



## Preparation and Adsorption Properties of 2,4-Dichlorophenoxyacetic Acid Magnetic Imprinted Polymers introducing $\beta$ -Cyclodextrin

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Magnetic molecularly imprinted polymers (Mag-MIPs) which contained  $\beta$ -cyclodextrin ( $\beta$ -CD) derivative as the functional monomer were successfully prepared using 2,4-dichlorophenoxyacetic acid as template molecule, methacrylic acid and *bismethacryloyl*- $\beta$ -cyclodextrin (BMA- $\beta$ -CD) as binary functional monomer, ethylene glycol dimethacrylate as polymeric matrix components,  $\text{Fe}_3\text{O}_4$  magnetite as magnetic component. Magnetic molecularly imprinted polymers were characterized by transmission electron microscope, Fourier transform infrared spectrometer, thermogravimetric analyzer. Competitive rebinding experiment results revealed that the magnetic molecularly imprinted polymers beads exhibited a higher specific recognition for the template than the non-imprinted polymers. Batch mode adsorption studies were carried out to investigate the specific adsorption equilibrium. Equilibrium dates in this study were analyzed with Langmuir isotherm model and Freundlich model, respectively. The analysis results show Langmuir isotherm model is fitted to the equilibrium date better than Freundlich model.

**Keywords:**  $\beta$ -Cyclodextrin, Molecularly imprinted polymers, Adsorption studies.

### INTRODUCTION

Molecularly imprinted technique is now a well-established method of preparing polymers with special selectivity by simulating recognition function of natural antibody. Molecularly imprinted polymers, which have so many advantages such as stability at extremes of pH and temperature, low cost and reusability, have been extensively used in chromatographic separation<sup>1-3</sup>, solid phase extraction<sup>4-6</sup>, chemical sensors<sup>7-9</sup> and catalysis<sup>10,11</sup>.  $\beta$ -Cyclodextrin ( $\beta$ -CD) is polysaccharide of glucose with a shape of a toroid and hollow truncated cavity with external hydrophilic rims and internal hydrophobic cavity. Compared with conventional molecularly imprinted polymers functional monomers,  $\beta$ -cyclodextrin possesses some unique advantages, for example,  $\beta$ -cyclodextrin can form inclusion with guest molecules through various kinds of intermolecular interactions (hydrophobic interaction, dipole-dipole interaction and hydrogen bond interaction) during the imprinting process<sup>12</sup>. So combining hydrogen bond based monomers and size-identified functional monomers would be a good way for molecularly imprinted polymers preparation<sup>13</sup>.

When it comes on the application of molecularly imprinted polymers in the separation and analysis of pollutants from environment, the economical efficiency should be taken into consideration. The magnetic molecularly imprinted polymers

can make separating fast, because it can be easily collected by an external magnetic field without additional centrifugation or filtration<sup>14,15</sup>. In this work, magnetic molecularly imprinted polymer beads were prepared using 2,4-dichlorophenoxyacetic acid as template, methacrylic acid and  $\beta$ -CD-MAA as binary functional monomers, ethylene glycol dimethacrylate as the crosslinker,  $\text{Fe}_3\text{O}_4$  magnetite as magnetic component by emulsion polymerization. The magnetic molecularly imprinted polymers were characterized by Fourier transform infrared spectrometer, transmission electron microscope and thermal-gravimetric analysis. The results indicate that the magnetic microspheres has a spherical structure and the desired magnetic susceptibility. Because the research about the absorption mode of magnetic molecularly imprinted polymers can help to assess the absorption efficiency and has the important significance on practical application of the particles, so the properties such as special binding and adsorption model were also investigated.

### EXPERIMENTAL

Bismethacryloyl- $\beta$ -cyclodextrin (BMA- $\beta$ -CD) was prepared by following the literature<sup>16</sup>. Ethylene glycol dimethacrylate (EGDMA) was purchased from Damao Reagent Plant (Tianjin, China) and was distilled under reduced pressure before use. All other chemicals used were commercially obtained.

Fourier transform infrared spectra (FT-IR) was recorded on a Nicolet NEXUS-470 fourier transform infrared spectrometer apparatus (USA). Ultraviolet visible (UV-visible) absorption spectra of 2,4-dichlorophenoxyacetic acid was recorded by a UV-2800 Shimadzu spectrophotometer (Japan). Thermal stability of the particles was measured using a diamond TG/DTA instruments (PerkinElmer, USA) under a nitrogen atmosphere up to 800 °C. Transmission electron microscopy was obtained on an Tecnai G20 instrument (FEI, USA).

**Preparation of Fe<sub>3</sub>O<sub>4</sub> particles:** The Fe<sub>3</sub>O<sub>4</sub> magnetite was synthesized by the coprecipitation method. 45 g FeCl<sub>3</sub>·6 H<sub>2</sub>O and 22.5 g FeSO<sub>4</sub>·7H<sub>2</sub>O were dissolved in 150 mL of water in a three-necked reactor (250 mL). The mixture was stirred vigorously and purged with nitrogen gas while the temperature increased to 80 °C, then 8 mol L<sup>-1</sup> NH<sub>3</sub>·H<sub>2</sub>O was added into it. After 1 h, the magnetic precipitate was isolated from the solvent by a permanent magnet and washed several times with distilled water. Finally, the obtained magnetic composites were dried in an oven at 60 °C for overnight.

**Preparation of magnetic molecularly imprinted polymers:** Magnetic molecularly imprinted polymers were synthesized according to previous literature with a few modifications<sup>14</sup>. First, 58.5 mg 2,4-dichlorophenoxyacetic acid was dissolved in 15 mL of DMSO and then 0.68 mL methacrylic acid and 2 g BMA-β-CD were added into the solution. This mixture was sonicated for about 0.5 h. Secondly, Fe<sub>3</sub>O<sub>4</sub> (1.1 g) was blended with 1 mL of oleic acid and 3.4 mL of ethylene glycol dimethacrylate, stirred in ultrasonic bath for 0.5 h. Then the pre-assembly solution was added into the mixture and stirred for another 0.5 h to prepare pre-polymerization solution. Thirdly, PVP (0.2 g) was dissolved into 75 mL of DMSO:H<sub>2</sub>O (9:1, v/v) in a three-necked round-bottom flask.

The mixture was stirred in N<sub>2</sub> atmosphere while the temperature increased to 60 °C. The pre-polymerization solution was added into the flask and the AIBN (0.1 g) used as initiator was added into the solution. The reaction was kept under 60 °C for 24 h. After the polymerization, the product was separated from the mixture by a magnet and washed with methanol: acetic acid (8:2) by Soxhlet extraction until the template molecule could not be detected by UV-visible spectrophotometer, then the polymer was washed with methanol several times and dried at 70 °C. The corresponding magnetic non-imprinted polymers (Mag-NIPs) were prepared in similar method as above, but without the addition of 2,4-dichlorophenoxyacetic acid. Mag-NIPs were used as the control for comparison in the characterization studies.

**Adsorption studies:** The binding experiment was carried out by adding 10 mg Mag-MIPs or Mag-NIPs in a glass tube containing 10 mL of 2,4-dichlorophenoxyacetic acid solutions which was prepared in methanol varied in the concentrations of 20 to 500 mg L<sup>-1</sup>. The solution was incubated for 24 h at room temperature and then the suspension was separated and analyzed by UV-visible spectrophotometer at 284 nm. The amount of 2,4-dichlorophenoxyacetic acid bound on the polymers was obtained by subtracting the free concentration from initial concentration of 2,4-dichlorophenoxyacetic acid added to the mixture.

## RESULTS AND DISCUSSION

Transmission electron microscope images (Fig. 1) indicated the particle diameter of Mag-MIPs was about 10-20 nm and had agglomeration phenomenon. Most of particles were of uniform spherical morphology and the imprinting layer thickness of Mag-MIPs was about several nanometers.

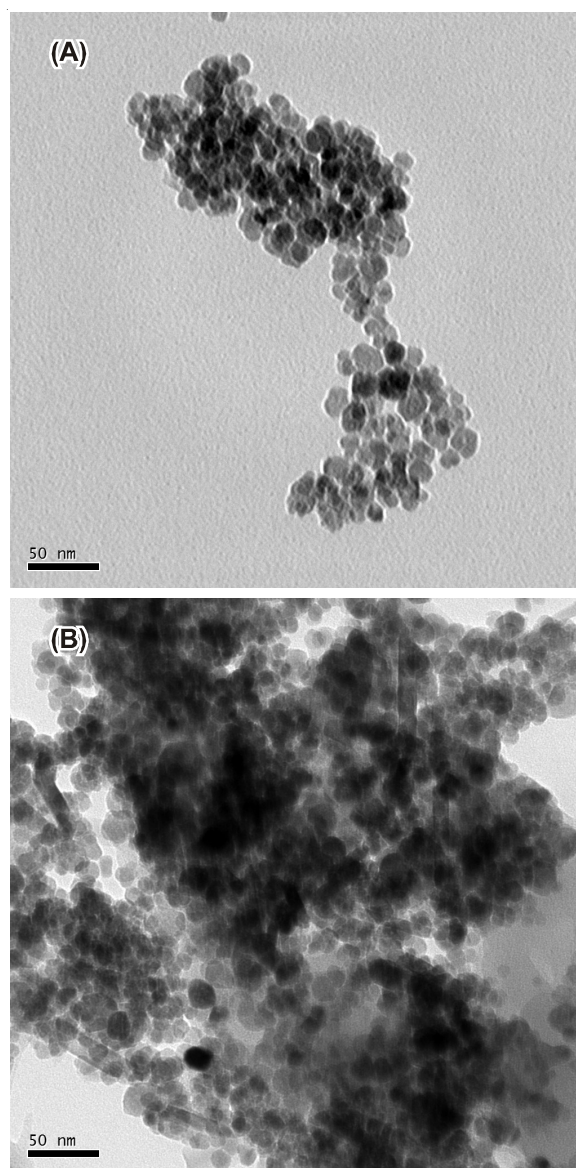


Fig. 1. Transmission electron microscope images of Fe<sub>3</sub>O<sub>4</sub> (A), magnetic molecularly imprinted polymers (B)

Fourier transform infrared spectrometer spectra of Fe<sub>3</sub>O<sub>4</sub>, Mag-MIPs were compared in Fig. 2. As illustrated, the adsorption band of Fe-O bond of Mag-MIPs at 572 cm<sup>-1</sup>, compared with Fe<sub>3</sub>O<sub>4</sub> of 563 cm<sup>-1</sup>, which proved that the Fe<sub>3</sub>O<sub>4</sub> embedded in Mag-MIPs, the characteristic feature of Mag-MIPs are C-O bond in carboxyl at 1723 cm<sup>-1</sup>, C-H band at 2923 and 2842 cm<sup>-1</sup> and the absorption band at 1153 cm<sup>-1</sup> was assigned to C-O asymmetric stretching vibration.

The stability of Fe<sub>3</sub>O<sub>4</sub>, Mag-MIPs were examined with thermal-gravimetric analyzer. As shown in Fig. 3, the magnetic Fe<sub>3</sub>O<sub>4</sub> showed a small weight loss of approximately 13 % in

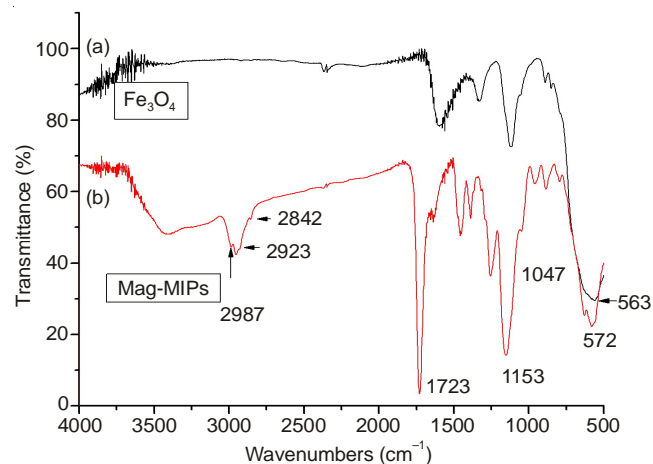


Fig. 2. IR spectrum of  $\text{Fe}_3\text{O}_4$  (a), and magnetic molecularly imprinted polymers (b)

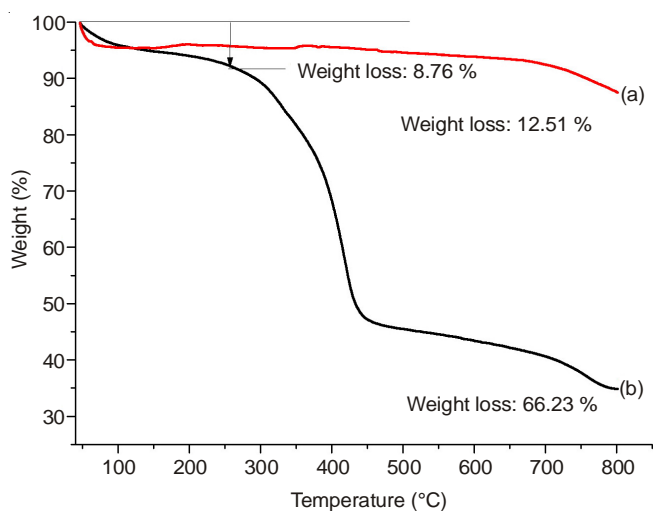


Fig. 3. Thermal gravimetric graph of  $\text{Fe}_3\text{O}_4$  (a) and magnetic molecularly imprinted polymers (b)

the whole process. Compared with the weight loss of  $\text{Fe}_3\text{O}_4$ , Mag-MIPs have obvious weight loss from 50 to 800 °C. The high weight decrease in the second stage from 280 to 445 °C, which is caused by the loss of imprinted polymer layer. The total mass loss is calculated to be 60.5 %. The residue can be attributed to the more thermally resistant  $\text{Fe}_3\text{O}_4$  magnetite, which showed the magnetite encapsulation efficiency was satisfactory.

Fig. 4 showed the magnetic hysteresis loop of  $\text{Fe}_3\text{O}_4$  and Mag-MIPs which had been dried at room temperature. The magnetic composites remained enough magnetic to meet the need of magnetic separation. Magnetization increased with an increase in the magnetic field.  $\text{Fe}_3\text{O}_4$  particles possessed better magnetic properties and the saturation magnetization of  $\text{Fe}_3\text{O}_4$  (10.95 emu/g) was slightly higher than that of Mag-MIPs (8.74 emu/g). Each sample exhibited an extremely small hysteresis loop and low coercivity, which is a typical characteristic of superparamagnetic particles. The inserted photograph of Fig. 4 showed the magnetic separation of Mag-MIPs particles. Initially, the magnetic beads were incubated in the distilled water. By reciprocated oscillation, the beads were fully dispersed. After a certain time, the beads were attracted to the wall of vial

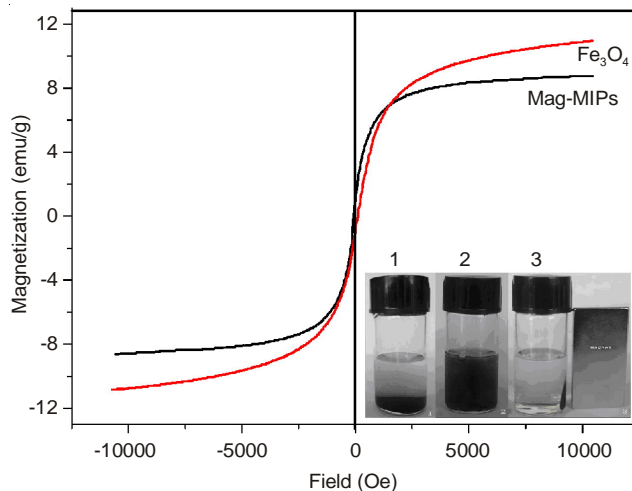


Fig. 4. Magnetic hysteresis loops of  $\text{Fe}_3\text{O}_4$  and magnetic molecularly imprinted polymers at 25 °C. The inset photographs showed the immersion (1), dispersion (2) and magnetic separation (3) of magnetic molecularly imprinted polymers

with the water becoming clear and transparent within in the presence of an external magnetic field. The superparamagnetism of the magnetic composites prevented them from aggregating and enabled them to re-disperse rapidly after the magnetic field was removed, which would facilitate the subsequent adsorption experiments.

**Adsorption isotherms:** The adsorption isotherm experiments for Mag-MIPs and Mag-NIPs were carried out in the 2,4-dichlorophenoxyacetic acid concentration range of 25-500 mg/L in 25 °C. The amount of 2,4-dichlorophenoxyacetic acid bound (mg/g) to the Mag-MIPs ( $Q$ ) was calculated by subtracting the amount of free 2,4-dichlorophenoxyacetic acid in the supernate from the amount of 2,4-dichlorophenoxyacetic acid initially added. It can be seen that the amount of absorbed 2,4-dichlorophenoxyacetic acid per unit mass of the polymer increase along with the increasing of 2,4-dichlorophenoxyacetic acid initial concentrations, while the binding amount of 2,4-dichlorophenoxyacetic acid on the imprinted polymer is always higher than that on the non-imprinted polymer in the whole concentration range, displaying the molecularly imprinted effect<sup>17</sup> (Fig. 5). The imprinted ratios of the Mag-MIPs prepared from different molar ratios were listed (Fig. 6). The imprinted ratio ( $\alpha$ ) was defined as the ratio of the binding capacity of the Mag-MIPs for 2,4-dichlorophenoxyacetic acid to the binding capacity of the corresponding Mag-NIPs for 2,4-dichlorophenoxyacetic acid. Although a value is not necessarily associated with concentration, but from the Fig. 6 the general change trend was obtained which the solution concentration was more dilute, the ratio was taller. This may be when solution concentration was higher, the nonspecific adsorption increased for this kind of Mag-MIPs and the imprinted ratio declined.

$$Q_t = \frac{(C_0 - C_t)V}{W}$$

In order to optimize the design of an adsorption system to separation 2,4-dichlorophenoxyacetic acid from solutions, it is important to establish the most appropriate correlation for the equilibrium curve. Theoretically the amount or adsorption capacity at equilibrium is commonly expressed by an adsorption

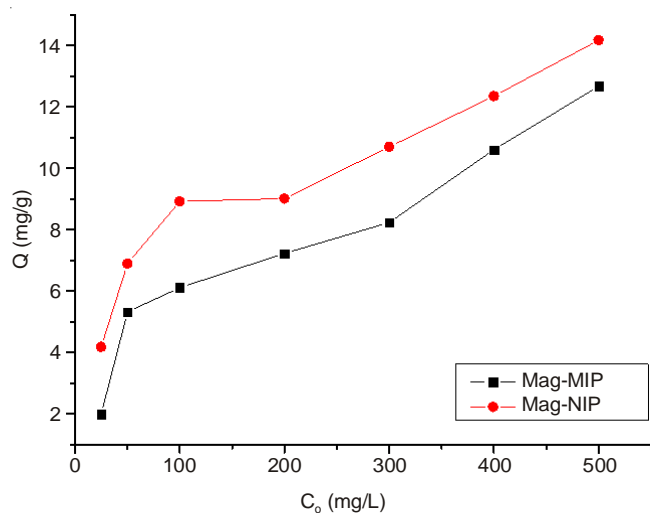


Fig. 5. Imprinted ratio of magnetic molecularly imprinted polymers and non-imprinted polymers

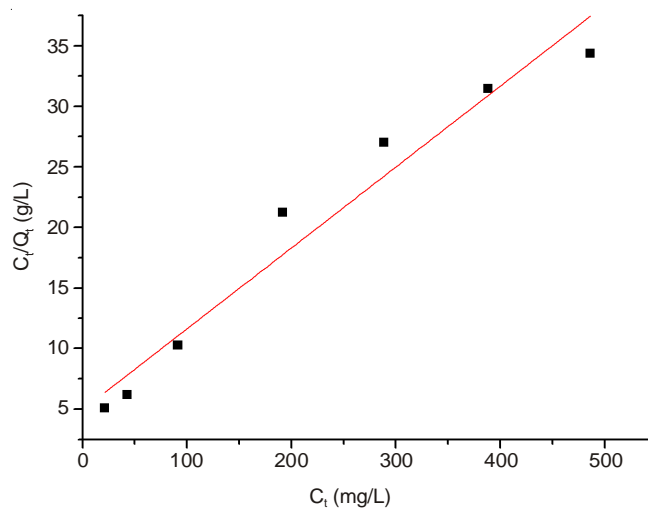


Fig. 7. Langmuir isotherm model onto magnetic molecularly imprinted polymers

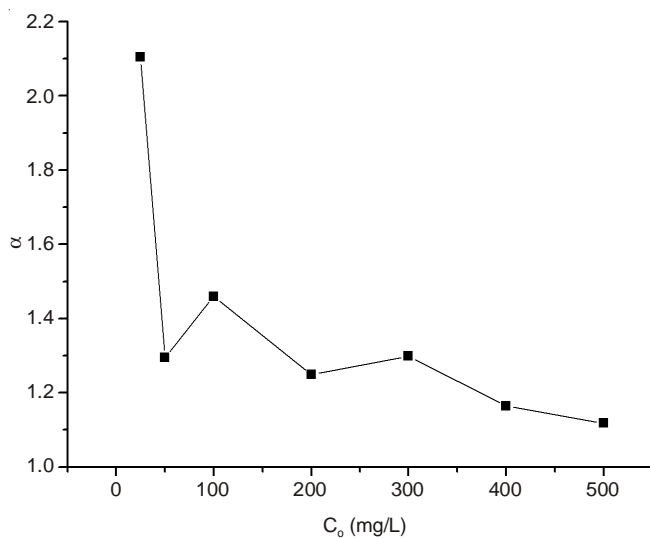


Fig. 6. Imprinted ratio of magnetic molecularly imprinted polymers

isotherm. Equilibrium data in this study were analyzed with two common isotherm models: Langmuir<sup>18</sup> and Freundlich<sup>14</sup> isotherm models. The Langmuir equation is given in the following equation:  $C_t/Q_t = C_t/Q_{\max} + 1/(KQ_{\max})$ , where  $C_t$  is the concentration of 2,4-dichlorophenoxyacetic acid at equilibrium ( $\text{mg L}^{-1}$ ),  $Q_{\max}$  is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface ( $\text{mg/g}$ ).  $Q_t$  is the adsorbate concentration in equilibrium ( $\text{mg g}^{-1}$ ) and  $K$  is the Langmuir constant ( $\text{L mg}^{-1}$ ). The obtained data were plotted according to the equation, it can be seen clearly in Fig. 7. The constant  $R^2$  is 0.9532.  $Q_{\max}$  is  $14.9678 \text{ mg g}^{-1}$  and  $K$  is 0.0135.

The Freundlich isotherm model is an empirical equation, which is employed to describe heterogenous systems and the linear forms which was given as follows:

$$\log Q_t = \log K_F + (1/n) \log C_t$$

where  $K_F$  is an indicative constant for adsorption capacity of the adsorption capacity of the adsorbent and  $1/n$ , ranging between 0 and 1, measures the adsorption intensity or surface heterogeneity. The obtained data were plotted according to the

equation, it can be seen clearly in Fig. 8. The constant  $R^2$  is 0.9140.  $K_F$  is 1.73,  $n$  is 3.01.

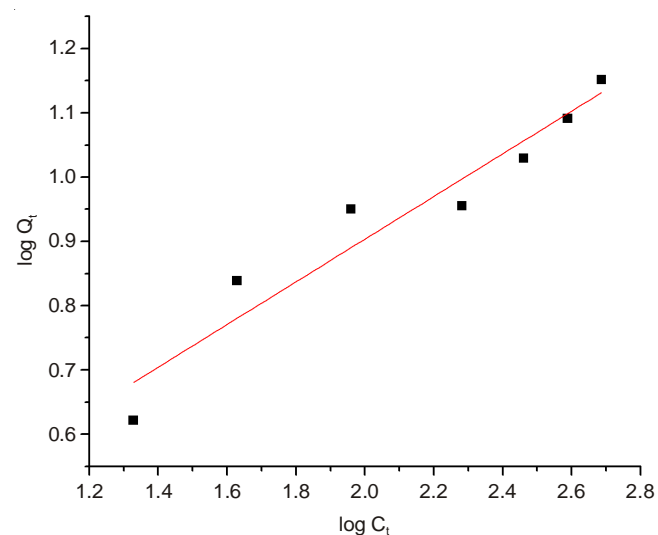


Fig. 8. Freundlich isotherm model onto magnetic molecularly imprinted polymers (Mag-MIPs)

The absorption research shows the two curves of the two absorption models are not a good linear relationship, which show recognition and adsorption is a complicated process between the mag-MIPs and substrate molecule, not only exists the interaction of Mag-MIPs and substrate, such as hydrophobic interaction, dipole-dipole interaction and hydrogen bond interaction, but also have relation with the structure of magnetic polymer itself and solvents *etc.* But from the data of the two absorption models, it can be observed the Langmuir isotherm model yielded a better fit than those by the Freundlich isotherm model.

## Conclusion

In this study, 2,4-dichlorophenoxyacetic acid imprinted magnetic polymers using  $\beta$ -cyclodextrin ( $\beta$ -CD) derivative as functional monomer were successfully synthesized. Magnetic response experimental results show that the magnetic mole-

cularly imprinted polymer particles can be rapidly and easily separated under a magnetic field. The adsorbing experiments indicate that magnetic imprinted polymers possess a higher affinity for 2,4-dichlorophenoxyacetic acid than the non-imprinted polymers. Such magnetic molecularly imprinted polymer particles might find applications in solid-phase extraction, drug delivery systems and other potential scientific fields.

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#### REFERENCES

- J.B. Jiang, Q. Zhou, C.C. Kang, S.Q. Wu, Y.W. Tang and X.J. Zuo, *J. Appl. Polym. Sci.*, **129**, 3425 (2013).
- K.I. Kitahara, I. Yoshihama, T. Hanada, H. Kokuba and S. Arai, *J. Chromatogr. A*, **1217**, 7249 (2010).
- X.Q. Chen, W.J. Yang, Y.M.H. Zhou and F.P. Jiao, *J. Porous Mater.*, **19**, 587 (2012).
- A. Bereczki, A. Tolokán, G. Horvai, V. Horváth, F. Lanza, A.J. Hall and B. Sellaergren, *J. Chromatogr. A*, **930**, 31 (2001).
- J. Jodlbauer, N.M. Maier and W. Lindner, *J. Chromatogr. A*, **945**, 45 (2002).
- M.T. Muldoon and I.H. Stanker, *Anal. Chem.*, **69**, 803 (1997).
- H.M. Zhao, Y.Q. Chen, H.B. Cheng, F. Yuan and X. Quan, *Appl. Mech. Mater.*, **303-306**, 170 (2013).
- J.P. Li, Y.P. Li, Y. Zhang and G. Wei, *Anal. Chem.*, **84**, 1888 (2012).
- A. Nezhadali, S. Pirayesh and R. Shadmehri, *Sens. Actuators B*, **185**, 17 (2013).
- K.J. Tong, S. Xiao, S.J. Li and J. Wang, *J. Inorg. Organomet. Polym.*, **18**, 426 (2008).
- Y. Kawanami, T. Yunoki, A. Nakamura, K. Fujii, K. Umamo, H. Yamauchi and K. Masuda, *J. Mol. Catal. Chem.*, **145**, 107 (1999).
- Y. Yang, Y.Y. Long, Q. Cao, K. Li and F. Liu, *Anal. Chim. Acta*, **606**, 92 (2008).
- Y. Zhang, Y.W. Li, Y.L. Hu, G.K. Li and Y.Q. Chen, *J. Chromatogr. A*, **1217**, 7337 (2010).
- W. Guo, W. Hu, J. Pan, H. Zhou, W. Guan, X. Wang, J. Dai and L. Xu, *Chem. Eng. J.*, **171**, 603 (2011).
- X. Wang, J.M. Pan, W. Guan, X.H. Zou, P.W. Huo, Y.S. Yan and W. Hu, *J. Sep. Sci.*, **34**, 3287 (2011).
- Z.F. Xu, D.Z. Kuang, G. Wen, F.X. Zhang, J.Q. Wang and J.H. Li, *Chemical J. Chinese Univ.*, **32**, 1727 (2011).
- M.S. Zhang, J.R. Huang, P. Yu and X. Chen, *Talanta*, **81**, 162 (2010).
- I. Langmuir, *J. Am. Chem. Soc.*, **38**, 2221 (1916).