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Magnetic dummy molecularly imprinted polymers based on multi-walled carbon nanotubes for rapid selective solid-phase extraction of 4-nonylphenol in aqueous samples

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ABSTRACT

In this paper, a highly selective sample clean-up procedure combining magnetic dummy molecular imprinting with solid-phase extraction was developed for rapid separation and determination of 4-nonylphenol (NP) in the environmental water samples. The magnetic dummy molecularly imprinted polymers (mag-DMIPs) based on multi-walled carbon nanotubes were successfully synthesized with a surface molecular imprinting technique using 4-tert-octylphenol as the dummy template and tetraethylorthosilicate as the cross-linker. The maximum adsorption capacity of the mag-DMIPs for NP was 52.4 mg g^{-1} and it took about 20 min to achieve the adsorption equilibrium. The mag-DMIPs exhibited the specific selective adsorption toward NP. Coupled with high performance liquid chromatography analysis, the mag-DMIPs were used to extract solid-phase and detect NP in real water samples successfully with the recoveries of 88.6–98.1%.

1. Introduction

Endocrine disrupting chemicals (EDC) are a kind of environmental exogenous chemicals including synthetic substances and naturally occurring hormones, which impair the normal function of the endocrine system of both wildlife and humans [1]. 4-nonylphenol (NP), a degradation product of nonylphenol ethoxylate used as nonionic surfactants in a variety of industrial and agricultural processes, has been identified in environmental compartments [2,3]. Currently, chromatographic methods involving high performance liquid chromatography (HPLC) and gas chromatography coupled with mass spectroscopy (GC–MS) have been used for the identification and quantification of NP [4,5]. While the key step of the chromatographic analysis method is efficient enrichment and extraction of traces of NP residues from complicated samples.

Molecular imprinting is a method for preparing an imprinted polymer with highly selective binding capacity toward the template [6]. Molecular imprinting coupling solid-phase extraction (SPE) has become the frequently used technique in enrichment and extraction of the trace analysis [7]. Qi et al. successfully synthesized 2, 4-dimethylphenol molecularly imprinted polymers for solid-phase selective extraction and enrichment traces of phenolic compounds in environmental water [8]. Guerreiro et al. prepared nonylphenol imprinted polymer for pre-concentration of nonylphenol from water samples coupled with HPLC [9]. However, complicated pretreatments, such as filtration and centrifugation, are required by applying these traditional MIPs. Recently, magnetic molecularly imprinted polymers (mag-MIPs) have attracted considerable attentions attributing to the fact that they not only exhibit specific selective binding for the template molecule, but also have outstanding magnetism [10]. Thus, the mag-MIPs can be isolated easily from samples with an external magnet without centrifugation or filtration step [11]. Currently, magnetic imprinted solid-phase extraction (M-SPE) has been the most accepted sample pretreatment method for the extraction and preconcentration of analytes in field of environmental, food and biological samples because of its convenience, time saving and simplicity [12]. Furthermore, M-SPE combined with chromatographic detection technology easily detects traces of endocrine disrupting chemicals in complex matrixes [13]. Although many mag-MIPs have been synthesized by different methods involving suspension polymerization, emulsion polymerization and surface imprinting polymerization [14,15], the use of mag-MIPs still faces challenges such as the template leakage, low binding capacity and slow mass transfer. To solve these problems, a dummy imprinting technique was developed to avoid the leakage of the template molecules [16].

In this study, novel magnetic dummy molecularly imprinted polymers (mag-DMIPs) based on multi-walled carbon nanotubes

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(MWNTs) were successfully synthesized using 4-tert-octylphenol (PTOP) as the dummy template by a surface imprinting technique for extraction and enrichment of 4-nonylphenol (NP) in aqueous samples. The MWNTs have been expected as an alternative surface imprinted support material due to their intriguing nanoscale dimensions, high specific surface area, mechanical strength, and chemical stability [17]. Thus, most recognition sites were situated at the surface of the imprinted complicated materials, which resulted in the target molecules faster to be rebound and easier to be removed [18]. Used as M-SPE adsorbents, the mag-DMIPs were separated via an external magnet easily, avoiding the steps of packed columns as the traditional SPE. The properties and application conditions of the mag-DMIPs were discussed in detail. Combined with HPLC, the mag-DMIPs were applied to rapidly separate and detect trace NP residues in environmental water samples with high selectivity and sufficient adsorption capacity.

2. Experimental

2.1. Chemicals

Multi-walled carbon nanotubes (MWNTs, diameters range of 20–40 nm) were obtained from Shenzhen Bill Corporation. Tetraethylorthosilicate (TEOS) and 4-vinyl pyridine (4-VP) were purchased from Beijing Chemical Reagent Factory (Beijing, China). 4-nonylphenol (NP), 4-tert-octylphenol (PTOP), nonylphenol ethoxylate (NPE), bisphenol A (BPA), and tetrabromobisphenol A (TBBPA) were obtained from Aladdin Reagents Company (Shanghai, China). Ferric chloride ($FeCl_3 \cdot 6H_2O$), sodium acetate (NaAc), acetic acid (HAC), dichloromethane, acetone, ethylene glycol (EG), polyethylene glycol (PEG, M_w=4000), ammonia solution ($NH_3 \cdot H_2O$), ethanol, acetonitrile (ACN), and methanol were purchased from Changsha Chemical Reagent Company (Hunan, China). The remaining chemical reagents were of analytical grade. Ultra-pure water was used throughout the experiment.

2.2. Instrumentation

The mag-DMIPs were characterized by transmission electron microscopy (TEM, JEM1010, Japan), vibrating sample magnetometer (VSM, M27407, Lake Shore Ltd.), and Fourier transform infrared spectra (FT-IR, Nicolet iS10, Thermo scientific, USA). High performance liquid chromatography (HPLC) analysis was performed with a LC2010AHT solution system (SHIMADZU, Japan). Chromatography analysis was achieved on a Spherigel C_{18} column (5 μm, 250 mm × 4.6 mm). The mobile phase is a mixture solution of acetonitrile and acetic acid (99:1, v/v) aqueous solution at pH 2.5 with a flow rate of 1.0 mL min^{-1}. The injection sample volume is 10.0 μL and the wavelength for a UV detector is 251 nm. All detected solutions were filtered through a 0.45 μm polytetrafluoroethylene membrane before use.

2.3. Preparation of magnetic dummy molecularly imprinted polymers

2.3.1. Pretreatment of multi-walled carbon nanotubes

An amount of 0.5 g MWNTs was added into 50 mL of HNO_3 under sonication for 10 min. Then, the mixture was stirred under 85 °C for 12 h. Cooled to room temperature (RT), the mixture was filtered through a 0.45 μm polycarbonate membrane and washed thoroughly with ultra-pure water for several times until the pH of the filtrate was neutral. The product was dried under vacuum for 12 h, obtaining carboxylic acid functionalized MWNTs (MWNTs–COOH).

2.3.2. Synthesis of magnetic multi-walled carbon nanotubes (MWNTs@Fe_3O_4)

First, 1.6 g of $FeCl_3 \cdot H_2O$ was dissolved in 40 mL of EG to form an orange solution. Then 400 mg of MWNTs–COOH was dispersed in this solution by sonication for 3 h. After that, 5.0 g of NaAc and 2.0 g of polyethylene glycol (PEG) were added under constant stirring for 30 min. The mixture was sealed in a Teflon-lined stainless steel autoclave and maintained at 200 °C for 8 h, then cooled to RT. The MWNTs@Fe_3O_4 composites were collected by an external magnet and rinsed six times with ethanol and purified water. Finally, the MWNTs@Fe_3O_4 composites were dried in a vacuum at 60 °C for 10 h.

2.3.3. Synthesis of magnetic dummy molecularly imprinted polymers (mag-DMIPs)

The preparation procedure of the mag-DMIPs was as follows. First, 1.0 mmol of PTOP and 4 mmol of 4-VP were dissolved in 50 mL of acetonitrile and stirred for 12 h at RT. Next, 10.0 mL of TEOS was added and the mixture was stirred for 5 min. Then, 500 mg of MWNTs@Fe_3O_4 which was dispersed in 10.0 mL of methanol and 2.0 mL of 1.0 mol L^{-1} acetic acid solution was added subsequently into above mixture. After the mixture was incubated for 15 h at RT under stirring, the product was collected by an external magnet and washed with the mixture solution of methanol and acetic acid (9:1, v/v) several times to remove the template. Finally, the resultant magnetic imprinted polymers (mag-DMIPs) were dried under vacuum at 60 °C for 24 h. For comparison, non-molecularly imprinted polymers based on magnetic multi-walled carbon nanotubes (mag-NIPs) were prepared using the same synthetic protocol in the absence of the template.

2.4. Adsorption experiment

Kinetic adsorption experiment was carried out as follows. First, 50.0 mg of the mag-DMIPs or the mag-NIPs was suspended in 20.0 mL of 50.0 μg mL^{-1} NP methanol solution. The suspensions were shaken continuously at 25 °C. Then the residual concentrations of analyte at intervals of 5, 10, 20, 30, 40, 60, 90 and 120 min were detected by HPLC. The adsorption capacity Q (mg g^{-1}) was calculated according to the following equation [19]:

$$Q = (C_o - C_{eq})V/m \quad (1)$$

where C_o (μg mL^{-1}) and C_{eq} (μg mL^{-1}) are the initial and equilibrium concentrations of NP, respectively. V (mL) is the total volume of the sample and m (mg) is the amount of mag-DMIPs or mag-NIPs.

To investigate the adsorption equilibrium of the mag-DMIPs toward NP, 10.0 mg of the mag-DMIPs or the mag-NIPs was suspended in 10.0 mL of methanol solutions with different initial NP concentrations range of 5.0–200.0 μg mL^{-1}. After 20 min, the mag-DMIPs or the mag-NIPs were separated by an external magnet and the supernatant was analyzed by HPLC. The saturated adsorption capacity was obtained according to Langmuir adsorption equation [20]

$$C_{eq}/Q = C_{eq}/Q_{max} + 1/kQ_{max} \quad (2)$$

where Q (mg g^{-1})and Q_{max} (mg g^{-1}) are the equilibrium adsorbed amount and theoretical maximum adsorption capacity of the adsorbent toward NP, respectively. C_{eq} (μg mL^{-1}) is the concentration of NP in equilibrium solution and K (L g^{-1}) is the Langmuir adsorption equilibrium constant towards NP.

In order to estimate the selectivity of the mag-DMIPs toward NP, 50.0 mg of the mag-DMIPs or the mag-NIPs was dispersed in 20.0 mL of 50.0 μg mL^{-1} NP, NPE, BPA and TBBPA mixture solution for 20 min. The mag-DMIPs or the mag-NIPs were separated by an external magnet and the supernatant was analyzed by HPLC.

2.5. Sample preparation

River water samples were collected from Donghe in Jishou city of Hunan province; the tap water sample was collected from the tap in the laboratory. The rain water sample was collected in Jishou on 27 September, 2013. All samples were filtered through a 0.45 μm nylon membrane before use.

3. Results and discussion

3.1. Preparation of mag-DMIPs

To improve the adsorption properties and eliminate the template leakage, the magnetic molecularly imprinted polymers based on MWNTs for specifically recognizing NP were synthesized using PTOP as the dummy template molecule. The schematic diagram of the mag-DMIPs preparation is shown in Fig. 1. It is a fact that the treatment of MWNTs with nitric acid could create considerable carboxyl groups on the surface of MWNTs, which resulted in the MWNTs surface to become negatively charged. Thus, the positive metal ions (ferric ions) would interact with the MWNTs via electrostatic attraction and serve as nucleation precursors. Then the ferric ions were in situ reduced into Fe_3O_4 with hydrothermal treatment, which resulted in Fe_3O_4 nanoparticles being grafted onto the MWNTs surface (MWNTs@Fe_3O_4). Finally, a thin MIPs film was grafted onto the surface of MWNTs@Fe_3O_4 by thermal polymerization using PTOP as the dummy template molecules, 4-VP as the functional monomers and TEOS as the cross-linkers.

Studies showed that the molar ratio of the template molecule: functional monomer (4-VP):cross-linker (TEOS) was a critical factor which influences the adsorption properties of the MIPs [21]. A series of mag-DMIPs were prepared with different molar ratios of the template: 4-VP:TEOS involving 1:2:5, 1:3:6, 1:4:8, and 1:5:10 and their adsorption performances were investigated. As shown in Table 1, the maximum adsorption capacity (Q_{max}) of these mag-DMIPs toward NP increased with increasing ratios of the functional monomer and cross-linker, while that of the non-specific adsorption of the mag-NIPs increased similarly. Considering the difference of Q_{max} between the mag-DMIPs and mag-NIPs, the molar ratio of 1:4:8 for the template: 4-VP:TEOS was selected to prepare the mag-DMIPs and mag-NIPs.

3.2. Characterization

Transmission electron microscopy (TEM) was employed to characterize the morphologies of the MWNTs, MWNTs@Fe_3O_4 and mag-DMIPs. As shown in Fig. 2a, the MWNTs were individual tube with the diameter of 20–40 nm. Fig. 2b shows that the Fe_3O_4 nanoparticles with the diameter of 20 nm were grafted on MWNTs successfully. After thermal polymerization, the imprinted polymers layer was grafted uniformly on the MWNTs surface (shown in Fig. 2c) and the diameter of the mag-DMIPs was 80–90 nm. Thus, the average thickness of the MIPs layer can be calculated as 30–35 nm.

Fourier transform infrared spectra (FT-IR) of the MWNTs (curve a), MWNTs@Fe_3O_4 (curve b) and mag-DMIPs (curve c) are shown in Fig. 3. The adsorption band at 3432 cm^{-1} corresponds to the

Table 1
Effect of the molar ratio of template/4-VP/TEOS on the performance of the mag-DMIPs.

	Template/4-VP/TEOS (molar ratio)	$Q_{mag\text{-}DMIPs}$ (mg g^{-1})	$Q_{mag\text{-}NIPs}$ (mg g^{-1})	$Q_{mag\text{-}DMIPs}/Q_{mag\text{-}NIPs}$
1	1/2/5	23.53	8.31	2.83
2	1/3/6	27.12	9.52	2.84
3	1/4/8	32.31	11.21	2.88
4	1/5/10	38.15	21.42	1.78

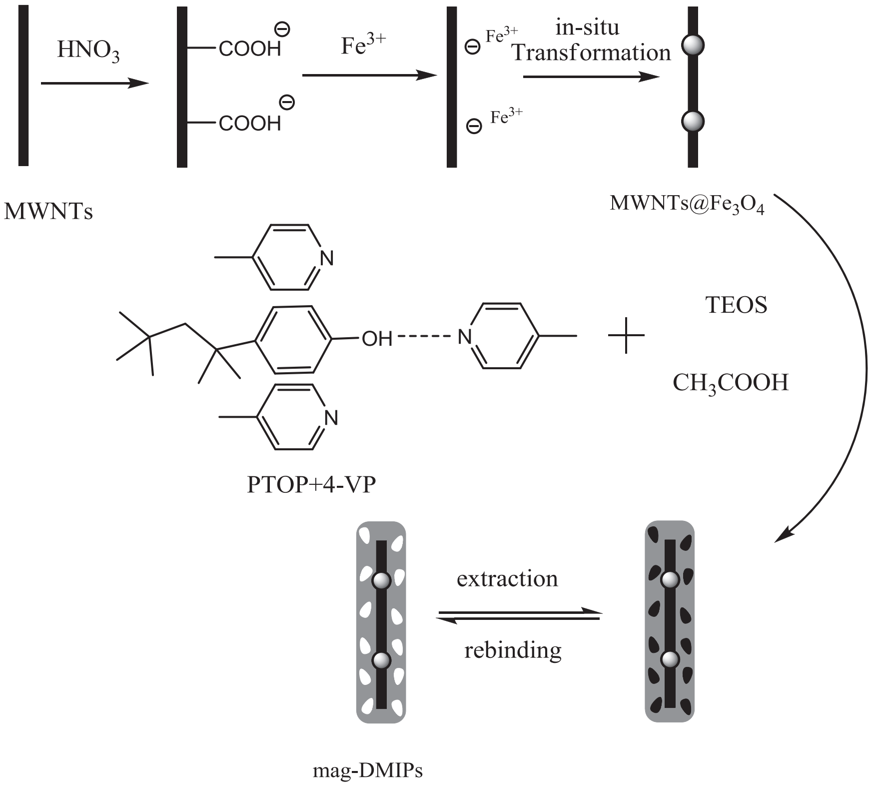

Fig. 1. The protocol for synthesis of mag-DMIPs.

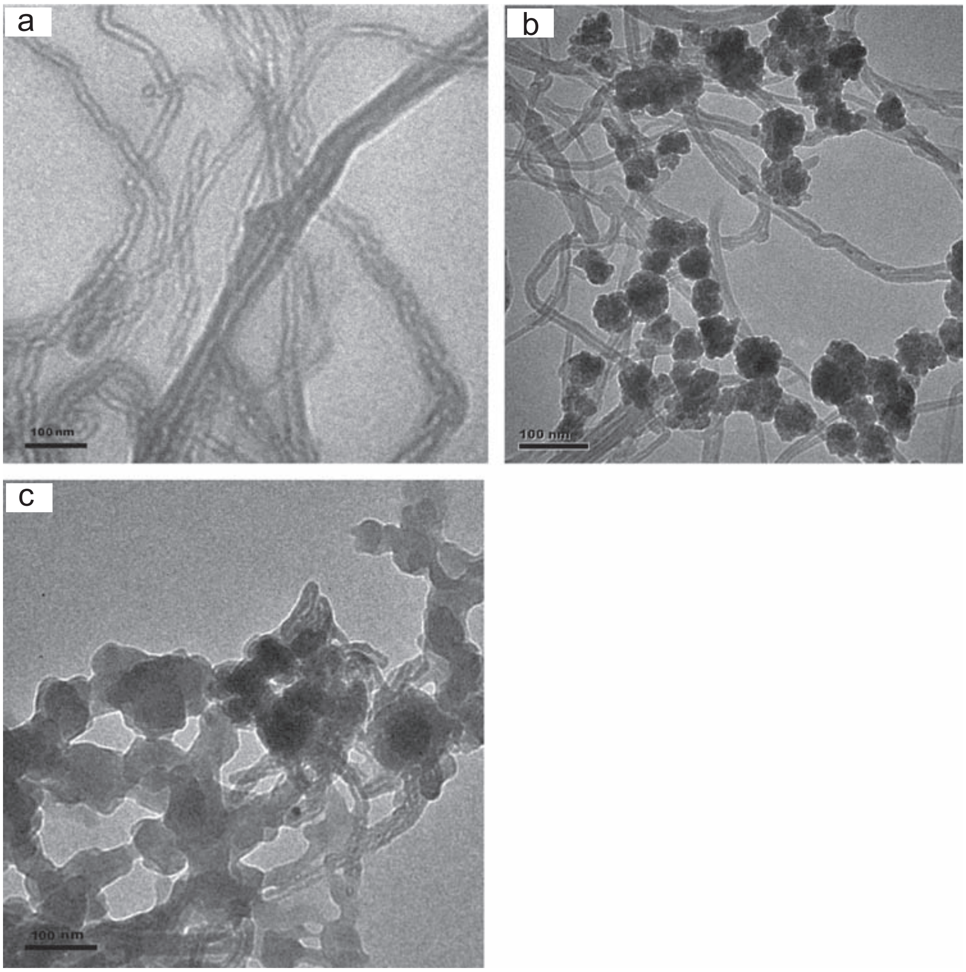

Fig. 2. TEM images of MWNTs (a), MWNTs@Fe_3O_4 (b) and mag-DMIPs (c).

stretching vibrations of O–H of MWNTs. The IR band at about 625 cm^{-1} is the characteristic vibration absorption of Fe–O bond. The adsorption bands at 1071 cm^{-1} and 791 cm^{-1} correspond to Si–O–Si and Si–O stretching vibrations, respectively. And the adsorption band at 1666 cm^{-1} and doublet bands at 1385 cm^{-1} and 1517 cm^{-1} are due to the stretching vibration of C–N and C–C of 4-VP. Based on the above results, it can be concluded that the mag-DMIPs were prepared successfully.

A vibrating sample magnetometer (VSM) was employed to study the magnetic property of the MWNTs@Fe_3O_4 and mag-DMIPs. The magnetic hysteresis loops of these samples are illustrated in Fig. 4. The saturation magnetizations of the MWNTs@Fe_3O_4 and mag-DMIPs were 40.69 emu g^{-1} and 26.52 emu g^{-1}, respectively. The decrease of saturation magnetization of the mag-DMIPs than that of the MWNTs@Fe_3O_4 was attributed to the formation of an imprinting layer on the surface of MWNTs@Fe_3O_4. As shown in the inset of Fig. 4, in the absence of an external magnet, a black homogeneous mag-DMIPs dispersion existed. When an external magnet was applied, the black mag-DMIPs were attracted to the wall of vial in a short time rapidly (about 60 s).

3.3. *Adsorption experiment*

Adsorption kinetic studies were carried out to investigate the adsorption process. The results showed that the mag-DMIPs reached adsorption equilibrium at 20 min, which is shorter than that of the traditional imprinted polymers [22]. The reason can be explained by the fact that NP easily reached the surface imprinting cavities of the mag-DMIPs, which resulted in less time needed to achieve the adsorption saturation. The results suggested that the nano-sized, surface imprinting and uniform structures of the mag-DMIPs allowed efficient mass transport [23], which overcame some drawbacks of traditionally imprinted materials.

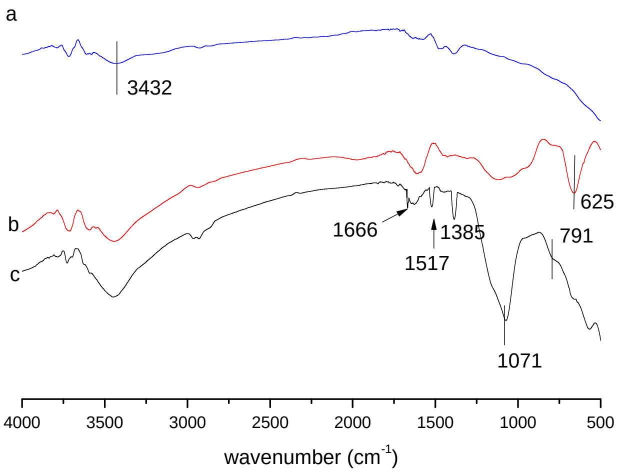

Fig. 3. FT-IR spectra of crude MWNTs (a), MWNTs@Fe_3O_4 (b) and mag-DMIPs (c).

The static adsorptions of the mag-DMIPs and mag-NIPs toward NP were investigated and the results are shown in Fig. 5. The mag-DMIPs exhibited a higher adsorption capacity than that of the

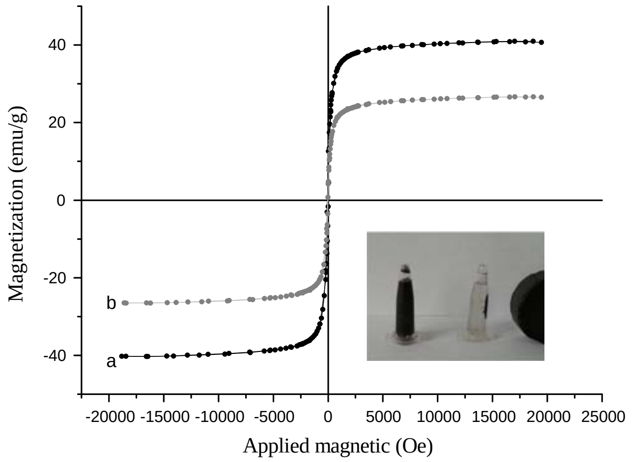

Fig. 4. Magnetization curves of MWNTs@Fe_3O_4 (a) and mag-DMIPs (b). The inset photograph shows the separation and redispersion process of mag-DMIPs in the presence (right) and absence (left) of an external magnet.

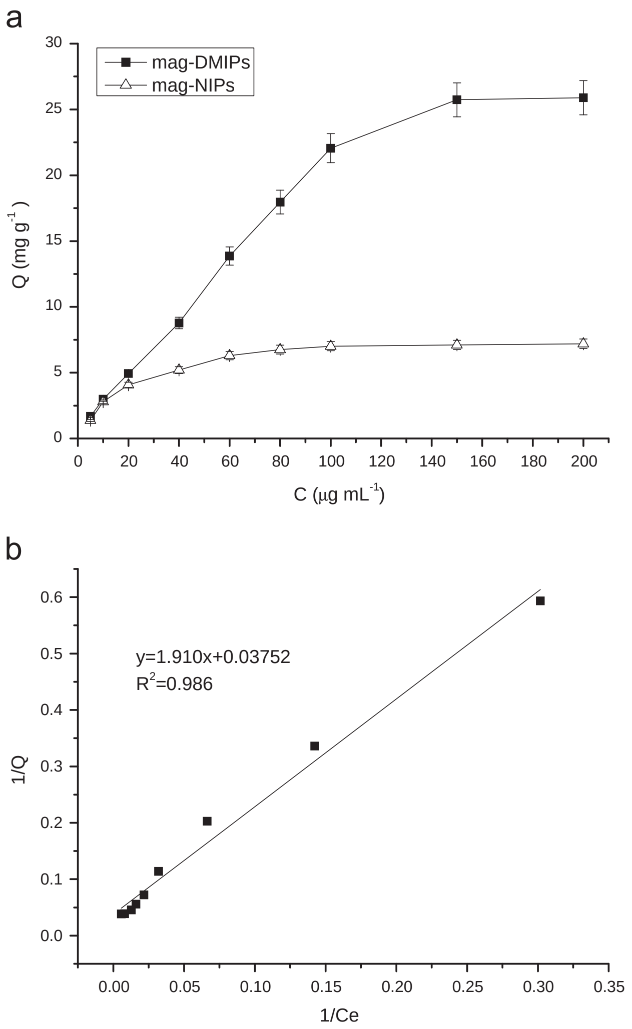

Fig. 5. (A) Adsorption isotherm of NP on mag-DMIPs and mag-NIPs. (B) Langmuir plots of mag-DMIPs.

mag-NIPs, which can be attributed to the fact that the mag-NIPs had not generated specific recognition sites due to the absence of template during the preparation process. According to the Langmuir adsorption equation, the fitted plots of the mag-DMIPs toward NP are shown in Fig. 5B, and the theoretical maximum adsorption capacity Q_{max} and Langmuir adsorption equilibrium constant K of the mag-DMIPs toward NP were calculated as 52.4 mg g^{-1} and 0.51 L g^{-1}, respectively.

In order to investigate the selectivity of the mag-DMIPs toward NP, three different analogs (NPE, BPA and TBBPA) were selected to test the binding characteristics of the mag-DMIPs and mag-NIPs. As shown in Fig. 6, the mag-DMIPs possessed the highest recovery toward NP among all four adsorbents, and the difference between the mag-DMIPs for every adsorbent followed the order NP > NPE > BPA > TBBPA.

The selectivity of the mag-DMIPs was evaluated further by imprinting factor (α) and selectivity factor (β) which are defined as follows [24]:

$$\alpha = Q_{(A)}/Q_{(B)} \tag{3}$$

$$\beta = \alpha_1/\alpha_2 \tag{4}$$

where $Q_{(A)}$ and $Q_{(B)}$ are the adsorption capacity of the mag-DMIPs toward NP and analog, respectively. In Eq. (4), α_1 is the imprinting factor toward NP and α_2 is the imprinting factor toward the analog. As shown in Table 2, α of NP is larger than that of others (NPE, BPA and TBBPA), which indicated that the selective adsorption capacity of the mag-DMIPs toward NP was stronger than that of others. Moreover, the selectivity factor (β) values of similar structurally compounds were 1.96 for NPE, 1.75 for BPA and 1.81 for TBBPA, which further indicated that the mag-DMIPs possessed high selectivity toward NP.

3.4. Optimization of magnetic solid-phase extraction

Before the proposed mag-DMIPs were applied to detect NP in real water samples, the extraction conditions involving the washing solvent, eluent solvent, and desorption time were investigated in detail. The extraction conditions were optimized by using 50.0 mg of the mag-DMIPs which was adsorbed saturated with 50.0 μg mL^{-1} for 20 min. When one parameter was changed, the other parameters were fixed at their optimized values.

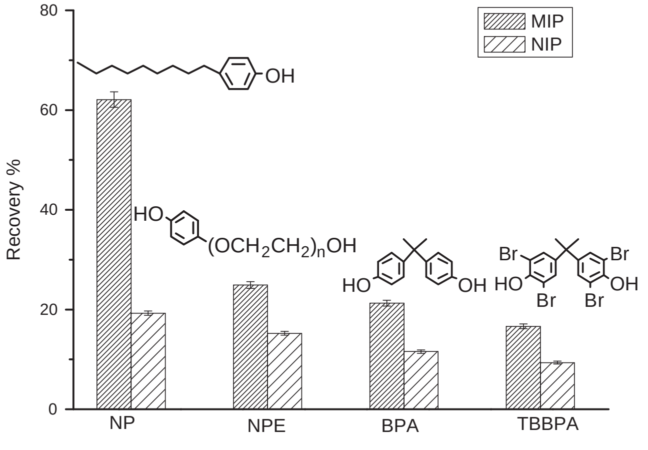

Fig. 6. Selective adsorption capacity of the mag-DMIPs and mag-NIPs.

Table 2
Imprinting factor (α) and selectivity factor (β) of the mag-DMIPs and mag-NIPs.

Target	$Q_{A(MIP)}$ (mg g^{-1})	$Q_{B(NIP)}$ (mg g^{-1})	α	β
NP	31.05	9.64	3.22	–
NPE	12.45	7.61	1.64	1.96
BPA	10.64	5.79	1.84	1.75
TBBPA	8.341	4.68	1.78	1.81

1) Washing solvent. The washing step was optimized to reduce the matrix interference and maximize the special interactions of the mag-DMIPs toward NP. In this study, six washing solutions involving methanol, chloroform, acetonitrile, and methanol/water mixture solutions with different ratios (20:80, 50:50, and 80:20, v/v) were investigated and the results are shown in Fig. 7a. The results showed that when 5.0 mL of methanol/water (80:20, v/v) mixture solution was used as washing solvent, the hydrophilic impurities in samples could be mostly cleaned up. Meanwhile, the lowest recovery of 5.2% NP was obtained from the mag-DMIPs, while 37.4% of that from the mag-NIPs. It demonstrated that methanol/water (80:20, v/v) mixture solution could affect the specific and nonspecific interactions between the mag-DMIPs and NP molecule. Therefore, 5.0 mL of methanol/water (80:20, v/v) mixture solution was selected as the washing solvent.
2) Eluent solvent. In order to obtain the highest recovery of the mag-DMIPs toward NP, different types of eluent solvents including dichloromethane/acetic acid (90:10, v/v), methanol/acetic acid (90:10, v/v), and acetonitrile/acetic acid (90:10, v/v) were investigated in the eluting step. As shown in Fig. 7b, methanol/acetic acid (90:10, v/v) offered the highest recovery of NP than that of other solvents. In addition, the dosage of eluent was investigated and the result showed that 2.0 mL of methanol/acetic acid (90:10, v/v) provided the best elution efficiency.
3) Desorption time. Different desorption time intervals of 10–120 min under the above optimum conditions were performed to investigate the desorption performance. Fig. 7c indicates that desorption was incomplete when the desorption time was less than 40 min, while the desorption no longer increased when the desorption time was over 40 min. Therefore, 40 min was chosen as the optimum desorption time for succeeding studies.

3.5. *Applications*

To demonstrate the ability of the mag-DMIPs to extract NP from real samples, different water samples including tap water, rain water and river water were separated and determined under the optimized conditions by coupling M-SPE with HPLC. The linearity of the established method for determination of NP was estimated over the range of 0.1–200.0 μg mL^{-1} with a limit of detection (LOD) of 0.15 ng mL^{-1}(R=0.997) based on a signal-to-noise ratio of 3. Fig. 8 shows the chromatograms obtained for a blank water sample (Fig. 8a), a spiked water sample (Fig. 8b) and eluate after M-SPE pretreatment (Fig. 8c). Comparing with Fig. 8a and b, few impurities are observed in the chromatograms shown in Fig. 8c, which indicated that the mag-DMIPs with M-SPE exhibited excellent selectivity and enrichment ability towards NP due to high surface area and special imprinted cavities which were complementary in size, shape, and functionality. The spiking concentrations for NP at three levels of 10.0, 20.0, and 50.0 ng mL^{-1} were subjected to extraction by the M-SPE under the optimized conditions as described in Section 3.4. According to the optimum conditions, 50.0 mg of mag-DMIPs was dispersed into 20 mL of different water samples spiked with 10.0, 20.0 and 50.0 ng mL^{-1} NP. After 20 min, the MMWNTs-MIPs were eluted with 2.0 mL of mixture solution of methanol/acetic acid (9:1, v/v) for 40 min and separated under an external magnetic field. A volume of 10.0 μL of sample solution was analyzed by HPLC at

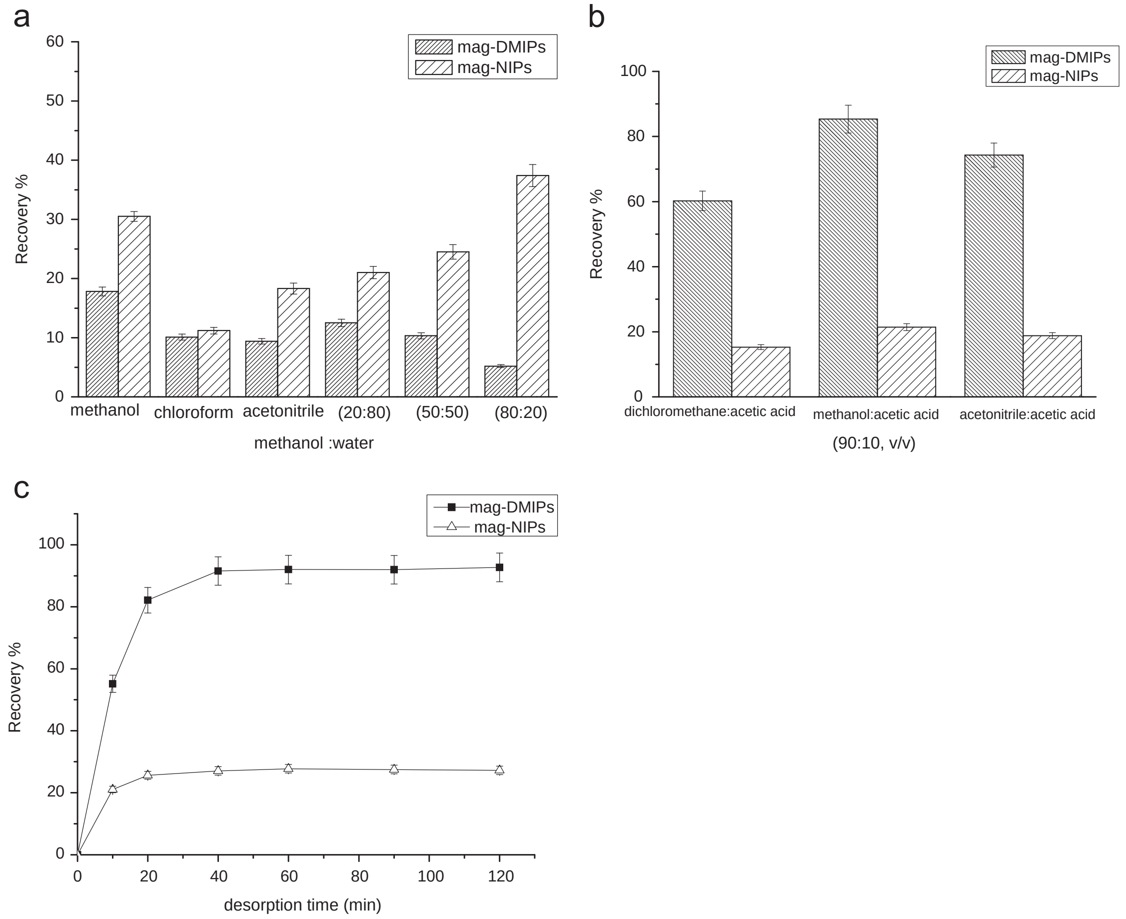

Fig. 7. Effects of washing solvent (a), elute solvent (b), and desorption time (c) on the adsorption of NP (n=3).

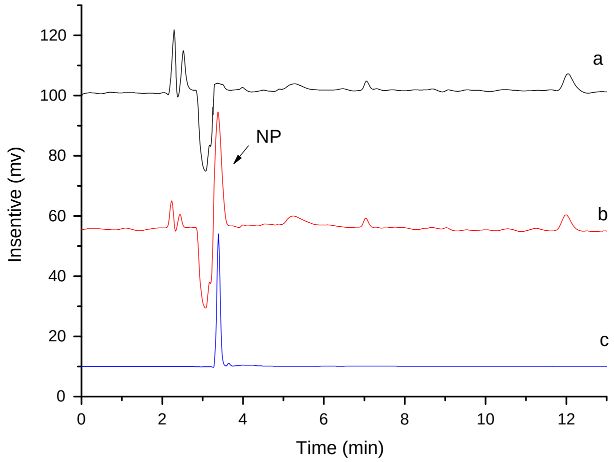

Fig. 8. Chromatograms of blank river water (a), spiked river water (b), eluate after M-SPE pretreatment (c). The NP was eluted with 2.0 mL of methanol/acetic acid (90:10, v/v) mixture solution for 40 min.

Table 3
Recoveries of NP at different spiked levels in aqueous solution.

Water samples	Spiked (ng mL^{-1})	Recoveries (%)	RSD (%) (n==5)
Tap water	10.0	97.3	3.4
	20.0	94.5	2.9
	50.0	98.1	4.2
Rain water	10.0	92.4	5.1
	20.0	94.5	2.8
	50.0	89.7	3.6
River water	10.0	90.2	2.3
	20.0	92.8	3.2
	50.0	88.6	3.8

251 nm. As shown in Table 3, the recoveries of NP in these spiked samples ranged from 88.6% to 98.1% with the relative standard deviation (RSD) less than 5.1%, which suggested that the mag-DMIPs are efficient SPE adsorbents for NP extraction from aqueous solutions.

4. Conclusions

A novel magnetic dummy molecularly imprinted polymer was synthesized successfully using 4-tert-octylphenol as the dummy template and MWNTs as the support matrix in this paper. The mag-DMIPs not only displayed outstanding magnetic property, but also had large adsorption capacity and high selectivity toward NP. Compared with traditional MIPs, the mag-DMIPs can be solid–liquid separated easily with aid of an external magnet. Combined with the magnetic solid phase extraction technique and high performance liquid chromatography, the mag-DMIPs can rapidly selectively separate and detect the trace NP from environmental water samples.

Acknowledgments

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