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Molecularly imprinted polyethersulfone membranes for the sieving, binding and recognition of bisphenol A

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ABSTRACT

Bisphenol A (BPA) molecularly imprinted polyethersulfone (PES) membranes were prepared by a liquid–liquid phase inversion technique. The BPA template molecules were then extracted from the solidified PES membranes by ethanol. BPA aqueous solutions with various concentrations were applied to the membranes to study the sieving performance. It was indicated that the sieving coefficient of the molecularly imprinted membranes was smaller than that of the non-imprinted ones due to the specific recognition sites. With the increase of BPA initial concentrations, the binding amounts of BPA increased. The recognition coefficients of BPA were 2.43, 2.18, and 1.91 for the BPA concentrations of 50, 100, and 150 μmol/L, respectively. Furthermore, it was observed that with the increase of operation pressure, the binding amounts for the imprinted membranes decreased dramatically, which, however, does not occur for the non-imprinted ones. The recognition coefficients of BPA under the pressures of 0.01, 0.03, and 0.06 MPa were 2.18, 1.64, and 1.39, respectively.

Keywords: Molecularly imprinted; Liquid–liquid phase inversion technique; Flat-sheet membrane; BPA; Recognition

1. Introduction

Endocrine disruptors (EDs), also known as endocrine-disrupting compounds or hormonally active agents, can affect and even alter the function of endocrine system, resulting in adverse health effects to human being [1]. Today, people are exposed to EDs in daily life, because they are found in low doses in thousands of products, especially in urban wastewater, which may affect the urban water cycle system severely [2,3]. Studies have revealed that low-level exposure of EDs might cause similar effects in animals and human beings [1]. Therefore, there is a growing interest in removal of EDs effectively from urban water cycle system during wastewater treatment [4–6]. Bisphenol A (BPA) is a well-known raw material for its wide use in the production of polycarbonate plastic and epoxy resins, along with other applications. However, it is also an endocrine disruptor which can affect the reproduction and development of animal organism even though at very low concentration [7–9].

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Membrane, a critical member of water treatment system, is usually combined with other treatment measures, e.g. adsorption, especially specific adsorption, in order to effectively remove harmful substances including EDs from water. In practice, polyethersulfone (PES) and PES-based membranes are usually used in water treatment because of the prominent oxidative, thermal, and hydrolytic stabilities with good mechanical and film-forming properties [10–12].

Molecular imprinting technique is a satisfactory means to achieve specific adsorption, and has been intensively studied due to its wide applications in many fields such as sensor design [13], adsorbents to environmental hormone [14,15], reaction catalysis [16], filtration biomolecules [17], removal of dye [18], etc. It has been developed by two essentially different approaches: covalent and non-covalent molecularly imprinting [19]. The major difference between them is that the imprint molecule is coupled to a polymerizable molecule by covalent bond, whereas the imprint molecule is mixed with functional monomers by the interaction of non-covalent bond in the non-covalent approach. The non-covalent approach has received extensive attention due to its wide range of applications. In our previous studies, specific adsorption of BPA had been achieved successfully by means of molecularly imprinted PES microspheres [20–22] and microfibers [23]. However, the study of BPA-imprinted PES membrane has rarely been reported. The originality of the present study lies in the dynamic adsorption of BPA molecules, which might be more useful in the industrial field.

In the present study, BPA-imprinted PES flat-sheet membranes were prepared by a liquid–liquid phase inversion technique, and used for the removal of BPA from aqueous solution. Moreover, the effect of BPA concentrations in aqueous solutions and operation pressure were investigated in order to find out the best operation condition.

2. Experimental

2.1. Materials

Polyethersulfone (PES, Ultrason E 6020P, CAS No. 25608-63-3) was purchased from BASF chemical company (Germany), and was used to prepare the polymeric membranes. Bisphenol A (BPA) was purchased from Shanghai Chemical Reagent Co. Ltd. (China) and used as the template. Dimethyl acetamide (DMAc) and ethanol were obtained from Chengdu Chemical Reagent Co. Ltd. (China). All the chemicals were of analytical grade and used without further purification unless otherwise described. Distilled water passed through ion-exchange columns was used throughout the study.

2.2. Preparation of the imprinted membranes

A liquid–liquid phase inversion method was carried out to prepare the molecularly imprinted PES membranes. Here, DMAc and water acted as the solvent and coagulant, respectively. The casting solution was prepared by dissolving template molecule (BPA, 5 wt.%) and PES (16 wt.%) in DMAc simultaneously at room temperature. The solution was stirred until the clear and homogeneous solution was obtained. After vacuum degassing, the solution was cast on a glass plate and coagulated in water at room temperature to prepare the membranes. The obtained membranes were incubated in water for over 2 days to remove the residual DMAc; and then extracted by ethanol for several days at 50°C until the entire template molecules were extracted. Afterwards, the membranes were rinsed with a large excess of water. By means of UV–Vis spectrophotometer U-200A (Shanghai Spectrum Instruments Co. Ltd., Shanghai, China), the extraction was confirmed with the disappearance of 276 nm BPA absorption in the extract solutions. Simultaneously, a PES solution with a concentration of 16 wt.% was used to prepare non-imprinted PES membranes as the control in the same manner. The molecularly imprinted PES membranes were named as MIM and the non-imprinted PES membranes were named as NIM.

2.3. Scanning electron micrograph (SEM)

For the SEM observation, the membrane samples were freeze-dried in a vacuum oven. Then, the membranes were quenched by liquid nitrogenous gas, cut with a single-edged razor blade, attached to the sample supports, and coated with a gold layer. A scanning electron microscope (JSM-5900LV, JEOL) was used for the morphology observation of the membrane cross-section.

2.4. Calculation of the porosity

The porosity of the membranes was calculated by Eq. (1):

$$\text{Porosity} = \frac{(W_B - W_A)/\rho_W}{W_A/\rho_P + (W_B - W_A)/\rho_W} \times 100\% \tag{1}$$

where W_B is the weight of the sample before drying; W_A is the weight of the sample after drying; $\rho_W = 1.0\,\text{g/cm}^3$ is the density of water; and $\rho_P = 1.43\,\text{g/cm}^3$ is the density of PES.

To investigate the pore size of the membranes, ultrafiltration of polyethylene glycol (PEG-4000) solution was evaluated, and a dead-end ultrafiltration cell with an effective membrane area of about 13.8 cm^2 was used. The feed solution with a concentration of 0.1 g/L was prepared by dissolving the PEG-4000 into double distilled water. The PEG solution passed through the filter for about 10 min to get steady state, and then the permeated solution was collected. The concentration of the PEG solution was determined by an UV–Vis spectrophotometer (Model 756, shanghai spectrophotometer instrument Co., Ltd., China) after Ninhydin reactions at the wavelength of 510 nm. Then the pore size was calculated as described in our earlier study [24].

2.5. Recognition experiments

As BPA could not be dissolved in water directly, the BPA solution was prepared by dissolving BPA in ethanol first. Then, the BPA ethanol solution was diluted in water to obtain BPA aqueous solutions with the concentrations of 50, 100, and 150 μmol/L, respectively.

The template recognition was carried out by a pressure-driven permeation method using an air compressor. And the same ultrafiltration apparatus described above was used.

The observed sieving coefficient (Sc) was calculated using Eq. (2):

$$\mathrm{Sc} = \frac{C_t}{C_0} \tag{2}$$

where C_0 (μmol/L) is the feed BPA concentration and C_t (μmol/L) is the BPA concentration in the permeate solution at time, t. The concentrations were measured by a UV–Vis spectrophotometer at the wavelength of 276 nm. Herein, the sieving coefficient can be termed instant sieving coefficient.

The concentration change (C_c, μmol/L) after the solution permeating the membrane, can be defined as Eq. (3):

$$C_c = (C_0 - C_t) \tag{3}$$

The binding amounts ($[S]_b$, μmol/g) of MIM and NIM were calculated by Eq. (4):

$$[S]_b = \frac{\int_0^V C_c \mathrm{d}V}{W} \tag{4}$$

where V (L) is the volume of the permeated BPA solution through the membrane and W (g) is the weight of the dried membrane used.

The recognition coefficient (α) was calculated using Eq. (5):

$$\alpha = \frac{[S]_{\text{imprinted}}}{[S]_{\text{non-imprinted}}} \tag{5}$$

where $[S]_{\text{imprinted}}$ (μmol/g) is the BPA binding amounts of MIM and $[S]_{\text{non-imprinted}}$ (μmol/g) represents that of NIM.

2.6. Selectivity of the BPA-imprinted membranes

For the selectivity of the BPA-imprinted membranes (BPA-MIM), it should selectively bind BPA molecule but no other molecules. The selectivity of the BPA-imprinted membranes was studied with 100 μmol/L aqueous solutions including BPA, phenol, or hydroquinone (HDQ) at the pressure of 0.01 MPa, since phenol and hydroquinone were BPA structurally related organic compounds. Then, the concentrations of these compounds at different time intervals were monitored by a UV–Vis spectrophotometer at 276 nm for BPA, 270 nm for phenol, and 288 nm for HDQ. Recognition coefficient (α) was used to evaluate the selectivity and can be calculated according to Eq. (5).

In addition, the influence of other hydrophobic molecules on membrane preparation process was investigated. Phenol molecularly imprinted membranes (phenol-MIM) and hydroquinone molecularly imprinted membranes (HDQ-MIM) were prepared with the same method mentioned above. And then the prepared membranes were investigated with 100 μmol/L BPA aqueous solutions at the pressure of 0.01 MPa.

3. Results and discussion

3.1. Characterization of the membranes

Liquid–liquid phase inversion technique was used to prepare the BPA-imprinted PES membranes from PES–BPA–DMAc solution. The coagulation medium was water, a common used non-solvent for the preparation of PES membranes. Here, water shows high intersolubility with DMAc but not with PES or BPA. When the solution of PES–BPA–DMAc was immersed into water, liquid–liquid phase separation occurred due to the rapid exchange of the solvent (DMAc) and the non-solvent (water). As a result of the poor intersolubility between water and BPA, the BPA template was preserved in the PES membranes. After the template was extracted by ethanol, molecularly imprinted PES membranes were prepared.

Additionally, in order to study the dynamic adsorption, a more porous structure was desired, which enables BPA to permeate though the membranes smoothly; therefore, in our present study, we choose 16 wt.% as the weight fraction of PES to secure the good structures of porous membranes, lower than that reported in our earlier studies [20,23]; thus the concentration of template molecule (BPA) was relatively higher in the dope, which is helpful for the formation of specific recognition sites on the surface of the membrane.

Cross-sections of the molecularly imprinted membranes (a, c) and the non-imprinted membranes (b, d) are illustrated in Fig. 1; and (a) and (b) were magnified at 1,000×, while (c) and (d) were magnified at 5,000 × . The thickness of the prepared membranes measured by a micrometer was $50 \pm 3\,\mu$m, and the SEM photographs showed the same results. As shown in Fig. 1, porous structure was observed both in MIM and in NIM. In addition, both MIM and NIM had skin layers and finger-like structures, which were the typical structures of the membranes prepared by the technique of liquid–liquid phase separation. The imprinted and non-imprinted membranes had no significant difference in terms of morphology.

By means of Eq. (1), the porosity of the molecularly imprinted membranes was calculated, which was 76.9%, and the porosity of the non-imprinted ones was 78.2%. There is no significant difference in porosity between the imprinted membranes and non-imprinted ones. The SEM photos revealed the porous structure of the membranes, which was consistent with the porosity results. The average pore size of the membrane surface was measured by ultrafiltration of PEG solution, and they were about 3–4 nm both for the imprinted and non-imprinted membranes. Actually, according to the SEM photos, there was almost no difference between the imprinted membrane and the non-imprinted one, since BPA is a small molecule with the molecular weight of 228.3 Da.

3.2. Sieving performance of the imprinted membranes

BPA aqueous solutions (50, 100, and 150 μmol/L) were applied to study the sieving performance of the BPA-imprinted membranes with the operation pressure of 0.01 MPa. According to Eq. (2), the sieving coefficients (Scs) of the molecularly imprinted membranes (MIM) and the non-imprinted membranes (NIM) are calculated and shown in Fig. 2.

The sieving coefficients for the imprinted and non-imprinted membranes increased with time. It was noted that the sieving coefficients for the molecularly imprinted membranes were smaller than those of the non-imprinted ones, due to the specific recognition site formed by BPA template in MIM. It also indicated

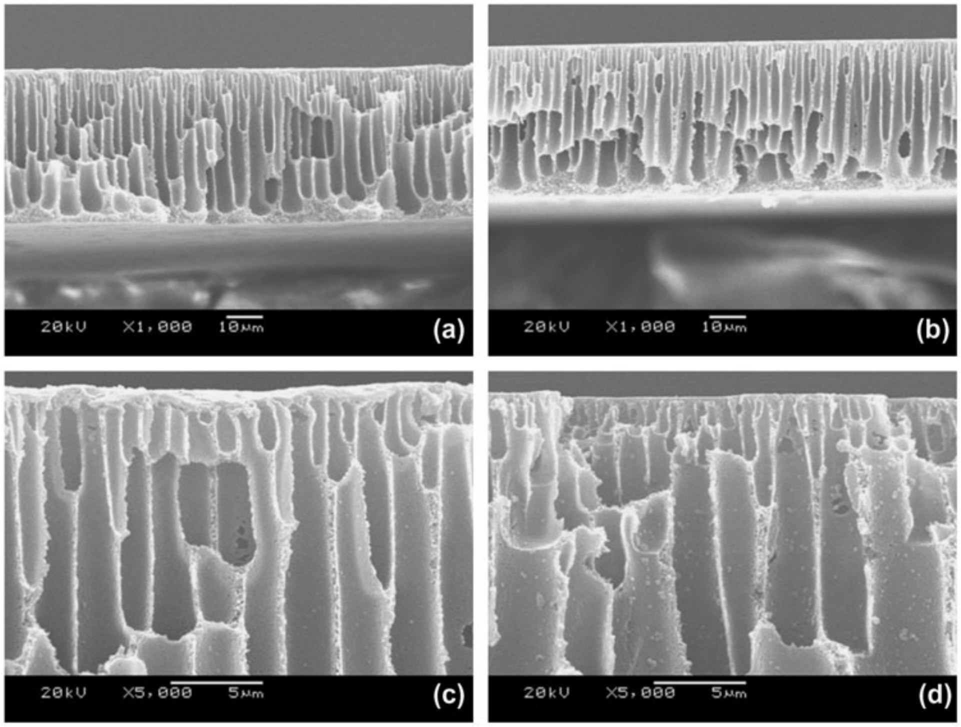

Fig. 1. SEM photographs of the cross-sections of the membranes. (a) and (c) were for the imprinted membranes; (b) and (d) were for the non-imprinted membranes. Voltage: 20 kV; magnification: (a), (b)×1,000, and (c), (d)×5,000.

that the concentration of BPA aqueous solution had no significant effect on the sieving coefficient. The concentration of the permeate solution was finally equal to that of the feed solution and the Sc climbed up to 1.0, which suggested that adsorption equilibrium was reached.

3.3. Binding and recognition of BPA in various concentrations of BPA solutions

The recognition ability of BPA-imprinted membranes was investigated in various BPA concentrations (50, 100, and 150 μmol/L) at room temperature. The concentration changes (Cc) of the imprinted and non-imprinted PES membranes were calculated by Eq. (3) and shown in Fig. 3.

Fig. 3 shows that the concentration change (μmol/L) decreased with the filtrate volume, and the minimum concentration change arrived at zero when the equilibrium of adsorption was reached. It was demonstrated that the concentration change for MIM was higher than those for NIM, which confirmed that the imprinted membranes had a larger binding ability of BPA.

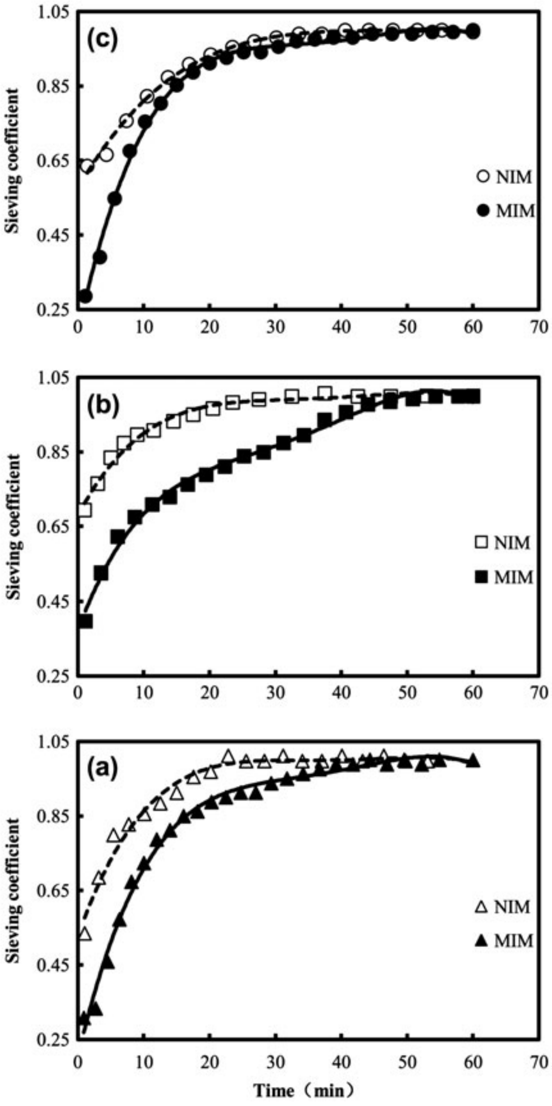

Fig. 2. Time course of sieving coefficients. Solid lines were for the imprinted membranes and dashed lines were for the non-imprinted membranes. The concentrations of BPA aqueous solutions were 50 (▲; △), 100 (■; □), and 150 (●; ○) μmol/L, respectively. The operation pressure was 0.01 Mpa.

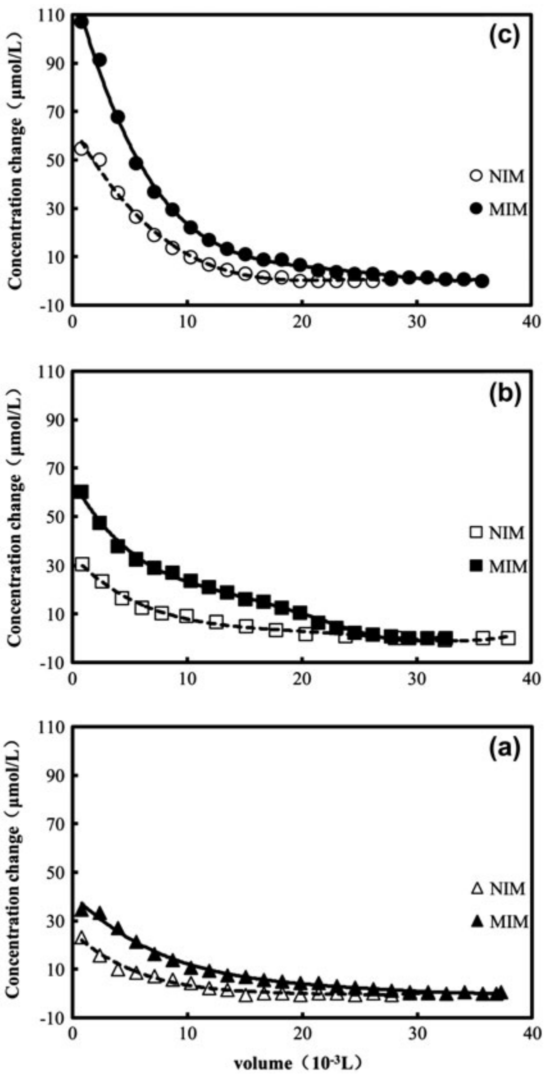

Fig. 3. Concentration change vs. filtrate volume. Solid lines and dashed lines were for the imprinted and non-imprinted membranes, respectively. The feed concentrations of BPA aqueous solutions were: 50 (▲; △), 100 (■; □), and 150 (●; ○) μmol/L. The operation pressure was 0.01 Mpa.

The binding amounts were calculated by Eq. (4), which showed the integral relationship of the binding amounts and the concentration change. Fig. 4 shows the binding amounts of BPA for the imprinted and non-imprinted membranes in various concentrations of BPA aqueous solutions.

As shown in the figure, the binding amounts (μmol/g) increased with time and the saturated binding was observed within 30–50 min. The binding amounts of BPA for the imprinted membranes reached a higher level than those for the non-imprinted ones. The saturated binding amounts of BPA were 17.5, 30.8, and 40.8 μmol/g for the imprinted PES membranes in 50, 100, and 150 μmol/L BPA aqueous solution, respectively, while those were 7.2, 14.1, and 21.4 μmol/g for the non-imprinted ones. It was obvious that with the increase of BPA concentrations, the binding amounts increased for both the imprinted and the non-imprinted membranes, although the absolute value of the former is larger. This phenomenon could be explained by the adsorption theory [25]. The adsorption of BPA in the non-imprinted membranes was attributed to the non-specific adsorption resulted from the large porosity of the membranes and the hydrophobic interaction between BPA and PES [26]. As for MIM, in contrast, besides the porosity and the hydrophobic interaction, there exist hydrogen bonds between the –OH in the BPA molecules and the $S(=O)_2$ in the PES molecules [20], by which specific recognition sites were form when BPA molecules were removed. According to the result, the specific sites have a positive influence to the adsorption of BPA in the imprinted membranes.

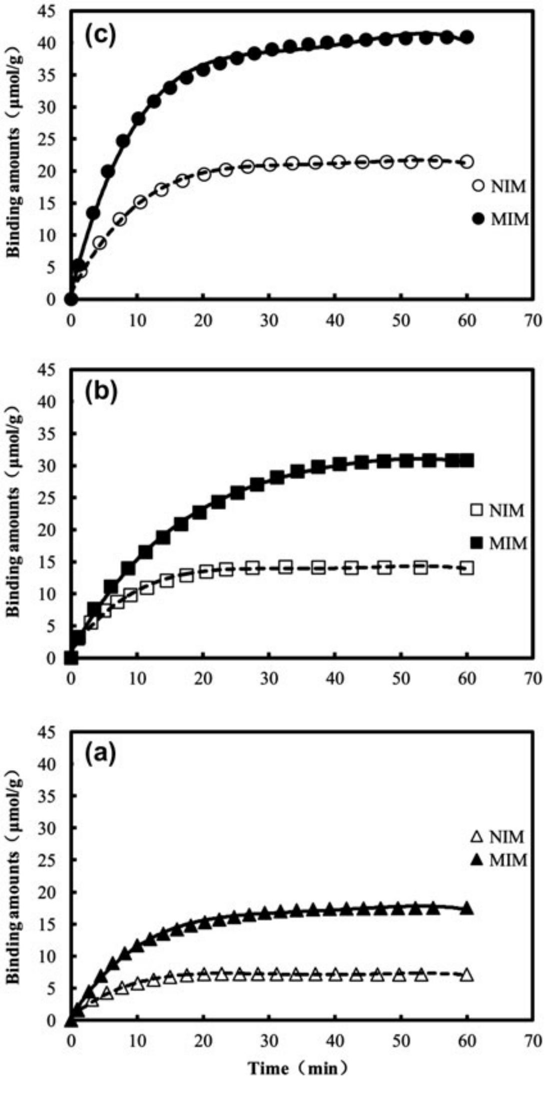

Fig. 4. Time course of binding amounts. Solid lines were for the imprinted membranes and dashed lines were for the non-imprinted membranes. The concentrations of BPA aqueous solutions were 50 (▲; △), 100 (■; □), and 150 (●; ○) μmol/L, respectively. The operation pressure was 0.01 Mpa.

According to Eq. (5), the recognition coefficients were calculated, which were 2.43, 2.18, and 1.91 for the BPA concentrations of 50, 100, and 150 μmol/L, respectively. Compared with our earlier work, the recognition coefficients are available to apply the MIM in the removal of endocrine disruptor BPA [16,19]. It suggested that with the increase of BPA concentration, the recognition coefficient decreased; a larger recognition coefficient represented a higher selective adsorption ability of BPA.

3.4. Effect of operation pressure on the binding and recognition of BPA

In order to study the effect of operation pressure on the binding and recognition ability of BPA, the membranes were applied under different pressures of 0.01, 0.03, and 0.06 Mpa, respectively. The concentration of BPA aqueous solution was set at 100 μmol/L and the results are shown in Fig. 5.

The saturated binding amounts of BPA were 30.8, 22.2, and 17.7 μmol/g for the imprinted PES membranes under the operation pressure of 0.01, 0.03, and 0.06 Mpa, respectively, while those were 14.1, 13.5, and 12.7 μmol/g for the non-imprinted counterparts. The results suggested that with the increase of operation pressure, the binding amounts for the imprinted membranes decreased obviously, which also occurred to the non-imprinted ones, but not as significant as the former. Furthermore, the recognition coefficients of BPA under the pressures of 0.01, 0.03, and 0.06 Mpa were 2.18, 1.64, and 1.39, respectively. Obviously, the

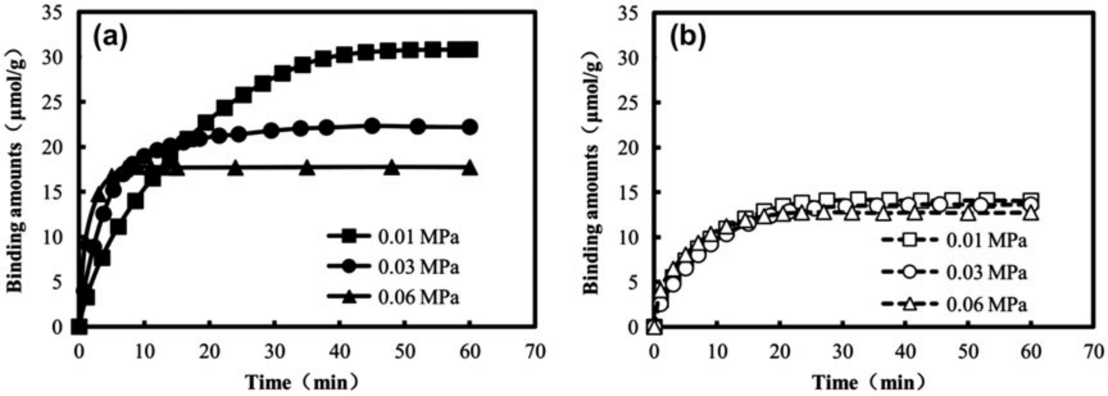

Fig. 5. Time course of binding amounts with the operation pressures of 0.01 (■; □), 0.03 (●; ○), and 0.06 (▲; △) Mpa, respectively. Solid lines were for the imprinted membranes and dashed lines were for the non-imprinted membranes. The concentration of BPA aqueous solution was 100 μmol/L.

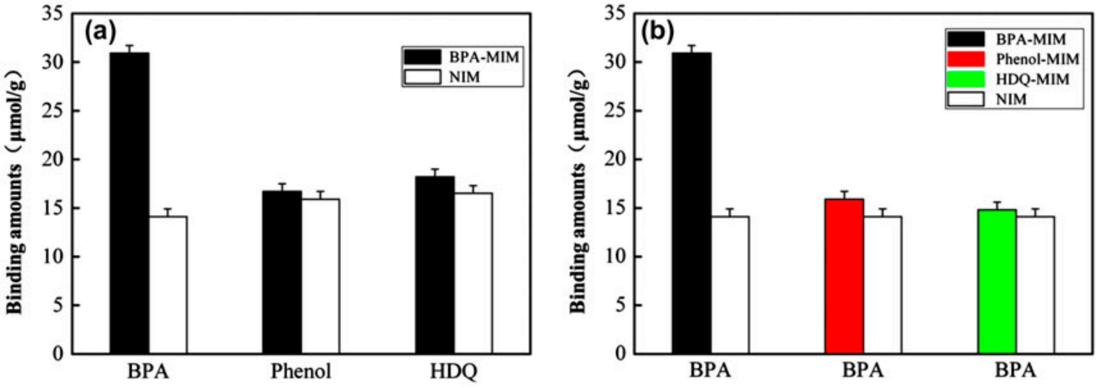

Fig. 6. (a) Binding amounts of BPA, phenol and HDQ for the BPA-imprinted (■) and non-imprinted (□) membranes; (b) Binding amounts of BPA for the different template imprinted membranes. The operation pressure was 0.01 MPa.

increase of operation pressure had a negative effect on the recognition coefficient. This may be attributed to the higher filtration rate at higher pressure.

In contrast to NIM, the BPA-imprinted PES membrane had a higher affinity to BPA due to the specific adsorption sites. Thus, during the process of water treatment, the BPA-imprinted PES membrane can not only act as the selective barrier to block macromolecular rententate that could not pass the pores, but also specifically adsorbs BPA, a small molecule ED. It can be expected that the design of molecularly imprinted polymeric membrane may play a role in removal of Eds during water treatment, especially wastewater treatment in urban area.

3.5. Selectivity of the BPA-imprinted membranes

To examine the selectivity, BPA-imprinted and non-imprinted membranes were applied in BPA, phenol, or HDQ aqueous solutions with the concentration of 100 μmol/g, respectively. Fig. 6(a) shows the binding amounts for BPA, phenol and HDQ to the BPA-imprinted membranes and non-imprinted ones, respectively. The binding amounts of BPA, phenol and HDQ were about 30.9, 16.7, and 18.2 μmol/g for the imprinted membranes, respectively; whereas those were about 14.1, 15.9, and 16.5 for the non-imprinted membranes, respectively. The recognition coefficients (α) of BPA, phenol and HDQ were 2.19, 1.05, and 1.09, respectively. The recognition coefficient of BPA-MIM for BPA was much higher than those for the others. Additionally, as shown in Fig. 6(b), the binding amounts of BPA for BPA-MIM, phenol-MIM, HDQ-MIM and NIM were 30.9, 15.9, 14.8, and 14.1 μmol/g, respectively. The binding amount for BPA–MIM was much higher than those of for other membranes. So the hydrophobic interactions between the template and PES membrane did little contribution to the selective effect of BPA. It can be deduced that specific recognition sites for BPA molecules were formed in the BPA-imprinted membranes, so that they showed selectivity for the BPA molecules.

4. Conclusions

Molecularly imprinted PES membranes can be easily prepared by a liquid-liquid phase inversion technique using a PES–DMAc solution containing BPA template. Besides the separation function of the membrane itself, the imprinted PES membrane also exhibited specific adsorption to BPA. The sieving coefficients were lower for the imprinted membranes than those for the non-imprinted ones due to the specific adsorption. The concentration of BPA aqueous solution did not affect the sieving coefficients evidently. With the increase of BPA concentrations, the binding amounts increased while the recognition coefficient decreased. It also indicated that with the increase of the operation pressure, the binding amounts of MIM decreased obviously, while the decrease of NIM was not significant; the increase of the operation pressure had a negative effect on the recognition coefficient. The design of BPA-imprinted PES membrane may play a role for the removal of EDs with high efficiency in the process of water treatment.

Symbols

W_B — the weight of the sample before drying (g)
W_A — the weight of the sample after drying (g)
ρ_W — the density of water (g/cm^3)
ρ_P — the density of PES (g/cm^3)
C_0 — the original BPA concentration (μmol/L)
C_t — the BPA concentration in the permeate solution at time, t (μmol/L)
Sc — the sieving coefficient (no unit)
Cc — the concentration change (μmol/L)
$[S]_b$ — the binding amounts of MIM and NIM (μmol/g)
V — the volume of the permeated BPA solution through the membrane (L)
W — the weight of the dried membrane used (g)
α — the recognition coefficient (no unit)
$[S]_{\text{imprinted}}$ — the BPA binding amounts of MIM (μmol/g)
$[S]_{\text{non-imprinted}}$ — the BPA binding amounts of NIM (μmol/g)

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