



# A sensitive and selective molecularly imprinted sensor combined with magnetic molecularly imprinted solid phase extraction for determination of dibutyl phthalate



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## ABSTRACT

A highly sensitive and selective molecularly imprinted (MIP) sensor combined with magnetic molecularly imprinted solid phase extraction (MMISPE) was developed for the determination of dibutyl phthalate (DBP) in complex matrixes. The magnetic molecularly imprinted polymer (MMIP) was synthesized as solid phase extraction (SPE) sorbent to extract DBP from complex matrixes and as sensing element to improve the selectivity of the imprinted sensor. The morphologies of MMIP and MIP-sensor were characterized by using scanning electron microscope (SEM) and transmission electron microscopy (TEM). The electrochemical performances of MIP-sensor were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The conditions of preconcentration, elution and electrochemical determination were studied in detail. Under the optimized experimental conditions, the response currents of the MIP-sensor exhibited a linear relationship towards DBP concentrations ranging from  $1.0 \times 10^{-8}$  g/L to  $1.0 \times 10^{-3}$  g/L. The limit of detection of the MMIP-sensor coupled with the MMISPE was calculated as 0.052 ng/L. The MMIP-sensor coupled with the MMISPE was applied to detect DBP in complex samples successfully.

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## 1. Introduction

Dibutyl phthalate (DBP) is extensively used as plasticizer in polyvinyl chloride plastics to improve its flexibility and plasticity. Other applications including nail polishes, paper coatings, dental materials, pharmaceuticals, and plastic food wraps have also been reported (Harris et al., 1997). Nevertheless, DBP has adverse effects on human health, which are regarded as endocrine disrupting compounds by means of their carcinogenic action (Naarala and Korpi, 2009). Since DBP is fat soluble component, it may be introduced into our food chains when foods, beverages and drinking waters are packed into plastic containers. Thus, it is significant to detect DBP in those complex matrixes. Indeed, several analytical methods have been successfully proposed for the determination of DBP in complex samples involving fluorescence (Zhang M.C. et al., 2006), high performance liquid chromatography (HPLC) (Castillo and Barceló, 2001), and gas chromatography (GC) (Gómez-Hens and Aguilar-Caballos, 2003). However, some of these techniques suffer from various drawbacks involving labor-intensive sample preparation,

expensive analysis settings and poor selectivity. Therefore, it is necessary to establish a new method with simplicity, high selectivity and sensitivity for determination DBP in complex samples.

Solid phase extraction (SPE) is a significant separation and preconcentration technique to reduce the influence of interferences with advantages of simplicity, low cost, and ease of use. Furthermore, it can be combined with determination technique easily involving HPLC, capillary electrophoresis, and electrochemical sensor to detect the trace amount component in complex matrixes (Junko, 2001; Bhim et al., 2007; Liu et al., 2011; Puig et al., 2007). Among these determination techniques, electrochemical sensor showed attractive advantages of simple, sensitivity, and label-free to analyze molecules in complex matrixes (Junko, 2001; Bhim et al., 2007). Thus, electrochemical sensor can be considered as a potential determination technique for DBP in complex matrixes. However, there are also several problems involving non-specific binding, low mass transfer, poor regeneration and limited response for electrochemical sensor application. Fortunately, these problems can be overcome by using highly selective sensing materials. Molecularly imprinted polymer (MIP) is one of these ideal sensing materials.

Molecularly imprinted polymer (MIP), which is prepared in presence of the template molecule, showed highly specific recognition performance toward the template molecule (Ellen et al., 2011;

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Chen et al., 2011). Up to now, MIP has been developed for the recognition of target environmental pollutants involving plasticizers, bisphenol A and peptides (He et al., 2010a; Dahlia et al., 2011; Stefan et al., 2011). As a novel imprinted polymer, magnetic molecularly imprinted polymer (MMIP), which can be isolated easily from samples by using an external magnetic field without complicated centrifugation or filtration step, is generally used to simplify the SPE steps and enhance the sensitivity of electrochemical sensor. Moreover, the MMIP showed great potential in the fields of biomedical and environmental applications because of their good biocompatibility, low toxicity and strong superparamagnetic property (Zhu et al., 2010; Zhang Z.C. et al., 2006; Gai et al., 2010; Jing et al., 2010). Researches on the application of MMIP in electrochemical sensors or SPE have been reported (Gai et al., 2010; Zhang et al., 2009; Hu et al., 2011). However, few papers on MMIP sensor combined with MMIP-SPE (MMISPE-MMIP sensor) by using MMIP both in SPE and electrochemical sensor were reported for separation and detection of DBP in complex matrixes.

In this work, we focused on development of a highly sensitive and selective MIP sensor combined with MMIP-SPE for the determination of DBP in complex matrixes. The electrochemical performances of MIP sensor were investigated by various electrochemical techniques in detail. The results showed that the combination of MMIP sensor and MMIP-SPE exhibits convenient, low cost, excellent selectivity and sensitivity for the determination of DBP. The proposed method was successfully employed to detect DBP in complex samples.

## 2. Experimental

### 2.1. Chemicals and apparatus

Methacrylic acid (MAA), ethyleneglycol dimethacrylate (EGDMA) and azodiisobutyronitrile (AIBN) were obtained from Beijing Chemical Reagent Company (Beijing, China). Dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP) and dioctyl phthalate (DOP) were obtained from Sinopharm Chemical Reagent Company (Shanghai, China). Iron (II) chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) and ammonium hydroxide ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ , 25%, w/w) were purchased from Shanghai Chemical Reagent Company (Shanghai, China). Chitosan, methanol and ethanol were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Vinyltriethoxysilane (VTES) and tetraethoxysilane (TEOS) were supplied by Hubei Wuda Organic Silicone Materials Co., LTD. (Hubei, China). All the other materials were of analytical grade. Redistilled water was used in all experiments.

Electrochemical measurements were performed using a CHI660B electrochemical workstation (Shanghai Chenhua Company, China) connected to a personal computer. A three-electrode system consisted of a bare or modified carbon working electrode, a saturated calomel reference electrode (SCE) and platinum counter electrode. Electrochemical experiments were conducted in an electrochemical cell containing 10 mL of 0.01 mol/L  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  and 0.1 mol/L phosphate buffer solution (PBS, pH 6.0). Scanning electron microscope (SEM, JSM-6700F) and transmission electron microscopy (TEM, JEM1010) were performed to characterize the morphologies of modified carbon electrodes. Vibrating sample magnetometer (VSM, M27407) was conducted to study the magnetic properties of the MMIP.

### 2.2. Preparation of nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2$

$\text{Fe}_3\text{O}_4$  nanoparticles (nano- $\text{Fe}_3\text{O}_4$ ) were prepared as previous study (Liu et al., 2005). Briefly, 6.48 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 2.26 g of

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were dissolved in 36 mL of 1.0 mol/L HCl solution under  $\text{N}_2$  atmosphere with mechanical stirring (800 rpm). Then, the obtained clear yellowish-green solution was added into 50 mL of ammonia solution (25%, v/v) under  $\text{N}_2$  atmosphere. After 30 min, the black nano- $\text{Fe}_3\text{O}_4$  was collected with help of an external permanent magnet. Finally, the nano- $\text{Fe}_3\text{O}_4$  was washed several times with ethanol and suspended in ethanol solution to obtain 5 g/L nano- $\text{Fe}_3\text{O}_4$  suspension.

Aqueous ammonia (4.5 mL), redistilled water (3.75 mL) and TEOS (0.1 mL) were added into 40 mL of nano- $\text{Fe}_3\text{O}_4$  suspension. The silica coated  $\text{Fe}_3\text{O}_4$  nanoparticles (nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2$ ) were obtained after vortex mixing for 10 h. Next, 150  $\mu\text{L}$  of vinyltriethoxysilane was dispersed into 40 mL of redistilled water containing 10% acetic acid under mechanical stirring (700 rpm) for 5 h. Then 250 mg of nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2$  was added into the above solution and the mixture solution was incubated at 60 °C for 5 h. Finally, the resulting product was obtained with the help of an external magnetic separation and washed with redistilled water to remove unreacted chemicals.

### 2.3. Preparation of MIP/nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2$

DBP-imprinted polymer based on nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2$  (MIP/nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2$ ) was prepared by the following procedure. First, 0.52 g of MAA and 0.28 g of DBP were mixed in 30 mL of ethanol under sonication for 30 min. Then 6.0 g of EGDMA and 0.02 g of AIBN were added dropwise into the mixture. The mixture was degassed and purged with nitrogen for 10 min. Subsequently, 0.25 g of nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2$  was added into the mixture solution and sonicated for 30 min. The mixture was incubated overnight at 60 °C. In the control experiment, the non-imprinted polymers (NIP/nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2$ ) were prepared in the same procedure without addition of the template molecule. The product was washed thoroughly with a mixture of methanol and acetic acid (volume ratio 6:1) and redistilled water for three times to elute the template DBP. Finally, these polymers were dried in an oven at 60 °C for 12 h.

### 2.4. Preparation of MIP/nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{CE}$

Prior to modification, carbon electrode was polished carefully to a mirror-like surface with 0.3, 0.1 and 0.05  $\mu\text{m}$  of alumina aqueous slurry and then washed successively in an ultrasonic cleaner with redistilled water and ethanol, respectively. Then, the bare carbon electrode was scanned with cyclic voltammetry (CV) in the potential range of  $-0.8 \sim +0.8$  V in phosphate buffer solution (PBS, 0.1 mol/L, pH 6.0) containing with 0.01 mol/L  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  until a pair of defined redox peaks were observed.

A 1.0% m/m chitosan stock solution was prepared by dissolving 200 mg of chitosan powder into 20 mL of 1.0% v/v acetic acid solution and sonicated for 15 min at room temperature. (Notice: Chitosan solution was stored under refrigeration at 4 °C when it was not in use.) Next, 10 mg of DBP-imprinted nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2$  was dispersed in 2.0 mL of 1.0% m/m chitosan containing 1.0% v/v acetic acid. Then 200  $\mu\text{L}$  of the MIP/nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2$  suspension was spreaded on the surface of carbon electrode and dried overnight to obtain the DBP-imprinted nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2$  modified carbon electrode (MIP/nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{CE}$ ). The nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2$  modified electrode (nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{CE}$ ) was prepared by spreading the dispersion of nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2$  onto a carbon electrode.

### 2.5. MMIP-sensor determination system coupled with MMISPE

For extraction and preconcentration of the analytes in complex samples, 20 mg of MIP/nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2$  and 20 mL of samples were mixed for 15 min into a 20-mL centrifuge tube. After equilibrium, the MIP/nano- $\text{Fe}_3\text{O}_4/\text{SiO}_2$  was isolated with the help

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