

# Dye-Molecular-Imprinted Polysiloxanes. II. Preparation, Characterization, and Recognition Behavior

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**ABSTRACT:** Microsphere silica (AMS) was prepared by the sol-gel method and used for the synthesis of dye-molecular-imprinted polysiloxanes. These were prepared by the cohydrolysis and polycondensation of the AMS with functional organosilicone monomers (*N*-phenylaminomethyl triethoxysilane, 3-aminopropyl triethoxysilane, and 4-aza-6-aminohexyl triethoxysilane) in the presence of a template molecule of disperse red (or disperse blue or water-soluble dye) followed by the removal of the template molecule. The molecular-imprinting and nonimprinting polysiloxanes were characterized by elemental analysis, diffuse-reflectance Fourier transform infrared spectroscopy, and scanning electron microscopy. Their adsorption behavior

toward the template molecule and nontemplate molecule was investigated. The molecular-imprinting polysiloxane exhibited higher selective recognition properties toward the template molecule than the nonimprinting polysiloxane. In the experimental conditions, their adsorption isotherms were a good fit with the Langmuir model. The distribution coefficient value of water-soluble-dye-imprinted polysiloxane was the highest among the three imprinting polysiloxanes under the experimental conditions. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 637–643, 2004

**Key words:** molecular imprinting; polysiloxanes; molecular recognition; adsorption; dyes/pigments

## INTRODUCTION

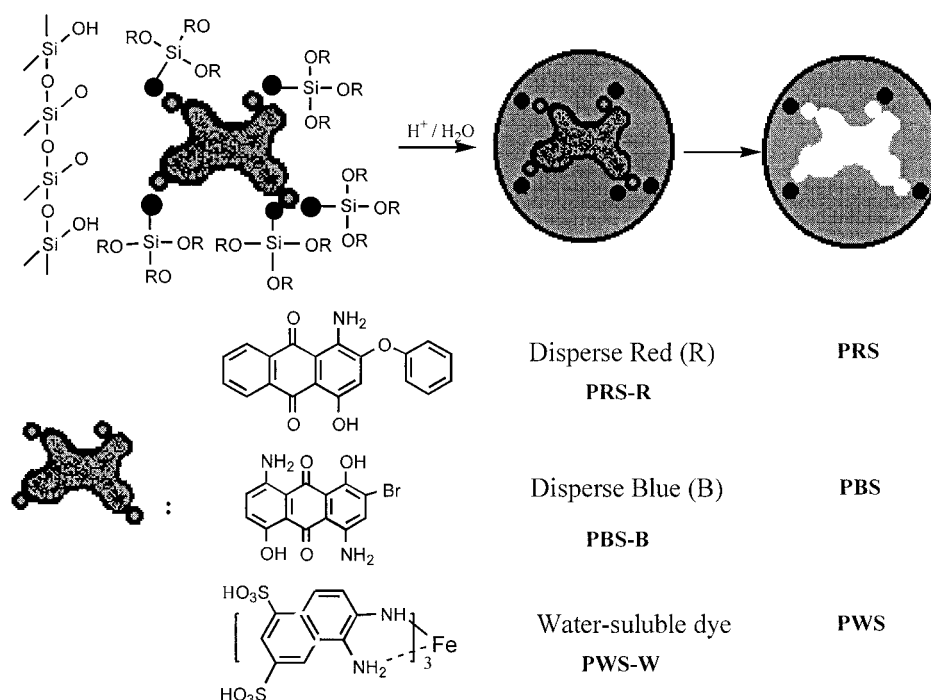
The molecular-imprinting technique has attracted considerable attention during the past few years.<sup>1–4</sup> This technique is a versatile method for producing imprints of template molecules in polymers, and the imprinted polymers display the behavior of selective molecular recognition. These imprinted polymers have been applied as selective absorbents,<sup>5,6</sup> chromatographic stationary phases,<sup>7,8</sup> biomimics,<sup>9–11</sup> and sensors.<sup>12,13</sup> Molecular-imprinting polymers are prepared by template-guide polymerization or by the cocondensation of functional organic monomers interacting with template molecules through covalent or noncovalent bonds; subsequently, the template molecules are removed, and cavities caused by molecular imprints are left in the polymers. The cavities, containing specific binding sites and a definite shape in the imprinting polymer, exhibit a memory function for the template molecules.

Interestingly, imprinting polymers have non-swelling properties, mechanical stability, and a uniform particle size and shape.<sup>14,15</sup> In recent years,

polymers of imprinting cavities on or in organic carriers, especially silica gels, have been reported. Katz and Davis<sup>4</sup> prepared the molecular imprinting of bulk and microporous silica and found that the cavity with spatially organized functional groups covalently anchored to the pore walls, and the imprinted silica could act as a shape-selective base catalyst. Markowitz et al.<sup>16</sup> reported that the surface of silica particles was molecularly imprinted with an  $\alpha$ -chymotrypsin transition-state analogue by template-guide-directed synthesis of mineralized materials. The silica particles of robust-surface-containing catalytic active sites exhibited very high catalytic activity in the hydrolysis reaction of the substrate. Akiyama et al.<sup>17</sup> prepared a molecular-imprinted polymer of cyclodextrin on silica gel supported via the template-guide copolymerization of acryloyl cyclodextrin with vinylated silica gel in the presence of a template molecule in water. They found that the molecular-imprinted polymer was an eminent stationary for high performance liquid chromatography (HPLC) in water. In this article, we report the preparation of molecular-imprinting microsphere polysiloxanes by the cohydrolysis and condensation of *N*-phenylaminomethyl triethoxysilane, 3-aminopropyl triethoxysilane, and 4-aza-6-aminohexyl triethoxysilane and with microsphere silica (AMS) with disperse red (or disperse blue or water-soluble dye) as the template molecule in acetonitrile or aqueous solvents. The recognition prop-

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**Scheme 1** The structure of three dye molecules and schematic representation of the preparation of their imprinted polysiloxanes.

erties of these polysiloxanes with imprinting molecular cavities on AMS surface toward the template molecule and nontemplate molecule were investigated.

## EXPERIMENTAL

### Materials

Ethanol, *n*-propanol, and ammonium hydroxide were analytical grade and were supplied by Shanghai Chemical Reagents Co. (Shanghai, China). The disperse red dye, disperse blue dye, and water-soluble dye were supplied by the Dye Plant of Wuhan (Wuhan, China) and were purified by column chromatography or recrystallization. Tetraethoxysilane, 4-aza-6-aminohexyl triethoxysilane, *N*-phenylaminomethyl triethoxysilane, and 3-aminopropyl triethoxysilane were supplied by the Chemical Plant of Wuhan University (Wuhan, China) and were purified by distillation under reduced pressure before use. Other chemicals were supplied by Shanghai Chemical Reagents Co.; they were analytical-reagent grade and were used without further purification.

### Measurements

Elemental analysis was carried out with an 1106 elemental autoanalysis apparatus (Carlo-Erba, Milan, Italy). The concentration of the adsorbing solution was determined on a UV-1601 ultraviolet-visible (UV-vis)

spectrometer (Hitachi, Tokyo, Japan). The IR spectra were recorded on a 360 Fourier infrared spectrometer (Nicolet, Madison, WI) by diffuse-reflectance Fourier transform infrared (DR-FTIR) spectroscopy. The scanning electron micrograph was measured by a X-650 SEM (Hitachi).

### Preparation and activation of the AMS

The AMS was prepared according to a procedure in the literature.<sup>18,19</sup> A mixed solvent of 100 mL of ethanol/*n*-propanol (3:1 vol/vol) was saturated with anhydrous ammonia, which was admitted through a dry column filled with sodium hydroxide pellets at 0°C. The concentration of ammonia in the solution was about 5 mol/L by titration with hydrochloric acid (0.1 mol/L). The alcoholic ammonia solution saturated by ammonia and ammonium hydroxide (20 mL, 130 mmol) was added to a 250-mL, three-necked, round-bottom flask equipped with a magnetic stirrer. Tetra-

**TABLE I**  
Elemental Analysis of Imprinting Polysiloxanes and NPs

Polysiloxane	C (%)	H (%)	N (%)	N (mmol/g)
PRS	10.99	2.65	2.59	1.85
PBS	11.21	2.71	2.66	1.90
PWS	11.47	2.90	2.72	1.94
NPS	10.64	2.51	2.57	1.84

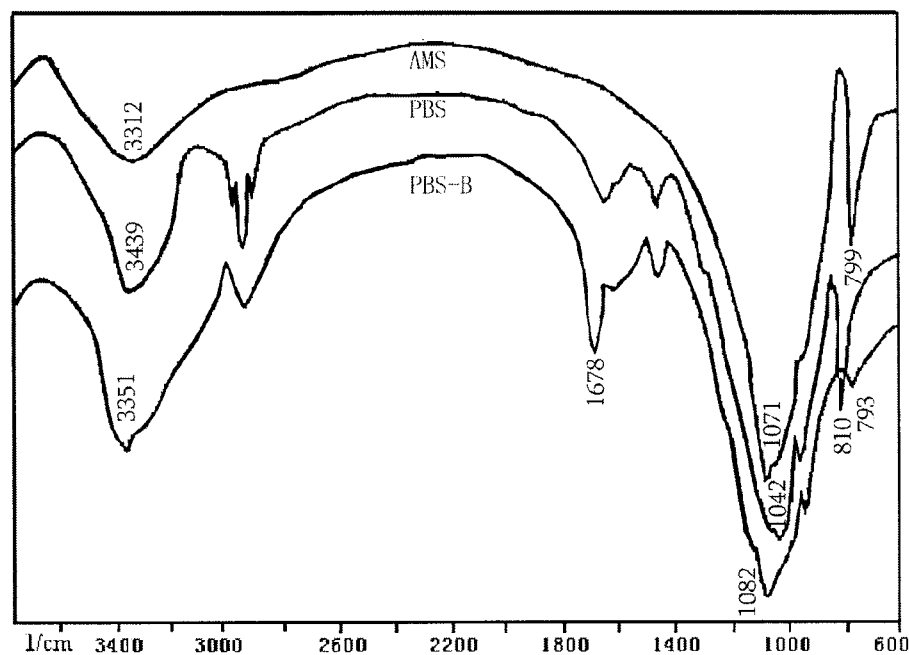


Figure 1 DR-FTIR spectra of AMS, PBS, and PBS-B.

thoxysilane (20 mL, 90 mmol) was added, and the mixture was slowly stirred at 0°C. The hydrolysis and condensation reaction of tetraethoxysilane proceeded with an accompanying increase in the opalescence of the reaction mixture. For quantitative condensation, the mixture was stirred continually at 0°C for 12 h, and the particles were kept in suspension. After filtration, washing with distilled water, and drying, 4.5 g of AMS was obtained. The yield was 83%.

The active AMS was prepared by immersion in hydrochloric acid (3 mol/L) for 24 h. They were then refluxed for 10 h to obtain the maximum number of silanol groups on the surface.<sup>20</sup> After activation, the AMS was filtrated, washed with distilled water, and dried at 120°C for 10 h.

#### Preparation of polysiloxanes imprinted with dye molecules<sup>19,21</sup>

The solution of disperse red (0.033 g, 0.1 mmol) in 20 mL of acetonitrile and the active AMS (2.0 g) were added to a 100-mL, three-necked, round-bottom flask and mixed thoroughly by stirring. Subsequently, *N*-phenylaminomethyl triethoxysilane (0.3 g, 1.15 mmol), 3-aminopropyl triethoxysilane (1.0 g, 4.65 mmol), and 4-aza-6-aminohexyl triethoxysilane (4.0 g, 15.3 mmol) were added and stirred for 2 h at room temperature under a nitrogen atmosphere to ensure that the organosilicone monomers with functional groups interacted abundantly with the template molecule. After 0.5 mL of hydrochloric acid (1.0 mol/L) was added, the mixture was heated at 90°C for 12 h to cohydrolyze and polycondense thoroughly with the

silanol groups on the surface of the AMS. After evaporation of the solvent under reduced pressure, the residue was cured at 90°C for 2 h. The polysiloxane imprinted by disperse red (PRS) was obtained by filtration, washing with sodium bicarbonate (0.01 mol/L) and distilled water, and Soxhlet extraction with acetonitrile for 10 h. It was then dried *in vacuo* at 110°C for 2 h and kept in a desiccator before use.

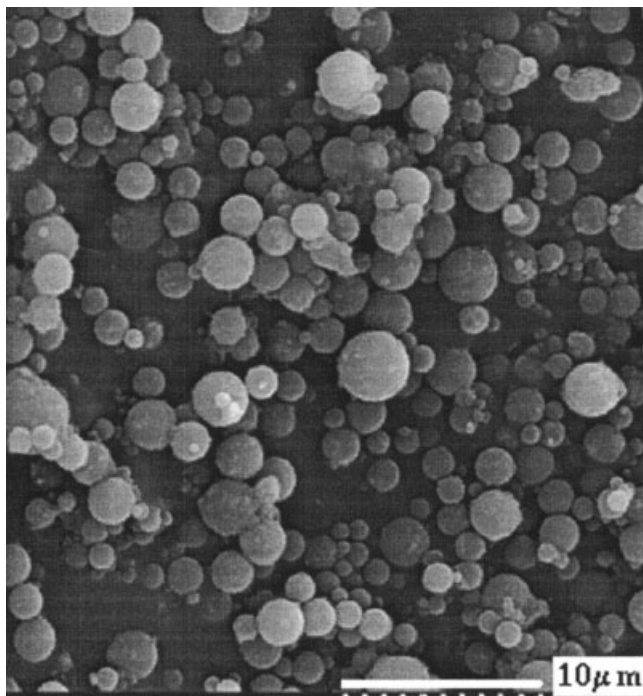
The polysiloxane imprinted by disperse blue (PBS) was prepared with the same method but with disperse blue (0.035 g, 0.1 mmol) instead of disperse red.

The polysiloxane imprinted by water-soluble dye (PWS) was prepared with the same method but with water-soluble dye (0.202 g, 0.2 mmol) and distilled water instead of disperse red and the acetonitrile solvent, respectively.

For comparison, we prepared nonimprinting polysiloxane (NPS) in the same way but with the absence of the template molecule. The disperse blue PBS inclusion compound (PBS-B) was obtained by the saturating adsorption of PBS toward the template molecule (disperse blue), washing with a little acetonitrile, and drying *in vacuo* at 110°C for 2 h.

#### Recognition behavior of imprinting polysiloxane and NPS

The adsorption behaviors of the three dye-molecular-imprinting polysiloxanes and NPS toward the template molecule and nontemplate molecule, respectively, were examined. The imprinting polysiloxane or NPS (20 mg; W) and the dye solution [2 mL (V) of acetonitrile or distilled water as the solvent] with



**Figure 2** Scanning electron micrograph of NPS.

known concentration ( $C_0$ ) were placed in a 10-mL test tube with a stopper. A series of such test tubes were shaken at a constant speed (100 times/min) at 30°C for 10 h. The concentration of the dye solution in the liquid phase after centrifugation ( $C_i$ ) was determined with a UV-vis spectrometer. The adsorption capacity ( $Q$ ) was calculated as follows:

$$Q = (C_0 - C_i)V/W \text{ (mg/g)}$$

## RESULTS AND DISCUSSION

### Preparation of molecular-imprinting polysiloxanes

The schematic representation of the preparation of the molecular-imprinting polysiloxanes and the three dye molecular structures are presented in Scheme 1. The organosilicone monomers were prearranged around the template molecule and interacted with it by non-covalent forces (e.g., hydrogen bonding); subsequently, they were subjected to cohydrolysis and polycondensation and were anchored to the surface of AMS by covalent bonding. After the removal of the substrate molecules by washing and extraction procedures, the cavities of the imprinting template molecule were left in the polysiloxane.

### Elemental analysis

The results of the elemental analysis of the imprinting polysiloxanes (PRS, PBS, and PWS) and NPS are

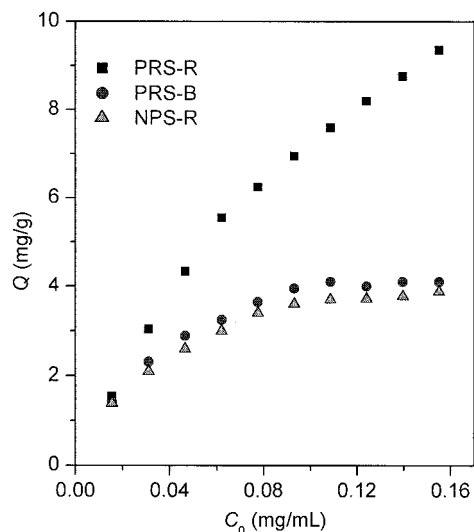
shown in Table I. The data show that the percentages of carbon, hydrogen, and nitrogen of the molecular-imprinting polysiloxanes (PRS, PBS, and PWS) were a little higher than those of NPS. This implies that the template molecule was not fully removed from the imprinting polysiloxanes. The molar concentrations of nitrogen (mmol/g) of the polysiloxanes were found according to the nitrogen content and are also listed in Table I.

### IR spectra

The typical IR spectra of AMS, PBS, and PBS-B were determined by DR-FTIR and are presented in Figure 1.

Figure 1 shows that the characteristic bands of the O—H stretching vibration and Si—O—Si asymmetric and symmetric stretching vibration of AMS presented at 3312, 1071, and 799  $\text{cm}^{-1}$ , respectively.<sup>22</sup> The bands of the O—H stretching vibration and Si—O—Si asymmetric and symmetric stretching vibration of PBS presented at 3439, 1042, and 810  $\text{cm}^{-1}$ . The bands of PBS at 2930, 1645, and 1464  $\text{cm}^{-1}$  were assigned as C—H stretching vibration and  $\text{NH}_2$  and  $\text{CH}_2$  bending vibration, respectively. This indicated that polysiloxanes with functional groups were bound on the surface of AMS. The bands of N—H and O—H stretching vibration were overlapped in the IR spectra of PRS.

Compared with the IR spectra of PBS, the bands of the N—H and O—H stretching vibration and  $\text{NH}_2$  bending vibration of PBS-B moved to a lower wave number (3350 and 1610  $\text{cm}^{-1}$ , respectively), and the strength of the band increased. This was attributed to the contribution of the stretching and bending vibrations of  $\text{NH}_2$  and O—H of the adsorbed template molecule. The new band presenting at 1678  $\text{cm}^{-1}$  was



**Figure 3** Adsorption isotherms of PRS and NPS toward the dye molecules (30°C).

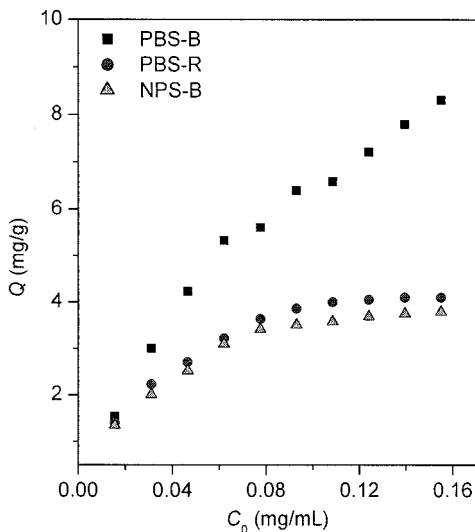


Figure 4 Adsorption isotherms of PBS and NPS toward the dye molecules (30°C).

regarded as the C=O stretching vibration of the template molecule.

Scanning electron microscopy

A scanning electron micrograph of NPS is presented in Figure 2. Figure 2 shows that the NPS-coated silica was microspherical and had a diameter of about 1–3 μm.

Adsorption isotherms

The isothermal adsorptions of PRS, PBS, and PWS toward their template molecules were deter-

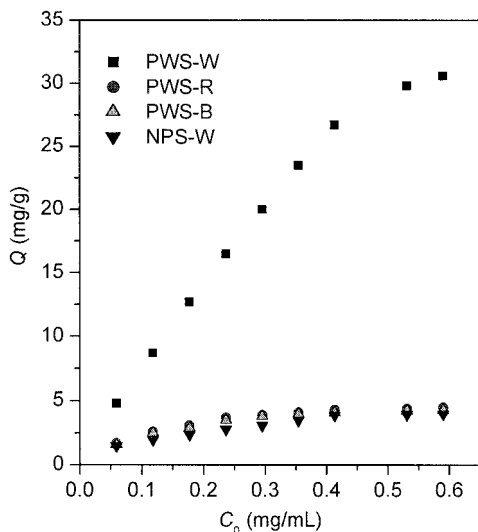


Figure 5 Adsorption isotherms of PWS and NPS toward the dye molecules (30°C).

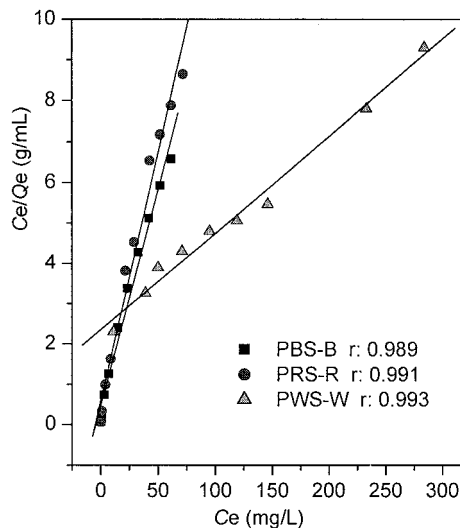


Figure 6 Linearized Langmuir isotherms (30°C).

mined.<sup>23–25</sup> For comparison, the isothermal adsorptions of NPS toward the three dye molecules were also determined. The experimental results are plotted in Figures 3–5. The results show that the adsorption capacities of the molecular-imprinting polysiloxanes toward their corresponding template molecules increased with increasing template molecule concentration. Compared to NPS, the increase in the adsorption capacity of PRS, PBS, or PWS toward its respective template molecule was obvious, especially for PWS. This indicated that the molecular-imprinting polysiloxanes prepared with different dyes as substrated exhibited memory functions for their respective substrates.

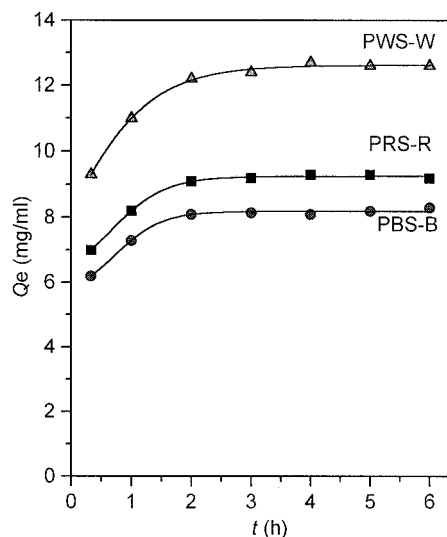


Figure 7 Curves of the adsorption dynamics of PRS, PBS, and PWS toward their corresponding template molecules ( $C_0 = 0.155$  mg/mL).

TABLE II  
 $K_D$  and  $\alpha$  Values of Different Dyes for the Imprinting Polysiloxanes and NPS

Substrate	PRS		PBS		PWS		NPS	
	$K_D$	$\alpha$	$K_D$	$\alpha$	$K_D$	$\alpha$	$K_D$	$\alpha$
Disperse red	152.2	1.00	36.0	3.14	40.9	6.21	33.4	4.55
Disperse blue	34.9	4.31	113.1	1.00	38.4	6.62	32.3	3.50
Water-soluble dye	—	—	—	—	254.0	1.00	34.8	7.30

Figures 3–5 also indicate that the adsorption isotherms of NPS toward disperse red (NPS-R), disperse blue (NPS-B), and water-soluble dye (NPS-W) or of imprinting polysiloxane toward nontemplate molecules (PRS toward disperse blue, PRS-B; PBS toward disperse red, PBS-R; PWS toward disperse red, PWS-R and disperse blue, PWS-B) were very close and tended toward saturation under the experimental conditions.

According to the linearized Langmuir isothermal equation<sup>26,27</sup>

$$C_e/Q_e = C_e/Q_s + 1/Q_s \times b$$

where  $C_e$  is the concentration of the substrate in the solution,  $Q_e$  is the adsorption capacity at the adsorption equilibrium, and  $Q_s$  is the saturated adsorption capacity. From this equation,  $C_e/Q_e$  versus  $C_e$  is plotted in Figure 6. Figure 6 indicates that the adsorption isotherms of PRS, PBS, and PWS toward their template molecules were a good fit with the Langmuir model in the experimental conditions. The saturated adsorption capacities of PRS, PBS, and PWS toward their template molecules were obtained by the linear slope ( $b$ ) and were 9.33, 8.2, and 40.1 mg/g, respectively.

The adsorption dynamics of PRS, PBS, and PWS toward their respective template molecules were determined at regular times. The experimental data are plotted in Figure 7. The curve of the adsorption dynamics shows that the three imprinting polysiloxanes had higher initial adsorption rates toward their respective template molecules. Adsorption equilibrium was reached in almost 2 h, which implied that the imprinting polysiloxane anchored on AMS surface was favorable for the transmission of the template molecule from a liquid phase to a solid phase.

### Recognition selectivity

The recognition selectivity of the imprinting polysiloxanes and NPS could be characterized by the distribution coefficient ( $K_D$ ) and separating factor ( $\alpha$ ) of static adsorption.<sup>28</sup>  $K_D$  and  $\alpha$  can be defined as follows:

$$K_D = Q_e/C_e$$

$$\alpha = K_{Dt}/K_{Ds}$$

where  $t$  and  $s$  represent the template and nontemplate molecules, respectively. When  $s = t$ ,  $\alpha = 1.0$ . The  $K_D$  and  $\alpha$  values of the imprinting polysiloxanes and NPS toward the template and nontemplate molecules at equilibrium adsorption were determined and are listed in Table II. The  $K_D$  values of all three imprinting polysiloxanes for their template molecules were higher than those for other substrates. The  $K_D$  values of the three dye molecules for NPS were similar. This implied that the cavities of characteristic recognition for the dye molecules were nonexistent in NPS. The  $K_D$  value of the template molecule for PWS was the highest among the three imprinting polysiloxanes under the experimental conditions. This was related to the good solubility of water-soluble dye in water.

### CONCLUSIONS

Molecular-imprinting-polysiloxane-coated AMS was prepared by the cohydrolysis and polycondensation of functional organosilicone monomers (*N*-phenylaminomethyl triethoxysilane, 3-aminopropyl triethoxysilane, and 4-aza-6-aminoethyl triethoxysilane) with AMS and disperse red (or disperse blue or water-soluble dye) as template molecules in nonaqueous or aqueous solvent. The molecular-imprinting polysiloxanes exhibited higher selective recognition properties toward their template molecules than NPS. The adsorption isotherms were a good fit with the Langmuir model under the experimental conditions.  $K_D$  of the water-soluble dye on PWS was the highest among the three imprinting polysiloxanes under the experimental conditions, which was related to the good solubility of the dye in water.

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