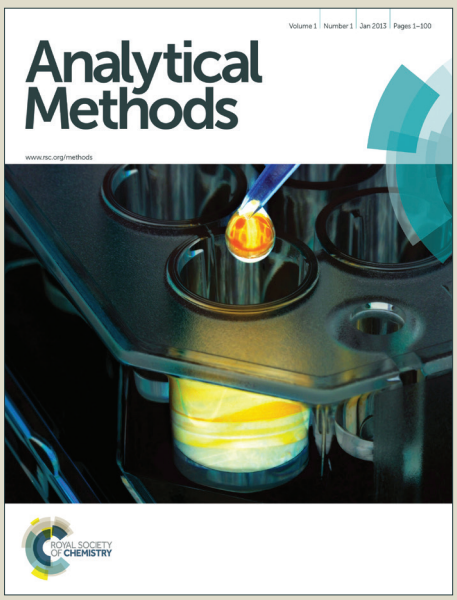
Analytical Methods

Accepted Manuscript



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Magnetic porous carbon based solid-phase extraction coupled with high performance liquid chromatography for the determination of neonicotinoid insecticides in environmental water and peanut milk samples

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Abstract Magnetic ordered porous carbon (MOPC-ZSM-5) was synthesized using zeolite ZSM-5 as a template and sucrose as a carbon source. It was used as a magnetic solid-phase extraction adsorbent for the extraction of four neonicotinoid insecticides (acetamiprid, imidacloprid, thiacloprid and thiamethoxam) from river water and peanuts milk samples prior to high performance liquid chromatography-ultraviolet detection. The calibration curves for the four neonicotinoid insecticides in water sample showed linearity from 1.0 to 200.0 ng mL^{-1} for thiamethoxam, imidacloprid, thiacloprid, and 0.5 to 200.0 ng mL^{-1} for acetamiprid. For peanuts milk sample, the linearity was observed in the range of 6.0-1000.0 ng mL^{-1} for thiamethoxam, imidacloprid, thiacloprid, and 3.0-1000.0 ng mL^{-1} for acetamiprid, respectively. The developed method has been successfully applied to the determination of the four neonicotinoid insecticides in river water and peanut milk samples, and a satisfactory result was obtained.

Keywords: Magnetic ordered porous carbon; Neonicotinoid insecticides; Peanut milk sample; Water sample; High performance liquid chromatography

Introduction

Due to their low bioaccumulation and broad spectrum of activity, neonicotinoid insecticides, as a new type of pesticides, are currently widely used for foliar and seed treatments in agriculture to control a wide range of plant pest insects, including mealy bugs, aphids and whiteflies. [1] Like nicotine, neonicotinoids are potent antagonists of nicotinic acetylcholine receptor agonists. Since the binding affinity of most neonicotinoids is higher for acetylcholine receptor agonists from insects than those from mammals, these insecticides are selectively more toxic to insects than mammals. [2] Neonicotinoid insecticides are commonly used on maize, rice, sunflowers, sugar beets, peanuts, rape, vegetables, fruits crops and potatoes. [3] However, their residues could give rise to a serious risk for the health and safety of the consumers. Therefore, sensitive, efficient and selective analytical methods for them are desirable to monitor trace levels of these compounds in food and environmental samples.

Due to their low volatility and high polarity, neonicotinoid pesticides are unsuitable for the direct analysis by gas chromatography (GC). [4] They are usually determined by high performance liquid chromatography (HPLC) with different detections including ultraviolet detection (UV), [5] thermal lens spectrometric detector (TLS), [6] diode array detection (DAD), [7-9] mass spectrometric detection (MS) [10-13] and fluorescence detection (FLD). [14] Although HPLC-MS or HPLC-MS-MS techniques for multiresidue determination of various pesticides are more sensitive and selective than the commonly used HPLC-UV, it is well known that the HPLC-MS or HPLC-MS-MS instrumentation is fairly expensive and they are not always available in all common analytical laboratories for pesticide residue analysis. Therefore, the analysis of pesticide residues by HPLC with UV detection is still highly desirable for the routine monitoring of pesticide residues. However, for the

determination of trace level of neonicotinoid residues in real samples by HPLC-UV, an effective prior sample pretreatment for the enrichment of the analytes is often necessary.

For the enrichment of neonicotinoid insecticide residues from food samples like milk, honey and vegetables, liquid–liquid extraction (LLE) [8, 15] and solid phase extraction (SPE) [11, 12] are the most commonly used sample preparation techniques. However, LLE and SPE suffer from some drawbacks, such as the consumption of large quantities of toxic organic solvents, multiple operation steps, relatively high cost, and possible interferences from co-eluted compounds. To overcome these shortcomings in LLE and SPE, a new mode of SPE named magnetic solid-phase extraction (MSPE) has been developed. [16] MSPE is an efficient extraction method which is based on the use of magnetic or magnetically modified nanoparticles as adsorbents for the SPE extraction. [17-19] MSPE is convenient, simple and economic since magnetic adsorbent used in MSPE can be readily isolated from the sample solution by only the use of a magnet but without the need of the procedures like filtrations or centrifugations often encountered in traditional SPE. The merit of using magnetic functionalized material as the adsorbent renders MSPE a promising technique for sample preparation. Since the adsorbent plays a key role in MSPE, various functionalized magnetic materials, such as C18, activated carbon, graphene and carbon nanotubes-based magnetic nanoparticles have been prepared and applied to enrich pesticides or extract environmental pollutants from environmental samples. [20-23]

Recently, porous carbon materials have been paid much attention due to their high specific surface area, tunable pore size, high chemical stability, low density, good corrosion resistance, and good electrical and thermal conductivity. [24, 25] Porous carbon materials have been extensively used as adsorbents [26, 27], catalyst supports, [28, 29] super capacitors [30] and fuel cells. [31, 32] A key challenge for

the applications of porous carbon materials is to build up a simple and efficient method to synthesize them. To achieve this goal, several methods have been developed to fabricate porous carbon materials in the recent years. [33, 34] Among them, the template method has attracted much attention for the preparation of porous carbon materials. [35, 36] So far, various templates including metal-organic frameworks, [37, 38] silica, [39, 40] and molecular sieve [41, 42] have been successfully used.

Recently, the zeolite ZSM-5 has been successfully employed as the template for the synthesis of mesoporous carbon materials. The zeolite ZSM-5 is a medium-pore molecular sieve with ellipsoidal tubular pores with 10-membered oxygen rings. However, there are only a very few reports about the applications of ZSM-5-based magnetic porous carbon materials as the adsorbent for the extraction or removal of organic pollutants. [43-45]

In this work, a magnetic ordered porous carbon (MOPC-ZSM-5) was synthesized using zeolite ZSM-5 as a template and sucrose as a carbon source. The MOPC-ZSM-5 was then explored as an adsorbent for the simultaneous extraction and concentration of four neonicotinoid insecticides (acetamiprid, imidacloprid, thiacloprid and thiamethoxam) from river water and peanut milk samples prior to HPLC-UV. To the best of our knowledge, this may be the first report about the application of such an adsorbent for the extraction of neonicotinoid insecticides from river water and peanut milk samples.

Experimental

Reagents and material

ZSM-5, MCM-41 and SBA-15 were obtained from Boaixin Chemical Reagents Company (Baoding,

China). Certified pesticide standards (99%) of imidacloprid (ICL), acetamiprid (ACT), thiamethoxam (TMX) and thiacloprid (TCL) were purchased from Agricultural Environmental Protection Institution (Tianjin, China). Their chemical structures are shown in Fig. 1. $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ were purchased from Chengxin Chemical Reagents Company (Baoding, China). HPLC-grade methanol was obtained from Sinopharm Chemical Reagent Co. (Beijing, China). Acetonitrile, H_2SO_4 (95%), acetone, $NH_3 \cdot H_2O$, sodium hydroxide (NaOH), hydrochloric acid (HCl), acetic acid, 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). The size and morphology of the MOPC-ZSM-5 were investigated by transmission electron microscopy (TEM) using a JEOL model JEM-2011(HR) at accelerating voltage of 200 kV and scanning electron microscopy (SEM) using an S-4800 field emission electron microscope operated at 5 kV. The TEM specimens were prepared by dispersing the MOPC-ZSM-5 on a copper grid.

A mixture stock solution containing each of imidacloprid, acetamiprid, thiamethoxam and thiacloprid at 20.0 μg mL^{-1} was prepared in methanol. The standard solutions were stored at 4 ^{o}C and protected from light.

Fig. 1

HPLC conditions

Chromatographic separations were performed on a Promosil C18 column (150 mm × 4.6 mm I.D., 5.0 μm) from Bonna-Agela technologies (Tianjin, China). HPLC was carried out on a LC-20AT liquid chromatography (Shimadzu, Japan) with two LC-20AT VP pumps and a SPD-20A UV/vis detector. The mobile phase was a mixture of acetonitrile-water (22:78 v/v) at a flow rate of 1.0 mL

min^{-1}. The UV monitoring wavelengths were chosen at 253 nm for thiamethoxam, 270 nm for imidacloprid, and 244 nm for both acetamipridand and thiacloprid, respectively.

Synthesis of magnetic micro-mesoporous nanocomposite MOPC-ZSM-5

MOPC-ZSM-5 were prepared according to the literature method [46] with some modifications. One gram of ZSM-5 template, 1.5 g of sucrose and 5 ml of distilled water were added to a 50-ml beaker. After being magnetically stirred for 50 min, 0.19 g of H_2SO_4 was added into the solution and then the mixture was magnetically stirred for another 10 min. Then, the mixture was heated at 100 ^oC for 6 h and at 160 ^oC for 6 h in an oven. 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. The product was dried in an oven and then ZSM-5 based ordered porous carbon (OPC) was obtained.

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 oxide and the reaction was carried out at 50 °C for 1 h under constant mechanical stirring. The precipitate was separated from the aqueous dispersion by an external magnetic field and washed with double-distilled water until the pH

became 7. Subsequently, the MOPC-ZSM-5 composite was dried under vacuum.

MOPC-MCM-41 and MOPC-SBA-15 were prepared according to the same procedures as described above except using MCM-41 and SBA-15 as template, respectively.

Sample preparation

Homogenized whole peanuts milk sample was purchased from local supermarket. Since the peanuts milk sample contained lipids and proteins, the pretreatment of peanut milk prior to MSPE was necessary. 20 mL of the peanut milk was vortex-mixed with 0.2 mL 36% acetic acid in a centrifuge tube for 1 min and then, the tube was centrifuged at 3000 rpm for 10 min. The resultant supernatant was transferred to a 50 mL volumetric flask and diluted with double-distilled water to the mark. Then, the mixture was stored at 4 ^{o}C for the next MSPE experiments.

MSPE procedures

Scheme 1 displays the MSPE steps for the extraction of the four neonicotinoid insecticides from the sample solution. Firstly, 10 mg MOPC-ZSM-5 was added into 50 mL sample solution. After the pH of the mixture was adjusted to 6.0 with 0.1 mol L^{-1} HCl, the mixture was shaken on a slow-moving platform shaker for 20 min. Then, MOPC-ZSM-5 was separated from the sample solution by placing a magnet at the bottom of the conical flask. After discarding the supernatant solution, the residual solution and MOPC-ZSM-5 was totally transferred to a 10 mL centrifuge tube, and then the MOPC-ZSM-5 was aggregated again by positioning a magnet to the outside of the tube wall so that the residual solution could be completely removed. Finally, the adsorbed neonicotinoid insecticides were eluted from the MOPC-ZSM-5 with 0.2 mL acetonitrile for three times (0.2 mL × 3). The

three desorption solutions were combined together. And finally, 10.0 μL of the resultant solution was injected into the HPLC system for analysis.

Scheme 1

Results and discussion

Characterization of MOPC-ZSM-5

The morphology of the zeolite ZSM-5 and MOPC-ZSM-5 was observed by both SEM and TEM (Fig. 2). It can be seen from Fig. 2C that the textile texture-like structure, a characteristic feature of the ordered porous materials, existed in ZSM-5. The TEM image of MOPC-ZSM-5 (Fig. 2D) shows that the structure order of ZSM-5 template is well preserved. The SEM image of MOPC-ZSM-5 (Fig. 2B) revealed that it has three-dimensional pore connection structure and ellipsoidal tubular pores. Both SEM and TEM images of MOPC-ZSM-5 show that Fe_3O_4 nanoparticles were dispersed well on the surface of the carbon material.

To further confirm the iron oxide nanoparticles were incorporated successfully on the MOPC-ZSM-5, the XRD pattern of MOPC-ZSM-5 was performed (Fig. S1, Supporting Information). The broad reflection peaks at *ca*. 25^o can be attributed to the turbostratic structure with randomly oriented porous carbon. All the other significant diffraction peaks of the MOPC-ZSM-5 matched well with the data from the JCPDS card (19-0629) for Fe_3O_4 (the diffraction angles at 2θ): 30.2°, 35.6°, 43.3°, 53.7°, 57.3°, and 62.8° can be assigned to (220), (311), (400), (422), (511), and (440) of crystal planes of Fe_3O_4).

As demonstrated in our previous paper, [47] the VSM magnetization curves of the MOPC-ZSM-5 exhibited a typical super paramagnetic behavior. The saturation magnetization intensity of the

MOPC-ZSM-5 was 46.5 emu $g^{-1,}$ which are sufficient for its magnetic separation from a solution with a strong magnet.

Fig. 2

Optimization of MSPE conditions

In our experiments, to obtain a high extraction efficiency of the MOPC-ZSM-5 for the analytes, various conditions that affect the MSPE of the four neonicotinoid insecticides, including the type and the amount of the adsorbent, sample pH, extraction time, and salt addition were investigated and optimized.

Comparison with other adsorbent materials

The MOPC-ZSM-5 adsorbent materials were compared with other two magnetic adsorbent materials MOPC-MCM-41 and MOPC-SBA-15 for their extraction efficiency of the four neonicotinoid insecticides. As shown in Fig. 3, the MOPC-ZSM-5 yielded the highest recoveries among the three adsorbents studied. Therefore, the MOPC-ZSM-5 was selected as the adsorbent for the extraction of the neonicotinoids.

Fig. 3

Effect of the amount of MOPC-ZSM-5

In order to evaluate the effect of the amount of the MOPC-ZSM-5 adsorbent on the extraction of the analytes, the addition of different amounts of MOPC-ZSM-5 (1, 3, 5, 7, 10, 15 and 20 mg) into the

sample solution was investigated. The results shown in Fig. 4 indicated that the extraction recoveries of the four neonicotinoid insecticides increased with increase of the MOPC-ZSM-5 dosage from 1 to 10 mg, and then almost unchanged with the further increase of the amount of the MOPC-ZSM-5. Therefore, 10 mg MOPC-ZSM-5 was selected for the experiments.

Fig. 4

Effect of extraction time

Since MSPE is a partition process of the analytes between the adsorbent and sample solution, the extraction time may be an important parameter that influences the extraction of the analytes. In this work, the extraction time profiles of the analytes were investigated by increasing the extraction time from 1 to 30 min. As shown in Fig. 5, the extraction recoveries of the four neonicotinoid insecticides reached a maximum at 20 min. It can be concluded that the extraction equilibrium between the adsorbent and the aqueous phase was nearly reached after 20 min. Hence, extraction time of 20 min was chosen.

Fig. 5

Effect of sample solution pH and ionic strength

The sample solution pH is expected to be a key factor that affects the extraction efficiency of the MOPC-ZSM-5 for the neonicotinoids. It can influence the existing forms of the analytes and the stability of the analytes. The sample solution pH was investigated in the range between 2.0 and 12 by adding different amounts of either 1 mol L^{-1} NaOH or 1 mol L^{-1} HCl solution into the sample solution. Fig. 6 shows that the extraction recoveries first increased when the pH was changed from 2 to 6, and then decreased when the pH was further increased from 6 to 12. The reason for this can be ascribed to that the neonicotinoids were unstable and could be hydrolyzed under alkaline

conditions. Moreover, they could be ionized under acidic conditions and the ionic forms of the analytes would greatly weaken the interactions between analytes and adsorbent, the ionized neonicotinoids were difficult to extract by the hydrophobic MOPC-ZSM-5 adsorbent. So, sample solution pH at 6.0 was selected for subsequent experiments.

The effect of ionic strength on the extraction recoveries of the analytes was investigated by adding NaCl into the sample solution in the range from 0% to 16% (w/v). The result showed that no significant variations in the extraction efficiency were observed with increased NaCl concentration. Therefore, no salt was added into the sample solution in further experiments.

Fig. 6

Effect of the desorption condition for the four neonicotinoids

It is necessary to choose an effective desorption solvent to achieve a high desorption efficiency, hence, the choice of desorption solvent should be carefully considered. For this purpose, the most commonly used three organic solvent (acetone, acetonitrile and methanol) were studied to elute the four neonicotinoids from the MOPC-ZSM-5 adsorbent. It was found that, under the same extraction and desorption conditions, no obvious difference was observed in the desorption efficiency of the four neonicotinoids among the three organic solvents. However, when acetonitrile was used as the desorption solvent, the shape of the chromatography peak (symmetry and sharp) of the four neonicotinoids was better than that when acetone or methanol was used. Based on the experimental results, acetonitrile was chosen as the desorption solvent for the subsequent experiments.

To examine the effect of the desorption solvent volume on the desorption efficiency of the analytes, different volumes of acetonitrile, i.e., 0.2 mL acetonitrile for one time desorption (0.2 mL), two times desorptions (0.2 mL × 2), three times desorptions (0.2 mL × 3) and four times

desorptions (0.2 mL × 4), were investigated. The results indicated that three times desorptions each time with 0.2 mL acetonitrile were sufficient to elute the neonicotinoids from the MOPC-ZSM-5 adsorbent. The desorption solutions were combined together and transferred to a 2 mL microcentrifuge tube, and then10 μL of it was injected into the HPLC system for analysis.

Analytical performance

Linearity and limits of detection (LODs) of the method

Calibration curves were established for all the analytes in the concentration range of 0.5–1000.0 ng ml^{-1} using six spiked concentrations in double-distilled water and neonicotinoids-free peanut milk sample. For each concentration level, five replicate extractions and determinations were performed. The characteristic calibration data obtained are summarized in Table 1. For water sample, good linearity was observed over the concentration range of 1.0-200.0 ng mL^{-1} for TMX，ICL and TCL and 0.5-200.0 ng mL^{-1} for ACT. For peanuts milk sample, the linear response was in the range of 6.0-1000.0 ng mL^{-1} for TMX，ICL and TCL and 3.0-1000.0 ng mL^{-1} for ACT. The limits of detection (LODs) were ranged from 0.1 to 0.2 ng mL^{-1} for water sample and from 1.0 to 2.0 ng mL^{-1} for peanut milk sample, which were calculated based on three times the average background noise.

Table 1

Analysis of environmental water and peanut milk sample

To validate the applicability of the developed method, the established MSPE method was applied to determine the four neonicotinoids in peanut milk and river water samples. The results are listed in

Table 2. As a result, 0.61 ng mL^{-1} of ACT was found in river water sample. 8.67 ng mL^{-1} of TMX and 3.69 ng mL^{-1} of ACT were found in peanut milk sample. In order to determine the accuracy of the method, river water sample were spiked with 5.0 and 50.0 ng mL^{-1} of each of the four neonicotinoids and peanut milk samples were spiked with 24.0 and 240.0 ng mL^{-1} of each of the four neonicotinoids. For each spiked concentration, five replicate analyses were performed. As a result, the recoveries for the four neonicotinoids fell in the range from 96.74% to 112.40%, showing that the method had a good accuracy. Fig. 7 shows the typical chromatograms of the four neonicotinoids for both spiked and unspiked river water and peanut milk samples.

Table 2

Fig. 7

Conclusions

In this work, MOPC-ZSM-5 was prepared as an adsorbent for the extraction of acetamiprid, imidacloprid, thiacloprid and thiamethoxam from river water and peanut milk samples. The new analytical method established with the combination of MPSE with HPLC–UV enabled a selective and sensitive analysis of the four neonicotinoid insecticides in peanut milk and environmental water samples at low levels. The results indicated that the MOPC-ZSM-5 has a good adsorption capacity for the four neonicotinoid insecticides. It can be concluded that the MOPC-ZSM-5 has a further potential as an adsorbent for the extraction of other environmental pollutants from complex samples.

Acknowledgements

Financial supports from the National Natural Science Foundation of China (No. 31171698), the

Innovation Research Program of Department of Education of Hebei for Hebei Provincial Universities (LJRC009), the Natural Science Foundations of Hebei (B2012204028) and the Scientific and Technological Research Foundation of Department of Education of Hebei Province (ZD20131033) are gratefully acknowledged.

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Table Captions

Table 1 Analytical performance data for the four neonicotinoid insecticides in water and peanut milk samples by the MSPE method.

Table 2 Recoveries obtained for the determination of the four neonicotinoid insecticides in environmental water and peanut milk samples.

Scheme Captions

Scheme 1. MSPE procedures for the four neonicotinoid insecticides using MOPC-ZSM-5 as the adsorbent.

Figure Captions

Fig. 1. Chemical structures of the four neonicotinoids.

Fig. 2 SEM images of zeolite ZSM-5 (A) and MOPC-ZSM-5 (B); TEM images of zeolite ZSM-5 (C) and MOPC-ZSM-5 (D).

Fig. 3 Comparison of the performance of the MOPC-ZSM-5 with MOPC-MCM-41 and MOPC-SBA-15 for the extraction of the analytes. Extraction conditions: sample volume, 50 mL; pH, 6.0; extraction time, 20 min; amount of the adsorbents, 10 mg; desorption solvent, 0.6 mL (0.2 mL × 3) acetonitrile; concentration of each of the analytes, 40 ng mL^{-1}.

Fig. 4 Effect of MOPC-ZSM-5 dosage on the extraction efficiency of the neonicotinoids. Extraction conditions: sample volume, 50 mL; extraction time, 20 min; pH, 6.0; desorption solvent, 0.6 mL (0.2 mL × 3) acetonitrile; concentration of each of the analytes, 40 ng mL^{-1}.

Fig. 5 Effect of extraction time on the extraction efficiency of the neonicotinoids. Extraction conditions: sample volume, 50 mL; pH, 6.0; amount of the sorbents, 10 mg; desorption solvent, 0.6 mL (0.2 mL × 3) acetonitrile; concentration of each of the analytes, 40 ng mL^{-1}.

Fig. 6 Effect of sample solution pH on the extraction efficiency of the neonicotinoids. Extraction conditions: sample volume, 50 mL; amount of the adsorbents, 10 mg; extraction time, 20 min; desorption solvent, 0.6 mL (0.2 mL × 3) acetonitrile; concentration of each of the analytes, 40 ng mL^{-1}.

Fig. 7 The typical chromatograms of blank peanut milk sample (a), the blank peanut milk sample spiked with neonicotinoids at each concentration of 90.0 ng mL^{-1} (b), blank water sample (c), and the blank water sample spiked with neonicotinoids at each concentration of 15 ng mL^{-1} (d). Peak identification: 1. TMX (253 nm), 2. ICL (270 nm), 3. ACT (244 nm), and 4. TCL (244 nm).

Table 1

Analytical performance data for neonicotinoid insecticides in water and peanut milk samples by the MSPE method.

Samples	Analytes	LRs (ng mL^{-1})	*r*	LODs (ng mL^{-1})	RSDs (%) (*n* = 5)
Water sample	TMX	1.0-200.0	0.9993	0.2	5.2
	ICL	1.0-200.0	0.9991	0.2	7.2
	ACT	0.5-200.0	0.9989	0.1	5.5
	TCL	1.0-200.0	0.9994	0.2	4.6
Peanuts milk sample	TMX	6.0-1000.0	0.9989	2.0	6.7
	ICL	6.0-1000.0	0.9992	2.0	5.6
	ACT	3.0-1000.0	0.9991	1.0	7.4
	TCL	6.0-1000.0	0.9987	2.0	4.8

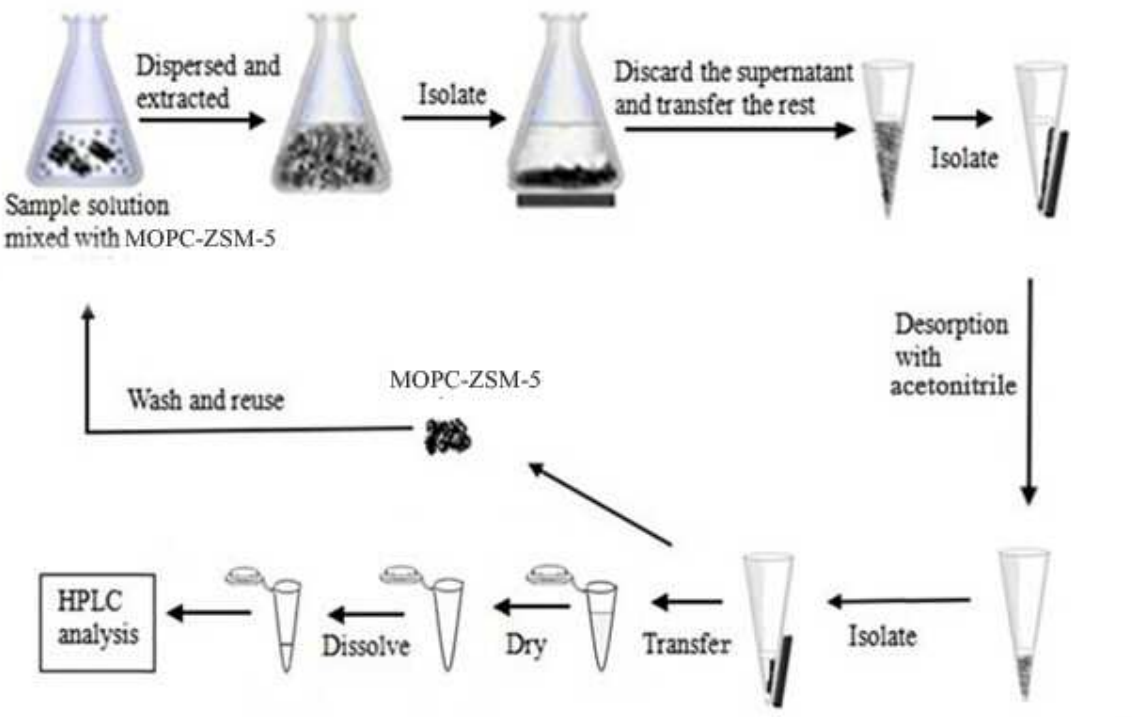
LR: linear range

Table 2

Recoveries obtained for the determination of TMX, ICL, ACT and TCL in environmental water and peanut milk samples.

Compound	Water sample (n = 5)				Peanuts milk sample (n = 5)			
	Spiked (ng L^{-1})	Found (ng mL^{-1})	R^b (%)	RSD (%)	Spiked (ng mL^{-1})	Found (ng mL^{-1})	R^b (%)	RSD (%)
TMX	0	nd			0	8.67		
	5	5.36	107.20	5.9	24	32.42	98.96	6.1
	50	48.57	96.74	6.1	240	247.96	99.70	5.3
ICL	0	nd			0	nd		
	5	5.62	112.40	5.4	24	23.64	98.50	6.4
	50	49.92	99.84	4.9	240	239.91	99.96	4.7
ACT	0	0.61			0	3.69		
	5	5.47	97.20	5.1	24	29.42	107.20	4.5
	50	55.43	109.64	6.2	240	258.47	106.16	6.1
TCL	0	nd			0	nd		
	5	5.52	110.40	5.3	24	23.69	98.71	4.2
	50	51.61	103.22	4.1	240	241.18	100.49	6.5

nd: not found.



Scheme1. Procedures for the MSPE of the four neonicotinoid insecticides with MOPC-ZSM-5 as the adsorbent.

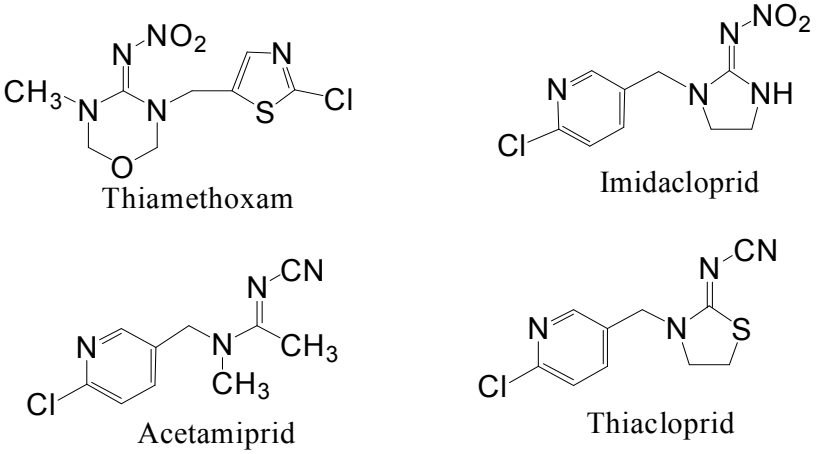
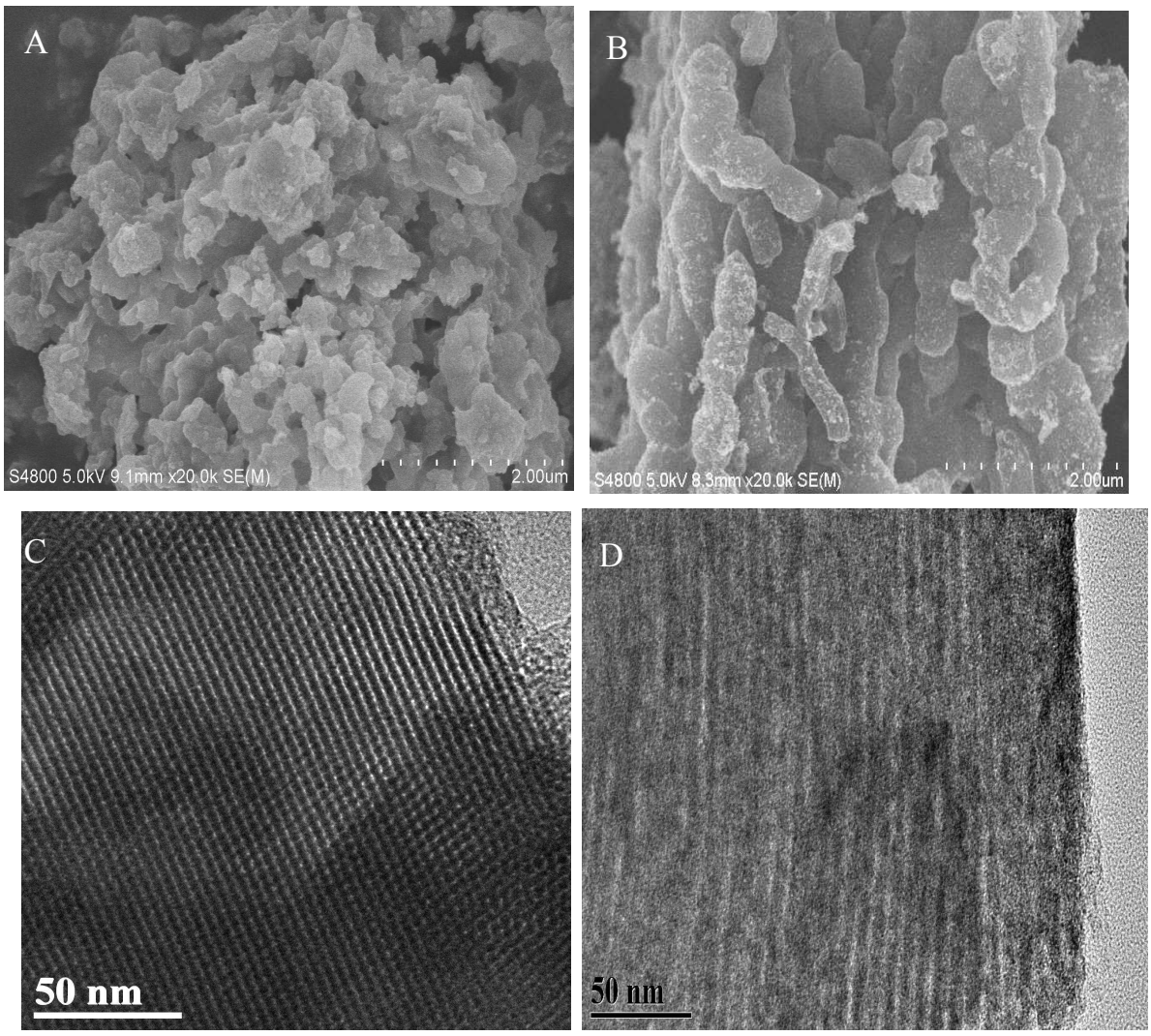


Fig. 1. Chemical structures of the neonicotinoid pesticides.



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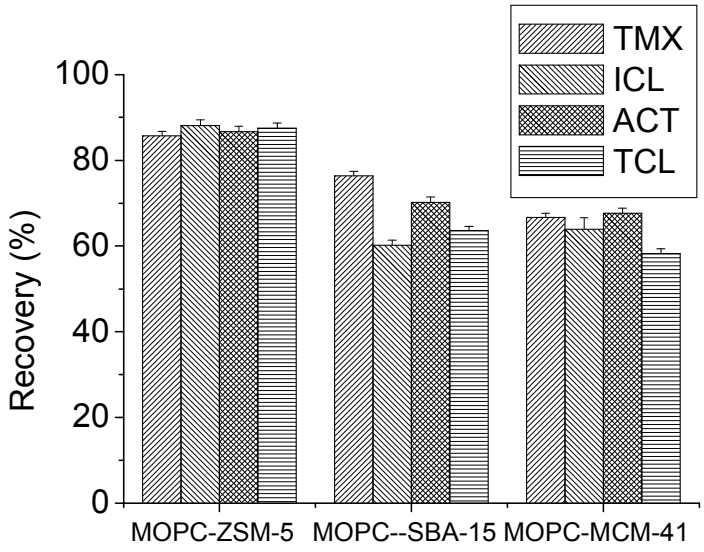

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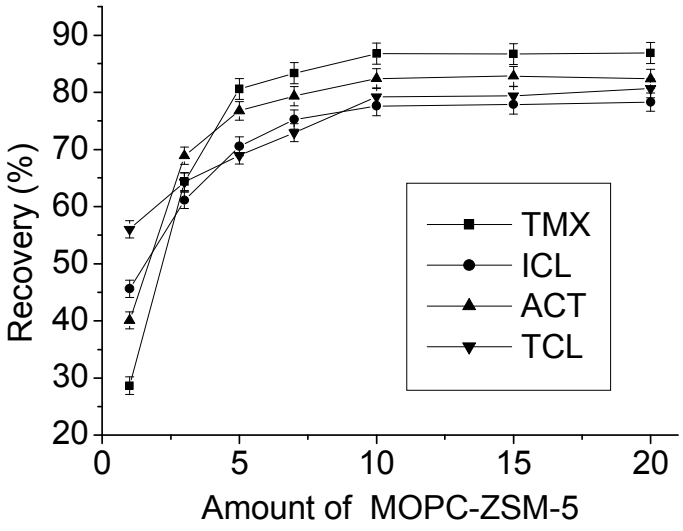

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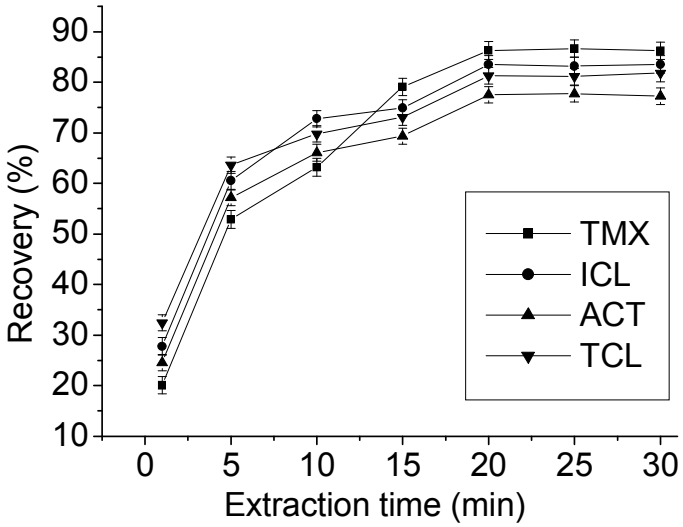


Fig. 5. Effect of extraction time on the extraction efficiency of the neonicotinoids. Extraction conditions: sample volume, 50 mL; pH, 6.0; amount of the sorbents, 10 mg; desorption solvent, 0.6 mL (0.2 mL × 3) acetonitrile; concentration of each of the analytes, 40.0 ng mL^{-1}.

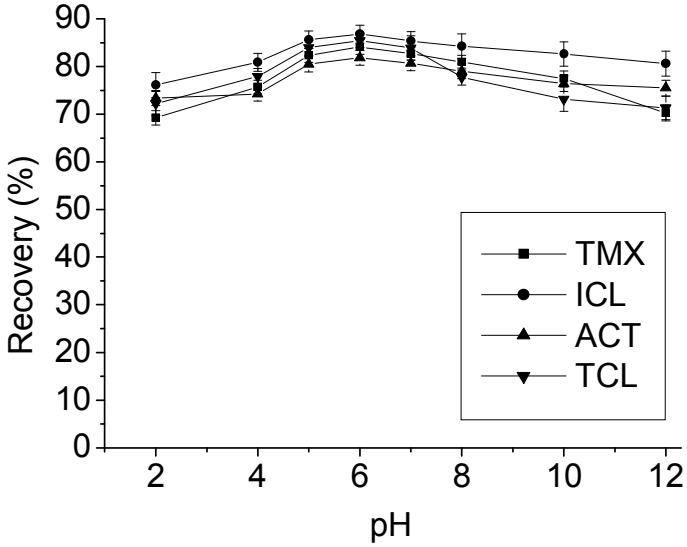
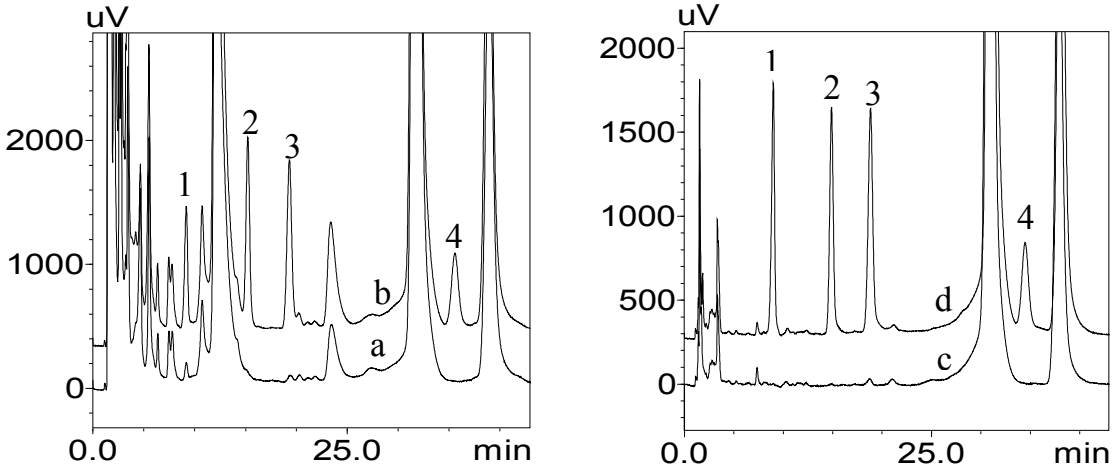


Fig. 6. Effect of sample solution pH on the extraction efficiency of the neonicotinoids. Extraction conditions: sample volume, 50 mL; amount of the adsorbents, 10 mg; extraction time, 20 min; desorption solvent, 0.6 mL (0.2 mL × 3) acetonitrile; concentration of each of the analytes, 40 ng mL^{-1}.



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Magnetic porous carbon based solid-phase extraction coupled with high performance liquid chromatography for the determination of neonicotinoid insecticides in environmental water and peanuts milk samples

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In this paper, magnetic ordered porous carbon (MOPC-ZSM-5) was synthesized using zeolite ZSM-5 as a template and sucrose as a carbon source. MOPC-ZSM-5 was used as an adsorbent for simultaneous extraction and concentration of four neonicotinoid insecticides from river water sample and peanuts milk sample prior to high performance liquid chromatography-ultraviolet detection.