Magnetic Molecularly Imprinted Polymer Particles Based Micro-Solid Phase Extraction for the Determination of 4-Nitrophenol in Lake Water

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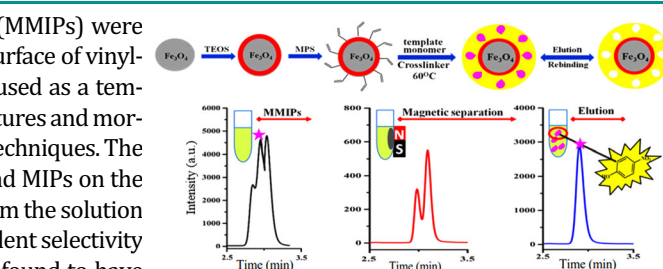[3] University of Leicester, Department of Chemistry, LE1 7RH, UK

Abstract: In this work, magnetic molecularly imprinted polymers (MMIPs) were prepared by the method of co-precipitation polymerization on the surface of vinyl-modified silica magnetic particles. Here, 4-nitrophenol (4-NP) was used as a template and vinylimidazole as a functional monomer. The structural features and morphology of MMIPs were characterized by SEM, FT-IR, TEM and XRD techniques. The results showed that the structures of MMIPs have a layer of silica and MIPs on the surface of the Fe_3O_4 particles, and they could be rapidly separated from the solution using a magnet. MMIPs possess higher adsorption capacity and excellent selectivity towards template (4-NP) than other structural analogues. And it is found to have good imprinting effect. MMIPs were used as micro-solid phase extraction sorbent for selective separation of 4-NP in lake water sample with high recoveries (90.63-95.63%) and low relative standard deviation values (RSD ≤ 3.2%, n = 3).

Keywords: molecularly imprinted polymers, magnetic separation, micro-solid phase extraction, 4-nitrophenol.

1. Introduction

The presence of phenol and its derivatives in food, in ground and surface of waters forms a considerable danger to human health and the environment. These compounds are considered as priority pollutants by the U.S. Environmental Protection Agency (USEPA) as well as by the European Union, because of their high toxicity and prevalent presence in the environment.[1] Among the phenolic compounds, 4-nitrophenol (4-NP) is one of the most important members of nitro aromatic compounds, which is used widely as precursor for the preparation of phenetidine and acetophenetidin, raw material for fungicides and petrochemical industry.[2] 4-NP can irritate the skin and eyes,[3-5] and can cause methemoglobin formation,[6] liver and kidney damage.[7] It's also dangerous to the fauna and flora in the biosphere.[8,9] Therefore, sensitive detection and effective removal of 4-NP from industrial water and ground water is essential to the environment.[10]

In the literature, a wide variety of methods were employed for the detection and quantification of 4-NP, such techniques include capillary electrophoresis,[11] high-performance liquid chromatography (HPLC),[12] fluorescence,[13] and electrochemical sensor.[14] Meanwhile selective adsorption and detection of 4-NP at low concentration from effluents are even more important. Since the contaminated water samples are complex, it requires more advanced methods to rapid and selective extraction of 4-NP.

In recent years, solid-phase extraction (SPE) becomes the most commonly used sample pretreatment technique.[15,16] Conventional SPE sorbents often has low selectivity, thus it is difficult to pretreated complex and low concentration samples. This problem can potentially be solved by use of molecularly imprinted polymers (MIPs).[17] MIPs as attractive materials have drawn immense attention. It is also considered as a modern technique for the separation and analysis of specific compound in complex matrix.[18] MIPs are featured for their high selectivity and efficient separation capability toward a target molecule,[19] which is removed by proper solvents. MIPs possess specific cavities which are complement to the target molecule in shape, size and functional groups.[20] However, MIPs are often prepared by the conventional bulk polymerization method and have drawbacks including heterogeneous distribution of the binding sites, slow binding kinetics, and poor site accessibility for template molecules.[21,22] In addition, the mass transfer of target molecules from solution to cavities is obstructed by the adsorption of the template on the surface of MIPs, which give rise to low binding affinity.[23] To solve these problems, recently, magnetic separation technology combined with the molecular imprinting technique has received growing attention.[24,25] Magnetic molecularly imprinted polymers (MMIPs) have the advantage of easy manipulation by an external magnetic field, as a result the tedious centrifugation step can be avoided. Also, it can be rapid and easy way for the extraction of template from complex matrices.[26] Therefore, MMIPs have been successfully applied to many fields,

such as sample preparation,[27] bioscience[28] catalysis[29] and environmental remediation.[30]

In a previous work from our group, imprinted polymers have been synthesized for the selective recognition of 4-NP in the aqueous samples.[31] On the base of the work, we successfully synthesized MMIPs by the method of co-precipitation polymerization on the surface of vinyl-modified silica magnetic particles and used to develop micro SPE (μ-SPE). μ-SPE possesses fast sample pre-treatment and much less organic solvent consumption comparing to SPE cartridges.[32,33] Here, vinylimidazole was selected as a functional monomer due to its higher imprinting factor comparing to that of 4-vinylpyridine. Finally, synthesized MMIPs was used for selective micro extraction of 4-NP from water samples.

2. Experimental

2.1. Materials

4-NP, phenol, toluene and anhydrous ferric chloride ($FeCl_3$) were purchased from Tianjin Chemical Reagent Factory (Tianjin, China). 4-chlorophenol and 4-vinylpyridine were purchased from Acros Organics (New Jersey USA). 3-(Trimethoxysilyl)-propyl-methacrylate (MPS), tetraethyl orthosilicate (TEOS) and vinylimidazole were purchased from J&K Chemicals (Beijing, China). Trimethylolpropane trimethacrylate (TRIM) was purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). 2,2-Azobisisobutyronitrile (AIBN) was supplied by Shanghai Reagent Factory (Shanghai, China). Acetonitrile, methanol and acetic acid were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) was purchased from Beijing Chemical Works (Beijing, China). Ammonia ($NH_3 \cdot H_2O$, 28%, w/w) was obtained from Xilong Chemical Co (Jiangsu, China).

2.2. Instrumentations

A DZF-6020 vacuum oven (Shanghai Yiheng Technology Co. Ltd., Shanghai, China). An 1810-B quartz automatic water double distiller (Shanghai, China). UV-vis 1800 spectrophotometer (Shimadzu Corporation, Japan). The structure morphology and size of the MMIPs were characterized by a S-4800 scanning electron microscope (SEM, Hitachi, Japan), an ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectrometry, which was performed using KBr pellets on an EQUINOX 55 (Bruker optics, Germany) between 400 and 4000 cm^{-1}. HPLC analysis was carried out on a Yilite UFLC series system equipped with a UV detector and connected to a Hypersil column (150×4.6 mm, 5 μm).

2.3. Preparation of Fe_3O_4 magnetic particles

The Fe_3O_4 magnetic particles were prepared by the modified co-precipitation method.[34] Typically, 2.78 g of $FeSO_4 \cdot 7H_2O$ (0.01 mol) and 5.41 g of $FeCl_3$ (0.02 mol) were placed in round-bottom flask which were dissolved in 80 mL distilled water with vigorous stirring for 10 min at room temperature under nitro-

gen atmosphere using N_2 balloon. After that, temperature was increased to 80 °C and 10 mL of $NH_3 \cdot H_2O$ (28%, w/w) was added dropwise into the mixture. Then the solution immediately turned into black and proceeded for 60 min with stirring (800 rpm) under nitrogen atmosphere. The obtained black products were separated from the liquid using a permanent magnet and then washed with distilled water until it was neutral. Finally, the products were dried under vacuum at 60 °C.

2.4. Synthesis of $Fe_3O_4@SiO_2$ particles

Magnetic particles (1.2 g) were placed in a round-bottom flask (250 mL) and dispersed in 80 mL ethanol and 16 mL distilled water, and then sonicated for 5 min. After adding 20 mL of $NH_3 \cdot H_2O$ (28%, w/w) and 8 mL TEOS in sequence, the mixture was purged with nitrogen gas for 10 min and reacted for 12 h at room temperature with continuous stirring. The resultant products were collected by external magnetic separation and then rinsed with diluted hydrochloric acid and water until the pH became neutral. Finally, the obtained $Fe_3O_4@SiO_2$ was dried in vacuum at 60 °C.

2.5. Preparation of $Fe_3O_4@SiO_2@MPS$ particles

MPS, the silane coupling agent, was employed for the connection between $Fe_3O_4@SiO_2$ and imprinted and non-imprinted polymer coatings.[35] In this procedure, 250 mg of $Fe_3O_4@SiO_2$ particles were dispersed in 50 mL of anhydrous toluene by sonication for 10 min, followed by the addition of MPS 5 mL. The mixture was reacted for 12 h under nitrogen atmosphere using N_2 balloon at 70 °C with continues stirring. The final product, $Fe_3O_4@SiO_2@MPS$ was separated by an external magnetic field and was washed several times with anhydrous toluene to remove the non-reacted chemicals. In the end, it was dried in vacuum at 60 °C for 4 h.

2.6. Preparation of the $Fe_3O_4@SiO_2@MIPs$

According to the prepolymer composition in Table 1, the template and the monomers were dissolved in 25 mL of solvent by sonication for 5 min, the mixture was gently shaken for 1 h at room temperature. Then cross-linker, initiator and 0.2 g of $Fe_3O_4@SiO_2@MPS$ was added sequentially and sonicated for 10 min. Following that the mixture was polymerized for 24 h under nitrogen atmosphere using N_2 balloon at 60 °C with continuous stirring. After separation by magnet, the particles were washed by the mixture of methanol/acetic acid (9:1, v/v) for removing template by Soxhlet apparatus.[36] After washing with methanol to remove acetic acid, the obtained MMIPs were dried under vacuum. The magnetic non-imprinted polymers (MNIPs) were prepared using same polymerization procedure without the template.

Table 1. Composition of the polymers(mmoL)^a

Polymer	Template (4-NP)	Monomer (VI)	Cross-linker (TRIM)	Initiator (AIBN)
MMIPs	0.20	0.80	4.00	0.05
MNIPs		0.80	4.00	0.05

^{a}25 mL acetonitrile was used as solvent

2.7. Adsorption studies

The batch adsorption experiment was performed to explore the adsorption capacity of MMIPs and MNIPs. 20 mg of MMIPs or MNIPs were dispersed in 5 mL of 4-NP (10 mg·L^{-1}) solution,[37] the mixture was shaken at room temperature. Then, the solution was separated by a magnet and filtered through a filter paper. The residual concentration of 4-NP was determined using UV-vis spectrophotometer at 318 nm. Binding capacity was calculated according to Eq. (1).[38]

$$Q = (C_o - C_e) \times V/m \qquad (1)$$

C_o (mg·L^{-1}) and C_e (mg·L^{-1}) are the initial and equilibrium concentrations of 4-NP, V (L) is the total volume of the sample and m (g) is the weight of MMIPs or MNIPs, respectively.

Selectivity experiment was conducted using 4-chlorophenol and phenol as structural analogues. 20 mg of MMIPs or MNIPs were dispersed into acetonitrile/phosphate buffer solution (45:55, $V:V$, pH=2.5) containing 10 mg·L^{-1} of 4-NP, 4-chlorophenol and phenol, respectively, then the mixture was shaken at room temperature. Finally, the concentration of 4-NP, 4-chlorophenol and phenol were determined by UV-vis at 318 nm, 280 nm and 270 nm, respectively. The recognition ability of MMIPs evaluated by the imprinting factor (IF),[39] which is calculated from the following formula:

$$IF = Q_{MMIPs}/Q_{MNIPs} \qquad (2)$$

Q_{MMIPs} and Q_{MNIPs} (mg·g^{-1}), represent the binding amount of MMIPs and MNIPs, respectively.
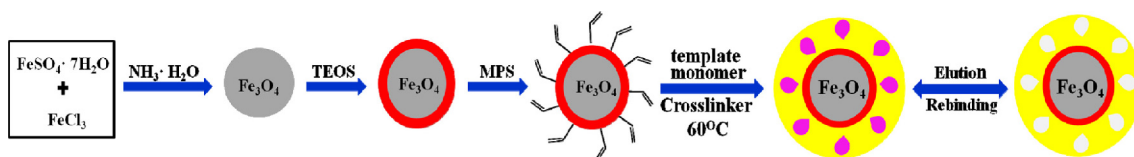
2.8. Analysis of 4-NP in lake water samples

The real water sample was collected from the Red lake (Xinjiang University, China). Working curve of 4-NP in acetonitrile/phosphate buffer solution (45:55, V:V, pH=2.5) was established in the concentration range of 0.1-10 mg·L^{-1}. The water samples were treated with 20 mg of MMIPs and separated with external magnet. Following, it was washed with 0.5 mL of buffer solution and desorbed with 1 mL methanol. The desorbed solution was collected and filtered with 0.22 μm membrane and then analyzed by HPLC. The chromatographic conditions were following: mobile phase was consisted of methanol and water 55:45 (V:V), column was held at room temperature and flow rate was 1.0 mL·min^{-1}, injection volume was 20.0 μL and UV detection at 318 nm.

3. Results and discussion

3.1. Preparation of MMIPs for 4-NP

In this work, MMIPs were successfully synthesized and enabled the selective recognition, easy separation and enrichment of the template from water samples. A schematic presentation of MMIPs preparation process was shown in Figure 1. It involves a couple of steps: firstly, magnetic Fe$_3$O$_4$ particles were produced using the co-precipitation method.[34] And then the magnetite particles were encapsulated in silica using TEOS to obtain Fe$_3$O$_4$@SiO$_2$. The silica shells prevent oxidation and weaken magnetic dipolar interactions between magnetite particles, thus favoring dispersion in liquid media.[40] Fe$_3$O$_4$@SiO$_2$ has a lot of -OH groups and grafted with MPS to further surface polymerization.[41] In the end, the MIPs were synthesized on the surface of Fe$_3$O$_4$@SiO$_2$ by the co-polymerization of vinyl groups of functional monomers (vinylimidazole) and cross-linker (TRIM) in the presence of template (4-NP).

One of the obstacles to the development of MMIPs are the effective removal of template after imprinting.[40] In order to overcome these difficulties, we used mixture of methanol/acetic acid (9:1, v/v) for 24 h to remove template *via* a Soxhlet extractor, which is quite effective method for the removal of the template.[36]

3.2. Optimization of MMIPs synthesis

The grafting degree of MPS plays a vital role during the synthesis of MMIPs.[42] In order to increase grafting of MPS, silanization process was optimized. Hydrochloric acid was chosen for the activation of Fe$_3$O$_4$@SiO$_2$, because hydrochloric acid benefits to have more -OH on the surface of Fe$_3$O$_4$@SiO$_2$. But, when the concentration of hydrochloric acid is too high, the magnetic performance of Fe$_3$O$_4$@SiO$_2$ is unsatisfactory. Therefore, the concentration of hydrochloric acid and activation time were optimized. Different concentration of hydrochloric acid solution 0.5 and 1.0 mol·L^{-1} and activation time 0.5-2.5 h was investigated (as shown in Figure 2(A)). It can be found from the Figure 2(A), in higher concentration of hydrochloric acid, IR transmission peak of both -OH (Figure 2(Aa-b)) and Fe-O (Figure 2(Ac-d)) are weaker than that of the lower concentration, it reveals that 0.5 mol·L^{-1} hydrochloric acid is better in contrast to 1.0 mol·L^{-1} hydrochloric acid. Furthermore, with the increasing of activation time the peaks of both -OH and Fe-O decreased. Meanwhile, when the time is 0.5 h, stretching vibration peaks of -OH and Fe-O are strong, which is beneficial to silanization. And that time was believed to be the appropriate condition for maintaining the magnetic properties and also higher degree at silanization. So, in the rest of experiment, 0.5 mol·L^{-1} concentration of hydrochloric acid and 0.5 h of activation time are used.

3.3. Characterization of MMIPs

3.3.1. FT-IR analysis
FT-IR spectroscopy of Fe$_3$O$_4$@SiO$_2$, activated Fe$_3$O$_4$@SiO$_2$, modified Fe$_3$O$_4$@SiO$_2$@MPS and MMIPs were shown in Figure 2(B).

Figure 1. Synthetic scheme of magnetic molecularly imprinted polymers.
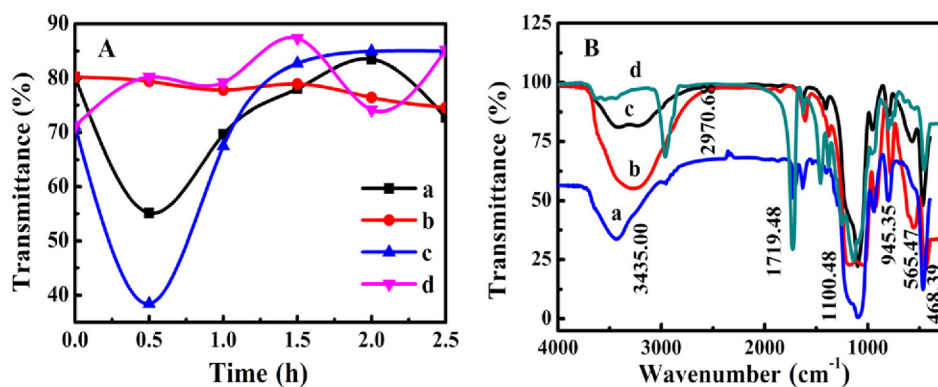
Figure 2. Effect of HCl concentration (0.5 and 1.0 mol·L^{-1}) and activation time on IR transmittance of functional groups of Fe$_3$O$_4$@SiO$_2$: (A-a and A-b) O-H and (A-c and A-d) Fe-O; IR spectra of Fe$_3$O$_4$@SiO$_2$: (B-a) before and (B-b) after activation; IR spectra of magnetic particles: (B-c) Fe$_3$O$_4$@SiO$_2$@MPS and (B-d) MMIPs.

Comparing to Fe$_3$O$_4$@SiO$_2$ (Figure 2(B-a)), the activated Fe$_3$O$_4$@SiO$_2$ (Figure 2(B-b)), showed strong absorption peak at 1100.48 cm^{-1} and 3600-3000 cm^{-1}, which are characteristic for stretching vibration of Si-O-Si and O-H group, respectively.[43] Absorption peak at 565 cm^{-1}, which is characteristic of Fe-O stretching vibration, can evidence successful formation of silica coating on Fe$_3$O$_4$ particles.[44] Using hydrochloric acid, the absorption peak at 3600-3000 cm^{-1} increased, which explained that the appropriate concentration of hydrochloric acid was favorable to produce more -OH. As for Fe$_3$O$_4$@SiO$_2$@MPS (Figure 2(B-c)), the absorption peak at 1719 cm^{-1} and 1630 cm^{-1} were assigned to the stretching vibration of C=O and C=C, and which could prove successful immobilization of MPS molecular. After polymerization (Figure 2(B-d)), the peak at 1730 cm^{-1} significantly enhanced, which demonstrated that the polymer was successfully grafted on the magnetic particles.

3.3.2. SEM and TEM analysis

The morphology of MMIPs were investigated by SEM and TEM. The SEM images of Fe$_3$O$_4$@SiO$_2$ and Fe$_3$O$_4$@SiO$_2$@MPS composite are shown in Figure 3(A)-(B). It can be clearly seen that, with layer by layer of modification, the size of particles gradually increased, and their average diameters are 550 nm and 610 nm respectively. The polymers particles were spherical and most of them were highly mono-dispersed, but there exists particle agglomeration, partly due to the magnetic attraction between the polymer particles.[39] Moreover, the TEM micrographs of MMIPs were shown in Figure 3(C), which indicated that polymers were successfully coated on Fe$_3$O$_4$ particles.

3.3.3. Investigation of magnetic property

Magnetic properties of polymer materials make the separation of the materials from solution easier, faster, and more efficient by simply applying a magnetic field.[45] As shown in the photograph of Figure 3(D)-(E), the fully dispersed MMIPs were easily and quickly concentrated on wall of a vial under a permanent magnet. This result showed that MMIPs exhibit a sufficient magnetic response for magnetic separation in the preparation and application of the materials .

3.3.4. XRD analysis

XRD measurement was used to identify the patterns of Fe$_3$O$_4$@SiO$_2$ and the MMIPs, as shown in Figure 4(a) and (b), respectively. As illustrated in the figure, both XRD spectra showed a series of
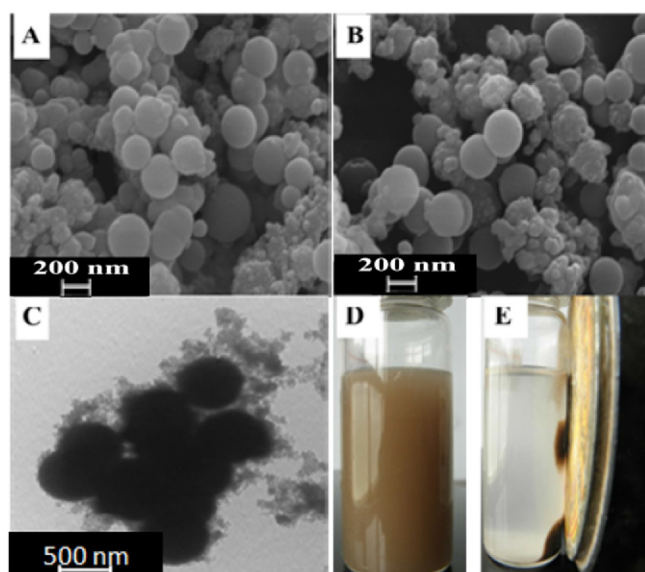
Figure 3. SEM image of magnetic particles: (A) Fe$_3$O$_4$@SiO$_2$ and (B) Fe$_3$O$_4$@SiO$_2$@MPS; (C) TEM images of MMIPs; photos of MMIPs suspension: (D) without and (E) with external magnet.
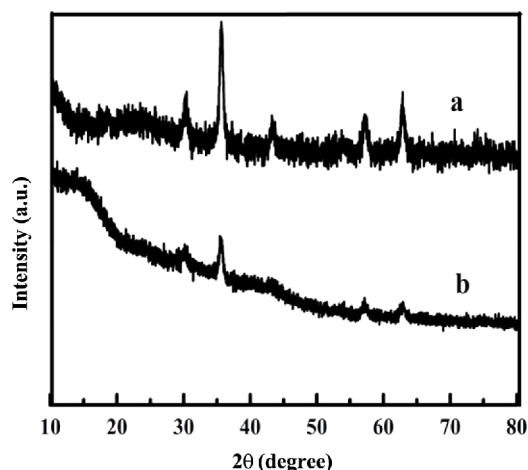

Figure 4. XRD patterns of magnetic particles: (a) Fe$_3$O$_4$@SiO$_2$ and (b) MMIPs.

peaks at 2θ=30.2°, 35.5°, 43.1°, 53.6°, 56.9°, and 62.7° respectively in the 2θ range of 25-80°, which are characteristic for Fe_3O_4, and also the data is well consistent with that of the database of magnetite in the JCPDS-International Center for Diffraction Data file.[46] This result indicated that the Fe_3O_4 nanoparticles were indeed incorporated into MIPs and the structure of Fe_3O_4 nanoparticles was not changed during the polymerization process. The intensities of the characteristic peaks of MMIPs are lower than that of $Fe_3O_4@SiO_2$, due to blocking of magnetic expression by the polymer layers on surface. And this is also consistent with the result that MMIPs have a larger diameter than $Fe_3O_4@SiO_2$. This result is almost same with those reported in publication.[47]

3.3.5. Adsorption property of MMIPs

Adsorption capacities of the imprinted and non-imprinted particles were investigated *via* batch binding experiment as shown in Figure 5(A). As shown in the figure, both MMIPs and MNIPs exhibited good adsorption to 4-NP and the IF was calculated according to Eq. (2). The IF was found to be 1.8, which indicated that the MMIPs have higher adsorption capacity than MNIPs. And the imprinting sites towards the target molecular 4-NP was successfully formed in MNIPs. The specific recognition ability of the materials was evaluated using 4-NP and two structurally similar compounds including 4-chlorophenol and phenol. The binding percentage of MMIPs toward 4-NP, 4-chlorophenol and phenol were calculated to be 93.2%, 26.1%, and 17.2%, as shown in Figure 5(B). It was found that the binding percentage of MMIPs for the template (4-NP) is much greater than that of the material for the other two analogues. There are numerous imprinting cavities in the MMIPs, which matched with 4-NP in size, shape, and functional groups, leading to the outstanding recognition behavior to the target molecules (4-NP). The low binding of the two analogues are due to absence of suitable binding for them. The material presented higher binding to 4-chlorophenol which is structurally much closer to the template than phenol does. This fact also proves that imprinting of the template is highly effective. Also, RSD values of binding test for 4-NP, 4-chlorophenol, and phenol are found to be 0.7%, 3.1%, and 3.2%, respectively. This result shows that the prepared MMIPs displayed high selectivity and reproducibility. In short, MMIPs display highly specific recognition for 4-NP, which could be used for the extraction of this target molecule in real water samples.
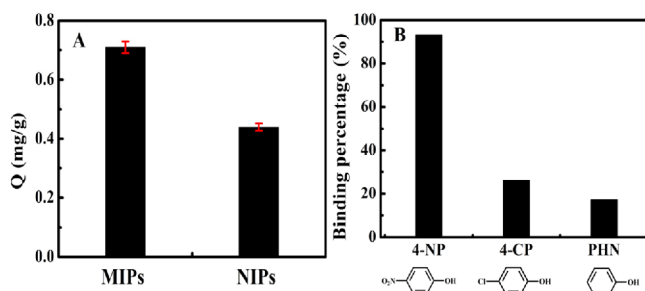
Figure 5. (A) Adsorption capacities of MIPs and NIPs particles for 4-NP; (B) MMIPs binding percentage of 4-NP, 4-chlorophenol and phenol. All analytes were tested at 10 mg·L^{-1} in acetonitrile/phosphate buffer solution (45:55, V:V, pH=2.5).

Table 2. Determination of enrichment factor of MMIPs for 4-NP

V (mL)	Binding percentage (%)	Enrichment factor
5.00	92.77	2.50
10.00	78.71	3.90
15.00	69.06	5.20
20.00	75.09	7.50
25.00	71.70	9.00
30.00	65.07	9.80

3.3.6. Investigation of enrichment factor

The concentration of 4-NP in water samples is comparatively very low, therefore it's hard to detect without concentration. For, the enrichment of the compound is quite important. According to the batch binding experiment, 20 mg of MMIPs were added to 4-NP solution of 2 mg·L^{-1} with different volume (5.0-30.0 mL). After washing with 0.5 mL of acetonitrile/phosphate buffer solution (45:55, V:V, pH=2.5), the polymer particles desorbed with 1 mL of methanol twice, and then 4-NP concentration of the eluted solution was measured. Enrichment factor was found out according to the Eq. (3), and it was found to be quite high, as shown in Table 2.

$$EF = C_{final}/C_{initial} \tag{3}$$

C_{final} and $C_{initial}$ represent initial and final concentrations of 4-NP.

3.4. Determination of 4-NP in lake water sample

The extraction recovery and application of MMIPs were evaluated by lake water samples spiked with 4-NP and it was analyzed by HPLC, as shown in Figure 6. Table 3 shows that recovery rate is more than 90% with RSD less than 5% (n=3). It proves that the MMIPs have great potential for the separation and detection of 4-NP in water samples.

4. Conclusions

In this paper, MMIPs were successfully prepared and characterized by SEM, FT-IR, TEM and XRD. The MMIPs were found
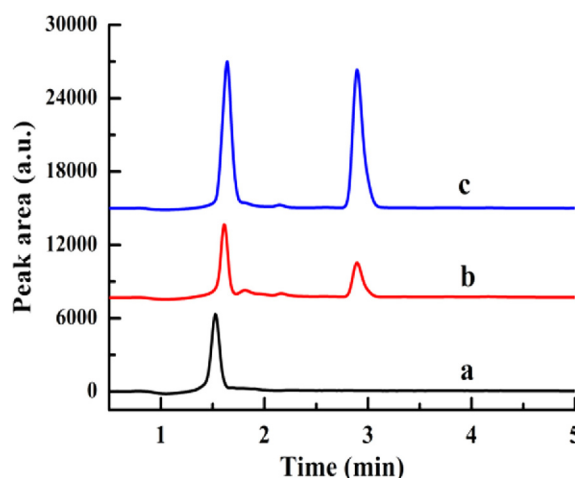
Figure 6. HPLC-UV chromatograms of water samples after extraction with MMIPs: (a) not spiked, (b) spiked with 4-NP at 0.5 mg·L^{-1} and (c) 2.0 mg·L^{-1}.

Table 3. Recoveries of 4-NP from spiked samples (n=3)[a]

Sample	Spiked (mg·L⁻¹)	Found (mg·L⁻¹)	Recovery (%)	RSD (%)
	0	N.D	-	-
Red lake water	0.50	0.45	90.63	4.77
	2.00	1.92	95.63	0.95

[a]N.D not detected.

to be easily collected by magnetic field. The adsorption capacity and selectivity of the MMIPs were studied. The results showed that the MMIPs have higher adsorption capacity and high selective recognition for the target molecule. The results attained in this study also demonstrated that the MMIPs were successfully evaluated as sorbent for solid-phase extraction of 4-NP. The novel MMIPs prepared *via* rational design was applied for the selective extraction of 4-NP in water sample.

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