Preparation of a novel magnetic microporous adsorbent and its adsorption behavior of p-nitrophenol and chlorotetracycline

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**HIGHLIGHTS**

- Acid resistance of Fe3O4 nanoparticles is enhanced by bilayer-silane-coatings.
- M150 is successfully synthesized with a high surface area of 1022.4 m²/g.
- The acid stability of M150 extends its application at low pH.
- M150 is superior in adsorption kinetics due to its smaller particle size.
- The microporous structure of M150 is beneficial to the adsorption of p-nitrophenol.

**ABSTRACT**

A novel method for fabricating hypercrosslinked magnetic polymer beads with improved acid resistance was developed. Magnetite nanoparticles were covered with tetraethoxysilane and vinyltriethoxysilane, followed by co-polymerization and post-crosslinking. The resulting M150 beads were highly stable at pH ≥ 2 and were superparamagnetic, with a saturation magnetization of 3.1 emu/g. M150 exhibited a specific surface area of 1022.4 m²/g and an average pore width of 2.6 nm. The adsorption of p-nitrophenol and chlorotetracycline (CTC) onto M150 and the commercial non-magnetic resins NDA 150 and XAD-4 followed both pseudo-first-order and pseudo-second-order equations. M150 displayed much faster kinetics than the other resins because of its small particle size and abundant macropores. The adsorption isotherm of p-nitrophenol onto the three resins fitted the Freundlich equation (R² > 0.98), whereas CTC adsorption was better described by the Langmuir isotherm. p-Nitrophenol adsorption was optimal at pH ≤ 4, whereas CTC adsorption was optimal at pH 5–6. All three sorbents showed high reusability for p-nitrophenol adsorption. XAD-4 demonstrated the highest reusability for CTC. The CTC adsorption capacities of M150 and NDA150 decreased by 12.42% and 20% after 10 adsorption–desorption cycles, respectively.

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**1. Introduction**

Magnetic polymer particles are widely used in biotechnology, analytical chemistry, and environmental engineering because of their convenient (rapid and easy) magnetic separation and high adsorption efficiency [1–5]. In the past decades, nanoscale and macroscale magnetic polymer particles have been produced using different methods, including in situ formation [6], core–shell production [7,8], and monomer copolymerization [9–11]. Most of the methods mainly focused on obtaining magnetic polymer beads with large adsorption capacity because uniform particle sizes, and high magnetite content. On one hand, various surface functional groups (such as amino and carboxyl) have been modified to the composite magnetic polymer particles to enhance the adsorption affinity between the sorbents and the targets [12,13]. On the other hand, significant adsorption capacity can also be achieved by improving the specific surface area of the sorbents. Hypercrosslinked resin is a typical polymer with a large specific surface area and has excellent adsorption properties for both hydrophilic and hydrophobic compounds [14].

The non-magnetic hypercrosslinked polymer resin beads were first synthesized in 1969 by Davankov et al. [15]. The common method for preparing such polymers is using a Friedel–Crafts catalyst such as FeCl3 to post-crosslink chloromethylated styrene–divinylbenzene copolymers [16]. During the reaction, chloromethyl groups are converted into methylene bridges to produce three-dimensional microporous resin beads with very small and uniform pores of about 2 nm in diameter [17]. The surface area of the resins exceeded 1000 m²/g owing to the abundant microporous structure [18]. Microporous resins have been

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successfully used in many fields, especially in wastewater treatment and resource reuse [19–22]. However, it is difficult to prepare the magnetic microporous resins with high surface area. Magnetic nanoparticles are typically around 10–20 nm in diameter [23]. Placing magnetic nanoparticles in the micropores of hypercrosslink resins is difficult using in situ methods, where ferrous/ferric salts are co-precipitated in a polymer solution [24]. Blockage of mesopores, which are important for the diffusion of adsorbates, reduces the adsorption capacity of the in situ formed magnetic resins [25]. Magnetic microporous resins could also be prepared by post-crosslinking the magnetic chloromethylated styrene-divinylbenzene beads produced through copolymerization process. However, the chloromethylation and the post-crosslinking processes are conducted under strongly acidic conditions, which rapidly erode the magnetite cores of the beads.

In this work, the hypercrosslinked magnetic resin M150 was prepared through silane coating, copolymerization, and post-crosslinking. The adsorption behavior of the hazardous compounds p-nitrophenol and CTC onto M150 were studied, with the nonmagnetic resins NDA150 and XAD-4 chosen as references.

2. Experimental

2.1. Materials

4-Vinylbenzyl chloride (VBC, 80 wt%, Changzhou Wujin Linchuan Chemical Co., Ltd., China) and divinylbenzene (DVB, 80 wt%, J&K Chemical Co., Ltd., China) were passed through an ion-exchange resin column to remove the inhibitors before use. Tetraethoxysilane (TEOS, 98%) and vinyltriethoxysilane (VTEO, 97%) were obtained from Sigma–Aldrich. Analytical reagent grade ferric chloride, ferric chloride hexahydrate (FeCl₃·6H₂O), ferrous chloride tetrahydrate (FeCl₂·4H₂O), aqueous ammonia (25 wt%), benzoperoxide (BPO), heptane, 1,2-dichloroethane (1,2-DCE), and methanol were purchased from Shanghai Chemical Reagent Corporation (China).

2.2. Synthesis of silane-coated Fe₃O₄ nanoparticles

The magnetite nanoparticles were synthesized by coprecipitating FeCl₃ and FeCl₂. 0.04 mol of FeCl₃·6H₂O and 0.02 mol of FeCl₂·4H₂O were dissolved in 500 mL of deionized water in a 1 L three-necked round-bottom flask, and deoxygenated by vigorous stirring under N₂ at room temperature. Afterwards, 25 mL of ammonia solution (25–28 wt%) was added and the mixture was heated to 358 K for 1 h. The magnetic precipitate was isolated using a permanent magnet and washed repeatedly with acetone. Subsequently, 15 g of TEOS dissolved in 250 mL of methanol was mixed with the magnetite nanoparticles, followed by the addition of 25 mL of ammonia solution (25–28 wt%). The reaction was allowed to proceed for 6 h at 313 K. The formation of the silane layer was terminated by washing away the excess TEOS with acetone. These steps were repeated using VTEO instead of TEOS to add vinyl groups to the magnetic nanoparticles, as shown in Scheme 1.

2.3. Synthesis of magnetic resin beads

The oil phase consisted of VBC (28.5 g), DVB (1.5 g), coated Fe₃O₄ nanoparticles (2.5 g), heptane (15 g), and benzoperoxide (BPO, 0.7 g). The sample was emulsified in 500 mL of aqueous phase containing dissolved polyvinyl alcohol (2 g) and sodium sulfate (0.1 g). Polymerization was carried out in a four-necked glass separator flask under N₂ protection at 353 K with stirring at 180 rpm. After 6 h, the magnetic precursor beads were separated using a permanent magnet, washed, and dried.

10 g of dry magnetic precursor beads were added to 50 mL of 1,2-dichloroethane (1,2-DCE) in a 100 mL four-necked round-bottomed flask. The mixture was stirred for 6 h under N₂ at room temperature to swell the beads. Afterwards, 2.0 g of FeCl₃ was added and dissolved by stirring for 1 h. The mixture was then heated to 363 K for 18 h. The released HCl gas was trapped by 250 mL of sodium hydroxide solution (28 wt%). The finished M150 hypercrosslinked magnetic resin beads were removed using a permanent magnet, washed, and then dried.

2.4. Characterization

The specific surface area and the pore size distribution of the obtained particles were determined by an ASAP-2010C automatic analyzer (Micromeritics, USA), with nitrogen as the adsorbate following the BET method. The transmission electron microscopy (TEM) micrographs were taken using a JEM-2000 instrument (JEOL, Japan). Scanning electron microscopy (SEM) micrographs were acquired using an S-3400N II instrument (Hitachi, Japan). Magnetic hysteresis loop measurements were performed using a vibrating sample magnetometer (EV7, ADE, USA). The amount of iron in the leachate was recorded by Perkin-Elmer 310 atomic absorption spectroscopy (Perkin-Elmer, USA). The crystalline type of the iron oxide species present in the polymer microspheres was characterized by powder X-ray diffraction (XTRA/3KW, Switzerland), with Cu KR radiation at 50 kV and 150 mA.

2.5. Adsorption experiment

The adsorption behavior of p-nitrophenol and CTC on hypercrosslinked magnetic resin (M150), commercial hypercrosslinked resin (NDA150), and commercial macroporous adsorption resin (XAD-4) were studied.

For the kinetic study, 0.500 g of each resin was washed with methanol and distilled water. The resins were then placed in 1000 mL conical flasks containing 500 mL of target solution. The
initial concentrations of the p-nitrophenol and CTC solutions were 200 mg/L. The adsorption experiments were conducted in a shaker at 140 rpm and 288 K. Samples were collected at different intervals, and the concentrations of p-nitrophenol and CTC were analyzed via HPLC after filtration. The pH of the solution was adjusted using 0.01 mol L\(^{-1}\) HCl or 0.01 mol L\(^{-1}\) NaOH. For regeneration, 50 mL of NaOH solution (pH 12) was used as the desorption agent.

Equilibrium adsorption studies of p-nitrophenol and CTC on M150, NDA150, and XAD-4 were carried out at 288, 303, and 318 K. About 0.100 g (W) of resin was introduced into a series of 250 mL conical flasks after washing with methanol and distilled water. About 100 mL of the p-nitrophenol solution and the CTC solution were added at known concentrations into each flask. The initial concentrations (\(C_0\)) of p-nitrophenol solution ranged from 200 mg/L to 2500 mg/L and those of CTC ranged from 50 mg/L to 200 mg/L. The flasks were then sealed and placed in a shaker at 120 rpm for 16 h. The shaker was completely covered to avoid light. The residual concentrations of p-nitrophenol and CTC in the aqueous phase (\(C_e\)) were then determined with HPLC.

Adsorption capacity \(Q_e\) (mg/g) was calculated using Eq. (1).

\[
Q_e = \frac{V(C_0 - C_e)}{W} \tag{1}
\]

3. Results and discussion

3.1. Preparation of M150

3.1.1. Synthesis of silane-coated Fe\(_3\)O\(_4\) nanoparticles

Nanosized magnetite particles were prepared by coprecipitating ferrous and ferric iron solutions. The resultant Fe\(_3\)O\(_4\) particles were 8–15 nm in diameter (Fig. 1a) and exhibited superparamagnetic characteristics with a saturation magnetization of 45.8 emu/g. The magnetic cores were then coated with a silane shell to enhance acid stability. As shown in Scheme 1, the magnetite nanoparticles were first coated with TEOS via a sol–gel process [26]. A strong IR absorption band at 1090 cm\(^{-1}\) confirmed the presence of the –O–Si–O bond (Fig. S1). The hydroxyl groups on the surface of the TEOS layer reduced the dispersibility of the Fe\(_3\)O\(_4\) nanoparticles in organic solvents, which hindered the subsequent copolymerization. Previous studies have indicated that the surface coating obtained from the sol–gel process was uniform but still porous [27]. Further coating with VTEO reduced the porosity of the silane coating and further protected the magnetite particles against acid erosion. The VTEO coating also rendered the particles soluble in 4-VBC which was the monomer in the following copolymerization procedure. The TEOS and TEOS + VTEO layers of the nanoparticles were clearly observed in the TEM micrographs (Fig. 1b and c). The dispersibility of the TEOS + VTEO-coated Fe\(_3\)O\(_4\) nanoparticles in 4-VBC was visibly better than their precursors only coated with TEOS (Fig. 1d).

3.1.2. Acid stability of coated Fe\(_3\)O\(_4\) nanoparticles

Leaching tests were conducted in acid solutions (pH 1–4) to evaluate the acid resistance of the silane-coated magnetite. The samples were incubated for 24 h at 293 K with continuous shaking. The results are summarized in Table 1. The TEOS silane coating significantly improved the stability of the Fe\(_3\)O\(_4\) nanoparticles under acidic conditions. Nearly 80 mg of iron per gram of nanoparticles was detected in the leachate at pH 1 after 24 h. By contrast, the value drastically decreased to 1.74 mg/g in the TEOS-coated magnetite under the same experimental conditions. When the TEOS-coated nanoparticles were further modified by VTEO, the amount of iron

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>Fe in HCl (mg/g)</th>
<th>Ms (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 1</td>
<td>pH 2</td>
</tr>
<tr>
<td>Fe(_3)O(_4)</td>
<td>79.71</td>
<td>9.23</td>
</tr>
<tr>
<td>TEOS-Fe(_3)O(_4)</td>
<td>1.74</td>
<td>0.42</td>
</tr>
<tr>
<td>TEOS + VTEO-Fe(_3)O(_4)</td>
<td>1.59</td>
<td>0.25</td>
</tr>
</tbody>
</table>
that leached out at pH 1 dropped to 1.59 mg/g. The improved acid resistance confirmed that VTEO had been successfully added to the particles.

The saturation magnetization data of the magnetite nanoparticles are listed in Table 1. As the non-magnetic silica coating represented a significant proportion of the mass of the modified particles, a downward trend in magnetization was observed during the coating procedure. The saturation magnetization values for the uncoated, TEOS-coated, and TEOS + VTEO-coated particles were 45.8, 36.2, and 34.7 emu/g, respectively (Fig. S2). Meanwhile, the silane-coated nanoparticles remained superparamagnetic.

3.1.3. Preparation of the magnetic hypercrosslinked resins

Hypercrosslinked resins are conventionally synthesized through the chloromethylation of polystyrene resin using chloromethyl ether at low pH [27]. In the current study, VBC was used as the monomer to avoid the chloromethylation, which is corrosive to the magnetic cores [23]. As shown in Scheme S1, the vinyl groups from the VTEO-coating also participated in the polymerization reaction, covalently linking the VBC–DVB polymer to the silane coating. As shown in Fig. 2a and b), the precursors had a relatively smooth surface with a few surface macropores. The presence of these surface macropores was caused by heptane, which is commonly used as porogen for producing mesopores and macropores in microporous polymers [28,29]. Quantification using the BET method with nitrogen as adsorbate indicated a specific surface area less than 1 m²/g.

The post-crosslinking reaction between the chloromethyl groups (internal electrophile from 4-VBC) and nearby benzene rings was catalyzed by FeCl₃ at high temperature (Friedel–Crafts reaction). The —CH₂— bridges that formed among the benzene rings generated abundant micropores and the desired large specific surface area. After post-crosslinking, the specific surface area increased to 1022.4 m²/g and a micropore volume of 0.52 cm³/g was obtained. Many surface macropores were also generated during post-crosslinking (Fig. 2c and d), probably because of the partial corrosion of Fe₃O₄ by the HCl generated during Friedel–Crafts reaction. The corrosion of magnetite also accounts for the decrease in specific saturation magnetization from the precursor beads (5.1 emu/g) to the finished beads (3.1 emu/g), as reflected in Fig. 3. The large surface area of the finished magnetic microbeads, combined with the macropores that facilitate efficient mass transfer, are crucial for high adsorption capacity and fast kinetics.

![Fig. 2. SEM micrographs of (a) the magnetic precursors; (b) the surface of the magnetic precursors; (c) M150; and (d) the surface of M150.](image-url)
3.2. Characterization of M150

To evaluate the acid resistance of the microporous magnetic polymer beads for practical applications, the finished M150 beads were treated with HCl at different concentrations for 24 h at 293 K. Fig. 4 shows that the beads were stable at pH 2–5 because their specific saturation magnetizations remained unchanged at 3.1 emu/g and iron was undetected in the leachate. At pH 1, however, the saturation magnetization was reduced by 25% to 2.3 emu/g because of magnetite corrosion. Fig. 4 also shows that the magnetization curves exhibited no hysteresis, validating that the microspheres remained superparamagnetic.

Fig. 5 shows that M150 has excellent magnetic responsivity when attracted by a permanent magnet for 30 s. As expected for superparamagnetic microbeads, a slight shake by hand immediately redispersed the microbeads.

The XRD patterns of the resultant hypercrosslinked magnetic polymer microspheres are depicted in Fig. 6. Six sharp diffraction peaks were observed, which indicates that they contained pure magnetite Fe₃O₄ crystals with an inverse cubic spinel structure. This finding is deduced from the superparamagnetic characteristics shown in Fig. 3. The broad peak from 13° to 23° resulted from the amorphous polymer encapsulating the magnetite cores.

Fig. 6 shows the N₂ adsorption–desorption isotherms of M150. The steep increase at low relative pressure (<0.01) demonstrates the microporous structure inside M150 [30]. The isotherm conformed to Type IV isotherm, which indicates the presence of mesopores and macropores. Moreover, the hysteresis loop was Type H4 loop, which signifies the dominance of micropores [31]. In addition, the pore size of M150 had a bimodal distribution at 0 nm to 1.1 nm and 100 nm to 1500 nm (Fig. S4), confirming the coexistence of micro pores and macropores. The surface properties of M150 and other two adsorbents are shown in Table 2. The dominant pores of M150 were micropores (0.52 cm³/g), occupying 80% of the total pore volume (0.65 cm³/g).

3.3. Adsorption performance for p-nitrophenol and CTC

3.3.1. Adsorption kinetics

Fig. 8 shows the adsorption kinetics of p-nitrophenol and CTC on the M150, NDA150, and XAD-4 resins at 288 K. The adsorption of p-nitrophenol onto 3 resins was much faster than that of CTC due to the smaller molecular size of p-nitrophenol (Fig. S5), which resulted in faster pore diffusion. CTC has a relatively larger size than p-nitrophenol, which gave it a higher diffusion resistance and significantly decreased its adsorption rates.

Pseudo-first-order, pseudo-second-order, and Weber–Morris kinetic models were utilized to fit the adsorption data to better
Table 2
Surface properties of the three adsorbents.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Specific area (m²/g)</th>
<th>Pore size (nm)</th>
<th>Micropore volume (cm³/g)</th>
<th>Mesopore volume (cm³/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Point of zero charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>M150</td>
<td>1022.4</td>
<td>2.6</td>
<td>0.52</td>
<td>0.09</td>
<td>0.65</td>
<td>3.5</td>
</tr>
<tr>
<td>NDA150</td>
<td>1150.5</td>
<td>3.3</td>
<td>0.45</td>
<td>0.58</td>
<td>0.95</td>
<td>3.9</td>
</tr>
<tr>
<td>XAD-4</td>
<td>846.8</td>
<td>5.8</td>
<td>0.07</td>
<td>1</td>
<td>1.23</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Fig. 8. Adsorption kinetics of p-nitrophenol (A–C) and CTC (D–F) onto M150, NDA150, and XAD-4 at 288 K.

Table 3
Kinetic parameters for p-nitrophenol and CTC adsorption onto the three resins at 288 K.

<table>
<thead>
<tr>
<th>Target</th>
<th>Resins</th>
<th>Pseudo-first-order model</th>
<th>Pseudo-second-order model</th>
<th>Weber-Morris model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>k₁ (10⁻³) qₑ R²</td>
<td>k₂ (10⁻⁵) qₑ R²</td>
<td>Kᵢ t R²</td>
</tr>
<tr>
<td>p-Nitrophenol</td>
<td>M150</td>
<td>0.19 148.24 0.9826</td>
<td>3.15 152.62 0.9968</td>
<td>42.30 −3.09 0.971</td>
</tr>
<tr>
<td></td>
<td>NDA150</td>
<td>0.017 153.60 0.9461</td>
<td>0.14 168.73 0.9770</td>
<td>8.64 13.21 0.991</td>
</tr>
<tr>
<td></td>
<td>XAD-4</td>
<td>0.035 90.63 0.9590</td>
<td>0.57 95.96 0.9891</td>
<td>7.42 −3.95 0.991</td>
</tr>
<tr>
<td>CTC</td>
<td>M150</td>
<td>0.202 164.03 0.944</td>
<td>2.18 169.18 0.9877</td>
<td>5.51 4.40 0.997</td>
</tr>
<tr>
<td></td>
<td>NDA150</td>
<td>0.003 109.92 0.9677</td>
<td>0.02 133.48 0.9802</td>
<td>3.90 −3.95 0.990</td>
</tr>
<tr>
<td></td>
<td>XAD-4</td>
<td>0.004 138.5 0.9814</td>
<td>0.03 163.25 0.9946</td>
<td>6.13 −12.11 0.987</td>
</tr>
</tbody>
</table>
describe the adsorption kinetics. The fitting parameters are shown in Table 3. The results show that the adsorption of p-nitrophenol and CTC onto the three resins followed both the pseudo-first-order and pseudo-second-order equations ($R^2 > 0.9$). The $k_1$ and $k_2$ values (rate constants) for the adsorption of p-nitrophenol and CTC onto M150 were almost two orders higher than those of NDA150 and XAD-4 because of its smaller particle size and its abundant macropores. The average particle size of the XAD-4 and NDA150 resins was around 500 μm, whereas that of M150 was 100 μm. The smaller particle size increased the contact surface between the sorbents and the solution; hence, the target analytes more rapidly diffused into the pores of the sorbents. Moreover, the abundant macropores of M150 provided effective diffusion channels for the adsorbates and accelerated the adsorption process.

The fitting results of the Weber–Morris model showed that none of the curves passed through the origin, which meant that the adsorption rates of p-nitrophenol and CTC were controlled by both intraparticle diffusion and external diffusion. The absolute value of $I$ (intercept) for p-nitrophenol adsorption was in the following order M150 > NDA150 > XAD-4. This finding implies that the boundary layer played the smallest role for M150. In addition, the much higher $K_i$ value (intraparticle diffusion rate constant) of the M150 implies the more effective diffusion of p-nitrophenol inside the pores of M150. By comparison, the $K_i$ values of CTC adsorption were lower than those of p-nitrophenol, which indicates a higher diffusion resistance.

The kinetic study indicates that M150 has distinct advantages in rapid adsorption equilibrium, which renders it suitable for complete-mixing water treatment processes.

Specific surface area influences the adsorption capacity of sorbents. The adsorption capacity of p-nitrophenol was consistent with the order of the specific area (NDA150 > M150 > XAD-4, Table 2). The XAD-4 resin exhibited a much lower adsorption capacity than the other two hypercrosslinked resins because it lacked micropores to adsorb p-nitrophenol. Meanwhile, XAD-4 exhibited a much higher adsorption capacity for CTC than M150 and NDA150.
Despite the high specific area, the dominant micropores (2 nm) of M150 inhibited the adsorption of larger molecules. CTC was better adsorbed by mesopores instead of micropores because of its larger size, which is consistent with previous studies on the removal of tetracycline using activated carbon and resins [32,33].

3.3.2. Adsorption isotherms

Fig. 9 describes the equilibrium adsorption isotherms of p-nitrophenol and CTC on M150, NDA150, and XAD-4 at 288, 303, and 318 K. The Langmuir and the Freundlich models were applied to fit the isotherm data. The fitting parameters are listed in Table 4. The adsorption of p-nitrophenol onto the three resins was better described by the Freundlich isotherm ($R^2 > 0.98$), which indicates heterogeneous adsorption and a multi-layer adsorption mechanism. This finding is mainly due to the small molecular size of the p-nitrophenol, which resulted in better micropore application. By contrast, the adsorption of CTC onto M150 and NDA 150 fitted better the Langmuir isotherm ($R^2 > 0.97$). Considering the porous structure of these two resins, we can deduce that CTC adsorption is a monolayer interaction because the molecular size of CTC is comparable to that of the micropores inside the resins. By comparison, the adsorption of CTC onto XAD-4 fitted both the Langmuir isotherm ($R^2 > 0.98$) and the Freundlich isotherm ($R^2 > 0.98$). The $n$ values of the Freundlich equations for p-nitrophenol adsorption all exceeded 1, which suggests that the adsorption of p-nitrophenol onto 3 resins is favorable. Moreover, the $n$ values of M150 and NDA 150 were higher than that of XAD-4, which indicates that hypercrosslinked resins with larger specific areas perform better in adsorbing p-nitrophenol. For CTC, despite its lower $Q_{eq}$ (maximum monolayer adsorption amount), M150 had a much higher $K_L$ (Langmuir constant) than both NDA 150 and XAD-4, which verifies the advantageous CTC adsorption of M150.

The adsorption of target compounds onto the adsorbents was also studied at different temperatures. As shown in Fig. 9, the adsorption capacity of p-nitrophenol onto the three resins decreased with increasing temperature, indicating an exothermic process. By contrast, the adsorption capacity of CTC increased with increasing temperature, indicating an endothermic process. Three forces may be involved during CTC adsorption: (1) Van der Waal’s forces, the planar structure of CTC produces stronger Van der Waal’s force for intensive physical adsorption; (2) $\pi-\pi$ interaction, the aromatic ring of CTC becomes an electron acceptor under the effect of electron-drawing groups such as ketone and acylaminogroup, which interact with the electron-rich aromatic rings in the sorbents via $\pi-\pi$ interaction; (3) cation–$\pi$ interaction, CTC forms ammonium groups with enhanced electron-drawing capability under acidic and neutral conditions, and then react with the aromatic ring in the sorbents. Thus, the adsorption of CTC onto the three sorbents is caused by synergistic physical and chemical adsorption. This result is consistent with the report of Ji et al. [34].

3.3.3. Effects of pH

The influence of pH on the adsorption of p-nitrophenol and CTC was studied because these two compounds have different forms at different pH. As shown in Fig. 10, the adsorption capacity of p-nitrophenol was very high at pH < 4 because it is in its molecular form at acidic pH, thereby favoring the intermolecular forces between p-nitrophenol and the sorbents. At pH above 4, p-nitrophenol ionizes, weakening the interactions between the adsorbates and the resins, as well as decreasing the adsorption capacity. At pH 12, p-nitrophenol was almost not adsorbed. Therefore, pH 12 is suitable for desorbing p-nitrophenol from the resins.

The species distribution of CTC at different pH is much more complicated (Fig. S6). At pH < 3.33, the dominant CTC species is CTC$. The $pzc$ values of the three resins (Table 2) show that the surfaces of the three resins are positively charged at these pH values. However, a portion of the functional groups on CTC remains in molecular form (parts A and B, Fig. S5) with strong electron-drawing capability. These functional groups interact with the aromatic rings in the sorbents via $\pi-\pi$ interactions. Moreover, the tertiary amine group of CTC reacts with $H^+$ under acidic conditions, and then interacts with the aromatic rings in the sorbents through cation–$\pi$ bonding. Therefore, despite the electrostatic repulsion between CTC$^+$ and the positive sorbent surfaces under acidic pH, $\pi-\pi$ bonding and cation–$\pi$ bonding ensured the high adsorption capacity of CTC. With increasing pH, CTC exhibited higher hydrophobicity, producing better adsorption on the sorbents. At pH 5–6, CTC was mainly in its molecular form, which is optimal for adsorption. Under such circumstance, physical adsorption and chemical adsorption were both involved. At pH higher than 6, certain functional groups (parts A and B, Fig. S5) gain electrons and lose their electron-drawing capability. At pH 9.33, CTC was mainly in its anionic CTC$^2-$ form. The resulting increase in water solubility inhibited adsorption. Meanwhile, the surfaces of the adsorbate and the sorbents were both negatively charged, which also negatively affected adsorption.

3.4. Reusability

The p-nitrophenol and CTC adsorption experiments onto the three resins were examined during 10 adsorption–desorption cycles to evaluate the reusability of these sorbents. As shown in Fig. 11, the three resins used to adsorb p-nitrophenol exhibited high adsorption and regeneration stability. The regeneration rates
reached nearly 100% after 10 repeated uses. For CTC adsorption, only XAD-4 was completely regenerated after 10 cycles, whereas the adsorption capacities of M150 and NDA150 dropped by 12.42% and 20%, respectively. Larger molecules are prone to accumulate on the resins, especially on microporous sorbents, hindering desorption. Hence, M150, with its abundant micropores have excellent removal efficiency for small molecules such as p-nitrophenol, but have lower adsorption capacities for larger molecules such as CTC.

### 4. Conclusions

In this work, a novel magnetic hypercrosslinked resin M150 with enhanced acid resistance was produced and utilized to eliminate p-nitrophenol and CTC from aqueous solution. The main conclusions are as follows:

1. Successively coating magnetite nanoparticles with TEOS and VTEO greatly improves their acid stability. The vinyl groups introduced by VTEO facilitate the interaction of the coated magnetite and the emerging poly-VBC during copolymerization.

2. Using VBC as the monomer prevents common chloromethylation using chloromethyl ether at low pH. The resultant M150 resin has a small particle size (100–150 μm) and a high specific area (1022.4 m²/g).

3. The specific surface area and micropore volume of the sorbents determine the adsorption capacity of p-nitrophenol, whereas a mesoporous structure is beneficial for CTC adsorption. The adsorption kinetics of M150 is superior to the other resins because of its smaller particle size and abundant macropores. M150 has a high removal efficiency and great reusability for adsorbing p-nitrophenol. The CTC adsorption capacity of M150 is inferior to that of XAD-4 because CTC accumulates in its pores.

4. p-Nitrophenol adsorption is exothermic, whereas CTC adsorption is endothermic. These two substances can be desorbed under alkaline conditions (pH 12).

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2013.12.015.
References


