

Preparation of Magnetic Molecularly Imprinted Polymer for Chlorpyrifos Adsorption and Enrichment

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Abstract. Magnetic molecularly imprinted polymer (MMIP) for chlorpyrifos was prepared and characterized. The adsorption performance of MMIP for chlorpyrifos was evaluated under various conditions. The results showed that the adsorption equilibrium was achieved within 1 h, the adsorption capacity was 16.8 mg/g, and the adsorption process could be well described by Langmuir isotherm model and pseudo-second-order kinetic model. The MMIP was used as the selective sorbent for solid-phase extraction of chlorpyrifos from environmental water and vegetable samples. Combined with gas chromatography–mass spectrometry, a LOD of 30 ng/L, spiked recovery of 89.6%–107.3% and RSD of 1.9%–3.8% for chlorpyrifos were obtained.

1. Introduction

Chlorpyrifos is the most widely used herbicide in agriculture and other applications. However, chlorpyrifos is associated with chromosomal damage and bladder cancer [1]. Nowadays, chlorpyrifos has been found in various environmental matrices and food samples. Consequently, it is necessary to develop suitable analytical methods for chlorpyrifos. Solid-phase extraction (SPE) is the most often used method for separation and enrichment of pollutants from various matrices [2-6].

Common adsorbents for SPE such as C18 lack adsorption selectivity. Molecularly imprinted polymer is a tailor-made material designed to present valuable molecular recognition properties for a target compound (template). Thus, MIP can selectively recognize the target molecules in a complex system [7].

Traditional SPE is always a tedious process. However, magnetically separation technology can provide an easy and rapid way for removal of magnetic particles from solution by applying a magnetic field [8, 9].

In this work, magnetic molecularly imprinted polymer (MMIP) for chlorpyrifos was prepared and characterized, and the adsorption behaviors of chlorpyrifos on the MMIP were investigated. Finally, the MMIP was used for preconcentration of chlorpyrifos from water and vegetable samples before instrumental determination.

2. Materials and methods

2.1. Chemicals

Chlorpyrifos was obtained from Dr. Ehrenstorfer GmbH (Germany), p-aminophenyltrimethoxysilane (APTMS) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Other



chemicals and materials were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China).

2.2. Apparatus

A 7890A-5975C GC-MS system (Agilent, USA) using a HP-5MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm) was utilized for separation and analysis. The injection volume was 1 μL without splitting. The quantification ion (m/z) for chlorpyrifos was 314.

2.3. Preparation of MMIP

Magnetic mesoporous silica ($\text{Fe}_3\text{O}_4@\text{mSiO}_2$) was synthesized according to the literature [10]. In the preparation of MMIP by surface imprinting technology with a sol-gel process [7], $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ was used as the carrier, chlorpyrifos as the template and APTMS as the functional monomer.

2.4. Sample analysis

Water samples were collected from the Peal River (Guangzhou, China) and the Center Lake (Higher Education Mega Center, Guangzhou, China), and stored at 4 °C until analysis. Vegetable samples were purchased from a market (Maoming, China). 2.00 g vegetable was extracted using 20 mL ethyl acetate.

20 mg of MMIP was added to sample solution. After shaking the mixture at 300 rpm for 20 min at room temperature, the MMIP were isolated from solution with a magnet. The chlorpyrifos adsorbed on the MMIP were eluted with 5 mL methanol/acetic acid (97:3, v/v) for 10 min. After drying with N_2 , the chlorpyrifos was redissolved in 1.0 mL dichloromethane. Then, 1 μL of which was injected into the GC-MS system for analysis.

3. Results and discussion

3.1. Characterization of MMIP

The FT-IR spectrum of the prepared MMIP was recorded. In the spectrum, the peak at 576 cm^{-1} was from the Fe-O stretching vibration, the peak at 1093 cm^{-1} was due to the Si-O-Si stretching vibration. The peaks at 1261 cm^{-1} and 1720 cm^{-1} were corresponded to the C-O vibration and C=O stretching vibration, respectively. These results indicated the successful preparation of MMIP.

The surface morphology of the MMIP was provided by SEM. From the SEM observation (figure 1), it was found that the MMIP were almost regular in shape with an average diameter of around 80 nm.

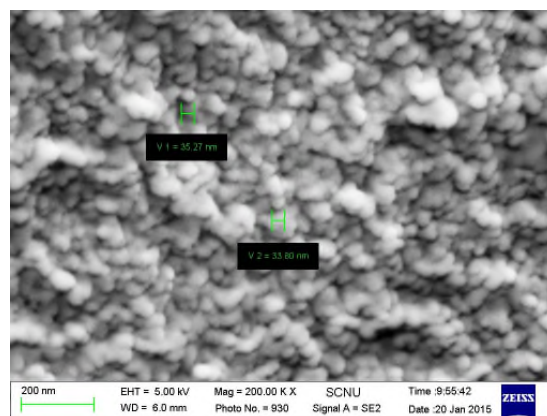


Figure 1. SEM image of MMIP.

The magnetic property of the MMIP was measured using a vibrating sample magnetometer. It was observed that its greatest saturation magnetization was 18.7emu/g, and both its remanence and coercivity were near zero, indicating the MMIP was superparamagnetic.

3.2. Adsorption properties of chlorpyrifos on MMIP

The adsorption of chlorpyrifos on MMIP was examined using batch experiments and conducted in duplicate. The adsorption capacities varied with initial chlorpyrifos concentrations (figure 2). Langmuir and Freundlich isotherms were used to describe the adsorption behaviors. Langmuir isotherm mode fitted the experimental data better ($R^2=0.9963$) than Freundlich model ($R^2=0.9118$), suggesting the adsorption of chlorpyrifos onto the MMIP followed the Langmuir model. The maximum adsorption capacity was 16.8 mg/g at an initial chlorpyrifos concentration of 20 mg/L.

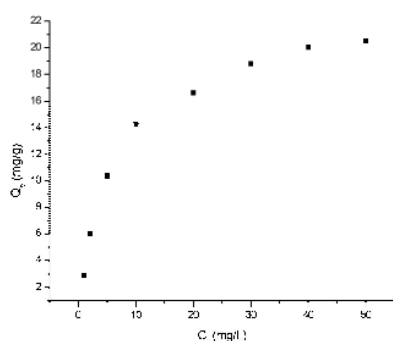


Figure 2. Chlorpyrifos adsorption on MMIP at different initial concentrations.

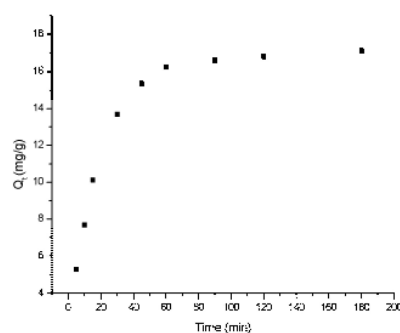


Figure 3. Effect of contact time on chlorpyrifos adsorption on MMIP.

The effect of contact time on chlorpyrifos adsorption with the MMIP was investigated using an initial concentration of 20 mg/L. The results (figure 3) showed that the adsorption occurred rapidly within the first 0.5 h and then gradually slowed down until reaching equilibrium (1 h). The kinetics of chlorpyrifos adsorption was studied by using pseudo-first-order and pseudo-second-order kinetic models. It was found that the pseudo-second order kinetic equation could preferably describe the adsorption process.

The selectivity coefficient (α) and imprinting coefficient (β) were used to estimate the selectivity properties of MMIP and MNIP toward chlorpyrifos and structurally similar compounds omethoate and dichlorphos.

$$\alpha = K_d(\text{chlorpyrifos}) / K_d(\text{M}) \quad (1)$$

$$\beta = \alpha_{\text{imprinted}} / \alpha_{\text{non-imprinted}} \quad (2)$$

where K_d is the distribution coefficient and M represents omethoate or dichlorphos.

As shown in table 1, the K_{MNIP} of chlorpyrifos for the MNIP was only slightly larger than those of omethoate and dichlorphos. However, the K_{MMIP} of chlorpyrifos for the MMIP was much higher than others, indicating that the template molecule chlorpyrifos had a higher affinity for the imprinted polymer than omethoate and dichlorphos.

Table 1. The selectivity parameters of MMIP and MNIP for chlorpyrifos.

Compounds	$K_{\text{MMIP}} (\text{L g}^{-1})$	$K_{\text{MNIP}} (\text{L g}^{-1})$	α_{MMIP}	α_{MNIP}	β
Chlorpyrifos	5.38	1.65	—	—	—
Omethoate	1.56	1.32	3.45	1.25	2.76
Dichlorphos	1.17	1.26	4.60	1.31	3.51

3.3. Determination of chlorpyrifos in water and vegetable samples

The MMIP was used as the sorbent for solid– phase extraction of chlorpyrifos from environmental water and vegetable samples. It was found that the proposed method had excellent linearity between the peak area and concentration over the range of 0.1–50 µg/ L for chlorpyrifos, with a correlation coefficient of 0.9925. The LOD calculated on the basis of signal to noise ratio of 3 was 30 ng/ L.

These water samples and vegetable extracting solution were analyzed, and the results were listed in table 2. Then, these samples were spiked with chlorpyrifos to assess the matrix effects and the results were also shown in table 2. It is obvious that the spiked recoveries of these samples were in the range of 89.6%–107.3%, with precision (RSD) of 1.9%–3.8%. Therefore, the developed method was sensitive, precise and rapid.

Table 2. Analytical results of chlorpyrifos in water and vegetable samples.

Sample	Added (ppb)	Found (ppb)	Recovery (%)	RSD (%)
River water	0	3.26	—	2.9
	5.0	8.50	107.3	2.4
Lake water	0	0.87	—	3.2
	1.0	1.92	105.7	1.9
Chinese cabbage	0	6.35	—	3.8
	10.0	15.69	89.6	2.7
Tomato	0	18.56	—	2.8
	20.0	36.05	94.83	2.4

4. Conclusions

Chlorpyrifos imprinted polymer on magnetic mesoporous silica was successfully synthesized and applied to adsorption of chlorpyrifos from solutions. The results suggested that the prepared MMIP could act as a selective SPE adsorbent for efficient separation and preconcentration of trace chlorpyrifos from environmental water and vegetable extract, and could be removed conveniently from sample solutions with the help of an external magnet. A new method for determination of trace chlorpyrifos in these samples was developed by using the MMIP based SPE coupled with gas chromatography–mass spectrometry. Results showed that the established method possessed good performance in terms of limit of detection, linearity, accuracy and reproducibility. Therefore, the synthesized MMIP can be a powerful alternative to common SPE adsorbents for chlorpyrifos, and the proposed method is a useful tool for routine analysis of chlorpyrifos due to its sensitivity, rapidity, selectivity and reliability.

5. References

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