

# Supporting information

## **A new core-shell magnetic mesoporous surface molecularly imprinted composite and its application as MSPE sorbent for determination of phthalate esters**

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## 1. DMSPE-GC/MS determination process and Conditions Optimization

DMSPE procedure for the extraction of PAEs was as follows: 10 mg of magnetic sorbents were added to 10 mL of sample solution in the tube with plug. After the tube was sealed and vibrated for 6 min, the magnetic sorbents were separated by external magnetic field. Then the magnetic sorbents were ultrasonicated for 10 min with 1.0 mL chloroform to desorb the PAEs, and then the solutions were dried with 0.5 g of anhydrous sodium sulfate. After the composite was separated by external magnetic field, the remaining solution was filtered through a 0.22  $\mu\text{m}$  syringe-driven filter and put into a sample bottle for GC-MS analysis. The conditions of pretreatment were optimized as follows:

### 1.1 Optimization of MSPE dosage

Accurately weighed 3 mg, 5 mg, 10 mg, 15 mg and 20 mg of MSPE and added them to 10 ml of ultrapure water samples which contained 100  $\mu\text{g/L}$  of six kinds of PAEs respectively. According to the "DMSPE-GC/MS procedure", investigated the adsorption efficiency of different amounts of materials for PAEs, to select the amount of materials with the highest adsorption efficiency. The results of material dosage optimization are shown in Fig.S.1: when the dosage was 3-10 mg, the recovery increased almost linearly; The recovery remained stable at 10 - 15mg and decreased slightly at 15 mg~20 mg, which may be due to the volume of eluent can't completely elute the targets absorbed in the material.

Considering the saturated adsorption capacity of the material and the volume of eluent, 10mg material was selected as the best amount of MSPE.

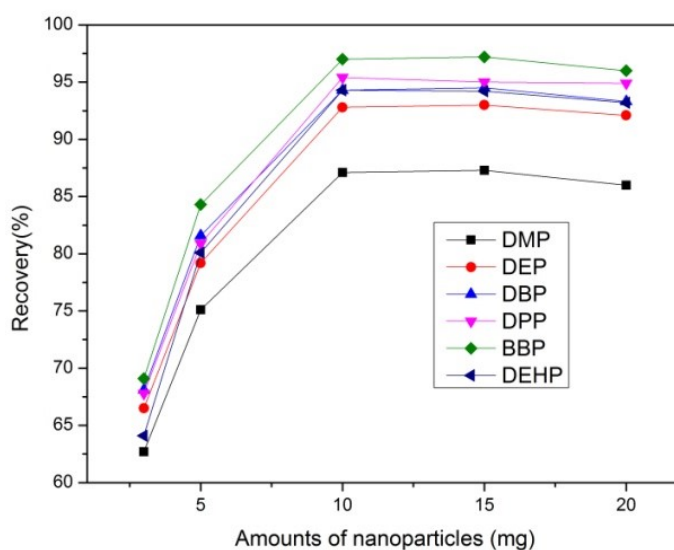


Fig.S.1. The effect of the amounts of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{mSiO}_2\text{-MIPs}$  nanoparticles

## 1.2 Optimization of the eluting solvent

Methanol, n-hexane and chloroform with different polarity and hydrophobicity were selected, and the amount of 1 ml solvent was used to elute PAEs, and their elution effects were compared. The elution efficiency of three different eluents is shown in Fig.S.2. The results showed that the elution effect of acetonitrile was slightly higher than that of methanol, and the elution effect of chloroform was the best, so chloroform was used as eluent.

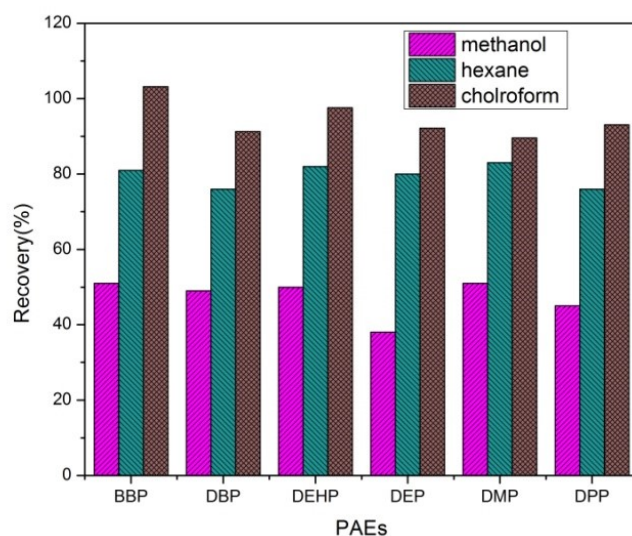


Fig.S2. Optimization of the eluting solvent

## 1.3 Optimization of eluent dosage

10 mg  $\text{Fe}_3\text{O}_4@\text{SiO}_2@m\text{SiO}_2$ -MIPs was added to 10 ml of ultrapure water samples which contained 100  $\mu\text{g/L}$  of six kinds of PAEs respectively. After shaking for 6 min, the material was magnetically separated, and the upper water phase was discarded. Chloroform with good elution effect reported in literature was selected as eluent, and 0.5 mL, 0.8 mL, 1.0 mL, 1.5 mL and 2.0 mL chloroform was used to elute the target substance respectively. After ultrasonic elution for 10 min, add 0.5 g anhydrous sodium sulfate to remove excess water. The organic phase was removed, filtered with 0.22  $\mu\text{m}$  membrane and analyzed. The results are shown in Fig.S.3. High recoveries were obtained with 1.0 mL and 1.5 mL chloroform. From the perspective of economic and environmental protection and to meet the needs of elution effect, 1.0 mL of chloroform was selected as the amount of eluent.

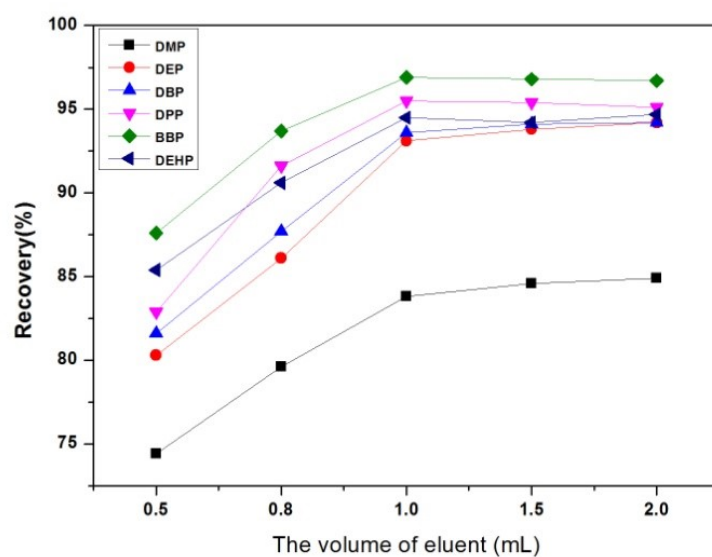


Fig.S.3. The effect of eluent dosage on extraction efficiencies

#### 1.4 Optimization of elution time

The elution time was investigated, and the samples were eluted by ultrasound for 3 min, 5 min, 10 min, 12 min and 15 min respectively. The results are shown in Fig.S.4. The experimental results showed that the recovery of each component increased with the increase of elution time at 3-10 min. At 10 min, the recoveries of the other five PAEs were above 90% except for DMP. Therefore, 10 min was chosen as the elution time.

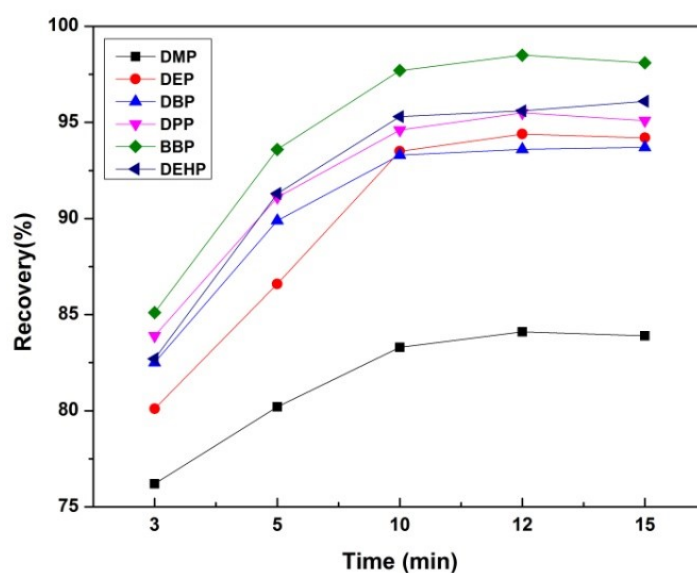


Fig.S.4. The effect of eluent time on extraction efficiencies

### 1.5 Optimization of pH value

10 mg  $\text{Fe}_3\text{O}_4@\text{SiO}_2@m\text{SiO}_2$ -MIPs was added to 10 ml of ultrapure water samples which contained 100  $\mu\text{g/L}$  of six kinds of PAEs respectively. Adjusted the pH value of the solution to 3, 5, 7, 8 and 9 (adjusted with hydrochloric acid and sodium hydroxide) and observed the change of the recovery of PAEs to optimize the best pH value. The results were shown in Fig.S.5: There was no significant difference in the recovery under different pH value, which showed that the elution process was not affected by pH value. Therefore, in order to simplify the experimental process and approach the real sample's condition (beverages and wines), we chose pH = 7 as the optimal condition.

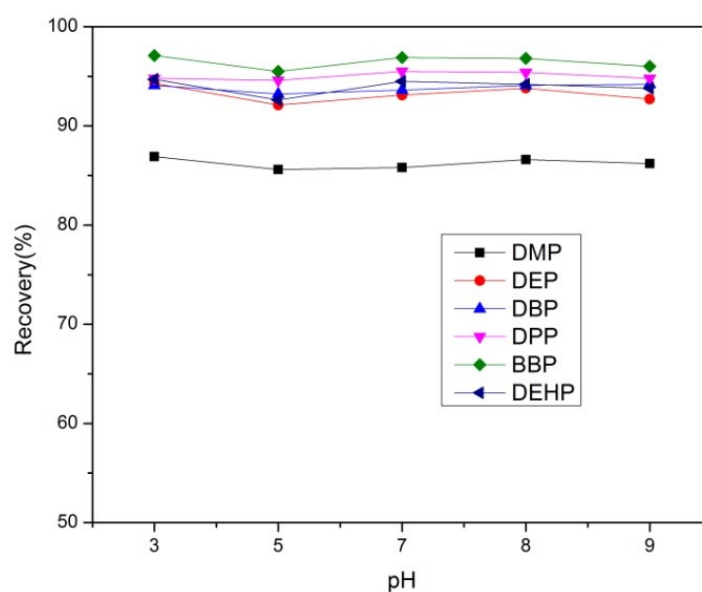


Fig.S.5. The effect of sample pH on extraction efficiencies

## 2. The fitting processes of adsorption kinetic models

Table S.1. Kinetic constants for the pseudo-first-order model and pseudo-second-order model

	Pseudo-first-order		Pseudo-second-order	
	$K_1(\text{min}^{-1})$	$R^2$	$K_1(\text{min}^{-1})$	$R^2$
$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{mSiO}_2\text{-MIPs}$	0.31118	0.34716	0.002384	0.9971
$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{mSiO}_2\text{-NIPs}$	-0.2382	0.58571	0.001842	0.99672

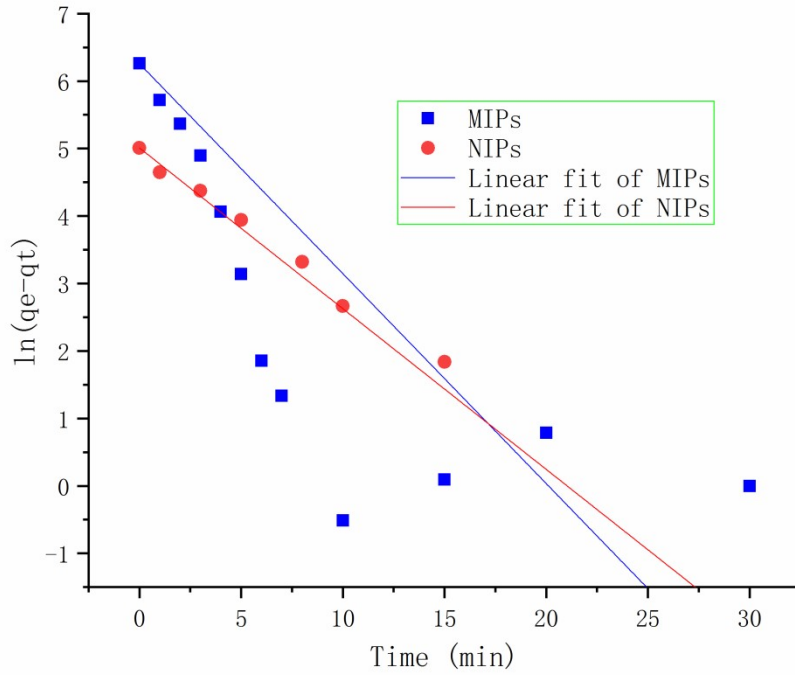


Fig.S.6. First-order kinetics model

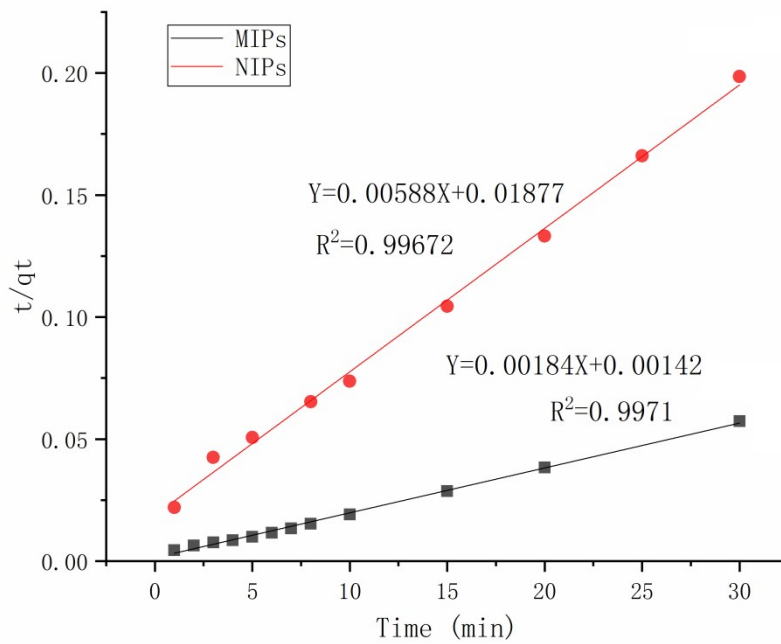


Fig.S.7. Second-order kinetics model

### 3. The fitting processes of isotherm kinetic models

Table S.2. Adsorption isotherm constants for Langmuir and Freundlich equations

	Langmuir			Freundlich		
	$Q_m$	$K_L$	$R^2$	$m$	$K_F$	$R^2$
$Fe_3O_4@SiO_2@mSiO_2$ -MIPs	598.1391	0.02295	0.94389	73.82336	-0.33897	0.84257
$Fe_3O_4@SiO_2@mSiO_2$ -NIPs	174.37625	0.00909	0.96467	15.23225	-0.35393	0.93768

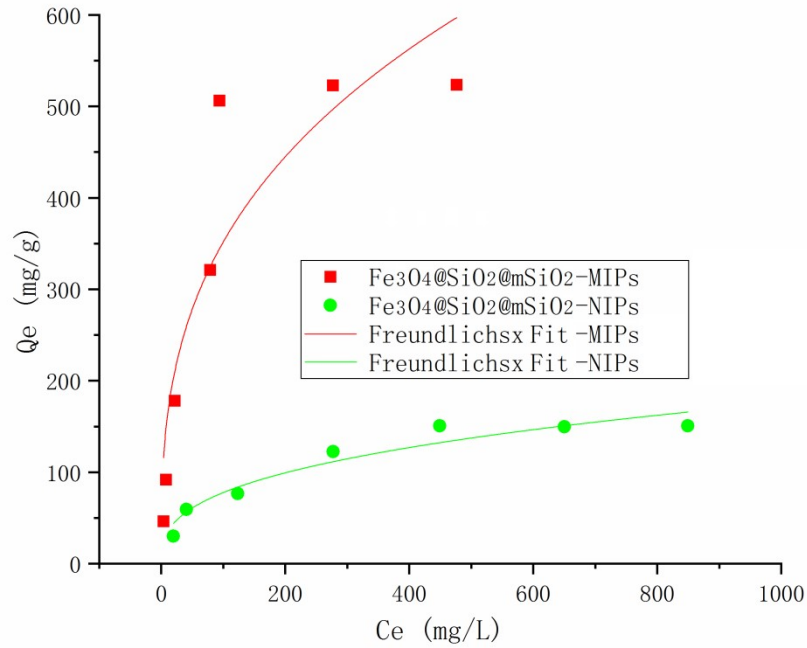


Fig.S.8. Fitted adsorption isotherms with Freundlich model simulation

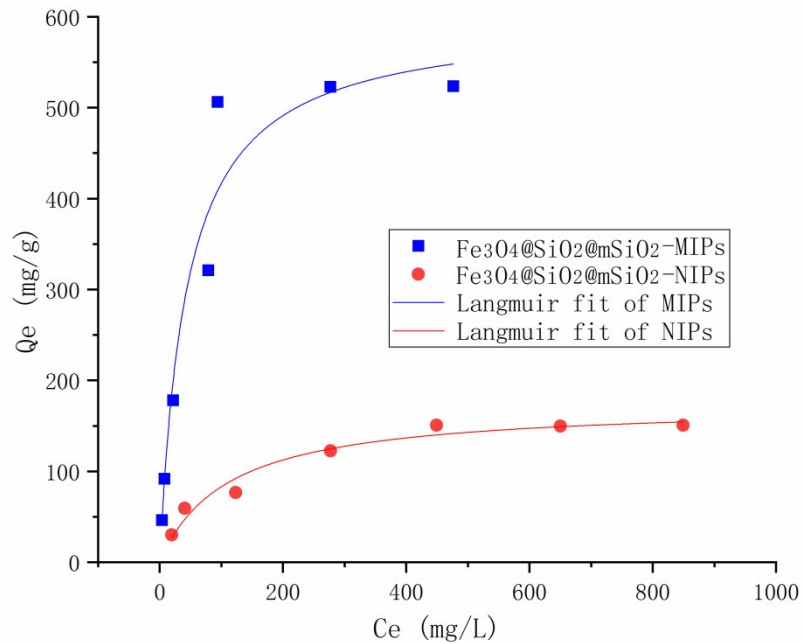


Fig.S.9. Fitted adsorption isotherms with Langmuir model simulation

4. Typical chromatograms of the mixed six PAEs standard solution (5.00  $\mu\text{g/mL}$ ).

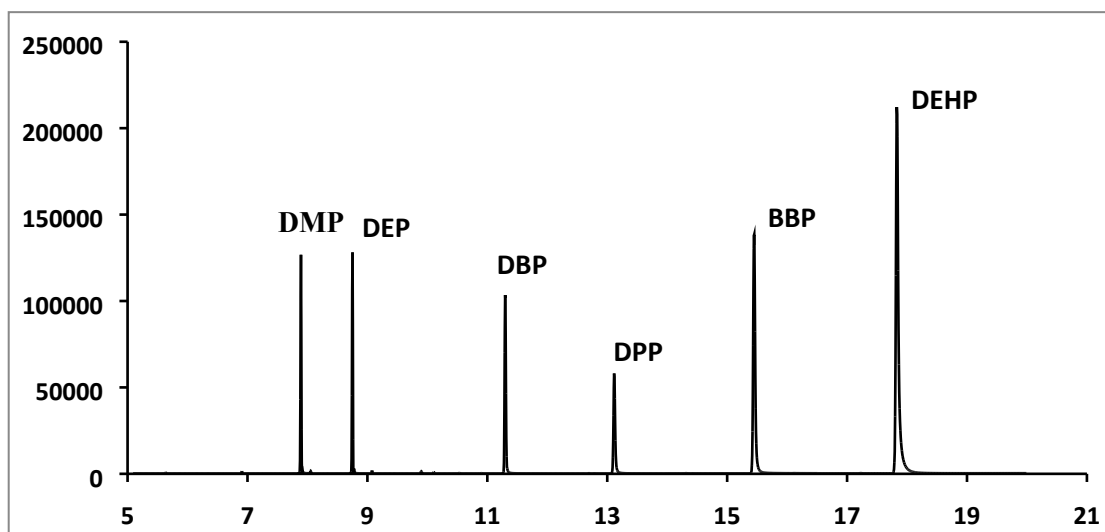


Fig.S.10. Typical chromatograms of the mixed six PAEs standard solution (5.00  $\mu\text{g/mL}$ ).