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Adsorption properties of dye imprinted polysiloxane composite microspheres using strong basic anion-exchange resin as matrix

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ABSTRACT

In this study, novel molecularly imprinted polysiloxane composite microspheres (MICS) have been synthesized on the surface of strong basic anion-exchange resin (001 × 7) through a surface molecular imprinting technique by using methyl orange (MO) as the template molecule, ethylenetri(β-methoxy)ethyoxysilane (KH-570) and γ-amidopropyltriethyoxysilane (KH-550) as the functional monomers in aqueous phase. The effects of species of silane, particle sizes, different templates on the adsorption and recognition properties of MICS were investigated. Langmuir adsorption model was employed to describe the isotherms and the maximum adsorption capacity was evaluated. It could be concluded that the adsorption and recognition performances of MICS prepared using two kinds of silane prove superior to those of MICS produced using only one type of silane; the imprinting efficiency of MICS is very high within five minutes and tends to be stable (2.5–2.8) with the time. Adsorption capacity of MO on MO-MICS is higher than that on methyl red imprinted composite microspheres (MR-MICS), indicating that the imprinted microspheres exhibit a certain adsorptive selectivity for the template. The imprinted polysiloxane composite microspheres also show excellent stability in rebinding of the imprint molecules after four adsorption–regeneration cycles.

Keywords: Strong basic anion-exchange resin; Methyl orange; Surface molecular imprinting; Polysiloxane; Recognition; Adsorption

1. Introduction

Dyes are widely utilized in various industries such as the textile, plastics, rubber, cosmetics, leather, food, and drug industries [1]. The dyes can contaminate bodies of water, change biological cycles, and affect photosynthesis. Continual contact with dye products can lead to toxic reactions such as skin allergy and can affect respiratory tract function [2,3]. Furthermore, dyes may exert serious harm to aquatic life and cause severe damage, such as reproductive system, dysfunction of the kidneys, liver, brain, and central nervous system [4–6].

It is extremely urgent and necessary for us to effectively detect and remove dyes from wastewater.

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However, the components of dyeing wastewater are becoming more and more complex as a consequence of the application of anthraquinone dyes and phthalocyanine dyes. Several methods, such as ultra-filtration through membranes [7], electrochemical [8], coagulation/flocculation [9], biological degradation [10], photocatalytic degradation [11] and physisorption [12]. have been employed in removing dyes from wastewater. But all of these methods mentioned previously were not very successful and barely satisfactory for enrichment detection or removal of dyes in water due to numerous restrictions [13].

Molecular imprinting technology is a feasible method to synthesize tailor-made molecular recognition materials with complementary binding sites by polymerizing suitable functional monomers in the presence of desirable template molecules. What molecular imprinting polymers (MIPs) take great advantages over natural identification materials is the chemical stability, excellent heat resistance, high-pressure resistance, organic solvent resistance, and low cost, which makes them considerably potential for applications in the areas of solid phase extraction, tailor-made separation, enzyme mimic, and electrochemical sensors [14–17]. Deng et al. [17] had successfully prepared conductive polypyrrole/TiO_2 nanocomposites through surface molecular imprinting technique using methyl orange (MO) as the template molecule to remove MO from wastewater. Luo et al. [18] had reported novel magnetic and hydrophilic molecularly imprinted polymers using 1-(α-methyl-acrylate)-3-methylimidazolium bromide as a new functional monomer by an inverse emulsion–suspension polymerization to remove water-soluble acid dyes from contaminated water. Li et al. [19] synthetized a novel adsorbent coupled with molecular imprinting technology and photo degradation technology through the immobilization of nanometer titanium dioxide on molecular imprinted chitosan matrices to degrade organic dyes and adsorb the heavy metal ions from wastewater.

Up to now, most MIPs are fabricated using water-insoluble functional monomers, such as 4-vinyl pyridine, 4-vinyl-benzene boronic acid, itaconic acid, acrylic ester and its derivatives in the organic phase. It is inevitable to give rise to pollution in the process of preparing MIPs in the organic phase. Silane and its derivatives can also be used as the functional monomers to produce MIPs [20]. However, there is no report about the MIPs prepared using strong basic anion-exchange resin as the matrix and using silane as the functional monomer. Strong basic anion-exchange resin (001 × 7) is copolymer of styrene and divinylbenzene with tertiary amine moiety ($–N(CH_3)_2$), which has advantages of high regeneration efficiency, considerable capacity of the exchange, good mechanical strength and strong pollution resistance ability. And also it can hydrolyze to generate hydroxyls in the acid media, effectively exchange inorganic acid and silicic acid group in the acid and approximately neutral media.

In this study, we present dye imprinted polysiloxane composite microspheres (MICS) based on strong basic anion-exchange resin as the matrix via surface molecular imprinting in aqueous phase with no added chemicals other than silane as functional monomers and MO as the template. The adsorption equilibrium, binding specificity and adsorption kinetics of the target molecules on the MICS were investigated. Regeneration and stability of MICS were also evaluated. The preparation of MICS was easy and took less time compared with other traditional polymerization methods. The resultant dye imprinted polysiloxane composite microspheres can be used for the enrichment detection and removal of the MO molecules from wastewater.

2. Experimental

2.1. Materials and apparatus

Ethylenetri(β-methoxy)ethyoxysilane (KH-570) and γ-amidopropyltriethyoxysilane (KH-550) were supplied by Tianjin Shengbin Chemical Plant (Tianjin, China), analytical grade. MO and methyl red (MR) were purchased from Beijing Xinjing Biological Technique Company (Beijing, China), analytical grade. Hydrochloric acid was from Tianjin No.2 Chemical Reagent Factory (Tianjin, China), chemical grade. Strong basic anion-exchange resin (001 × 7) was from LangFang HengTai Energy Chemical Building Material Co., Ltd (Hebei, China).

UV–vis spectrophotometer (UV-1901, Hitachi High-Technologies Corporation production) was used for absorbance determination.

2.2. Preparation of molecularly imprinted composite microspheres (MICS)

2.2.1. Preparation of MICS and NICS

About 20 ml of MO or methyl red solution (0.5 mM) was added to each conical flask containing a certain amount of strong basic anion-exchange resin (1.0 g). When the mixture above in each conical flask was heated to 90℃ under stirring, 5 ml of KH-570, KH-550 or the mixture of KH-550 and KH-550 were, respectively, introduced into each conical flask. Then, 10 ml of hydrochloric acid (0.01 M) was injected to each conical flask. The reaction was performed for

1.5 h under the conditions of refluxing and stirring at about 90–95 ℃. The freshly prepared spheres were collected and intensively washed with distilled water to remove the unreacted functional monomer. Finally, the sample was repeatedly washed with hydrochloric acid (0.01 M) to remove MO or methyl red and dried at 60 ℃. The dried MICS were passed through different mesh sieves and the microspheres with the diameters of 100–125 μm and 450–550 μm were collected for re-adsorption test. The MO imprinted microspheres were noted as MO-MICS and the MR imprinted microspheres were noted as on methyl red imprinted composite microspheres (MR-MICS).

Also, the composite microspheres without the template MO were prepared for non-imprinted polysiloxane composite microspheres and noted as NICS. The same process was carried out to treat NICS like MICS.

2.2.2. Adsorption experiments of MICS and NICS

Adsorption experiments of MO on the MICS and NICS were carried out using a batchwise adsorption method. Accurately measured 0.10 g dry MICS or NICS were added to each glass bottle and mixed with MO solutions (5 ml) of a constant initial concentration (0.025 mM) for evaluating imprinting efficiency, or varying concentrations (0.1–0.4 mM) for determinating adsorption isotherms. The suspensions were oscillated (145 rpm) in a shaking incubator at 25 ℃ for 12 h to reach adsorption equilibrium. After adsorption, the MO concentration after centrifugation was measured by a UV spectrophotometer at 463.5 nm. Equilibrium adsorption capacity Q_e (mg/g) was calculated by mass balance according to the following Eq. (1):

$$Q_e = (C_0 - C_e)V/W \tag{1}$$

where Q_e (mg/g) is the equilibrium absorption, C_0 (mM) is the initial MO concentration, C_e (mM) is the final concentration of MO at equilibrium, V (ml) is the volume of the MO solution, and W (g) is the weight of the polysiloxane composite microspheres incubated in the solution. The imprinting efficiency (IE) of the microspheres was defined as follows:

$$\mathrm{IE} = Q_{\mathrm{MIP}}/Q_{\mathrm{NIP}} \tag{2}$$

where Q_{MIP} and Q_{NIP} are the Q_e of the imprinted and corresponding nonimprinted microspheres. The higher the IE is, the better recognition effect the MICS is.

In dynamic adsorption experiments, capped bottles each containing the polysiloxane composite microspheres (0.10 g) and 0.025 mM of MO solution (5 ml) were agitated in a shaking incubator at 25 ℃. The MO concentration of the supernatant in each bottle was measured at certain intervals.

The adsorbance Q_t (mg/g) was calculated according to a formulation similar to Eq. (1):

$$Q_t = (C_0 - C_t)V/W \tag{3}$$

where C_t (mM) is the MO concentration in the supernatant at time t.

The adsorption capacity of MICS and NICS for MR is also investigated following the steps above.

2.2.3. Recognization performance of MO-MICS

The molecular recognition selectivity of molecular imprinted microspheres can be evaluated by the static distribution coefficient K_{D} and the separation factor α, which are defined in the following equations:

$$K_{\mathrm{D}} = C_{\mathrm{P}}/C_{\mathrm{S}} \tag{4}$$

where C_{p} (mM) is the concentration of the template molecules on microspheres, and C_{S} (mM) is the concentration in the solution.

$$\alpha = K_{\mathrm{D1}}/K_{\mathrm{D2}} \tag{5}$$

where K_{D1} and K_{D2} are the static distribution coefficients of the template and the other molecules, respectively.

In order to compare differences of molecular recognition properties on MICS and NICS, the relative separation factors β is introduced and defined as follows:

$$\beta = \alpha_{\mathrm{I}}/\alpha_{\mathrm{N}} \tag{6}$$

where α_{I} is the separation factor of MICS for the template, α_{N} is the separation factor of NICS for the template. The value of β reflects the difference of molecular recognition and selection performances on MICS and NICS. The bigger the value of β is, the better the imprinting effect is.

3. Results and discussion

3.1. Preparation and recognition mechanism of MICS for template molecule

Fig. 1 shows the schematic representation of imprinting and recognition process of MO-MICS. The –NH– and $–NH_2$ groups in functionalized organic silane monomers could interact with the $–NH_2$ and

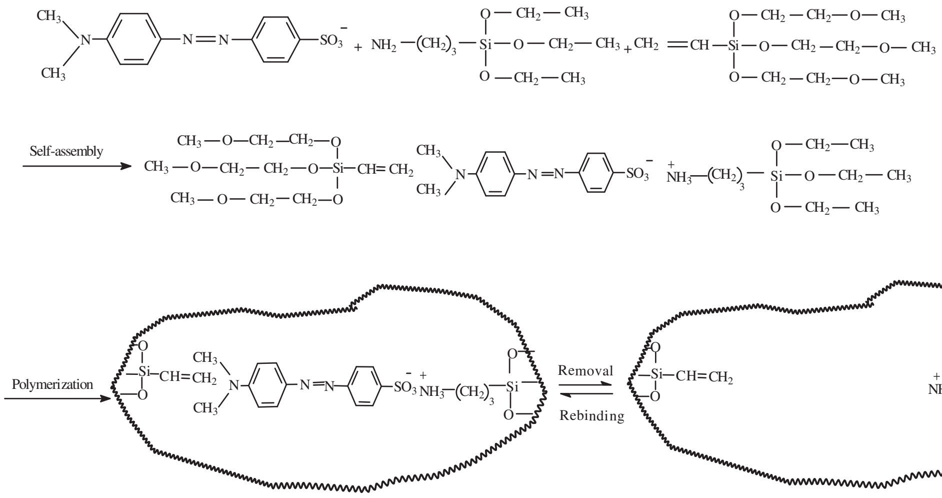


Fig. 1. Schematic representation of imprinting and recognition process of MO-MICS.

–OH groups in the dye molecules via noncovalent bond (mainly hydrogen bond). Si–O– bonds generated reactive silanols through hydrolysis caused by acid catalysis. Reactive silanols around the template molecules and hydroxyl groups on the surface of the matrix were polycondensed to produce polysiloxane network.

Reversible reaction between the template and silane was formed involving varying types of noncovalent interactions, for example ionic, hydrophobic and hydrogen bonds. In pre-assembly process, the template molecules were likely to combine with the hydrophobic groups in KH-570 through hydrophobic interaction and interact with the $–NH_2$ groups in KH-550 via ionic bonds. The subsequent crosslinking of silanols and hydroxy groups on the surface of anion-exchange resin resulted in the formation of polysiloxane network, in which the template molecules were immobilized. Then, MICS were obtained after removal of the template molecules from the polysiloxane network using dilute hydrochloric acid. So the template molecules may be selectively rebound by the sites on the surface of the matrix because of the complementary groups in silanols and the structural elements.

3.2. *Influence of types of silane on adsorption performance of MICS*

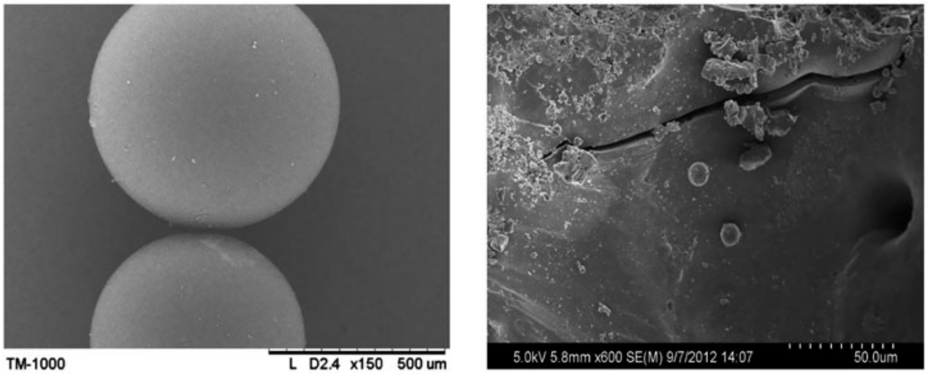
Fig. 2 shows the SEM micrographs of strong basic anion-exchange resin and MO-MICS. In Fig. 2(a), it can be seen that strong basic anion-exchange resin with highly rigid matrix displayed spherical shapes and smooth surface. From Fig. 2(b), we can see that MICS exhibited a rough surface containing many micropores, indicating that molecularly imprinted polysiloxanes were formed on the surface of anion-exchange resin. The average diameter of MICS is nearly the same as that of anion-exchange resin [21].

3.3. *Influence of types of silane on adsorption performance of MICS*

Adsorption dynamic studies were carried out for MO-MICS prepared with different functional monomers to investigate the adsorption process. It can be seen from Fig. 3 that the adsorption performance of MICS prepared using two kinds of silane was superior to those of MICS prepared using only one kind of silane. Adsorption rate of the template molecules on three kinds of MICS was so fast so as to reach adsorption equilibrium within 50 min.

The adsorption process was considered to proceed in two steps, permeating and combining. Firstly, MO molecules in solution permeated into molecularly imprinted cavities, after which the molecules combined with the functional groups arranged in the cavities (as shown in Fig. 1). In the present work, the $–NH_2$ groups in silane KH-550 can combine with the $–SO_3^-$ moieties in MO of target molecules via ionic bonds. The $–CH{=}CH_2$ groups in silane KH-570 can interact with MO through hydrophobic interaction, which is weaker than electrostatic interaction produced by silane KH-550. The MICS prepared using only KH-570 had no $–NH_2$ groups and could not form ionic bonds with MO. So the adsorption capacity of MO on MICS prepared using KH-550 is higher than that on MICS prepared using only KH-570.

Silane KH-550 hydrolyzed rapidly in acid aqueous solutions to generate silanols with a hydrophilic group ($–NH_2$). While silane KH-570 hydrolyzed more



(a) anion exchange resin

(b) MO-MICS

Fig. 2. SEM photos of strong basic anion-exchange resin and MO-MICS.

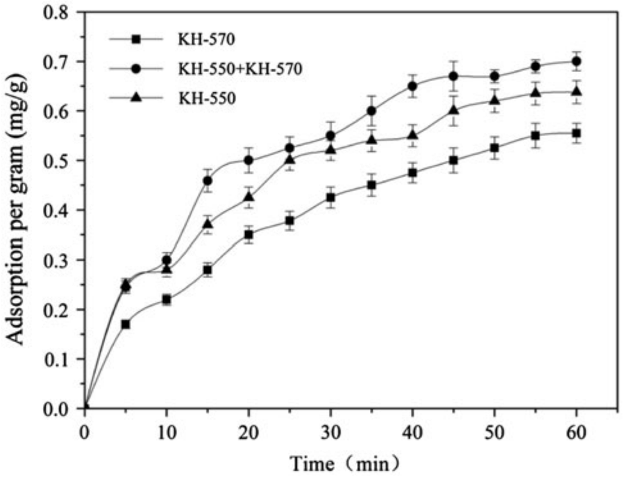


Fig. 3. Adsorption dynamics of MO on MO-MICS prepared with different silanes. Experimental conditions: $V = 5.0$ ml; $C_0 = 0.025$ mM; the mass of dry MICS 0.10 g; temperature 25 ℃.

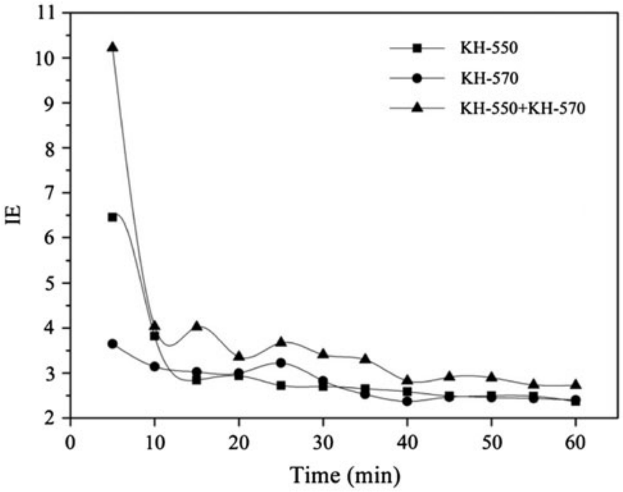


Fig. 4. Curves of imprinting efficiency of MO-MICS prepared with different functional monomers.

slowly and generated silanols with hydrophobic groups. Both KH-570 and KH-550 were applied to fabricate the MICS, which demonstrated the most desirable adsorption capacity and selective properties.

Fig. 4 shows the IE curves of MO-MICS prepared with different silanes. From Fig. 4, we can see that the IE of MICS prepared using only one kind of silane KH-550 was higher than that of MICS fabricated using only one kind of silane KH-570, while the IE of MICS prepared using two kinds of silane outweighed that of MICS prepared using only one kind of silane. The IE of three types of MICS was all very high within five minutes, then gradually decreased and tended to be stable (2.5–2.8) with the time. Addition of two kinds of silane can make full use of electrostatic interaction and hydrophobic interaction to achieve better imprinting effect. The MICS could be used in speedy enrichment detection for MO in waste water.

3.4. Influence of particle sizes on the adsorption performance of MICS

Fig. 5 shows the adsorption dynamics curves of MO-MICS of different diameters prepared using two kinds of silian. Form Fig. 5, we can see that the adsorption capacity of MO on MICS with small diameter was higher than that on MICS with bigger diameter. It is widely acknowledged that the smaller the particle size is, the greater the specific surface area is on the equal mass of MICS, the more recognization sites and cavities on the surface of MICS can be formed. However, the difference in adsorption capacity caused by diameters was slight.

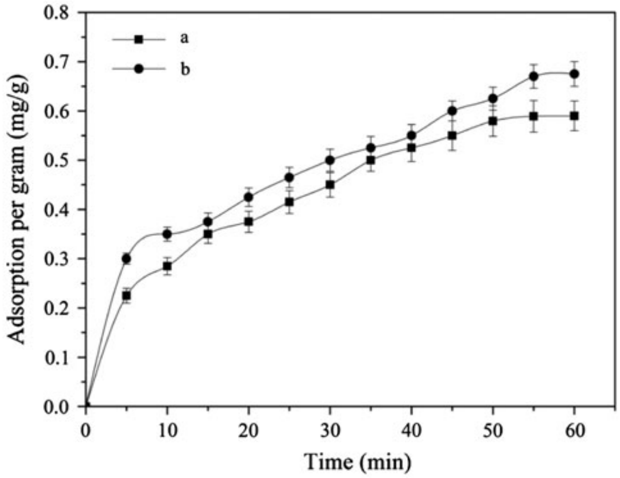


Fig. 5. Curves of adsorption dynamics of MO-MICS of different diameters prepared using two kinds; (a) 450 μm ⩽ R⩽550 μm (b) 100 μm ⩽ R⩽125 μm.

3.5. Adsorption performance of MICS prepared with different template molecules

Fig. 6 shows the adsorption dynamics curves of MO-MICS, MR-MICS, and NICS and the structural formulae of the template molecules with which each kind of imprinting microspheres were prepared were marked in the Fig. 6. The adsorption capacity of MO on MO-MICS was higher than that on NICS and MR-MICS. The adsorption capacity of MO on MR-MICS was lower than that on MO-MICS because MO-MICS had special recognization sites for MO on their surfaces. It was indicated that the imprinted microspheres exhibited a certain recognization performance for their template molecules.

3.6. Adsorption thermodynamics

The curve of adsorption thermodynamics was demonstrated by the plot of adsorption per gram (Q_e) vs. initial concentration of MO (C_0) when MO-MICS were used to adsorb MO at room temperature [21]. It is showed in Fig. 7 that the adsorption capacity of MICS and NICS increased with the increasing concentration of MO. For both MICS and NICS the Q_e and C_0 were found to be good linearity at lower concentration (< 0.1mM). C_0/Q_e vs. C_0 was plotted and the intercept and slope were obtained (Fig. 8). According to Langmuir model, the saturated adsorption capacities of MICS and NICS were 9.73 mg/g and 3.48 mg/g, respectively. It was found that MICS rebinded more MO than NICS did, indicating that the imprinted polysiloxane composite microspheres exhibited good recognition property.

3.7. Recognition performance

Table 1 shows the recognition property of MICS, we can see that the adsorption capacity of MO on MO-MICS is higher than that of MR on MO-MICS, while the adsorption capacity of MR on MR-MICS is higher than that of MO on MR-MICS. The K_D values of their template molecules on MICS were higher than that of other molecules. The separation factors (α_I)) of MO-MICS and MR-MICS were all about 1.2, definitely indicating that they exhibited a certain selective recognition performances. The separation factor (α_N) of NICS was less than one, showing that NICS has no molecular recognition performance. Anion-exchange

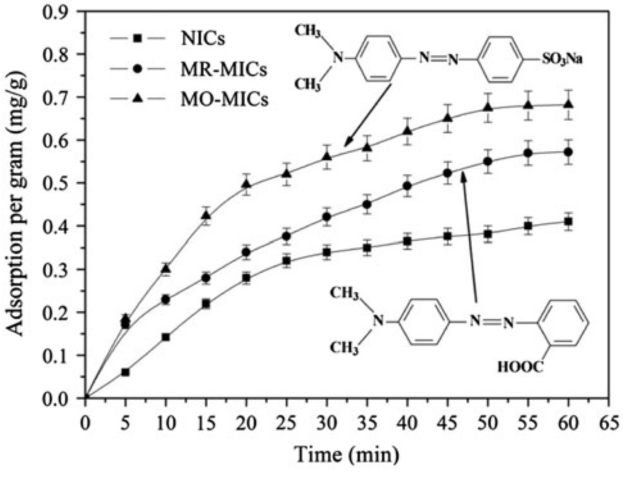


Fig. 6. Adsorption dynamics of MO on MICS prepared with different templates. Experimental conditions: $V = 5.0$ ml; $C_0 = 0.025$ mM; the mass of dry MICS 0.10 g; temperature 25 ℃.

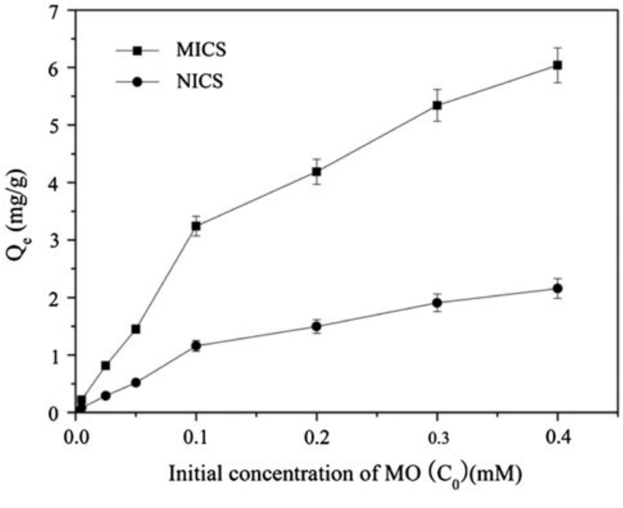


Fig. 7. Curves of adsorption thermodynamics of MICS and NICS. Experimental conditions: $V = 5.0$ ml; $C_0 = 0.1$–0.4 mM; the mass of dry MICS 0.10 mg; temperature 25 ℃; time 12 h.

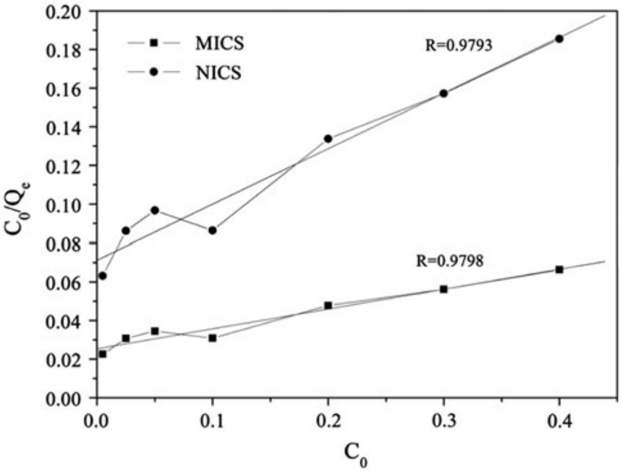


Fig. 8. Curves of C_0/Q_e to C_0.

Table 1
Molecule recognition of MO-MICS

Adsorbent	K_D (ml/g)		α	β
	For MO	For MR		
NICS	57.04	58.6	0.97	/
MO-MICS	87.38	69.17	1.26	1.30
MR-MICS	63.28	76.36	1.21	1.25

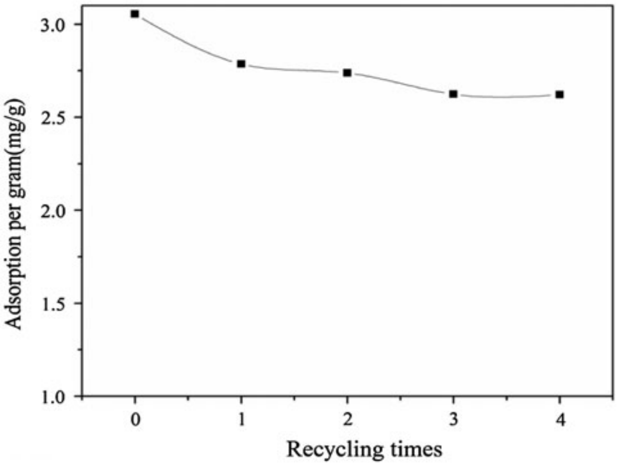


Fig. 9. Curves of regeneration performance of MO-MICS with recycling times. Experimental conditions: $V = 5.0$ ml; $C_0 = 0.1$ mM; the mass of dry MICS 0.10 g; temperature 25˚C; time 12 h.

resin contains a great many porosities and high-specific surface. Strong basic anion-exchange resin can also adsorb MO and MR, so the separation factor α and the relative separation factors β are poor.

3.8. Regeneration performance

Regeneration performance of MIPs is important for practical applications. Fig. 9 shows the regeneration performance of MO-MICS with recycling times. With the increase in recycling times, the adsorption capacity of the MICS slightly declined, but the rate of decline gradually decreased. The adsorption capacity turned out to be stable at 85.8% of initial adsorption capacity after 4 recycling times. That was because the surface of MICS was crosslinked by polysiloxane networks, most of the formed recognition sites had good stability and were able to withstand several cycles of elution treatment. MICS can be used for the enrichment detection and removal of the dye molecules in the water samples.

4. Conclusion

MO-MICS and MR-MICS were fabricated using silane KH-570 and silane KH-550 as functional monomers and strong basic anion-exchange resin as the matrix through surface imprinting in aqueous phase. This method was simple and feasible, to avoid the organic pollution. Adsorption rate of MO on MICS prepared using either of KH-570 or KH-550 as the functional monomer was very low, while the adsorption rate of MO on MICS prepared using both KH-570 and KH-550 was quick and the equilibrium adsorption capacity was high. The smaller the particle size was, the bigger the specific surface area was on the equal mass of MICS, and therefore, adsorption capacity was higher. MICS exhibited a certain recognization performance for MO or MR, while NICS had no recognization performance for MO or MR under the equal conditions. With the increase of recycling times, not only the adsorption capacity of MO on MICS slightly declined, but also the rate of decline gradually decreased, and the adsorption capacity turned out to be stable at 85.8% of initial equilibrium adsorption capacity after 4 recycling times.

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