Computer assisted preparation and adsorption properties of electrospinning imprinted nanofibers

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Abstract. Dimethyl phthalate (DMP) was used as template molecule to prepare dimethyl phthalate imprinted polymer. The difference of characterization between MINFs and NINFs was analyzed by infrared spectroscopy (FTIR) and scanning electron microscope (SEM). The adsorption performance of imprinted nanofibers was studied through static experiment, isothermal experiment, and selective experiment, respectively. Simultaneously, the nanofibers was applied to analysis for water samples as packing material for solid phase columns. The results of adsorption kinetics showed that MINFs had high sensitivity and selectivity. MINFs showed better binding capacity than NINFs. The maximum binding capacity of MINFs was $4.6 \times 10^{-2}$ mmol/g, and that of NINFs was $2.6 \times 10^{-2}$ mmol/g. Solid phase extraction (SPE) was used to detect the concentration of DMP in real water samples, the recovery rate reaches 99.45%.

Keywords: Dimethyl phthalate, Molecular imprinting, Electrospinning, Adsorption property

1. Introduction

With the inspiration of specific molecular recognition between antigens and antibodies in nature, the template molecule recognition site was introduced into the polymer materials. Molecularly imprinted technology (MIT) was a superior technology used to identify specific chemical substances [1]. Take the target molecule as a template, polymerized through cross-linking reaction, and then remove small molecules, the generated three-dimensional imprinted hole structure can match the spatial structure and binding site of the specific target molecule, thereby, based on this principle, obtained molecularly imprinted materials with predetermined selectivity [2-3].

Dimethyl phthalate (DMP) was used as a plasticizer in the synthetic materials, accounted for about 70% of all plasticizer consumption. The environmental estrogens of plasticizers were released into the environment and accumulated in the human body, threaten health of humans and other creatures [4-5]. At present, the detection methods related to DMP include ultraviolet spectrophotometry, high-performance liquid phase chromatography, liquid-mass spectrometry, etc. But there are many problems such as: the amount of released in the environment was very small, the environmental matrix was complex, and there had many interfering components, which were difficult to be enriched and detected. Solid phase extraction was an efficient and simple methods of enrichment [6]. The imprinted molecules
filled in the extraction column had special recognizability and can also enrich trace analytes effectively, which improved corresponding detection accuracy [7-8]. At present, there are few reports about the preparation and application of DMP imprinted fibers in water environment detection. In this article, Dimethyl phthalate imprinted nanofibers were synthesized through molecularly imprinted technology, the characterization and performance were studied, the nanofibers were applied to water sample analysis as packing material for solid phase columns. The results showed that molecularly imprinted nanofibers had high sensitivity and selectivity. Compared to non-imprinted fibers, the imprinted nanofibers showed better binding capacity and better results when applied to water samples analysis.

2. Experiment

2.1. Reagents and Instruments
N, N-Dimethylformamide (DMF) was purchased from Tianjin Bodi Chemical Co. LTD. Dimethyl Phthalate (DMP) was purchased from Tianjin Fuchen Chemical Co.LTD. Ethanol and Methanol were purchased from Jiangsu Qiangsheng Functional Chemical Co.LTD. Diisooctyl Phthalate (DIOP) was purchased from Shanghai Zhanjun Chemical Co.LTD. Diethyl Phthalate (DEP) was purchased from Aladdin reagent Co. LTD. Polyethersulfone Resin (PES, Purity> 99.5%) was purchased from Sinopharm reagent Co. LTD. Methanol (Chromatographic Pure) was purchased from Shanghai Ling Feng Chemical Reagent Co.LTD. Dioctyl phthalate (DOP) was purchased from Wuxi Yatai Chemical Co.LTD.

HPLC analysis was performed on LC-2010A high performance liquid chromatography, Shimadzu Corporation, Japan. Infrared spectra were recorded on Nicolet Nexus 470 Fourier transform infrared spectrometer, Nicolet Corporation, USA. Scanning electron microscope (SEM) images were taken with a JSM-7001F Scanning Electron Microscope, JEOL Co.LTD.

2.2. Preparation of molecularly imprinted nanofibers
Weighed about 2.5g of PES and placed it in a beaker, added the mixed solution of 210μL DMP and 10mL DMF, heated in a water bath, stirred until dissolved to obtain molecularly imprinted spinning solution. Put the prepared spinning solution into a glass syringe, fixed it on the micro-infusion pump, cut a piece of aluminum foil paper of appropriate size, and fixed it on the receiving plate to receive the electrospun fibers. The positive electrode was connected with the needle of the glass injection. One end of the negative electrode was fixed on the receiving plate, the plate spacing was controlled at about 20cm, the positive voltage was adjusted to 14.25 kV, and the negative voltage was adjusted to 2.25 kV to start spinning to prepare molecularly imprinted nanofibers.

The prepared molecularly imprinted nanofibers were wrapped with filter paper and placed in a soxhlet extractor, using methanol:acetic acid(9:1,V:V) as the extractant, and extracted for 72 hours at 60° C under the condition of a constant temperature water bath, vacuum dried for use.

As a control, non-imprinted nanofibers (NINFs) were prepared similar to molecularly imprinted nanofibers except DMP was omitted.

2.3. Characterization of imprinted materials
2.3.1. Scanning electron microscope analysis. The structure of surface molecularly imprinted polymers had a greater impact on the adsorption performance. In this paper, the internal structure of molecularly imprinted nanofibers (MINFs) and non-imprinted nanofibers (NINFs) were characterized by scanning electron microscopy.
It can be clearly observed from the figure that both MINFs and NINFs scanning electron microscopy images had obvious silk structures, with a diameter of about 500-800nm, smooth surface, uniform thickness, and tightly arranged.

2.3.2. **Infrared analysis.** To characterize imprinted polymers, molecular imprinted nanofibers (MINFs) and non-imprinted nanofibers (NINFs) were detected by infrared spectroscopy, as shown in Figure 3. Observed from the figure, it was found that the difference in the infrared spectrum was not obvious. The characteristic peak at 1737cm⁻¹ or 1738cm⁻¹ was the stretching vibration peak of the C=O bond in the carboxyl group. 1157cm⁻¹ or 1164cm⁻¹ was the stretching vibration peak of C-O and C-C.1446cm⁻¹ or 1445cm⁻¹ and 920 cm⁻¹ were produced by the deformation stretching vibration of the O-H bond in the carboxyl group in the polymer, 1153.24cm⁻¹ was O=S=O symmetric stretching vibration doublet.
2.4. Adsorption experiment

2.4.1. Formulation of DMP standard curve. Prepared 0.01-0.10mmol/L and 0.1-0.5mmol/L DMP solutions respectively, measured the absorbance at the characteristic peak at 280nm, and drew a standard curve. The standard curve equation was $y=0.00131+1.40671x$, the correlation coefficient was 0.99894 in Figures 4, and $y=0.00672+1.33266x$, the correlation coefficient was 0.99958 in Figures 5.
2.4.2. Static adsorption experiment. Accurately weighed twelve groups of 25mg NINFs and MINFs respectively into a 50ml beaker, added 25mL of 0.08mmol/L DMP standard solution, placed in a constant temperature incubator, and shook at room temperature 25°C and rotation speed 150 rpm. At 20min, 40min, 1h, 2h, 3h, 4h, 5h, 8h, 12h, 20h, 24h, 36h, 48h, took sample 50μL respectively, filtered with 0.22μm filter membrane, and measured the absorbance at each sampling point, Measured the concentration of the target substance according to the standard curve, and investigated the adsorption kinetics of molecularly imprinted nanofibers on DMP.

Determined the change value of the solution concentration before and after adsorption, and calculated the binding capacity to the substrate according to formula (1).

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Q = \frac{(C_0 - C) \times V}{m}
\]

Q: binding capacity (mg/g).
C₀: concentration of substrate in solution before adsorption (mg/mL).
C: concentration of substrate in solution after adsorption (mg/mL).
V: volume of adsorption solution (mL). Take the average of three parallel determinations.
m: mass of nanofibers (g).

2.4.3. Isothermal adsorption experiment. Prepared different concentrations of DMP (0.02mmol/L, 0.04 mmol/L, 0.06 mmol/L, 0.08mmol/L, 0.10 mmol/L and 0.15mmol/L, 0.2mmol/L, 0.25mmol/L, 0.3mmol/L) Adsorption solution, each take 25mL, add 0.025 mg molecular imprinted nanofibers membrane, and perform adsorption experiments under the conditions of 298K, 308K, 318K and 328K, respectively. When the adsorption reached equilibrium, the concentration of DMP in the solution was measured and the adsorption capacity of nanofibers was calculated.

2.4.4. Selective adsorption experiment. The 0.2mmol/L DMP, DEP, DOP and DIOP solutions were prepared respectively, and the molecularly imprinted nanofibers with or without template were put into the corresponding four solutions. After 6 hours, the supernatant was taken and the UV was measured to obtain the corresponding absorbance, the equilibrium concentration was obtained from the standard curve.
2.5. Solid phase extraction of water sample

The imprinted nanofibers are used to fill a solid phase extraction column, and the prepared and eluted imprinted nanofibers membrane was cut into a suitable size to make a fiber column. The fiber column was first wetted and eluted with methanol/water solution in a volume ratio of 1:1, and then washed with pure water to remove residual methanol. The simulated water samples of DMP with different concentrations of 0.20μmol/L, 0.50μmol/L, 1.00μmol/L, 1.50μmol/L, 2.00μmol/L, passed through the solid phase extraction column. Methanol was used for elution, and the absorbance of the eluted solution was measured by ultraviolet, and the DMP concentration was obtained from the standard curve.

3. Results and discussion

3.1. Study on adsorption performance

3.1.1. Static adsorption analysis. Drew the adsorption kinetic curve. As shown in Figure 6, MINFs and NINFs had an obvious upward trend in the first 24 hours, indicated that the amount of adsorption gradually increased with the increase of adsorption time. After 24 hours, it tended to be smooth. When the maximum binding capacity was reached, and the adsorption capacity in the first 2h rises linearly, which fully indicated that the adsorption rate was very fast. The adsorption rate slowed down after 2h. However, it was obvious that the binding point of MINFs was higher than that of NINFs, so the binding effect of the template was better than that of the non-template.

The static adsorption method was used to determine the adsorption capacity of MINFs and NINFs on DMP. Both the adsorption capacity of MINFs and NINFs on DMP increased with the increase of adsorption time, but the adsorption capacity of MINFs was larger. The specific recognition site can specifically recognize DMP through hydrogen bonding and spatial matching, so it had a greater adsorption capacity for DMP.

![Figure 6. The relationship between DMP binding amount and time](image)

3.1.2. Isothermal adsorption analysis. As shown in Figure 7, the adsorption capacity of the template molecule DMP by the molecularly imprinted nanofibers was different at different temperatures. As the temperature increases, the adsorption capacity of the adsorption medium on the target molecule decreases. At the same time, the higher the concentration, the stronger the adsorption capacity. The
concentration reached equilibrium at 0.2 mmol/L, which were 0.256 mmol/g, 0.247 mmol/g, 0.218 mmol/g, 0.176 mmol/g, respectively.

Figure 7. Effect of temperature on DMP adsorption

3.1.3. Selective adsorption analysis. As shown in Figure 8, the binding capacity of MINFs was higher than the binding capacity of NINFs. MINFs can also adsorb DIOP, DOP and DEP to a certain extent, but it adsorbed very little compared with DMP. Therefore, compared with the other three structural analogs, DMP had the best adsorption capacity. The imprinted pores of MINFs can be complementary to the three-dimensional structure of the target substance, coupled with the role of specific functional groups, so the adsorption capacity of MINFs to template molecules was higher than that of compounds with similar spatial structures.

Figure 8. Binding amount of different substances on imprinted polymer and blank polymer
3.2. Solid phase extraction of water samples

The imprinted nanofibers were applied with water samples for solid phase extraction, the detection wavelength was 277nm, and methanol was the blank control solution. The results were shown in Table 1. It can be seen from the solid phase extraction efficiency that the extraction effect was better, the recovery rate was 99.45%, and the relative error of the experiment was very small, indicated that the effect of using molecularly imprinted polymers as SPE was better and can be greatly improved.

| Concentration of sample (μmol/L) | Concentration of determination (μmol/L) | Recovery rate (%) | RE (%) |
|----------------------------------|----------------------------------------|-------------------|--------|
| 2.00                            | 1.989                                  | 99.45             | 0.19   |
| 1.50                            | 1.488                                  | 99.2              | 0.11   |
| 1.00                            | 0.997                                  | 99.7              | 0.09   |
| 0.50                            | 0.497                                  | 99.4              | 0.18   |
| 0.20                            | 0.198                                  | 99                | 0.20   |

4. Conclusion

DMP imprinted nanofibers with uniform distribution and better dispersion were prepared by electrospinning technology. Three adsorption experiments were used to study adsorption kinetics, thermodynamics and adsorption specificity. The results of adsorption experiments showed that MINFs had better adsorption performance than NINFs. The adsorption capacity of the template molecule DMP by the molecularly imprinted nanofibers were different at different temperatures. As the temperature increased, the adsorption capacity of the target molecule by the adsorption medium decreased. Through selective adsorption of the structural analogues of DMP (dioctyl phthalate, disoioctyl phthalate and diethyl phthalate), it was found that MINFs preferentially adsorb the template molecule DMP, and the adsorption amount was larger, when it was applied for actual water sample analysis, the recovery rate reached 99.45%, which improved the sensitivity of detection.

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