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Molecularly imprinted polymers of allyl-β-cyclodextrin and methacrylic acid for the solid-phase extraction of phthalate

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ABSTRACT

β-Cyclodextrin was derived by allylic bromine (allyl-β-CD). A new kind of molecularly imprinted polymers (MIPs) with selective adsorption for phthalate were prepared using allyl-β-CD and methacrylic acid (MAA) as the binary functional monomers. The allyl-β-CD-MIPs were characterized by scanning electron micrograph (SEM) and Fourier transform-infrared spectroscopy (FT-IR). In this work, dipentyl phthalate (DPP) was selected as template; the interaction of DPP with MAA, acrylamide (AM) and methyl methacrylate (MMA) were compared by UV spectroscopic techniques. Facts of adsorption solvent, adsorption kinetics and adsorption selectivity were studied in the static adsorption methods. The scatchard plot suggested that the template-polymer system has two site of adsorption behavior with adsorption capacities of 1.170 mg/g and 6.244 mg/g, respectively. The (allyl-β-CD)-MIPs were used as selective sorbents for the solid-phase extraction (SPE) in the dynamic methods. The results indicated that (allyl-β-CD)-MIPs have specific recognition selectivity and excellent adsorption affinity for DPP. Finally, the (allyl-β-CD)-MIPs were used for molecularly imprinted solid-phase extraction (MISPE) to analyze the phthalates in cow milk.

1. Introduction

Molecularly imprinted polymers (MIPs) were designed and constructed using biomimetic receptor system by molecularly imprinting technology (MIT). MIT has attracted increasing attentions due to its outstanding advantages, involving predetermined recognition ability (Haupt & Mosbach, 1998), and relative ease and low cost of preparation (Gao, Li, & Zhang, 2010). Recently, MIPs are widely used in chromatography (Fairhurst, Chassaing, Venn, & Mayes, 2004), adsorbents (Sellergren, 1994; Koohpaei, Shahtaheri, Ganjali, Forushani, & Golbabaei, 2008), membranes (Ulbricht, 2004) and sensors (Patel, Sharma, & Prasad, 2009). Molecularly imprinted solid-phase extraction (MISPE) combined the advantages of both molecular recognition and traditional separation method. Now MISPE has become the most favorite research field of MIPs due to its merits like simple processes and low cost of preparation methods (Min, Da, Feng, & Li, 2005).

Cyclodextrin (CD) was frequently used in the enantiomer separation and drug delivery systems for their unique property to form inclusion compounds with other small molecules (Tsai & Syu, 2005). Recently, beta-Cyclodextrin (β-CD) and its derivatives were selected as specific functional monomers in the synthesis of MIPs. In earlier reports, MIPs based on β-CD (β-CD-MIPs) were synthesized using β-CD or its derivatives as single function monomer (Tsai & Syu, 2005; Ning, Byun, & Bittman, 2001). Now, β-CD-MIPs are usually prepared with β-CD (or its derivatives) combined with other functional monomers as binary functional monomers. Some β-CD-MIPs prepared with binary functional monomers have also been reported. Of with β-CD were derived from methacryloyl chloride or 4,4′-(1,4-phenylenediisopropylidene)bisphenol (Xu, Kuang, Lan, & Deng, 2007; Xu, Li, Kuang, Zhang, & Wang, 2008; Xu, Li, Kuang, Zhang, & Wang, 2010). The β-CD-MIPs showed greater adsorption properties with the addition of β-CD.

Phthalates are a series of compounds used in most of the plastics as plasticizers. It is reported that phthalates have adverse effects on human health. The phthalates are regarded as endocrine disrupting compounds by means of their carcinogenic action (Naarala & Korpi, 2009; Blandeau, 1999). There are only a few reports about the phthalate MIPs, for the phthalates are a series of compounds with similar physical and chemical properties. In this paper, β-CD was derived by allylic bromine (allyl-β-CD). The (allyl-β-CD)-MIPs were prepared using dipentyl phthalate (DPP) as the template and allyl-β-CD and methacrylic acid (MAA) as binary functional monomers. The testing results demonstrated that the (allyl-β-CD)-MIPs have

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greater adsorption capacity and better selective adsorption than the MIPs synthesized by conventional methods (He, Lv, Zhu, & Lu, 2010).

2. Experimental

2.1. Chemicals

N,N-Dimethylformamide (DMF), allylic bromine, 2,2-azoisobutyronitrile (AIBN), methylacrylic acid (MAA), acrylamide (AM), β-CD, methyl methacrylate (MMA), dimethyl phthalic(DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), dipentyl phthalate (DPP), bis(2-ethylhxyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), dimethyl terephthalate (DMT) and diallyl m-phthalate (DAIP) were purchased from Sinopharm Chemical Reagent Company (China). β-CD was recrystallized from water and dried under vacuum at 120 °C with phosphorus pentoxide for 24 h. AIBN was recrystallized from ethanol and dried under vacuum. MAA was redistilled and DMF was dried over molecular sieves before being used. NaH, Ethylene dimethacrylate (EDMA) were obtained from Sigma–Aldrich (USA), EDMA was removed of the polymerization inhibitor before being used. C_{18} SPE was purchased from Agela Technologies. All the reagents used in these experiments were of analytical grade.

2.2. Instruments and operation parameters

The UV–vis spectrophotometer (UV-2450) was from Shimadzu (Japan). Scanning electron microscopy (SEM) images studied on a SEM model-Hitachi S-3400N (Japan). Fourier transforms infrared (FT-IR) spectra studies were performed on the FT-IR 650 FT-IR spectrophotometer (Tianjin Gangdong Sci & Tech. Development. Co., Ltd., China). Agilent 6890N/5973N gas chromatography mass spectrometry detector (USA) with DB-5ms capillary column (60 m × 0.32 mm, 1.00 μm, J&W) was used for chromatographic studies.

The GC oven was set at an initial temperature of 120 °C for 0.5 min. The temperature program-control was set to raise the oven temperature from 120 °C to 250 °C at 40 °C/min and held for 3 min; from250 °C to 280 °C at 10 °C/min and held for 1 min; from 280 °C to 300 °C at 5 °C/min and held for 16 min. The injector temperature was 250 °C and the helium flow was maintained at a flow rate of 1 mL/min. The sample was injected at the splitless mode and the delay time was 6.0 min. The volume of injected sample was 1 μL and the injection was set to the direct injection mode. The MSD was operated with electron impact ionization at selected ion monitoring (SIM) mode. The ions selected for each analysis were the following target ions-*m/z* DMP: 163, 77; DEP: 149, 177; DBP: 149, 223; DPP: 149, 237; DEHP: 149,167; DNOP: 149, 279. The dwell time was 30 ms for each ion. The source temperatures for GC–MS interface and MS system were 250 °C.

2.3. Spectrophotometric analysis

The solutions were prepared in acetonitrile, in which the molar ratio of DPP to the functional monomers (MAA, AM and MMA) was 1:4. A series of solutions in acetonitrile were prepared with a molar ratio of DPP to MAA varying at 1:0. 1:1, 1:2, 1:4; 1:10, 1:15, 1:20, 1:30, respectively.

2.4. Synthesis of (allyl-β-CD)-MIPs

An amount of 2.29 g of β-CD was dissolved in 30 mL of dry DMF, and then slowly added with 0.25 g of NaH. The suspension was stirred at room temperature under the protection of N_2 until no more gas evolved. The excess NaH was removed by filtering, and the filtrate was added with 0.5 mL of allylic bromide and stirred at room temperature under the protection of N_2. After 24 h, 2 mmol of DPP, 12 mmol of MAA and 60 mmol of EDMA were added, stirred for 1 h, followed by an addition of 40 mg of AIBN. The mixture was stirred under 60 °C for 24 h under the protection of N_2.

The obtained polymers were ground and the particles sieved between 200 and 400 meshes sieves were selected. The selected particles were Soxhlet extracted with a mixture of methanol–acetic acid (4:1, v/v) until no DPP was detected. The obtained particles were washed with methanol to remove the residual acetic acid, dried under vacuum and stored in a desiccator. The non-imprinted polymers ((allyl-β-CD)-NIPs) were prepared by the same procedure except for the addition of DPP.

2.5. Adsorption experiments

2.5.1. Adsorption isotherm

About 30 mg of (allyl-β-CD)-MIPs or (allyl-β-CD)-NIPs were suspended in 5 mL of DPP solution with initial concentrations ranging from 2 μg/mL to 100 μg/mL. The suspensions were sealed and kept thermostatic at 20 °C. After 24 h, the mixture was filtrated using a 0.22 μm filter. The concentration of the filtrate was determined by UV spectrophotometer. The amount of substrate bound to the polymer (Q, mg/g) was calculated using the formula:

$$Q = \frac{V(c_o - c_b)}{m}$$

where V represents the volume of solution (mL), C_o represents the initial concentration (μg/mL), C_b represents the solution concentration after adsorption (μg/mL), and m represents the quantity of (allyl-β-CD)-MIPs or (allyl-β-CD) NIPs (g).

The scatchard plots of (allyl-β-CD)-MIPs to varied DPP concentrations were constructed as per the equation:

$$\frac{Q}{c_b} = \frac{Q_{\max} - Q}{K_d}$$

where K_d is the dissociation constant (μg/mL) and $Q_{\max}$ is the apparent maximum adsorption amount (mg/g).

2.5.2. Adsorption kinetic

About 30 mg of the (allyl-β-CD)-MIPs were suspended in 5 mL of 32 μg/mL DPP hexane solution and were incubated at 20 °C. The mixture solution was filtrated through a 0.22 μm filter at a defined time and the filtrate was measured by spectrophotometer.

2.5.3. Adsorption selectivity

About 30 mg of (allyl-β-CD)-MIPs or (allyl-β-CD)-NIPs were suspended in 5 mL hexane solution of DMP, DEP, DBP, DPP, DNOP and DAIP with an initial concentration of 20 μg/mL. After an incubated at 20 °C for 24 h, the mixture solution was filtrated through a 0.22 μm filter and the filtrate was measured using the spectrophotometer.

2.6. Dynamic adsorption experiment of MISPE

The MISPE columns were prepared by packing 200 mg of (allyl-β-CD)-MIPs into 2 mL empty glass syringes. There are frits both at the top and bottom of the syringes to protect the sorbents. The analog compounds of DPP and DMT were selected for the SPE experiment. The initial concentration for each of the compound was 20 μg/mL. The solution were flown through the SPE at a rate of 0.25 mL/min, the filtrate was detected for every 1 mL volume. The dynamic adsorption experiment of (allyl-β-CD)-NIPs were operated in the same way by packing 200 mg of (allyl-β-CD)-NIPs into 2 mL empty glass syringes.

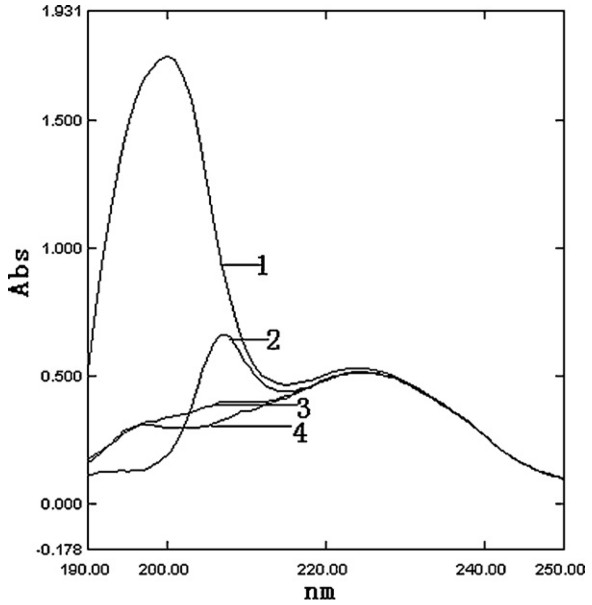

Fig. 1. UV absorption spectrum of DPP to different functional monomer. Curves 1–4 stand for DMP, DMP to MMA, DMP to AM, DMP to MAA, respectively. The molar ratio of DMP to functional monomer is 1:4.

2.7. Analysis of real samples

The cow milk was purchased from the supermarket. The cow milk samples were pretreated before MISPE analysis as followed (Yin, Xu, Wu, Wang, & Gu, 2010): 5 mL of cow milk was transferred into a glass colorimetric tube and added with 10 mL hexane, the mixture solution was mixed by whirlpool concussion and then extracted by ultrasonic action for 15 min. The suspension was centrifuged at 4000 r/min for 5 min. Some saturated NaCl solution was added in to the supernatant fluid, and then centrifuged for 2 min. The supernatant was taken out and made with hexane up to a volume of 10 mL. The cow milk extracted solution was then stored at 4 °C.

The MISPE columns were activated with 5 mL of hexane. The extracted solution was allowed to pass through MISPE column at a flow rate of 1 mL/min, and the column was washed with 0.5 mL of hexane. About 3 mL of a mixture of hexane–acetic acid (85:15, v/v) was flown through the column to elute the phthalates. The collected solution was dried by using N_2 and was made to a volume of 1 mL using hexane for further usage for GC–MS analysis.

3. Results and discussion

3.1. Selected functional monomers by UV spectrophotometer

In this work, MIPs were prepared by non-covalent molecularly imprinted technology. The reactions between the templates and the functional monomers are important factors in the subsequent affinity and selectivity properties of the imprinted polymers (Karim et al., 2005). There reported are three different functional monomers (MMA, AM, MAA) as per evaluation.

As shown in Fig. 1, the absorption peak of DPP in 200 nm was significantly red-shifted and even disappeared when the functional monomers were used. The absorption wavelength changed as follows: MAA > MMA > AM. Therefore, MAA was chosen as the functional monomer for the following experiments.

In order to study the interaction between DPP and MAA at different ratios, the concentration of DPP was kept at 0.06 mmol/L while the concentration of MAA varied. As shown in Fig. 2, the absorption value in 200 nm becomes increasingly weaker with an increasing of the MAA concentration, denoting the interactions of template-monomer structure.

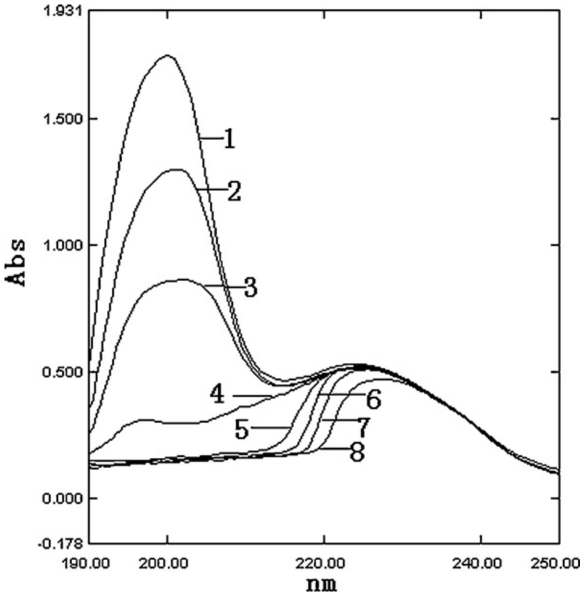

Fig. 2. UV absorption spectrum of DPP to different molar ratio of MAA. Curves 1–8 stand for DMP to MAA from 1:0, 1:1, 1:2, 1:4, 1:10, 1:15, 1:20, 1:30, in molar ratio, respectively.

3.2. Characteristics of (allyl-β-CD)-MIPs

The β-CD and (ally-β-CD)-MIPs were characterized by FT-IR spectroscopy. In the FT-IR absorption curs of β-CD, the typical feature of β-CD was the peak around 2930.31 cm^{-1}, and all the absorption peaks fits the standard FT-IR absorption curs of β-CD. This result confirms that the materials that be used in these experiments were β-CD. In the FT-IR absorption curs of (allyl-β-CD)-MIPs, the carbonyl groups from MAA and EDMA were confirmed by the absorption peak at 1736.10 cm^{-1}, and the methyl group from MAA and EDMA and the methylene group from β-CD were confirmed by the absorption peak at 2990.09 cm^{-1}, 2961.16 cm^{-1}, 1457.92 cm^{-1} and 1395.25 cm^{-1}. There are carbon-carbon double bond existing on the allyl-β-CD molecules, MAA molecules and EDMA molecules. But there are no absorption peak of carbon–carbon double bond were found in the FT-IR absorption curs of (allyl-β-CD)-MIPs. These results showed that the carbon-carbon double bond from allyl-β-CD, MAA and EDMA were reacted with each other, but the carbonyl groups, methyl group and methylene group were preserved in the (allyl-β-CD)-MIPs.

The surface morphologies of (allyl-β-CD)-NIPs and (allyl-β-CD)-MIPs were characterized by SEM. As shown in Fig. 3A and B, the surface of (allyl-β-CD)-MIPs were rough and multiporous while the surface of (allyl-β-CD)-NIPs were smooth and homogeneous. For (allyl-β-CD)-MIPs, the irregular rough morphology is probably due to specific adsorption sites which has been created from the templates. And space holes were formed when the templates were washed out from (allyl-β-CD)-MIPs.

3.3. Adsorption properties of molecularly imprinted polymers

3.3.1. Influence of solvent on adsorption

Different solvents (hexane, methanol, acetonitrile) were evaluated in the adsorption testing of (allyl-β-CD)-MIPs. The results showed that the (allyl-β-CD)-MIPs have the best adsorption capacity in the solvent of hexane, and the adsorption capacity increased with the growth of DPP from initial concentration. This is probably

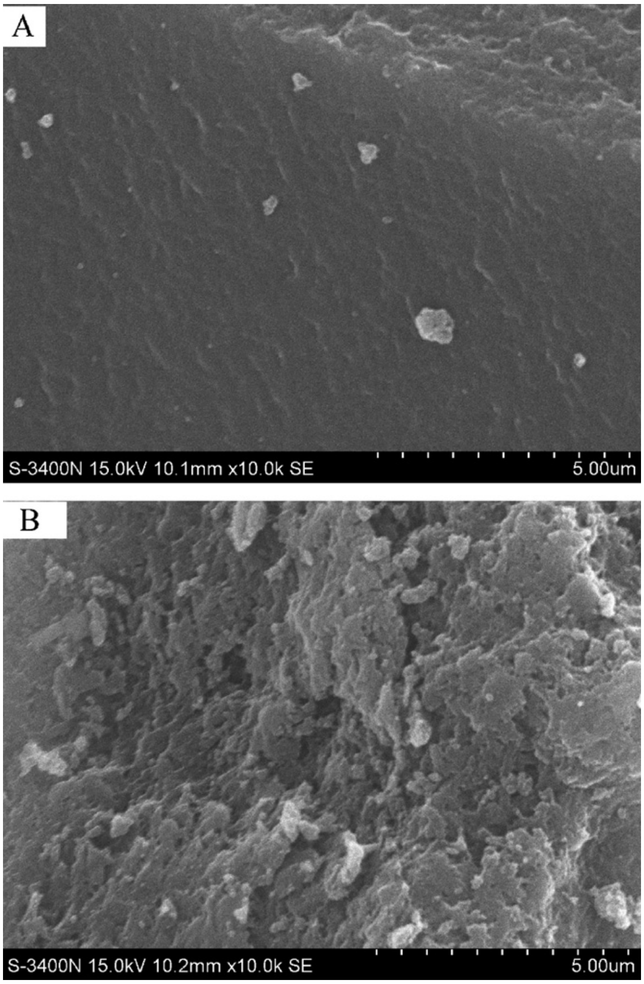

Fig. 3. SEM micrographs of (allyl-β-CD)-NIPs (A) and (allyl-β-CD)-MIPs (B).

because of the low polarity of hexane having no influence over the hydrogen bonding between polymers and DPP. Thus hexane was chosen as the solvent for the following adsorption experiments.

3.3.2. *Adsorption kinetics*

The adsorption kinetics profile was carried out in the DPP solution with an initial concentration of 32 μg/mL. As shown in Fig. 4, there are two steps of the adsorption progress. In the first 1 h, the adsorption rate is greater than that in the followed 2–6 h. After about 6 h, the (allyl-β-CD)-MIPs achieved the maximal adsorption capacity. This result indicates that there are a large number of imprinted cavities existing on the (allyl-β-CD)-MIPs, which can adsorb to the template easily in the initial phase. But also some non-imprinted functional monomers (β-CD and MAA) existing on the (allyl-β-CD)-MIPs, which can also adsorb the templates late on.

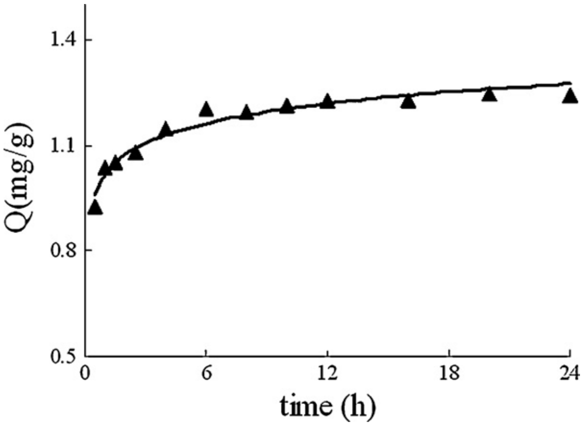

Fig. 4. Adsorption kinetic of BPP-(allyl-β-CD)-MIPs.

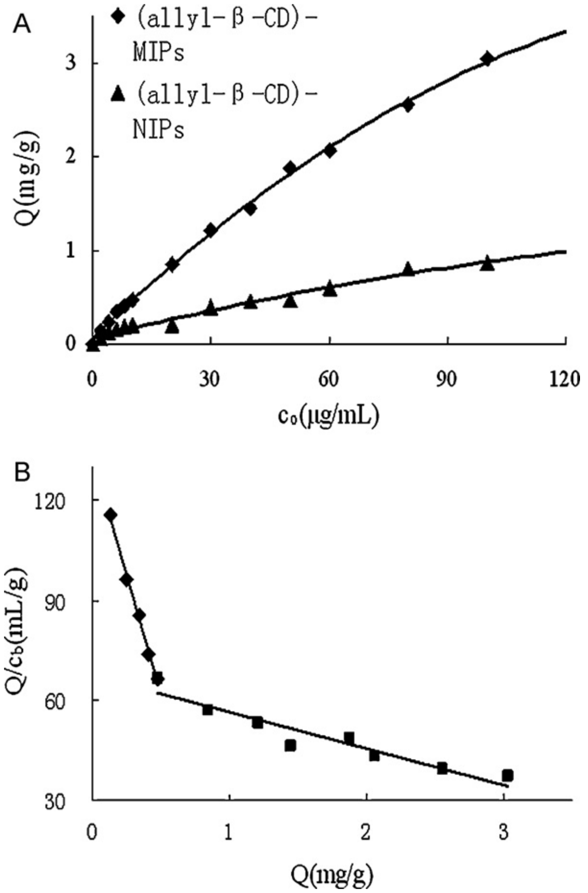

Fig. 5. Adsorption isotherm of (allyl-β-CD)-MIPs and (allyl-β-CD)-NIPs (A) and scatchard plot of (allyl-β-CD)-MIPs to DPP (B).

3.3.3. *Adsorption isotherm and scatchard plot*

In order to research out the adsorption performance of (allyl-β-CD)-MIPs and (allyl-β-CD)-NIPs, the adsorption isotherm experiments were employed in the DPP solutions with initial concentrations ranging from 2 μg/mL to 120 μg/mL (Fig. 5A). Obviously, the adsorption capacity of (allyl-β-CD)-MIPs is greater than that of (allyl-β-CD)-NIPs. The adsorption capacity of (allyl-β-CD)-MIPs was increasing with a rising of initial concentrations while the adsorption capacity of (allyl-β-CD)-NIPs got saturated so soon.

The scatchard plot of (allyl-β-CD)-MIPs to DPP were analyzed in Fig. 5B. There are two linear parts with different slopes in the figure, which means the adsorption sites could be classified into two groups with specific adsorption properties (Xu et al., 2010). These results corresponded with the prediction that was declared in Section 3.3.2. The linear regression equations for the two linear regions are $Q/c_b = -114.7Q + 134.2$ ($r = 0.9931$) and $Q/c_b = -10.78Q + 67.23$ ($r = 0.9096$), respectively. The K_d and $Q_{\max}$ of the lower affinity adsorption sites were 8.718 μg/mL and 1.170 mg/g respectively, and of the higher affinity adsorption site were 92.76 μg/mL and 6.244 mg/g, respectively. These results were greater than that of the conventional imprinted polymers reported earlier (He et al., 2010).

Table 1
Recovery of phthalates in spiked cow milk analyzed by MISPE and C_{18} SPE (spiked level: 1 μg/mL).

Analytes	Linearity of standard solution (10^4)	R^2	Recovery	
			MIP-SPE (%)	C_{18}-SPE (%)
DMP	$y = 12.762x - 0.7637$	0.9996	62.74	35.47
DEP	$y = 12.257x - 1.0836$	0.9993	82.86	26.40
DBP	$y = 15.949x - 1.7918$	0.9990	93.25	63.32
DPP	$y = 15.376x - 1.2828$	0.9994	93.73	56.89
DEHP	$y = 10.923x + 0.4260$	0.9996	67.36	57.94
DNOP	$y = 13.549x - 0.8553$	0.9997	86.54	48.71

3.4. Adsorption selectivity

Structural analogs (DAP, DEP, DBP, DPP, DNOP, DAIP) were adopted to testing the adsorption selectivity of (allyl-β-CD)-MIPs (Fig. 6). The adsorption amount of DAP, DEP, DBP, DPP and DNOP in (allyl-β-CD)-MIPs were obviously greater than that of (allyl-β-CD)-NIPs. The adsorption amount of DAIP in (allyl-β-CD)-MIPs was very close to that in (allyl-β-CD)-NIPs. This is probably due to the fact that DAP, DEP, DBP, DPP and DNOP have the similar space structure, but the space structure of DAIP is much different from that of others. These results thus indicated that the (allyl-β-CD)-MIPs possessed excellent selective adsorption ability.

3.5. Dynamic adsorption

The dynamic adsorption curves of (allyl-β-CD)-MIPs and (allyl-β-CD)-NIPs are given in Fig. 7. The cures in Fig. 7B indicate that there are no selectivity adsorptions of (allyl-β-CD)-NIPs to DPP or DMT and the DPP and DMT leakage occurs almost at the same time. But in Fig. 7A, the DPP and DMT show leakage at different volumes. The (allyl-β-CD)-NIPs could reserve DPP and DMT because both of them could react with (allyl-β-CD)-NIPs using hydrogen bonding and hydrophobic force. For (allyl-β-CD)-MIPs besides the hydrogen bonding and hydrophobic force reacting with DPP and DMT, the imprinted space caverns possess the selective adsorption for DPP as well. There is no specific adsorption for (allyl-β-CD)-MIPs to DMT, so DMT leakage is earlier than DPP in the dynamic adsorption of (allyl-β-CD)-MIPs.

3.6. Real sample analysis

The real samples were then analyzed by MISPE and C_{18} SPE in this work. The progress of C_{18} SPE was performed according to the previous report (Niu, YE, Fang, Xue, & Sun, 2006). The recoveries of spiked cow milk analyzed by MISPE and C_{18} SPE are shown in Table 1. The extracts obtained from C_{18} showed lower recoveries for the spiked cow milk samples. In contrast, higher recoveries were obtained by using MISPE as sorbents, which is due to its high affinity and specific adsorption to the analytes. In the testing of C_{18} SPE, it is found that there are some phthalates eluted from the SPE tube when no samples or standard solutions were loaded, but there are no phthalates eluted from the glass SPE tube. It is probably because of fact that the commercial SPE tubes were made of plastics, phthalates in the plastics are eluted normally by the eluting solution.

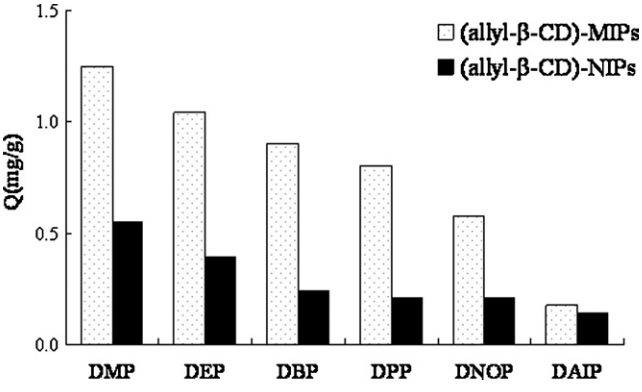

Fig. 6. The adsorption amount of DMP, DEP, DBP, DPP, DNOP and DAIP.

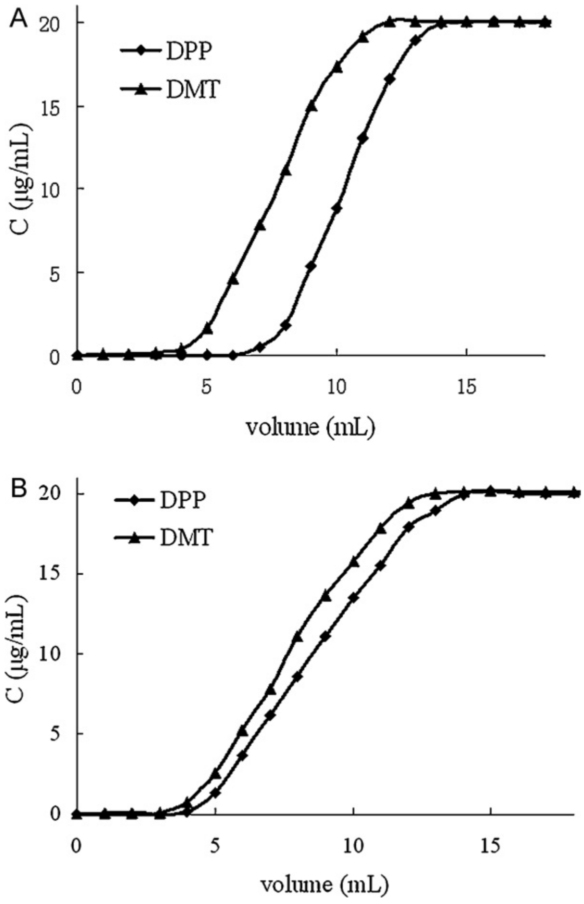

Fig. 7. Dynamic adsorption curves of DPP and DMT for (allyl-β-CD)-MIPs (A) and (allyl-β-CD)-NIPs (B).

4. Conclusions

The functional monomers of MAA, MMA and AM were evaluated by UV spectrophotometry, MAA was selected as functional monomers in this experiment. A novel (allyl-β-CD)-MIPs prepared with the binary functional monomers of MAA and allyl-β-CD were successfully accomplished. The synthesized products were characterized by FT-IR and SEM. The results of the static adsorption experiments showed the (allyl-β-CD)-MIPs with higher adsorption capacity to template. In the selective adsorption and dynamic adsorption, (allyl-β-CD)-MIPs can separate the template and its analog clearly, which confirmed the good selective adsorption performance of (allyl-β-CD)-MIPs. The testing results thus demonstrated that the (allyl-β-CD)-MIPs possessed greater adsorption capacity and better selective adsorption than MIPs synthesized by conventional method. When the MISPE made of (allyl-β-CD)-MIPs were used for the real sample analysis, the results demonstrated that (allyl-β-CD)-MIPs can be used as selected sorbents in SPE techniques for real sample analysis.

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