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Synthesis and evaluation of molecularly imprinted core–shell carbon nanotubes for the determination of triclosan in environmental water samples

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ABSTRACT

Synthetic core–shell molecularly imprinted polymers (MIPs) were prepared for the extraction of trace triclosan in environmental water samples. The synthesis process combined a surface molecular imprinting technique with a sol–gel process based on carbon nanotubes (CNTs) coated with silica. The morphology and structure of the products were characterized by transmission electron microscopy and Fourier transform infrared spectroscopy. The adsorption properties of the polymers were demonstrated by equilibrium rebinding experiments and Scatchard analysis. The prepared imprinted materials exhibited fast kinetics, high capacity and favorable selectivity. The process of synthesis was quite simple and different batches of MIPs and non-imprinted polymers (NIPs) showed good reproducibility in the template binding. The feasibility of determination of triclosan from real samples was testified using spiked river and lake water samples. The recoveries of river water and lake water samples were ranged from 92.1 to 95.3% and 90.7 to 93.6%, respectively, when the environmental water samples were spiked with 0.1, 0.3, and 0.5 $\mu g\,L^{-1}$ of TCS. In addition, the reusability of MIPs and NIPs without any deterioration in capacity was demonstrated for at least 10 repeated cycles.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) contain a large number of chemicals for human usage. PPCPs and their metabolites are continually introduced into the environment [1,2], which may affect water quality and potentially impact the ecosystem and human health, and they have become a new concerned area of environmental science. Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) is an important PPCP used in various personal care products such as soaps, detergents, toothpastes, disinfectants, cosmetics and pharmaceuticals [3]. Although triclosan has not been reported to be toxic to mammals [4], it is very toxic to certain algae species, e.g., *Scenedesmus subspicatus* [5]. Furthermore, some findings indicate a possible bacterial resistance to triclosan, which may result from its property to block lipid biosynthesis by specifically inhibiting the enzyme enoyl-acyl carrier protein reductase [6,7]. In order to prevent the deleterious effects of triclosan on the aquatic environment, the development of new sorbents for selective removal and determination of triclosan in environmental matrices is of great importance.

Several analytical methods have been described to determine the levels of triclosan, such as gas chromatography (GC) and high-performance liquid chromatography (HPLC) coupled with mass spectrometry (GC/MS, HPLC/MS/MS) or electrochemical sensor [8–12]. Because of the interference of complex matrix in real samples, these analytical methods required extensive sample pretreatment like liquid–liquid extraction and solid-phase extraction (SPE) [13,14]. Generally, the samples were pretreated using the SPE technique. This technique is fast and simple compared with the traditional liquid–liquid extraction, but lacks selectivity. Accordingly, there is considerable interest in developing an effective extraction method prior to the measurement. As economical, rapid and selective clean-up methods are needed, the application of SPE procedures involving the use of synthetic antibody mimics, such as molecularly imprinted polymers (MIPs), has received more and more attentions over the past decade as an attractive alternative for the analysis of complex samples [15,16].

Molecular imprinting technique is an outstanding method for the preparation of MIPs as selective sorbents [17,18]. Due to their mechanical/chemical stability, easy preparation and low cost, MIPs have been widely used in a variety of applications, such as separation media [19], mimicking antibody [20], selective removal and

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determination of environmental pollutants [21,22], chemical and biomimetic sensors [23]. Herein, a new type of selective sorbent was prepared by anchoring MIP shells on the surface of carbon nanotubes (CNTs) via a surface molecular imprinting sol–gel process. This method combined the merits of surface molecular imprinting and nanotechnique. Surface molecular imprinting shell and nanocomposite core enabled the template-imprinting sites to situate at the surface or in the proximity of the materials' surfaces, providing the advantages of favorable selectivity, high capacity and fast association/dissociation kinetics [24–27]. The process of this method was quite simple and different batches of imprinted materials showed good reproducibility as a sorbent for triclosan. The resulted MIPs were coupled with HPLC for the determination of trace triclosan in environmental water samples.

2. Experimentals

2.1. Materials

Multiwalled carbon nanotubes (CNTs, diameter: 60–100 nm, length: 5–15 μm) were provided by Shenzhen Nanotech Port Co., Ltd., China. Tetraethoxysilicane (TEOS), 3-aminopropyltriethoxysilane (APTES), phenyltrimethoxysilane (PTMOS) and triclosan (TCS) were purchased from Alfa Aesar Chemical Company. *p*-Chlorophenol (*p*-CP), 2,4,6-trichlorophenol (2,4,6-TCP), cetyltrimethylammonium bromide (CTAB), ammonium hydroxide (25%), acetic acid (HAc), ethanol and methanol were purchased from Tianjin Chemicals Ltd. The highly purified water (18.0 MΩ cm^{-1}) obtained from a WaterPro water system (Aquapro Corporation, AFZ-6000-U, China) was used throughout the experiments. Environmental water samples were collected from local lake and river and filtered through 0.22 μm filters, stored in precleaned glass bottles. All reagents used were of at least analytical grade.

2.2. Instruments and HPLC analysis

A Tecnai G2 T2 S-TWIN transmission electron microscope (TEM) was used to examine TEM images of CNTs, CNTs@SiO_2 and CNTs@TCS-MIPs. The infrared spectra of CNTs, CNTs@SiO_2, CNTs@NIPs and CNTs@TCS-MIPs were recorded with Nicolet AVATAR-360 Fourier transform infrared (FT-IR) spectrometer.

The HPLC analyses were performed on a Shimadzu LC-20A HPLC system including a binary pump and a variable wavelength UV detector (Shimadzu, Kyoto, Japan). The instrument control and data processing were carried out by the LC solution software. A Shimadzu VP-ODS C_{18} (5 μm particle size, 150 mm × 4.6 mm) analytical column was used for analyte separation. The mobile phase was methanol-H_2O-HAc (70/20/10, v/v/v) delivered at a flow rate of 1.0 mL min^{-1}. The injection volume was 20 μL, and the column effluent was monitored at 281 nm.

2.3. Coating SiO_2 on CNTs (CNTs@SiO_2)

The impurities such as amorphous carbon and metallic catalyst in the CNTs sample were removed using a HNO_3 solution (2.6 M) contained in a three neck flask with vigorous stirring (500 rpm) at 85 °C for 48 h. The suspension was then filtered through a 0.22 μm filter to recover the CNTs, followed by washing repeatedly with highly purified water until the pH reached 7.0, and then dried under vacuum at 80 °C for further use. The SiO_2 coating on the CNTs was performed according to the reported method [28]. In a typical synthesis procedure, 250 mg of pristine CNTs, 0.5 mL of APTES, 100 mg of cetyltrimethylammonium bromide (CTAB), and 48 mL of highly purified water were added in a conical flask and sonicated for 20 min at 40 °C, and then stirred for another 3 h, resulting in mixture A. 5 mL of TEOS, 3 mL of highly purified water and 50 mL of ethanol were treated exactly as mixture A, resulting in mixture B. Subsequently, A and B were mixed together and then sonicated for 60 min at 40 °C, followed by stirring for 10 min. Ammonia hydroxide (25%) was added dropwise until the pH value reached 9.5. After the coating progress, the product was washed for several times by centrifugation and redispersing in ethanol to remove the surfactants thoroughly. Finally, the product was dried under vacuum at 80 °C for further work.

2.4. Preparation of triclosan-imprinted polymer (CNTs@TCS-MIPs) and non-imprinted polymers (CNTs@NIPs)

To prepare the CNTs@TCS-MIPs, 1 g of TCS (Fig. 1) was dissolved in 20 mL of ethanol, and mixed with 2 mL of APTES (or 2 mL of PTMOS, or 1 mL of APTES and 1 mL of PTMOS). The mixture was stirred for 20 min, then 4 mL of TEOS was added. After stirring for 5 min, 1 g of CNTs@SiO_2 and 1 mL of 1 M HAc (as catalyst) were added. The mixture began to co-hydrolyse and co-condense after stirring for a few minutes, and then the mixture was incubated for 10 h at room temperature. The product was centrifuged and dried in a vacuum oven at 100 °C for 8 h. Thus, the surface of the CNTs@SiO_2 was grafted with the complex of TCS and APTES or PTMOS. The sorbent was extracted with 25 mL of ethanol and 25 mL of 1 M HCl under stirring for 2 h to remove TCS. The product was isolated by centrifugation, washed with ethanol/6 M HCl (1:1, v/v), neutralized with 0.1 M NaOH, and washed with highly purified water. Finally, the sorbent was dried under vacuum at 80 °C for 12 h. For comparison, the CNTs@NIPs was also prepared following the same procedure in the absence of TCS.

2.5. Binding experiments of CNTs@TCS-MIPs and CNTs@NIPs

In kinetic adsorption experiments, 50 mg of CNTs@TCS-MIPs were mixed with 20 mL ethanol solution of TCS at a concentration of 30 μg mL^{-1}, and incubated at regular time intervals, and then the supernatants and polymers were separated by centrifugation. The TCS concentration of the supernatants was measured by HPLC analysis.

In steady-state binding experiments, 50 mg of CNTs@TCS-MIPs and CNTs@NIPs were mixed with 10 mL ethanol solution of TCS of various concentrations from 0.01 to 40 μg mL^{-1}. CNTs@TCS-MIPs and CNTs@NIPs were isolated by centrifugation after incubation for 30 min at room temperature. The amount of TCS bound to the CNTs@TCS-MIPs and CNTs@NIPs were determined by HPLC.

2.6. Reproducibility and reusability of CNTs@TCS-MIPs and CNTs@NIPs

The reproducibility of CNTs@TCS-MIPs and CNTs@NIPs were evaluated by using 50 mg of six batches of products which were prepared on different days. These products were added to the solutions of TCS in 10 mL of ethanol with a concentration of 30 μg mL^{-1}. After incubation for 30 min at room temperature, the bound amount of TCS was measured by HPLC.

To estimate the reusability of CNTs@TCS-MIPs and CNTs@NIPs, 50 mg polymers were added to the solutions of TCS in 10 mL of ethanol with a concentration of 30 μg mL^{-1} and incubated at room temperature while gently stirred on a rocking table for 30 min. Then, CNTs@TCS-MIPs and CNTs@NIPs were removed by centrifugation and the bound amount of TCS was quantified by HPLC. The recovered CNTs@TCS-MIPs and CNTs@NIPs were washed with a mixture of ethanol/6 M HCl (1:1, v/v) in Soxhlet extractor till we ensure complete removal of residual TCS in the polymers and washed with ethanol for several times, then dried under vacuum at 60 °C and reused for adsorption of TCS.

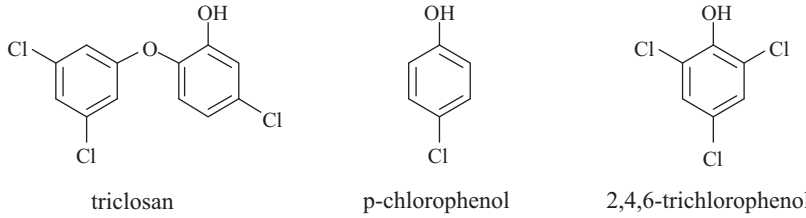

Fig. 1. Molecular structures of chlorophenols used in this study.

2.7. Separation and determination of TCS in environmental water samples

The river and lake water samples collected from the Xiaoyin River and Mati Lake (Tianjin, China) were selected for the spiked sample analysis. 100 mL river and lake water were spiked with TCS at three levels 0.1, 0.3 and 0.5 μg L^{-1}, respectively, and then stored in closed amber glass containers at room temperature in the dark until they were analyzed within 24 h after sampling. 100 mg of CNTs@TCS-MIPs and CNTs@NIPs were added to 50 mL of the spiked river and lake water samples, then incubated for 30 min at room temperature. Next, the mixture was centrifuged at 5000 rpm for 8 min. Finally, after the supernatant solution was discarded, CNTs@TCS-MIPs and CNTs@NIPs which absorbed target molecule were eluted with a mixture of ethanol/6 M HCl (1:1, v/v) solution, collected, and evaporated to dry under a stream of nitrogen and dissolved with 2 mL of methanol and measured by HPLC.

3. Results and discussion

3.1. Preparation and characterization of CNTs@TCS-MIPs

The synthesis of CNTs@TCS-MIPs *via* a multistep procedure is involved in the formation of template (TCS)-aminosilica monomer (APTES) complex, silica–shell deposition on the surface of CNTs, MIP-functionalized onto the silica surface, and final extraction of TCS to generate the recognition sites (Fig. 2). This method contained two sol–gel processes: one was to transform silica shell to the surface of purified CNTs using TEOS and APTES in the presence of cationic surfactant CTAB to produce the CNTs@SiO_2 with core–shell structure; the other was to anchor an MIP shell on the surface of CNTs@SiO_2 using HAc as the catalyst to obtain core–shell CNTs@TCS-MIPs nanocomposite.

TEM images of the CNTs, CNTs@SiO_2 and CNTs@TCS-MIPs are shown in Fig. 3. The average diameter of CNTs adopted was about 60–80 nm (Fig. 3A). After coating with thin SiO_2, the diameter of the CNTs@SiO_2 was increased to about 80–100 nm, corresponding to a 10–20 nm thick SiO_2 layer covered on CNTs (Fig. 3B). The SiO_2 layers with a thickness of 10–20 nm were uniformly coated on CNTs for all the samples, and there were hardly any free SiO_2 particles as observed by TEM. CNTs having a silica shell provided good biocompatibility, non-toxic coating, a hydrophilic surface and high dispersion in all solvents, Furthermore, the silanol groups on the surface of silica-coated CNTs could be easily modified to link with bioconjugators by the sol–gel method with interesting biofunctionalities. The TEM image in Fig. 3C shows the formation of CNTs@TCS-MIPs core@shell structured nanocomposites after the template–monomer complex was reacted on the surface of the CNTs@SiO_2 via sol–gel reaction. It was observed that the thickness of the silica film could be increased by repeating the sol–gel reaction. The diameter of the CNTs@TCS-MIPs nanocomposite was increased to 100–120 nm after the TCS-imprinting process, which corresponds to a roughly 15–20 nm thick imprinted SiO_2 layer covered on CNTs@SiO_2. The thickness of the imprinted polymer layer was 15–20 nm, which would be effective to the mass transport between solution and the surface of CNTs@TCS-MIPs.

The FT-IR spectra of CNTs, CNTs@SiO_2, CNTs@TCS-MIPs and CNTs@NIPs were compared in Fig. 4. There was no obvious peak in the spectrum of the blank CNTs (Fig. 4a). The strong peak at about 1069 cm^{-1} is attributed to the stretch of Si–O–Si, and the –OH vibration was detected at 3442 and 1636 cm^{-1}. The above peaks indicated the formation of silica film on the surface of

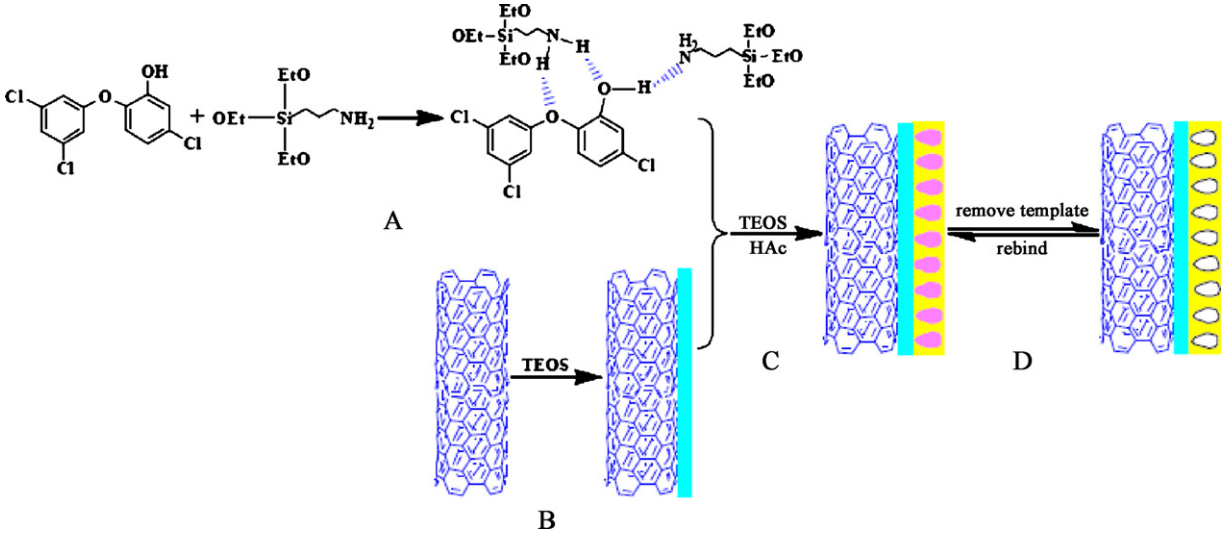

Fig. 2. Scheme of the synthetic route for CNTs@TCS-MIPs: (A) formation of template (TCS)-aminosilica monomer (APTES) complex; (B) transformation of the surface of purified CNTs to silica shell by a sol–gel process using TEOS and APTES in the presence of CTAB to obtain core@shell CNTs@SiO_2; (C) reaction of CNTs@SiO_2 with template-silica monomer complex to produce silica surface functionalized with TCS-imprinted polymer; (D) removal of the TCS from polymer shells and the CNTs@TCS-MIPs were obtained.

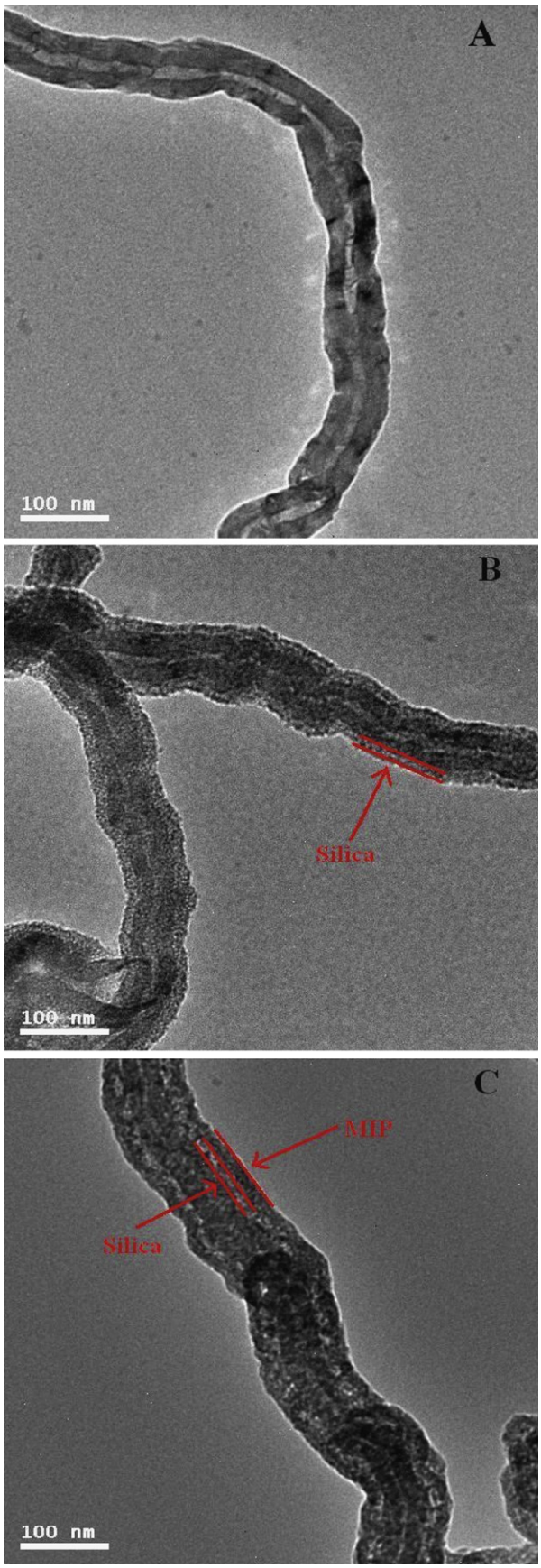

Fig. 3. TEM images of (A) blank CNTs; (B) CNTs@SiO_2; (C) CNTs@TCS-MIPs.

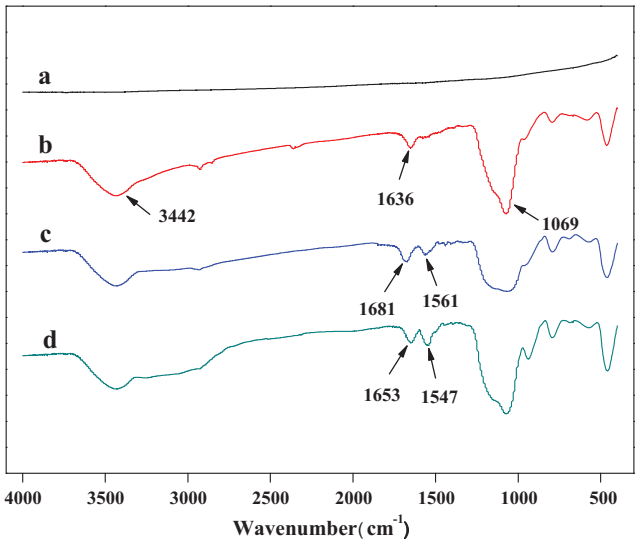

Fig. 4. FT-IR spectra of (a) blank CNTs; (b) CNTs@SiO_2; (c) CNTs@NIPs; (d) CNTs@TCS-MIPs.

CNTs (Fig. 4b). A characteristic feature of CNTs@TCS-MIPs and CNTs@NIPs when compared with the CNTs@SiO_2 was N–H bond at 1653 and 1547 cm^{-1} (Fig. 4d), 1681 and 1561 cm^{-1} (Fig. 4c). These results suggested that–NH_2 could be grafted onto the surface of CNTs@SiO_2. CNTs@TCS-MIPs and CNTs@NIPs showed similar location and appearance of the major bands.

3.2. Monomers selection for molecular imprinting

One of the important factors for successful molecular imprinting is the presence of functional monomers in the polymer matrix. The role of monomers is to assist in the creation of the specific binding cavity by exposing interacting chemical functions after the polymerization is situated within the cavity in an optimal position for rebinding. According to the structure and features of template molecule including polarity, hydrophobicity, and acidity, the specific functional monomers were tailored to the designed template. When inspecting template TCS, the functional groups on this molecule that one can use as anchors are the phenyl group, the hydroxyl group and the O atom link. We selected APTES, PTMOS and the mixture of APTES and PTMOS (1:1, v/v) as functional monomers to examine the capacity of corresponding polymers. 50 mg of CNTs@TCS-MIPs and CNTs@NIPs prepared with different functional monomers were mixed with 10 mL ethanol solution of TCS at a concentration of 30 $\mu g\,mL^{-1}$, to investigate the effect of functional monomer on the uptake capacity. The results are shown in Fig. 5. We found that APTES as functional monomers were much better than PTMOS and the mixture of APTES and PTMOS, not only in adsorption capacity, but also in imprinting effect. This might result from the interaction between functional monomers and the template molecule TCS. The monomer APTES provides amine group which can form hydrogen bonds with O atom and interact with hydroxyl group through the acid/base interaction, and also provides the hydrophobic ether-like Si–O–Si bond (for interaction, e.g., with the Ar–O–R moiety) [29]; while PTMOS provides the phenyl group for π–π interactions with the phenyl residue. TCS possesses two O atoms, which have the ability to form multiple hydrogen bonds with the –NH_2 of APTES and the acid/base interaction. The hydrogen bonds and the acid/base interaction between functional monomer APTES and TCS might be much stronger than π–π interactions between TCS and PTMOS. Because of its superiority, APTES was chosen as the functional monomer in the work.

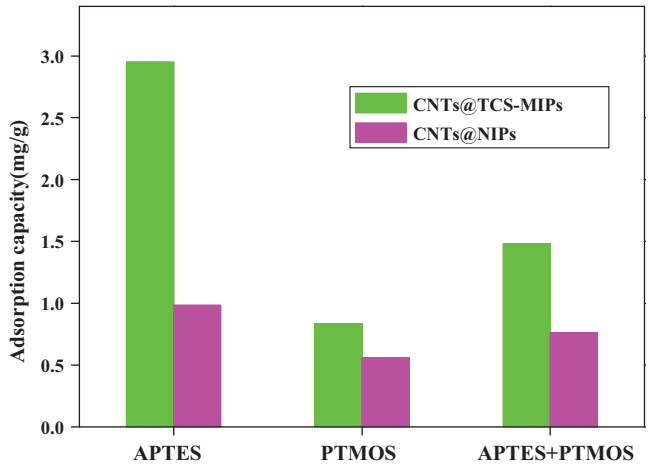

Fig. 5. The effect of different functional monomers on the imprinting of CNTs@TCS-MIPs and CNTs@NIPs.

3.3. Binding characteristics of imprinted materials

Fig. 6A presents the adsorption kinetics of TCS solution onto CNTs@TCS-MIPs. The adsorption capacity was increased with time and the imprinted polymers exhibited a high adsorption rate. In the first 30 min, the adsorption rate was increased rapidly and reached equilibrium after 60 min. Such a time profile indicated an initial rapid increases in the adsorption capacity and later a slower increase to reach the adsorption equilibrium. For imprinted materials of non-thin films, it takes generally 12–24 h to reach adsorption equilibrium [30]. However, imprinted materials of thin films only need 30–200 min to reach adsorption equilibrium for different templates [25,26]. Therefore, in our case, TCS reached the surface imprinting cavities of CNTs@TCS-MIPs easily and took less time to reach adsorption saturation, which implied that the nanosized, surface imprinting and uniform structures of CNTs@TCS-MIPs allowed efficient mass transport, thus overcoming some drawbacks of traditionally packed imprinted materials.

To investigate the affinity of CNTs@TCS-MIPs and CNTs@NIPs, a steady-state binding method and subsequent Scatchard analysis were carried out. The binding isotherms of TCS to CNTs@TCS-MIPs and CNTs@NIPs were determined in the concentration range of 0.01–40 μg mL^{-1} (initial concentration) and the results were shown in Fig. 6B. The data indicated the amount of TCS bound to the CNTs@TCS-MIPs was increased quickly along with increased initial concentration when it was below 30 μg mL^{-1}. When the initial concentration was over 30 μg mL^{-1}, the adsorption curve became relatively flat and reached saturation at high TCS concentration. However, the amount of TCS bound to CNTs@NIPs at equilibrium experiment was only increased along with increased initial concentration of TCS and did not reach saturation at high TCS concentration obviously in the studied range. These results indicated the amount of TCS bound to CNTs@TCS-MIPs was dramatically higher than that of CNTs@NIPs at the same initial concentration. Therefore, the high surface/volume ratios of nanosized imprinted CNTs@TCS-MIPs were expected not only to improve the binding capacity, but also to provide an excellent accessibility to target molecules.

The saturation binding data were further processed to generate a Scatchard equation to estimate the binding properties of CNTs@TCS-MIPs. The Scatchard equation was as follows:

$$\frac{Q}{[\mathrm{TCS}]} = \frac{Q_{\max} - Q}{K_{\mathrm{D}}}$$

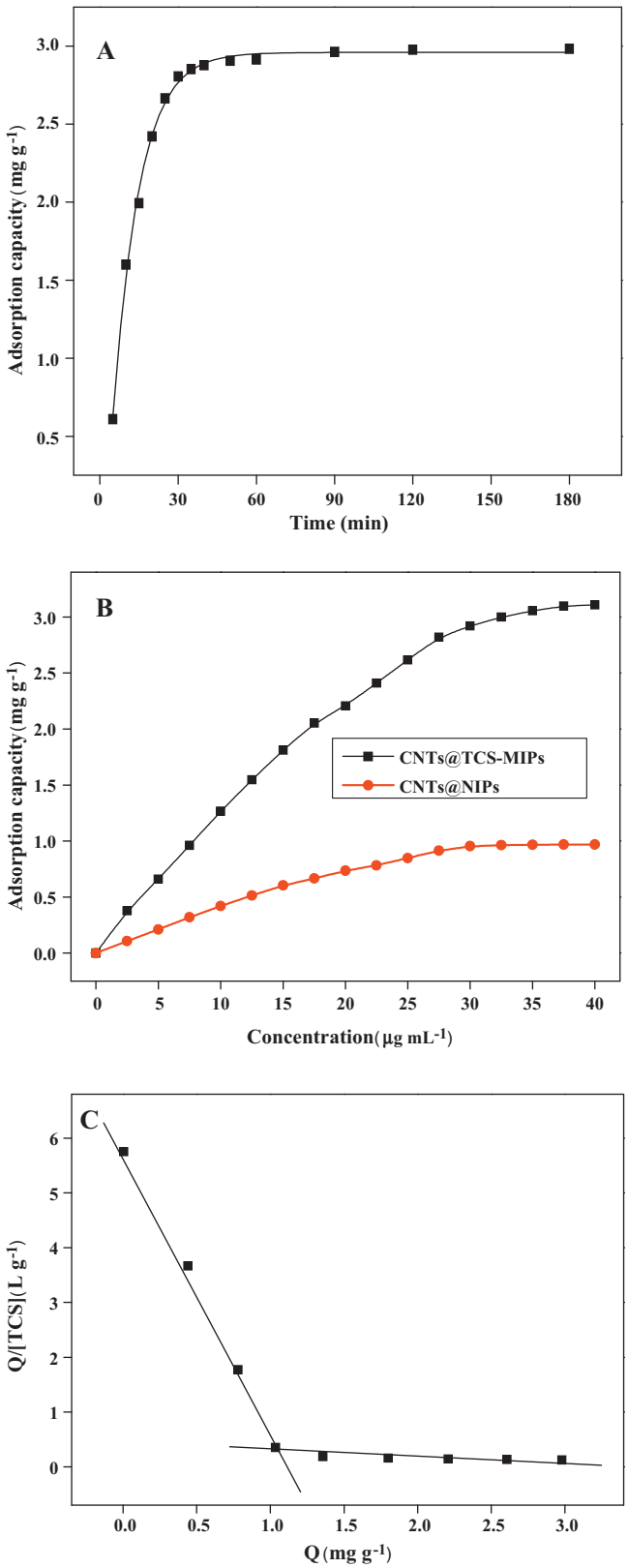

Fig. 6. Curves of (A) adsorption kinetics of CNTs@TCS-MIPs; (B) adsorption isotherm of TCS onto CNTs@TCS-MIPs and CNTs@NIPs; (C) Scatchard plot to estimate the binding nature of CNTs@TCS-MIPs.

Table 1
The adsorption capacity, partition coefficients, imprinting factors and selectivity coefficients of TCS, *p*-CP and 2,4,6-TCP onto CNTs@TCS-MIPs and CNTs@NIPs.[a]

Analytes	Q_{MIP}[b] (mg g^{-1})	Q_{NIP}[b] (mg g^{-1})	K_{MIP} (mL g^{-1})	K_{NIP} (mL g^{-1})	*IF*	*SC*
p-CP	1.026	0.9471	347.9	305.1	1.141	3.592
2.4.6-TCP	0.5824	0.4148	151.8	99.46	1.526	2.684
TCS	1.816	0.8055	973.6	237.7	4.096	–

[a] In this experiment, 100 mg of CNTs@TCS-MIPs and CNTs@NIPs were incubated with the mixture of TCS, *p*-CP and 2, 4, 6-TCP at a concentration of 30 μg mL^{-1} in 10 mL of ethanol for 30 min at room temperature ($n = 3$).
[b] Corner marks MIP and NIP represent the imprinted and non-imprinted polymers, respectively.

where Q is the amount of TCS bound to CNTs@TCS-MIPs at equilibrium, Q_{max} is the apparent maximum adsorption capacity, [TCS] is the free analytical concentration at equilibrium and K_D is the dissociation constant. The values of K_D and Q_{max} could be calculated from the slope and intercept of the linear curve plotted as Q/[TCS] versus Q.

The Scatchard analysis of CNTs@TCS-MIPs was performed. It was observed that two straight lines were obtained in the plot region (Fig. 6C), which indicated that there existed two kinds of binding sites of high and low affinity. The linear regression equations for the left and right slope of the biphasic curve is $Q/[TCS] = 5.849 - 5.244Q$ ($r = 0.9992$) and $Q/[TCS] = 0.2304 - 0.03746Q$ ($r = 0.9722$). From the slope and the intercept of the biphasic curve obtained, the values of K_D were 0.1907 and 26.69 g L^{-1}, and Q_{max} were 1.115 and 6.149 mg g^{-1}, respectively.

3.4. Binding specificity of CNTs@TCS-MIPs and CNTs@NIPs

In order to verify the selectivity of the CNTs@TCS-MIPs and CNTs@NIPs to TCS, two chlorophenols (*p*-CP and 2, 4, 6-TCP) were selected as analogues. The adsorption of CNTs@TCS-MIPs and CNTs@NIPs to the mixture of TCS, *p*-CP and 2, 4, 6-TCP with a concentration of 30 μg mL^{-1} in 10 mL of ethanol was listed in Table 1.

The specificity of CNTs@TCS-MIPs and CNTs@NIPs was estimated by the partition coefficients of the selected chlorophenols between polymers and the solution. The partition coefficient K was determined according to the following formula:

$$K = \frac{C_p}{C_s}$$

where C_p was the amount of test analytes bound by CNTs@TCS-MIPs and CNTs@NIPs nanocomposites, and C_s was the concentration of test analytes remaining in the solution.

Additionally, the imprinting factor (*IF*) and selectivity coefficient (*SC*) were generally used to evaluate the selectivity properties of CNTs@TCS-MIPs and CNTs@NIPs toward TCS and structurally related chlorophenols *p*-CP and 2, 4, 6-TCP. The *IF* and *SC* were calculated by the following formulas:

$$\text{Imprinting factor}\,(IF) = \frac{K_i}{K_c}$$

$$\text{Selectivity coefficient}\,(SC) = \frac{IF_{TCS}}{IF_i}$$

where K_i and K_c represent the partition coefficients of analytes for CNTs@TCS-MIPs and CNTs@NIPs, IF_{TCS} and IF_i are the imprinting factors for TCS and the other two chlorophenols, respectively.

As shown in Table 1, the bound amount of TCS for CNTs@TCS-MIPs was much higher than that of the other two chlorophenols, suggesting that the template molecule had a relatively higher affinity for the imprinted polymer than its analogues. Moreover, the *IF* of TCS was also much higher than those of two other chlorophenols. As shown in Fig. 1, TCS had two O atoms, however, *p*-CP and 2, 4, 6-TCP both only had one O atom. Therefore, the interaction of CNTs@TCS-MIPs with TCS through hydrogen bond might be much stronger than *p*-CP and 2, 4, 6-TCP. In addition, TCS was imprinted on silica layers during the preparation of imprinted polymers. After removal of TCS, the complementary cavities in imprinted polymers in the positioning of the functional groups and in the shape of the template were formed. These results further verified the satisfactory imprinting efficiency of the imprinted polymers for TCS in the present work.

3.5. Reproducibility of CNTs@TCS-MIPs and CNTs@NIPs

The reproducibility of CNTs@TCS-MIPs and CNTs@NIPs were investigated by using six batches of CNTs@TCS-MIPs and CNTs@NIPs prepared on different days. Three independent replicates were used for each batch. The mean adsorption capacity of every batch with the relative standard deviation (RSD) was listed in Table 2. The results showed that the reproducibilities of six batches of CNTs@TCS-MIPs and CNTs@NIPs were all satisfactory with a RSD less than 12%.

3.6. Adsorption–desorption of CNTs@TCS-MIPs and CNTs@NIPs

A stable performance is expected when the polymers are to be used repeatedly. To examine the reusability of MIPs and NIPs, the adsorption–desorption cycle was repeated six times by using the same CNTs@TCS-MIPs and CNTs@NIPs. Fig. 7 shows the change of the amount of adsorbed TCS after six regeneration cycles. It could be seen that the MIPs lost more than 7.6% of its affinity on average over six cycles, while the affinity of NIPs remained unchanged. It is probable that some recognition sites in the network of CNTs@TCS-MIPs could be jammed after regeneration or destructed after rewashing, and thus, they were not fit for the template molecule anymore. On the other hand, the affinity of CNTs@NIPs was nonspecific and the effect of washing is negligible. The MIPs and NIPs could be regenerated after the removal of the bound TCS by washing and retain their recovery efficiency for at least six adsorption–desorption cycles upon treatment with ethanol/6 M HCl (1:1, v/v) and highly puri-

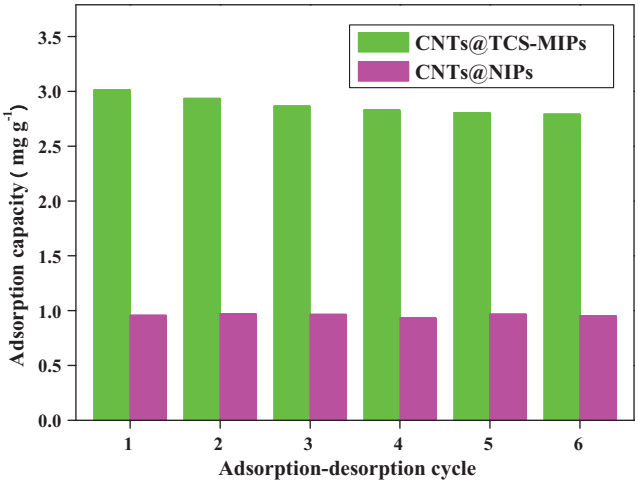

Fig. 7. Reusability of CNTs@TCS-MIPs and CNTs@NIPs.

Table 2
Reproducibility of CNTs@TCS-MIPs and CNTs@NIPs.

Polymers	Batch	1	2	3	4	5	6	Average
CNTs@TCS-MIPs	Q (mg g^{-1})	2.913	3.026	2.857	2.946	2.781	3.125	2.941
	RSD	6.7	7.9	8.4	4.1	11.4	10.3	8.9
CNTs@NIPs	Q (mg g^{-1})	0.9761	0.9452	0.9505	0.9618	0.9753	0.9346	0.9573
	RSD	7.1	8.6	6.9	5.8	9.7	11.2	8.2

Table 3
Recoveries of CNTs@TCS-MIPs binding TCS for spiked river and lake water samples (n = 5).

Samples	TCS					
	0.1 μg L^{-1}		0.3 μg L^{-1}		0.5 μg L^{-1}	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
River water	92.1	5.6	93.4	3.8	95.3	2.1
Lake water	90.7	8.4	91.8	6.9	93.6	3.5

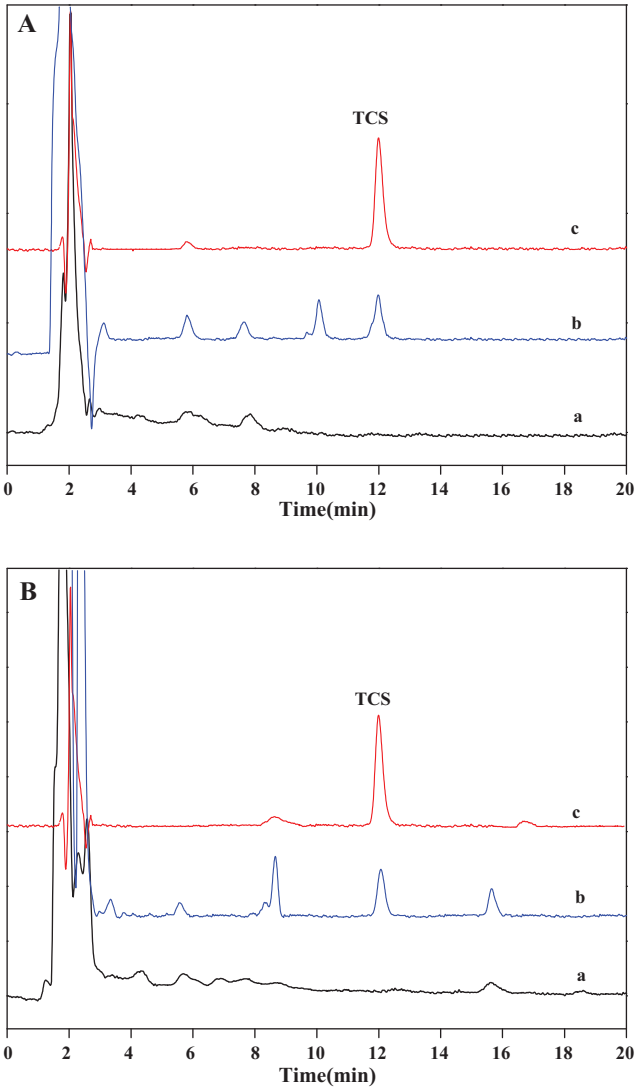

Fig. 8. Chromatograms of (A) river and (B) lake water samples. (a) Samples spiked with TCS at the concentration of 0.5 μg L^{-1}, elution of (b) CNTs@NIPs and (c) CNTs@TCS-MIPs washed with a mixture of ethanol/6 M HCl (1:1, v/v) after CNTs@TCS-MIPs and CNTs@NIPs adsorbing 100 mL of river or lake water spiked samples, respectively.

fied water. These results demonstrated reusability of the imprinted and non-imprinted materials over several adsorption–desorption cycles.

3.7. Application of imprinted and non-imprinted materials in environmental water samples

The application of CNTs@TCS-MIPs and CNTs@NIPs to selective adsorption of TCS in environmental water samples was also investigated. After adsorption of CNTs@TCS-MIPs and CNTs@NIPs to 100 mL of river or lake water samples spiked with TCS at the concentration of 0.5 μg L^{-1}, the adsorbed CNTs@TCS-MIPs and CNTs@NIPs were washed with a mixture of ethanol/6 M HCl (1:1, v/v). The chromatograms of samples spiked with TCS at the concentration of 0.5 μg L^{-1}, and elution of adsorbed CNTs@TCS-MIPs and CNTs@NIPs to TCS are displayed in Fig. 8. The peak of TCS could not be seen from chromatograms of the environmental water samples spiked with TCS at the concentration of 0.5 μg L^{-1} (Fig. 8a). After the enrichment of spiked river or lake water samples with CNTs@TCS-MIPs, and washing by ethanol/6 M HCl (1:1, v/v), the peak of TCS appeared distinctly at 11.98 min and other irrelevant compounds in the environmental water samples were nearly eliminated (Fig. 8c). The chromatograms confirmed that TCS in spiked environmental water samples were selectively enriched by CNTs@TCS-MIPs and could be recovered by the washing step. As shown in Fig. 8b, the extraction efficiency and selectivity of CNTs@NIPs are much lower than those of CNTs@TCS-MIPs. The enrichment of CNTs@NIPs showed a lack of selectivity, and some other unconcerned compounds were enriched besides the TCS.

To evaluate the accuracy and application of the developed method, the environmental water samples spiked with three levels of TCS (0.1, 0.3, and 0.5 μg L^{-1}) were analyzed. At each concentration, five measurements were performed (Table 3). The recoveries of river water and lake water samples were ranged from 92.1 to 95.3% and 90.7 to 93.6%, respectively. The relative standard deviation (RSD) was less than 8.4%. These results revealed that CNTs@TCS-MIPs could be directly used for selective adsorption and determination of TCS in environmental water samples. The characteristics of the CNTs@TCS-MIPs are stable, which could be used for over six cycles with lost of less than 6.9% of its recovery on average.

4. Conclusion

A simple method was developed to synthesize core–shell molecularly imprinted polymers for the extraction of triclosan by combining a surface molecular imprinting technique with a sol–gel process based on carbon nanotubes coated with silica.

The MIPs nanocomposites combined the merits of surface molecular imprinting and carbon nanotubes. The prepared imprinted materials possessed fast kinetics, high capacity and favorable selectivity. Different batches of MIPs showed good reproducibility and the reusability of MIPs without any deterioration in capacity was demonstrated for at least six repeated cycles. The MIPs developed could be used for the selective adsorption and determination of triclosan from environmental matrices. The MIPs developed in this research can also be applied as selective coatings for electrochemical and quartz crystal microbalance (QCM) sensors to monitor trace amounts of environmental pollutants.

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