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Direct Synthesis of Surface Molecularly Imprinted Polymers Based on Vinyl-SiO_2 Nanospheres for Recognition of Bisphenol A

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ABSTRACT: Molecularly imprinted polymers (MIP) with high performance in selectively recognizing bisphenol A (BPA) were prepared by using a novel and facile surface molecular-imprinting technique. Vinyl-functionalized, monodispersed silica spheres were synthesized by a one-step emulsion reaction in aqueous solution. Then, BPA surface molecularly imprinted polymers (SMIP) were prepared by polymerization with 4-vinylpyridine as the functional monomer and ethylene glycol dimethacrylate as the crosslinker. Maximal sorption capacity (Q_{max}) of the resulting SMIP was up to 600 μmol g^{-1}, while that of nonimprinted polymers was only 314.68 μmol g^{-1}. Kinetic binding study showed that sorption capacity reached 70% of Q_{max} in 20 min and sorption equilibrium at 80 min. SMIP had excellent accessibility and affinity toward BPA, for the selectivity coefficients of SMIP for BPA in respect to phenol, *p*-*tert*-butylphenol, and *o*-phenylphenol were 3.39, 3.35, and 3.02, respectively. The reusage process verified the SMIP owning admirably stable adsorption capacity toward BPA for eight times. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 3846–3852, 2013

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INTRODUCTION

As a typical endocrine disruptor,[1,2] bisphenol A (BPA) can potentially interfere with the endocrine system of wild animals and humans. Many evidences have shown that BPA has toxic properties.[3] By interfering the action of endogenous gonadal steroid hormones, it will induce estrogenic endocrine disruption, even abnormal variation of reproductive organs, and occurrence of tumorigenic progression. BPA is used as an important monomer for the production of polycarbonate plastics and epoxy resins, such as baby bottles, one-off tableware, dental sealants, glasses, and other plastic packaging materials.[4] Therefore, BPA will be inevitably released into the environment during manufacture, use, and disposal processes and easily migrate into human body to cause profound and adverse effect on health. As a consequence, it is very essential to effectively remove the BPA from the environmental samples.

Molecular imprinting is known as a technique for generating tailor-made recognition sites with memory of the shape, size, and functionality of templates after removal of the template molecules.[5,6] Then, molecularly imprinted polymers (MIP) have attracted extensive research interest for being facilely prepared and showing specific affinity when facing a mixture of various species.[7–10] However, conventional MIP for BPA are prepared by bulk polymerization or precipitation polymerization[11–15]; thus, the residual template molecules and recognition sites are embedded deeply in the matrix due to the high-cross-linking nature of MIP, which results in incomplete template removal, small binding capacity, and slow mass transfer. As a result, traditional polymer materials often exhibit high selectivity but low-rebinding capacity and poor site accessibility to target species. Recently, surface imprinting[16–20] as a new technology promising to overcome the problems of traditional materials has caused considerable attention, in which the imprinted templates are controlled to situate at the surface of supporters. Using silica nanospheres as supporters, the surface-imprinted materials will realize mechanical/chemical stability, low cost, narrow size distribution, and easy preparation process. Surface molecular-imprinting materials provide complete removal of templates, better accessibility to the target species, and faster binding kinetics, comparing to traditional MIP.[21]

As the original silica carriers have no functional groups on its surface, there is a need to introduce active organic groups (such as vinyl, amine, and thiol) into the silica colloids. Often, two methods, postgrafting and cocondensation, are used to modify them. In the current material field, some directly process commercial silica gel with organosilanes,[22,23] while others first

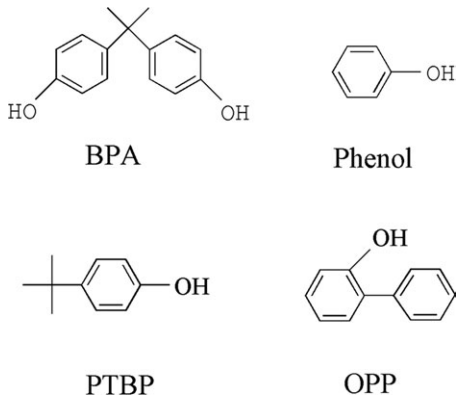


Figure 1. The molecular structures of BPA, phenol, PTBP, and OPP.

prepare silica spheres by Stöber et al.[24] method and conduct postmodification[17–19] work in order to realize the following polymerization. The multistep process is sophisticated and time consuming, and particle surfaces can only be partially modified.[25] The resultant functional groups on silica nanospheres may not be stable enough when reacting in the following process. If a one-step approach is used to prepare silica nanospheres with functional groups uniformly and simultaneously forming at the surface, it will save plenty of time, and the resultant nanospheres may remain stable for the robust chemical bond.

Herein, we applied surface molecular-imprinting technology to the synthesis of BPA-imprinted polymer using silica nanospheres as carriers. Highly monodispersed, 150-nm-sized vinyl–SiO_2 nanospheres were facilely prepared by a one-step approach in aqueous solution.[25,26] Then, a highly binding ability surface molecularly imprinted polymer (SMIP) for BPA was directly synthesized on the surface of vinyl–SiO_2 nanospheres for the first time. The polymers were characterized by Fourier transform infrared spectrometer (FTIR), scanning electron microscope (SEM), and transmission electron microscope (TEM). Materials' functional evaluations included static and dynamic-binding processes, Scatchard analysis, selective binding tests in four kinds of analogues, and reusable performance in the same condition for eight times. The results demonstrated that BPA–SMIP nanospheres not only possessed of great rebinding capacity and efficiently recognizing ability for template, but also exhibited steady and excellent reusable property.

EXPERIMENTAL

Materials and Chemicals

BPA (purity > 98%), phenol, *o*-phenylphenol (OPP, purity > 99%), and *p*-*tert*-butylphenol (PTBP, purity > 99%) were purchased from Aladdin reagent Co. (China). 4-Vinylpyridine (4-VP, Alfa Aesar, 96%) and ethylene glycol dimethacrylate (EGDMA, Alfa Aesar, 98%) were purified by distillation under vacuum. Azobisisobutyronitrile (AIBN, chemical grade) was purchased from Shanghai No. 4 Reagent & H.V. Chemical Company (China) and purified through recrystallization in ethanol before use. Sodium dodecylbenzene sulfonate (SDBS) was purchased from Sinopharm Chemical Reagent Co. (China). Vinyltriethoxysilane (VTES) was purchased from Nanjing Union Silicon Chemical Co. (China). Ammonium hydroxide (28%) and toluene were purchased from Shanghai Chemical Reagent Co. (China). Doubly distilled water used throughout the experiment processes were obtained from the laboratory purification system.

Instrumentation

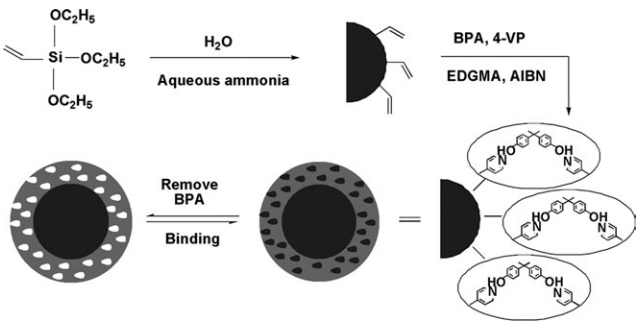
FTIR spectra were recorded on a Tensor-27 FTIR spectrometer (Bruker, Germany) with a resolution of 2 cm^{-1} and a spectral range of 4000–400 cm^{-1}. The morphologies and structures of BPA-imprinted silica nanospheres were observed by a SIRION200 SEM (FEI, Holland) and a JEM-2011 TEM (JEOL, Japan) with measurements operating at 5 and 200 kV, respectively.

The BPA amount was analyzed by the high-performance liquid chromatography (HPLC) system (Shimadzu, Japan), which consisted of a LC-15C pump, SIL-10AF injector with 50 μL loop, and a SPD-15C dual-wavelength absorbance detector. The mobile phase used for HPLC experiments was a mixture of methanol and water (90 : 10, v : v), and all separations were carried out on a GL Sciences C18 column (5 μm, 150 mm × 4.6 mm) with a flow rate of 1.0 $mLmin^{-1}$. The detecting wavelength of the UV detector was set at 228 nm for BPA and 276 nm for the mixtures of BPA and analogues.

Procedure for the Preparation of Molecularly Imprinted Polymer

One-Step Preparation of Vinyl–SiO_2 Nanospheres. Vinyl–SiO_2 nanospheres were synthesized according to the literature-reported approach.[25,26] VTES (3.8 g) and SDBS (0.0039 g) were added into 30 mL of doubly distilled water under vigorous stirring until an emulsion formed. After 1 h, $NH_3{\cdot}H_2O$ (0.5 mL) was added to the emulsion, and the mixture was kept stirring at 50°C for 24 h. The resulting nanospheres were separated from the reaction medium by centrifugation and washed with doubly distilled water several times.

Imprinting of BPA Molecules at the Surface of Vinyl–SiO_2 Nanospheres. In a typical synthesis, vinyl–SiO_2 nanospheres (0.5 g) were dispersed in 20 mL of toluene by ultrasonic bath. 4-VP (0.421 g), EGDMA (1.132 mL), BPA (0.228 g), and AIBN (0.08 g) were subsequently dissolved into the above solution. The mixing solution was purged with nitrogen for 30 min while being cool in ice bath. The polymerization was made at 40°C for 4 h and then at 60°C for 18 h. The final polymerization was completed after further aging at 75°C for another 6 h to obtain



Scheme 1. Schematic procedure of molecular imprinting at the surface of vinyl-SiO_2 nanospheres.

Table I. Effect of Different Solvent Volumes in Imprinted Process

Template (BPA) mmol	Monomer (4-VP) mmol	Cross-linker (EGDMA) mmol	Solvent (toluene) mL	Q_{SMIP} (μmol g^{-1})	Q_{SNIP} (μmol g^{-1})
1.0	4	5.5	200	204.3	194.5
1.0	4	5.5	100	194.2	181.8
1.0	4	5.5	50	183.5	160.9
1.0	4	5.5	20	150.6	91.3

a high-cross-linking density. Magnetically, stirring at a rate of 300 rpm was kept throughout the experiment. The resultant SMIP were collected by filtration and washed with a mixing methanol/acetic acid solvent (9 : 1, v : v). Original BPA templates in the imprinted shells were removed by Soxhlet extraction in 200 mL of mixing methanol/acetic acid (9 : 1, v : v) solution until no residual BPA could be detected. Finally, the polymers were washed with methanol to neutral and dried at 60°C for 12 h. For comparison, the surface nonimprinted polymer (SNIP) was also prepared by an exactly identical method except that no template molecules were added during the polymerization process.

Measurements of Recognition Properties of SMIP. The static and dynamic tests of rebinding BPA molecules were investigated using HPLC. Ten milligrams of SMIP particles was suspended in 10 mL toluene solution with various BPA concentrations (0.01–4 $mmolL^{-1}$), respectively. After shaking at room temperature for 12 h to facilitate full adsorption, the amounts of BPA in the supernatants were detected. The binding amount of BPA was determined by measuring the difference between the initial and final amount in solution. The same procedure was performed on the SNIP. Meanwhile, the binding kinetics was carried out using 10 mg of SMIP, which were added into 10 mL toluene solution containing 0.5 $mmolL^{-1}$ BPA by monitoring the temporal residual BPA concentration in the solutions at certain time intervals.

Selectivity of SMIP. To explore the selectivity of the SMIP toward BPA, the selective recognition assays of BPA from BPA and its analogues (phenol, PTBP, and OPP) were investigated on SMIP and SNIP. Their chemical structures were shown in Figure 1. The mixed solutions contained the same concentration of BPA, phenol, PTBP, and OPP with a series of concentration from 0.1 to 4 $mmolL^{-1}$. Then the adsorption was performed as the process mentioned earlier, and the final compounds in the residual solutions were analyzed by HPLC.

Reusage of SMIP. About 100 mg of SMIP particles was suspended in 30 mL toluene solution with a BPA concentration of 2 $mmolL^{-1}$. Then the adsorption was proceeded as mentioned earlier. After the adsorption, the material was washed with methanol three to four times and dried at 60°C to constant weight. The sorption–desorption cycle was repeated eight times.

RESULTS AND DISCUSSION

Preparation and Characterization of SMIP Nanospheres

Preparation of SMIP Nanospheres. The possible schematic illustration of the routes for the preparation of BPA imprinting at the surface of silica nanospheres was shown in Scheme 1. It could be seen that the vinyl layer of the silica surface directed the selective occurrence of imprinting polymerization at the surface of silica through the copolymerization of vinyl groups with cross-linking agents. 4-VP, the monomer, and BPA, the template, would be connected together by hydrogen bond and polymerized on the surface of silica nanospheres to form SMIP. After the removal of BPA template, large quantities of tailor-made cavities for BPA were obtained on the surface.

The volume of solvent was a critical factor to influence the adsorption properties of the SMIP.[27] Different volumes of toluene were chosen to optimize the conditions, and the results were listed in Table I. It was obvious that the adsorption capacity of the SMIP for BPA increased with increasing volume of solvent, while that of the nonspecific adsorption on SNIP also drastically augmented. Consider the difference of binding capacity between SMIP and SNIP, 20 mL toluene and the molar ratio of the template, functional monomer, and cross-linker-1 : 4 : 5.5[19] were chosen for the synthesis of the SMIP and SNIP sorbents.

Characterization of SMIP and SNIP. To confirm the existence of functional vinyl groups on the surface of silica nanospheres and carbonyl group in SMIP and SNIP, the FTIR spectra of silica nanospheres, SMIP, and SNIP were obtained and shown in Figure 2. The IR bands at about 3000–3063, 1603, and 1412 cm^{-1} indicated the presence of C=C groups on the prepared vinyl–SiO_2 nanospheres. Compared to vinyl–SiO_2 nanospheres, a characteristic adsorption feature of the SMIP and SNIP was

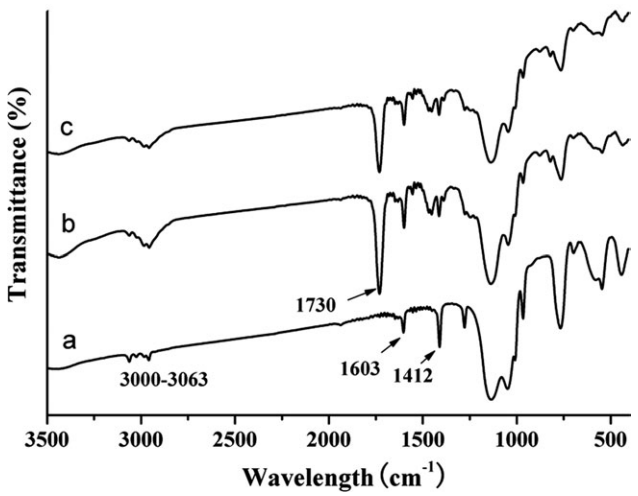


Figure 2. FTIR spectra of (a) vinyl-SiO_2 nanospheres, (b) SMIP, and (c) SNIP.

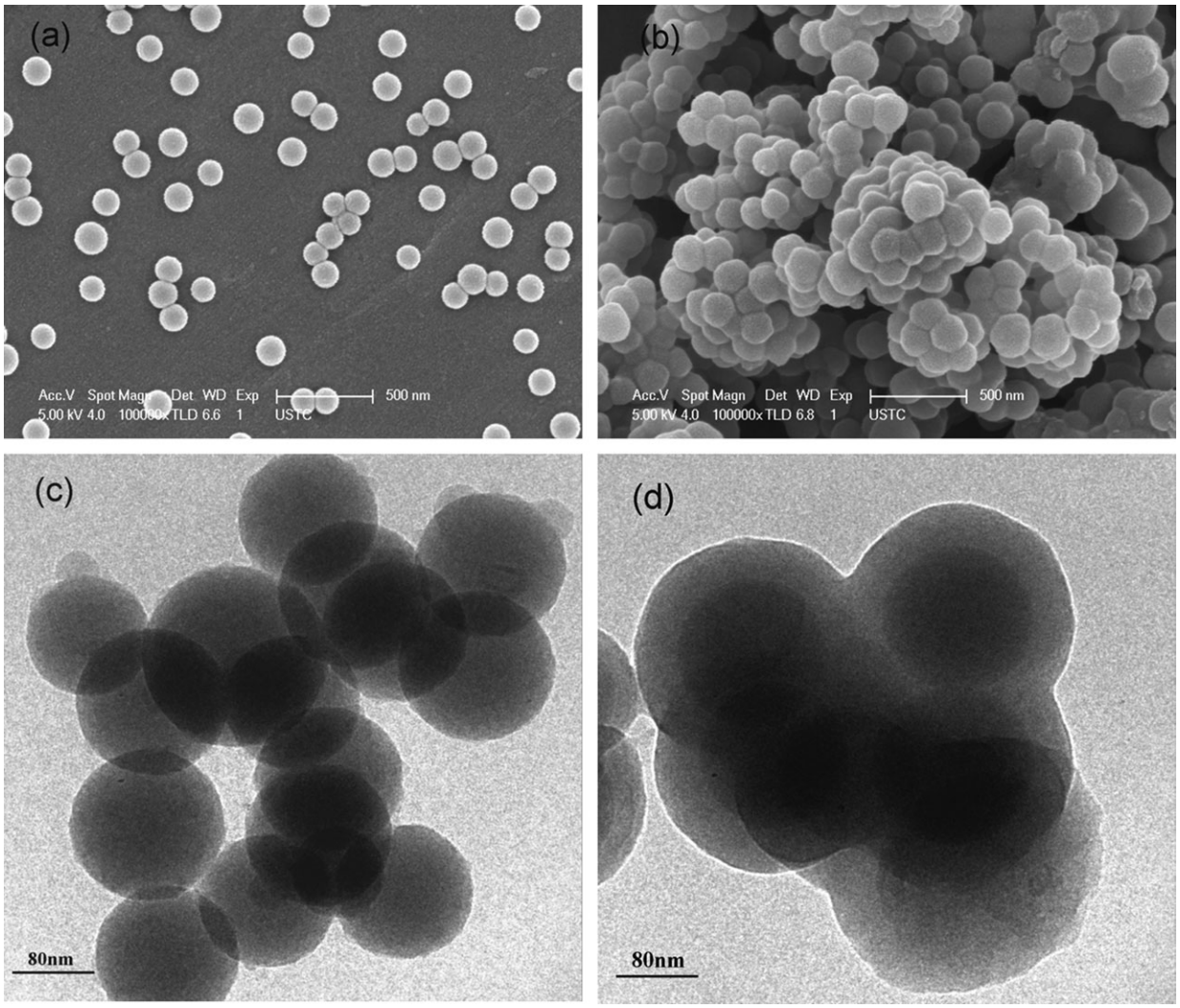


Figure 3. (a) SEM image of vinyl-SiO_2 nanospheres, (b) SEM image of SMIP, (c) TEM image of vinyl-SiO_2 nanospheres, and (d) TEM image of SMIP.

clearly observed at 1730 cm^{-1}, which was the proof of the existing of C=O groups in the final imprinted polymers.

SEM and TEM images were taken for the vinyl–SiO_2 nanospheres and SMIP. As shown in Figure 3, the vinyl–SiO_2 nanospheres and SMIP were highly spherical. The obtained vinyl–SiO_2 particles were about 150 nm in size and relatively monodispersed. The layer thickness of SMIP was estimated to be about 50 nm. It could be observed from the TEM spectra that surface polymerization successfully occurred on the surface of silica nanospheres and core-shell structure formed.

Evaluation of the Adsorption Character of SMIP and SNIP. For the sake of its further application, the adsorption capacity of SMIP and SNIP sorbents was investigated in BPA of toluene solutions with different concentrations ranging from 0.01 to 4 $mmolL^{-1}$.

The sorption capacity Q (μmol g^{-1}) is calculated by the following equation:

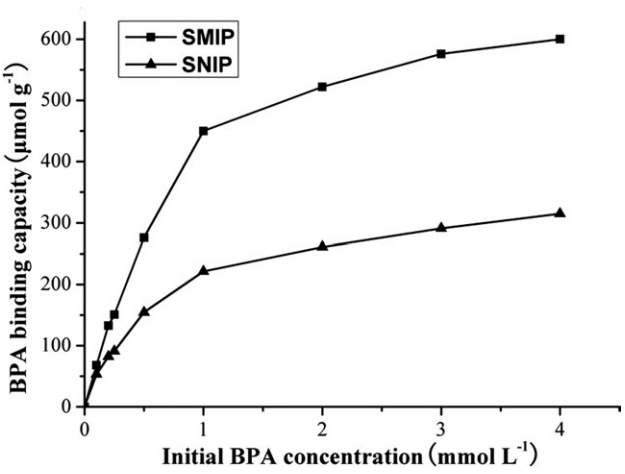


Figure 4. Static adsorption isotherms of the SMIP and SNIP sorbents for BPA (0.1–4 $mmolL^{-1}$).

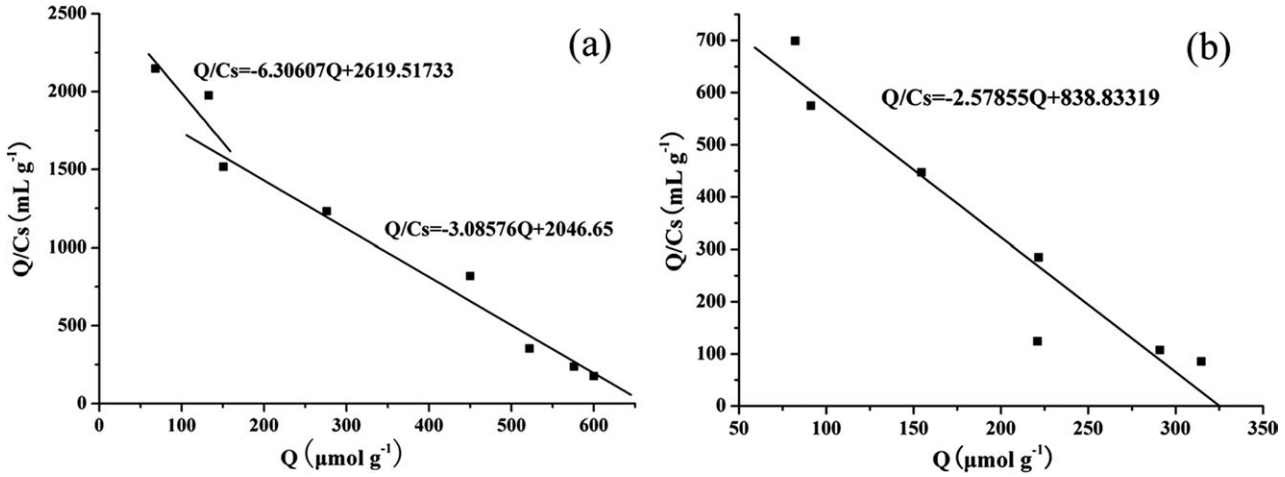


Figure 5. Scatchard plot for BPA in (a) SMIP sorbent and (b) SNIP sorbent.

$$Q = \frac{(C_0 - C)V}{W} \quad (1)$$

$$\frac{Q}{C_s} = \frac{Q_{max} - Q}{K_d} \quad (2)$$

where C_0 and C are the initial and final template concentrations (μmol L^{-1}) in the solutions, respectively, V (L) is the volume of the bulk solution, and W (g) is the weight of the materials.

Figure 4 showed the static binding isotherm of BPA on these two sorbents. It was obvious to find that the adsorption capacities of SMIP and SNIP increased with the increasing initial concentration of BPA. The maximum adsorption of SMIP for BPA was calculated to 600 μmol g^{-1}, which was nearly two times as large as that of corresponding SNIP (314.68 μmol g^{-1}). Then, it could be concluded that the SMIP displayed much stronger affinity to BPA compared to the SNIP. And the sorption capacity of the SMIP prepared was favorably superior to those reported in the previous literature.[22,28–30]

The binding affinity and theoretical binding site number for template of the imprinted polymers are mainly estimated by Scatchard analysis with the data of static adsorption experiment. Scatchard analysis is provided by the Scatchard equation, which is described as follows:

where Q (μmol g^{-1}) is the equilibrium adsorption capacity, Q_{max} (μmol g^{-1}) is the apparent maximum adsorption capacity, C_s (μmol mL^{-1}) is the equilibrium concentration of BPA, and K_d (μmol mL^{-1}) is the equilibrium dissociation constant. In Figure 5, the steeper line exhibits the specific binding sites, and the flatter line exhibits nonspecific binding sites. According to the slope and intercept of regression model, K_{d1} for specific binding sites and K_{d2} for nonspecific binding sites for SMIP were calculated to 158.58 and 342.07 μmol L^{-1}, respectively. Likewise, an equilibrium dissociation constant for the SNIP was calculated to 387.81 μmol L^{-1}. It showed that the SMIP had high selectivity for BPA.

Dynamic adsorption test of SMIP for BPA was carried out at different time intervals. The results in Figure 6 indicated that an initial rapid increased in the adsorption capacity within a short

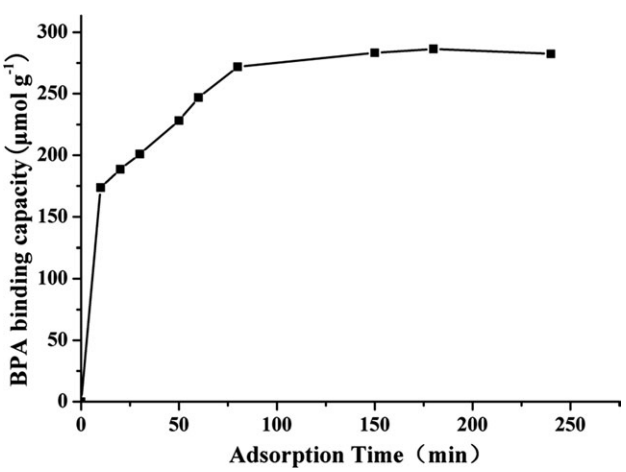


Figure 6. Adsorption kinetics of the SMIP for BPA (0.5 mmolL^{-1}).

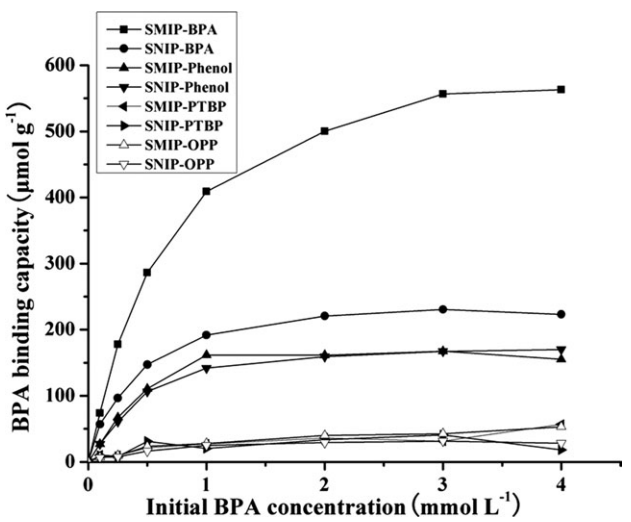


Figure 7. Static adsorption curves of BPA, phenol, PTBP, and OPP on SMIP and SNIP sorbents (0.1–4 mmolL^{-1}).

Table II. Competitive Binding Tests of BPA and Three Analogues on the BPA-Imprinted and Nonimprinted Silica Sorbents (0.25 mmolL^{-1})

	K_d				K			K'		
Sorbents	BPA	Phenol	PTBP	OPP	BPA/Phenol	BPA/PTBP	BPA/OPP			
SMIP	2457.81	368.06	39.50	39.93	6.68	62.22	61.55	3.39	3.35	3.02
SNIP	630.58	320.72	34.00	30.93	1.97	18.55	20.39			

shaking period of 20 min, and the equilibrium was obtained in 80 min. It implied that SMIP with specific recognition cavities at surface reduced the mass transfer resistance to make it easier for targets to access to and led to rapid binding kinetics, compared to MIP synthesized in the traditional method that cost several hours to achieve the equilibrium.[7,31]

Selectivity of SMIP. The structurally similar compounds—phenol, PTBP, and OPP—were chosen as the competitive species with BPA for the selective recognition study. Selectivity of the imprinted and nonimprinted sorbents was evaluated by some factors, which were calculated by the following eqs. (3)–(5).[32] Distribution coefficient (K_d) stood for the character of a substance adsorbed by a sorbent, and selectivity coefficient of the sorbent (k) represented the otherness of two analogues adsorbed by the same sorbent, while relative selectivity coefficient (k') suggested the otherness of two different sorbents.

$$K_d = \frac{C_i - C_f}{C_f} \times \frac{V}{W} \tag{3}$$

where C_i and C_f represent the initial and equilibrium concentrations (μmol L^{-1}), and V (mL) and W (g) are volume of solution and mass of sorbent.

$$k = \frac{K_{\text{dBPA}}}{K_{\text{danalogue}}} \tag{4}$$

$$k' = \frac{K_{\text{imprinted}}}{K_{\text{nonimprinted}}} \tag{5}$$

Figure 7 indicated that SMIP possessed higher recognition capability and affinity toward BPA. The absorption capacity of SMIP to BPA was 19 times as large as that to PTBP or OPP and 2.6 times to phenol. PTBP and OPP could hardly be adsorbed on SMIP. The material had affinity to phenol, but the binding capacity on SMIP and SNIP was similar, so that the adsorption was not specific. The $K_{(\text{BPA/analogue})}$ value of the BPA-imprinted silica sorbent in Table II showed that the BPA-imprinted silica sorbent had higher selectivity for BPA over the structurally similar compounds. These facts proved the strong interactions between the template and the functional monomer to favorably form high-affinity-binding sites and improve the selectivity of the polymers. The relative selectivity coefficient (k') values were 3.39, 3.35, and 3.02, respectively. It was clear that the BPA-imprinted silica sorbent had more significant selectivity than the nonimprinted silica sorbent.

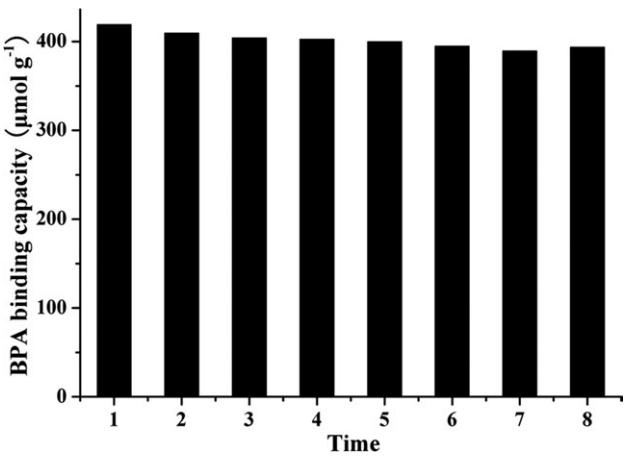


Figure 8. Reuse results of SMIP for eight times.

Reusage of SMIP. A sorption–desorption cycle was repeated eight times by using the same SMIP to evaluate its reusable performance. The results in Figure 8 showed that the binding capacity of BPA remained a high level of over 390 μmol g^{-1} during the cycle, which indicated that the recognizing sites were stable, and the material could be reusable after a regeneration process. Few researches about the reusage performance of SMIP were reported. So, the characteristics of the sorbents were superior to those traditional materials that the SMIP could save the costs for the pretreatment of samples.

CONCLUSIONS

In this work, a highly recognition capability BPA–SMIP was first directly synthesized by molecular-imprinting technique on the surface of vinyl–SiO_2 nanospheres forming a one-step emulsion reaction in aqueous solution. The adsorption properties of the core-shell nanostructure SMIP were evaluated, and the material showed large adsorption capacity, fast binding kinetics, and excellent selectivity toward BPA, which were superior to those of SNIP. The results demonstrated that surface-imprinted polymer could significantly improve the binding capacity and kinetics for its recognition sites situating at the surface. The SMIP also exhibited steady and excellent reusable performance toward BPA in eight sorption–adsorption cycles.

This class of new imprinted materials may become a powerful tool for the study of enrichment and purification of trace BPA from complex matrix samples. Because of its nice reusable performance, it may be available to achieve coupling technique with SPE–HPLC in the future. The merits make the surface-imprinting materials to be one of the most promising candidates for various applications, including chemical and biochemical separation, recognition elements in biosensors, and drug delivery.

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