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Molecular imprinted material prepared by novel surface imprinting technique for selective adsorption of pirimicarb

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Abstract

In this paper, a molecular imprinted material with high performance for recognizing pirimicarb, which is a kind of carbamate pesticide, was prepared by adopting the novel surface molecular imprinting technique put forward by us previously. Firstly, the functional macromolecule poly(methacrylic acid) (PMAA) was grafted on the surface of silica gel particles in the manner of "grafting from" using 3-methacryloxypropyl trimethoxysilane (MPS) as an intermediate, and the grafted particle PMAA/SiO_2 was formed. Afterwards, the molecular imprinting was carried out towards the macromolecule PMAA grafted on the surface of silica gel particles using pirimicarb as template and ethylene glycol diglycidyl ether (EGGE) as crosslinking agent via the intermolecular hydrogen bond and electrostatic interaction, and pirimicarb imprinted material MIP-PMAA/SiO_2 was obtained. The combining characteristic of MIP-PMAA/SiO_2 for pirimicarb was studied profoundly with static method. The experimental results show that the surface-imprinted material MIP-PEI/SiO_2 has excellent combining affinity and recognition selectivity for the template molecules of pirimicarb. Before imprinting, PMAA/SiO_2 has greater adsorption capacities for pirimicarb as well as for the contrast substances, atrazine and propoxur, whose structures are similar to pirimicarb, and the selectivity coefficients of PMAA/SiO_2 for pirimicarb with respect to atrazine and propoxur are only 1.523 and 0.612, respectively. However, after imprinting, the combining capacities of MIP-PMAA/SiO_2 towards atrazine and propoxur decrease remarkably, whereas that of MIP-PMAA/SiO_2 for pirimicarb still remains higher. The coefficients of MIP-PMAA/SiO_2 for pirimicarb with respect to atrazine and propoxur were enhanced greatly, and they are 12.20 and 14.15, respectively. Besides, MIP-PMAA/SiO_2 adsorbing pirimicarb in a saturated state has fine elution and reuse properties.

Keywords: Pirimicarb; Poly(methacrylic acid); Surface imprinting

1. Introduction

Various pesticides, such as carbamates, organophosphorus and chlorinated phenoxyacids, are widely used in agriculture. These chemicals directly applied onto the ground are rapidly transported into groundwater and natural water is frequently contaminated by them [1–4]. Due to the high toxicity of these pesticides for humans and all animals and the long-term persistence in the environment, legislation poses several limits on the presence of these pesticides as residues and make them a suitable subject of trace analysis [5,6]. Generally, the trace analysis of complex environment samples needs a preconcentration step in order to reduce the matrix interference and enrich the analytes, and this treatment is often performed by solid-phase extraction (SPE) [7,8]. The technique of SPE is more rapid, simple and economical than the traditional liquid–liquid extraction. In order to carry out SPE effectively and attach a more selective preconcentration of the analytes, it is needed to develop sorbents with high selectivity. Molecular imprinted polymers (MIPs) as synthetic antibody mimics appear as excellent candidates to accomplish such requirement [9–11].

The conventional method to prepare molecular imprinted polymers (MIPs) is a entrapment way, and the process is generally as follows: functional and crosslinking monomers are copolymerized (with bulk or solution polymerization method) in the presence of template molecules, and before

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copolymerization, the functional monomers initially are arranged around the template molecules through either non-covalent or covalent interactions; subsequently the template molecules are removed, molecular cavities remain in the polymer, which are complementary to the template in size, shape and spatial arrangement of functional groups; finally the obtained monolith is ground and sieved to the required particle dimensions. Obviously, the molecular imprinted polymers prepared by the conventional technique have some disadvantages: (1) the imprinted polymer matrices are usually thick and the number of recognition sites per unit volume of the polymer is relatively low [12]; (2) the template molecules are embedded in the matrices too deeply so that not only the elution is difficult, but also the diffusion barrier for the template molecules is introduced [12,13], the rate of mass transfer is lower, and the template molecules are not easy to bind with recognition sites. In order to overcome these drawbacks, various surface molecular printing techniques have been developed in recent years [14–17], and the obtained thin molecular imprinted polymer films in which the imprinted cavities are distributed are more effective for recognizing the template molecules. In the previous study [18], we put forward a novel approach of surface imprinting on the surface of silica gel particles based on the graft polymerization: firstly functional macromolecule polyethyleneimine (PEI) was grafted on the silica gel particle surfaces in the manner of ‘‘grafting to’’, secondly ion printing was performed using heavy-metal ions as templates and epichlorohydrin as crosslinking agent via coordination bond action, and finally ion-imprinted material IIP-PEI/SiO_2 with high performance was obtained.

In the present work, the principle of the novel surface imprinting technique described above was adopted, and a molecular imprinted material, MIP-PMMA/SiO_2, for selectively combining pirimicarb, which is a kind of carbamate pesticide, was prepared. The combining performance of this material for pirimicarb was evaluated. In comparison with the preparation of the previous ion-imprinted material IIP-PEI/SiO_2, there are some obvious developments in this research: (1) poly(methacrylic acid) (PMMA) is used as functional macromolecule and it is grafted on the surface of silica gel particles in the manner of ‘‘grafting from’’, instead of ‘‘grafting to’’; (2) the crosslinking agent used in the imprinting process is the compound with two end epoxy groups, ethylene glycol diglycidyl ether; (3) the interaction between the functional macromolecule of PMMA and the template molecule, pirimicarb, is hydrogen bond and electrostatic interaction, instead of coordination bond action.

Pirimicarb molecule-imprinted polymers were prepared by Pingarrón et al. [5] for the preconcentration of pirimicarb and by Fung and Sun [19] for the recognition of pirimicarb with the conventional molecular imprinting technique and using methacrylic acid (MMA) as functional monomer. In this study, the pirimicarb molecule-imprinted material, MIP-PMMA/SiO_2, with high performance was prepared by adopting the surface imprinting technique. As compared with the pirimicarb imprinted polymers prepared by the conventional technique, MIP-PMMA/SiO_2 not only is highly effective for recognizing pirimicarb, but also its preparation is convenient and timesaving.

2. Experimental section

2.1. Materials and equipment

Silica gel (120–160 mesh, about 125 μm in diameter, Qingdao Ocean Chemical Ltd., Province Shandong, China) was received. Methacrylic acid (MAA; Ruijin Chemical Ltd., Tianjin, China) was of analytical grade and was purified by distillation under vacuum before use. Ammonium persulphate (Shanghai Chemical Reagent Plant, Shanghai, China) and γ-methacryloylpropyl trimethoxysilane (MPS; Nanking Chuangshi Chemical Aux Ltd., Province Jiangsu, China) were of analytical grade. Pirimicarb (Shanda Chemical Engineering Ltd., Province Jiangsu, China) was received. Propoxur (Changlong Chemical Engineering Ltd., Province Jiangsu, China) and atrazine (Qiaochang Chemical Ltd., Province Shandong, China) were received. Ethylene glycol diglycidyl ether [2,2′-(ethylenebis(oxymethylene))bisoxirane] (EGGE, crosslinking agent; Wuxi Wanrong Material Ltd., Province Jiangsu, China) was of chemical grade. Other reagents were commercial chemicals with analytical grade and purchased from Chinese companies.

The instruments used in this study were as follows: Unic-2602 UV spectrophotometer (Unic Company, Shanghai), Perkin–Elmer 1700 infrared spectrometer (Perkin–Elmer Company, USA), PHS-2 acidimeter (The Second Analytical Instrument Factory, Shanghai, China), TG16-WS high-speed centrifuge with desk type (Changsha Xiangyi Centrifuge Factory, Province Jiangsu, China), THZ-92C constant temperature shaker equipped with gas bath (Boxun Medical Treatment Equipment Factory, Shanghai, China) and STA449 thermogravimetric analyzer (TGA, Netzsch Company, Germany).

2.2. Preparation of grafted particle PMAA/SiO_2 and study on its adsorption property for pirimicarb

2.2.1. Preparing PMAA/SiO_2

According to the procedures described in Ref. [20], poly(methacrylic acid) was allowed to be grafted onto the surface of silica gel particles in the manner of ‘‘grafting from’’. The typical process was as follows: 10 g of silica gel particles activated with methane sulfoacid and 15 ml of coupling agent MPS were added into 200 ml of a mixed solvent of ethanol and water (v/v = 1:1), and the contents were maintained at 50 °C and were reacted for 24 h, resulting in the formation of the surface-modified particles MPS–SiO_2, on which polymerisable double bonds were attached chemically. Afterwards, 6 g of MPS–SiO_2 particles and 20 g of methacrylic acid were added into 400 ml of water, and the graft polymerization was performed by the initiating of $(NH_4)_2S_2O_8$ (0.018 g, 0.6 wt% of monomer) under N_2 atmosphere at 70 °C for 7 h. The product particles were extracted with ethanol in a Soxhlet extractor to remove the polymers attached physically to the particles, dried under vacuum, and finally the grafted particles PMAA/SiO_2 were gained. The grafting degree of PMAA/SiO_2 was determined with TGA method. The PMAA/SiO_2 particles used in this study have a grafting degree of 15.54 g/100 g.

2.2.2. Determination of adsorption property of PMAA/SiO_2 for pirimicarb

The adsorption dynamic behaviours of PMAA/SiO_2 for pirimicarb in aqueous medium and non-aqueous mediums, ethanol and carbon tetrachloride (CCl_4), were measured to determine the time during which the adsorption reached to equilibrium (it was about 6 h). On the basis of adsorption dynamic determination, the adsorption isotherms of PMAA/SiO_2 for pirimicarb in the three mediums were determined. The adsorption experiments were conduced in a constant temperature shaker. The changes of pirimicarb concentration before and after adsorption were determined with UV spectrophotometry.

2.2.3. Examining the effect of pH value on adsorption of PMAA/SiO_2 for pirimicarb in aqueous medium

The pH values of the aqueous solutions of pirimicarb were adjusted with dilute solution of HCl and NaOH. The isothermal adsorption experiments of PMAA/SiO_2 for pirimicarb were carried out in the solutions with different pH values to examine the effect of pH value on the adsorption capacity and to study the adsorption mechanism of PMAA/SiO_2 for pirimicarb.

2.3. Preparation of imprinted material MIP-PMAA/SiO_2 and study on its combining characteristic for pirimicarb

2.3.1. Preparing pirimicarb molecule-imprinted material MIP-PMAA/SiO_2

PMAA/SiO_2 (1 g) with a grafting degree of 15.54 g/100 g was added into 50 ml of pirimicarb solution of 8 mmol/l, and the pH value was adjusted to 8 with dilute NaOH solution. The mixture was shaken on a constant temperature shaker for 6 h until PMAA grafted on silica gel particles was fully swelled and the adsorption reached equilibrium. After filtrating, the PMAA/SiO_2 particles, which had adsorbed pirimicarb in a saturated state, were dried under vacuum. A certain amount of the PMAA/SiO_2 particles which adsorbed pirimicarb was placed in a mixed solution of water and ethanol (v/v = 1:1), in which pirimicarb with a concentration of 4 mmol/l was contained. The pH value of the solution was adjusted to 8, and a certain amount of crosslinking agent EGGE (0.1 g, 0.6 mmol) was added. The crosslinking reaction was performed at 50 °C for 8 h. The product particles were washed repeatedly with a mixed solvent of methanol, acetic acid and water (volume ratio = 7:2:1) to remove the template pirimicarb and the crosslinking agent EGGE. After filtrating, pirimicarb molecule-imprinted material MIP-PMAA/SiO_2 was obtained. The infrared spectrum of MIP-PMAA/SiO_2 was recorded.

2.3.2. Measuring combining isotherm

The adsorption dynamic behaviour of MIP-PMAA/SiO_2 for pirimicarb was firstly measured, and the time during which the adsorption reaches equilibrium was determined (it was also 6 h). Then, the combining isotherm was measured. Numbers of 30 ml of pirimicarb solutions with different concentrations were taken and transferred into conical flasks. MIP-PMAA/SiO_2 particles with the same mass were added into these solutions. These mixtures were shaken on a constant temperature shaker, centrifuged after reaching combining equilibrium, and the equilibrium concentrations of pirimicarb in the supernatants were determined with spectrophotometry (at 243 nm). The equilibrium combining amounts of MIP-PMAA/SiO_2 towards pirimicarb were calculated according to Eq. (1), and the binding isotherm was plotted.

$$Q_e = \frac{V(C_0 - C_e)}{m} \tag{1}$$

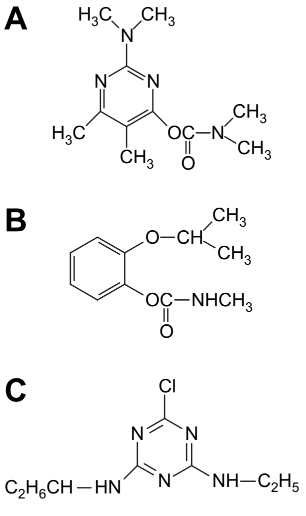
where C_0 (mg/ml) is the initial concentration of pirimicarb and C_e is the equilibrium concentration of pirimicarb; V (l) is the volume of the pirimicarb solution; m (g) is the mass of the solid absorbent MIP-PMAA/SiO_2; Q_e (mg/g) is the equilibrium combining quantity of MIP-PMAA/SiO_2 for pirimicarb.

2.3.3. Selectivity experiments

Propoxur is a kind of carbamate pesticide like pirimicarb and its chemical structure is similar to pirimicarb to a certain extent. Atrazine is a kind of herbicide, and the size and structure of atrazine molecule are quite analogous to pirimicarb. Thus, both propoxur and atrazine are selected as the contrast substances for examining the recognition selectivity of MIP-PMAA/SiO_2 for pirimicarb. The molecular structures of the three substances are schematically shown in Scheme 1.

In order to compare the binding selectivity of MIP-PMAA/SiO_2 for pirimicarb, the isotherms of MIP-PMAA/SiO_2 as well as PMAA/SiO_2 for propoxur and atrazine were determined with spectrophotometry (at 210 and 220 nm, respectively), separately.

In order to further show the specificity of MIP-PMAA/SiO_2 for pirimicarb, the competitive adsorptions of pirimicarb with



Scheme 1. Schematic expression of chemical structures of (A) pirimicarb, (B) propoxur and (C) atrazine.

respect to propoxur and atrazine were studied. The binary mixed solutions of propoxur/pirimicarb and atrazine/pirimicarb were prepared, respectively, and the concentrations of the three substances in the two mixed solutions were all the same, and were 8 mmol/l. MIP-PMAA/SiO_2 (0.3 g) was added into 30 ml of the two solutions, and the static adsorption experiments were performed. After combining equilibriums were reached, the concentration of each substance in the two supernatants was determined with spectrophotometry. Two-band method was used, and the two bands were selected as 210 and 243 nm for the mixed solution of propoxur/pirimicarb, and as 222 and 243 nm for the mixed solution of atrazine/pirimicarb. The distribution coefficient for each substance was calculated according to Eq. (2), and this equation was originated from Ref. [21].

$$K_d = \frac{Q_e}{C_e} \tag{2}$$

where K_d represents the distribution coefficient (ml/g); Q_e (mg/g) is the equilibrium combining quantity; C_e (mg/ml) is the equilibrium concentration.

The selectivity coefficient of MIP-PMAA/SiO_2 for the combining of pirimicarb with respect to the competition species (assigned as B) can be obtained from the equilibrium combining data according to Eq. (3).

$$k = \frac{K_d(\text{pirimicarb})}{K_d(\text{B})} \tag{3}$$

where k is the selectivity coefficient and B represents propoxur or atrazine. The value of k allows an estimation of selectivity of MIP-PMAA/SiO_2 for pirimicarb. A relative selectivity coefficient k' can be defined as expressed in Eq. (4) [21], and the value of k' can indicate the enhanced extent of adsorption affinity and selectivity of imprinted material for the template molecule with respect to non-imprinted material.

$$k' = \frac{k_{\text{impr}}}{k_{\text{non-impr}}} \tag{4}$$

where k_{impr} is the selectivity coefficient of MIP-PMAA/SiO_2 for pirimicarb with respect to the competition species B and $k_{\text{non-impr}}$ is the selectivity coefficient of PMAA/SiO_2 for pirimicarb with respect to the same competition species B.

2.3.4. Desorption experiment

A certain amount of MIP-PMAA/SiO_2 particles adsorbing pirimicarb in a saturated state was packed into a piece of glass pipe with an internal diameter of 0.8 cm, and the bed volume (BV) of the packed column was 2 ml. The mixed solvent of methanol, acetic acid and water with a volume ratio of 7:2:1 as eluent was allowed to flow gradually through the column at a rate of two bed volumes per hour (2 BV/h) in countercurrent manner. The effluent with one volume (1 BV) interval was collected and the concentration of pirimicarb was determined with spectrophotometry. The dynamic desorption curve was plotted and elution property of MIP-PMAA/SiO_2 was examined.

3. Results and discussions

3.1. Preparing processes of MIP-PMAA/SiO_2

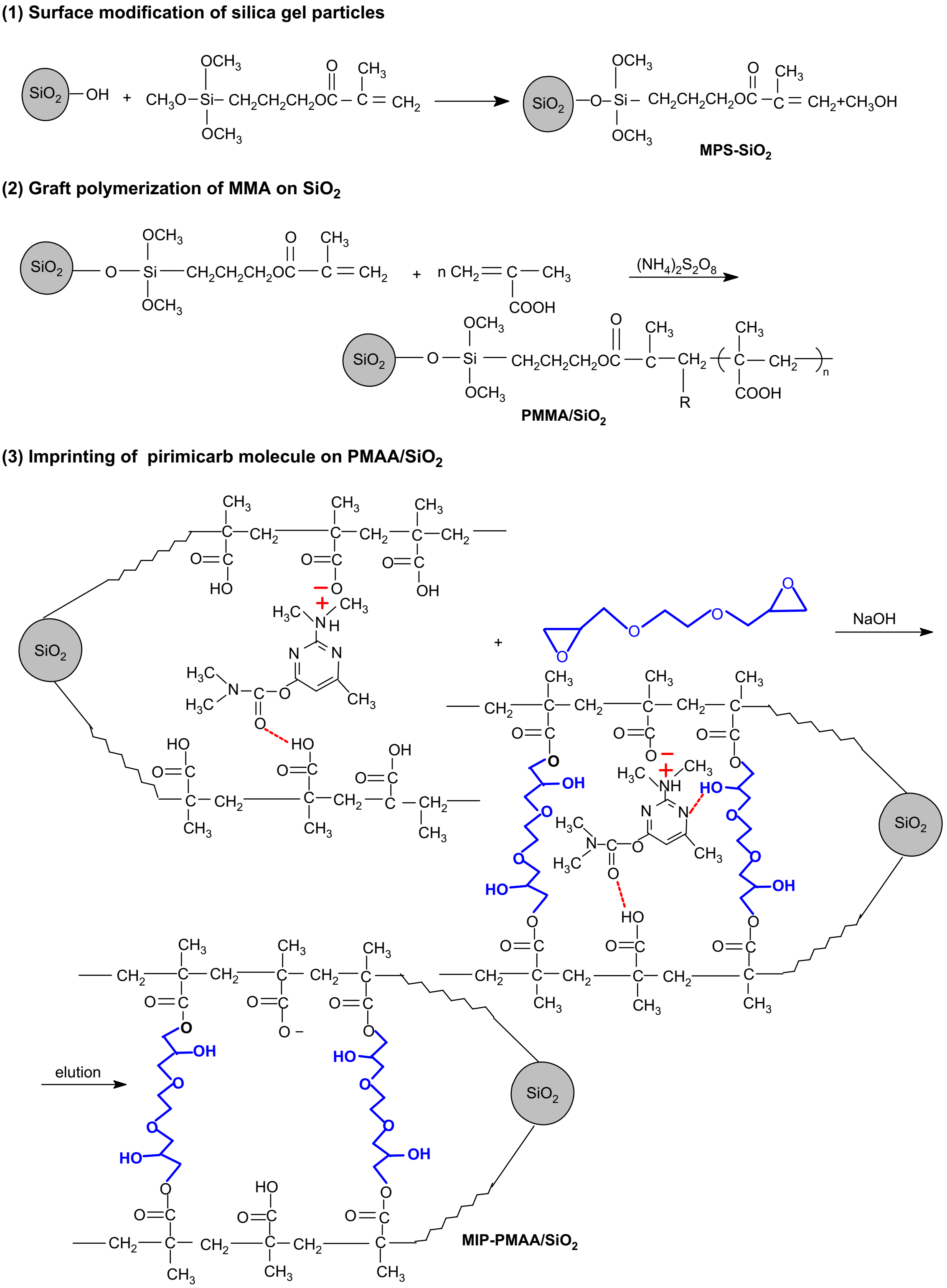
In this study, 3-methacryloxypropyl trimethoxysilane (MPS) was chosen as the intermediate to link silica gel and PMAA. After silica gel particles were chemically modified with MPS, polymerizable double bonds were attached chemically on the surface of the silica gel particles. Therefore, the graft polymerization of MAA on the silica gel particles in the manner of ‘‘grafting from’’ was allowed to be realized, and the grafted particles PMAA/SiO_2 were resulted in. As the adsorption of PMAA/SiO_2 towards pirimicarb reached a saturated state, the crosslinking agent EGGE was added. In the presence of NaOH, the ring-opening reactions between the two terminal epoxy groups of EGGE and the carboxyl groups of the grafted macromolecules PMAA can be carried out favorably, leading to the crosslinking of macromolecules PMAA. As a result, pirimicarb molecules were enveloped in the crosslinking networks. As the template molecules were washed away, a great deal of pirimicarb caves will remain in the thin polymer layer on the surface of silica gel particles, and the pirimicarb molecule-imprinted material MIP-PMAA/SiO_2 was obtained. The whole preparation process of MIP-PMAA/SiO_2 is shown in Scheme 2. The infrared spectrum characterization result shows that a new and obvious band at 1575 cm^{-1} appeared in the infrared spectrum of MIP-PMAA/SiO_2 in comparison with that of PMAA/SiO_2, and it should be ascribed to the characteristic absorption of methylene $-CH_2-$ linking with ether bond in the crosslinking bridge of EGGE. The absorption bands of other groups produced after the crosslinking reaction, such as C–O–C bond of ester group, C–O–C bond of ether linkage and $>$C–OH group of secondary alcohol, were covered up by the absorption bands of PMAA/SiO_2.

3.2. Adsorption and action mechanism of PMAA/SiO_2 towards pirimicarb

3.2.1. Adsorption properties of PMAA/SiO_2 for pirimicarb in different mediums

Pirimicarb was dissolved in water, carbon tetrachloride and ethanol, respectively. The isothermal adsorptions of PMAA/SiO_2 for pirimicarb were carried out in the three mediums. The adsorption isotherms are given in Fig. 1.

It can be found from Fig. 1 that in the medium of CCl_4, PMAA/SiO_2 has stronger absorption action. Pirimicarb is a kind of carbamate insecticide. It can be seen from its molecular structure as shown in Scheme 1 that there are multi-sites of hydrogen bond acceptor, such as oxygen atom of carbonyl group and nitrogen atoms of tertiary amine and imine groups. The carboxyl group in the grafted PMAA macromolecule not only is the hydrogen bond acceptor, but also is the hydrogen bond donor. Based on the above analysis for the molecular structure of pirimicarb, it can be speculated that the driving



Scheme 2. Schematic expression of preparing process of MIP-PMAA/SiO_2.

force for the stronger absorption of PMAA/SiO_2 towards pirimicarb in the medium of CCl_4 should first be attributed to hydrogen bond interaction. Besides, it is probable that there is another acting force for the adsorption of pirimicarb onto PMAA/SiO_2 in CCl_4. CCl_4 is a solvent with weak polarity, whereas PMAA and pirimicarb are substances with stronger polarity. It is obvious that in solvent CCl_4, pirimicarb will be adsorbed onto PMAA/SiO_2 by right of polarity interaction probably, i.e. in right of ‘surfactant inverse micelle’-like behaviour.

In the medium of ethanol, PMAA/SiO_2 at all has no adsorption action for pirimicarb. The reason for this is that a strong hydrogen bond interaction between the grafted PMAA and the

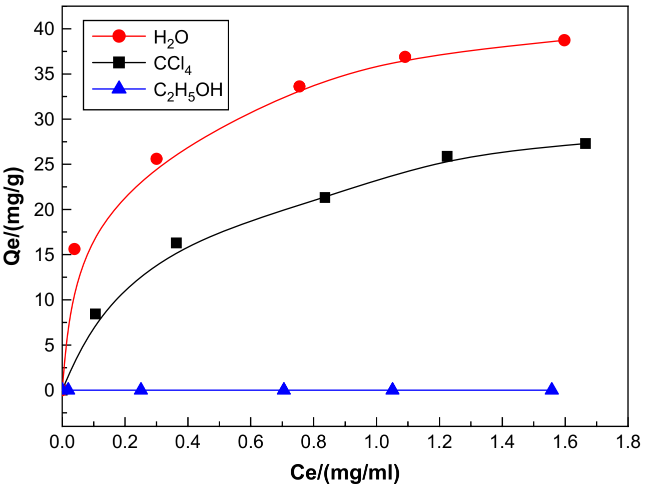


Fig. 1. Adsorption isotherms of $PMAA/SiO_2$ for pirimicarb in three mediums. Temperature: 30 °C; pH = 7 (in aqueous medium).

solvent ethanol will be produced, and the solvent molecules will occupy the total action sites on the $PMAA/SiO_2$. As a consequence, the hydrogen bond interaction between $PMAA/SiO_2$ and pirimicarb is intensively inhibited. The action of the competition and inhibition of the solvent molecules leads to the non-adsorptive phenomenon of the solid sorbent for the solute [22]. Besides, in ethanol, PMMA was not charged, so there is no electrostatic interaction between $PMMA/SiO_2$ and pirimicarb basically. It is also one of the reasons for no adsorption of pirimicarb onto $PMMA/SiO_2$.

It can also be observed from Fig. 1 that in the aqueous medium, the adsorption capacity of $PMAA/SiO_2$ towards pirimicarb is much higher than that in CCl_4. In all reason, analogous to ethanol, the hydrogen bond interaction between $PMAA/SiO_2$ and pirimicarb also will be intensively inhibited and weakened by water molecules. However, in the aqueous medium $PMAA/SiO_2$ can produce quite strong adsorption action towards pirimicarb. The fact suggests that there is still other intermolecular interaction between $PMAA/SiO_2$ and pirimicarb in the aqueous medium. This intermolecular interaction should be electrostatic interaction. In aqueous medium, the carboxyl groups of PMAA will dissociate partially and negatively charged carboxylate groups will be produced. In aqueous medium, the nitrogen atoms of tertiary amine and imine groups of pirimicarb will be protonized to a certain extent and will be positively charged. It is obvious that a strong electrostatic interaction will be produced between $PMAA/SiO_2$ and pirimicarb, resulting in strong adsorption action of $PMAA/SiO_2$ towards pirimicarb. Therefore, it is possible that in aqueous medium, the adsorption driving force is the synergy between hydrogen bond and electrostatic interaction, furthermore, hydrogen bond is produced by the driving of the electrostatic interaction. It needs to be pointed out that in the aqueous solution, the hydrogen bond interaction arises from the interaction between un-disassociated carboxyl groups of PMAA and un-protonized nitrogen atoms of amine and imine groups of pirimicarb. The adsorption mechanism will be further discussed below. Besides, it can be seen from the shape of the adsorption isotherm that the adsorption of $PMAA/SiO_2$ towards pirimicarb in aqueous medium belongs to Freundlich-type adsorptions and is a kind of typical monolayer adsorption.

3.2.2. *Adsorption mechanism of $PMAA/SiO_2$ towards pirimicarb in aqueous medium*

The pH values of the aqueous solutions of pirimicarb were adjusted and under different pH conditions the isothermal adsorption experiments were conducted. Fig. 2 gives the adsorption isotherms under different pH conditions. In order to display the effect of pH value on the adsorption capacity, the equilibrium adsorption data at the equilibrium concentration of 1 mg/ml are taken from Fig. 2, and the equilibrium adsorption amount as a function of pH is plotted as shown in Fig. 3.

The following facts can be observed from Fig. 3: at lower pH, the adsorption capacity of $PMAA/SiO_2$ for pirimicarb is very low; afterwards, the adsorption capacity is enhanced rapidly with increasing pH value; it reaches a maximum value as pH is increased to 8; subsequently, the adsorption capacity turns to decrease with the increase of pH value. The change of the adsorption capacity with pH value reflects the special adsorption mechanism.

When pH value of aqueous medium is very low, although the nitrogen atoms of amino groups of pirimicarb are in highly protonized state, the carboxyl groups of grafted PMAA on $PMAA/SiO_2$ nearly do not dissociate. In such a case, the electrostatic interaction between $PMAA/SiO_2$ and pirimicarb is quite weak, namely, the force driving them to close up each other is very infirm. Thus, the hydrogen bond between them is difficult to be formed, resulting in very low adsorption capacity. When pH value is increased, the dissociation degree of the carboxyl groups of grafted PMAA increases and the electrostatic interaction between them is strengthened. By the driving of this electrostatic interaction, pirimicarb molecules approach the surface of $PMAA/SiO_2$ particles; the various acceptor sites of hydrogen bond of pirimicarb are allowed

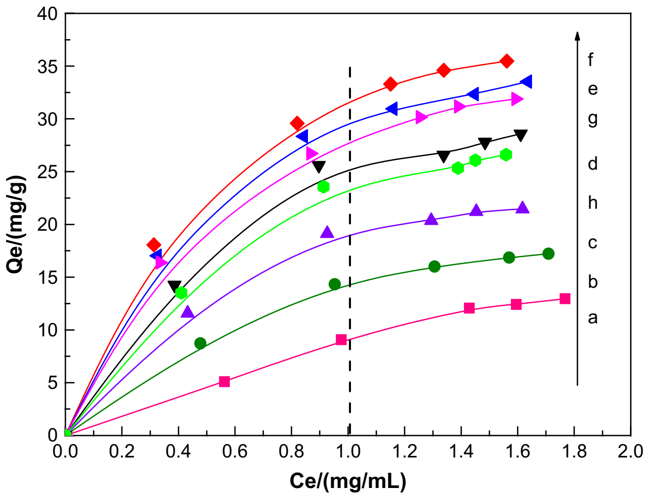


Fig. 2. Adsorption isotherms of $PMAA/SiO_2$ for pirimicarb at different pH values. Temperature: 30 °C; pH value: (a) 2; (b) 3; (c) 4; (d) 6; (e) 8; (f) 9; (g) 10; (h) 11.

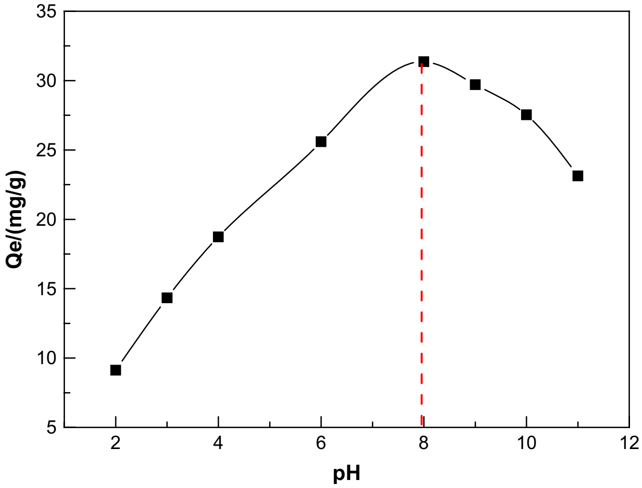


Fig. 3. Equilibrium adsorption amount as a function of pH value. Temperature: 30 °C; $C_e = 1$ mg/ml.

to be fully closed to the donor sites of PMAA/SiO_2. As a consequence, the hydrogen bond between them is formed. Therefore, the synergy between hydrogen bond and electrostatic interaction makes the adsorption capacity of PMAA/SiO_2 towards pirimicarb to be enhanced rapidly with the increase of pH value. In the meantime, the protonized degree of the nitrogen atoms of amino groups of pirimicarb is gradually weakened with the increase of pH value, and this is adverse to the electrostatic interaction between PMAA/SiO_2 and pirimicarb. As $pH > 8$, the effect of weakening of the electrostatic interaction on the adsorption is displayed obviously, leading to that the adsorption capacity turns to decrease with the increase of pH value. Thus, after explaining the effect of pH value on the adsorption capacity, a conclusion can be drawn: in aqueous medium, there exists intermolecular hydrogen bond and electrostatic interaction between PMAA/SiO_2 and pirimicarb, and just about the synergy between the two interactions leads to the very strong adsorption action of PMAA/SiO_2 towards pirimicarb.

3.3. Combining characteristic of MIP-PMAA/SiO_2 for pirimicarb

Based on the strong adsorption ability of PMAA/SiO_2 for pirimicarb, surface-imprinted material MIP-PMAA/SiO_2 of pirimicarb molecule was prepared as described in Section 2.2. The combining characteristic of MIP-PMAA/SiO_2 for pirimicarb was studied with static method. In Figs. 4 and 5, the combining isotherms are given. Fig. 4(A) displays the adsorption isotherms of the non-imprinted material PMAA/SiO_2 for pirimicarb and propoxur, whereas (B) displays the combining isotherms of MIP-PMAA/SiO_2 for pirimicarb and propoxur. Because the solubility of pirimicarb in water is limited, in Fig. 4, the equilibrium concentration of substances can be extended only to 1.6 mg/ml. Fig. 5(A) displays the adsorption isotherms of the non-imprinted material PMAA/SiO_2 for pirimicarb and atrazine, whereas (B) displays the combining isotherms of MIP-PMAA/SiO_2 for pirimicarb and atrazine. Because the solubility of atrazine in water is very small, in Fig. 5, the range of the substance concentration is very small.

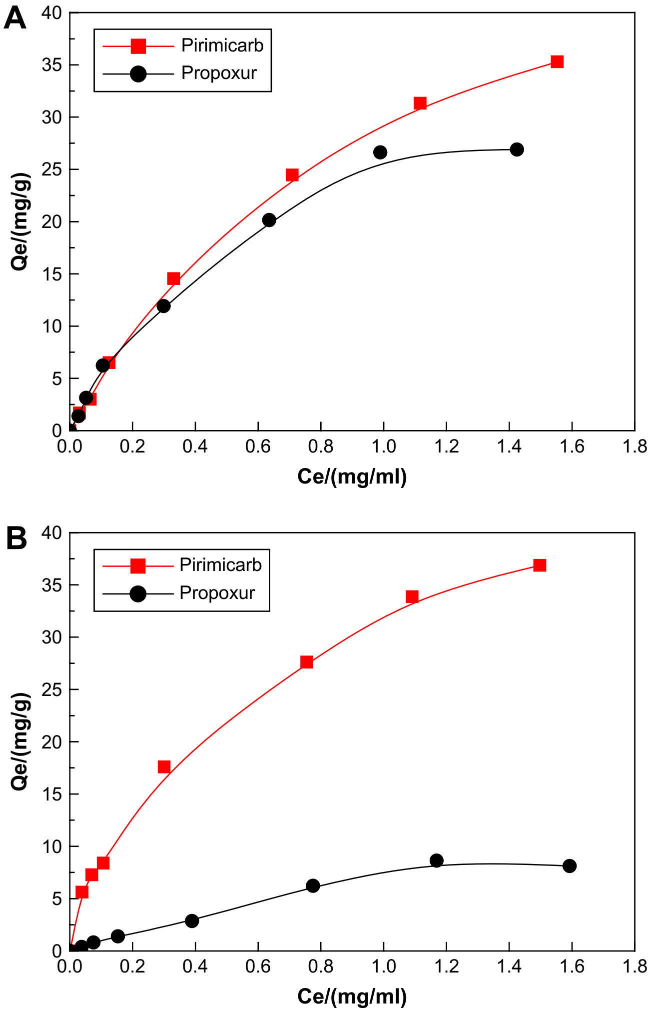


Fig. 4. (A) Adsorption isotherms of pirimicarb and propoxur on PMAA/SiO_2. Grafting amount of PMAA/SiO_2: 15.54 g/100 g; temperature: 30 °C; pH = 7; (B) combining isotherms of pirimicarb and propoxur on MIP-PMAA/SiO_2. Grafting amount of PMAA/SiO_2: 15.54 g/100 g; temperature: 30 °C; pH = 7.

The following facts can be observed from Fig. 4: (1) analogous to PMAA/SiO_2, in aqueous medium, MIP-PMAA/SiO_2 also has strong combining ability for pirimicarb. The action force for the combining also should be hydrogen bond and electrostatic interaction. The shape of the combining isotherm still has the characteristic of Freundlich-type adsorptions, so the adsorption behaviour still belongs to monolayer adsorptions. (2) The adsorption capacities of the non-imprinted material PMAA/SiO_2 for pirimicarb and propoxur are very similar. (3) After imprinting of pirimicarb molecule, the combining capacity of MIP-PMAA/SiO_2 for pirimicarb still remains high, but the combining capacity of MIP-PMAA/SiO_2 for propoxur is remarkably decreased, and the recognition selectivity of MIP-PMAA/SiO_2 for pirimicarb is fully displayed. It can be seen from Fig. 5 that before imprinting, the adsorption capacity of PMAA/SiO_2 for atrazine is greater than that for pirimicarb. However, after imprinting of pirimicarb molecule, the combining capacity of MIP-PMAA/SiO_2 for atrazine

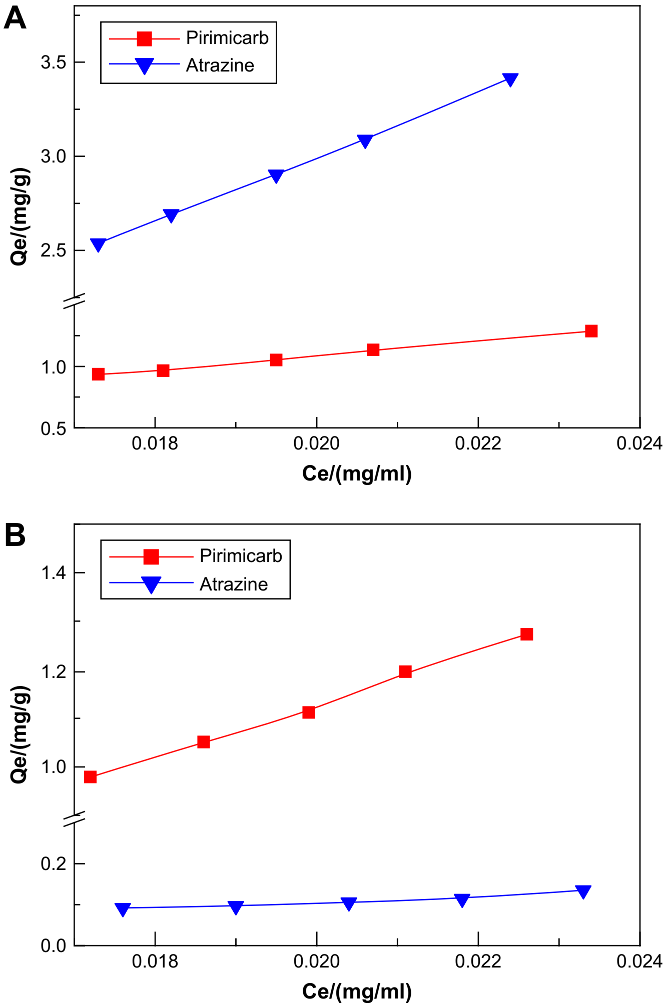


Fig. 5. (A) Adsorption isotherms of pirimicarb and atrazine on PMAA/SiO_2. Grafting amount of PMAA/SiO_2: 15.54 g/100 g; temperature: 30 °C; pH = 7; (B) combining isotherms of pirimicarb and atrazine on MIP-PMAA/SiO_2. Grafting amount of PMAA/SiO_2: 15.54 g/100 g; temperature: 30 °C; pH = 7.

is strikingly decreased and actually is negative to the combining capacity for pirimicarb. This fact clearly reveals the combining affinity and recognition selectivity of MIP-PMAA/SiO_2 for pirimicarb.

Competitive adsorptions of pirimicarb/propoxur and pirimicarb/atrazine on MIP-PMAA/SiO_2 from their mixtures were researched. Table 1 summarizes the data of the distribution coefficients K_d, selectivity coefficients k and relative selectivity coefficients k'. About the combining affinity and recognition selectivity of MIP-PMAA/SiO_2 for pirimicarb, the further explanation can be given from these data shown in Table 1.

From the data shown in Table 1 the following facts can be found: (1) the selectivity coefficients of PMAA/SiO_2 for pirimicarb in relation to propoxur and atrazine are very low and are 1.523 and 0.612, respectively. This implies that the adsorption ability of PMAA/SiO_2 for the three substances is approximate. The little differences of adsorption ability of PMAA/SiO_2 towards them are only caused by the differences of intermolecular forces due to their different structures. (2) The selectivity coefficients of MIP-PMAA/SiO_2 for pirimicarb with respect to propoxur and atrazine are remarkably enhanced, and are 12.20 and 14.15, respectively. (3) The relative selectivity coefficients of MIP-PMAA/SiO_2 for pirimicarb/propoxur and pirimicarb/atrazine are 8.01 and 22.79, respectively. The above facts suggest that the combining abilities of MIP-PMAA/SiO_2 for pirimicarb are far stronger than that for propoxur and atrazine, and it has high recognition ability and excellent combining selectivity for pirimicarb in comparison with the non-imprinted material PMAA/SiO_2.

The reason for the above facts can be accounted for as follows. The cavities imprinted by pirimicarb molecules in the thin layer of PMAA on the surface of MIP-PMAA/SiO_2 are not suited to propoxur and atrazine molecules in size, shape and spatial arrangement of action sites. Although propoxur is also a kind of carbamate insecticide and the size of its molecule is smaller than that of pirimicarb, propoxur molecules are difficult to be combined by MIP-PMAA/SiO_2 owing to unsuitable combining sites. Similarly, although the size of atrazine molecule is similar to that of pirimicarb, propoxur molecules are also difficult to be combined by MIP-PMAA/SiO_2 due to inappropriate combining sites. Obviously, the fine recognition ability and high combining selectivity of MIP-PMAA/SiO_2 for pirimicarb come from a great deal of the suited imprinting caves.

3.4. Desorption property of MIP-PMAA/SiO_2

The dynamic desorption curve of MIP-PMAA/SiO_2 adsorbing pirimicarb in a saturated state is given in Fig. 6. The mixed solvent of methanol, acetic acid and water (in a volume ratio of 7:2:1) as the eluent passes through the column packed with MIP-PMAA/SiO_2 at a flow rate of 2 bed volumes per hour (2 BV/h) upstream. It can be seen that the desorption curve is cuspidal and without trail formation. The calculation result shows that the desorption ratios in 12 BV and in 18 BV reach 96.16 and 98.72%, respectively. The above desorption data indicate that pirimicarb combined on MIP-PMAA/SiO_2 is easy to be desorbed, namely, MIP-PMAA/SiO_2 has excellent eluting property. This is convenient for the reuse of surface-imprinted material MIP-PMAA/SiO_2.

Table 1
Distribution coefficient and selectivity coefficient data

Adsorb material	K_d (ml/g)		k	k'	K_d (ml/g)		k	k'
	Pirimicarb	Propoxur			Pirimicarb	Atrazine		
MIP-PMAA/SiO_2	31.3	2.567	12.20	8.01	60.51	5.45	14.15	22.79
PMAA/SiO_2	25.02	16.43	1.523		51.82	89.27	0.612	

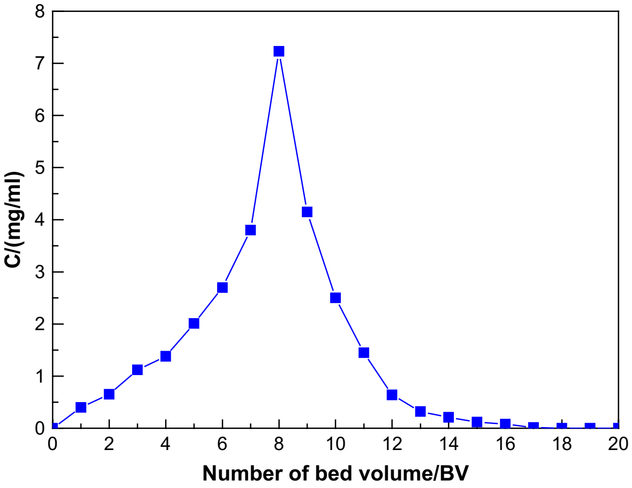


Fig. 6. Elution curve of pirimicarb on MIP-PMAA/SiO_2 column.

4. Conclusions

In this paper, imprinting pesticide pirimicarb towards poly(methacrylic acid) on the surfaces of silica gel particles was carried out successfully using ethylene glycol diglycidyl ether as the cross-linker, and novel molecular imprinted material MIP-PMAA/SiO_2 was obtained. MIP-PMAA/SiO_2 possesses excellent recognition ability and combining selectivity for pirimicarb, whereas its combining capacity for the contrast substances, propoxur and atrazine, whose structures are approximate to pirimicarb, is very poor. MIP-PMAA/SiO_2 has fine eluting property, and pirimicarb combined on MIP-PMAA/SiO_2 is easy to be desorbed by the eluent. In this study, the innovative surface molecular imprinting technique put forward by us previously was further developed. Pirimicarb molecule-imprinted material MIP-PMAA/SiO_2 was prepared by utilizing the intermolecular forces of hydrogen bond and electrostatic interaction between the grafted macromolecules and template molecules. This class of new imprinted materials like pirimicarb molecule-imprinted Material MIP-PMAA/SiO_2 can be widely used in the monitoring and analyzing of pesticides, and it is significant and valuable for environmental protection.

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