

# Thermoresponsive and magnetic molecularly imprinted polymers based on iron oxide encapsulated carbon nanotubes as a matrix for the selective adsorption and controlled release of 2,4,5-trichlorophenol

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**ABSTRACT:** Thermoresponsive and magnetic molecularly imprinted polymers (TMMIPs) based on magnetic carbon nanotubes (MCNTs) were prepared and applied to the switched recognition and controlled release of 2,4,5-trichlorophenol (2,4,5-TCP) from aqueous solution. In this study, MCNTs were first synthesized via the encapsulation of  $\text{Fe}_3\text{O}_4$  nanoparticles into the tunnel of carbon nanotubes by a wet impregnation technology. Then, the TMMIPs were synthesized with *N*-isopropyl acrylamide as a thermal functional monomer by free-radical polymerization. The magnetic sensitivity and stability of the prepared materials were tested with a vibrating sample magnetometer (saturation magnetization = 1.4 emu/g) and atomic absorption spectrophotometer (in the pH range 3.0–8.0), respectively. The thermoresponsive properties of the TMMIPs were evaluated by two means, including the results of ultraviolet–visible spectroscopy and the controlled release of 2,4,5-TCP at 30 and 40°C, respectively. The effects of the pH, initial concentration, and contact time on adsorption were examined with batch mode experiments, and several other compounds were selected as model analytes to evaluate the selective recognition performance of the TMMIPs. This demonstrated that the TMMIPs had a higher affinity for 2,4,5-TCP than did the thermoresponsive and magnetic nonimprinted polymers. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42087.

**KEYWORDS:** adsorption; composites; magnetism and magnetic properties

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## INTRODUCTION

Carbon is a fascinating and very versatile element. It is able to form various different architectures at the nanoscale, such as carbon nanotubes (CNTs), nanofibers, graphene, fullerene, and carbon nanospheres.<sup>1</sup> These carbon materials have been applied in many fields, including nanoelectronics, nanometer materials science, nanomechanics, nanobiology, and environmental science, because of their better performance, including their special structure, better crystallinity, faster mass transfer, and large surface area.<sup>2–6</sup> Among them, CNTs have demonstrated the best performance up to this point, and related study articles started to increase in number almost exponentially after Sumio Iijima<sup>7</sup> confirmed the existence of CNTs in 1991 using electron diffraction. They have been intensively studied and have received much attention for their applications in various areas because of their excellent properties, which include a high specific surface area, extremely high mechanical stability, and electron emission.<sup>8–10</sup> CNTs have mostly been used as adsorption materials because of their extraordinary mechanical strength and relatively large specific area.<sup>11,12</sup> Earlier studies demonstrated that

CNTs may be an excellent adsorption material for use in wastewater treatment. However, CNTs have the drawback of no specific adsorption to certain pollutants; this limits their application in the enrichment, separation, and detection of contaminants.

Molecular imprinting technology is an approach for incorporating affinity binding sites for target molecules in synthetic polymers; these are called *molecularly imprinted polymers*.<sup>13</sup> This molecular recognition characteristic has been applied in several different fields, including catalysis, solid-phase extraction, chromatography, biomedical applications, and sensors.<sup>14–18</sup> A surface molecular imprinting technique was established on the basis of molecular imprinting through the fabrication of the molecularly imprinted polymer layer on the surface of a supporting substrate; this resulted in the improvement of the mass transfer and a reduction in the permanent entrapment of templates in traditional molecules.<sup>19</sup> Thus, CNTs could be a promising supporting substrate for surface molecular imprinting processes.

The application of magnetic particles to solve environmental problems has received considerable attention in recent years.

Magnetic particles can be used as adsorbents to adsorb contaminants directly.<sup>20</sup> Because magnetic nanoparticles are likely to aggregate and dissolve in acid solution, they have been encapsulated in other adsorption materials, such as silica, carbon, and polymers.<sup>21–23</sup> The drawback is that the adsorption capacity is relatively small. In this study, magnetic carbon nanotubes (MCNTs) were synthesized via the encapsulation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles into the tunnel of CNTs by a wet impregnation technology. Thus, with this method, we obtained an excellent composite adsorption material that could be separated from the medium by an applied magnetic field.

Functional materials with reversibly switchable physicochemical properties have received increasing interest. Thus, stimuli-responsive materials can be controlled via changes in environmental factors, such as the temperature, pH, ionic strength, light, and electrical properties.<sup>24–28</sup> Particularly, thermoresponsive materials as drug-delivery systems, sensors, and solute separation systems have been investigated by many groups. Poly(*N*-isopropyl acrylamide) (PNIPAM) is a kind of typical functional polymer that undergoes a phase separation from a swollen, hydrophilic state to a collapsed, hydrophobic state in water at temperatures higher than its lower critical solution temperature (LCST).<sup>29</sup> In this article, we report an effective method for achieving thermoresponsive and magnetic molecularly imprinted polymers (TMMIPs) based on MCNT composites; we were able to selective recognition and controlled release of the template molecules in response to environmental temperature changes.

Chlorophenols have widespread use and are persistent organic contaminants in the environment. They are used as a fungicide in the paper industry and as a precursor in the herbicide industry.<sup>30</sup> 2,4,5-Trichlorophenol (2,4,5-TCP), as a typical chlorophenol, has been listed by the U.S. Environmental Protection Agency as one of 31 high-priority pollutants.<sup>31</sup> Commonly, even low levels of 2,4,5-TCP in drinking water may pose a serious threat to human health and natural ecosystems. The selective recognition and separation of the target 2,4,5-TCP from complex matrices in aquatic systems is of great importance.

Inspired by the aforementioned work, we first obtained the encapsulation of Fe<sub>3</sub>O<sub>4</sub> particles within the tubular structure of CNTs by a wet impregnation technique. Then, *N*-isopropyl acrylamide (NIPAM) was adopted as a thermoresponsive monomer, and TMMIPs based on MCNTs were prepared by free-radical polymerization. Then, TMMIPs were applied to the selective adsorption and controlled release of 2,4,5-TCP from aqueous solution.

## EXPERIMENTAL

### Instruments and Apparatus

The morphology of the MCNTs and TMMIPs were examined by transmission electron microscopy (TEM; JEM-2010HR) analysis. Magnetic measurements were carried out with a vibrating sample magnetometer (7300, Lakeshore) under a magnetic field up to 10 kOe. Thermogravimetric analysis (TGA) of the samples were performed for powder samples (ca. 10 mg) with a Diamond Thermogravimetric/Differential Thermal Analysis

(TG/DTA) instrument (PerkinElmer) under a nitrogen atmosphere up to 800°C with a heating rate of 5.0°C/min. A TBS-990 atomic absorption spectrophotometer (Beijing Purkinge General Instrument Co., Ltd., Beijing, China) with a deuterium background correction and a GF990 graphite furnace atomizer system was used to study the leakage of magnetite from TMMIPs at different pH values. A BI-200SM instrument (BrookHaven Instruments) was used to determine the size and size distribution of the polymers.

### Reagents and Materials

CNTs were obtained from Zhengzhou Jinyanguang China-ware Co., Ltd. (Henan, China). Fe(NO<sub>3</sub>)<sub>3</sub>, ferrocene, propionic acid, ethylene glycol dimethacrylate (EGDMA), acrylamide (AM), dimethyl sulfoxide (DMSO), NIPAM, oleic acid, and poly(vinyl pyrrolidone) were all purchased from Chemical Reagent Corp. 2,2'-Azobisisobutyronitrile was supplied by Shanghai No.4 Reagent & H. V. Chemical Co., Ltd. (Shanghai, China). 2,4,5-TCP, 2,4-dichlorophenol (2,4-DCP), sesamol, thymol, and 3-(methacryloyloxy)propyl trimethoxysilane (MPS) were all purchased from Aladdin Reagent Co., Ltd. (Shanghai, China).

### Preparation of the MCNTs

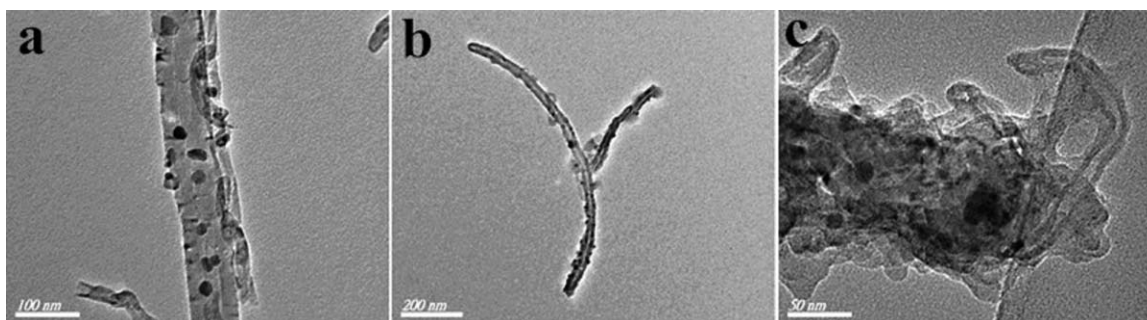
**Method 1.** Amounts of 0.22 g of CNTs and 0.1 g of Fe(NO<sub>3</sub>)<sub>3</sub> were dissolved in 10 g of ethanol and sonicated for 1.0 h. The solution was dried at 60°C for 12 h to obtain the dry powder. The products were steamed with propionic acid at 80°C for 15 h in a tube furnace and then heated at 260°C in an N<sub>2</sub> atmosphere for 2.0 h. The black products were separated by an externally applied magnetic field and washed several times with water and ethanol. Finally, the obtained MCNTs were dried at 60°C for 6.0 h.

**Method 2.** CNTs and ferrocene (CNT/ferrocene mass ratio = 1 : 1) were placed in tube furnace. The tube furnace was sealed with N<sub>2</sub> and maintained at 350°C for 2.0 h. After they were cooled to room temperature, the resulting MCNTs were collected and washed with ethanol several times to remove unreacted ferrocene. Then, they were dried at 60°C *in vacuo* for 6.0 h.

### Synthesis of the TMMIPs

First, the MCNTs were modified with MPS to make active vinyl organic function groups grafted onto the surface of MCNTs. An amount of 1 g of MCNTs was dispersed into 165 mL of an ethanol/water mixture (10 : 1 v/v). The mixture was stirred for 0.5 h at room temperature, and then, 3.5 mL of MPS was added to the mixture under a temperature of 40°C for 24 h. The resulting modified CNTs were collected by an Nd-Fe-B permanent magnet. After they were washed several times by ethanol and water, the resulting CNTs were dried at 50°C *in vacuo* for 5.0 h.

Second, the modified MCNTs were coated with the temperature-sensitive molecularly imprinted polymer layer. The template molecules 2,4,5-TCP (1.0 mmol), NIPAM (0.4 g, 3.5 mmol), and AM (0.1 g, 1.4 mmol) were dispersed into DMSO (10 mL), and the mixture was sonicated for 1.0 h to allow for the self-assembly of the template molecules and functional monomer. An amount of 0.25 g of modified MCNTs were

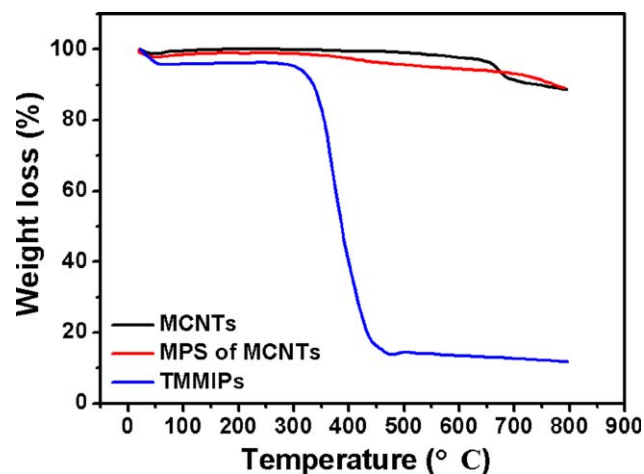


**Figure 1.** TEM images of the (a) MCNTs synthesized by method 1, (b) MCNTs synthesized by method 2, and (c) TMMIPs.

dispersed in 2.0 mL of oleic acid and stirred for 1.0 h. Then, the previous preassembly solution and EGDMA (1.46 mL) were added to the mixture of MCNTs and oleic acid under stirring. After 30 min, 0.4 g of polyvinylpyrrolidone and 100 mL of DMSO/water (9 : 1 v/v) were added under violent stirring (300 rpm) for 15 min. After we purged the oxygen with nitrogen gas for 10 min, 0.1 g of 2,2'-azobisisobutyronitrile was added to the solution. The mixture was heated to 50°C in an N<sub>2</sub> atmosphere for 6.0 h. While the temperature was increased to 70°C, the mixture was stirred for 18 h under N<sub>2</sub> protection. After the polymerization, the TMMIPs were collected by an Nd–Fe–B permanent magnet. The template molecules were removed by extensive washing with a mixture of methanol/acetic acid (95 : 5 v/v) with Soxhlet extraction until no 2,4,5-trichlorophenol leakage was observed from the eluant. Finally, the obtained magnetic molecularly imprinted polymers (MMIPs) were dried at 50°C *in vacuo*. In comparison, the magnetic non-imprinted polymers (MNIPs) were also prepared as a blank in parallel but without the addition of 2,4,5-TCP.

#### Batch Mode Binding Studies

The influence of the pH in solution, contact time, and initial concentration of 2,4,5-TCP on the adsorption were studied. The specific steps were as follows: 10 mg of adsorbents [TMMIPs or thermoresponsive and magnetic nonimprinted polymers (TMNIPs)] were dispersed in a solution of 2,4,5-TCP (10 mL).



**Figure 2.** TGA curves of the MCNTs, modification of the MCNTs, and TMMIPs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The concentration of the testing solution was prepared according to the requirements of the different experiments. After the required adsorption time, the TMMIPs or TMNIPs were isolated by an Nd–Fe–B permanent magnet. Finally, the concentration of the template in the solvent phase was determined with an ultraviolet–visible (UV–vis) spectrophotometer at 293 nm. In addition, all of the experiments were maintained at room temperature.

#### Controlled Release of 2,4,5-TCP

The controlled release of the captured 2,4,5-TCP from TMMIPs was carried out. A series of adsorption experiments was first implemented as follows: 10 mg of TMMIP adsorbent was dispersed in 10 mL of a testing solution of 2,4,5-TCP (100 mg/L) for 12 h at 25°C. Then, the TMMIPs were collected by an Nd–Fe–B permanent magnet, washed with water, and finally placed in 10 mL of deionized water at 30 and 40°C for different times, respectively. The concentration of released 2,4,5-TCP was determined with a UV–vis spectrophotometer at 293 nm.

#### Procedure for the Selective Binding Experiments

To measure the specific adsorption of the TMMIPs to 2,4,5-TCP, 10 mg of the TMMIPs or TMNIPs was added to a 10-mL solution with 200 mg/L of 2,4,5-TCP, 2,4-DCP, bisphenol A (BPA), thymol, and sesamol, respectively. The concentration was determined with a UV–vis spectrophotometer at 293, 285, 276, 273, and 296 nm.

#### Magnetite Leakage Studies

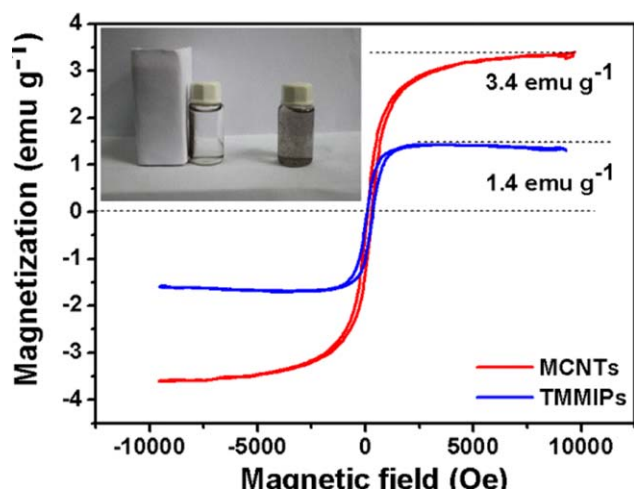
To testify the resistance to acid corrosion, 10 mg of MCNTs and TMMIPs were placed in 10 mL of deionized water with different pH values (ranging from 3.0 to 8.0), respectively. After 6 h, the TMMIPs were isolated by an Nd–Fe–B permanent magnet, and the amount of magnetite that was likely to leach from the materials into the media was determined by a graphite furnace atomic absorption spectrophotometer.

## RESULTS AND DISCUSSION

#### Characteristics of the TMMIPs

The morphology of the MCNTs of methods 1 and 2 and the TMMIPs were analyzed with TEM, as shown in Figure 1. As shown in Figure 1(a), there was a sporadic decoration with Fe<sub>3</sub>O<sub>4</sub> nanoparticles in the tube of the CNTs. We also found that Fe<sub>3</sub>O<sub>4</sub> nanoparticles were approximately spherical and about 20 nm in size and were encapsulated in the inner space of the CNTs. A few magnetic nanoparticles attached to the





**Figure 3.** Magnetization curves of the MCNTs and TMMIPs and photographs of the TMMIPs suspended in water in the absence and presence of an externally placed magnet (inset). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

surface of the CNTs. Compared with Figure 1(a), Figure 1(b) shows the MCNTs synthesized by method 2, which were decorated with  $\text{Fe}_3\text{O}_4$  nanoparticles on the surface of the CNTs. Thus, the materials did not effectively resist oxidation and acid corrosion. In this study, the MCNTs used as support materials were prepared by method 1. As shown in Figure 1(c), the surface of TMMIPs was coated with an imprinting layer of about 25 nm; this could benefit the template reaching the binding sites within a short time.

Figure 2 shows the TGAs of different samples. The TGA curves of the MCNTs were found to rapidly decrease after the temperature reached  $675^\circ\text{C}$ ; this could be ascribed to the decomposition of hydroxyl on the surface of the CNTs. The TGA trace of the vinyl-functionalized MCNTs showed an 11% weight loss between 25 and  $800^\circ\text{C}$  continuously; this described the successful modification of MPS. TGA of the TMMIPs showed an 89% weight loss in the range between 350 and  $800^\circ\text{C}$ ; this was due to the fact that the imprinting polymers layered, and a total of 11 wt % remained at  $800^\circ\text{C}$ . Thus, the remaining weights of the TMMIPs were attributed to the thermal resistance of the MCNT composites.

Figure 3 shows the magnetic hysteresis loops of the MCNTs and TMMIPs. The saturation magnetization values obtained at room temperature were 3.4 and  $1.4 \text{ emu/g}$  for MCNTs and TMMIPs, respectively. The saturation magnetization value of the TMMIPs significantly decreased to  $1.4 \text{ emu/g}$ ; this resulted from the imprinting of the polymers. However, the TMMIPs still possessed enough magnetic response to meet the need of magnetic separation, as can be observed in Figure 3 (inset). In the absence of an external magnetic field, the adsorbents dispersed uniformly in deionized water. When an external magnetic field was applied, the black TMMIPs were attracted to the wall of the vial in a short time. To verify the resistance to acid corrosion of MCNTs, the amounts of magnetite that was likely to leach from the  $\text{Fe}_3\text{O}_4$ , MCNTs, and TMMIPs were estimated.

The results showed that no magnetite was determined from MCNTs and TMMIPs, suggesting that the wall of CNTs prevented magnetite leakage successfully.

#### Factors Influencing the Adsorption of 2,4,5-TCP

First, we studied the effects of the pH and mechanism on the adsorption of 2,4,5-TCP; this was important for the batch mode experiments. The template molecular of 100 mg/L was selected as the initial concentration, and the adsorption capacities at different pHs for the TMMIPs and TMNIPs are shown in Figure 4(a). It is obvious that the curves show almost no changes for both the TMMIPs and TMNIPs over the pH range 3.0–5.0 and then decreased rapidly from 5.0 to 9.0, respectively. The possible mechanism was that the pH of the solution affected the degree of ionization of the template molecule; this subsequently led to a change in the surface charge for both adsorbents and adsorbates.<sup>32</sup> The fact that the neutral molecules of phenolic compounds benefitted the formation of hydrogen bonds with template molecules was also been reported in our previous work.<sup>33</sup> At a lower pH, the adsorption capacity was enhanced because the 2,4,5-TCP were under the undissociated state, and the molecular structures easy linked with the binding sites. Under higher pH conditions, the adsorption capacity significantly decreased because of the dissociation of hydroxyl groups, the repulsion of the negatively charged 2,4,5-TCP, and AM species decreased the hydrogen-bonding interactions between the template and monomer.<sup>34</sup> It was obvious that the maximum adsorption capacity was at pH 5.0; this was close to the value of the environmental system. Thus, 5.0 was selected as the optimal value for the adsorption medium in the following studies. Moreover, the adsorption capacity for the TMMIPs was greater than those of the TMNIPs; this strongly indicated the imprinting effect.

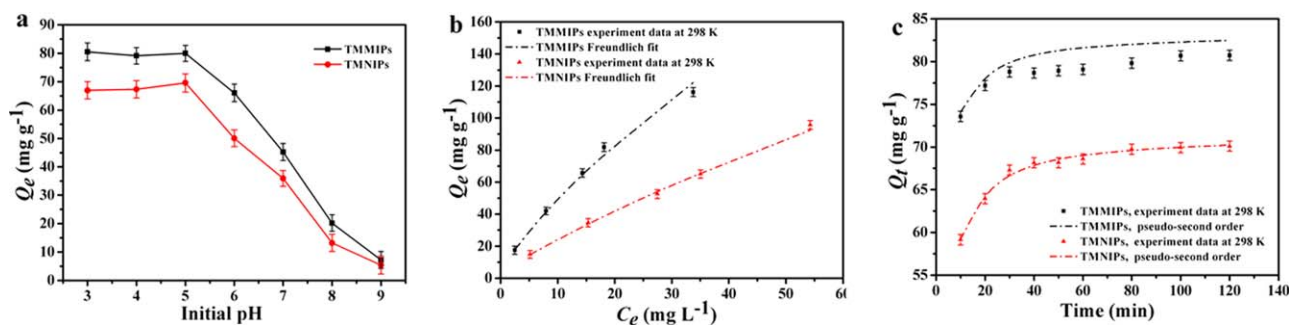
In our study, the effect of the initial concentration on the adsorption of 2,4,5-TCP onto the TMMIPs and TMNIPs were studied by static equilibrium adsorption, and then, two common isotherm models Langmuir<sup>35</sup> and Freundlich<sup>36</sup> were applied to fit the experimental data of adsorption equilibrium. The values of the resulting parameters and regression coefficients ( $R^2$ s) for the TMNIPs and TMMIPs at 298 K are listed in Table I. Moreover, the Freundlich isotherm model for the 2,4,5-TCP molecular adsorption onto the TMMIPs and TMNIPs with increasing initial concentration with nonlinear regression is also illustrated in Figure 4(b).

The Langmuir equation, which fits monolayer adsorption onto a surface with a finite number of identical sites and no interaction among the molecules, is expressed by the following equation:<sup>37</sup>

$$Q_e = \frac{K_L Q_m C_e}{1 + K_L C_e} \quad (1)$$

where  $C_e$  is the equilibrium concentration of the adsorbate in solution (mg/L),  $Q_e$  is the equilibrium adsorption capacity (mg/g),  $Q_m$  is the maximum adsorption capacity of the sorbent, and  $K_L$  is the Langmuir binding constant, which is related to the free energy of adsorption (L/mg).

In practice, it is not realistic that there exists only one type of binding site and that there is no interaction among molecules adsorbed onto the adsorbents. The Freundlich isotherm model



**Figure 4.** Factors influencing adsorption: (a) pH, (b) initial concentration, and (c) time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

is an empirical equation instead of an assumption of homogeneity, such as equally available adsorption sites, monolayer surface coverage, and no interaction between adsorbed species, and it is given as follows:

$$Q_e = K_F C_e^{1/n} \quad (2)$$

where  $K_F$  is an indicative constant for the adsorption capacity of the sorbent (mg/g) and the value of  $1/n$  indicates the intensity of the adsorption, with a range from 0.1 to 1.0 representing favorable adsorption conditions.

By comparing the results presented in Table I and Figure 4(b), we observed that the plots of the Freundlich model showed a higher correlation ( $R^2 > 0.99$ ), which was higher than those of the other models. As shown in Figure 4(b), 2,4,5-TCP adsorbed on the TMMIPs was greater than that of the TMNIPs; this could be attributed to the good specificity of the TMMIPs. Simultaneously,  $Q_e$  for 2,4,5-TCP turned larger for both the TMMIPs and TMNIPs with the initial concentration increasing.

Except for the pH and initial concentration, the contact time is also an important factor in adsorption processes. To investigate whether the mechanism of 2,4,5-TCP adsorption depended on the physical or chemical characteristics of the adsorbent, the kinetic data were fitted to a pseudo-first-order rate equation and pseudo-second-order rate equation,<sup>38,39</sup> respectively. They are described in eqs. (3) and (4):

$$Q_t = Q_e - Q_e e^{-k_1 t} \quad (3)$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (4)$$

where  $Q_e$  and  $Q_t$  are the amount of adsorbate (mg/g) on the adsorbent at equilibrium and time  $t$  (min), respectively.  $k_1$  and

**Table I.** Adsorption Isotherm Constants of 2,4,5-TCP by the TMMIPs and TMNIPs

Adsorption isotherm mode	Constant	TMMIPs	TMNIPs
Langmuir equation	$R^2$	0.963	0.846
	$Q_m$ (mg/g)	250	250
	$K_L$ (L/mg)	0.011	0.028
Freundlich equation	$R^2$	0.997	0.998
	$K_F$ (mg/g)	9.099	4.064
	$1/n$	0.738	0.782

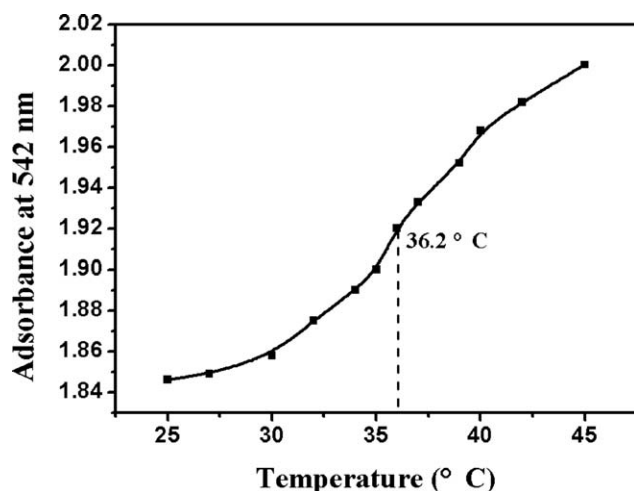
$k_2$  are the rate constant of pseudo-first-order rate equation and pseudo-second-order rate equation, respectively. The values of  $k_1$  (L/min) and  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) were calculated from plots of  $\ln(Q_e - Q_t)$  versus  $t$  and  $t/Q_t$  versus  $t$ , respectively.

The adsorption rate constants and regression values are summarized in Table II, and the pseudo-second-order rate equation for 2,4,5-TCP adsorption onto the TMMIPs and TMNIPs with nonlinear regression is shown in Figure 4(c). As shown in Figure 4(c), it was obvious that the adsorption capacities of 2,4,5-TCP by the TMMIPs and TMNIPs increased more rapidly in the initial stages, and then, the adsorption capacities were both almost constant. The required times to reach to adsorption equilibrium were 40 and 80 min for the TMMIPs and TMNIPs, respectively; the possible reason may have been that the adsorption rate depended on the specific binding sites on the surface of the TMMIPs after 40 min. The adsorption of 2,4,5-TCP followed pseudo-second-order kinetics because of the favorable fit between the experimental and calculated values of  $Q_e$  ( $R^2 = 0.999$ ). Thus, we assumed that the chemical process could be the rate-limiting step in the adsorption process for 2,4,5-TCP. On the basis of the second-order model, the initial adsorption rate ( $h$ ;  $\text{mg g}^{-1} \text{min}^{-1}$ ) is also summarized in Table II according to the following equation:<sup>40</sup>

**Table II.** Kinetic Constants of 2,4,5-TCP by the TMMIPs and TMNIPs

Adsorption kinetics mode	Constant	MMIPs	MNIPs
Pseudo-first-order equation	$R^2$	0.870	0.930
	$Q_{e,c1}$ (mg/g)	16.478	22.309
	$k_1$ ( $\text{min}^{-1}$ )	0.052	0.055
Pseudo-second-order equation	$R^2$	0.999	1
	$Q_{e,c2}$ (mg/g)	83.333	71.429
	$k_2$ ( $\text{min}^{-1}$ )	0.0096	0.0068
half-equilibrium time	$T_{1/2}$	1.250	2.071

$Q_{e,c}$  ( $\text{mg g}^{-1}$ ) is the calculated value of  $Q_e$ ;  $k_1$  ( $\text{L min}^{-1}$ ) is the rate constant of first-order adsorption that was obtained from the plot of  $\ln(Q_e - Q_t)$  versus  $t$ ;  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the rate constant of second-order adsorption that was obtained from the plot of  $t/Q_t$  versus  $t$ ;  $h$  ( $\text{mg g}^{-1} \text{min}^{-1}$ ) is the initial adsorption rate;  $T_{1/2}$  (min) is the half-equilibrium time.



**Figure 5.** Optical absorbance of the TMMIP aqueous solutions at various temperatures.

$$h = k_2 Q_e^2 \quad (5)$$

The comparison of  $h$  once more suggested that the TMMIPs possessed a faster  $h$  than the TMNIPs; this could also be attributed to the successful formation of binding sites by the TMMIPs.

### Thermoresponsive Properties

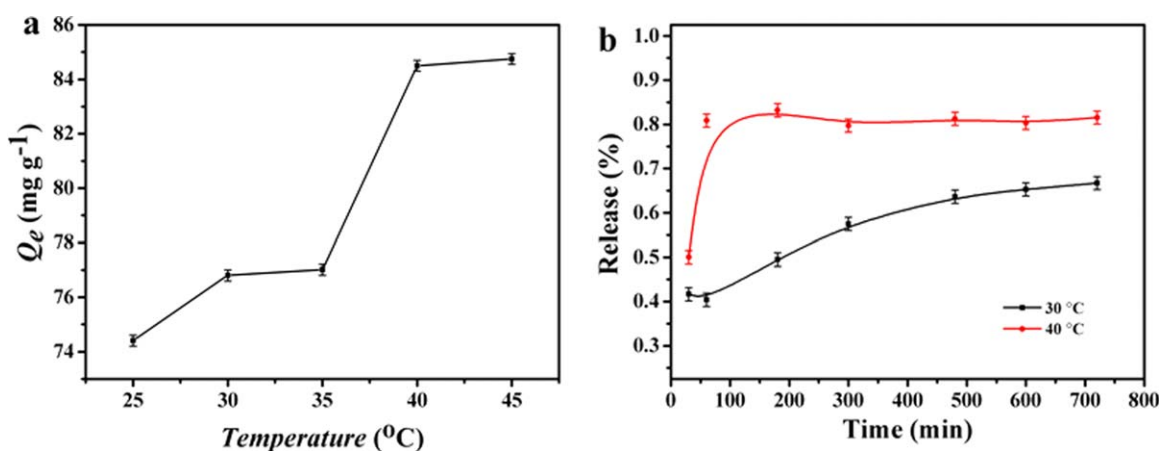
To determine whether the synthesized materials exhibited a thermal response, the LCST of the TMMIPs was tested by the monitoring of the absorbance change of aqueous polymer solutions at 542 nm as a function of the temperature by UV spectroscopy<sup>41</sup> (Figure 5). We observed that the TMMIPs exhibited an absorbance increase when the solutions were heated from 25 to 45°C, and the LCST of the TMMIPs was 36.2°C; this was higher than that of the pure PNIPAM. According to previous studies, an elevated LCST could be attributed to the introduction of hydrophobic EGDMA as the crosslinking agent and the terminal carboxylic acid groups of methacrylic acid (MAA) into the PNIPAM chains; this changed the LCST behavior (both the response rate and LCST value).<sup>42</sup>

The materials we synthesized in our study possessed thermoresponsive properties. Thus, we also studied the factor of tempera-

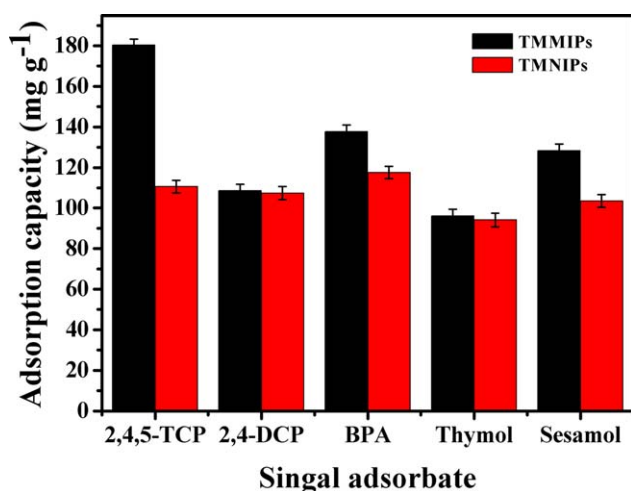
ture on the adsorption capacities and release properties. Figure 6(a) shows the adsorption capacity at different temperatures ranging from 25 to 45°C, and Figure 6(b) shows the dynamic release rates of 2,4,5-TCP at 30 and 40°C. As shown in Figure 6(a), it was obvious that  $Q_e$  increased with temperature, and between 35 and 40°C, the adsorption capacity increased dramatically. In this curve, the adsorption was shown to be an endothermic process. In addition, at 36.2°C, the thermoresponsive properties played a major role in adsorption; they changed the conformation of the PNIPAM chain from an expanded coil to a collapsed globular structure, and then, the collapsed TMMIPs decreased the distance between 2,4,5-TCP and MAA in the polymer matrix<sup>43</sup> and thus increased the adsorption capacity. Moreover, after the adsorption reached the equilibrium step at 25°C, the dynamic controlled release of 2,4,5-TCP was conducted at 30 and 40°C in water, as shown in Figure 6(b). Through calculation, the maximal release rates of the TMMIPs at 30 and 40°C were found to be 66 and 83%, respectively; this indicated that the release rate increased with increasing temperature. The same result was also reported in our previous work.<sup>44</sup> At LCST, namely, 36.2°C, the polymer chains of the TMMIPs shrunk and tended to be in the hydrophobic state; this resulted in an inhibited access to the imprinted binding sites.<sup>45</sup> Because the collapse of the polymers resulted from the destruction of the spatial integrity of the imprinted binding sites, most of the captured 2,4,5-TCP was released from the binding sites. In addition, the effect of time for the release rate at 40°C was different from that of 30°C. The release rate slightly increased with increasing release time at 30°C; the reason was that the TMMIPs would not shrink upon the LCST. These facts further supported the idea that the switched recognition and release ability were supplied by the temperature-responsive imprinted polymers.

### Selectivity of the TMMIPs toward 2,4,5-TCP

To measure the adsorption selectivity of the TMMIPs, selective binding experiments onto the TMMIPs and TMNIPs were carried out for 2,4,5-TCP and its four structural analogs, which were 2,4-DCP, BPA, thymol, and sesamol, respectively. In Figure 7, the adsorption capacities of TMMIPs for 2,4,5-TCP, 2,4-DCP, BPA, thymol, and sesamol were 180.322, 108.594, 137.687,



**Figure 6.** (a) Switched adsorption and (b) controlled release of 2,4,5-TCP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 7.** Adsorption selectivity of 2,4,5-TCP onto the TMMIPs and TMNIPs in five phenolic compounds (single solute). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

96.115, and 128.36 mg/g, respectively. This suggested that the TMMIPs had the highest adsorption capacity for 2,4,5-TCP among all five comparative compounds; this indicated the specific adsorption for the 2,4,5-TCP. Moreover, to further confirm the selectivity of TMMIPs toward 2,4,5-TCP, the distribution coefficients ( $K_d$ 's; L/g), selectivity coefficients ( $k_s$ ), and relative selectivity coefficient ( $k'$ ) of 2,4-DCP, BPA, thymol, and sesamol with respect to 2, 4, 5-TCP were obtained according to eqs. (6) and (7).

$$K_d = \frac{Q_e}{C_e} \quad (6)$$

The  $k$  value for the binding of a specific compound was obtained according to the following equation:

$$k = \frac{K_d(LC)}{K_d(X)} \quad (7)$$

where X is a comparative compound.  $k'$  can be defined with eq. (8):

$$k' = \frac{k_M}{k_N} \quad (8)$$

where  $k_M$  and  $k_N$  are the selectivity coefficients of the TMMIPs and TMNIPs, respectively.

The values of  $K_d$ ,  $k$ , and  $k'$  are summarized in Table III. The  $k$  values of the TMMIPs for 2,4-DCP, BPA, thymol, and sesamol

**Table III.** Adsorption Selectivity Parameters of TMMIPs and TMNIPs

Comparative compound	TMMIPs		TMNIPs		$k'$
	$K_d$ (L/g)	$k$	$K_d$ (L/g)	$k$	
2,4,5-TCP	0.9016		0.6528		
2,4-DCP	0.5430	1.661	0.5370	1.216	1.366
BPA	0.6884	1.310	0.5879	1.110	1.180
Thymol	0.4806	1.876	0.4705	1.387	1.352
Sesamol	0.6418	1.405	0.5179	1.260	1.115

were 1.661, 1.310, 1.876, and 1.405, respectively; this suggested that the selective recognition for comparative compounds followed the order 2,4,5-TCP > BPA > Sesamol > 2,4-DCP > Thymol.  $k'$  is an indicator for expressing the adsorption affinity of the recognition sites to the template molecules. The  $k'$  value for the four structural analogs were all greater than 1; this indicated the specific function of the TMMIPs for 2, 4, 5-TCP.

## CONCLUSIONS

In this work, novel TMMIPs based on MCNTs were prepared and applied to the switched recognition and controlled release of 2,4,5-TCP from aqueous solution. The batch mode binding study for 2,4,5-TCP was investigated. The experimental environment conditions, such as the pH, initial concentration, and contact time, had great effects on the adsorption capacity for 2,4,5-TCP onto the TMMIPs and TMNIPs. Simultaneously, the TMMIPs showed a good selective recognition for 2,4,5-TCP. Moreover, it could switch the adsorption and release of the template by just changing the temperature and be separated through magnetic field easily and fast. The magnetic stability was effectively improved by the encapsulation of the  $Fe_3O_4$  nanoparticles in the CNTs. The TMMIPs could be further applied to the drug release and controlled separation of pollutants in an aqueous environment.

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