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ORIGINAL PAPER

A new molecularly imprinted polymer prepared by surface imprinting technique for selective adsorption towards kaempferol

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Abstract A new molecularly imprinted polymer (KAE-MPS/SiO$_2$) with high performance for recognizing kaempferol (KAE) was prepared by adopting the surface molecular imprinting technique with silica nanoparticles modified with 3-methacryloxypropyltrimethoxysilane (MPS) as a carrier material, 2-vinylpridine as the functional monomer and ethylene glycol dimethacrylate as the crosslinker. The static adsorption experiments indicated that KAE-MPS/SiO$_2$ had significantly higher adsorption capacity for KAE than its non-imprinted polymers. Scatchard analysis revealed that two classes of binding sites were formed in KAE-MPS/SiO$_2$ with dissociation constants of 0.26 and 2.34 μmol/mL, and the maximum apparent binding capacity was 3.33 and 16.16 μmol/g, respectively. The selectivity coefficients of KAE-MPS/SiO$_2$ for KAE in relation to competition species myricetin and chlorogenic acid were 2.51 and 4.24, respectively, which suggested that KAE-MPS/SiO$_2$ had high recognition selectivity and binding affinity for the template KAE. Dynamic binding study showed that the KAE-MPS/SiO$_2$ had good site accessibility and mass transport for KAE. The KAE-MPS/SiO$_2$ can be reused many times without decreasing their adsorption capacities significantly.

Keywords Surface molecular imprinting · Adsorption · Selectivity · Nanoparticle · Tailor-made polymer

Introduction

Molecular imprinting is a rapidly developing technique to prepare polymers possessing high recognition properties [1, 2], and the polymers prepared by this

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technique, molecularly imprinted polymers (MIPs), have been utilized as materials of molecular recognition in many scientific and technical fields, such as solid-phase extraction, chromatograph separation, membrane separations, sensors, drug releases, catalysts, etc. [3–9]. The conventional method to prepare MIPs is an entrapment way. In this process, polymerizable functional monomers are pre-arranged around a template molecule in organic solvent. The resulting pre-polymer complexes are copolymerized with an excess of crosslinker in the presence of a free radical initiator under thermal or photochemical conditions. After the removal of the template by extraction, binding sites complementary to the template molecule both in shape and chemical functionality are left within the polymer matrices that allow rebinding of the template with high specificity. However, the molecular imprinted polymers prepared by conventional methods have some disadvantages, such as time-consuming and complicated preparation process, less recognition sites inside matrices particles obtained via crushing and grinding the imprinted polymeric monolith and greater diffuse barrier for the template molecules coming from thick matrices, leading to poor binding capacity and lower binding kinetic of MIPs for the template molecules. In order to overcome these drawbacks effectively, the surface imprinting technique has been developed in recent years [10–15]. The material with binding sites situated at the surface present many advantages including high selectivity, more accessible sites, fast mass transfer and binding kinetics [16].

Kaempferol (KAE) (3,5,7,4′-tetrahydroxy flavone), a major representative of the flavonol subclass, has received much attention during the past few years because of its anticarcinogenic, antiatherogenic, antioxidant, antiphlogistic, osteogenic properties and other biological activities [17–22]. However, traditional separation of KAE is tedious and inefficient due to poor affinity and selectivity (e.g., silica-gel, polyamide, ion exchange types and reversed-phase column) [23]. Development of a new technique for large-scale separation and purification of KAE is thus of essential importance for the potential application of KAE. In this study, a new molecularly imprinted polymer (KAE-MPS/SiO_2) with high performance for recognizing KAE was prepared by adopting the surface molecular imprinting technique using silica nanoparticles as carrier material. This allows us not only to understand their underlying origin of selective adsorption, but also to be able to evaluate their parameters which were important in determining the ability of the KAE-MPS/SiO_2 to adsorb the template. Consequently, the binding characteristics of the KAE-MPS/SiO_2 were explored using static and dynamic binding experiments; the quantity of binding sites of the KAE-MPS/SiO_2 was examined by using Scatchard analysis. In addition, the binding selectivity of the KAE-MPS/SiO_2 and their reusability were also explored in detail.

Experimental

Materials

Silica nanoparticles (20 nm) were purchased from Nanjing Haitai nano-material Co. Ltd. (Nanjing, Jiangsu, China). 3-Methacryloxypropyltrimethoxysilane (MPS) was obtained from Jiangsu Chenguang Co. Ltd. (Zhenjiang, Jiangsu, China). Kaempferol (KAE; 98%), Myricetin (MYR; 98%) and Chlorogenic acid (CHA; 98%) were purchased from Nanjing Sorun Herbal Technology Development Co. Ltd. (Nanjing, Jiangsu, China). 2-Vinylpridine (2-Vpy) was obtained from Alfa. Ethylene glycol dimethacrylate (EDMA) was purchased from Shanghai Haiqu Chemical Co. Ltd. (Shanghai, China). 2,2′-Azobisisobutyronitrile (AIBN) was purchased from Shanghai No. 4 reagent & H. V. Chemical Co. Ltd. (Shanghai, China). 2-Vpy and EDMA were distilled under vacuum before used. AIBN was purified by recrystallization from ethanol. All other reagents used were all of analytical reagent grade.

Instruments

The instruments used in this study were as follows: UV-2450 Ultraviolet–Visible Spectrophotometer (Shimadzu, Japan); SHZ-82 constant temperature bath oscillator (Zhongda Instrument, Jiangsu, China); KQ2200DB ultrasonic cleaner (Kunshan Ultrasonic Instrument Co., Ltd. Jiangsu, China); YXJ-II high-speed centrifuge (Zhongda Instrument, Jiangsu, China); FT-IR (Nicolet, America) and Element analysis instrument (CE, Italy).

Preparation of imprinted polymer KAE-MPS/SiO_2

Preparing MPS/SiO_2

The composite material MPS/SiO_2 was prepared according to the steps described in Ref. [24], and a typical preparing process was as follows: silica nanoparticles were treated for activation by drying under vacuum at 110 °C for 12 h to eliminate surface water and activate the surface silanol groups for silanization. Dried activated silica (AS) (6 g) was dispersed in absolutely dry toluene (150 mL) in three-necked round-bottomed flask under the atmosphere of nitrogen with continuous stirring. The coupling agent MPS (4.5 mL) and triethylamine (1 mL) were added into the flask, the reaction was carried out at 90 °C for 24 h. MPS was grafted onto silica nanoparticles surface in a coupling manner. The product particles were separated from the mixture via centrifugation and washed with acetone and methanol. Finally, the grafted particles MPS/SiO_2 were gained by drying under vacuum at 80 °C for 24 h.

Preparing KAE-MPS/SiO_2

To prepare the KAE-MPS/SiO_2, the template KAE (0.25 mmol) and the functional monomer 2-Vpy (2 mmol) were dissolved in methanol (20.0 mL) in a glass vial (50 mL volume). After shaking for 6 h, MPS/SiO_2 (8.770 g), the crosslinking agent EDMA (10 mmol) and initiator AIBN (22 mg) were added. The mixture was fully stirred for 4 h at room temperature, followed by purging thoroughly with nitrogen for 10 min, and then sealed under vacuum. The polymerization was started by thermal initiation in a water bath at 50 °C for 6 h, and then continued at 60 °C for 24 h [22]. The product particles were washed repeatedly with a mixed solvent of methanol and acetic acid ($V_{CH_3OH} : V_{CH_3COOH} = 90 : 10$) to remove the template and the remaining monomer. Finally, the surface-imprinted polymer (KAE-MPS/SiO_2) was obtained by filtrating and drying. As a contrast, the non-imprinted material (NIP-MPS/SiO_2) was prepared in the absence of the template and treated by using the same method.

Determination of adsorption property of KAE-MPS/SiO_2 for KAE

Binding experiments

The adsorption dynamic behaviour of KAE-MPS/SiO_2 for KAE was first measured, 0.2 g KAE-MPS/SiO_2 was accurately taken into a 5.0 mL centrifuge tube and then 3.0 mL of KAE methanol solution was added. The mixture was shaken on a constant temperature shaker. After an interval of time, the mixture was centrifuged, and the supernatant solution was collected after filtrating with microporous membrane and diluted with methanol to a certain times. Finally, the equilibrium concentration of KAE in the supernatant was determined by UV spectrophotometer. The binding amount, which was defined as micromole of template molecule KAE bound per gram polymers, was calculated by the following Eq. 1, the curve of the binding amount versus time was plotted, and the time in which the adsorption reached to equilibrium was determined.

$$Q = \frac{(C_0 - C_t)V}{W}, \tag{1}$$

where Q (μmol/g) is the binding amount of KAE on KAE-MPS/SiO_2, C_0 (μmol/mL) is the initial concentration of KAE, C_t (μmol/mL) is the concentration of KAE at the time of t, V (mL) and W (g) are the volume of the solution and the mass of the absorbent KAE-MPS/SiO_2, respectively.

Adsorption isotherm of KAE-MPS/SiO_2 for KAE was determined in batch mode, 3.0 mL of KAE methanol solution with different concentrations were taken and transferred into a 5.0 mL centrifuge tube, KAE-MPS/SiO_2 or NIP-MPS/SiO_2 particles with the same mass (50.0 mg) was accurately added into these solutions. These mixtures were shaken on a constant temperature shaker. After reaching adsorption equilibrium, the mixture was centrifuged, and the supernatant solutions were collected after filtrating with microporous membrane and diluted with methanol to a certain times. Finally, the equilibrium concentrations of KAE in the supernatants were determined by UV spectrophotometer. The equilibrium binding amounts were calculated by the following Eq. 2.

$$Q = \frac{(C_0 - C)V}{W}, \tag{2}$$

where Q (μmol/g) is the equilibrium binding amount of KAE-MPS/SiO_2 for KAE, C_0 (μmol/mL) is the initial concentration of KAE, C (μmol/mL) is the equilibrium concentration of KAE and V (mL) and W (g) are the volume of the solution and the mass of the absorbent KAE-MPS/SiO_2, respectively.

The binding parameters of KAE-MPS/SiO_2 are mainly estimated by Scatchard analysis with the data of static binding experiment. Scatchard equation is described by the following Eq. 3.

$$\frac{Q}{C} = \frac{(Q_{\max} - Q)}{K_d}, \tag{3}$$

where Q (μmol/g) is the equilibrium binding amount of KAE on KAE-MPS/SiO_2, $Q_{\max}$ (μmol/g) is the apparent maximum binding amount, C (μmol/mL) is the equilibrium concentration of KAE and K_d (μmol/mL) is the equilibrium dissociation constant.

Selectivity experiments

MYR and CHA are both of the functional factors of traditional Chinese medicines. The size and structure of MYR are quite analogous to KAE. The chemical structure of CHA is similar to KAE to a certain extent. Both MYR and CHA are selected as the contrast substances for examining the recognition selectivity of KAE-MPS/SiO_2 for KAE. The molecular structures of the three substances are schematically shown in Fig. 1.

The binding amounts of KAE-MPS/SiO_2 for KAE and the competition species were calculated as above. The distribution coefficient for each substance was calculated according to Eq. 4,

$$K_D = \frac{C}{C_e}, \tag{4}$$

where K_D represents the distribution coefficient (mL/g); C (μmol/g) is the equilibrium binding amount and C_e (μmol/mL) is the equilibrium concentration.

The selectivity coefficient of KAE-MPS/SiO_2 for KAE relative to the competition species is evaluated by α, which can be defined as expressed in Eq. 5,

$$\alpha = \frac{K_{Di}}{K_{Dj}}, \tag{5}$$

where α is the selectivity coefficient, i and j represent the template and competition species, respectively. The value of α allows an estimation of selectivity of KAE-MPS/SiO_2 for KAE.

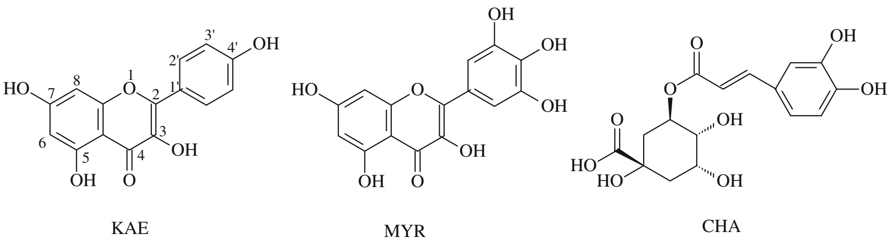

Fig. 1 The structures of KAE, MYR and CHA

A relative selectivity coefficient (α') can be defined as expressed in Eq. 6, and the value of α' can indicate the enhanced extent of adsorption affinity and selectivity of imprinted material for the template molecule relative to non-imprinted material.

$$\alpha' = \frac{\alpha_{\mathrm{MIP}}}{\alpha_{\mathrm{NIP}}}, \tag{6}$$

where α_{MIP} is the selectivity coefficient of KAE-MPS/SiO_2 for KAE relative to the competition species and α_{SNIP} is the selectivity coefficient of NIP-MPS/SiO_2 for KAE relative to the same competition species.

Reusability experiments

Reusability experiments were carried out for KAE-MPS/SiO_2 particles to investigate the regeneration property. The adsorption–desorption experiment was repeated six times by using the same KAE-MPS/SiO_2 particles. 0.2 g KAE-MPS/SiO_2 was accurately taken into a 5.0 mL centrifuge tube, and then 3.0 mL of KAE methanol solution was added. The mixture was shaken on a constant temperature shaker for 6 h. The mixture was centrifuged, and the supernatant solutions were collected after filtrating with microporous membrane and diluted with methanol to a certain times. The concentrations of KAE in the supernatants were determined by UV spectrophotometer, the binding amounts were calculated by Eq. 2. Afterwards, the KAE-MPS/SiO_2 particles were washed with a mixed solvent of methanol and acetic acid ($V_{\mathrm{CH_3OH}} : V_{\mathrm{CH_3COOH}} = 90 : 10$) to remove the template KAE for the next adsorption–desorption cycle.

Results and discussion

Preparing processes of KAE-MPS/SiO_2

The whole preparation process of KAE-MPS/SiO_2 is shown in Fig. 2. Silica particles possess siloxane groups (Si–O–Si) in the bulk and silanol groups (Si–OH) on its surface. The surface silanol groups facilitate the introduction of the organic groups which covalently bind to the silica surface. In this study, MPS was chosen as the coupling agent to link AS and polymers. After AS was chemically modified with MPS, polymerizable double bonds were attached chemically on the surface of the silica particles.

It is of obvious importance that the functional monomers strongly interact with the template and form stable host–guest complexes before polymerization. 2-Vpy is frequently used as functional monomer for imprinting acidic template species. It is a kind of basic functional monomer which serves as not only a proton donor, but also a proton acceptor. The KAE molecule contains four hydroxyl groups and one carbonyl group. From the structure of KAE shown in Fig. 1, the hydroxyl group (No. 5) of the KAE molecule can form strong intramolecular hydrogen bonds with the carbonyl group (No. 4), and therefore the intermolecular interaction between the template and monomer is weakened. The remained three hydroxyl groups as main imprinting functional groups can react with the nitrogen atom of 2-Vpy via

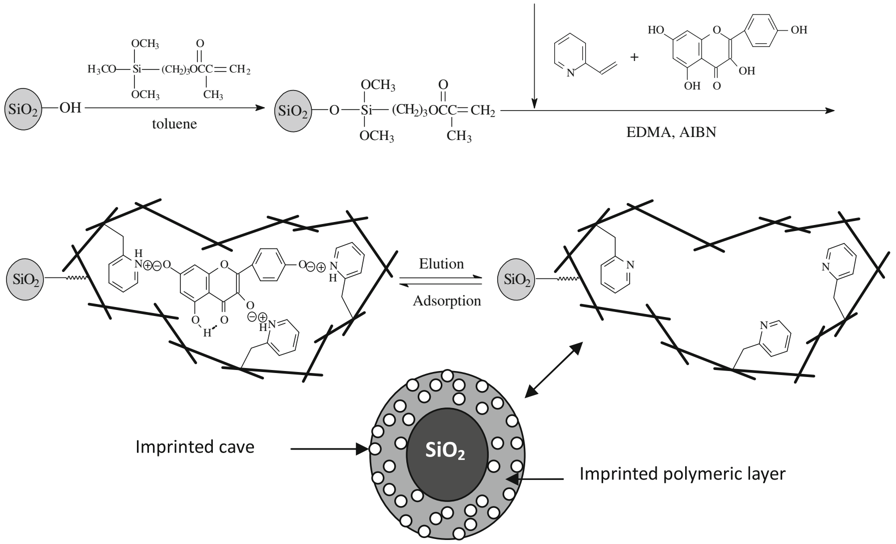

Fig. 2 Schematic illustration for synthesis of KAE-MPS/SiO_2

electrostatic interaction mode in solution. As the interaction between KAE and 2-Vpy reached stably, the modified silica particles, crosslinking agent EDMA were added. And then, with the initiator AIBN, the graft polymerization was favourably carried out on the surface of the silica particles. KAE molecules were enveloped in the crosslinking networks. After the template molecules were washed away, the surface-imprinted functionalized silica sorbent which contained a great deal of tailor-made cavities for KAE was formed.

Characteristic of elemental analysis and FT-IR spectra

Table 1 summarizes elemental analysis results of the silica samples following each functionalization step. It can be seen from Table 1 that the carbon and hydrogen content of MPS/SiO_2 were 5.444 and 1.104%, respectively. The carbon content of MPS/SiO_2 was higher than that of SiO_2 (AS). It demonstrated that MPS had been successfully grafted onto the surface of AS. According to the carbon and hydrogen contents of the MPS/SiO_2 and SiO_2 (AS), the graft density on the surface of AS was calculated about 0.648 mmol/g. In this process, the AS gave an estimated 6.10 mmol/g capacity of silanol groups. The capacity of functionalized silanol groups was 4.156 mmol/g if the three methoxy groups of the silane reagent were supposed to react, and thus, 68.1% of silanol groups were still not functionalized. After polymerization, the carbon content of KAE-MPS/SiO_2 was even higher than that of MPS/SiO_2. This provided an evidence for the presence of grafted polymer.

FT-IR spectra of SiO_2 (AS), MPS/SiO_2, KAE-MPS/SiO_2 and NIP-MPS/SiO_2 were measured and shown in Fig. 3a–d, respectively. The observed features around 1057 cm^{-1} indicated Si–O–Si and Si–O–H stretching vibrations, respectively. The bands around 792 and 465 cm^{-1} resulted from Si–O vibrations. Compared with the spectra of a and b, the

Table 1 Elemental analysis of SiO_2 (AS), MPS/SiO_2, $KAE-MPS/SiO_2$ and $NIP-MPS/SiO_2$

Samples	C%	H%
SiO_2 (AS)	0.000	0.610
MPS/SiO_2	5.444	1.104
$KAE-MPS/SiO_2$	12.880	2.091
$NIP-MPS/SiO_2$	12.738	1.998

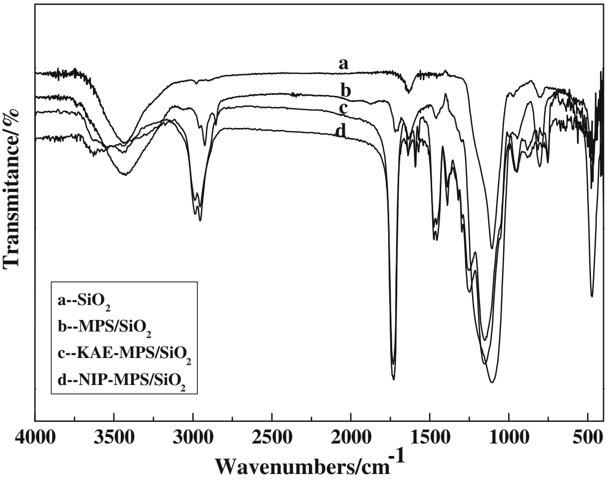

Fig. 3 FT-IR spectra of SiO_2 (AS), MPS/SiO_2, $KAE-MPS/SiO_2$ and $NIP-MPS/SiO_2$

vibration absorption of O–H bond groups appeared at 3450 cm^{-1}, and it indicated that silanol groups were not silanized completely, which was corresponding with the elemental analysis. The vinyl groups introduced onto the surface of the AS by immobilization of a long chain group played a space-shield effect on the surrounding silanol groups, which was why so many silanol groups were still not derivatized.

It was found that the new absorption peaks at 2960 and 1711 cm^{-1} in the spectrum of MPS/SiO_2 were attributed to the stretching vibration absorption of saturated C–H band and carbonyl C=O in ester groups, respectively. These results suggested that MPS had been grafted successfully onto the surface of SiO_2 (AS). Compared with MPS/SiO_2, the spectra of the imprinted and non-imprinted materials showed that the stretching vibration absorption of saturated C–H band and carbonyl C=O in ester groups were strengthened distinctly, which resulted from polymerization crosslinking process. The infrared data proved that the surface-imprinted polymer $KAE-MPS/SiO_2$ had been obtained.

Adsorption properties of $KAE-MPS/SiO_2$ for KAE

Dynamic adsorption curve

The dynamic adsorption curve of $KAE-MPS/SiO_2$ for the template KAE is given in Fig. 4. As seen in this figure, the adsorption amounts of KAE on $KAE-MPS/SiO_2$

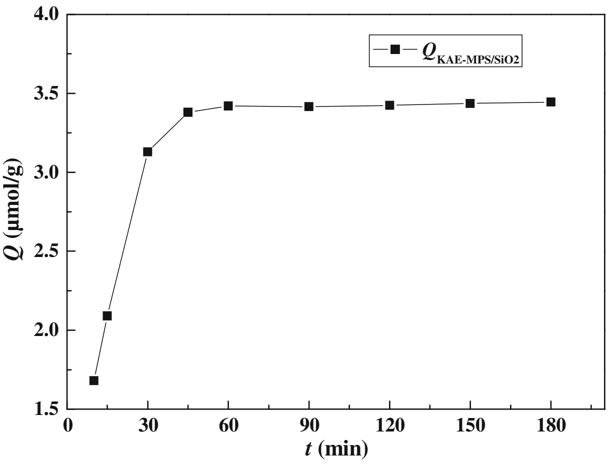

Fig. 4 Adsorption dynamics of KAE-MPS/SiO_2

increased quickly with the time during the first 45 min and then adsorption amounts increased slowly with the time and about 60 min later, the adsorption process reached equilibrium. It is reasonable to assume that a large number of imprinted cavities exist on the surface of the imprinting material, so the template KAE is easy to enter into the cavities and bind with the recognition sites. After the recognition sites on the surface of KAE-MPS/SiO_2 were filled up with the template KAE, the diffusion resistance would lead to make the molecules enter into the cavities and bind with the recognition sites difficultly, then the rate of adsorption drops gradually. In this study, the fast adsorption process indicated that the diffusion resistance for KAE is smaller, and the KAE-MPS/SiO_2 has good site accessibility and mass transport for KAE.

Adsorption isotherms

The binding ability of KAE-MPS/SiO_2 and NIP-MPS/SiO_2 for KAE was studied with static equilibrium binding experiments. Figure 5 shows the adsorption isotherms of KAE onto the KAE-MPS/SiO_2 and NIP-MPS/SiO_2, respectively. As shown in this figure, the binding amounts increased gradually with the increase of concentration of KAE in the initial solution, and ultimately inclined to reach a stable value, the adsorption reached saturation. The difference of adsorption amounts between KAE-MPS/SiO_2 and NIP-MPS/SiO_2 was getting larger with the increasing concentration of the template. The KAE-MPS/SiO_2 exhibited a higher adsorption capacity for KAE than that of NIP-MPS/SiO_2 at either low or high concentration. The above facts fully displayed that the two kind of polymer particles with almost the same element are remarkably different in their space structure, the non-selective physical adsorption occurred between NIP-MPS/SiO_2 and KAE. In contrast, the KAE-MPS/SiO_2 adsorbed much more template than that of NIP-MPS/SiO_2 since KAE-MPS/SiO_2 had generated specific recognition sites in imprinting cavities.

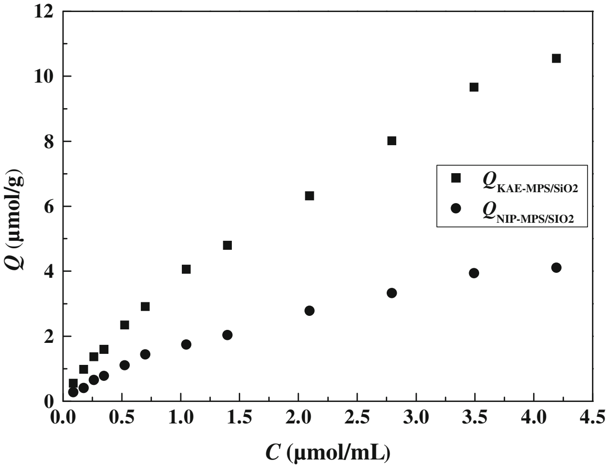

Fig. 5 Adsorption isotherm of KAE-MPS/SiO_2 and NIP-MPS/SiO_2

Scatchard analysis was used to evaluate the binding affinity and the theoretical binding site number for template of the molecularly imprinted material. Figure 6 shows the Scatchard plot of the adsorption of KAE-MPS/SiO_2 for KAE. As seen in this figure, there are two distinct linear sections within the plot. It suggests that there exist two classes of binding sites in respect to the affinity for KAE in the imprinted polymer particles, one is of high selectivity or affinity with a high binding energy, and the other is of low affinity with a low binding energy. From the slopes and intercepts of the two straight lines, the K_d and Q_{max} values can be calculated, and the results are listed in Table 2.

Adsorption selectivity

The structurally similar compound MYR and CHA were chosen as the competitive species with KAE for the adsorption selectivity study. Figure 8 illustrates the adsorption amounts of KAE-MPS/SiO_2 and NIP-MPS/SiO_2 for KAE, MYR and CHA, respectively. Table 1 shows value of distribution coefficient (K_D), selectivity coefficient of the sorbent (α) and the relative selectivity coefficient (α') which were obtained in these selectivity experiments. From the data shown in Fig. 7 and Table 3, the following facts can be found: (1) KAE-MPS/SiO_2 showed a significantly higher adsorption capacity for KAE than that for MYR and CHA. Compared with CHA, the adsorption capacity of KAE-MPS/SiO_2 for MYR is higher. The adsorption capacity of NIP-MPS/SiO_2 for the three substrates was approximate. The results indicates that KAE-MPS/SiO_2 obviously differs from NIP-MPS/SiO_2 in the space structure, and the binding abilities of KAE-MPS/SiO_2 for KAE are far stronger than that for MYR and CHA. The adsorption behaviour of NIP-MPS/SiO_2 for the three substrates has no selectivity. (2) The selectivity coefficients of KAE-MPS/SiO_2 for KAE relative to MYR and CHA are higher, 2.51 and 4.24, respectively. The selectivity coefficients of NIP-MPS/SiO_2 for KAE

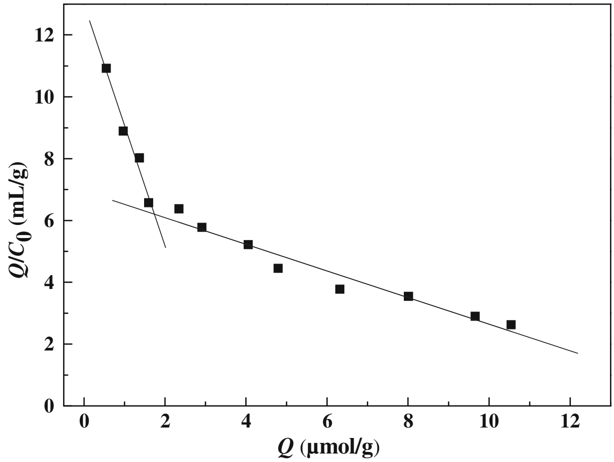

Fig. 6 Scatchard plot of the adsorption of KAE-MPS/SiO_2 for KAE

Table 2 The results of the Scatchard analysis

Binding site	Linear equation	K_d (μmol/mL)	Q_{max} (μmol/g)
Higher affinity site	$Q/C_0 = 12.99–3.90Q$ ($r^2 = 0.9585$)	0.26	3.33
Lower affinity site	$Q/C_0 = 6.95–0.43Q$ ($r^2 = 0.9406$)	2.34	16.16

r relative coefficient

relative to MYR and CHA are lower, 1.28 and 1.76, respectively. This implies that the KAE-MPS/SiO_2 had high absorption selectivity for KAE over the structurally similar compounds MYR and CHA. (3) The relative selectivity coefficients of KAE-MPS/SiO_2 for KAE relative to MYR and CHA are 1.96 and 2.40, respectively, which is greater than 1 and showed the KAE-MPS/SiO_2 had higher absorption selectivity than that of the NIP-MPS/SiO_2.

The reason for the above facts can be accounted for as follows. It is well known that the fine adsorption ability and high binding selectivity of molecular imprinting material for template come from a great deal of the suited imprinting cavities. In this study, the cavities imprinted by KAE molecules do not suit to MYR and CHA molecules in size, shape and spatial arrangement of action sites. The size and shape of MYR molecule are similar to those of KAE. Although, MYR molecule is able to enter into the cavities, it is also difficult to be binded by KAE-MPS/SiO_2 due to inappropriate binding sites, resulting in that the binding ability of KAE-MPS/SiO_2 for MYR is poor. Similarly, the size of CHA molecule is larger to that of KAE, it is more difficult to enter into the cavities and be binded by KAE-MPS/SiO_2 owing to unsuitable binding sites, resulting in that the binding ability of KAE-MPS/SiO_2 for CHA is weaker. Therefore, the high binding ability of KAE-MPS/SiO_2 for the template KAE stemmed mainly from existence of cavities which were perfectly complementary both in shape and functional groups with KAE. And KAE-MPS/SiO_2 exhibited not only strong effect binding for template but also steric effect

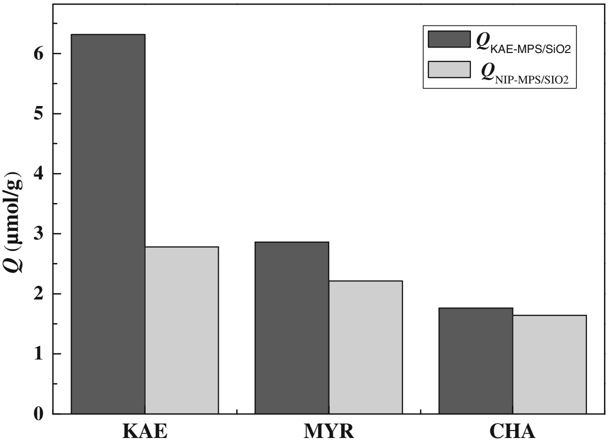

Fig. 7 Adsorption amounts of the polymers for KAE, MYR and CHA

Table 3 Distribution coefficient and selectivity coefficient data of the polymers

Polymer	K_D (mL/g)		α	α'	K_D (mL/g)		α	α'
	KAE	MYR			KAE	CHA		
KAE-MPS/SiO_2	3.77	1.50	2.51	1.96	3.77	0.89	4.24	2.40
NIP-MPS/SiO_2	1.45	1.13	1.28		1.45	0.82	1.76	

hindering non-template from being binded. The binding capacity of NIP-MPS/SiO_2 for the substrates was due to physical adsorption which was non-specific adsorption and had no selectivity. The above facts clearly revealed that KAE-MPS/SiO_2 had high recognition selectivity and binding affinity for the template KAE.

Reusability of the KAE-MPS/SiO_2

In order to show the reusability of the KAE-MPS/SiO_2 particles, the adsorption–desorption cycle was repeated six times using the same imprinted particles. As seen in Fig. 8, the adsorption amounts of KAE on KAE-MPS/SiO_2 decrease gradually for the first three times, and then the adsorption amounts are nearly change no longer and maintained their recovery rate at almost constant value of 92.0%. It is reasonable to assume that the KAE-MPS/SiO_2 can be reused many times without decreasing their adsorption capacities significantly.

Conclusions

In this study, the novel KAE imprinted polymer KAE-MPS/SiO_2 with high performance has been prepared by adopting the surface molecular imprinting technique for the first time. Both the static and dynamic binding experiment

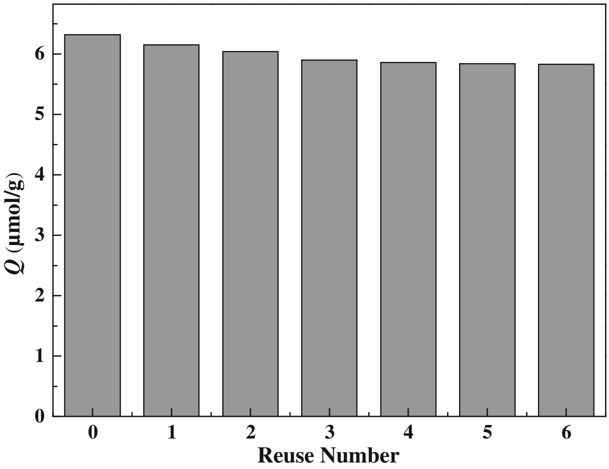

Fig. 8 Reusability of the KAE-MPS/SiO_2 particles

revealed that the KAE-MPS/SiO_2 possessed strong affinity for the template KAE, and displayed high special adsorption capacity, good site accessibility and significantly good mass transport property. The selectivity experimental results show that the KAE-MPS/SiO_2 has excellent selectivity for the KAE relative to the competition species. In addition, KAE-MPS/SiO_2 has fine reuse property. This class of new surface-imprinted polymer like KAE imprinted on the surface of modified silica particles KAE-MPS/SiO_2 can be widely used in the monitoring and analyzing of KAE, and it is significant and valuable for the study of separation and enrichment of the effective ingredient from traditional Chinese medicine.

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