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A Core-Shell Spherical Silica Molecularly Imprinted Polymer for Efficient Selective Recognition and Adsorption of Dichlorophen

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Abstract: A core-shell surface-imprinted polymer was successfully synthesized on the surface of silica spheres by precipitation polymerization. The polymers were used to selectively identify dichlorophen in complex environmental system. The physical-chemical properties of the silica sphere molecularly imprinted polymers were analyzed by scanning electron microscopy and transmission electron microscopy scans characterization. The adsorption properties of core-shell polymers were examined by adsorption isotherms, kinetics and selectivity experiments. The Langmuir adsorption isotherm well fitted the adsorption experimental data, and an increase of temperature enhanced the adsorption capacity. The maximum binding capacity of imprinted polymers reached 72.46 mg g^{-1} at 318 K. Meanwhile, the adsorption data of binding experiments were well-fitting by the pseudo-second-order equation. Compared with nonimprinted polymer, the imprinted polymer not only has specific selectivity towards dichlorophen but also has higher adsorption performance. Moreover, via the regeneration experiments, it has been demonstrated that the MIPs have certain stability to the adsorption for the target, which provides a good reference for the adsorption of dichlorophen by the imprinted polymer in water.

Keywords: Molecular imprinting, Precipitation polymerization, Selective recognition, Dichlorophen

Introduction

Industrial Bactericide, such as dichlorophen, as an important group of Pharmaceuticals and Personal Care Products (PPCPs), have been commonly used as the active ingredient in cleaning and disinfecting products [1,2]. As a result, trace residues of chlorinated disinfectants are potentially harmful to the environment and human health [3-5]. Removal of PPCPs from wastewater has some successful technologies, such as activated carbon adsorption [6], ozone oxidation [7], oxidation and membrane filtration [8]. Zhu *et al.* [9] investigated the effect of different adsorbents on the removal of PPCPs in actual water environment. The results of these experiments have shown that adsorption can be an effective method for removing drugs and personal care products (PPCP). However, most dichlorophen are hydrophobic and easily accumulate in organisms and sediments. As a trace of organic pollutants, it has been increasingly concerned by the whole society. It is thus of great necessity to develop efficient and reliable methods for the removal of dichlorophen from aquatic environment. The great advantages of selective adsorption technology have extended its wide application as a new type of adsorbent.

Molecular imprinting has a special recognition function, which vividly portrayed a "human lock" technique for "molecular key" [10,11]. The basic principle of molecular imprinting techniques is to obtain a polymer that exactly matches a template molecule in the spatial structure and binding site. Due to the special recognition of high affinity for target molecules, it has been widely applied in many fields, such as solid phase extraction [12,13], chromatographic separation [14], sensors [15-17], simulated enzyme catalysis [18], molecularly imprinted membrane [19]. In many cases, the imprinted polymer acts as a good adsorbent to remove organic contaminants from the water [20]. Many studies have been reported about the adsorption of contaminants by molecularly imprinted polymers, but few reports have been published on the preparation of imprinted polymers using dichlorophen as a template molecule [21].

The molecularly imprinted polymer, as the product of molecular imprinting technology, is prepared by the traditional method would result in incomplete elution of the template molecule and deep embedding of the imprinting site. In the present work, surface imprinting has been proposed to overcome those limitations [22,23]. Core-shell imprinted polymers have higher binding capacities, faster mass transfer and binding kinetics, which contribute to their wider application [24]. Most of those polymers are based on solid materials, such as Fe_3O_4 [25], quantum dots [26], silica nanospheres [27,28]. Spherical silica not only has a large specific surface area, but also the presence of hydroxyl groups leads to its strong reactivity [29]. However, its inherently superior hydrophilicity causes precipitation polymerization of silica in the organic phase [30], which is inevitably restricted in practice. As we know, 3-(methacryloyloxy) propyltrimethoxysilane can be used for the modification of silica surface to change its physical and chemical properties. Therefore, the modified spherical silica can be used as an imprinting carrier to improve the adsorption performance of

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the imprinted polymer [31,32].

In this work, we prepared molecularly imprinted polymers (MIPs) with core-shell structures by surface precipitation polymerization method. The obtained surface-imprinted polymers exhibited a highly controllable spherical shaped morphology. The advantages of our approach are affordable and synthetically viable. The physical and chemical properties of the prepared particles were mainly characterized by SEM and TEM. Batch adsorption experiments and adsorption isotherms, adsorption kinetics, selectivity experiments and reuse experiments were studied.

Experimental

Materials

Dichlorophen (98 %), acrylamide (AAm, ≥99 %), ethylene glycol dimethacrylate (EGDMA), 2,2'-azobis (2-methylpropionitrile) (AIBN, ≥98 %), 2,4-dichlorophenol (2,4-DCP, >98 %), 2,6-dichlorophenol (2,6-DCP, 99 %), chlorophene (>97.0 %) were all analytical reagents and purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Tetraethyl orthosilicate (TEOS) was purchased from Tianjin Fuchen Chemical Reagent. 3-(methacryloyloxy) propyltrimethoxysilane (MPTMS) was purchased from Shandong Yousuo Chemical Technology Co., Ltd. Ethanol, deionized water, ammonia, acetonitrile, methanol, acetic acid were all analytical reagents and purchased from Guangzhou Jinhuada Chemical Reagent Co. Ltd.

Method

Preparation of Spherical Silica

The synthesis steps of silica are as follows: in brief, 110 m*l* of ethanol, 50 m*l* of deionized water and 20 m*l* of aqueous ammonia were added in a 500 m*l* flask. After vigorous magnetic stirring was completed, 10 m*l* of TEOS was added and the mixture was stirred at room temperature for 2.0 h. The product were centrifuged and washed alternately with deionized water and ethanol several times, then was dried under vacuum at 60 °C for 12 h.

Modification of Silica Spheres

The silica surface was modified with the vinyl groups by using MPTMS. In brief, 0.5 g of the prepared silica spheres were dissolved in 50 m*l* ethanol and sonicated for 15 minutes. Then, 2.0 m*l* of MPTMS was added dropwise while constantly stirring, and then the mixed solution was heated to 50 °C in a water bath and reflux for 12 h to obtain the modified silica spheres. Finally, the products were washed several times with ethanol, and then dried under vacuum at 60 °C for 12 h.

Preparation of Core-shell MIPs

The core-shell MIPs were prepared on the modified spherical silica surface by precipitation polymerization. 60 m*l* of acetonitrile, 0.1 mmol of dichlorophen, 0.4 mmol of acrylamide, 100 mg of MPTMS-modified silica, 1.6 mmol of EGDMA and 10 mg of AIBN were added in a 250 m*l* round-bottomed flask. The mixture was sonicated for 15 min, deoxidized with nitrogen, and then sealed. Then the flask was placed into a constant temperature water batch shaker, and carried out a two-step polymerization process. The first step was at 50 °C for 6.0 h and the second step was at 60 °C for 24 h. The products were separated by centrifuged, washed with ethanol several times to remove unreacted material, and then dried under vacuum at 60 °C for 12 h. The dichlorophen molecules in the polymer were extracted with a mixed solution of methanol and acetic acid (9:1, V:V). After the template molecules were removed, the core-shell MIPs products were obtained and dried under vacuum at room temperature. The non-imprinted polymers were prepared under the same condition, except that no template molecules were added in the polymerization process.

Batch Binding Experiments

To investigate the adsorption capacity of the polymers, batch binding experiments were carried out in this study. In the adsorption experiment, the solution of ethanol and deionized water (1:3, V:V) was used as a solvent, 2.0 mg of imprinted polymer were added to 10 m*l* solvent with the initial concentrations arranging from 10 to 100 mg/*l*. The solutions were placed for 12 h at 298, 308, and 318 K to reach adsorption equilibrium, respectively. The concentrations of free dichlorophen in the solutions were measured by a UV-Vis spectrophotometer at 285 nm. The amount of adsorbed dichlorophen can be calculated by the reduction of the remaining concentration from the initial concentration. The equilibrium binding amount of dichlorophen Q_e (mg/g) was calculated according to the following equation:

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

where C_0 and C_e (mg/*l*) were the initial and equilibrium concentration of dichlorophen, respectively, $V(l)$ was the volume of the solution and m(g) was the mass of polymers.

In the study of the binding kinetics, 2.0 mg of imprinted polymers was added into 50 mg/*l* dichlorophen solution (ethanol and deionized water 1:3, V:V). The solutions were then incubated at 298, 308, and 318 K at different react times, respectively. The adsorption capacities of dichlorophen Q_t (mg/g) were calculated as follows:

$$Q_t = \frac{V(C_0 - C_t)}{m} \tag{2}$$

where C_t (mg/*l*) was the free concentration of dichlorophen at any time t (min).

In order to study the selectivity properties of the dichlorophen imprinted polymers, 2.0 mg of MIPs was separately placed in 10 m*l* solution with 2,4-dichlorophenol, 2,6-dichlorophenol and dichlorophen, respectively. The initial concentrations of the three solutions was the same

(50 mg/*l*). Meanwhile, the adsorption property of non-imprinted polymers was also studied. All the measurement data that mentioned were carried out in triplicate, and the mean values were used.

Regeneration Performance of MIPs

For the purpose to study the regeneration performance of MIPs for adsorption of dichlorophen, 2.0 mg of MIPs were added into 50 mg/*l* dichlorophen solution at 298 K and the solution was incubated for 0.5 h. The amount of remaining material in the solution was measured. The template molecules in the polymer were then washed off and the above procedures were repeated 6 times.

Results and Discussion

Preparation of Core-shell MIPs

The synthetic route of the core-shell MIPs is shown in Figure 1. It illustrates the process of preparing a core-cell structured silica polymer via a surface imprinted method. The synthesis of surface imprinted polymers with highly controlled morphology is generally carried out as follows: (1) the spherical silica with a smooth and uniform surface was synthesized, and the obtained materials were modified via a simple and feasible method, and then the double bond was introduced by MPTMS which could facilitate the polymerization; (2) the template molecule, functional monomer, cross-linking agent and initiator were added to the reaction system, pre-polymerized at 50 °C for 6 h, and polymerized at 60 °C for 24 h. During the precipitation polymerization process, the hydrogen bond might be formed between the template molecule and the functional monomer. The template molecule was then removed using an organic solvent, and the imprinted product with silica as a support core were obtained. The obtained imprinted polymers had specific recognition sites with excellent compatibility of size, shape and chemical interactions which could selectively and sensitively rebind the template molecules.

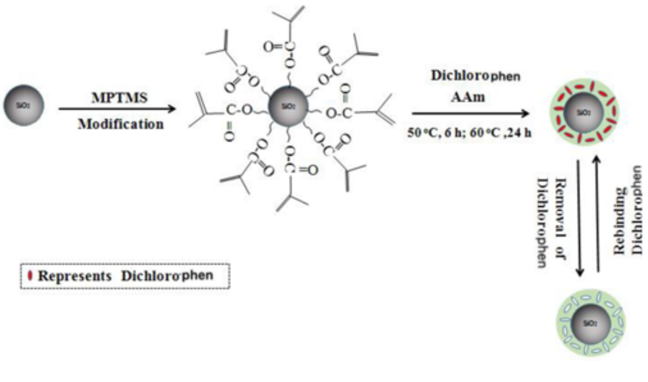

Figure 1. Synthetic route for core-shell molecularly imprinted nanoadsorbents.

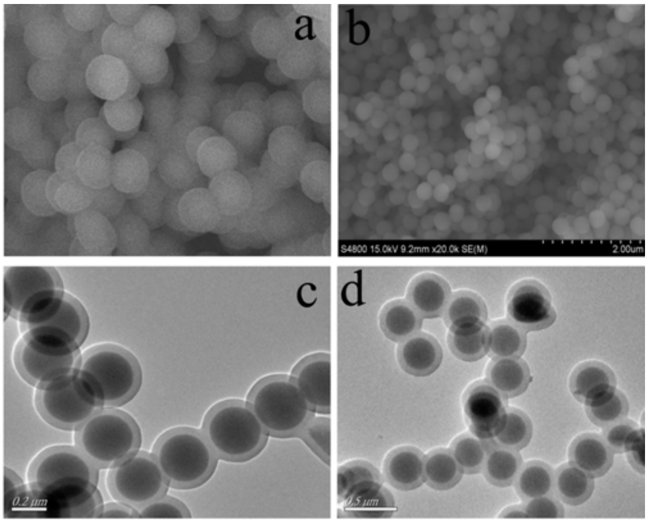

Figure 2. SEM images of the MIPs (a, b) and TEM image of the MIPs (c, d).

Characterization of MIPs

The characteristics of the MIPs were observed by SEM and TEM. The results are shown in Figure 2(a, b) and (c, d), respectively. In Figure 2(a, b), the prepared silica were spherical particles with a diameter about 200-260 nm, which had a regular shape and a uniform size. Compared with the spherical polymers prepared in the previous report, the imprinted layer of the core-shell imprinted polymer prepared in this experiment was very uniform and thin [33].

As can be seen from the Figure 2(c, d), the thickness of the imprinted polymeric layer on the surface of the silicon sphere is approximately 50 nm. This facilitates selective adsorption to reach equilibrium in a shorter period of time.

Adsorption Isotherms

For the study of the equilibrium adsorption capacity of the imprinted polymer to dichlorophen, the static adsorption data were mainly fitted by Langmuir and Freundlich isotherm models [34]. The linear forms of isotherm models were respectively expressed as the equations (3) and (4):

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \tag{3}$$

$$\text{In}Q_e = \text{In}K_F + \left(\frac{1}{n}\right)\text{In}C_e \tag{4}$$

where Q_m (mg/g) was the maximum adsorption capacity of the polymers, K_L (*l*/mg) was the Langmuir adsorption equilibrium constant, K_F and n were the adsorption equilibrium constant of Freundlich, respectively.

Some of the parameters involved in the isotherm equations are listed in Table 1. The adsorption behavior of the polymer to dichlorophen was fitted using the linear equation of the

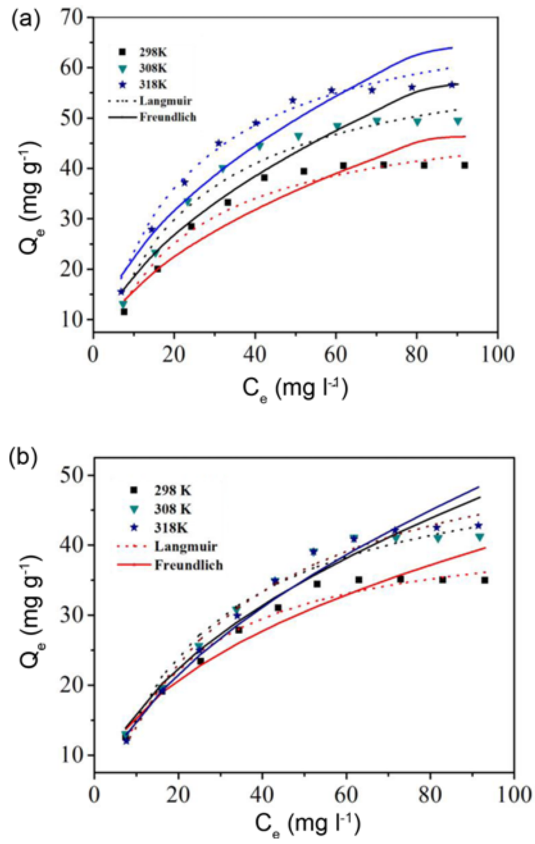

Figure 3. Fitting curves of the Langmuir and Freundlich isotherm of dichlorophen onto MIPs (a) and NIPs (b).

Langmuir and Freundlich isotherm model at three different temperature and the results were shown in Figure 3. The figure shows that with the increase of initial concentration, the adsorption amount of MIPs is increased rapidly at the beginning, then the growth rate tends to be slow, and finally reaches the dynamic equilibrium after a period of time. Also, it is obviously that with the increasing of react temperature, the binding amount improved in the whole concentration range. The maximum adsorption amounts of the target molecules on the polymer surface were 52.91 mg g^{-1}, 65.35 mg g^{-1} and 72.46 mg g^{-1} at 298, 308 and 318 K, respectively. This may be due to the fact that the molecularly imprinted polymer layer was located on the surface of the spherical silica to facilitate the adsorption. The higher temperature may increase the pore volume and the specific surface area of the adsorbent. Compared with the non-imprinted polymer adsorption value 43.47-58.52 mg g^{-1}, the existence of the imprinting site was implied. Compared the R^2 of the two adsorption models, it can be seen that the Langmuir isotherm adsorption model (R^2>0.981) can well fit the adsorption process for dichlorophen on the imprinted polymer. This indicates that the adsorption process of the imprinted polymer for the target is monolayer molecular layer adsorption.

Adsorption Kinetics

The adsorption kinetics data of MIPs and NIPs for dichlorophen at different temperatures are shown in Figure 4. The adsorption rate of MIPs to dichlorophen was faster in the initial period of time, and the adsorption equilibrium was achieved within 90 min, owing to the imprinted polymeric layer was located on the surface of the carrier. The study of the kinetics of the adsorption reaction at different temperatures and different reaction times shows that as the temperature and time increase, the amount of adsorption also increases. It can be seen that the adsorption capacity of MIPs is always higher than NIPs because there are a large number of imprinted sites in the imprinted polymer layers.

The adsorption kinetics of polymer for dichlorophen were studied by pseudo-first-order and pseudo-second-order kinetics [35]. The linear forms of the kinetic equation were respectively expressed as the equations (5) and (6)

$$\mathrm{In}(Q_e - Q_t) = \mathrm{In}Q_e - k_1 t \tag{5}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{6}$$

where k_1 (min^{-1}) was the pseudo-first-order rate constant, and k_2 (g μmol^{-1} min^{-1}) was the pseudo-second-order rate constant.

The constants used in the kinetic model are listed in Table 2. Compared with the two kinetic formulas, the R^2 value of the pseudo-second-order kinetic model is closer to 1 than the pseudo-first-order model, and the pseudo-second-order

Table 1. Isotherm constants for Dichlorophen adsorption onto MIPs and NIPs

Samples	T (K)	Q_e (mgg^{-1})	Langmuir			Freundlich		
			Q_m (mgg^{-1})	K_L (Lmg^{-1})	R^2	K_F ((mgg^{-1}) (Lmg^{-1}))	n	R^2
MIPs	298	40.5	52.91	0.0450	0.9891	4.963	1.987	0.905
	308	49.4	65.36	0.0419	0.9813	5.597	1.915	0.913
	318	56.0	72.46	0.0468	0.990	7.176	2.022	0.9261
NIPs	298	35.0	43.47	0.053	0.991	5.874	2.376	0.9535
	308	41.1	54.34	0.040	0.987	5.291	2.072	0.9645
	318	42.8	59.52	0.032	0.989	4.419	1.899	0.9642

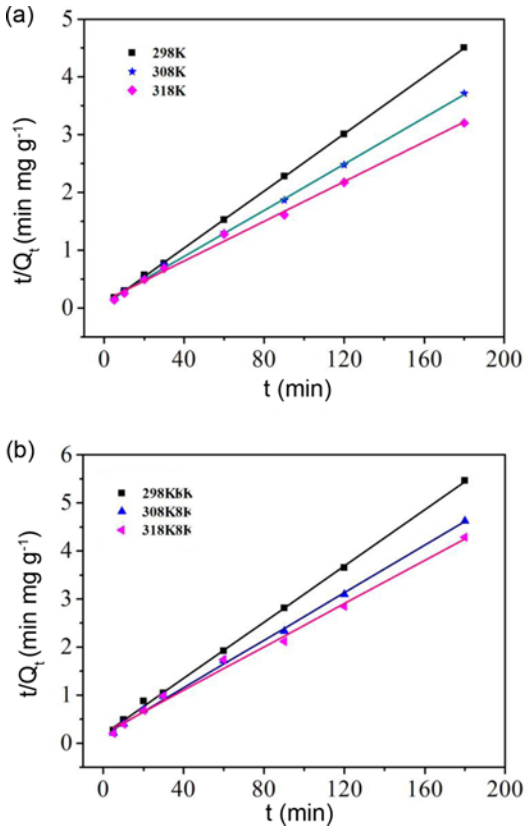

Figure 4. Adsorption kinetic polts of MIPs (a) and NIPs (b) towards dichlorophen and fitting curves to the pseudo-second-order kinetic model at three temperature.

model can better fit the adsorption process. At three different temperatures, the $Q_{e,c}$ calculated by the pseudo-second-order model is closer to the $Q_{e,\mathrm{exp}}$ value obtained from the experiment, which further proves that both the adsorption of dichlorophen by MIPs and NIPs are in accordance with pseudo-second-order kinetic model. Pseudo-second-order kinetic equation can better fit the silica surface imprinted polymer selective identification of dichlorophen kinetic data, indicating that the selective recognition is a chemical adsorption process. Meanwhile, the pseudo-second-order rate constant k_2 increased with increasing temperature and the initial concentration of dichlorophen, indicating that the adsorption kinetics of dichlorophen was largely related to temperature and initial concentration.

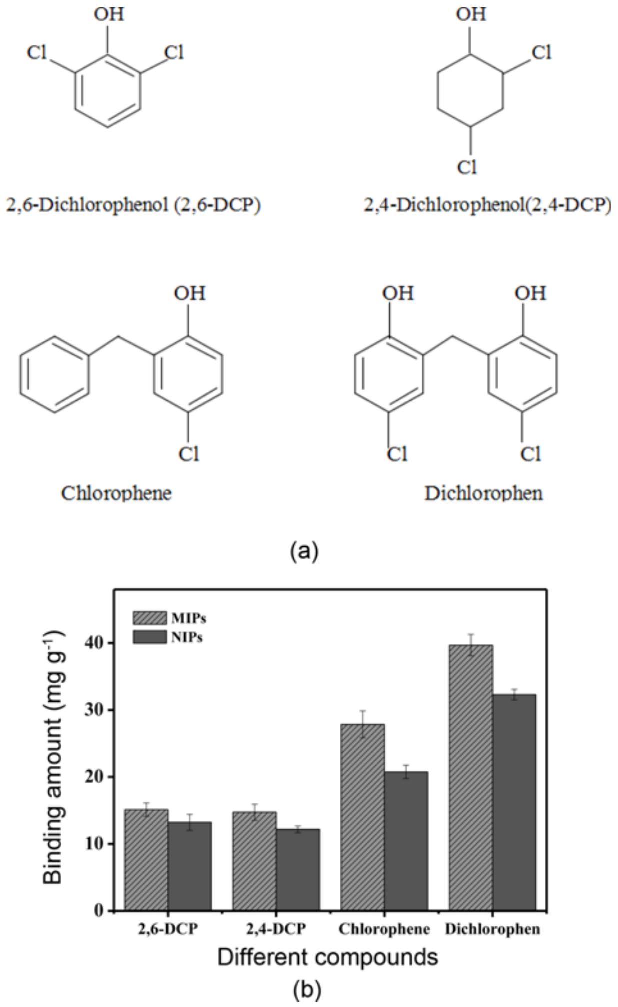

Figure 5. The chemical structures of the tested four different compounds (a) and selective adsorption performance of MIPs and NIPs to dichlorophen (b).

Table 2. Constants of the adsorption kinetic constants for dichlorophen onto MIPs and NIPs

Adsorption	T (K)	$Q_{e,\mathrm{exp}}$ (mgg^{-1})	Pseudo-first-order			Pseudo-second-order		
			$Q_{e,c}$ (mgg^{-1})	k_1 (min^{-1})	R^2	$Q_{e,c}$ (mg g^{-1})	k_2 (gmg^{-1}min^{-1})	R^2
MIPs	298	39.68	32.58	0.0166	0.7617	39.38	0.0122	0.9990
	308	47.81	39.95	0.0165	0.8541	47.77	0.0045	0.9995
	318	53.59	52.18	0.0391	0.8573	53.14	0.0024	0.9964
NIPs	298	32.30	26.76	0.0153	0.8476	32.14	0.0046	0.9992
	308	37.81	31.71	0.0154	0.8746	37.72	0.0037	0.9987
	318	40.28	34.10	0.0146	0.7981	40.18	0.0025	0.9944

Table 3. Selective recognition and adsorption properties of various MIPs

Morphology	Template molecule	Adsoption capacity (Q_m)	Equilibrium time	Reference
Irregular	Tetracycline	3.84 mg g^{-1}	24 h	36
Core-shell	Atrazine	1.5 mg g^{-1}	12 h	37
Core-shell nanosphere	Dichlorophen	72.46 mg g^{-1}	1.5 h	This study

Selectivity Performance

The ability of imprinted polymers to selectively recognize and adsorb target molecules is an important index for evaluate its application. As shown in Figure 5(a), we chose 2,6-DCP, 2,4-DCP and chlorophene with different chemical structures as research objects. These substances have a great environmental impact on the environment. Figure 5(b) shows the adsorption capacities of MIPs and NIPs to the four substances under the same conditions. It can be seen from the figure that the adsorbed amount of dichlorophen on MIPs was obviously higher than that of 2,6-DCP, 2,4-DCP and chlorophene. Because the surface of MIPs has the function of completely matching the result of dichlorophen and the functional group spots, these sites have the ability to selectively recognize and bind dichlorophen. In addition, it can also be seen from the figure that the adsorbed amount of MIPs to any one substance is higher than NIPs. However, the difference between the adsorption amounts of dichlorophen, chlorophene, 2,6-DCP and 2,4-DCP for MIPs and NIPs were not the same. The binding capacities of dichlorophen and chlorophene onto MIPs were 39.68 and 27.85 mg g^{-1}, respectively. In addition, MIPs had higher adsorption capacity for chlorophene than 2,4-DCP and 2,6-DCP, due to similar chemical structure of chlorophene with dichlorophen. The image shows the binding capacities of the NIPs onto chlorophene, which were similar to that of 2,6-DCP and 2,4-DCP, indicating the NIPs had no specific sites for template molecule. In Table 3, the selectivity, adsorption capacity and equilibrium time of MIPs collected from various references are listed. It can be shown that MIPs have strong selectivity and adsorption capacities to the template molecule.

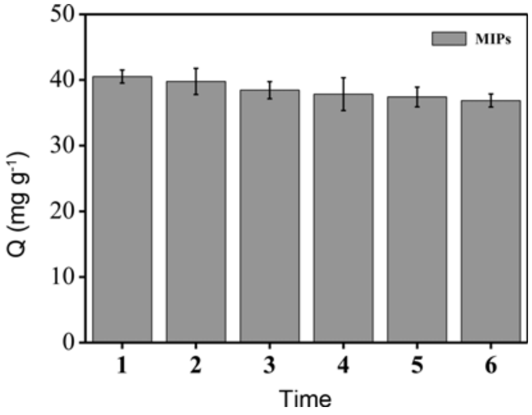

Figure 6. Stability and reuse of MIPs.

Regeneration Property of MIPs

Repeated six experiments can be used to demonstrate the regeneration and stability of MIPs. The adsorption results of MIPs after each adsorption in the experiment were listed in Figure 6. As can be seen from the graph, MIPs can be well used in practical applications for recycling.

Conclusion

In this study, surface imprinting method was used to synthesize imprinted polymers. From the characterization results of the polymer, it was found that a polymeric layer with template molecules was successfully imprinted on the silica surface. The batch adsorption experiments demonstrated that the increase of temperature could improve the adsorption properties of the polymer. The adsorption isotherms and kinetics studies have shown that the polymer adsorption of dichlorophen monolayer adsorption and in line with pseudo-second-order kinetic equation. Selective experiment shows that the adsorption capacity of MIPs for dichlorophen was significantly higher than that of NIPs, and the MIPs could be successfully applied in practice. The research of imprinted polymers with core-shell structures not only enriches the potential application of MIP, but more importantly provides a good reference value for the adsorption and removal of trace amounts of dichlorophen from the water environment.

Acknowledgments

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