Preparation and selective adsorption of organic pollutants by an inorganic molecular imprinted polymer

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ABSTRACT

A novel inorganic molecular imprinted polymer (MIP) was synthesized by adding Al$^{3+}$ to the Fe/SiO$_2$ gel with Acid Orange II (AO II) as the template. The MIP was characterized by scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy and nitrogen adsorption-desorption measurement. Compared with the non-imprinted polymer (NIP), the MIP enhanced the adsorption capacity of the target pollutants AO II. The selective adsorption capacity study indicated that the MIP adsorbed more AO II than the interferent Bisphenol A (BPA), which also has the structure of a benzene ring, thus proving the selective adsorption capacity of the MIP for template molecules AO II. In addition, the adsorption of AO II over MIP belonged to the Langmuir type and pseudo-second adsorption kinetics, and Dubinin-Radushkevich model indicates that the adsorption process of AO II over MIP and NIP are both given priority to chemical adsorption. The MIP reusability in performance was demonstrated in at least six repeated cycles.

Key words | Acid Orange II, Al$^{3+}$ ion, molecular imprinting, selective adsorption

ABBREVIATIONS

MIP | Molecular imprinted polymer
NIP | Non-imprinted polymer
AO II | Acid Orange II
BPA | Bisphenol A
TPAOH | Tetrapropylammonium hydroxide
TEOS | Tetraethoxysilane
SEM | Scanning electron microscope
XRD | X-ray diffraction
BET | Brunauer–Emmett–Teller
FT-IR | Fourier transform infrared spectroscopy

INTRODUCTION

Molecular imprinting is a useful technique for the preparation of polymers with selective molecular recognition abilities (Zhao et al. 2015). For the molecular imprinted polymer (MIP), its internal imprinting holes are complementary to the template molecules on the shape and chemical structure. After removing the template, these holes possess the affinity and selectivity similar to a natural antibody, thus MIPs have a specific adsorption capacity for specific target compounds (Reddithota et al. 2010). Molecular imprinting technique has been widely evaluated and studied in separation (Serrano et al. 2015), sensors (Chen et al. 2012), and selective catalysis (Saumya et al. 2011) for its excellent molecular recognition ability. At present, MIP has been extensively applied to wastewater treatment. For example, Du et al. (2015) prepared a novel water-compatible surface-imprinted core-shell microsphere by employing molecular imprinting technique, which showed good adsorption capacity and specific recognition for template peptide. Xu et al. (2014) prepared a dual-template molecularly imprinted polymer-coated stir bar for the analysis of estrogens in complex wastewater. This paper also aimed at preparing a novel MIP and using it to treat wastewater containing a kind of dye AO II.

doi: 10.2166/wst.2016.244
Generally, MIPs can be divided into three types, namely, the organic, inorganic and organic-inorganic hybrid MIPs (Wu et al. 2015). The hybrid MIP combines the advantages of both inorganic and organic imprinting materials and shows a better application prospect. But many problems exist in hybridization form, material selection, synthesis methods and so on. Therefore, the synthesis and application of hybrid MIP are still in the exploratory stage (Gu et al. 2015). Organic polymer-based MIP is extensively employed due to the easy availability for various monomers, and MIPs are usually organic. However, they may shrink or swell when exposed to different mobile phases, so it may lead to the change of the morphology of the polymer network and the decrease of the adsorption performance (Yu & Mosbach 2000). Compared with the organic MIP, the inorganic MIP has ideal mechanical strength, large specific surface area and better stability (Shen et al. 2009), so this work aims at the preparation of an inorganic MIP. In inorganic molecular imprinting, silica-based MIP can offer excellent mechanical strength and good solvent resistance (Huang et al. 2009), and the silica gel prepared by the sol-gel method has advantages like high purity and uniformity, accurate chemical measurement and so forth (Sohrabi et al. in press). Therefore, this paper intends to develop an inorganic MIP based Fe/Si gel prepared by sol-gel method.

In this study, Acid Orange II (AO II), a common dye with the nature of Lewis base, is used as the target. Al$^{3+}$, as a Lewis acid site, can specifically recognize Lewis base (Shimada et al. 1993). For example, Bragazze et al. (2014) prepared a bi-functionalized molecularly imprinted silica in which aluminum ions were inserted in the silica matrix to form Lewis acid sites for the specific extraction of quercetin. So, aluminum ions were introduced to MIP to specifically identify the target (AO II). To summarize, this paper aims at the preparation of a novel inorganic molecularly imprinted material with Fe/Si gel as the base and AO II as the template molecules. BPA, which also has the benzene ring, is chosen as the interferent to verify the selective adsorption ability of MIP.

## MATERIALS AND METHODS

### Chemicals and materials

FeCl$_3$·6H$_2$O, AlCl$_3$·6H$_2$O, C$_2$H$_5$OH (ethyl alcohol) and BPA (Bisphenol A) were supplied by Guangzhou Chemical Reagent Company, China. NaOH, NO$_3$·H$_2$O and HCl were provided by Tianjin Chemical Reagent Co., Ltd. Tetrapropylammonium hydroxide (TPAOH) was supplied by Tianjin Guangfu Fine Chemical Research Institute, China. Tetraethoxysilane (TEOS) was supplied by Shanghai Chemical Reagent Company. All the chemicals were of analytical reagent grade and used as received without further purification. High-performance liquid chromatography (HPLC) grade methanol was obtained from Tedia. The 0.45 µm microfiltration membranes (nylon 66, diameter 90 mm) were purchased from Tianjin Jinteng Experiment Equipment Co., Ltd (China).

### Preparation of MIP

The MIP was prepared via a route given in Figure 1, in which the Lewis acid (Al$^{3+}$) acted as the functional group to combine with the target pollutant AO II.

#### Synthesis of Fe/SiO$_2$ particles

The Fe/SiO$_2$ particles were prepared via sol-gel method. 10.8 g FeCl$_3$·6H$_2$O was added to a mixture solution of ethanol (1 mol) and water (11 mol) at room temperature, stirring with a magnetic mixer (85-2A, Jintan Medical Instrument Factory) for about 10 min. After completely dissolved, TPAOH (0.06 mol) and TEOS (0.2 mol) were introduced and fiercely stirred by a magnetic mixer for 30 min. Then the solution pH was adjusted to 7 by adding NH$_3$·H$_2$O solution (in mass % of 1.25) quickly with stirring by hand and then the sol could be obtained. With about 20 min standing, it turned into the gel. The gel was washed with deionized water and vacuum dried at 70 ℃ for 24 h, and the Fe/SiO$_2$ particles were obtained.

#### Synthesis of Al$^{3+}$ loaded Fe/SiO$_2$ particles

20 g Fe/SiO$_2$ particles and 60 g AlCl$_3$·6H$_2$O were added to 200 mL deionized water, then the mixture was aged for 3 h with keeping the solution pH and temperature at 6.5 and 80 ℃, respectively. Next, the particles were washed with diluted hydrochloric acid (pH = 4) to remove the Al(OH)$_3$ on the surface. Finally, the Al$^{3+}$ loaded Fe/SiO$_2$ particles were obtained after being washed with deionized water and dried at room temperature in turn.

#### Synthesis of molecular imprinting particles

First, 10 g Al$^{3+}$ loaded Fe/SiO$_2$ particles were added to 100 mL deionized water, and 200 mL aqueous solution containing 40 g molecules (AO II) was poured simultaneously.
Then, the solution pH was adjusted to 4 and the mixed system was kept at 80°C for a week, in order to make the template molecules enter into the SiO₂ particles and form the footprints. After the solution was filtered, the obtained particles were washed with ethanol, diluted hydrochloric acid, and deionized water in order. Finally, the wet particles were dried under natural light for 5 days. The obtained particles were named as MIP. As a reference, the prepared adsorbent without adding the template molecules AO II in the process of synthesis were named as non-imprinted polymer (NIP).

Characterization of MIP

The profile was observed with a scanning electron microscope (SEM, model S-3400N, America). Fourier transform infrared (FT-IR) spectra were taken on a Nicolet iS50 FT-IR spectrometer. X-ray diffraction (XRD) spectra was measured on an XRD (D/MAX-2500V) operated under the condition of 40 kV and 40 mA with CuKα radiation (λ = 0.1541 nm). Specific BET (Brunauer–Emmett–Teller) surface area was determined with a Quantachrome NOVA4200e apparatus by nitrogen adsorption at 77 K.

Evaluation of the performances of MIP

Adsorption experiments were carried out in a 250 mL conical flask with cover. 100 mg adsorbent were added to 200 mL AO II or BPA solution with certain initial concentration and pH. The vessel was put in a constant temperature water bath oscillator (SHA-B, Jintan Medical Instrument Factory) at 30°C. At different time intervals, samples for analysis were taken and filtered through 0.45 μm microfiltration membrane to remove adsorbent particles. The measure of AO II concentration was performed by a UV-vis spectrophotometer (UV-3150, Shimadzu) with a maximum absorbance at 484 nm. The analysis of BPA was performed by HPLC (LC20AD, Shimadzu).

RESULTS AND DISCUSSION

Characteristics of MIP

The BET specific surface area of MIP was measured as 298 m²/g, and that of which increased by nearly 20% compared with that (250 m²/g) of NIP. It may be attributed to the effect of molecular imprinting and the removing of the template molecules.

The SEM examination in Figure 2 indicates the different morphology of NIP (a) and MIP (b). The NIP particles without imprinting showed a relatively smooth surface and layered structure, while the surface of MIP particle was rough and some hole shape structures were observed. This may be attributed to the fact that the imprinting template molecular AO II was driven into the Fe/SiO₂ particle first.
and then washed out, forming the imprinting cavities in accordance with a favorable imprinted shell with selectivity as reported by Tripta Kamra (Kamra et al. 2016).

Figure 3(a) compares the FT-IR spectrum of NIP and MIP, and they are almost the same. The peak at 3,418 and 1,034 cm\(^{-1}\) are assigned to the fundamental stretching vibration of O-H and the asymmetric stretching vibration of Si–O–Si (Teleki et al. 2008). The peak at 1,640 cm\(^{-1}\) correspond to the vibration of Al–O–Si due to the doping of Al\(^{3+}\) (Zhong et al. 2006), indicating the existence of Al ions combining with SiO\(_2\) through oxygen atoms.

No new peaks emerge in the XRD pattern of MIP (Figure 3(b)) compared with NIP, indicating that the phase composition does not significantly change after the imprinting. The peak at 2\(\theta\) angles of 26.2\(^\circ\), 35.9\(^\circ\), 49.4\(^\circ\), and 54.0\(^\circ\) were well matched with published JCPDS data (file no: 47-1144) for SiO\(_2\). The peaks at 2\(\theta\) values of 24.2\(^\circ\), 33.2\(^\circ\), 35.7\(^\circ\), and 40.9\(^\circ\) correspond to the \(\alpha\)-Fe\(_2\)O\(_3\) structure (file no: 33-0664). The diffraction peaks at 21.7\(^\circ\), 26.3\(^\circ\), and 33.7\(^\circ\) are assigned to Fe\(_2\)Al\(_4\)Si\(_5\)O\(_{18}\) (file no: 31-0615). All above indicate that the adsorbent prepared mainly contains SiO\(_2\), \(\alpha\)-Fe\(_2\)O\(_3\), and Fe\(_2\)Al\(_4\)Si\(_5\)O\(_{18}\).

The effect of pH on the adsorption performance of MIP

Figure 4 shows the effect of pH value on the adsorption of AO II over MIP. The isoelectric point of \(\alpha\)-Fe\(_2\)O\(_3\), which is contained in MIP, was reported at pH 6.8 in the aqueous solution (Kosmulski 2014), so the \(\alpha\)-Fe\(_2\)O\(_3\) and MIP are positively charged when pH is less than 6.8 and are negatively charge while pH is higher than 6.8. As a result, the adsorption quantity of AO II increased dramatically from pH 6.8 to pH 2 through an enhanced static interaction between positively charged \(\alpha\)-Fe\(_2\)O\(_3\) and negatively charged AO II. Once the solution pH was greater than isoelectric point 6.8, MIP would be negatively charged, which would have a great influence on the adsorption of AO II. Although the adsorption quantity is higher at lower pH, under a strong acidic condition is not conducive to the stability of MIP (Chen et al. 2010). For better studying the influence of
other factors, the pH was set to a value less than 6.8, so it was chosen at 4.

Enhanced adsorption activity and selectivity of MIP in single system

In order to verify the adsorptive selectivity, the sorption effect of MIP and NIP for AO II or BPA in single system was analyzed. The sorption kinetics of AO II (20 mg L\(^{-1}\)) on MIP and NIP are presented in Figure 5(a). It is easily seen that the time to achieve the adsorption/desorption equilibrium were both about 25 min, but the adsorption quantity of MIP were significantly higher than that of NIP at the same time due to the molecular imprinting process. Compared with NIP, the saturated adsorption amount (24.4 μmol g\(^{-1}\)) of MIP was about double of that (12.3 μmol g\(^{-1}\)) of NIP. This indicates that MIP has strong adsorption ability to the target molecule AO II.

To further examine the selective adsorption of MIP, the comparison of MIP and NIP on the adsorption effect for the interferent BPA (100 mg L\(^{-1}\)) are shown in Figure 5(b). The adsorption equilibrium were reached at 90 min, which was longer than AO II because of its high concentration. The adsorption capacity (212.4 μmol g\(^{-1}\)) of NIP was higher than that (176 μmol g\(^{-1}\)) of MIP. This is attributed to the special binding sites of MIP formed in the process of molecular imprinting, which make it easier to combine with target pollutants and other matters, so it results in a decrease accordingly for the BPA adsorption. This is in accord with literature reported by Wei et al. (2015).

Adsorptive selectivity of MIP in binary system

The adsorptive selectivity was also estimated in binary solutions containing AO II (20 mg L\(^{-1}\)) and the interferent BPA (100 mg L\(^{-1}\)). The experimental results are shown in Figure 6. The adsorption quantity for AO II of MIP was higher than that of NIP, while for BPA, adsorption amount of MIP was less than NIP. This was further evidence of the selectivity of MIP. The adsorptive selectivity of the adsorbent is focused on in Table 1. The rate constant of AO II adsorbed over MIP is 0.03722 g μmol\(^{-1}\) min\(^{-1}\), being 2.4 times that of the non-target BPA (0.01553 g μmol\(^{-1}\) min\(^{-1}\)). When the adsorption is carried out over NIP, the \(k\) value of AO II is decreased to 0.00251 g μmol\(^{-1}\) min\(^{-1}\), being only 73% of that of BPA (0.00341 g μmol\(^{-1}\) min\(^{-1}\)). The selectivity of MIP for AO II is 3.29. These results further indicate that MIP still has a high selectivity with the interferent at high levels.
Adsorption isotherm and dynamics research for template molecule AO II

The adsorption mechanism can be ascertained through the study of the adsorption isotherm. The adsorption for AO II under different initial concentrations and the fitting data are shown in Figure 7. The fitting of the data suggested that the adsorption of AO II on MIP and NIP obeyed the Langmuir isotherm (1) (Wimalasiri et al. 2015)

$$Q_e = \frac{Q_m b C_e}{1 + b C_e}$$  \hspace{1cm} (1)

where $Q_e$ is the amount of AO II adsorbed per unit mass of the adsorbent ($\mu$mol g$^{-1}$), $C_e$ is the concentration of AO II in solution ($\mu$mol L$^{-1}$), $Q_m$ is an index of the adsorption capacity of the adsorbent ($\mu$mol g$^{-1}$), and $b$ is Langmuir adsorption constant.

In addition, Dubinin-Radushkevich isothermal model (2–4) can distinguish that the adsorption process is mainly physical ($E < 8$ KJ mol$^{-1}$) or chemical ($8$ KJ mol$^{-1} < E < 16$ KJ mol$^{-1}$) (Dang et al. 2009). According to calculations and Figure 8(a), the average free energies were 10.64 and 11.18 KJ mol$^{-1}$ for MIP and NIP, respectively, indicating that the adsorption process of AO II over MIP and NIP

### Table 1

<table>
<thead>
<tr>
<th></th>
<th>Over MIP</th>
<th>Over NIP</th>
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<tbody>
<tr>
<td>$k_{\text{target}}$ ($10^{-3}$ g mol$^{-1}$ min$^{-1}$)</td>
<td>37.22</td>
<td>2.51</td>
</tr>
<tr>
<td>$k_{\text{non-target}}$ ($10^{-3}$ g mol$^{-1}$ min$^{-1}$)</td>
<td>15.53</td>
<td>3.41</td>
</tr>
<tr>
<td>$R$</td>
<td>2.40</td>
<td>0.73</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>3.29</td>
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$R$ is the ratio of $k_{\text{target}}/k_{\text{non-target}}$ and $\alpha$ is the ratio of the $R$ value over MIP to that over NIP.
are both given priority to chemical adsorption, which may be on account of the interaction between Lewis acid $\text{Al}^{3+}$ and Lewis base AO II.

\[
\ln Q_e = \ln Q_m - K_D \varepsilon^2
\]  

(2)

\[
\varepsilon = RT \ln \left(1 + \frac{1}{C_0} \right)
\]  

(3)

\[
E = \frac{1}{\sqrt{2K_D}} \times 10^{-3}
\]  

(4)

where $Q'_e$ and $Q'_m$ are the quantity (mol g$^{-1}$) in equilibrium adsorption and D-R model adsorption, respectively; $K_D$ is adsorption constant (mol$^2$ J$^{-1}$); $\varepsilon$ is the Polanyi potential energy; $R$ is the molar gas constant and with a value of 8.314 J mol$^{-1}$ K$^{-1}$; $C_e$ is the solute concentration when equilibrium adsorption; $E$ is the average free energy (kJ mol$^{-1}$).

The data in Figure 8(b) suggests that the adsorption of AO II over MIP and NIP obeyed pseudo-second-order reaction kinetics after fitted by pseudo-first-order kinetics Equation (5) and pseudo-second-order kinetics Equation (6),

\[
\log (Q_e - Q_t) = \log Q_e - \frac{k_1 t}{2.303}
\]  

(5)

\[
t = \frac{1}{(k_2 Q_e^2)} + t \frac{1}{Q_e}
\]  

(6)

where $Q_t$ (μmol g$^{-1}$) is the sorption amount of AO II at time $t$, $k_1$ (min$^{-1}$) and $k_2$ (g min$^{-1}$ μmol$^{-1}$) are the rate constants. B, $k_2$ (0.346 g min$^{-1}$ μmol$^{-1}$) for MIP is about 13.4 times of that (0.0259 g min$^{-1}$ μmol$^{-1}$) of NIP.

**Stability of MIP**

Furthermore, to ensure a high selectivity of MIP, this experiment also aims at MIP with excellent stability. To evaluate the lifetime of MIP, it was put into the AO II solution with a concentration of 20 mg/L for 3 h. Then it was taken out of the solution, washed with distilled water and the above experiment was repeated five times. The results are shown in Figure 9; the adsorption capacity for the first six cycles of adsorption were measured in turn as 175, 172, 168, 166, 165 and 167 μmol g$^{-1}$. This indicates that MIP can be recovered and reused in the adsorption of organic pollutants.

**Confirming the role of molecular imprinting**

To further demonstrate the role of molecular imprinting, the target pollutant AO II and the interferent BPA were
exchanged. The imprinted polymer with BPA as template molecular was prepared, and the sorption kinetics of AO II (20 mg L\(^{-1}\)) and BPA (100 mg L\(^{-1}\)) are presented in Figure 10. The adsorption amount of imprinted adsorbent (290 \(\mu\)mol g\(^{-1}\)) for BPA was significantly higher than that (207 \(\mu\)mol g\(^{-1}\)) of the non-imprinted. For the interferent AO II, the adsorption capacity of the adsorbent imprinted with BPA (7.2 \(\mu\)mol g\(^{-1}\)) decreased significantly compared with the non-imprinted adsorbent (12.4 \(\mu\)mol g\(^{-1}\)), let alone the adsorption capacity of MIP (24.2 \(\mu\)mol g\(^{-1}\)) imprinted with AO II. The above results further confirmed that the molecular imprinted adsorbent owns specific recognition of the template molecules and the exclusion of non-template molecules.

CONCLUSIONS

By loading Al\(^{3+}\) on Fe/SiO\(_2\) gel prepared with sol-gel method, we prepared a novel MIP with high selectivity for the target AO II and characterized it with SEM, FT-IR, XRD and BET surface area. MIP could specifically recognize template molecules for the imprinting process, so MIP has strong selective adsorption ability to AO II in single and binary systems. Moreover, MIP has high stability.

ACKNOWLEDGEMENTS

This research was supported by Nature Science Foundations of China (21267002, 21367003, 41473118, and 41273139), the National Key Basic Research Program of China (No. 2013CB956102), Nature Foundations of Guangxi Province (2015GXNSFBB139009, 2014GXNSFAA118296, 2014GXNSFBA118217, 2015 GXNSFEA053001) and the BaGui Scholars Program Foundation (2014).

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First received 15 December 2015; accepted in revised form 9 May 2016. Available online 22 June 2016.