

Preparation of atrazine surface-imprinted material MIP-PSSS/SiO₂ and study on its molecule recognition character

Yanbin Li, Tao Chen, Baojiao Gao[†], and Zongwen Qiao

Department of Chemical Engineering, North University of China, Taiyuan 030051, P. R. China
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Abstract—By using a novel molecular surface-imprinting technique, “synchronously graft-polymerizing and imprinting” method established by our group, a pesticide molecule surface-imprinted material was prepared successfully for the removal of pesticide residues from water. The micron-sized silica gel particles were first surface-modified with coupling agent γ -aminopropyltrimethoxysilane (AMPS), obtaining the modified particles AMPS-SiO₂, onto whose surfaces primary amino groups were introduced. The anionic monomer sodium p-styrenesulfonate (SSS) was used as functional monomer and *N,N*-methylenebisacrylamide (MBA) was used as crosslinker. In aqueous solution, the monomer molecules were arranged around the template molecule, atrazine molecule that is an extensively used herbicide, through electrostatic interaction. By initiating of the redox surface-initiating system of -NH₂/S₂O₈²⁻, the graft/cross-linking polymerization of SSS on SiO₂ particles and the surface imprinting of atrazine molecule were simultaneously carried out, forming atrazine molecule surface-imprinted material MIP-PSSS/SiO₂. With propoxur and pirimicarb, which are also two pesticides as two contrast substances, the recognition performance of the atrazine molecule surface-imprinted material MIP-PSSS/SiO₂ was investigated in depth. The experimental results show that MIP-PSSS/SiO₂ particles possess special recognition selectivity and excellent binding affinity for atrazine. The binding capacity of atrazine on MIP-PSSS/SiO₂ particles can get up to 61 mg/g, and relative to propoxur and pirimicarb, the selectivity coefficients of MIP-PSSS/SiO₂ for atrazine are 9.69 and 8.79, respectively.

Keywords: Pesticide Residues, Atrazine, Surface Imprinting Technique, Graft Polymerization, Molecule Recognition

INTRODUCTION

Molecular imprinting is a technology to create recognition sites in a macromolecular matrix using a template molecule, and so molecularly imprinted polymers (MIPs) have special recognition ability and predesigned selectivity for the template molecule. In recent years, MIPs as highly selective solid sorbents have been widely used in separation, purification and determination [1-3]. MIPs have been also used in the water environmental protection and control area to effectively remove those toxic substances [4-7]. The conventional method to prepare MIPs is entrapment, but it has some disadvantages including being a time-consuming and complicated preparation process, having fewer recognition sites inside the particles obtained via crushing and grinding the imprinted polymeric monolith, and greater diffuse barrier for the template molecules coming from thick matrices. These drawbacks lead to poor binding capacity and lower binding kinetic of MIPs towards the template molecules [8,9], and severely limit the applications of MIPs in various areas. To overcome these drawbacks, many researchers developed molecule surface-imprinting techniques [10-13], and tried to make the imprinted caves to lie on the surfaces of solid particles. The surface-imprinted materials are more effective for recognizing and binding the template molecules than the imprinted materials prepared with the conventional method. Our group also has been devoting our-

selves to molecule surface-imprinting techniques. In recent years, we put forward two novel molecule surface-imprinting techniques, pre-graft polymerizing and post-crosslinking/imprinting method [14-16] and synchronously graft-polymerizing and imprinting method [17], and both of them are successful.

Now, pesticides (insecticide and herbicide) are widely used to increase the yield of crops around the world. However, pesticides are highly toxic for living organisms and they are difficult to degrade, and so they have persistent bioaccumulative effects. The excessive use of pesticides has constituted a risk for water quality because residual pesticides can pass through the soil and subsoil, and cause the pollution of surface waters and groundwater. Besides, the water pollution of pesticides may come from agricultural drainage [18-21]. In a word, pollution of surface and ground waters caused by residual pesticides is a major environmental problem faced by modern society that leads to ecological disequilibrium and health hazards [22-25]. Therefore, it is important to develop new technologies and materials to promote the efficient removal of pesticide residues from water. Several techniques for the pesticide removal from water are known such as oxidation process, membrane filtration, biodegradation, photo-catalysis and adsorption [26-30]. Among these, adsorption has been used as a simple and effective method for removing the residual pesticides from water, and various solid adsorbents are developed [31-33]. However, those solid adsorbents have a common drawback, the lack of selectivity. Molecularly imprinted materials can specially recognize and bind the template molecules because inside MIPs a great deal of imprinted cavities designed for the target template molecule are distributed, and these cavities are comple-

[†]To whom correspondence should be addressed.

E-mail: gaobaojiao@126.com

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mentary to the template molecule in shape, size and functionality, so they are the solid adsorbents with the best selectivity. Some researchers have prepared pesticide molecule-imprinted materials and described the feasibility of using such imprinted materials in the pesticide removal as well as in analysis and detection of pesticide residues in water although there are only a few reports about pesticide molecule-imprinted materials. For example, Li et al. prepared molecularly imprinted microspheres for selective recognition and removal of 2,4-dichlorophenol that is used extensively in the manufacture of pesticides and herbicides from contaminated water [34], Chimuka et al. developed a selective extraction technique based on the combination of membrane assisted solvent extraction and molecularly imprinted solid phase extraction for triazine herbicides [35], and Lu et al. prepared high density imprinted layer-coated silica nanoparticles and used them in selective recognition and fast enrichment of chlorpyrifos from complicated matrices [36]. The goal of this study is to prepare pesticide imprinted material with high performance by using the novel surface imprinting technique of synchronously graft-polymerizing and imprinting method established by our group, and to examine its recognition property so that a valuable reference for more effectively removing residual pesticides in water by using pesticide surface-imprinted materials is supplied.

In the present study, atrazine (it is an extensively used herbicide) was used as template molecule, anionic monomer sodium p-styrenesulfonate (SSS) was used as functional monomer, and the atrazine molecule surface-imprinted material was prepared with micron-sized SiO₂ as matrix. In the preparation process of the surface-imprinted material stated above, there were three main technical points: (1) By right of electrostatic interaction, the template atrazine molecule combined with monomer SSS; (2) A surface-initiating system was constituted by the amino group (primary amino group) on the modified silica gel particles and the persulfate in the aqueous solution. (3) The surface-initiated graft-polymerization of SSS and the imprinting process of atrazine molecule were synchronously carried out, and after removing the template molecules, atrazine molecule surface-imprinted material MIP-PSSS/SiO₂ was formed. In this investigation, on the basis of preparing the imprinted material MIP-PSSS/SiO₂, its recognition and binding properties for atrazine were examined in depth. The study results show that the preparation of atrazine molecule surface-imprinted material MIP-PSSS/SiO₂ is successful, and it possesses high combining ability and special recognition selectivity for atrazine. Pesticide molecule surface-imprinted materials can be used for highly effectively removing pesticide residues from water, and so such study is significant and valuable in the field of water environment protection.

EXPERIMENTAL SECTION

1. Material and Equipment

Silica (about 125 μm of diameter, Ocean Chemical Limited Company, Qingdao City, China) was of reagent grade. γ-Aminopropyltrimethoxysilane (AMPS, Nanking Chuangshi Chemical Aux Ltd., Province Jiangsu, China), sodium p-styrenesulfonate (SSS, Shanghai Kantuo Chemical Reagent Co. Ltd., China), ammonium persulfate (APS, Shanghai Fushu Chemical Engineering Co. Ltd., Shanghai, China), and *N,N'*-methylenebisacrylamide (MBA, Shanghai Yuanye Bio-Technique Co. Ltd., Shanghai, China) were all of

analytical grade, purchased from Chinese companies, and used as received. Atrazine (Shangdong Qiaochan Chemical Co. Ltd., Province Shangdong, China), pirimicarb (Jiansu Shanda Chemical Co. Ltd., Province Jiansu, China) and propoxur (Hunan Haili Chemical Co. Ltd., Province Hunan, China) were chemically pure.

The instruments used in this study were as follows: Perkin-Elmer 1700 infrared spectrometer (Perkin-Elmer Company, USA); LEO-438VP scanning electronic microscope (SEM, LEO Company, UK); UV-2602 UV/VIS spectrophotometer (Shanghai Younike Instrument Co. Ltd., Shanghai, China); THZ-92C constant temperature shaker equipped with gas bath (Shanghai Boxun Medical Treatment Equipment Factory, Shanghai, China); Zetasizer Nano-Zeta potential analyzer (Malvern Instrument Company, UK); STA449 thermogravimetry analyzer (TGA, Netzsch Company, German), air atmosphere, a heating rate of 10 °C/min.

2. Preparing Grafted Particles PSSS/SiO₂ and Examining Interaction between Grafted PSSS and Atrazine

The goal of this work was to prepare atrazine imprinting material with SSS as functional monomer, so the interaction between SSS and atrazine molecule needs to be first examined. For this purpose, we prepared the grafted particles PSSS/SiO₂ by using surface-initiated graft-polymerization method, and investigated the adsorption action of the grafted particles PSSS/SiO₂ towards atrazine. The examining of the interaction between the grafted PSSS and atrazine can be equivalent to the estimating of the interaction between the monomer SSS and atrazine molecule. Referring to the procedure described elsewhere [37], the grafted particles PSSS/SiO₂ were prepared: (1) the micron-sized silica gel particles were surface-modified with coupling agent 3-aminopropyltrimethoxysilane (AMPS), and primary amino groups were introduced onto the surfaces of silica gel particles, obtaining the modified particles AMPS-SiO₂; (2) by the initiating of amino group/persulfate system, the surface-initiated graft-polymerization of SSS was conducted, obtaining the grafted particles PSSS/SiO₂.

The FTIR spectrum of the grafted particles PSSS/SiO₂ was determined to characterize their structure, and their zeta potentials at different pH values were determined to verify their surface electrical property. Atrazine aqueous solutions with different concentrations were prepared in a range of 1-30 mg/mL, and the isothermal adsorption tests of PSSS/SiO₂ for atrazine were performed.

3. Preparation and Characterization of Atrazine Molecule Surface-imprinted Material MIP-PSSS/SiO₂

The atrazine molecule surface-imprinting was conducted in an aqueous solution. Atrazine (2.85 g) and SSS (13.63 g) were dissolved in 100 mL of distilled water and the pH of this solution was adjusted to pH=4 with a diluted aqueous solution of HCL. The solution was added into a four-necked flask equipped with a mechanical agitator, a reflux condenser, a thermometer and a N₂ inlet, followed by added 1.2 g of the modified particles AMPS-SiO₂ and 1.46 g of crosslinker MBA. N₂ was bubbled for 30 min to exclude air. The content was heated to 35 °C, and 0.136 g of initiator APS was added. The graft/cross-linking polymerization reaction was carried out under N₂ atmosphere at 35 °C for 12 h. The resultant particles were collected by filtering. To remove the template atrazine, the product particles were fully soaped and washed with a diluted aqueous solution of NaOH (pH=11), and finally washed with distilled water until atrazine could not be detected by UV spectrophotom-

etry in the cleaning liquid. Through vacuum drying, the atrazine molecule surface-imprinted material, MIP-P(SSS-co-MBA)/SiO₂ (simplified as MIP-PSSS/SiO₂) was obtained. For comparison, the non-imprinting material P(SSS-co-MBA)/SiO₂ (simplified as NMIP-PSSS/SiO₂) was also prepared in the absence of template atrazine under the same conditions stated above.

The FTIR spectrum of MIP-PSSS/SiO₂ particles was determined to characterize their chemical structure, and their morphology change was observed with SEM. The grafting degree of copolymer P(SSS-co-MBA) on MIP-PSSS/SiO₂ particles was determined by TGA (by subtracting the weight loss rate of AMPS-SiO₂ from that of MIP-PSSS/SiO₂), and the experimental result indicated that the grafting degree of MIP-PSSS/SiO₂ particles was 20.23 g/100 g. At the same time, the non-imprinting material NMIP-PSSS/SiO₂ (P(SSS-co-MBA)/SiO₂) has a grafting degree of 20.01 g/100 g, showing that the grafting degrees of both particles were similar.

4. Study of Combination and Recognition Properties of MIP-PSSS/SiO₂ for Atrazine

4-1. Isothermal Binding Experiments

The adsorption kinetics experiment was first conducted to determine the time of equilibrium adsorption, and it was about 6 h. On that basis, the isothermal binding property of MIP-PSSS/SiO₂ particles for atrazine was investigated. At the constant temperature of 25 °C, atrazine solutions of 70 mL with different concentrations were placed into a number of conical flasks with cover, and about 0.01 g of MIP-PSSS/SiO₂ particles weighted accurately was added into these solutions, respectively. These mixtures were shaken in a constant temperature oscillator for 6 h, and the binding process was allowed to reach equilibrium. After centrifugal separation, the atrazine concentrations of the supernatants were determined by UV spectrophotometry ($\lambda=221$ nm). The equilibrium binding amount of atrazine, Q_e (mg/g), was calculated according to Eq. (1), and the isothermal binding curve was figured.

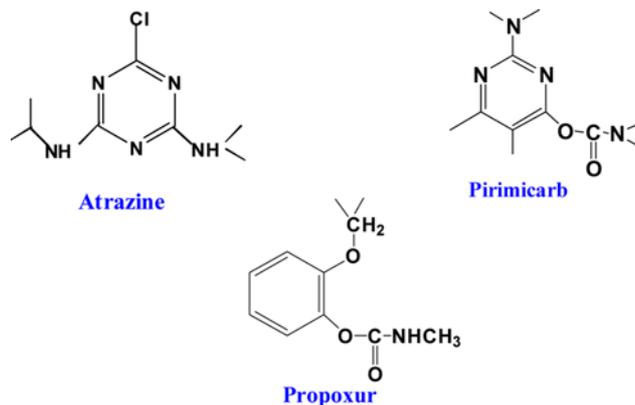
$$Q_e = \frac{V(C_0 - C_e)}{m \times 1000} \quad (1)$$

where C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentration of atrazine, respectively, V (mL) is the volume of atrazine solution, and m (g) is the mass of the used adsorbent MIP-PSSS/SiO₂ particles.

Like atrazine, both propoxur and pirimicarb are two pesticides, but they are two insecticides. The chemical structures of propoxur and pirimicarb have some similarity to that of atrazine, and especially for both pirimicarb and atrazine, they are hexahydroxy N-containing aryl compounds. Therefore, in this investigation, propoxur and pirimicarb were selected as two contrast substances to examine the recognition property of MIP-PSSS/SiO₂ for atrazine. The molecular structures of all of the three pesticides are schematically expressed in Scheme 1. According to the same method described above, the isothermal binding curves of propoxur and pirimicarb were determined, and their concentration in the supernatants were determined by UV spectrophotometry at 216 nm for propoxur and at 313 nm for pirimicarb, respectively.

4-2. Binding Selectivity Experiments

To further examine the recognition specificity of MIP-PSSS/SiO₂ particles for atrazine, competitive adsorption experiments in mixed solutions were carried out. Two binary mixed solutions, atrazine/



Scheme 1. Schematic expression of molecular structures of three pesticides.

propoxur and atrazine/pirimicarb, were prepared, and the concentration of each substance in the two mixed solutions was the same, 0.3 mg/mL. The two binary mixed solutions (70 mL) were placed into two conical flasks with cover, respectively, and 0.01 g of MIP-PSSS/SiO₂ particles weighted accurately was added into the two solutions, respectively. The isothermal binding experiments were conducted. After reaching binding equilibriums (6 h), the equilibrium concentration of each substance in the two supernatants was determined by dual-band UV spectrophotometry, and the distribution coefficient for each substance was calculated according to Eq. (2) [38,39].

$$K_d = \frac{Q_e}{C_e} \quad (2)$$

where K_d represents the distribution coefficient (mL/g) of a substance; (mg/g) is its equilibrium combining quantity; C_e (mg/mL) is its equilibrium concentration.

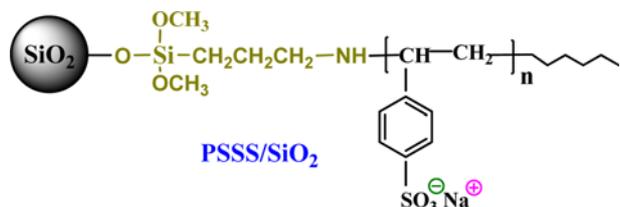
Relative to a certain competition substance, propoxur or pirimicarb, the selectivity coefficient k of MIP-PSSS/SiO₂ particles for atrazine can be obtained from the distribution coefficient data according to Eq. (3), and the value of k marks the recognition selectivity of MIP-PSSS/SiO₂ for the template atrazine.

$$k = \frac{K_d(\text{Atrazine})}{K'_d} \quad (3)$$

where $K_d(\text{Atrazine})$ is the distribution coefficient of atrazine, whereas K'_d represents the distribution coefficient of a certain competition substance [38, 39].

5. Desorption Experiment

MIP-PSSS/SiO₂ particles with a certain amount, which had adsorbed atrazine in a saturation state, were packed into a piece of glass pipe with an internal diameter of 1.0 cm, and the bed volume (BV) of the packed column was made to be about 2 mL. A diluted aqueous solution of NaOH (pH=11.5) was used eluent. The eluent was allowed to flow gradually through the packed column at a rate of two bed volumes per hour (2 BV/h) in a countercurrent manner. The effluents with one volume (1 BV) interval were collected, and the concentrations of atrazine in these effluents were determined. The dynamic desorption curve was plotted, and the elution property of MIP-PSSS/SiO₂ particles was examined.



Scheme 2. Schematic expression of chemical structure of grafted particles PSSS/SiO₂.

RESULTS AND DISCUSSION

1. Structure of Grafted Particles PSSS/SiO₂ and their Adsorption Property for Atrazine

1-1. Structure of Grafted Particles PSSS/SiO₂

In an aqueous solution system, a surface-initiating system was constituted by the amino group (primary amine group) on the modified particles APMS-SiO₂ and the ammonium persulfate in the aqueous solution, and so primary free radicals were generated on the surfaces of APMS-SiO₂ particles [37]. These free radicals on the surfaces of the particles initiated monomer SSS to produce graft-polymerization, forming the grafted particles PSSS/SiO₂. The chemical structure of the grafted particles PSSS/SiO₂ can be schematically expressed in Scheme 2. It is obvious that the grafted macromolecule PSSS is an anionic polyelectrolyte carrying a great deal of sulfonate group.

Fig. 1 gives the FTIR spectra of the three particles, SiO₂, the modified particles APMS-SiO₂ and the grafted particles PSSS/SiO₂.

As compared with the spectrum of SiO₂, in the spectrum of APMS-SiO₂, the band at 3,440 cm⁻¹ that is associated with the silanol group has been weakened. At the same time, two new bands at 2,920 cm⁻¹ and 690 cm⁻¹ appear. The former is the asymmetrical stretching vibration absorption of C-H bond and the latter is attributed to the bending vibration absorption of N-H bond of the primary amine group. The above spectrum data show that the coupling agent APMS has bound onto the surfaces of silica gel particles and the modified particles APMS-SiO₂ have been formed. In the spectrum of PSSS/SiO₂, the characteristic vibration absorption of the sulfonate group appears at 1,010 cm⁻¹. At the same time, the out-plane flexural vibration absorption of C-H bond of benzene ring appears at 674 cm⁻¹ (other characteristic absorption bands of benzene are covered). The above spectrum changes demonstrate that the anionic monomer SSS has produced surface-initiated graft-polymerization by initiating of amino group/persulfate system and the grafted particles PSSS/SiO₂ have

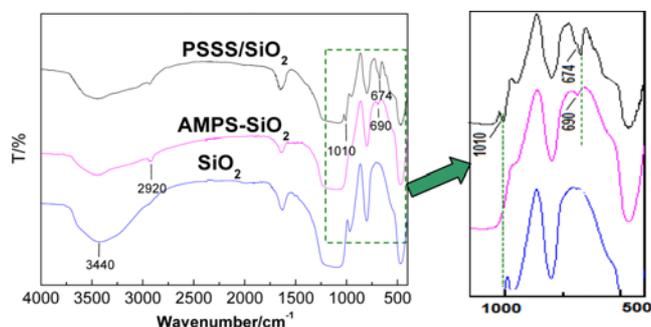


Fig. 1. Infrared spectra of three kinds of particles.

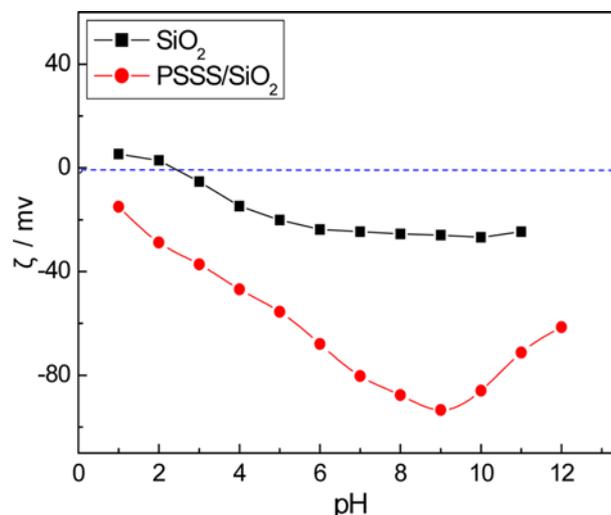


Fig. 2. Zeta potential curve of grafted particles PSSS/SiO₂.

been formed. It needs to be pointed that all of the above various absorption bands of PSSS/SiO₂ look very weak by affecting of the strong absorption background of SiO₂.

1-2. Zeta Potential of Grafted Particles PSSS/SiO₂

Fig. 2 gives the zeta potential curves of PSSS/SiO₂ and SiO₂ particles. From Fig. 2, the following facts can be seen. Although the zeta potential of SiO₂ particles is negative in a greater range of pH, the absolute values are small. However after the graft-polymerization of SSS, the zeta potential of PSSS/SiO₂ particles has changed fundamentally. In a greater range of pH, not only the zeta potential of the grafted particles PSSS/SiO₂ is negative, but also the absolute values are very large. It implies that there are negative charges with high density on the surfaces of PSSS/SiO₂ particles, and it arises from the negative ions of sulfonate groups of the grafted PSSS.

1-3. Interaction between PSSS/SiO₂ and Atrazine

The isothermal adsorption experiments of PSSS/SiO₂ particles for atrazine were performed in acidic solutions of pH=4, and Fig. 3 gives the adsorption isotherms.

Fig. 3 shows that silica gel particles can adsorb atrazine but the

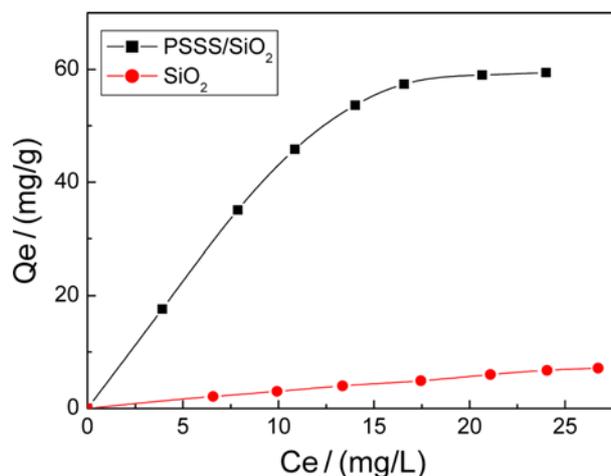


Fig. 3. Adsorption isotherm of grafted particles PSSS/SiO₂ for atrazine. Temperature: 25 °C; pH=4.

adsorption ability is very weak. However, the grafted particles PSSS/SiO₂ have very strong adsorption ability for atrazine and the adsorption capacity can get up to 60 mg/g, suggesting that there is a strong interaction between PSSS/SiO₂ particles and atrazine molecules. Based on the molecular structure of atrazine displayed in Scheme 1 and the chemical structure of PSSS/SiO₂ particles shown in Scheme 2, this experimental fact is easy to explain. There are five N atoms in a molecule of atrazine and they will become positive ions by protonating in acidic solutions and even in neutral solutions. Whereas, there are negative charges with high density on the surfaces of the grafted particles PSSS/SiO₂, which arise from the negative ions of the sulfonate groups of the grafted macromolecule PSSS. It is inevitable that the strong electrostatic interaction between the host-guest (the grafted particles PSSS/SiO₂ and atrazine molecules) will be produced, leading to a high adsorption capacity of PSSS/SiO₂ particles for atrazine. Through the strong electrostatic interaction, a great deal of atrazine molecules will be adsorbed onto the surfaces of PSSS/SiO₂ particles. At the same time, the above experimental facts also demonstrate that there exists strong electrostatic interaction between the anionic monomer SSS and atrazine molecule, and so it lays a full theory foundation for realizing atrazine molecule surface-imprinting with SSS as functional monomer.

To evaluate the effect of pH value on the interaction between PSSS/SiO₂ particles and atrazine, isothermal adsorption experiments of PSSS/SiO₂ particles for atrazine were carried out at different pH values. Fig. 4 presents the relationship curve between the saturated adsorption amounts of atrazine on PSSS/SiO₂ particles and pH value.

It can be seen that the adsorption capacity of atrazine on PSSS/SiO₂ particles first increases and then decreases with pH value, and there is a maximum adsorption capacity at pH 4, suggesting that at pH 4, the interaction between PSSS/SiO₂ particles and atrazine is the greatest. This is explained as follows. As pH value is small, there is great deal of H⁺ ion in the solution, and they as counterions can enter into the compact layer of the double layer on the surfaces of PSSS/SiO₂ particles. As a result, the zeta potential of PSSS/SiO₂ particles will decrease as shown in Fig. 2, and it will cause the interaction between PSSS/SiO₂ particles and atrazine to become small, leading to small adsorption capacity of atrazine. The zeta potential

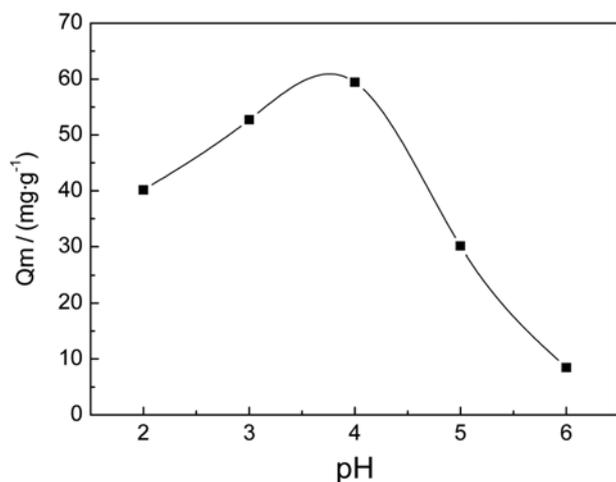


Fig. 4. Variation of saturated adsorption amount with pH value. Temperature: 25 °C.

of PSSS/SiO₂ particles will increase with the increasing of pH value, and it makes the adsorption capacity of atrazine to become larger. However, the protonating degree of the N atoms in atrazine molecule will weaken with the increasing of pH value, and it is disadvantageous to the interaction between PSSS/SiO₂ particles and atrazine. As pH < 4, the negative effect does not appear; but as pH > 4, the negative effect will appear. Therefore, at pH = 4, the interaction between PSSS/SiO₂ particles and atrazine is the greatest, and a maximum adsorption capacity is led to. Based on this consideration, the pH value of the medium is always adjusted to be at pH 4 in the imprinting process as indicated in Section 2.3 as well as in the isothermal adsorption experiments.

2. Preparation Processes of Atrazine Molecule Surface-imprinted Material MIP-PSSS/SiO₂

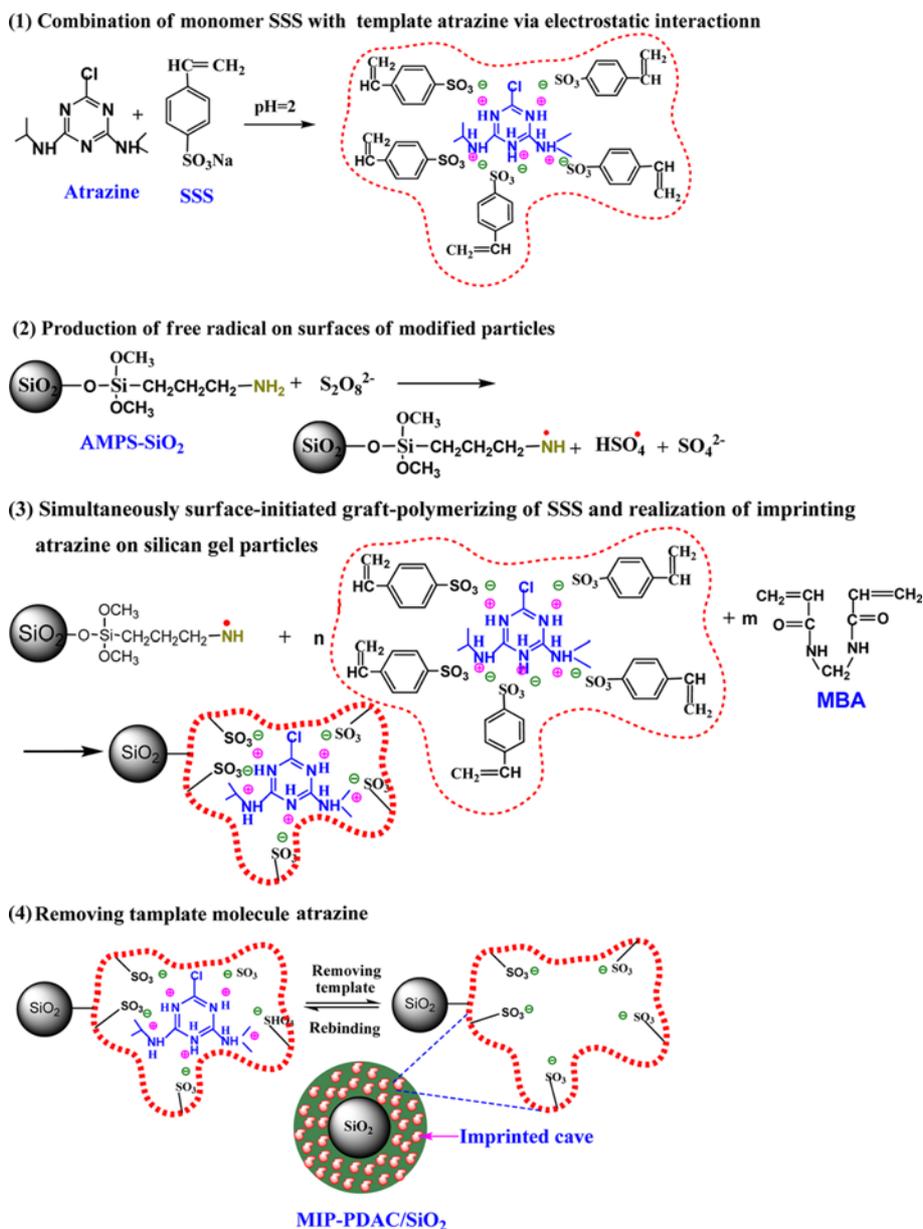
(1) In aqueous solution, by electrostatic interaction, the anionic monomers SSS are first combined around atrazine molecule that carries positive charge because of the protonation of N atoms. (2) A redox surface initiation system is constituted by the amino group (primary amine group) on the modified particles APMS-SiO₂ and the ammonium persulfate in the aqueous solution, and so primary free radicals are generated on the surfaces of APMS-SiO₂ particles. (3) These free radicals on the surfaces of the particles initiate monomers SSS around atrazine molecule as well as crosslinker MBA to produce graft/cross-linking polymerization, forming a thin layer of copolymer on the surfaces of silica gel particles. Meanwhile, atrazine molecules are enveloped in the crosslinking networks, namely, atrazine molecule surface-imprinting is realized. (4) After washing the enveloped template molecules from the crosslinking networks, large numbers of atrazine molecule-imprinted caves will remain within this thin polymer layer on the surfaces of silica gel particles (it can be proved by the following recognition specificity of the obtained imprinted material for atrazine molecule). Thereupon, the atrazine molecule surface-imprinted material MIP-PSSS/SiO₂ is obtained. The procedure described above can be schematically expressed in Scheme 3.

3. Characterization of Atrazine Molecule Surface-imprinted Material MIP-PSSS/SiO₂

3-1. Infrared Spectrum

Fig. 5 gives the infrared spectra of two particles, the grafted particles PSSS/SiO₂ and atrazine molecule surface-imprinted particles MIP-PSSS/SiO₂.

As compared with the spectrum of PSSS/SiO₂, in the spectrum of MIP-PSSS/SiO₂ (i.e., MIP-P(SSS-co-MBA)/SiO₂), except for the characteristic vibration absorption of sulfonate group absorption at 1,010 cm⁻¹ and the out-plane flexural vibration absorption of benzene ring appears at 674 cm⁻¹, two new absorption bands at 1,680 and 1,545 cm⁻¹ appear. The former should be ascribed to the stretching vibration absorption of the carbonyl group of amide group (amide I band), and the latter should be attributed to the in plane bending vibration absorption of N-H bond of amide group (amide II band). The two bands come from the units of the crosslinker MBA in the grafted crosslinked copolymer P(SSS-co-MBA) of MIP-PSSS/SiO₂. These spectrum changes mentioned above fully demonstrate that it is the surface initiating system of amino group/persulfate that initiates the graft/cross-linking polymerization of SSS and MBA, and leads to the formation of atrazine molecule surface-imprinted layer on silica gel particles.



Scheme 3. Schematic expression of chemical reaction process to prepare MIP-PSSS/SiO₂.

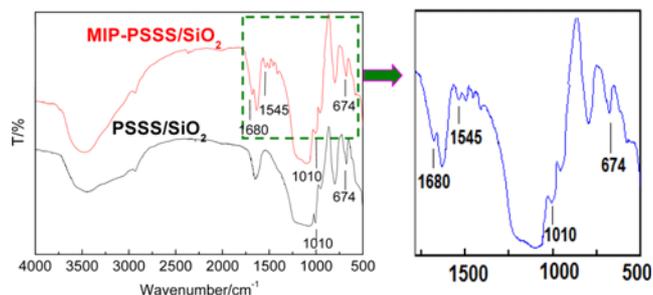


Fig. 5. Infrared spectra of PSSS/SiO₂ and MIP-PSSS/SiO₂ particles.

3-2. Morphology

Fig. 6(a) and Fig. 6(b) present the SEM images of raw silica gel particles and the imprinted particles MIP-PSSS/SiO₂. It can be found that the surfaces of raw silica gel particles are rough and scraggy.

After the graft/cross-linking polymerization, the surfaces of the imprinted particles MIP-PSSS/SiO₂ become smoother and flatter. This is led to by the coating and filling up action of the crosslinking copolymer (P(SSS-co-MBA)) layer.

4. Binding and Recognition Performance of MIP-PSSS/SiO₂ for Atrazine

4-1. Binding Isotherms

In acidic solutions of pH=4, the adsorption experiments for three substances, atrazine, propoxur and pirimicarb, were performed with the non-imprinted material NMIP-PSSS/SiO₂ and the imprinted material MIP-PSSS/SiO₂, respectively. Fig. 7 gives adsorption isotherms of NMIP-PSSS/SiO₂ (non-imprinted material) for the three substances, whereas Fig. 8 gives the binding isotherms of MIP-PSSS/SiO₂ (imprinted material) for the three substances. It needs to be indicated that in Fig. 6 and Fig. 7, the three isotherms are devised into two pictures because of the different solubilities of the three

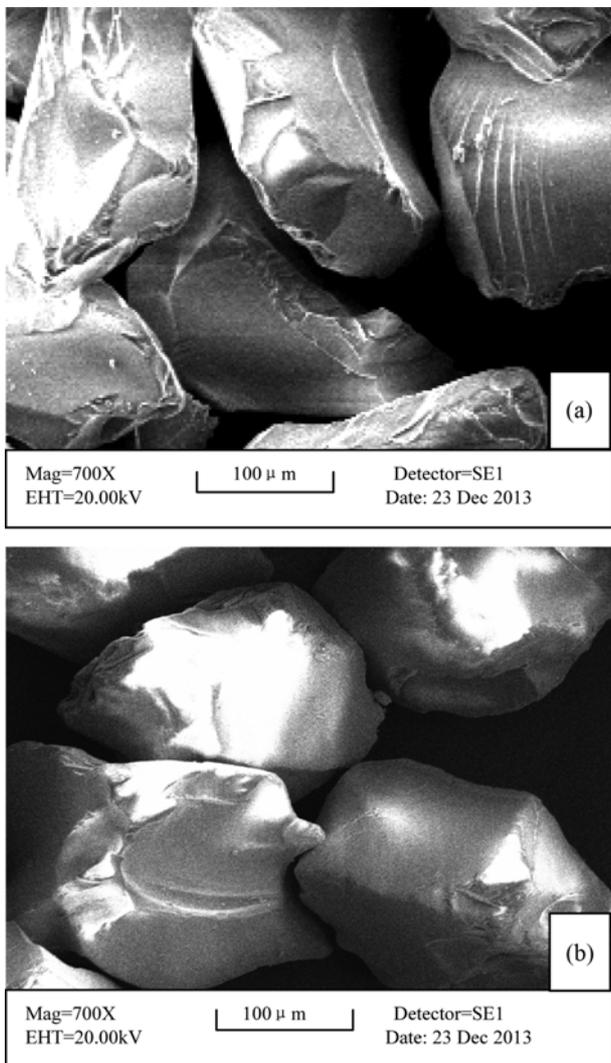


Fig. 6. SEM photographs of SiO₂ and MIP-PSSS/SiO₂.

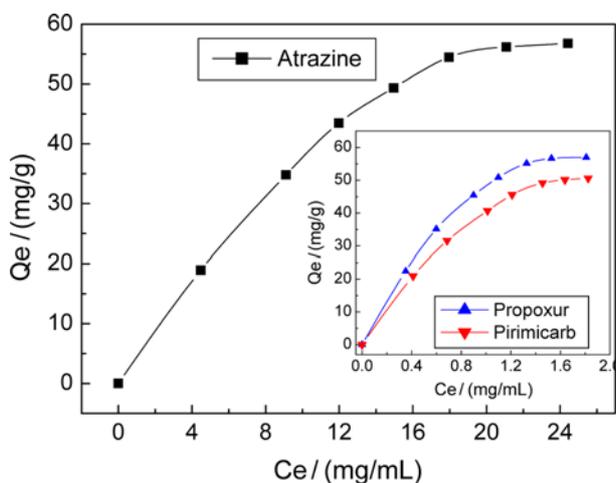


Fig. 7. Adsorption isotherms of NMIP-PSSS/SiO₂ for three pesticides. Temperature: 25 °C; pH=4.

pesticides in water.

It is displayed in Fig. 7 that the non-imprinted material NMIP-

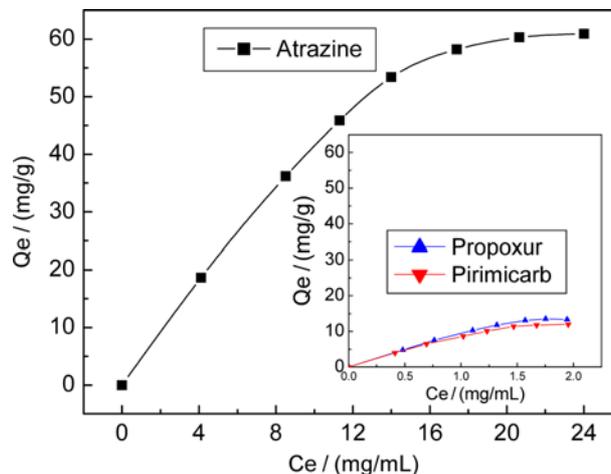


Fig. 8. Binding isotherms of MIP-PSSS/SiO₂ for three pesticides. Temperature: 25 °C; pH=4.

PSSS/SiO₂ has high adsorption ability for all of the three substances, and the adsorption capacity is in a range of 51-57 mg/g. Fig. 7 shows that NMIP-PSSS/SiO₂ particles for the three pesticides have the similar adsorption abilities, and they are without adsorption selectivity.

Fig. 8 indicates clearly that the binding capacities of the imprinted material MIP-PSSS/SiO₂ for the three pesticides have changed fundamentally. The binding capacity of atrazine still maintains a high value (61 mg/g). However, the binding capacity of propoxur remarkably decreases from 57 mg/g to 13 mg/g, and that of pirimicarb also significantly decreases from 51 mg/g to 12 mg/g. Obviously, the imprinted material MIP-PSSS/SiO₂ displays high combining affinity and special recognition selectivity for the template molecule, atrazine. For MIP-PSSS/SiO₂ particles, a great quantity of atrazine molecule-imprinted caves is distributed within the thin polymer layer on the surfaces of silica gel particles. These caves are highly matched with atrazine molecule in size, steric shape and combination sites, and it leads to the specific recognition ability and strong binding action of MIP-PSSS/SiO₂ particles towards atrazine molecules. For both propoxur and pirimicarb, there are some molecular structure differences between them and atrazine. Therefore, these imprinted caves are unmatched with propoxur molecule and pirimicarb molecule in size, steric shape and combination sites (see Scheme 1). It is these mismatches that make these imprinted caves to be difficult to accept the two kinds of contrast molecules, resulting in weak combination action and low combination capacities of MIP-PSSS/SiO₂ particles for propoxur and pirimicarb. Since the imprinted material MIP-PSSS/SiO₂ has special recognition selectivity and high combining affinity for atrazine as described above, it can be used as an effective solid adsorbent for the removal of atrazine from water. Similarly, the imprinted materials of other pesticides with high performance can also be prepared using the same method. Therefore, the novel molecule surface-imprinting technique of synchronously graft-polymerizing and imprinting is promising in the pesticide pollution treatment.

Besides, the adsorption models of three materials, NMIP-PSSS/SiO₂, MIP-PSSS/SiO₂ and the grafted particles PSSS/SiO₂ for the three pesticides were evaluated, and the adsorption behaviors fitted to

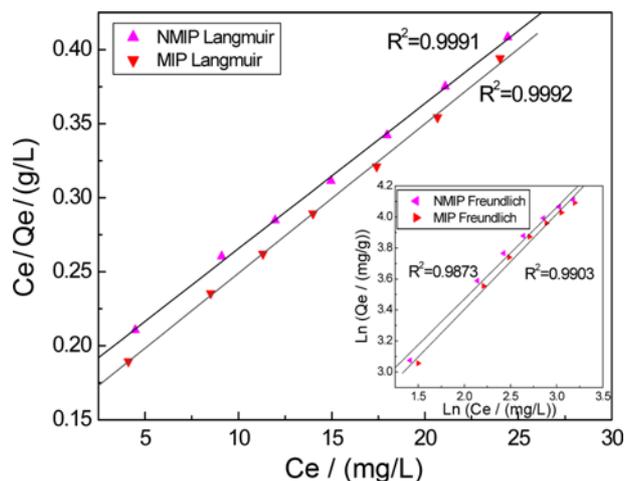


Fig. 9. Fitted straight lines according to two isothermal equations.

the Langmuir equation. It is explained as follows by taking the adsorptions of NMIP-PSSS/SiO₂ and MIP-PSSS/SiO₂ particles for atrazine as examples. The adsorption isotherms of NMIP-PSSS/SiO₂ and the binding isotherm of MIP-PSSS/SiO₂ for atrazine (shown in Fig. 7 and Fig. 8) were treated with the straight line forms of the Langmuir equation (C_e/Q_e versus C_e) and Freundlich equation ($\ln Q_e$ versus $\ln C_e$) shown in Eq. (4) and Eq. (5), respectively, and four fitted straight lines, which are divided in two groups, are resulted in as displayed in Fig. 9. By comparing the linear correlation coefficients for the lines of the two groups, it is obvious that there is a good linear relativity between C_e/Q_e and C_e , namely, the adsorption behaviors of NMIP-PSSS/SiO₂ and MIP-PSSS/SiO₂ particles for atrazine fit to the Langmuir equation.

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \quad (4)$$

$$\ln Q_e = \ln k + n \ln C_e \quad (5)$$

4-2. Selectivity Coefficients

Two binary mixed solutions, atrazine/propoxur and atrazine/pirimicarb, were prepared, and the competitive adsorption experiments of MIP-PSSS/SiO₂ in the two solutions were conducted. In Table 1 the data of the distribution coefficients K_d for each substance and the selectivity coefficients k of MIP-PSSS/SiO₂ for atrazine are summarized.

It can be found from the data in Table 1 that in the two binary

Table 1. Distribution coefficient and selectivity coefficient data for two binary systems

Adsorbing material	Adsorbed substance	K_d /(mL/g)	k
NMIP-PSSS/SiO ₂	Atrazine	27.01	1.06
	Pirimicarb	25.37	
	Atrazine	27.45	1.02
	Propoxur	26.97	
MIP-PSSS/SiO ₂	Atrazine	30.85	8.79
	Pirimicarb	3.51	
	Atrazine	31.66	9.69
	Propoxur	3.27	

mixed solutions, both the selectivity coefficients of the non-imprinted material NMIP-PSSS/SiO₂ for atrazine are close to 1, implying the NMIP-PSSS/SiO₂ particles have no recognition selectivity for atrazine molecule. Whereas for MIP-PSSS/SiO₂ material, its selectivity coefficients for atrazine relative to propoxur is 9.69, and its selectivity coefficients for atrazine relative to pirimicarb is 8.79. It is apparent that in comparison to NMIP-PSSS/SiO₂ particles, the atrazine molecule-imprinted material MIP-PSSS/SiO₂ exhibits special molecule recognition property for atrazine. The special recognition specificity of MIP-PSSS/SiO₂ for atrazine molecule still comes from a great deal of the imprinted caves matched with atrazine molecule within the thin polymer layer on the surfaces of silica gel particles. The result of competitive adsorption experiments again demonstrates that the atrazine molecule-imprinted material MIP-PSSS/SiO₂ has specific recognition selectivity for atrazine. Therefore, we can draw the conclusion that the pesticide molecule surface-imprinted materials prepared with the novel molecule surface-imprinting technique of "synchronously graft-polymerizing and imprinting" will be the solid adsorbents with high performance for the efficient removal of pesticide residues from water.

5. Elution Property MIP-PSSS/SiO₂

A diluted aqueous solution of NaOH (0.001 M, pH=11.5) was used as the eluent. The eluent was allowed to upstream pass through the column packed with MIP-PSSS/SiO₂ particles having adsorbed atrazine molecule in a saturated state, and the dynamic desorption experiment was conducted. In Fig. 10, the dynamic desorption curve is presented.

It can be seen in Fig. 8 that this desorption curve is cuspidal and without trailing, indicating that the template ions combined in the packed column are easy to be washed off, namely, MIP-PSSS/SiO₂ particles have excellent eluting property. By calculating, the desorption ratios of atrazine in 19 BV and 21 BV reach 96.84% and 99.28%, respectively. This experimental fact shows that atrazine molecules combined in the imprinted caves on MIP-PSSS/SiO₂ particles are easy to be desorbed or eluted because those atrazine molecule-imprinted caves are distributed within the thin polymer layer on the surfaces of MIP-PSSS/SiO₂ particles, and it leads to the little diffusion resistance for template molecules. Therefore, the template

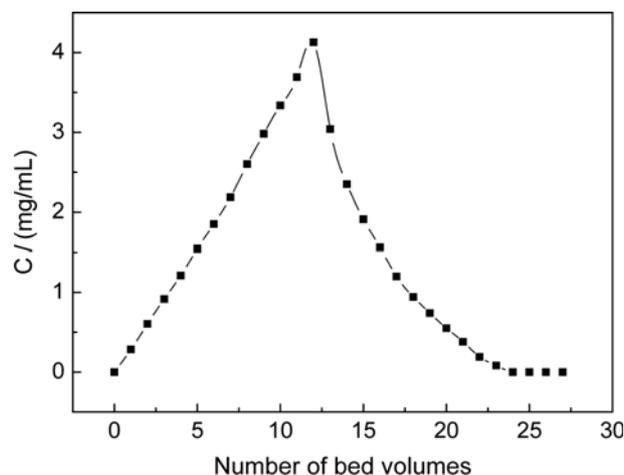


Fig. 10. Elution curve of atrazine on MIP-PSSS/SiO₂ column. Temperature: 25 °C.

molecules can be washed off rapidly, and the column can be recovered quickly. This demonstrates that the recovery and reuse of the surface-imprinted material MIP-PSSS/SiO₂ is feasible and very convenient.

CONCLUSIONS

By using the novel molecular surface-imprinting technique of “synchronously graft-polymerizing and imprinting,” atrazine molecule surface-imprinted material was prepared successfully. The anionic monomers SSS are combined around the template atrazine molecule by the mutual strong electrostatic interaction; and by initiating of a surface-initiating system consisting of the amino group on silica gel particles and persulfate in the aqueous solution, atrazine molecule surface-imprinting was smoothly carried out on the surfaces of silica gel particles, obtaining atrazine molecule surface-imprinted material MIP-PSSS/SiO₂. As a result there are a great deal of atrazine molecule-imprinted caves within the thin polymer layer on the surfaces of silica gel particles; the imprinted material MIP-PSSS/SiO₂ possesses special recognition selectivity and high binding affinity for atrazine molecule. It can be anticipated that the surface-imprinted materials of various pesticides with high performance can be prepared by using the new surface-imprinting method. With these surface-imprinted materials as solid absorbents, pesticide residues in water can be effectively removed. Such researches are significant and valuable in the management and protection of the water environment.

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