Preparation and Characteristics of a Dummy Molecularly Imprinted Polymer for Phenol

Yunhong Huang,[1,2] Yang Xu,[1] Qinghua He,[1] Bibai Du,[1] Yusheng Cao[1]

[1]State Key Laboratory of Food Science and Technology, Sino-Germany Joint Research Institute, Nanchang University, Nanchang 330047, People's Republic of China

[2]College of Life Science, Jiangxi Normal University, Nanchang 330022, People's Republic of China

Correspondence to: Y. Cao (E-mail: yyssccc@hotmail.com)

ABSTRACT: A dummy molecularly imprinted polymers (DMIP) for phenol was synthesized by a thermal polymerization method with acrylamide as the functional monomer, ethylene dimethacrylate as the crosslinker, 2,2-azobisisobutyronitrile as the free-radical initiator, acetonitrile as the porogenic solvent, and sulfadiazine, a phenol analogue, as the template. In comparison to other adsorbents, the synthesized DMIP showed a higher capacity and rate of adsorption. The adsorption amount of the DMIP adsorbents for phenol reached 6.09 ± 0.15 mg/g, and the adsorption rate of the DMIP was about 0.406 ± 0.01 mg g^{-1}·min^{-1}. The results indicate that the Freundlich model fit the adsorption model of DMIP for phenol. The adsorption model of DMIP for phenol was multilayer adsorption. This showed that the DMIP synthesized by bulk polymerization could be used as a novel adsorbent for the removal of phenol from contaminated water. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Phenol has been identified as a highly toxic compound in the past decades because of their carcinogenic nature and pungent odor. The major sources of phenolic waste are petroleum refineries, petrochemical plants, steel mills, coke oven plants, coal gas, synthetic resins, and pharmaceutical plants. Many countries have put rigid limits on the acceptable level of phenol because it is highly toxic and difficult to degrade biologically. The U.S. Environmental Protection Agency has included phenol on the priority pollutants list.[1–4] The World Health Organization prescribed 1 mg/L as the maximum permissible concentration of phenol in drinking water and 0.001 mg/L as the maximum permissible concentration in potable water.[5] In view of its high toxicity and the wide prevalence and poor biodegradability of phenol, it is necessary to develop a promising method to remove it from wastewaters before they are discharged into water bodies.

Several processes have been used for the removal of phenol from wastewater, including solvent extraction,[6,7] oxidation,[8,9] biological degradation,[10,11] and adsorption.[12–15] Among these treatments, adsorption is still the most versatile and widely used because it can effectively remove many types of pollutants and is easy to design and operate. Great effort has been exerted to develop new adsorbents and stabilizers, including activated carbon fibers, green macroalga, activated carbon, and surfactant-modified zeolites. However, there are some problems with these adsorbents, such as low adsorption capacities, high cost, inability to be reused, and bad mechanical stability.[16,17] In recent years, molecularly imprinted polymers (MIPs) have been developed as new smart materials. They have good adsorption capacities and are cost effective, able to be reused, chemically and thermally stable, and compatible with all solvents. MIPs have a vast range of prospective uses in the extraction and refining of compounds.

Wulff and Sarhan[18] put forward the technology of molecular imprinting in 1972. The technology of molecular imprinting was developed quickly since 1993, when an MIP with theophylline as its template was reported by Mosbach et al.[19] MIPs are a new smart material and have remarkable identification properties. The working principles of MIPs involve the formation of cavities, which have a size, shape, and functionality complementary to the target analyte.[20–22] There has been very active research on MIPs as new adsorbents in recent years. Feng et al.[23] successfully demonstrated MIPs as solid-phase extraction adsorbents, which could extract phenolic compounds in environmental water samples. The MIP with phenol as a template could extract phenol in the water; however, the adsorption capacity of the MIP for phenol was so low that the MIP as a solid-phase extraction adsorbent is not used widely.[24]
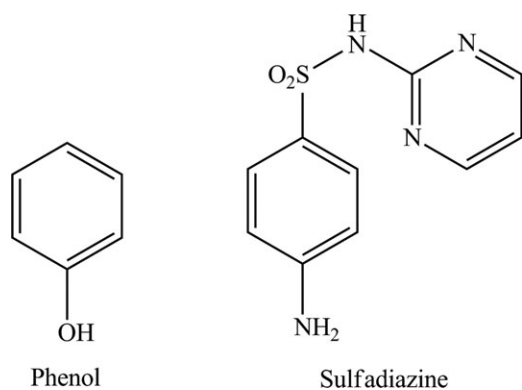
Figure 1. Chemical structures of the phenol and SD.

According to the resemblance between the template molecule and the analyte, the polymers synthesized by the technology of molecular imprinting were classified into two categories: MIPs and dummy molecularly imprinted polymers (DMIPs). In the former, both the template molecule and analyte were identical, whereas the template molecule and analyte were analogues in the latter.[25,26] The use of a template molecule that mimics the structure of a putative imprinting molecule appears to be a potential solution that not only solves the problem of template bleeding but also provides an alternative procedure when the original template is very expensive, involves safety considerations in the manipulation of the compound, or when the conditions used to polymerize the template (thermal or UV irradiation) could result in unwanted compound degradation. Navarro-Villoslada andUrraca[27] and Lucci et al.[28] synthesized DMIPs for zearalenone (ZON) by thermal polymerization with cyclododecyl 2,4-dihydroxybenzoate, a ZON analogue, as a template and successfully demonstrated that DMIP, as a solid-phase extraction adsorbent, could extract ZON from organic solvent. Feás et al.[29] synthesized a DMIP for cyproheptadine by bulk polymerization with an analogue of cyproheptadine, namely, azatadine, as the template and demonstrated that the DMIP, as a solid-phase extraction adsorbent, could extract cyproheptadine. Zhao et al.[30] successfully synthesized a DMIP for bisphenol A with 4,4-dihydroxybisphenyl and 3,3′,5,5′-tetrabromobisphenylas as dummy templates and showed that the DMIP was successfully applied to solid-phase extraction coupled with high performance liquid chromatography with ultraviolet (HPLC/UV) to determine the amount of trace bisphenol A in real water samples. The working principles of the MIP and DMIP are similar, involving formation of cavities that have the size, shape, and functionality complementary to the target analyte. During the imprinting process, the size and shape of the cavity will correspond to those of the template. The chemical structures of phenol and sulfadiazine (SD) are shown in Figure 1. The size and shape of the SD molecule was bigger than those of the phenol molecule, and both the amine of the SD and the hydroxyl of the phenol could interact with acrylamide (AM) by hydrogen bonding. To prevent the leakage of the residual phenol template molecules, the structural analogue of phenol, SD, was used as a template. A DMIP for phenol has not been reported in recent years.

In this study, a DMIP for phenol was synthesized by a thermal polymerization method with AM as the functional monomer, ethylene dimethacrylate (EDMA) as the crosslinker, 2,2-azobisisobutyronitrile (AIBN) as the free-radical initiator, acetonitrile as the porogenic solvent, and an analogues of phenol, namely, SD, as the template. The surface morphologies and characteristics of the DMIP synthesized were investigated with scanning electron microscopy (SEM) and batch adsorption experiments.

EXPERIMENTAL

Materials
SD (4-amino-2 -N-pyrimidinyl benzene sulfonamide) was purchased from China Institute of Veterinary Drugs Control (Beijing, China) with a purity of 100%. The phenol was purchased from Guangzhou Analysis and Testing Center Keli Technical Development Corp. (Guangzhou, China). The functional monomer, AM, and the free-radical initiator, AIBN (>98%), were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). The crosslinking agent, EDMA, was purchased from Shanghai Hechuang Chemical Co., Ltd. (Shanghai, China). High performance liquid chromatography (HPLC)-grade acetonitrile and methanol were purchased from Tianjin Yongda Chemical Reagent Development Center (Tianjin, China). All chemicals were analytical grade.

Main Apparatuses
The UV spectra of the functional monomer and the different concentrations of the SD solution were analyzed with a UV–visible spectrophotometer (UV-3100, GE Amersham Corporation, London, UK). The surface morphologies of the DMIP and nonimprinted polymer (NIP) adsorbents were examined with SEM (SU-1510, Hitachi Corporation, Tokyo, Japan). The DMIP and NIP adsorbents were characterized by Brunauer–Emmett–Teller (BET) nitrogen adsorption/desorption analysis. The infrared spectrum analyses were taken on a TENSOR37 Fourier transform infrared spectrometer (Bruker Corporation, Bremen, Germany). The effects of the functional monomer on the chemical shift of the amino protons of SD were analyzed with a superconductive nuclear magnetic resonance spectrometer (Avance 400, Bruker corporation, Fällanden, Switzerland).

Synthesis of the DMIP and NIP
The DMIP was synthesized by bulk polymerization. The prepolymerization mixture consisted of 1 mmol of template SD, and 4 mmol of AM was dissolved in 10 mL of acetonitrile prepared in a 50-mL borosilicate glass bottle with a screw cap. The previous mixture was prepolymerized for 30 min. Then, 4 mmol of EDMA and 1 mmol of AIBN were added. The prepolymerization mixture was purged with argon for 5 min to remove oxygen, Thermal polymerization was initiated by the placement of the borosilicate glass bottle in a conduction oil bath at 60°C for 24 h. The NIP was synthesized under the same conditions but without the addition of the template.

The bulk polymers obtained were crushed, ground, and sieved. The particle size fraction from 0.18 to 0.28 mm was collected. The resulting particles were placed in a Soxhlet extraction apparatus and washed with methanol/acetic acid (9:1 v/v) to remove the template molecules until SD could no longer be detected at 260 nm in the eluent. Then, the product was dried *in vacuo* at 50°C for further study.
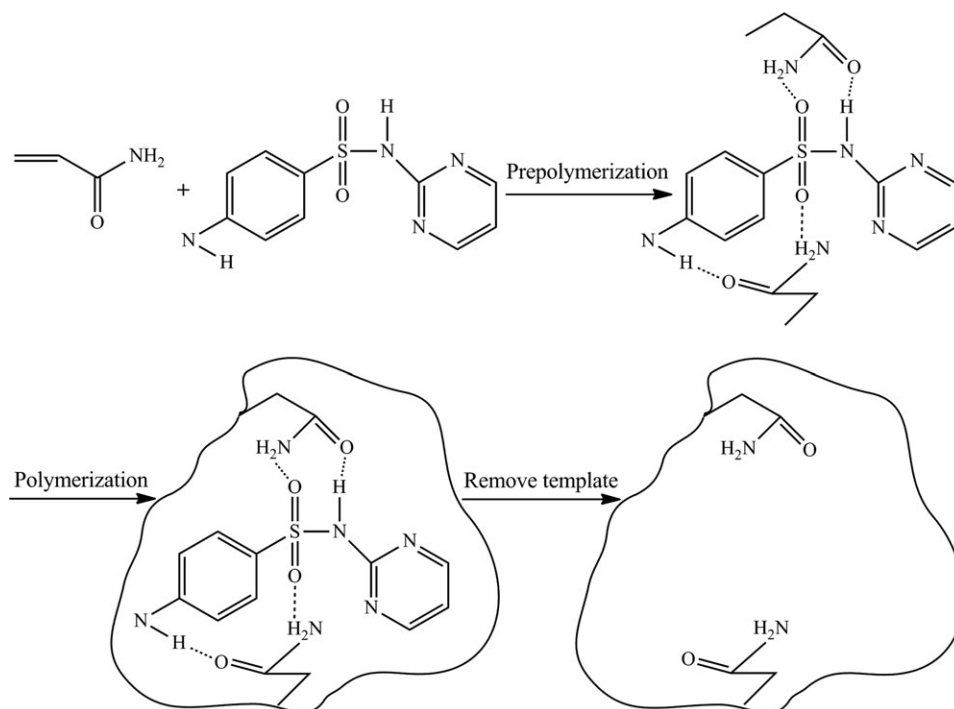
Figure 2. Schematic representation of the dummy molecular imprinting process. (a) The dummy template molecule (SD) was initially dissolved in the porogen solvent and allowed to form noncovalent interactions with the functional monomer (AM). (b) After the addition of the crosslinker (EDMA) and initiator (AIBN), these complexes were fixed by bulk polymerization (at 60°C for 24 h). (c) Finally, the dummy template was removed by washing (9:1 v/v MeOH/acetic acid), and (d) the DMIP was ready for rebinding (association/dissociation) studies with phenol.

Adsorption Kinetics of the DMIP

The phenol adsorption experiments were conducted with a batch method. The dry DMIP (100 mg) was immersed in 100 mL of a water solution containing 50 μg/mL of phenol, and the pH value of the solution was 7. The mixture in a conical flask with stopper was incubated at 25°C on a rotary shaker at 200 rpm for 40 min. After centrifugation, the supernatant was analyzed by UV spectroscopy at 270 nm to quantify the concentration of the residual phenol.

To investigate the adsorption capacity of DMIP, NIP was done under the same conditions. The adsorption experiments were performed in triplicate.

The adsorption capacity (Q; mg/g), was calculated on the basis of the difference in the phenol concentration before and after adsorption, the volume of the aqueous solution, and the mass of the dry DMIP according to the following:

$$Q = (C_0 - C_t)V/1000m \qquad (1)$$

$$\Delta V = Q/t \qquad (2)$$

where C_0 is the initial phenol concentration (μg/mL), C_t is the phenol concentration (μg/mL) at different times, V is the volume of the phenol solution (mL), m is the mass of dry DMIP (g), ΔV is the rate of adsorption for phenol (mg g^{-1}·min^{-1}), and t is the time of equilibrium adsorption (min).

Adsorption Isotherm of DMIP

To investigate the adsorption isotherm of the DMIP in water, 100 mg of DMIP and 100 mL of solution at different concentra-

tions of phenol ranging from 50 to 300 μg/mL at an initial pH of 7 were, placed into a 250-mL conical flask with a stopper. The mixture was incubated at 25°C on a rotary shaker at 200 rpm for 30 min and then centrifuged at 3000 rpm for 10 min. The supernatant was analyzed by UV spectroscopy at 270 nm to quantify the concentration of residual phenol. The adsorption experiments were performed in triplicate.

The equilibrium adsorption capacity (Q_e; mg/g) was calculated on the basis of the difference in the phenol concentration before and after equilibrium adsorption, the volume of the aqueous solution, and the mass of the dry DMIP according to the following:

$$Q_e = (C_0 - C_e)V/1000m \qquad (3)$$

where C_e is the equilibrium concentration of phenol (μg/mL) and m is the mass of dry DMIP (g).

Regeneration of DMIP

The dry DMIP (100 mg) was immersed in 100 mL of a water solution containing 50 μg/mL of phenol, and the pH value of the solution was 7. The mixture in the conical flasks with a stopper were incubated at 25°C on a rotary shaker at 200 rpm for 30 min. After centrifugation, the supernatants were analyzed by UV spectroscopy at 270 nm to quantify the concentration of the residual phenol. The recovered DMIP were placed in a Soxhlet extraction apparatus and washed with methanol/acetic acid (9:1 v/v) to remove phenol, dried *in vacuo*, and reused for the adsorption of phenol.
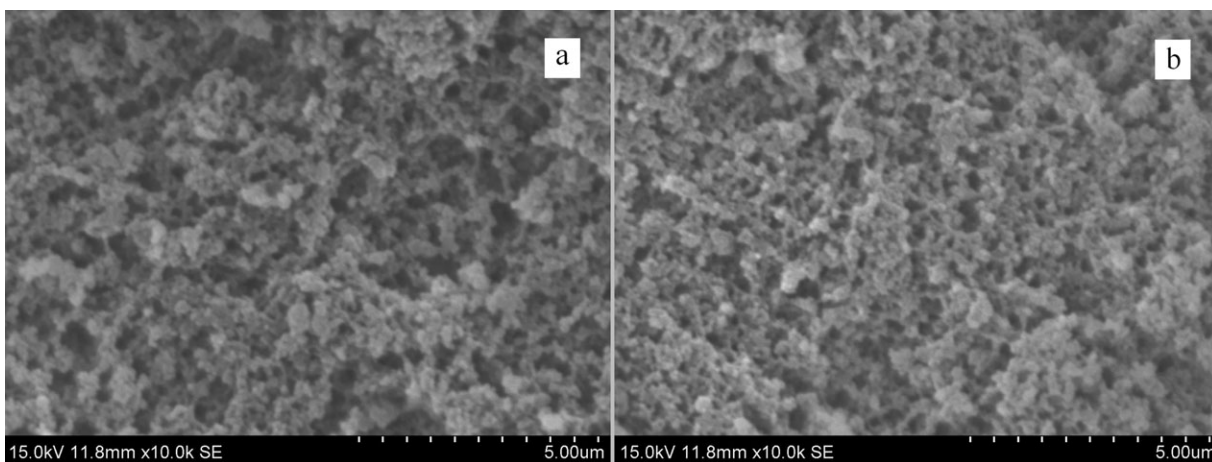
Figure 3. SEM images of (a) DMIP and (b) NIP.

RESULTS AND DISCUSSION

Preparation of the DMIP

The possible preparation process of DMIP is shown in Figure 2. The figure illustrates that the template (SD), functional monomer, free-radical initiator, and crosslinker were copolymerized in acetonitrile. After the residues of the reactants and the template were removed, a large number of tailor-made cavities microparticles were formed, and the DMIP was finally obtained. Herein, the DMIP was synthesized by a noncovalent imprinting method. The all-noncovalent interactions, such as hydrogen bonding, electrostatic interaction, and hydrophobic interaction were significant in the process of molecular imprinting.

Characterization of DMIP

The surface morphologies of both polymeric particles were observed by SEM. It was necessary to cover the surface of the polymer with a thin, electrically conductive layer by gold sputtering before the SEM observation of the samples because polymers are insufficiently conductive on their own. We found that the SEM images of the NIP and DMIP showed appreciable differences in morphology. The surface of the DMIP exhibited a bigger porous structure than the NIP (Figure 3). The bigger porous structure of the DMIP was due to the fact that specific binding sites had been created for the polymer. The cavities in the DMIP were probably caused by the structure of the target molecule, SD. The nitrogen adsorption/desorption analysis of BET was used to evaluate the pore volume and the specific surface area of the NIP and DMIP, which are shown in Table I. The BET surface area of the DMIP was 182.2 m^2/g and that of the NIP was 125.6 m^2/g. The pore volume of the DMIP was 0.095 cm^3/g, and that of the NIP was 0.065 cm^3/g. This also showed that the NIP and the DMIP particles were significantly different in these aspects. The phenomenon showed that the DMIP could be successfully synthesized with bulk polymerization.

The wave numbers from the FTIR spectra, ranging from 450 to 4000 cm^{-1}, of SD, the DMIP, and the NIP are presented in Figure 4. The results indicate that the DMIP and NIP show the occurrence of major bands at similar locations; this indicated chemical similarity in the backbone structure of the polymers. The NIP showed strong absorption peaks; the band at about

3446 cm^{-1} was associated with the N&bond;H stretching vibration, and the strong absorption band at about 1730 cm^{-1} was ascribed to C&dbond;O stretching vibrations. The characteristic absorption peaks of N&bond;H and C&dbond;O from the DMIP shifted to low wave numbers compared with those of the NIP. This phenomenon was attributed to an association between the monomer and template molecules via hydrogen bonding. Compared with SD, the DMIP did not showed similar characteristic absorption peaks. This showed that no template molecules were retained on the DMIP.

The formation of an intermediate between the functional monomer and template molecules via hydrogen bond is a prerequisite for molecular imprinting because the affinity and selectivity of the imprinted polymer are manifested by the interaction strength in the precursor. In the mixture solution, the amino group (&bond;NH_2) and the carbonyl group (C&dbond;O) in a molecule of AM can interact with the functional group (amino group and carbonyl group) of the template molecule and lead to the formation of the precursor through hydrogen bonding. Such an association between the functional monomer and the template molecule was confirmed by UV absorption and ^1H-NMR spectroscopy.

The UV absorption spectra of the functional monomer and the mixture of the functional monomer and template were measured in acetonitrile, as shown in Figure 5. It was clearly observed that the decreased absorption peak of the mixtures and the redshift effect were attributed to an association between the monomer and template molecules via hydrogen bonding.

Figure 6 shows a comparison of the ^1H-NMR spectra for SD and the mixture of SD and AM. The resonances between 6.006

Table I. Porosities of the Polymers as Determined by BET Analysis

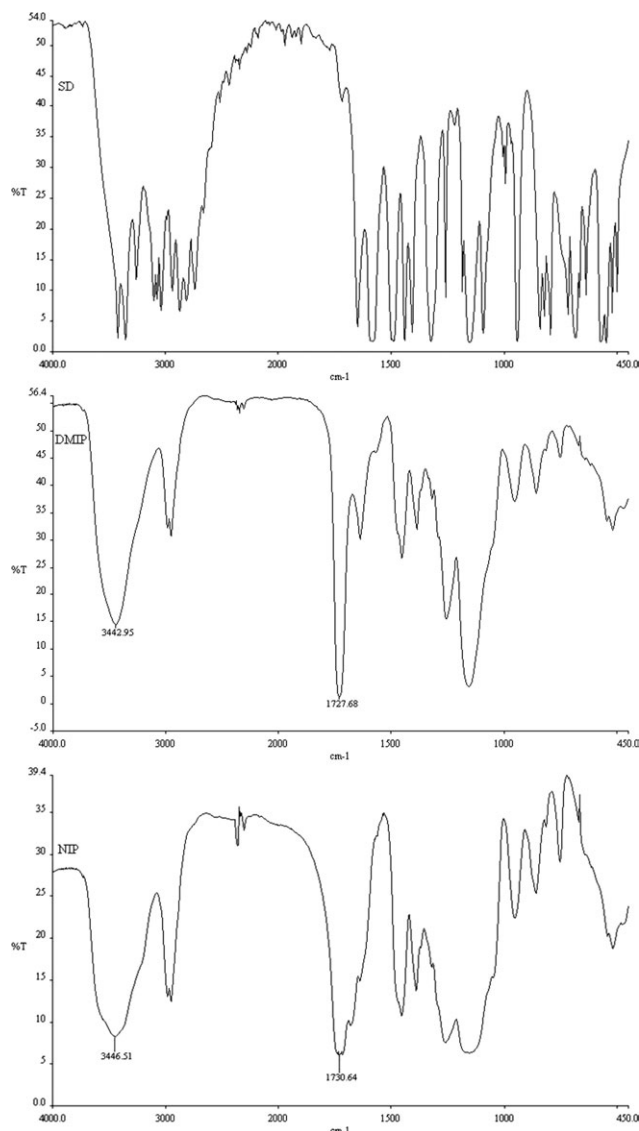| Sample	MIP	NIP
Pore volume (cm^3/g)	0.095	0.065
BET surface area (m^2/g)	182.2	125.6
Pore size (nm)	2.09	2.04

Figure 4. FTIR spectra of the polymers SD, DMIP, and NIP. SD was a template molecule, DMIP was an imprinted molecular polymer, and NIP was a nonimprinted polymer.

Figure 5. UV absorption spectra of (a) 20 mmol/L AM in acetonitrile, (b) the mixture of 20 mmol/L AM and 40 mmol/L SD, and (c) the mixture of 20 mmol/L AM and 80 mmol/L SD.

3). According to adsorption rate design formulas, the adsorption rate of the DMIP was 0.406 ± 0.01 mg g^{-1}·min^{-1}. In comparison with other adsorbents, the DMIP adsorbent had a higher adsorption capacity and adsorption rate for phenol. It was reported that the adsorption amount of the modified fly-ash-based zeolite adsorbent for phenol only reached about 0.7 mg/g.[31] The adsorption rate of the carbonylated hypercrosslinked polymeric adsorbent was about 0.24 mg g^{-1}·min^{-1}.[32] The adsorption rate of the physiochemically activated coconut shell was about 0.167 mg g^{-1}·min^{-1}.[33] The adsorption rate of the post-crosslinked polymeric adsorbent (PDM) was about 0.262 mg g^{-1}·min^{-1}.[14] It was apparent that the DMIP adsorbent quickly reached equilibrium and had a good adsorption capacity.

Adsorption Isotherm of the DMIP

The adsorption activity of MIPs is often investigated by the description of the adsorption isotherm. There are the Langmuir model, Freundlich model, and Langmuir–Freundlich model in the analysis of adsorption isotherm.[34,35] The Freundlich model

and 11.262 ppm in the spectrum were two amino protons of SD, which exhibited an obviously downfield shift in the presence of AM. These ^{1}H-NMR data strongly supported the formation of hydrogen bonds between AM and SD molecules.

Adsorption Kinetics of the DMIP

The adsorption kinetics of the DMIP were analyzed with a batch method. Figure 7 presents the adsorption kinetics of the DMIP and NIP adsorbents for phenol. The adsorption of both the DMIP and NIP adsorbents was time dependent, and their kinetic profiles for phenol were similar. It took only 15 min for the DMIP and NIP adsorbents to achieve equilibrium. We noted that the adsorption amount of the DMIP adsorbents for phenol reached 6.09 ± 0.15 mg/g after 15 min of adsorption; this was higher than the 4.63 ± 0.12 mg/g of the NIP adsorbents and suggested a good imprinting effect of the DMIP adsorbents. The relative standard deviation (RSD) of the test was less than 3% ($n =$
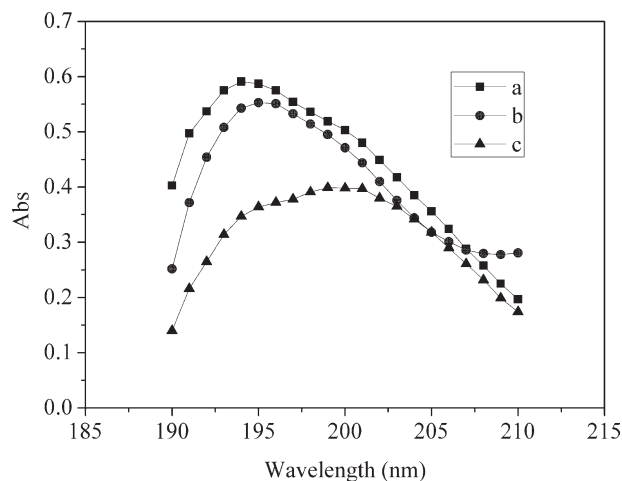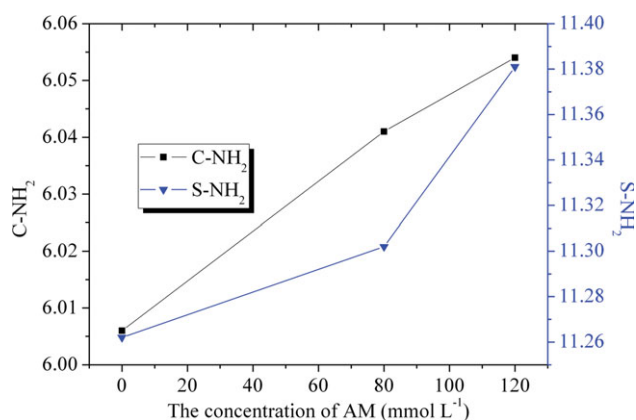

Figure 6. Effect of the functional monomer on the chemical shift of amino protons of SD on the ^{1}H-NMR spectra. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
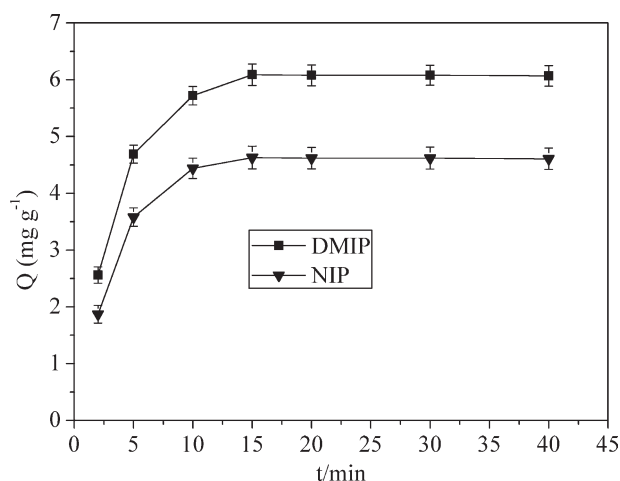
Figure 7. Adsorption kinetics of the DMIP and NIP for phenol. The data were obtained by adsorption in triplicate. The RSDs of the DMIP test were 1.89, 2.04, 2.1, 2.45, 2.41, 2.3, and 2.37% ($n = 3$). The RSDs of the NIP test were 2.01, 2.11, 2.35, 2.56, 2.43, 2.49, and 2.44% ($n = 3$).

is widely applied to describe the adsorption isotherm curves of noncovalent MIPs under conditions in which the concentration of the adsorbed substance is lower.[36] The Freundlich equation is described as follows:

$$Q_e = KC_e^{1/n} \qquad (4)$$

$$\ln Q_e = 1/n \ln C_e + \ln K \qquad (5)$$

where K and n are the adsorption equilibrium constants.

The adsorption isotherm of the DMIP for phenol is generally estimated by Freundlich equation. The adsorption capacity of the DMIP for phenol increased when the concentration of phenol increased. Linear plots of $\ln Q_e$ versus $\ln C_e$ showed that adsorption of phenol from wastewater on the DMIP also followed the Freundlich isotherm (Figure 8). The linear regression
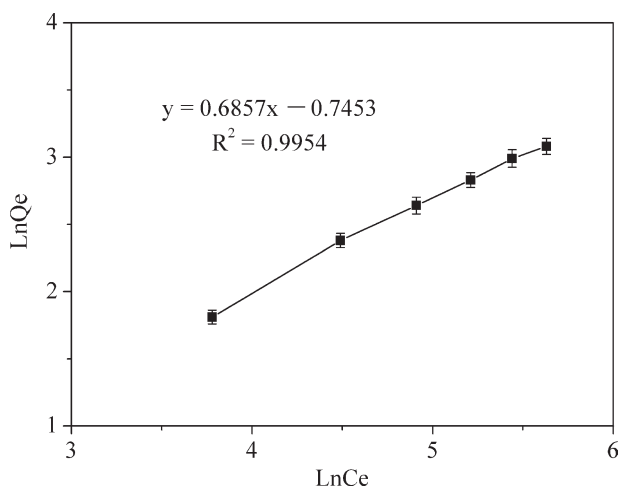

Figure 8. Adsorption isotherm of DMIP for phenol derived from the Freundlich equation. The data were obtained by adsorption in triplicate. The RSDs of the test were 2.56, 2.67, 3.1, 2.81, 3.24, and 2.97% ($n = 3$).
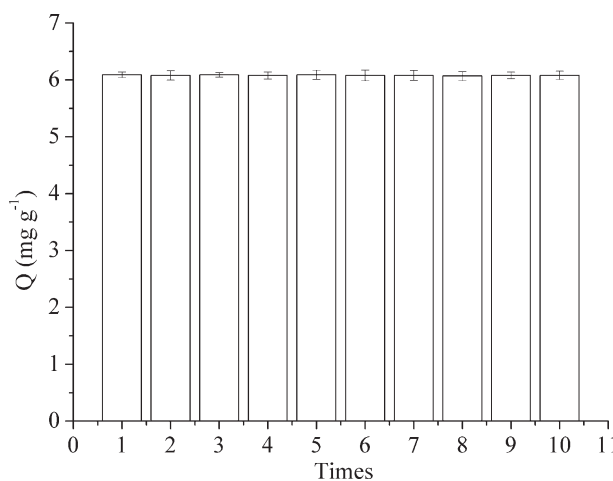

Figure 9. Phenol removal efficacy of the DMIP after regeneration. The data were obtained by adsorption in triplicate. The RSDs of the test were 2.45, 4.1, 2.09, 3.12, 4.04, 4.67, 4.31, 3.89, 2.96, and 3.72% ($n = 3$).

equation for the experimental dots in Figure 8 is $y = 0.6857 x - 0.7453$. The regression constant was calculated to be 0.9954. Values of K and n were calculated from the intercepts and slopes of the plots. The parameter n was calculated to be 1.456. The results suggest that phenol from wastewater was favorably adsorbed by the DMIP and that the Freundlich model fit the adsorption model of DMIP for phenol. The adsorption model of DMIP for phenol was multilayer adsorption.

Regeneration of DMIP
Experiments were performed to determine whether the phenol bound to the DMIP could be desorbed–released and the DMIP reused. As shown in Figure 9, the DMIP could be regenerated after the bound phenol was removed by washing with methanol/acetic acid (9/1 v/v), and it retained the same removal efficiency in the 10 binding/removal cycles tested. The reusability of the DMIP demonstrated through 10 adsorption–desorption cycles was an advantage over other adsorbents, and the adsorption amount of the DMIP adsorbent for phenol retained 6.082 ± 0.006 mg/g. The RSD of the test was less than 5% ($n = 3$). This showed that the DMIP by bulk polymerization method had good regeneration and reusability and could be applied to remove phenol from contaminated water.

CONCLUSIONS

A DMIP for phenol was successfully synthesized by a thermal polymerization method with AM as the functional monomer, EDMA as the crosslinker, AIBN as the free-radical initiator, acetonitrile as the porogenic solvent, and an analogue of phenol, SD, as the template. In comparison to other adsorbents, the synthesized DMIP showed an increase in the capacity and the rate of adsorption. The results indicate that the Freundlich model fits the adsorption model of the DMIP for phenol. The adsorption model of the DMIP for phenol was multilayer adsorption. The DMIP had good regeneration and reusability. The DMIP, as a novel adsorbent, could be applied to remove phenol from contaminated water.

ACKNOWLEDGMENTS

REFERENCES

1. Jiang, Y.; Wen, J. P.; Bai, J.; Wang, D. Q.; Hu, Z. D. *Biochem. Eng. J.* **2006,** *29*, 227.

2. Kamble, S. P.; Mangrulkar, P. A.; Bansiwal, A. K.; Rayalu, S. S. *Chem. Eng. J.* **2008,** *138*, 73.

3. Lua, A. C.; Jia, Q. P. *Chem. Eng. J.* **2009,** *150*, 455.

4. Tziotzios, G.; Teliou, M.; Kaltsouni, V.; Lyberatos, G.; Vayenas, D. V. *Biol. Biochem. Eng. J.* **2005,** *26*, 65.

5. Mukherjee, S.; Kumar, S.; Misra, A. K.; Fan, M. *Chem. Eng. J.* **2007,** *129*, 133.

6. Yang, C.; Qian, Y.; Zhang, L.; Feng, J. *Chem. Eng. J.* **2006,** *117*, 179.

7. Hameed, B. H.; Rahman, A. A. *J. Hazard. Mater.* **2008,** *160*, 576.

8. Esplugas, S.; Gimenez, J.; Contreras, S.; Pascual, E.; Rodriguez, M. *Water Res.* **2002,** *36*, 1034.

9. Rodgers, J. D.; Jedral, W.; Bunce, N. *J. Environ. Sci. Technol.* **1999,** *33*, 1453.

10. Wang, L. M.; Li, Y.; Yu, P.; Xie, Z. X.; Luo, Y. B.; Lin, Y. W. *J. Hazard. Mater.* **2010,** *183*, 366.

11. Liu, Y. J.; Zhang, A. N.; Wang, X. C. *Biochem. Eng. J.* **2009,** *44*, 187.

12. Girods, P.; Dufour, A.; Fierro, V.; Rogaume, Y.; Rogaume, C.; Zoulalian, A.; Celzard, A. *J. Hazard. Mater.* **2009,** *166*, 491.

13. Cherifi, H.; Hanini, S. *Desalination* **2009,** *244*, 177.

14. Zeng, X.; Fan, Y.; Wu, G.; Wang, C.; Shi, R. *J. Hazard. Mater.* **2009,** *169*, 1022.

15. Wang, S. L.; Tzou, Y. M.; Lu, Y. H.; Sheng, G. *J. Hazard. Mater.* **2007,** *147*, 313.

16. Park, S. J.; Jang, Y. S.; Shim, J. W.; Ryu, S. K. *J. Colloid Interface Sci.* **2003,** *260*, 259.

17. El-Naas, M. H.; Al-Zuhair, S.; Alhaija, M. A. *J. Chem. Eng.* **2010,** *162*, 997.

18. Wulff, G.; Sarhan, A. *Angew. Chem. Int. Ed. Engl.* **1972,** *11*, 341.

19. Vlatakis, G.; Andersson, L. I.; Miillcr, R.; Mosbach, K. *Nature* **1993,** *361*, 645.

20. Zhang, Z. L.; Wang, B. *J. Appl. Polym. Sci.* **2009,** *113*, 1050.

21. Lai, E. P. C.; Maleki, Z. D.; Wu, S. *J. Appl. Polym. Sci.* **2010,** *116*, 1499.

22. Zhu, X. L.; Zhu, Q. S. *J. Appl. Polym. Sci.* **2008,** *109*, 2665.

23. Feng, Q. Z.; Zhao, L. X.; Lin, J. M. *Anal. Chim. Acta.* **2009,** *650*, 70.

24. Lv, Y. Q.; Lin, Z. X.; Feng, W.; Tan, T. W. *Chromatography* **2007,** *66*, 339.

25. Matsui, J.; Fujiwara, K.; Takeuchi, T. *Anal. Chem.* **2000, 72, 1810.**

26. Urraca, J. L.; Marazuela, M. D.; Merino, E. R.; Orellana, G.; Moreno-Bondi, M. C. *J. Chromatogr. A* **2006,** *1116*, 127.

27. Navarro-Villoslada, F.; Urraca, J. L. *Sens. Actuators B* **2007,** *121*, 67.

28. Lucci, P.; Derrien, D.; Alix, F. *Anal. Chim. Acta.* **2010,** *672*, 15.

29. Feás, X.; Seijas, J. A.; Vázquez-Tato, M. P. *Anal. Chim. Acta.* **2009,** *631*, 237.

30. Zhao, W. H.; Sheng, N.; Zhu, R.; Wei, F. D.; Cai, Z.; Zhai, M. J.; Du, S. H.; Hu, Q. *J. Hazard. Mater.* **2010,** *179*, 223.

31. Kamble, S. P.; Mangrulkar, P. A.; Bansiwal, A. K.; Rayalu, S. S *J. Chem. Eng.* **2008,** *138*, 73.

32. Huang, J. H. *J. Hazard. Mater.* **2009,** *168*, 1028.

33. Mohd Din, A. T.; Hameed, B. H.; Ahmad, A. L. *J. Hazard. Mater.* **2009,** *161*, 1522.

34. Xing, W. L.; He, X. W. *Talanta* **1997,** *44*, 959.

35. Antonio, P.; Iha, K.; Suárez-Iha, M. E. V. *Talanta* **2004,** *64*, 484.

36. Zheng, H.; Liu, D. *J. Hazard. Mater.* **2009,** *167*, 141.