Selective Adsorption of Di(2-ethylhexyl) Phthalate by Surface Imprinted Polymers with Modified Silica Gel as Functional Support

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Summary： A novel surface molecularly imprinted polymer (SMIP) selective for di(2-ethylhexyl) phthalate (DEHP) was prepared on the surface of silica gel, which was modified by aminopropyltriethoxysilane and acryloyl chloride in a two-step method, with DEHP as template, methyl acrylic acid (MAA) as functional monomer, ethyleneglycol dimethacrylate (EGDMA) as cross-linker and azobisisobutyronitrile (AIBN) as initiator. The prepared SMIP was characterized by Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), and nitrogen adsorption-desorption analysis. The adsorption properties of the SMIP for DEHP were investigated. The results showed that the SMIP was porous and rough. Its specific surface area and pore volume were 292.05 m^2/g and 0.299 cm^3/g, respectively, which increased to 15 and 10 times that of silica gel, respectively. The adsorption performance is optimal under the conditions of pH value in the range 6~7. The adsorption equilibrium time was about 150 min. The isothermal adsorption process and adsorption kinetics could be well described by Langmuir and the pseudo-second-order kinetic model respectively. The saturated adsorption capacity is 16.08 mg/g. The SMIP exhibited excellent adsorption selectivity for DEHP. The SMIP prepared is a desirable solid-phase extraction agent for separation and enrichment of DEHP in complicated environmental samples.

Keywords: di(2-ethylhexyl) phthalate; Silica gel; Molecularly imprinted polymer; Selective adsorption; Adsorption isotherm; Adsorption kinetics

Introduction

Phthalates are a group of organic esters known as estrogen-like chemicals or environmental hormone. The most common phthalate is di(2-ethylhexyl) phthalate (DEHP), which is widely used as plasticizer in industry [1]. Generally, it was added to the resin, plastic, rubber, adhesives and other materials mainly to increase the flexibility, ductility and scratchability of the products [2-3]. Plasticizers were widely distributed in the ecological system and were regarded as one of the most abundant content of environmental pollutants in nature. Literature showed that toys, food packaging materials, medical blood bags and tubing, edible oil, dairy products, personal care products and so on were all polluted by plasticizers [4]. Phthalates were the refractory substances in the environment. If they were long-term accumulated in the human body, they would lead to hormonal imbalance and the decrease of immunity. They could affect the human reproductive capacity and cause baby gender confusion, cardiovascular disease and even genotoxicity [5]. Therefore, the detection and control of DEHP in the environment and food is very important. Usually it is extensively disseminated and at very low levels, the traditional detection method was to use the non-specific liquid-liquid extraction and solid phase extraction to enrich the phthalates in samples before testing, the sample handling process was cumbersome and poorly selective [6].

The imprinting hole of molecularly imprinted polymers (MIPs) has the same molecular structure with the template and can achieve specific recognition of the template molecular. Molecular imprinting technique provides a new choice for selective separation of target from complex matrix. Currently, many researchers have synthesized MIPs for dimethyl phthalate [7], dibutyl phthalate [8], aniline [9], melamine [10], bisphenol A [11], nonylphenol [12] and other environmental pollutants. As a kind of chiral pollutant, the interference with endocrine system of DEHP is enantioselective, it is of great significance in separating the toxic racemate of DEHP with MIPs as the stationary phase, but few researches have focused their attention on the preparation of MIPs for DEHP. Huma Shaikh groups [1] prepared MIPs for DEHP using bulk polymerization method, but about 15% of the product appeared agglomerating so as to abate the adsorption capacity of the polymer. Recently, a novel surface imprinting technique, which can fix the recognition sites of molecularly imprinted polymers on the surface of support materials, has been developed to avoid agglomeration and slow mass transfer of the

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polymer and damage of imprinting cavities due to grinding and sieving of MIPs [13-16].

The available supports for SMIP were silica gel, carbon nanotube, magnetic ferroferric oxide, alumina, chitosan and resin etc [17-19]. Among them, silica gel with stable chemical properties, high thermal stability and firm mechanical strength were considered as favorable supporting matrix. In order to improve their poor performance in chemical and affinity with organic molecules and polymers, functional groups were required to graft or coat onto the surface of silica gel prior to the imprinting process. In recent investigations, the silane coupling agents such as aminopropyl triethoxysilane (KH-550) [20], γ- (2,3–epoxy propoxy) trimethoxysilane (KH-560) [21], γ-methacryloyloxy propyl trimethoxy silane (KH-570) [22] or vinyl triethoxysilane (VTES) [23] were selected to be grafted onto the surface of silica gel by one-step modification. The terminal group on silica gel surface grafted by KH-550 or KH-560 was amino-group or 2,3-epoxypropoxyl, respectively, which has weak affinity with monomers or polymers, so that MIP film was not easy to be attached on the surface of silica gel and thus reduced its chemical stability. The SMIP based on silica gel grafted by KH-570 or VTEO with C=C group represented better chemical stability. However, self-polymerization happened during the grafting process, resulting in decrease in C=C group on the surface of silica gel and consequent unhomogeneity of coverage of the MIP on the surface of silica gel. In order to overcome the drawbacks mentioned above, in this work, KH-550 was firstly grafted onto the surface of silica gel, and then followed by acylation reaction with acryloyl chloride to obtain modified silica gel with -C=C-. This two-step modification method could not only avoid the self-polymerization of the silane coupling agent during the modification process, but also made the silica gel surface grafted with the structure containing C=C to improve affinity between supporting material and MIP film. SMIP selective for DEHP was prepared on the surface of modified silica gel with DEHP as template, methyl acrylic acid (MAA) as functional monomer, ethyleneglycol dimethacrylate (EGDMA) as cross-linker and azobisisobutyronitrile (AIBN) as initiator. This work was the first report to prepare the SMIP for DEHP using silica gel as supporting matrixes which was functionalized in a two-step method. The structural characteristics, morphological information and imprinting mechanism of the prepared SMIP were discussed in details. The adsorption performances of SMIP and non-imprinted polymer (SNIP) for DEHP were investigated. And the SMIP was used to prepare a molecularly imprinted solid-phase extraction (MISPE) column for extraction and enrichment of DEHP in environmental sample.

Experimental

Materials

Di(2-ethylhexyl) phthalate (DEHP), dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), di-*n*-octyl phthalate (DNOP), methacrylic acid (MAA), acrylic acid (AA), methyl methacrylate (MMA), acrylamide (AM), azobisisobutyronitrile (AIBN), methanol, acetic acid, ethanol, acetonitrile, triethylamine, toluene and silica gel(100-200 mesh) were purchased from Sinopharm Chemical Reagent Co. Ltd., China. γ-aminopropyltriethoxysilane (KH-550) was obtained from Shanghai YuanYe biotechnology Co., Ltd., and used after vacuum distillation. Aacryloylchloride was purchased from Beijing Zhongsheng Huateng Technology Co., Ltd. Ethylene glycol dimethacrylate (EGDMA) was purchased from the Energy Chemical Co. Ltd. All chemicals were of analytical grade.

Activation and modification of silica gel

Activation of silica gel: 15 g of silica gel was added into a three-necked flask (500 mL capacity), and 200 ml of 10% hydrochloric acid solution (W/V) added to the three-necked flask, and then stirred under reflux for 24 h at 120℃, to remove trace impurities at the silica surface and increase the number of hydroxyl groups on the surface of silica gel. After the reaction, the silica gel was alternately washed with acetone and ethanol, and then washed with distilled water to pH neutral, finally dried under vacuum at 150ºC for 12 h.

Preparation of amino-silica gel: 5 g of the activated silica gel and 50 mL toluene was added into a three-necked flask, dispersed and degassed by ultrasonic for 30 min. 15 mL of KH-550 and 5 mL of triethylamine was added dropwise into the mixture liquid under nitrogen protection, and then stirred under reflux for 12 h at 90℃. The silica gel treated as described above was washed with toluene, acetone and methanol, respectively, for several times, and then washed with distilled water, finally dried under vacuum at 60℃ for 12 h.

The acylation of amino-silica gel: 4 g of the amino-silica gel and 80 mL of toluene was added into

a three-necked flask, 5 mL of acryloyl chloride was added dropwise into the three-necked flask under nitrogen protection, after stirring for 10 min, 12mL of triethylamine was added dropwise to the mixture. Then the mixture was stirred at room temperature for 24 h. The product was filtered and washed with toluene, methanol and distilled water for several times and then dried under vacuum at 60℃ for 12 h.

Synthesis of Surface Molecularly Imprinted Polymer

2 mmol DEHP, 8 mmol MAA were dissolved in 50 ml of toluene. After ultrasonic mixing for 30 min, 2 g of acylated silica gel, 24 mmol EGDMA and 24 mg AIBN were added into the mixture under nitrogen protection. The above mixture was stirred under reflux for 24 h at 60℃. After the reaction is finished, the product was filtered and washed with toluene, acetone, methanol and distilled water, respectively, and then was Soxhlet eluted with methanol/acetic acid (9:1, V/V) for 24 h to remove the imprinted molecule. The eluted sample was dried under vacuum at 60℃ for 12 h. Non-imprinted polymer (SNIP) was also synthesized in the same way without addition of DEHP.

The schematic illustration of synthetic route for SMIP was presented in Fig. 1.
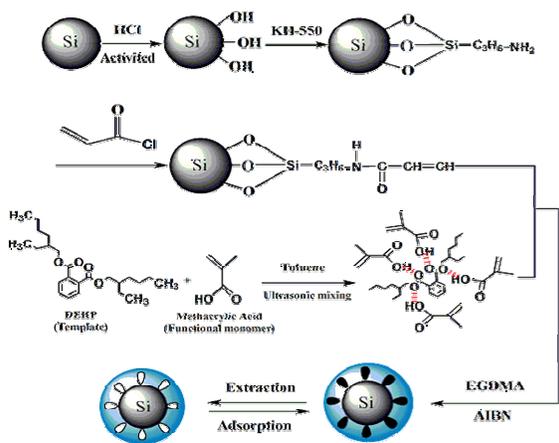
Fig. 1:   The schematic illustration of synthetic route for SMIP.

Characterization of Surface Molecularly Imprinted Polymer

TENSOR 27 Fourier transform infrared spectrometer (Bruker Company, Germany) was used to collect the infrared spectra of the SMIP, SNIP and silica gel. S-4800 field emission scanning electron microscopy (SEM) (Japan, Hitachi) was used to observe the morphology of the SMIP and silica gel. Nitrogen adsorption-desorption method was used to determined the specific surface area and pore size distribution of SMIP, SNIP and silica gel.

Adsorption Studies

Influence of pH on Adsorption

100 mg SMIP(or SNIP) were added into10 mL DEHP/methanol solution in each conical flask with the same initial concentration of 50 mg/L and varied pH (2, 3, 4, 5, 6, 7, 8, 9,10) , the pH were adjusted with H_2SO_4 and NaOH solution in the concentration of 2mol/L, respectively. And then the conical flasks were sealed and placed in an water-bath shaker for 10 h at 25℃. After the adsorption was finished, the equilibrium concentration of DEHP in each flask was determined by HPLC and a parallel was measured three times and averaged. The adsorption capacity was calculated by eq. (1) [24].

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (1)$$

where, q_e (mg/g) is the equilibrium adsorption capacity, C_0 (mg/L) is the initial concentration of DEHP, C_e (mg/L) is the equilibrium concentration of DEHP, V (ml) is the volume of DEHP/methanol solution; W (g) is the weight of SMIP (or SNIP).

Measurement of Adsorption Isotherm

100 mg SMIP(or SNIP) were added into10 ml DEHP/methanol solution in each conical flask with varied concentration (1, 3, 5, 10, 15, 20, 25, 30, 40, 50, 100, 200, 400, 600, 800 mg/L) , and the conical flasks were sealed and placed in an water-bath shaker for 10 h to achieve adsorption equilibrium at 25, 35, 45℃, respectively. The equilibrium concentration of DEHP in each flask was determined by HPLC and a parallel was measured three times and averaged. The adsorption capacity was calculated by eq.(1).

Adsorption Kinetics

100 mg SMIP(or SNIP) were added into10 mL DEHP/methanol solution in a series of conical

flasks with an initial concentration of 50 mg/L and pH 6 , and each the conical flasks were sealed and placed in an water-bath shaker at 25℃. One of the flasks was taken out form the shaker every certain time interval, and the concentration of DEHP was determined by HPLC and a parallel was measured three times and averaged. The adsorption capacity was calculated according to eq. (2).

$$q_{t} = \frac{(C_0 - C_t)V}{W} \qquad (2)$$

where, q_t (mg/g) is the adsorption capacity at different times, C_t (mg/L) is the concentration of DEHP at different times, C_0 (mg/L) is the initial concentration of DEHP, V (ml) is the volume of DEHP/methanol solution; W (g) is the weight of SMIP (or SNIP).

Measurement of Adsorption Selectivity

DMP, DEP, DBP, DNOP were chosen as the analogues for DEHP to estimate the selective adsorption of SMIP and SNIP. The chemical structure of DEHP and its analogues are shown in Fig. 2. 100 mg SMIP (or SNIP) were added in 10mL toluene solution containing DMP, DEP, DBP, DNOP and DEHP with initial concentrations of 10mg/L of each substance. The mixture was placed in a water-bath shaker at 25℃ for 10 h to achieve adsorption equilibrium. The equilibrium concentrations of DMP, DEP, DBP, DNOP and DEHP were determined by HPLC and a parallel was measured three times and averaged.
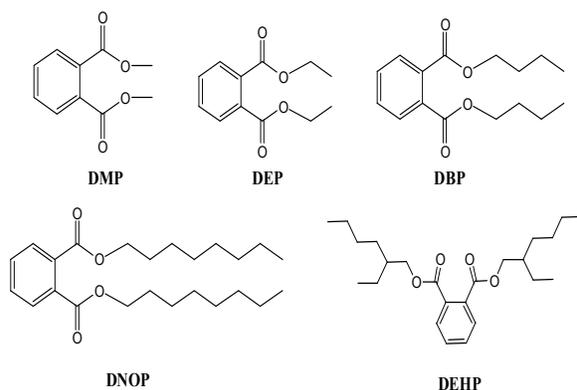
Fig. 2:   Chemical structure of DEHP and its analogues.

Determination of DEHP, DBP, DNOP, DEP and DMP

DEHP, DBP, DNOP, DEP and DMP were determined by HLPC (Shimadzu, Japan) with Inertsil ODS-SP C_{18} column (250 mm×4.6 mm×5 μm). The column temperature was 35℃, the mobile phase was CH_3OH/H_2O (95/5, V/V), the flow rate was 0.5 ml/min, the wavelength of UV detector was 254 nm.

Results and Discussion

Characterization of SMIP

FT-IR Spectra

The FT-IR spectra of activated silica gel, ammoniated silica gel, acylated silica gel and SMIP were shown in Fig. 3.

From Fig.3(b) we can see, the bending vibration peak of N-H appeared at 1551cm^{-1}, the peak at 3250-3650 cm^{-1} decreased significantly and the Si-OH peak at 970 cm^{-1} also weakened compared with Fig.3(a), indicating that parts of the Si-OH from silica gel reacted with silane and amino-group were introduced to the surface of silica gel. The symmetric and asymmetric stretching vibration peak of -CH$_2$- at 2935 cm^{-1} also confirmed that KH-550 was successfully grafted to the surface of silica gel.

As shown in Fig.3(c), the absorption peak of C=C appeared at 1573 cm^{-1}, the bending vibration peak of -NH$_2$ at 1551 cm^{-1} weakened compared with Fig.3(b) and amide bands appeared obviously at 686 cm^{-1}, indicating that the amino groups on the surface of silica gel reacted with acryloyl chloride and the C=C was successfully grafted onto the surface of silica gel.

In Fig.3(d), the ester carbonyl peak at 1730 cm^{-1} might result from cross-linker ethyleneglycol dimethacrylate. The absorption peak of C=C at about 1573 cm^{-1} disappeared, indicating that the C=C grafted on the surface of silica gel, functional monomer MAA and the cross-linking agent were completely reacted with each other. The stretching vibration peak of saturated C-H at 2935 cm^{-1} may be attributed to the propyl of KH-550 and the methyl of MAA and EGDMA [25]. These all proved that the cross-linking polymerization carried out and molecularly imprinted polymer was successfully synthesized on the surface of silica gel.

The bending and stretching vibration of Si-O-Si at 466 cm^{-1},780 cm^{-1},1098 cm^{-1} appeared in all the four spectra in Fig. 3, proving that silica gel remained the original structure during reaction. The band at 3450 cm^{-1} may be attributed to the O-H stretching vibration, indicating that the -OH at the surface of silica gel reacted with others incompletely.
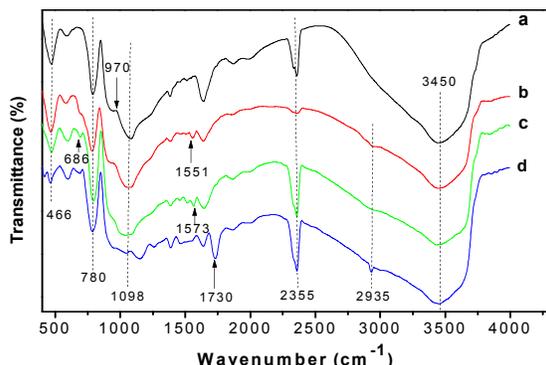
Fig. 3:　　FT-IR spectra of activated silica gel (a), ammoniated silica gel (b), acylated silica gel (c) and SMIP(d).

SEM

Fig. 4 was SEM of silica gel and SMIP with different magnifications (800×, 30000×). We could see that the surface of SMIP was rough and multi-porous while the surface of silica gel was smooth and homogeneous. The irregularly rough morphology was probably because the polymer film was coated on the surface of silica gel, and the film had various mesh hole structure. The template molecules were through these holes approaching the determined recognition sites and thus forming adsorption.
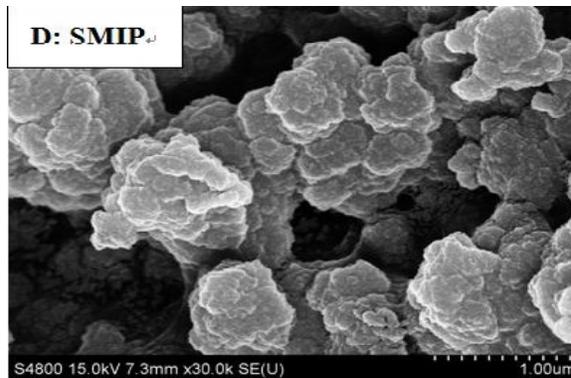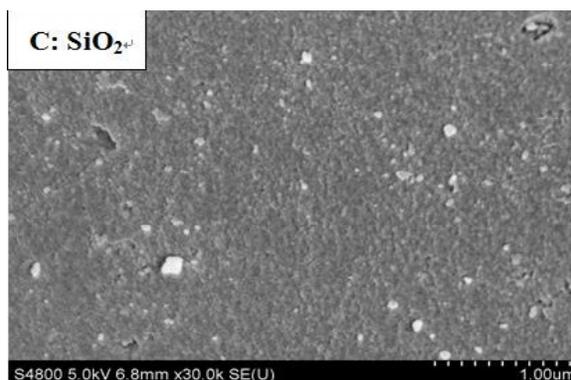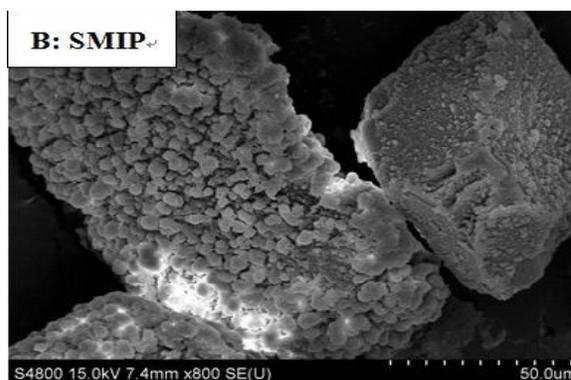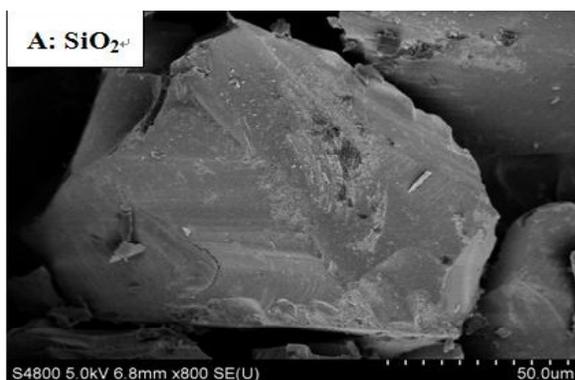
Fig. 4 SEM photographs of silica gel and SMIP

Specific Surface Area

To obtain the pore diameter and surface area information of silica gel, SNIP and SMIP, the adsorption and desorption isotherms of nitrogen and pore size distribution were measured and shown in Fig. 5. As seen from Fig. 5, hysteresis loop exist in the higher P/P_0 region (0.5-0.9) in the adsorption-desorption isotherm, this may be attributed to capillary condensation [26]. The specific surface area, average pore diameter and pore volume were calculated by using BET model and shown in

Table-1. It could be seen that there was little difference between SiO$_2$ and SNIP in specific surface area, pore diameter and pore volume, but the specific surface area and pore volume of SMIP have increased significantly compared with SiO$_2$ and SNIP, suggesting that the template molecules was effectively eluted to leave many new imprinting cavities.

Table-1: Specific surface area, pore size and pore volume of the materials.

Sample	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
SiO$_2$	19.0209	0.02702	3.49
SNIP	19.6987	0.02612	3.51
SMIP	292.05	0.2992	3.59
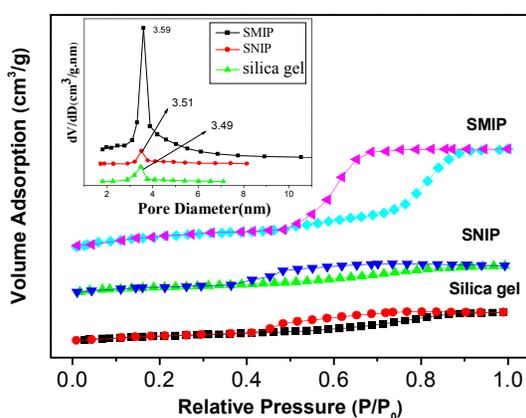
Fig. 5:   Adsorption-desorption isotherms of nitrogen for silica gel, SNIP and SMIP

Adsorption Studies

Effect of pH on the Adsorption

The static adsorption method was employed to investigate the adsorption capacity of SMIP and SNIP for DEHP at varied pH (2.0 ~10.0), the results were shown in Fig. 6.

As can be seen from Fig.6, adsorption capacity of SMIP for DEHP increased with increasing pH in the range of 2-6 and reaches a maximum at pH 6-7, but decreased significantly with further increase in pH up to 10. The pH dependence of adsorption can be explained as follows: (1)Under the acidic conditions, the electrostatic shielding effect, resulting from accumulation of free H$^+$ around the oxygen atoms in ester function of DEHP molecule via electrostatic forces, made it difficult for DEHP molecules to bind with the recognition sites in SMIP. (2) Under alkaline conditions, interaction between

OH$^-$ in the solution and –COOH groups in the polymer made the hydrogen bonding action between the polymer and DEHP weakened, resulting in adsorption capacity descended.
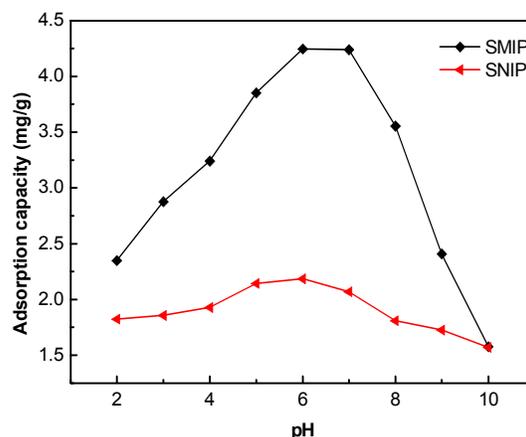
Fig. 6:   Effect of pH on adsorption capacities.

The Adsorption Isotherm

Fig.7 presents the adsorption isotherms of SMIP and SNIP for DEHP. In this work, Langmuir and Freundlich isotherm model were employed to correlate the experimental data of adsorption isotherm, and the adsorption constants calculated by linear-regression analysis were listed in Table-2.

Table-2:   Adsorption isotherm constants of SMIP.

	Langmuir				Freundlich		
T/K	q^0(mg/g)	*b*(L/mg)	*R*^{2}		*K*$_f$	1/*n*	*R*^{2}
298	16.08	0.014	0.9902		0.8179	0.4728	0.9691
308	12.56	0.037	0.9937		0.4042	0.5795	0.9632
318	11.17	0.010	0.9674		0.2966	0.6080	0.9656

The linear Langmuir and Freundlich model are expressed as equations (3) and (4), respectively [11].

$$\frac{C_e}{q_e} = \frac{1}{q^0 b} + \frac{1}{q^0} C_e \qquad (3)$$

$$\log q_e = \log k_f + \frac{1}{n} \log q_e \qquad (4)$$

Where, C_e (mg/L) is the equilibrium concentration in the solution, q_e(mg/g) is the equilibrium adsorption capacity, Langmuir constants q^0 (mg/g) and b (L/mg) are related to the adsorption capacity and energy of adsorption. K_f and 1/n are Freundlich constants

related to the adsorption capacity and heterogeneity factors, respectively.
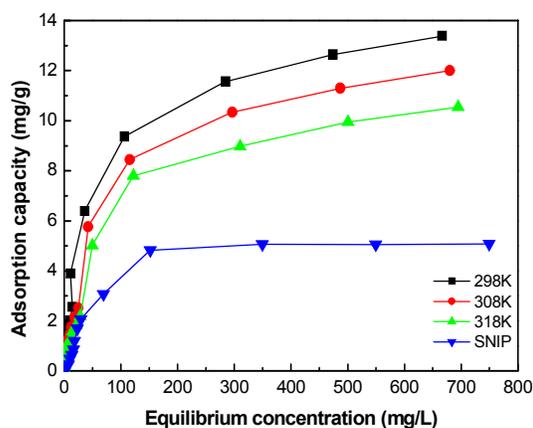
Fig. 7:   Adsorption isotherms of SMIP and SNIP.

As shown in Fig.7, the adsorption capacity of SMIP for DEHP was obviously higher than that of SNIP. This is because that the SMIP contained the cavities matching with DEHP molecules and regularly arranged functional groups interacting with DEHP due to the participation of DEHP during the preparation of SMIP and exhibited the better specific adsorption ability, while SNIP showed nonspecific adsorption due to the absence of imprinted holes of DEHP molecular although it had identical chemical structure with SMIP [27]. In addition, it also could be found that adsorption capacity of SMIP decreased obviously with temperature increased from 298 K to 318 K. This was because the adsorption relies mainly on the force of hydrogen bond produced between DEHP molecular and SMIP, while the hydrogen bond could be weakened with the increase in temperature [28].

Table-2 shows that Langmuir and Freundlich models could well describe the adsorption of DEHP onto SMIP. The Freundlich characteristic parameter n value was found to be more than 1, indicating that the adsorption process can carry out easily [29]. Correlation coefficient R^2 indicated that the Langmuir model was better suitable for adsorption of SMIP for DEHP than Freundlich models, suggesting monolayer molecular adsorption of SMIP for DEHP. So it is conclude that the adsorption sites on SMIP were uniformly distributed.

In order to further estimate the binding properties of the SMIP, the experimental data of adsorption isotherm were analyzed by Scatchard equation, which was expressed as [30]:

$$\frac{q_e}{C_e} = \frac{(q_{max} - q_e)}{K_d} \qquad (5)$$

where, q_e(mg/g) is the equilibrium adsorption capacity, C_e (mg/L) is the equilibrium concentration of DEHP in solution, K_d (mg/L)is the dissociation constant of the binding sites and q_{max} (mg/g) is the apparent maximum binding amount of the binding sites. Scatchard curves were plotted in q_e/C_e versus q_e and shown in Fig.8.
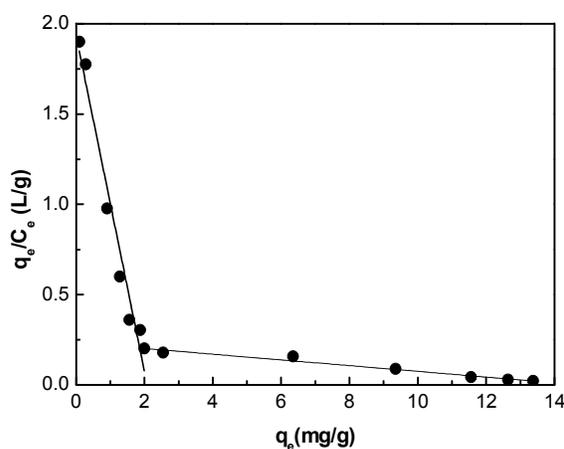
Fig. 8 Scatchard plots of SMIP

From Fig. 8, it was observed that the plot of SMIP contains two straight lines, suggesting the presence of two classes of binding sites in the SMIP. For higher affinity sites, linear equation is q_e/C_e=-0.0159q_e+0.2323 (R^2= 0.9728), and the values of K_d and q_{max}, calculated from the slope and intercept of Scatchard plots, are 62.893mg/L and 14.610 mg/g, respectively. For lower affinity sites, linear equation is q_e/C_e=-0.9298q_e+1.9368 (R^2 = 0.9696), the values of K_d and q_{max} are 1.076mg/L and 2.083 mg/g, respectively.

According to Scatchard analysis, it is believed that there are at least two distinct groups with different specific binding forces in the SMIP for DEHP molecules. There are two kinds of oxygen atoms in ester group of DEHP, and they could combine with hydrogen in -COOH of monomer MAA via hydrogen bond with two different kinds of binding force, which is speculated and illustrated in Fig. 1.

Adsorption Kinetics

The adsorption kinetics was investigated by examining the influence of contact time on DEHP adsorption, and the results are depicted graphically in Fig. 9. It could be seen from Fig. 9 that the adsorption rates of SMIP and SNIP for DEHP were fairly rapid at the initial stages of adsorption. After a rapid adsorption, the DEHP adsorption rates declined slowly and the equilibriums were reached at 150 min and 60 min, respectively.
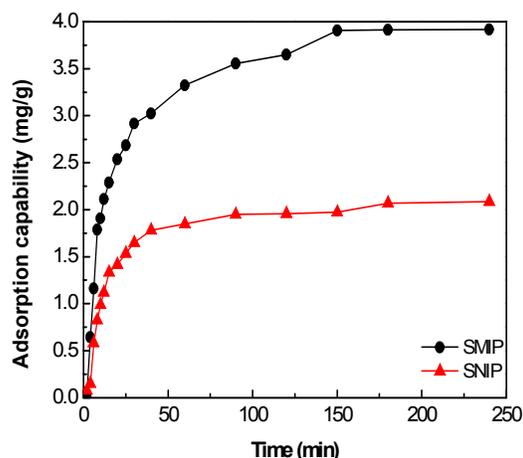
Fig. 9:   Kinetic curve of adsorption for DEHP

In this work, pseudo-first-order (eq.(6)) and pseudo-second-order(eq.(7)) kinetics models [31] were employed to simulate the adsorption process, and the results were listed in Table-3.

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \qquad (6)$$

$$\frac{\text{t}}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

where, q_e (mg/g) and q_t (mg/g) are the adsorption capacity at equilibrium and t (min), respectively. k_1(min^{-1}) and k_2 (g/(mg·min)) are the first-order and the second-order rate constant, respectively.

As can be seen from Table-3, the pseudo-second-order kinetics model gave better correlation (R^2>0.99) than pseudo-first-order kinetics

model. The experimental q_e value (3.916 mg/g) perfectly agreed with the calculated q_e value (3.912 mg/g) by the pseudo-second-order model. Although the correlation coefficient ($R^2 = 0.9281$) obtained via the pseudo-first-order kinetic model was in the range of the allowable statistics error, the calculated q_e (3.319 mg/g) had an obvious deviation from the experimental value q_e (3.916 mg/g). Thus, the pseudo-second-order kinetic model is better suitable for describing the adsorption of DEHP onto the SMIP prepared, indicating that the chemo-adsorption might be the rate-limiting step controlling adsorption process of the SMIP.

Adsorption Selectivity

Four different phthalates DMP, DEP, DBP and DNOP were selected as structural analogs to investigate adsorption selectivity of SMIP and SNIP for DEHP, The adsorption of SMIP and SNIP for the mixture of DEHP, DMP, DEP and DBP was given in Fig.10.
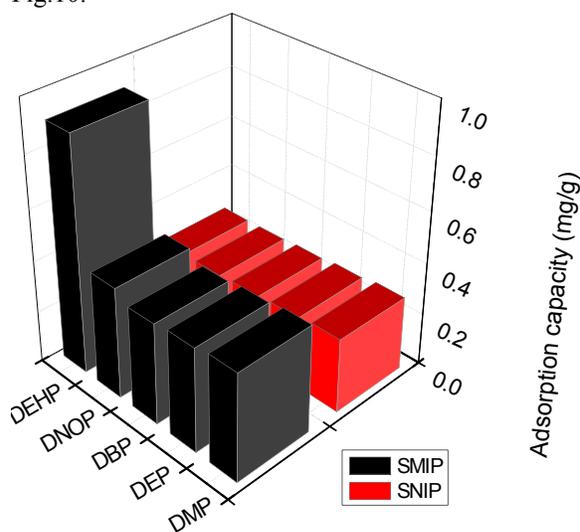
Fig. 10 Selective adsorption of SMIP and SNIP

As given in Fig.10, adsorption capacity of SMIP for DEHP was significantly higher than that for the other four phthalates, indicating that SMIP can specifically recognize DEHP due to imprinting cavities and binding sites. Otherwise, the adsorption of SNIP for DEHP and the other the four phthalates had no selectivity.

Table-3:   The kinetics parameters of adsorption of the SMIP for DEHP.

Model	Parameters		Correlation coefficient (R^2)	Kinetis equation
pseudo-first-order	k_1 (min^{-1}) -0.0185	q_e (mg/g) 3.319	0.9281	$\ln(q_e-q_t)=-0.0329t + 1.20$
pseudo-second-order	k_2 [g/(mg·min)] 4.8624	q_e (mg/g) 3.912	0.9992	$t/q_t=0.2411t+3.154$

The selectivity of SMIP and SNIP was estimated by the partition coefficients of selected phthalates between polymers and the solution. The partition coefficient K was determined according to eq.(8).

$$K=q_e/C_e \qquad （8）$$

Where, q_e is the equilibrium adsorption capacity, and C_e is the equilibrium concentration.

Additionally, the imprinting factor (IF) and selectivity coefficient (SC) were used to evaluate the selectivity properties of SMIP and SNIP toward DEHP and its structural analogs DMP, DEP, DBP and DNOP.

The IF and SC was calculated by following eq.(9) and eq. (10) [1].

$$IF = K_i /K_c \qquad (9)$$
$$SC = IF_{DEHP}/IF_i \qquad (10)$$

Where K_i and K_c represent the partition coefficients of analytes for SMIP and SNIP, respectively; IF_{DEHP} and IF_i was the imprinting factors for DEHP and the other four phthalates, respectively.

The adsorption capacity, partition coefficients, *IF* and *SC* of SMIP and SNIP for DEHP and its analogs were listed in Table-4.

Table-4:   The partition coefficient K, IF and SC of SMIP and SNIP for DEHP and its analogues.

Analytes	K_{SMIP}(mL/g)	K_{SNIP}(mL/g)	IF	SC
DMP	0.071	0.040	1.775	16.16
DEP	0.067	0.038	1.763	16.27
DBP	0.064	0.036	1.778	16.13
DNOP	0.075	0.035	2.140	13.40
DEHP	0.975	0.034	28.68	—

As shown in Table-4, the *IF* for DEHP was much higher than those for the other four phthalates, suggesting that template molecule had a relatively higher affinity for the imprinted polymer than the other four analogs. There were two possible factors influencing the selectivity of the imprinted molecule over the analogs. One was the molecular volume and the other was the strength of the interaction between the target molecule and binding sites. In this work,

DEHP and its analogues have the same esterfunction which can produce binding site with monomer via hydrogen bonding. But, their shape and size was unique and different from each other. As shown in Fig. 2, DEHP had branched alkyl chain, while its analogues only had straight alkyl chain. Further more, the alkyl chain length of DEHP was longer than that of DMP, DEP and DBP. Because DEHP was selected as imprinting template, after DEHP was eluted, the cavities and functional groups which are complementary with template molecule and the shape of the template were fixed in the imprinted polymer. This is why SMIP had selectivity for DEHP. It can be concluded that the different molecular volume and dimensional structure between the binding sites in the polymer and the targets determined the selectivity of DEHP molecular recognition.

In order to further investigate the adsorption selectivity of SMIP for DEHP. A molecularly imprinted solid-phase extraction (MISPE) column was prepared with SMIP as solid-phase extraction agent. Then DEHP and its analogs in environmental sample were separated and enriched by the MISPE and commercially available C18 solid-phase extraction column, and the recovery rates were shown in Fig. 11. We could see clearly that the recovery rate of the MISPE column for DEHP was 101.76% and significantly higher than that of the other four analogs. This is due to highly selective adsorption of SMIP for DEHP over its analogs.

We could also see from Fig. 11 that the recovery rate of the MISPE column for DEHP (101.76%) was much higher than that of the commonly used C18 solid-phase extraction column (56.35%), which indicated that the MISPE column had better adsorption capacity for DEHP than C18 column. Moreover, the C18 solid-phase extraction column had little selectivity for DEHP over the four analogs. Compared to the C18 solid-phase extraction column, MISPE column is more suitable for separating DEHP from the other phthalates in environmental samples. It is suggested that SMIP prepared in our laboratory is a desirable solid-phase extraction agent for separation and enrichment of DEHP in complicated environmental samples.
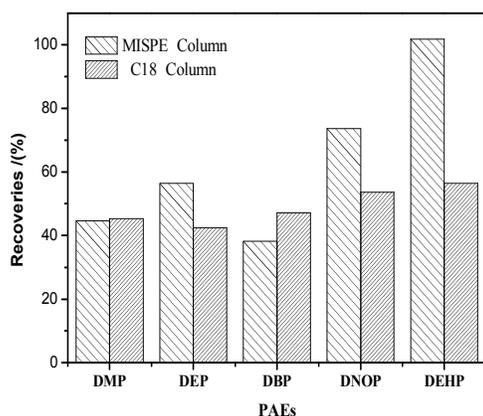
Fig. 11: Recovery of different SPE column for DEHP and its analogs.

Conclusions

Molecularly imprinted polymer selective for DEHP was successfully synthesized on the surface of silica gel. KH-550 was first grafted onto the surface of silica gel, and then followed by acylation reaction with acryloyl chloride to obtain modified silica gel with C=C groups. The polymerization was carried out by using modified silica gel as functional support, DEHP as template, MAA as functional monomer, EGDMA as cross-linker and AIBN as initiator. The group C=C, grafted on the surface of silica gel, took participation in polymerization to improve the stability of imprinted polymer. The SMIP was found porous and rough. It has much larger specific surface area, compared with silica gel, which could provide more binding sites for adsorption. The adsorption kinetics of SMIP for DEHP follows Pseudo-second-order kinetic model very well (R^2 = 0.9992) and reached the equilibrium at 150 min. According to the adsorption isotherms, the maximum adsorption capacity of the SMIP has been found to be 16.08 mg/g, and the SMIP had much higher adsorption capacity than the SNIP. The selectivity coefficients of SMIP for DEHP with respect to DMP, DEP, DBP and DNOP were 16.16, 16.27, 16.13 and 13.40, respectively. These experimental results demonstrated that the prepared SMIP exhibited excellently specific adsorption and selectivity for DEHP. It would have a promising application in solid-phase extraction to selectively extract or enrich DEHP in complicated environmental samples.

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