

Selective Extraction and Determination of Di(2-ethylhexyl) Phthalate in Aqueous Solution by HPLC Coupled with Molecularly Imprinted Solid-phase Extraction

Chen, Fangyan^{*+}; Yang, Zhan; Tang, Yubin; Wang, Xingang

School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212018, CHINA

ABSTRACT: Surface Molecularly Imprinted Polymer (SMIP) for selective adsorption of 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. The prepared SMIP was used to prepare Molecularly Imprinted Solid-Phase Extraction (MISPE) column for selective extraction of DEHP from aqueous solution. The results suggested that MISPE column had high affinity and excellent selectivity for DEHP. And adsorption property of MISPE column was significantly superior to commercial C18 column. The MISPE column was reusable. An analytical method MISPE-HPLC was developed for extraction and determination of the DEHP residues in environmental water samples. The results showed that the linear relationship of the peak area and the concentration of DEHP were as follow: $y=2354.6x+1663.5$ with a good correlation coefficients ($R^2=0.9997$) and the detection and quantification limits reached 0.012 mg/L and 0.039 mg/L, respectively. The spiked recoveries of DEHP in river water and lake water sample were in the range from 93.3% to 102.3 % at the spiked level of 50~1000 $\mu\text{g/L}$. The Relative Standard Deviations (RSD) were less than 5.2%.

KEYWORDS: Surface molecularly imprinted polymer; Solid-phase extraction; High Performance Liquid Chromatography; Di(2-ethylhexyl) phthalate; Selective extraction; Spiked recovery.

INTRODUCTION

Phthalic esters (PAEs) are a kind of environmental endocrine disruptors. They are widely distributed in environment and reluctant to be degraded naturally. They are internationally recognized as persistent organic pollutants [1]. If they were accumulated in the human body, they would lead to hormonal imbalance, decline

in immunity and reproductive capacity, baby gender confusion, cardiovascular disease and genotoxicity [2]. Di(2-ethylhexyl) phthalate (DEHP) is the largest amount PAEs used in industry, and has been listed as priority control toxic pollutant by many countries[3]. As a result, it is very necessary to detect trace DEHP rapidly and

* To whom correspondence should be addressed.

+ E-mail: chenfangyan@just.edu.cn

1021-9986/2017/3/127-136

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sensitively in the environment samples. High-Performance Liquid Chromatography (HPLC) or Gas Chromatography (GC) was usually applied in determination of DEHP. Moreover, it is vital to enrich and extract DEHP from complex environmental samples. Solid-Phase Extraction (SPE) provides an effective way for enrichment and extraction of target analytes from complicated matrixes [4-10]. Nevertheless, SPE can result in co-extraction of impurity components which interference with the determination of target analytes, due to application of traditional adsorbents lack of adsorption selectivity.

Molecularly Imprinted Polymers (MIPs) have spatial structure and binding sites matching with the templates, resulting in selective adsorption for the target molecule. So MIPs have been widely used in SPE to extract the trace analytes selectively from complex samples, and have been considered as one of the most promising SPE agents [11-13]. For instance, MIPs for phenylalanine racemate [14], erythromycin [15], melamine [16], cephalexin [17], diethylstilbestrol [18], nonylphenol [19], 2,4-dichlorophenoxyacetic acid [20], 4-chloro-2-methylphenoxy acetic acid [21] have been synthesized and applied in SPE successfully. A few of MIPs for PAEs and their application in SPE have been reported in literatures. He Juan et al [22] prepared DBP imprinted polymer by bulk polymerization and established the MISPE-GC-MS method for the detection of DBP in milk sample. DEHP imprinted polymers were synthesized by suspension polymerization and was used in the solid-phase extraction to establish the MISPE-GC method for the detection of DEHP in water samples [23]. Nevertheless, to our knowledge, there are few reports on the exploitation of MISPE-HPLC method for the detection of DEHP in environmental water samples. In present work, Silica gel was modified by two-step method. KH-550 was firstly grafted onto the surface of silica gel, and then followed by acetylation 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 stability of MIP on silica gel. DEHP imprinted polymers have been synthesized on the surface of modified silica gel and have been used as the stationary phase to prepare molecularly imprinted solid-phase

extraction (MISPE) column, and MISPE-HPLC method was established for the detection of DEHP in water samples. The established methods had high selectivity for enrichment and rapid analysis of DEHP residues in water samples.

EXPERIMENTAL SECTION

Reagents and Instruments

γ -aminopropyltriethoxysilane (KH-550) was obtained from Shanghai YuanYe biotechnology Co., Ltd., China, and used after vacuum distillation. Acryloyl chloride was purchased from Beijing Zhongsheng Huateng Technology Co., Ltd., China. Ethylene glycol dimethacrylate (EGDMA) was purchased from the Energy Chemical Co. Ltd., China. 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), Acrylamide (AM), Methyl methacrylate (MMA), azobisisobutyronitrile (AIBN), methanol, ethanol, ethyl acetate, acetonitrile, acetic acid, triethylamine, toluene and silica gel (100-200 mesh) were purchased from Sinopharm Chemical Reagent Co. Ltd., China. SiliaSphere C18 was purchased from Beijing Greenherbes Science and Technology Development Co. Ltd., China. All chemicals were of analytical grade.

LC-20A high performance liquid chromatography was purchased from Shimadzu Corporation, Japan.

Preparation of SMIP

KH-550 was firstly grafted onto the surface of silica gel, and then followed by acetylating reaction with acryloyl chloride to obtain modified silica gel.

2 mmol of DEHP, 8 mmol of MAA were dissolved in 50 mL of toluene. After ultrasonic mixing for 30 min, 2 g of modified 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 °C. 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 for 12 h 60°C, and the SMIP was obtained. Non-imprinted polymer (SNIP) was also synthesized in the same way without addition of DEHP.

Adsorption procedure

0.1g of SMIP and 10 mL of DEHP/methanol solution with an initial concentration of 50 mg/L and pH 6 were added into a conical flask, and the conical flask was sealed and shaken at 25°C for 10 h to achieve adsorption equilibrium. The equilibrium concentration of DEHP was determined by HPLC and a parallel was measured three times and averaged. The adsorption capacity was calculated by equation (1).

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

Where, Q (mg/g) is 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.

Optimization of MISPE**Preparation of MISPE column**

0.5g of the prepared SMIP were weighed and fully dispersed in 20mL of methanol and then poured slowly and equably into an empty glass SPE column. The columns were washed with 10mL of methanol and 10mL of distilled water, respectively, so as to remove the impurities and to activate adsorbents in the solid-phase extraction column.

NISPE column and C18 column were prepared by an identical method with SNIP and SiliaSphere C18 as adsorbent, individually.

Optimization of loading flow rate

10mg/L DEHP aqueous sample was loaded onto the MISPE column at a flow rate of 0.5mL/min, 1.0 mL/min, 2.0 mL/min, respectively. DEHP solution sample was collected at the outlet of the MISPE column once every 10 min, and was analyzed by HPLC to determine the concentration of DEHP. A plot of DEHP concentration versus time of sample loading was drawn to obtain breakthrough curve.

Optimization of washing solution

20mL of 10mg/L DEHP aqueous sample was loaded onto the MISPE column at a flow rate of 1.0 mL/min. The column was washed with 10mL of methanol/water solution with different concentration of methanol (0%,

10%, 20%, 30%, 40%, v/v) respectively, and then was eluted with 10mL of ethyl acetate. DEHP eluted from the MISPE column was measured by HPLC. The recovery of DEHP was calculated according to Equation (2).

$$\text{recovery (\%)} = \frac{C_2 V_2}{C_1 V_1} \times 100\% \quad (2)$$

Where, C_1 (mg/L) and C_2 (mg/L) is the concentration of DEHP in the loading sample and in the eluent, respectively. V_1 (mL) and V_2 (mL) represents the volume of loading sample and eluent, respectively.

Optimization of eluting solvent

20mL of 10mg/L DEHP aqueous sample was loaded onto the MISPE column at a flow rate of 1.0 mL/min. After being washed with 10mL of 10% methanol/water, the MISPE column was eluted with various eluting solvent. The eluent was analyzed by HPLC, and the recovery of DEHP was calculated according to equation (2).

Optimization of volume of eluting solvent

The MISPE column was loaded with 20mL of 10mg/L DEHP aqueous sample at a flow rate of 1.0 mL/min and then washed with 10mL of 10% methanol/water. DEHP was eluted from the MISPE column with ethyl acetate of various volumes, and was determined by HPLC. The recovery of DEHP was calculated according to Equation (2).

Selectivity of MISPE column

20mL of aqueous sample containing 10mg/L DMP, DEP, DBP, DNOP and DEHP was loaded onto the MISPE column, NISPE column and C18 column at a flow rate of 1.0 mL/min, respectively. The three kind of SPE column was washed with 10mL of 10% methanol/water, eluted with 4mL of ethyl acetate. The five kinds of analytes were measured by HPLC, and their recoveries were calculated by Equation (2).

Reusage of MISPE column

The MISPE column was loaded with 20mL of 10mg/L DEHP aqueous sample at the rate of 1.0 ml/min, washed with 10mL of 10% methanol/water solution, and then eluted with 4mL of ethyl acetate at the rate of 1.0 mL/min. The procedure was repeated for 10 times to respect the reusability of the MISPE column.

Application of MISPE to environmental water samples

Two kinds of real water samples, lake water and river water, were collected from the Ancient Canal and Jinshan Lake in China, respectively. The spiked water samples with different spiked levels (50 μ g/L, 200 μ g/L, 600 μ g/L and 1000 μ g/L) were obtained by adding a micro volume of solution containing four different concentrations of DEHP to the two environmental water samples. 20mL of each water samples and each spiked water sample was loaded onto the MISPE column at a flow rate of 1.0 mL/min, respectively. The columns were washed with 10mL of 10% methanol/water solution, eluted with 4mL of ethyl acetate at a rate of 1.0 mL/min. DEHP in the eluent were measured by HPLC.

HPLC conditions

DEHP, DBP, DNOP, DEP and DMP were determined by LC-20A high performance liquid chromatography with Inertsil ODS-SP C₁₈ column (250 mm \times 4.6 mm \times 5 μ m). HPLC conditions were as follows: Column temperature was 35 °C; mobile phase was methanol: water (95:5, V/V); flow rate was 0.5 mL/min; wavelength of UV detector was 254 nm.

RESULTS AND DISCUSSION

Preparation of SMIP

To a large extent, affinity of the imprinted polymers depends on intermolecular reactions between the templates and the functional monomers. Therefore, it is vital to choose an appropriate functional monomer. In this work, four different monomers, MAA, AA, AM and MMA, were employed to prepare different SMIPs and the adsorption capacity of DEHP on to these prepared SMIPs were presented in Fig. 1. It was found that the adsorption capacity of DEHP on to the SMIP prepared by using MAA as monomers was maximal. MMA combine with DEHP only rely on the intermolecular electrostatic force, lack of hydrogen bonding conditions. MAA, AA and AM all can combine with DEHP via hydrogen bond. Nevertheless, because of the electron-donating effect of Methyl, MAA can combine more easily with oxygen atoms in ester group of DEHP via hydrogen bond compared to AA and AM. Stronger binding force between MAA and DEHP resulted that the SMIP prepared with MAA as functional monomer contained more cavities and binding sites matching with DEHP

molecules, exhibiting the better specific adsorption ability. So, MAA was therefore selected as functional monomer for preparation of SMIP.

The polarity of the polymerization media are expected to affect the efficiency of interactions between the template molecules and monomer during the imprinting process. So, in the present work, the effect of different solvents, Acetonitrile, methanol and toluene on adsorption capacity of the prepared SMIPs for DEHP was investigated and the results were showed in Fig. 2. As seen in Fig. 2, the adsorption capacity of DEHP on to the SMIP prepared in toluene was far more than that on the other two polymerization media. Thus, toluene was used as optimum solvent for preparation of SMIP.

The molar ratio of the template (DEHP): functional monomer (MAA): cross-linker (EGDMA), polymerization temperature and Polymerization time have critical influences on the adsorption properties of the SMIP. Orthogonal test was carried out to determine the optimal technology condition for preparation of SMIP. The orthogonal table L₉(3) are used to arrange the experiments, the results and analysis of the orthogonal experiment were listed in Table 1. K represents the average of Q at the same level of each factor. If value of K is the largest, the corresponding level was the optimal. R is defined as remainder of maximal K value minus minimal K value for the same factor. The magnitude of R reflects the effect of each factor on adsorption capacity of the prepared SMIP. If the magnitude of R is large, the influence is great, and the factor is the major one, vice versa [24]. The value of R given in Table 1 showed that the order of effect of every factor on adsorption capacity of DEHP onto the SMIP prepared, from main to secondary, is as follows: the molar ratio of the template: functional monomer: cross-linker > polymerization temperature > polymerization time. According to analysis of the value of K for each factors, the molar ratio of 1:4:12 for the template: functional monomer: cross-linker, polymerization temperature of 60°C and polymerization temperature of 24h was chosen as optimal condition for preparation of the SMIP. Adsorption capacity of DEHP onto the SMIP prepared in the optimal condition was 3.914mg/g, which indicates that SMIP has high affinity to DEHP. It would have promising application in extraction of DEHP from environmental samples.

Table 1: Results and analysis of orthogonal experiments.

NO.	A	B (°C)	C (h)	Q(mg/g)
1	1:4:8	55	12	2.816
2	1:4:8	60	18	3.173
3	1:4:8	65	24	3.094
4	1:4:12	55	18	3.692
5	1:4:12	60	24	3.914
6	1:4:12	65	12	3.068
7	1:4:16	55	24	3.089
8	1:4:16	60	12	3.125
9	1:4:12	65	18	2.791
K ₁	3.028	3.199	3.003	
K ₂	3.558	3.404	3.219	
K ₃	3.002	2.984	3.366	
R	0.556	0.420	0.363	

Note: A: The molar ratio of the template (DEHP): functional monomer (MAA): cross-linker (EGDMA), B: polymerization temperature, C: polymerization time (h). Q: adsorption capacity of SMIP for DEHP. Initial concentration of DEHP was 50 mg/L.

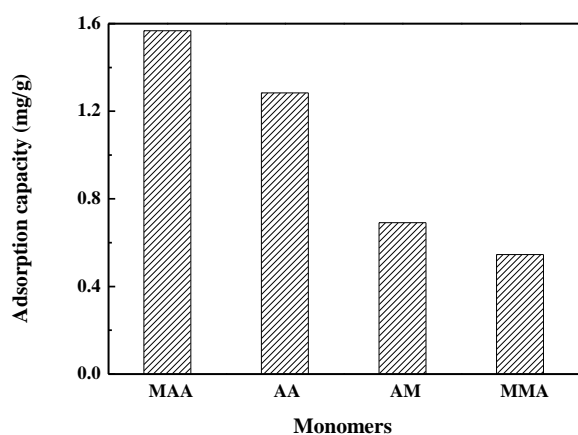


Fig. 1: Influence of different functional monomer on the adsorption of SMIP.

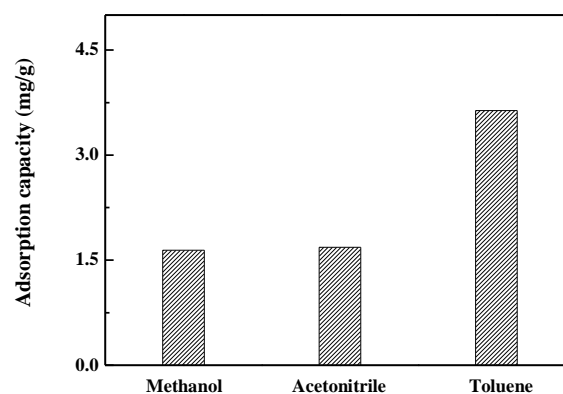


Fig. 2: Influence of different functional monomer on the adsorption of SMIP.

Optimization of MISPE

Selection of solvent of loading sample

Solvent of loading sample should play an important role in the enrichment of the analyte in virtue of its impact on microenvironment of the binding reaction and the stability of analyte. Nevertheless, in this study, the objective was to detect the concentration of DEHP in water samples, so aqueous samples were chosen as the loading sample in order to simplify pretreatment of samples. The maximum concentration of DEHP

in loading aqueous sample was selected as 10mg/L due to its low solubility in water.

Selection of loading flow rate

Loading flow rate have a vital influence on retention of analytes on SPE column. If the flow rate is too high, the analytes would be hard to enter into the imprinted holes, resulting in inefficient retention of the analytes, even leakage of the analytes from the column [25]. The plot of analyte concentration at the outlet of the SPE

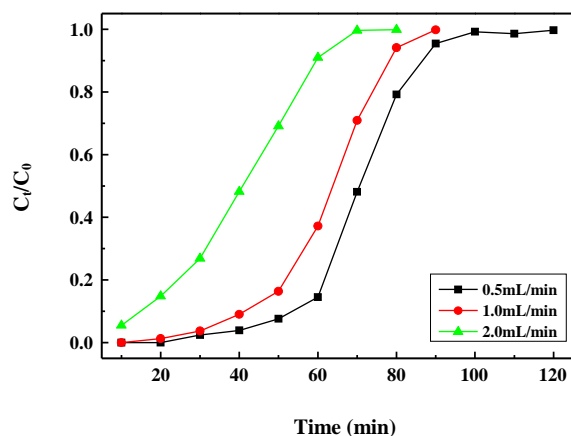


Fig. 3: Breakthrough curves at different flow rate.

column versus time of sample loading is called as breakthrough curve. Customarily, breakthrough time is considered as the time when the analytes concentration in outlet reaches to 5% - 10% of initial concentration of analytes in the loading sample. Breakthrough volume, a key factor representing the enrichment ability of the adsorbents for analytes with low concentrations, is equal to the product of flow rate and breakthrough time [26]. In order to determine the optimal loading flow rate, the breakthrough curves at different flow rate (0.5 mL/min, 1.0 mL/min and 2.0 mL/min) was tested and shown in Fig. 3.

As seen in Fig. 3, when the flow rate of loading sample was 0.5 mL/min, 1.0 mL/min and 2.0 mL/min, breakthrough time was 50 min, 35 min and 10 min, and breakthrough volume was 25 mL, 35 mL and 20 mL, respectively. It is obvious that a flow rate of 1.0 mL/min can result in larger breakthrough volume, which is beneficial to the enrichment of DEHP. Thus, a flow rate of 1.0 mL/min was selected as optimal flow rate. To ensure no breakthrough occurs during MSPE, volume of loading sample should be less than breakthrough volume. Therefore, 20 mL of DEHP aqueous solution was loaded onto the MISPE at a flow rate of 1.0 mL/min in following experiments.

According to breakthrough volume, concentration of DEHP in loading sample and mass of prepared SMIP packed in column, the exact capacity of the prepared column for DEHP adsorption can be calculated be 0.7 mg/g at a flow rate of 1.0 mL/min. The prepared column had enough capacity to ensure complete adsorption for trace DEHP in environment sample.

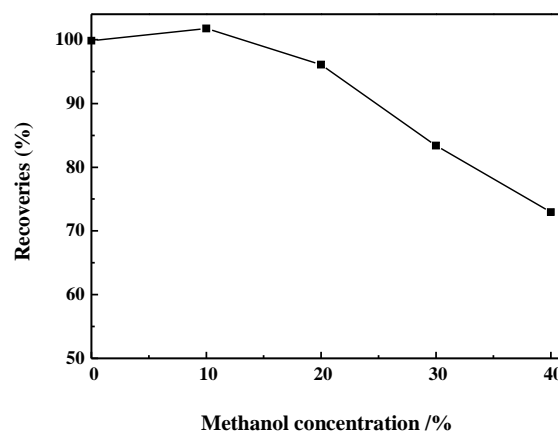


Fig. 4: Recoveries of DEHP in MISPE column washed with different concentration of methanol/water solution.

Optimization of washing solution

In SMPE procedure, the aim of washing was to wash away the interfering component, but avoid the analytes from being washing away. For this purpose, the strength of washing solvent should be slightly stronger than or equal to that of the loading samples [27]. Due to loading sample being aqueous, the MISPE column was washed with methanol/ water solution in different concentration of 0%, 10%, 20%, 30%, 40% (v/v), and the recoveries were presented in Fig. 4. As shown in Fig. 4, when the MISPE column was washed with pure water and 10% methanol/water solution, the recoveries were more than 99%. When the methanol concentration exceeded 10%, recoveries decreased with the increasing concentration of methanol/ water solution. It was suggested that pure water or 10% methanol/ water solution was desirable washing solution. However, washing solution should be required to wash away the hydrophobic impurities, so 10% methanol/water solution was chosen as washing solution in later experiments.

Optimization of eluting solvent

Eluting is the crucial step in the solid-phase extraction process. It is required that the eluting solvents have sufficiently strong polarity and selectively toward analytes, so that the analytes can be eluted from the MISPE column and the impurities can be kept on MISPE column [28]. In this study, six kinds of eluting solutions with different polarity, such as hexane, acetonitrile, acetone, 10% acetic acid/methanol, ethyl acetate, were

investigated. As presented in Fig. 5, the recoveries of DEHP were all less than 90% when the MISPE column was eluted with hexane, acetonitrile, acetone, 10% acetic acid/methanol solution. While ethyl acetate eluted almost 100% of the loaded DEHP, this is attributed to their similar polarity. Therefore, ethyl acetate was selected as eluting solvent in all experiments.

Optimization of volume of eluting solvent

Amount of eluting solvent has important influence on enrichment factor of the analytes. To optimize the amount of eluting solvent, the effect of volume of eluting solvent on recovery of DEHP was discussed and the results were given in Fig. 6. It can be seen from Fig. 6 that recoveries increased as increasing volume of eluting solvent. When the MISPE column was eluted with 4 mL of ethyl acetate, recovery was 97.6%, indicating that more than 4 mL of ethyl acetate was sufficient to elute DEHP completely from the MISPE column. The less amount of volume of eluting solvent is, and the larger enrichment factor is. So, 4 mL of ethyl acetate was used as eluting solution in following experiments so as to improve enrichment factor of DEHP.

Selectivity of MISPE column

To verify the selectivity of the MISPE, DMP, DEP, DBP and DNOP were selected as the analogues of DEHP, and their recoveries on MISPE, NISPE and C18 column at the optimized extraction condition were investigated. As shown in Fig. 7, the recovery of DEHP on MISPE column was significantly higher than that of the four analogues on the MISPE column. Moreover, recoveries of DMP, DEP, DBP, DNOP and DEHP on both NISPE and C18 column was less than 56%, and was little different from each other. The results revealed that MISPE column have excellent selectivity for DEHP compared to NISPE and C18 column. This is because SMIP, used as adsorbents on the MISPE column, have spatial structure and binding sites matching with the DEHP, resulting in selective adsorption to DEHP. During the preparation of SMIP, DEHP was used as template molecular and fixed in the backbone of the polymer, after DEHP being eluted, the imprinting cavities and binding sites were thus formed in the MIP [29]. It was also found from Fig. 7 that the recovery of DEHP on the MISPE column (101.76%) was much higher than that on the

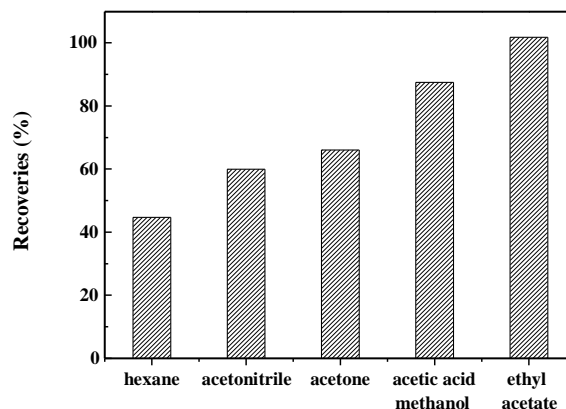


Fig. 5: Recoveries of DEHP in MISPE column eluted with different eluting solvent.

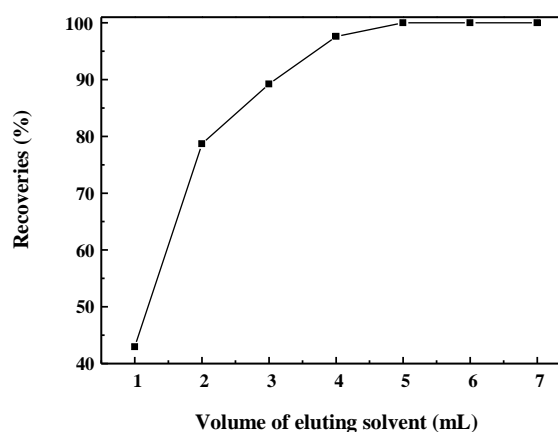


Fig. 6: Influence of volume of eluting solvent on recovery of DEHP.

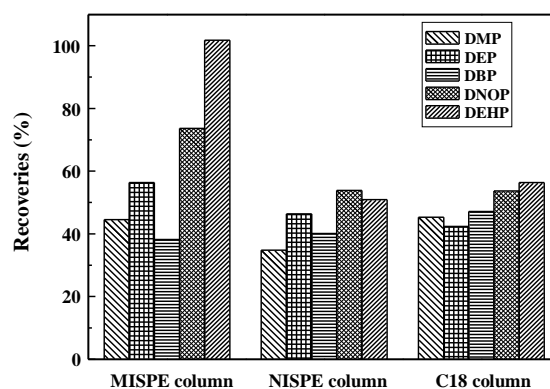
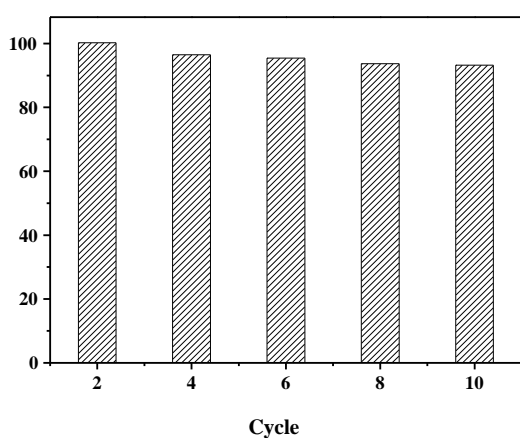


Fig. 7: Recoveries of DEHP and its analogues on MISPE, NISPE and C18 column.

Table 2: Recoveries of DEHP at various spiked level in environmental water samples.

Sample	Spiking level($\mu\text{g/L}$)	Recoveries(% , n=6)	RSD(% , n=6)	DEHP content($\mu\text{g/L}$)
River water	50	102.3	4.51	24.9
	200	99.7	4.07	
	600	97.3	3.94	
	1000	93.3	2.86	
Lake water	50	99.3	6.08	15.5
	200	96.6	5.86	
	600	94.2	5.19	
	1000	93.8	4.45	

**Fig. 5: Reusability of the MISPE column.**

traditional and commonly used C18 solid-phase extraction column (56.35%), which suggested that MISPE column is a desirable SPE column for extraction and enrichment of DEHP from complicated environmental samples

Reusability of MISPE column

The evaluation of reusability of the MISPE column was carried out and the results were given in Fig. 8. As seen from Fig. 8, the MISPE column was reusable, because the recoveries of DEHP were all more than 93% for reusability of ten times. It is suggested that spatial structure and binding sites matching with the DEHP was stable after generation process.

Application of MISPE to environmental water samples

Calibration curves were established by analyzing DEHP standard solution with various concentrations (0, 5, 10, 20, 40, 50, 80 and 100mg/L) to carry out a linear

regression analysis. The results showed that the linear relationship of the peak area and the concentration of DEHP were as follow: $y=2354.6x+1663.5$ with a good correlation coefficients ($R^2=0.9997$). RSD is 2.48% (n=6) at 10mg/L of DEHP, and the Limit Of Detection (LOD) and the Limit Of Quantification (LOQ) was estimated according to three times and ten times the Signal-to-Noise ratio (S/N) to be 0.012mg/L and 0.039mg/L, respectively.

In order to evaluate day-to-day reproducibility, three concentrations (5mg/L, 50mg/L, 100mg/L) of DEHP standard solution were analyzed for six consecutive days, and six replicates for each concentration were analyzed in the same day. Recoveries and RSD values within a day were calculated. The quite good recoveries (92.8-105.3%) were obtained in all cases, and similar RSD values (2.52-7.65%) were obtained among the days. The results demonstrate the high accuracy and good reproducibility.

To validate suitability and potential application of the MISPE for real environmental sample, a river water sample and a lake water sample was respectively spiked with different concentration of DEHP standard solution and processed by MISPE procedure. The spiked recoveries were listed in Table 2. It can be seen from Table 2 that the MISPE had high accuracy and precision with good recoveries from 93.3% to 102.3% and low RSD from 2.86 to 6.08, and the tested river and lake water sample contain DEHP of 24.9 and 15.5 $\mu\text{g/L}$. It is concluded that MISPE-HPLC method developed in this study was reliable and applicable for determination of trace DEHP in environmental water samples.

CONCLUSIONS

Surface molecularly imprinted polymer for selective adsorption of DEHP was successfully prepared by using silica gel modified by aminopropyltriethoxysilane and acryloyl chloride in a two-step method as support, DEHP as template, methyl acrylic acid as functional monomer and ethyleneglycol dimethacrylate as cross-linker. The Molecularly Imprinted Solid-Phase Extraction (MISPE) column was prepared with the SMIP as adsorbent. The recovery of DEHP on MISPE column was significantly higher than that of its analogues DMP, DEP, DBP, DNOP, and recovery of DEHP on MISPE column was obviously higher than that on commercial C18 column. The MISPE column was reusable. These results revealed that SMIP column can selectively extract and efficiently enrich DEHP in water sample. An analytical method MISPE-HPLC was developed in this study. Good precision and accuracy and low detection limit demonstrated the developed method was feasible for determination of trace DEHP in environmental water samples. The prepared SMIP provide a promising SPE adsorbent for selective extractions of DEHP.

Acknowledgement

This work was financially supported by Natural Science foundation of Jiangsu Province of China (NO. : BK2012272)

Received : Sep. 29, 2015 ; Accepted : Sep. 26, 2016

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