a PHS-3C digital pH meter (Hangzhou Dongxing Instrument Factory, Hangzhou, Zhejiang, China).

The size and morphology of the MC 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-3000N microscope (Hitachi, Japan). The Brunauer–Emmett–Teller (BET) surface areas were determined from the $N_2$ adsorption at 77 K using Tristar Ⅱ 3020 (USA).

**Synthesis of MC**

Mesoporous carbon material was synthesized using MCM-41 molecular sieve as a template and sucrose as a carbon source according to the reported methods[28-30] with some modifications. The typical synthetic procedures are as follows. Typically, 1 g MCM-41 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, 0.11 mL $H_2SO_4$ (98 wt%) was added. After being stirred for 10 min, the mixture was heated in an oven at 100 ℃ for 6 h and at 160 ℃ 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, 0.06 mL of $H_2SO_4$ (98 wt%) and 5 ml of distilled water, the mixture was treated again at 100 ℃ for 6 h and at 160 ℃ for 6 h. The obtained MCM-41/sucrose composite was carbonized in a conventional furnace at 900 ℃ for 2 h in nitrogen flow. Subsequently, the MCM-41 template was removed by mixing the composite with 20 ml of HF (25% wt%) for 10 h and the obtained mesoporous carbon was rinsed with ethanol and distilled water, respectively, to neutralize the material surface. Finally, the MC material was air-dried and then introduced into hollow fiber system for the extraction of target analytes from samples. The overall preparation process is illustrated in Scheme 1.

**Sample preparation**

Water samples were filtered through 0.45 μm filter prior to extraction by MC-HF-LPME. Soil samples were air-dried at room temperature, pulverized and passed through 250-μm sieve. 5.0 g of the soil sample was accurately weighed and put into a 50 mL centrifuge tube, to which 10.0 mL

double-distilled water was added. The resultant sample mixture was first vigorously shaken on a vibrator for 30 min and then centrifuged at 4000 rpm for 5 min. After that, the sediment was washed with 1.0 mL acetonitrile by vortex for 1 min, and then centrifuged. This washing process was repeated again. All the supernatants were combined together and double-distilled water was added into the supernatants to complete the volume of 20.0 mL.

**MC reinforced HF-LPME procedures**

The polypropylene hollow fiber tubes were cut into 6.0-cm segments. Each piece was employed only once to avoid any possible memory effect. Before use, the segments were ultrasonically cleaned in acetone for 5 min in order to remove any impurities and then dried in air. After that, the fiber was immersed entirely in 1-octanol for 30 s. The excess of 1-octanol was carefully removed by washing the hollow fiber with double-distilled water under ultrasound. The acceptor phase (15.0 μL of 1.5 mg $mL^{-1}$ MC in 1-octanol) was injected into the lumen of the hollow fiber with a 25-μL syringe. Then both sides of the fiber were sealed with heated tweezers.

For each extraction, the impregnated and filled fiber was placed in a 30 mL screw cap glass vial containing 20.0 mL of the sample solution, 3.0 g NaCl and a magnetic stir bar. The extraction process was performed at 800 rpm stirring rate for 30 min. Then, the fiber was taken out from the glass vial carefully and transferred into a 500 μL micro-vial. The analytes were desorbed from the fiber with 50.0 μL of acetonitrile by vortex for 2 min. Finally, 20.0 μL desorption solution was injected into HPLC for analysis.

## Results and discussion

**Characterization of the MC nanocomposite**

The MCM-41 molecular sieve was used as a template to prepare the mesoporous carbon. The morphology of the silica particles and their structural characteristics are preserved in the MC. This can be deduced from the SEM and TEM images (Fig. 1). The carbon replica, like the MCM-41 molecular sieve, was nanoporous carbon with interconnected hierarchical pore structures. Fig. 2 shows the sorption isotherm of the carbon material exhibits broad capillary condensation steps, which suggests that the porosity is made up of pores of a wide range of sizes. The MC has a BET surface area of 302 $m^2$ $g^{-1}$ and a pore volume of 0.34 $cm^3$ $g^{-1}$. The mesopores

network with size 4.5 nm has been generated by the removal of the silica walls.

**Optimization of HPLC conditions**

For the separation of phenylurea herbicides, reversed-phase HPLC has been most commonly employed[1-3]. In this study, different ratios of methanol to water as mobile phase were investigated on a Centurysil $C_{18}$-BDS column (250 mm × 4.6 mm I.D., 5.0 μm) for the separation of phenylurea herbicides in water and soil samples. As a result, the best separation was achieved with methanol-water (85:15, v/v) as mobile phase at a flow rate of 1.0 mL $min^{-1}$. Since the maximum absorption wavelengths of the target pesticides were at 254 nm, DAD monitoring wavelength was chosen at 254 nm for quantification data handling. In such conditions, there were no interfering peaks coming from sample co-extractives.

**Optimization of the MC-HF-LPME conditions**

In order to choose the optimum experimental conditions, 20.0 mL double-distilled water spiked with 50.0 ng $mL^{-1}$ each of the four phenylurea herbicides was used to study the extraction performance under the following different experimental conditions. All the experiments were performed in triplicate and the means of the results were used for evaluation.

**Selection of extraction solvent for the acceptor phase**

Organic extraction solvents in HF-LPME play a key role in achieving a good extraction performance for the analytes. Generally, the selected organic solvent has to satisfy the following requirements[15-16]. Firstly, the organic solvent should be compatible with the hollow fiber to fill the pores of the fiber completely. Secondly, it should have high partition coefficient for the analytes. Thirdly, it should be immiscible with sample solution and nonvolatile to prevent solvent loss over the extraction time. Finally, in this study, a good dispersion capability for MC is also necessary. Based on these criteria and previous experiment exploration in HF-LPME[13-17], four organic solvents, i.e., 1-octanol, *n*-hexane, ethyl acetate and methylene chloride, were investigated. As a result, 1-octanol exhibited the highest extraction efficiency for the analytes and therefore was selected as the extraction solvent for the acceptor phase.

**Effect of the concentration of MC**

In order to evaluate the effect of the addition of MC into the acceptor phase on the extraction efficiency, the concentration of MC ranging from 0 to 3 mg $mL^{-1}$ was tested. As shown in Fig. 3, the extraction efficiency increased with increased concentration of MC. When the concentration of MC exceeded 1 mg $mL^{-1}$, the peak areas of the analytes remained almost the same. In order to guarantee the MC was enough to adsorb the analytes at the upper limit of the standard curve, 1.5 mg $mL^{-1}$ of the MC was chosen for the following studies.

**Fiber length**

In the proposed method, the amount of sorbent material is relevant to the hollow fiber length. In general, extraction efficiency will increase with the increasing of the length of hollow fiber. In order to evaluate the influence of the length of hollow fiber on the extraction, the length of hollow fiber ranging from 3 to 8 cm was tested. Fig. 4 showed that the peak areas of the analytes were increased by increasing the length of hollow fiber from 3 to 6 cm and then remained almost unchanged. The reason could be that when the fiber was longer than 6 cm, the fiber could not be immersed completely in the sample solution, which resulted in no further increase in extraction efficiency. Accordingly, a 6 cm hollow fiber was used for subsequent experiments.

**Effect of extraction time**

The extraction time is an important factor in HF-LPME procedure because it influences the partition of the target analytes between the sample matrix and the organic solvent, and subsequently between the organic solvent and the MC. Compared with the conventional HF-LPME mode, nanoparticles adsorbent reinforced HF-LPME could lead to a longer equilibrium time since the mass transfer involved a process of diffusion through the nanometer sized pores of the adsorbent [13]. In this work, a series of extraction times from 10 to 60 min were tested to investigate the effect of extraction time. The result showed that the peak areas for the analytes increased by increasing the extraction time up to 30 min and then no significant changes were observed. This result indicates that the extraction equilibrium could be achieved within 30 min. Although HF-LPME is not an exhaustive extraction process, maximum sensitivity is attained at equilibrium conditions. Therefore, an extraction time of 30 min was chosen for the experiment.

**Effect of stirring rate**

According to mass-transfer theory, in the multiphase systems, the rate of agitation plays a dominant

role. The contact area of the phases can be increased with a higher agitation rate. In fact, an appropriate stirring rate can increase extraction efficiency and reduce the extraction equilibrium time because it can increase the contacting frequencies between the analytes and the fiber, and improve the mass-transfer rate of the analytes from the donor phase into the acceptor phase. So stirring rate is an important parameter that requires to be optimized. In this study, the effect of the stirring rate was investigated in the range from 200 to 1000 rpm. The results revealed that increased stirring rate resulted in an enhanced extraction efficiency before 800 rpm and then extraction efficiency remained almost unchanged when the stirring rate was above 800 rpm, which may be due to the fact that the higher stirring speed led to mechanical stress of the fiber, and exacerbated fiber collisions with the wall of the vial and the formation of air bubbles on the hollow fiber surface, affecting the extraction accuracy and reproducibility. So a stirring rate of 800 rpm was chosen.

**Effect of the sample solution pH**

The sample solution pH can sometimes influence the existing forms of the analytes**,** and then influence the extraction efficiency. Therefore, in the present work, the effect of the sample solution pH was surveyed from 2 to 10 by adjusting it with 0.1 mol $L^{-1}$ hydrochloric acid or 0.1 mol $L^{-1}$ sodium hydroxide solution. Fig. 5 shows that the extraction efficiency of the analytes remained almost constant at pH between 2.0 and 7.0. When the pH was higher than 7.0, the extraction efficiency decreased slightly, which could be ascribed to the decomposition of the phenylureas at higher pH values. The phenylureas are urea derivatives, and they are neutral compounds. Therefore, the pH of the sample solution had a negligible effect on the extraction efficiency, which was in agreement with the reported result [3,17,31]. The pH of the water and soil sample solutions was normally at about 5-6, thus there is no need to adjuste the pH of the sample solution before extraction.

**Effect of salt addition**

The addition of salt to the sample solution can decrease the solubility of the analytes and therefore enhance extraction efficiency. The effect of salt concentration on the extraction efficiency of the analytes was evaluated by adding different amounts of NaCl ranging from 0 to 25% (w/v). The results indicated that the peak area increased when the concentration of salt was increased from 0% to 15%, and the peak areas remained nearly constant when the concentration of salt was further increased. Therefore, the 15% concentration of salt was selected.

**Effect of the desorption condition**

After extraction, the analytes should be desorbed using an organic solvent from the MC reinforced HF-LPME system for HPLC analysis. In this experiment, three different organic solvents, i.e., acetonitrile, methanol and acetone, were evaluated for this purpose since they are HPLC compatible solvents. The results showed that these solvents provided similar desorption power, but a better chromatographic peak shape was obtained when acetonitrile was used. Thus, acetonitrile was selected as the desorption solvent. The volume of acetonitrile was optimized in the range from 30 to 100 μL and as a result, 50 μL yielded the best desorption result. When the acetonitrile volume was lower than 50 μL, it was not enough for the complete desorption of the analytes. On the other hand, the higher volumes could reduce the enrichment factor of the method. The desorption time was investigated by vortex for the time in the range from 1 to 5 min. It was found that peak areas of the analytes reached the highest values at desorption time of 2 min. Hence, desorption time of 2 min was chosen for further study.

**Validation of the method**

Based on the above optimization, the analytical characteristics of the optimized MC-HF-LPME method in terms of its linear range (LR), limits of detection (LODs) and repeatability were investigated for water and soil samples.

For water sample, a series of working solutions containing each of the phenylureas at six concentration levels of 0.2, 0.3, 0.5, 1.0, 10.0, 50.0 and 100.0 ng $mL^{-1}$ were prepared for the construction of the calibration curves. For soil sample phenylureas -free soil sample was used as blanks for matrix-matched standard calibrations. An appropriate amount of mixture standard solution of the analytes was added into 5.0 g of the homogenized soil sample, and then the sample was prepared according to the procedures described in section 2.3. A series of standard samples containing the four phenylureas at six concentration levels of 2.0, 5.0, 10.0, 50.0, 100.0 and 300.0 ng $g^{-1}$ were prepared for the construction of the calibration curves. For each level, five replicate extractions and determinations were performed under the optimized experimental conditions. The results are listed in Table 1. A good linear relationship between the corresponding peak areas and the concentrations was obtained for both water and soil samples, with the correlation coefficients ($r$) of 0.9929-0.9992. The LODs (S/N= 3) of the method were between 0.05 and 0.1 ng $mL^{-1}$ for water sample, between 0.5 and 1.0 ng $mL^{-1}$ for soil samples. The repeatability study was carried out by

five parallel experiments at the concentration of 10.0 ng $g^{-1}$ each of the phenylureas under the optimal conditions. The relative standard deviations (RSDs) varied from 4.6% to 6.8%. These results showed that the method has a high sensitivity and good repeatability. To further validate the method, the present method was compared with the previously reported graphene reinforced HF-LPME methods for the determination of phenylureas in terms of the linear range, LODs, and RSD. The comparison results are shown in Table 2, from which one can see that the RSD of the present method are comparable with that of graphene reinforced HF-LPME method, but the current method has much lower LODs and wider linear range than that obtained with graphene reinforced HF-LPME method, which prove that MC has higher adsorption ability for the phenylureas than graphene, and this technique is very effective sample preparation/pre-concentration technique.

**Analysis of real samples**

To evaluate the applicability of the developed method, the extraction and determination of the phenylureas in river water and soil samples were performed under the optimized experimental conditions. As a result, chlortoluron, isoproturon, and monolinuron were found at 0.91 ng $mL^{-1}$, 0.44 ng $mL^{-1}$, and 0.48 ng $mL^{-1}$ in water sample, respectively. In soil sample, only monolinuron was found to be at 3.78 ng $g^{-1}$.

In order to validate the accuracy of the method, the water samples were spiked with the standards of the phenylureas at the concentration of 2.0 and 20.0 ng $mL^{-1}$, and soil samples were spiked at 30.0 and 100.0 ng $g^{-1}$, respectively. For each concentration level, five parallel experiments were carried out. The results showed that the recoveries for the phenylureas were in the range from 91.8% to 106.5% with RSDs between 4.9% and 7.3% (see Table 3), which indicated that the new method was applicable for the analysis of the analytes in real samples. Fig. 6 shows the typical chromatograms of the extracted analytes from water and soil sample before and after being spiked with each of the four phenylureas.

## Conclusions

In this work, the MC reinforced HF-LPME method was developed for the first time and successfully applied for the analysis of four phenylureas in real samples. Because of the combination of the outstanding adsorption capability of MC and the excellent clean-up efficiency of the HF-LPME, this method has exhibited good precision and high sensitivity. The hollow fiber is disposable, so the single use of the hollow fiber reduces the risk of cross-contamination and carry-over problems. In addition, the MC-HF-LPME combined with HPLC is simple and low-cost

technique, and would have a significant application potential for the analysis of other environmental pollutants.

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## Table Captions

**Table 1** Analytical performance data for the phenylurea herbicides in river water and soil samples by the the MC-HF-LPME technique.

**Table 2** Comparison of MC reinforced HF-LPME method with Graphene reinforced HF-LPME for the determination of the phenylurea herbicides.

**Table 3** Determination of the four phenylurea herbicides and recoveries in river water and soil samples.

## Scheme Caption

**Scheme 1.** Schematic illustration of the preparation processes of the MC-HF

## Figure Captions

**Fig. 1** The SEM (a) and TEM (b) images of the mesoporous carbon.

**Fig. 2** The $N_2$ adsorption–desorption isotherms of the mesoporous carbon.

**Fig. 3** Effect of the concentration of mesoporous carbon in acceptor phase. Extraction conditions: sample volume; 20 mL; fiber length; 6 cm; stirring rate; 800 rmp; extraction time; 30 min; concentration of NaCl; 15%; desorption solvent; acetonitrile 50 μL; concentration of analytes; 100 ng $mL^{-1}$.

**Fig. 4** Effect of the fiber length. Extraction conditions: sample volume; 20 mL; concentration of ordered mesoporous carbon in acceptor phase;1.0 mg $mL^{-1}$; stirring rate; 800 rmp; extraction time; 30 min; concentration of NaCl; 15%; desorption solvent; acetonitrile 50 μL; concentration of analytes; 50 ng $mL^{-1}$.

**Fig. 5** Effect of the sample solution pH. Extraction conditions: sample volume; 20 mL; concentration of ordered mesoporous carbon in acceptor phase;1.0 mg $mL^{-1}$; fiber length; 6 cm; stirring rate; 800 rmp; extraction time; 30 min; concentration of NaCl; 15%; desorption solvent; acetonitrile 50 μL; concentration of analytes; 50 ng $mL^{-1}$.

**Fig. 6** The typical chromatograms for soil sample (A) and the soil sample spiked with phenylurea herbicides at each concentration of 80.0 ng $g^{-1}$ (B); river sample (C) and the river sample spiked with phenylurea herbicides at each concentration of 5.0 ng $mL^{-1}$ (D). Peak identification: 1. Chlortoluron; 2. Isoproturon; 3. Monolinuron; 4. Buturon.

**Table 1** Analytical performance data for the phenylurea herbicides in river water and soil samples by the the MC-HF-LPME technique.

| Herbicides | River water sample ($n$ = 5) | | | | Soil sample ($n$ = 5) | | | |
|---|---|---|---|---|---|---|---|---|
| | LR (ng $mL^{-1}$) | $r$ | LOD (ng $mL^{-1}$) | RSDs (%) | LR (ng $g^{-1}$) | $r$ | LOD (ng $g^{-1}$) | RSDs (%) |
| Chlortoluron | 0.2-100.0 | 0.9979 | 0.05 | 4.6 | 2.0-300.0 | 0.9929 | 0.5 | 6.6 |
| Isoproturon | 0.2-100.0 | 0.9992 | 0.05 | 5.8 | 2.0-300.0 | 0.9952 | 0.5 | 6.8 |
| Monolinuron | 0.2-100.0 | 0.9987 | 0.05 | 6.2 | 2.0-300.0 | 0.9974 | 0.5 | 6.4 |
| Buturon | 0.3-100.0 | 0.9985 | 0.1 | 5.4 | 5.0-300.0 | 0.9945 | 1.0 | 5.7 |

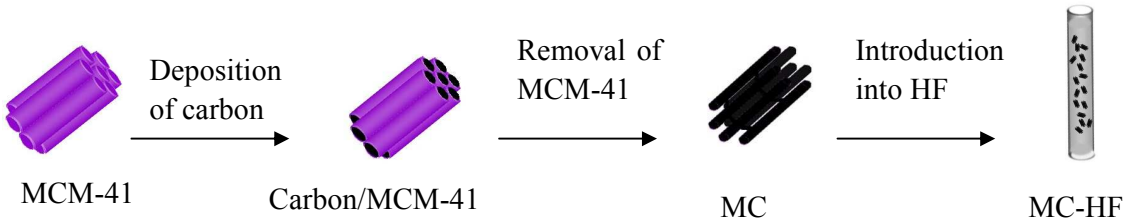
**Table 2** Comparison of MC reinforced HF-LPME method with Graphene reinforced HF-LPME for the determination of the phenylurea herbicides.

| Methods | Sample | Linearity ($ng\ mL^{-1}$) | LOD ($ng\ mL^{-1}$) | RSD (%) | References |
|---|---|---|---|---|---|
| Graphene reinforced HF-LPME | milk | 10.0-400.0 | 1.6-2.0 | 5.2-7.4 | [17] |
| MC reinforced HF-LPME | water | 0.2-100.0 | 0.05-0.1 | 4.6-6.2 | This method |
| | soil | 2.0-300.0 ($ng\ g^{-1}$) | 0.5-1.0 ($ng\ g^{-1}$) | 5.7-6.8 | |

**Table 3** Determination of the four phenylurea herbicides and recoveries in river water and soil samples.

| Herbicides | River water sample ($n$ = 5) | | | | Soil sample ($n$ = 5) | | | |
|---|---|---|---|---|---|---|---|---|
| | Spiked (ng mL$^{-1}$) | Found (ng mL$^{-1}$) | R[a] (%) | RSDs (%) | Spiked (ng g$^{-1}$) | Found (ng g$^{-1}$) | R[a] (%) | RSDs (%) |
| Chlortoluron | 0 | 0.91 | | | 0 | nd[b] | | |
| | 2.0 | 3.03 | 106.0 | 6.5 | 30.0 | 31.32 | 104.4 | 7.2 |
| | 20.0 | 21.44 | 102.6 | 5.7 | 100.0 | 103.44 | 103.4 | 5.9 |
| Isoproturon | 0 | 0.44 | | | 0 | nd[b] | | |
| | 2.0 | 2.53 | 104.5 | 6.3 | 30.0 | 31.75 | 105.8 | 7.3 |
| | 20.0 | 20.77 | 101.7 | 6.6 | 100.0 | 106.47 | 106.5 | 6.8 |
| Monolinuron | 0 | 0.48 | | | 0 | 3.78 | | |
| | 2.0 | 2.33 | 92.5 | 6.1 | 30.0 | 32.11 | 94.4 | 6.5 |
| | 20.0 | 19.45 | 94.8 | 5.4 | 100.0 | 100.24 | 99.5 | 4.9 |
| Buturon | 0 | nd[b] | | | 0 | nd[b] | | |
| | 2.0 | 1.94 | 97.0 | 6.4 | 30.0 | 28.94 | 96.5 | 6.4 |
| | 20.0 | 18.35 | 91.8 | 5.5 | 100.0 | 98.37 | 98.4 | 5.6 |

R[a]: recovery of the method; nd[b]: not detected.




**Scheme 1.** Schematic illustration of the preparation processes of the MC-HF

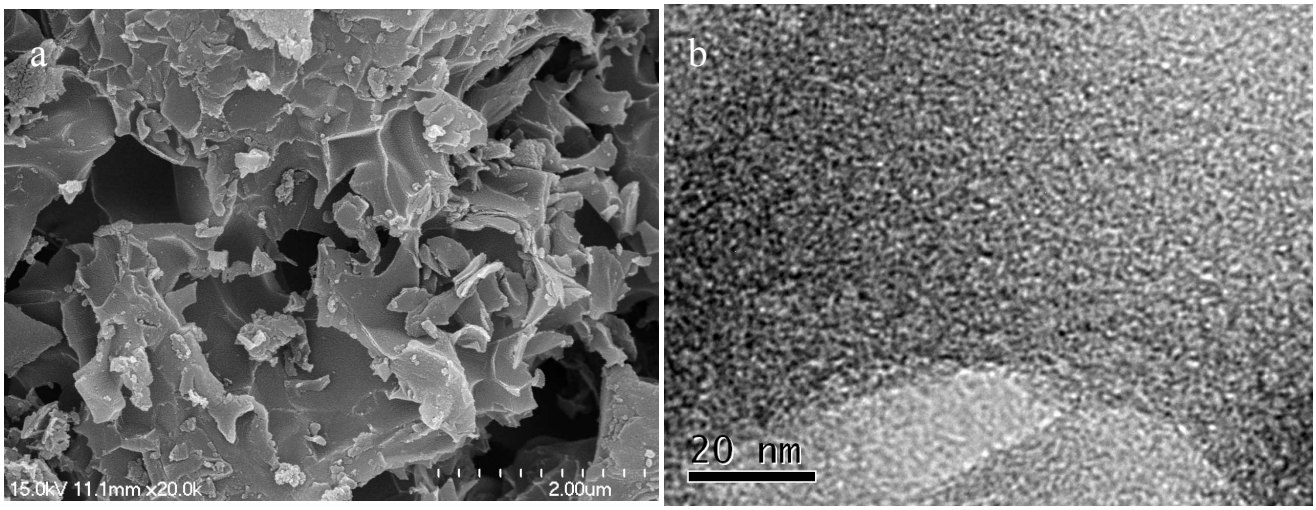



**Fig. 1** The SEM (a) and TEM (b) images of the mesoporous carbon.

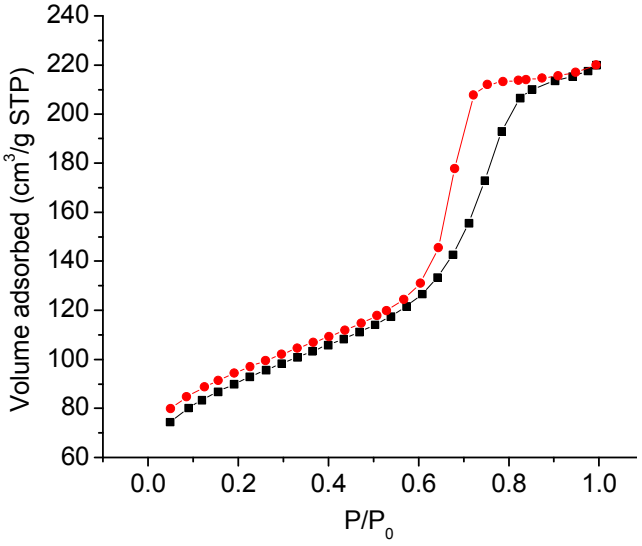



**Fig. 2** The $N_2$ adsorption–desorption isotherms of the mesoporous carbon.

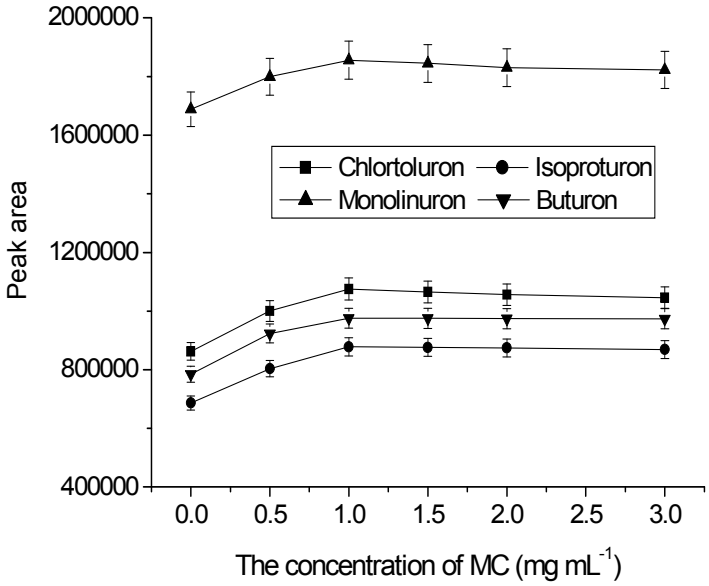



**Fig. 3** Effect of the concentration of mesoporous carbon in acceptor phase. Extraction conditions: sample volume; 20 mL; fiber length; 6 cm; stirring rate; 800 rmp; extraction time; 30 min; concentration of NaCl; 15%; desorption solvent; acetonitrile 50 μL; concentration of analytes; 100 ng $mL^{-1}$.

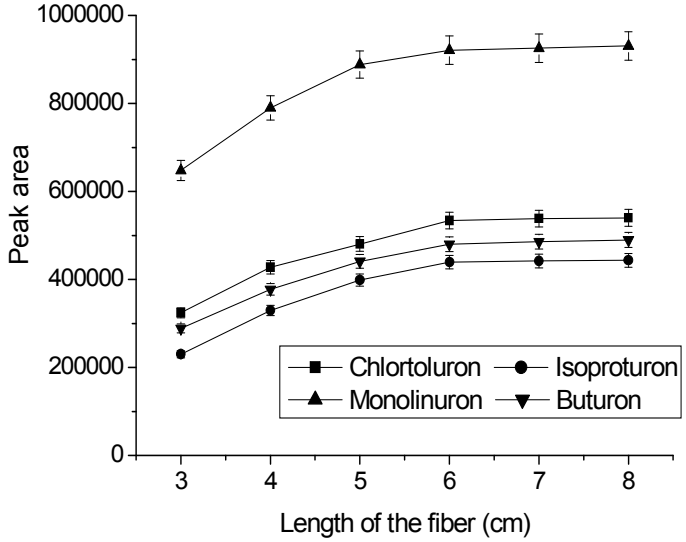



**Fig. 4** Effect of the fiber length. Extraction conditions: sample volume; 20 mL; concentration of ordered mesoporous carbon in acceptor phase;1.0 mg $mL^{-1}$; stirring rate; 800 rmp; extraction time; 30 min; concentration of NaCl; 15%; desorption solvent; acetonitrile 50 µL; concentration of analytes; 50 ng $mL^{-1}$.

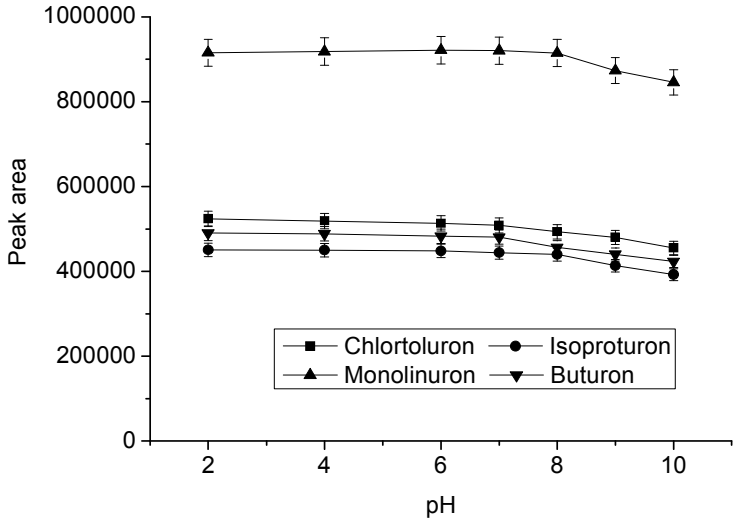



**Fig. 5** Effect of the sample solution pH. Extraction conditions: sample volume; 20 mL; concentration of ordered mesoporous carbon in acceptor phase;1.0 mg $mL^{-1}$; fiber length; 6 cm; stirring rate; 800 rmp; extraction time; 30 min; concentration of NaCl; 15%; desorption solvent; acetonitrile 50 μL; concentration of analytes; 50 ng $mL^{-1}$

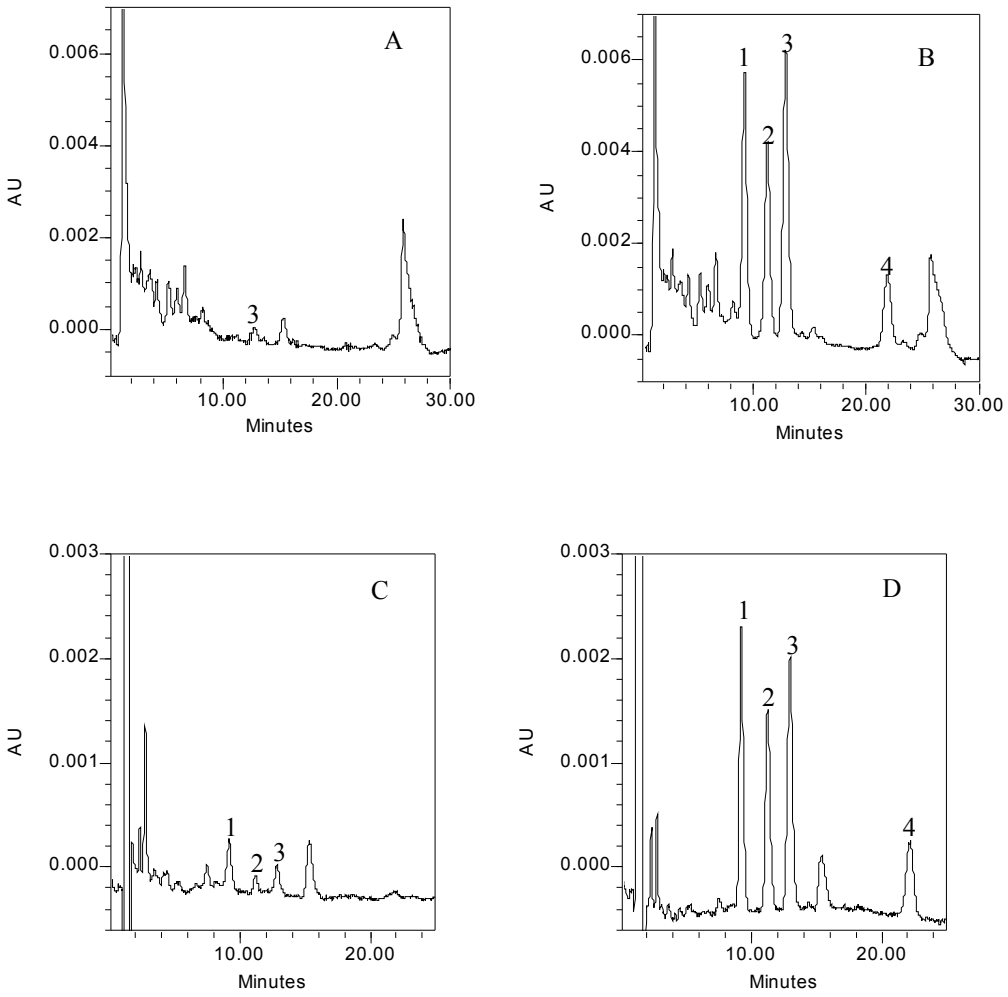



**Fig. 6** The typical chromatograms for soil sample (A) and the soil sample spiked with phenylurea herbicides at each concentration of 80.0 ng $g^{-1}$ (B); river sample (C) and the river sample spiked with phenylurea herbicides at each concentration of 5.0 ng $mL^{-1}$ (D). Peak identification: 1. Chlortoluron; 2. Isoproturon; 3. Monolinuron; 4. Buturon.