M-PGMA as a new water treatment agent to remove oxytetracycline from water
Cheng Liu, Bin Wang, Yang Deng, Jie Wang, Wei Chen and Yu Liu

ABSTRACT
Magnetic ion exchange resin is a strong base anion exchange resin with magnetic properties that can be used to remove negatively charged materials from water. Magnetic poly glycidyl methacrylate resin (m-PGMA), a new type of resin, has shown better removal performance for humics than MIEX®. Removal of oxytetracycline (OTC) in water by m-PGMA, and factors influencing the removal, were examined, and in addition, the removal of OTC by MIEX and powdered activated carbon (PAC) were used as a comparison. Results showed that m-PGMA could remove more OTC than MIEX and PAC. The removal performance was greatly affected by dosage of m-PGMA, inorganic anions, organics and pH value. At a contact time of 30 min, the removal rates of OTC were 45%, 52% and 63% when the dosage was 5 ml/L, 10 ml/L and 20 ml/L, respectively. In comparison the removal rate of OTC by MIEX was 45% with a dosage of 10 ml/L and a contact time of 30 min. The removal of OTC was significantly increased when the pH value was above 7.3, as the OTC molecule exists as an anion in alkaline medium. In conclusion, m-PGMA is more effective than MIEX and PAC in the removal of OTC in water, and can be one of the choices to remove trace organics like OTC.

Key words | anion, drinking water, magnetic ion exchange resin (m-PGMA), MIEX®, oxytetracycline (OTC)

INTRODUCTION
Oxytetracycline (OTC) has been widely applied in animal feeding as a growth promoter for livestock and in drug therapy (Heberer 2002; Sarmah et al. 2006; Madden et al. 2009). The OTC discharged from animals and human beings, in addition to the OTC remaining in the effluent of pharmaceutical wastewater treatment plants, can enter into natural water bodies, as well as soil and sediments (Hirsch et al. 1999; Kolpin et al. 2002; Calamari et al. 2003; Choi et al. 2007). Among the most common antibiotics, OTC can increase the resistance of bacteria against drugs, spread the antibiotic resistance genes among bacterial populations, and subsequently threaten public health (Costanzo et al. 2005; Pei et al. 2007). Unfortunately, conventional drinking water and wastewater treatment plants are not specifically designed for such emerging contaminants, and the reported OTC removal efficiencies are quite poor (Ternes et al. 2002; Watkinson et al. 2007).

Ion exchange is a common treatment method to remove charged pollutants (e.g., certain anions or cations) from water. The treatment capability of ion exchange relies heavily upon resin materials. Recently, two resin types in water treatment, magnetic ion exchange resin (MIEX®) and magnetic polyglycidyl methacrylate resin (m-PGMA), have received much attention (Chen et al. 2013; Comstock & Boyer 2014). MIEX, developed jointly by Orica Watercare, Commonwealth Scientific Industrial Research Organization, and South Australian Water Corporation, is a strong base anion exchange resin with certain magnetic properties. It can be employed to remove negatively charged water pollutants (Mergen et al. 2008; Bond et al. 2009).
MIEX, as a pre-treatment, can improve the reduction of dissolved organic carbon (DOC) and disinfection by-product (DBP) precursors (Boyer et al. 2008), and mitigate membrane fouling (Kim & Dempsey 2010; Gan et al. 2013). Similar to MIEX, m-PGMA is another new magnetic anion exchange resin developed in our earlier work (Liu et al. 2015). Three unique features differentiate m-PGMA from other resins. First, the m-PGMA beads (100–200 μm) are of much smaller size than conventional anion exchange resins (AERs), thereby providing much greater specific surface areas. Second, m-PGMA backbones containing a high fraction of magnetic iron oxides allow the fine resin beads to settle down rapidly. Last, compared with MIEX, m-PGMA has a bigger specific surface area and pore volume, resulting in greater adsorption efficiency (Chen et al. 2013). Both MIEX and m-PGMA can remove humic acids (HA) from water, and the latter appeared to exhibit a better removal performance (Chen et al. 2013). However, MIEX and m-PGMA removal of synthetic organic compounds such as OTC have not been reported.

In this paper, the factors controlling OTC removal by m-PGMA were evaluated. In particular the OTC removal efficiencies of m-PGMA were compared with those of MIEX. In addition, powdered activated carbon (PAC), a commonly used organic removal material, was used for comparison.

**MATERIALS AND METHODS**

**Materials and chemicals**

All the chemicals used were of analytical grade, except as noted. MIEX resins were provided from Orica Water Care of Australia. PAC was provided by Xin-hua Chemical Co., Ltd. m-PGMA was prepared in the environmental engineering laboratory at Hohai University, China, using the method which was reported in our previous research paper (Chen et al. 2013). OTC was purchased from the National Institute for the Control of Pharmaceutical and Biological Products of China, and was used without any further purification. Methanol (HPLC) was obtained from Fluka Co. Ltd. Other reagents, including azobisisobutyronitrile (AIBN), sodium chloride, methylcellulose (MC), polyethylene glycol 6000 (PEG), glycidyl methacrylate (GMA), divinylbenzene (DVB), methylbenzene, cyclohexanone, atoleine, HA, phosphoric acid, sodium hydroxide, hydrochloric acid, sodium chloride, iron trichloride hexahydrate pure, ferrous sulfate heptahydrate, sodium hydroxide, oleic acid, ethanol, trimethylammonium chloride and sodium sulfate were purchased from CANSPEC, Shanghai, China. High purity deionized water was produced from a Merck Millipore pure water system (Elix 20).

**Preparation of m-PGMA**

m-PGMA was synthesized using the method previously described (Chen et al. 2013) with minor modifications. The first step was to prepare Fe3O4 nanoparticles. A mixture of FeCl3·6H2O (0.046 mol), FeSO4·7H2O (0.023 mol) and 2 g NaCl was dissolved in 100 mL distilled water and extracted using a Soxhlet extractor with methyl alcohol for 12 h to remove remaining porogens and nonencapsulated magnetite. The product was washed with excess tepid distilled water and ethanol three times before being stored in ethyl alcohol.

To prepare m-PGMA, 50 mL Fe3O4 nano-particles, 3 g AIBN, distilled water (30 mL), and absolute ethyl alcohol (20 mL) were added and mixed in a 500 mL four-necked flask equipped with a stirrer, a Graham condenser and a nitrogen gas pipe. The solution was rapidly stirred at 65 °C for 10 min before the addition of GMA (25 mL), DVB (12.7 g), 5% NaCl solution (12.5 mL), 0.01% methylcellulose (MC) solution (12.5 mL), 8% PEG solution 100 mL, methylbenzene (13.7 g), cyclohexanone (2.4 g), and atoleine (4.1 g). To obtain magnetic polymer microspheres, suspension polymerization proceeded at 75 °C for 1.5 h and then at 80 °C for 0.5 h. After the suspension polymerization was complete, the product was washed with excess tepid distilled water and extracted using a Soxhlet extractor with methyl alcohol for 12 h to remove remaining porogens and nonecapsulated magnetite. The product was dried at 40 °C, and the final product was sieved successively through...
200 μm and 100 μm strainers. Dried magnetic polymer microspheres mixed with 50% trimethylammonium chloride solution (magnetic polymer microspheres:trimethylammonium chloride = 1:2.5) were decanted into a three-necked flask. The solution was stirred at 80 °C for 10 h. The final product was rinsed with excess 1 M HCl solution and then with excess distilled water until the supernatant reached pH 7.

**Experimental methods**

A desired concentration of 5 μg/L OTC was freshly prepared using pure water without adjusting the pH value in all experiments, except to investigate the effect of pH value. The solution pH was adjusted by adding either 0.1 M HCl or NaOH solutions. Adsorption tests were conducted in a batch mode using jar test apparatus (ZhongRun Water Co. Ltd, ShenZhen, China), in which 1,000 mL 5 μg/L OTC solution were added to 1-L circular jars. To ensure a completely mixed state during the treatment tests, vigorous stirring at 200 rpm was used. Initial pH was adjusted with 0.1 M HCl and NaOH solutions in the tests to study the effect of pH. For all the other tests, the solution pH was not controlled. Once appropriate amounts of the resin or PAC were added, the adsorption was initiated. At a designated sampling time, 50 mL were collected and then filtered through pre-rinsed 0.45 μm filters (XinYa Purification Parts Plant, Shanghai, China) prior to analysis. The pH of the solution used in the experiment was about 6.5, which is mainly due to the pure water.

According to previous studies (Drikas et al. 2011), regeneration of OTC saturated m-PGMA was achieved using sodium chloride solution. Due to the similar characteristics of m-PGMA, the optimized conditions for the regeneration of saturated MIEX can be used. The removal performance of the regenerated m-PGMA was evaluated with the removal efficiency for the initial concentration of 5 μg/L OTC solutions and resin dose of 10 mL/L at pH 7.0 ± 0.2 for 0.5 h.

Coagulation of raw water (taken from Taihu Lake; the main water parameters are shown in Table 1) using polyaluminium chloride (PACl) in the presence of OTC (coagulation test) was performed in order to investigate the contribution of m-PGMA pretreatment to the enhancement of coagulation efficiency. The main steps are as follows: 1,000 mL of each sample were put into a circular jar and agitated with a shaking apparatus at 150 rpm for 50 min to complete the m-PGMA pretreatment. Then, PAC was added to each sample at certain concentrations, and the samples were mixed at 100 rpm for 20 min and at 60 rpm for 15 min. Samples were left for 20 min, and then each sample’s supernatant (100 mL) was collected using a U-shaped pipette in order to avoid the suction of precipitated solids. The samples were used to determine the turbidity, etc.

All the treatment tests were conducted in duplicate and the results are reported as the average values.

**Analytical methods**

Before the OTC measurement, OTC in samples was extracted and concentrated using a solid-phase extraction method developed by Flores et al. (2011). OTC was quantified using high performance liquid chromatography (Agilent 1100) coupled with a XDB-C18 reversed phase column (250 mm × 4.6 mm, 5 μm, Agilent, USA) at 35 °C. The mobile phase was 0.01 M methanol-phosphoric acid (70/30, v/v) at a flow rate of 0.8 mL/min. A UV detector was used at a wavelength of 277 nm.

Inorganic anions (i.e., Cl− and SO4²−) were measured using a Dionex ion chromatograph with an IonPac AG11-HC guard column and an AS11-HC analytical column. The 30 mM KOH effluent was automatically generated by eluent delivery at an eluent flow rate of 1.0 mL/min. Solution pH was measured with a Sartorius standard pH meter PB-10. Nitrogen adsorption analysis was carried out using a Belsorp-mini apparatus at −196 °C. Samples were degassed at 200 °C with an overnight nitrogen flow prior to the analyses. Specific surface areas (SA) were determined

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**Table 1** | The main parameters of Taihu Lake

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC (mg L⁻¹)</td>
<td>4.1–5.2</td>
</tr>
<tr>
<td>UV₂⁵⁴ (cm⁻¹)</td>
<td>0.075–0.106</td>
</tr>
<tr>
<td>pH</td>
<td>7.78–8.15</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>14.6–326.7</td>
</tr>
<tr>
<td>Alkalinity (mgL⁻¹as CaCO₃)</td>
<td>56–89</td>
</tr>
<tr>
<td>Algae cell count (×10⁴ cell L⁻¹)</td>
<td>10–5,986</td>
</tr>
</tbody>
</table>
with the Brunauer–Emmett–Teller (BET) method, and using a P/P₀ range between 0.0 and 0.5. Pore volumes (PV) were calculated from adsorption isotherms at a relative pressure of 0.99 atm. Average pore diameters (MPD) were determined by the Barrett–Joyner–Halenda (BJH) method using either the adsorption branch or desorption branch, depending on their isotherm hysteresis types.

RESULTS AND DISCUSSION

Characterization of m-PGMA, MIEX and PAC

According to a former study (Liu et al. 2015), although derived from MIEX, m-PGMA has some special features different from MIEX. Therefore, the pore size distributions of m-PGMA and MIEX have been determined and are shown in Figure 1.

As seen in Figure 1, the pore sizes of m-PGMA are mostly concentrated in a narrow range between 4–20 nm, indicating that m-PGMA is a meso-porous sorbent. In contrast, MIEX has pores varying from a few nm to 50 nm, representing a much broader pore diameter distribution.

Basic physicochemical parameters of m-PGMA, MIEX and PAC are shown in Table 2. The difference in the exchangeable group, particle size and exchange capacity was not significant between the two resins. Higher specific surface area, greater total pore volume and larger average pore diameter were observed in m-PGMA than MIEX. According to the removal mechanism of the two resins, these parameters may be the crucial ones in accounting for the adsorption difference between m-PGMA and MIEX.

The PAC used in the study is a kind popularly used in water treatment plants in China, which has about 1,000 m²/g of specific surface area and 0.56 cm³/g of pore volume. In addition, the zero charge point of the PAC is about 6.5.

Removal efficiency of OTC by m-PGMA, MIEX and PAC

Removal kinetics of OTC

Kinetics data of OTC adsorption to m-PGMA, MIEX and PAC are shown in Figure 2.

At their normally used dosage (10 mL/L for m-PGMA and MIEX, 20 mg/L for PAC), the removal of OTC increased over time. However, all the adsorption curves almost reached chemical equilibrium after about 50 min. At any specific time, m-PGMA could achieve higher removal efficiency than MIEX due to higher specific surface areas and larger pore volumes, and both m-PGMA and MIEX removed more OTC than PAC as the OTC molecule has negative charge at neutral pH. At 30 min, nearly 52% and 47% OTC were removed by m-PGMA and MIEX; the removal results are better than those of many other trace organic pollutants such as geosmin and 2-MIB, of which less than 10% is removed by MIEX (Liu et al. 2011). This finding is probably due to the fact that a fraction of OTC dissolved in pure water is negatively charged. Previous studies (Liu et al. 2015) showed that OTC exists predominantly as a zwitterion, resulting from the dimethylammonium group being protonated and

Figure 1 | Pore size distribution of (a) m-PGMA and (b) MIEX.
the loss of proton from the phenolic diketone moiety between pH 3.3 and 7.3. At this pH range, although OTC molecules are neutral, the dimethylammonium groups are positively charged, while the other part of the group is negatively charged.

Table 2 shows the key physicochemical parameters of m-PGMA and MIEX.

Table 2 | Key physicochemical parameters of m-PGMA and MIEX

<table>
<thead>
<tr>
<th>Parameter</th>
<th>m-PGMA</th>
<th>MIEX</th>
<th>PAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable group</td>
<td>-Cl</td>
<td>-Cl</td>
<td>–</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>52.16</td>
<td>65.82</td>
<td>–</td>
</tr>
<tr>
<td>Bulk density (g/mL)</td>
<td>1.15</td>
<td>1.20</td>
<td>1.05</td>
</tr>
<tr>
<td>Particle size (μm)</td>
<td>100–200</td>
<td>150–180</td>
<td>75 (90%)</td>
</tr>
<tr>
<td>Alkali base exchange capacity (mmol/g)</td>
<td>2.36</td>
<td>2.23</td>
<td>–</td>
</tr>
<tr>
<td>Magnetic material content (%)</td>
<td>6.08</td>
<td>8.52</td>
<td>–</td>
</tr>
<tr>
<td>Specific saturation magnetization (emu/g)</td>
<td>10.79</td>
<td>4.42</td>
<td>–</td>
</tr>
<tr>
<td>Specific surface area (m²/g)</td>
<td>40.026</td>
<td>4.341</td>
<td>1,065</td>
</tr>
<tr>
<td>Coercive field strength (G)</td>
<td>0.17</td>
<td>2.1</td>
<td>–</td>
</tr>
<tr>
<td>Zero charge point</td>
<td>6.2</td>
<td>6.4</td>
<td>6.5</td>
</tr>
<tr>
<td>Total pore volume (cm³/g)</td>
<td>0.1852</td>
<td>0.018</td>
<td>0.56</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>18.509</td>
<td>16.962</td>
<td>–</td>
</tr>
<tr>
<td>Element analysis</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C%</td>
<td>69.88</td>
<td>39.02</td>
<td>–</td>
</tr>
<tr>
<td>H%</td>
<td>7.14</td>
<td>5.27</td>
<td>–</td>
</tr>
<tr>
<td>O%</td>
<td>2.27</td>
<td>34.43</td>
<td>–</td>
</tr>
<tr>
<td>Distribution of pore diameter (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;2 nm</td>
<td>0</td>
<td>3.37</td>
<td>25.6</td>
</tr>
<tr>
<td>2 nm–100 nm</td>
<td>99.98</td>
<td>96.63</td>
<td>30.3</td>
</tr>
<tr>
<td>&gt;100 nm</td>
<td>0.02</td>
<td>0</td>
<td>44.1</td>
</tr>
</tbody>
</table>

Figure 2 | Removal kinetics of OTC by m-PGMA, MIEX and PAC.

Table 3 shows the results fitted to two kinetic models. It was suggested from the values of $R^2$ that the adsorption of OTC on m-PGMA and MIEX followed the pseudo-first-order model better than the pseudo-second-order model. According to the typical characteristics of m-PGMA and MIEX particles, the adsorption of OTC onto m-PGMA and MIEX may be considered to consist of two processes: (1) the

Table 3 | Kinetics parameters for OTC removal by m-PGMA, MIEX and PAC

<table>
<thead>
<tr>
<th>Initial concentration (μg/L)</th>
<th>Resin category</th>
<th>First-order kinetics</th>
<th>Second-order kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$K_1$ (L/min)</td>
<td>$q_e$</td>
</tr>
<tr>
<td>5</td>
<td>m-PGMA</td>
<td>0.44647</td>
<td>47.0077</td>
</tr>
<tr>
<td></td>
<td>MIEX</td>
<td>0.40888</td>
<td>42.0101</td>
</tr>
<tr>
<td></td>
<td>PAC</td>
<td>0.2783</td>
<td>34.3832</td>
</tr>
</tbody>
</table>
transport of OTC from bulk solution to the surface of the resins and (2) the attachment of OTC to resins. Due to a greater surface area and shorter transport distance, the effects of mass transport were decreased significantly and the attachment of OTC onto the two resins became the main limiting step. However, according to former studies, the attachment phase was almost instantaneous. Therefore, the removal process was found to follow the pseudo-first-order kinetic model.

It can also be seen from Figure 2 that the adsorption of OTC by PAC can not provide better removal results than other trace organics, as it only removes 33% of OTC with a dosage of 20 mg/L and contact time of 30 min. The reason lies in the fact that the OTC molecule is usually negatively charged at neutral pH due to the quantity of hydroxyls and amino groups on the molecule. According to the dosage usually used in water treatment plants, PAC is not a better choice for the removal of OTC.

Removal capacities of OTC

The Langmuir and Freundlich isotherm models were used to describe the equilibrium adsorption isotherms of m-PGMA and MIEX to remove OTC from water. The isotherm points at different equilibrium concentrations and the results of fitting the data to the models are shown in Figure 3 and Table 4.

The results show that the Freundlich isotherm model fitted the removal data relatively well, while the Langmuir isotherm model could not fit the data well. As the Freundlich isotherm model is an empirical equation applicable to adsorption on heterogeneous surfaces as well as multilayer adsorption (Morales et al. 2013), the parameters gained from the fitting equation did not have real meaning for the adsorption. However, as seen from the removal curve, the adsorption performance of m-PGMA was better than that of MIEX.

Effects of influencing factors

According to the results of OTC removal performance, m-PGMA showed significant advantages in OTC removal compared to MIEX and PAC. Therefore, to better understand its removal characteristics, the factors influencing the removal of OTC by m-PGMA were investigated.

Effect of chemical dose

Kinetics data on m-PGMA adsorption of OTC at different doses are shown in Figure 4.

At any specific time, the OTC removal rate increased with the increasing m-PGMA dose. At 30 min, OTC was removed by 40%, 47% and 58% with 5 mL/L, 10 mL/L and 20 mL/L m-PGMA, respectively. This finding is due to

| Table 4 | Comparison of removal capacity with m-PGMA and MIEX |
|----------------|----------------|----------------|
| Resin category | $C_{\text{initial}}$ (ng/L) | pH | Fitting equation | $R^2$ |
| m-PGMA     | 5,000           | 7.05 | $q_e = 0.0471 C_e^{0.9146}$ | 0.9681 |
| MIEX       | 5,000           | 7.05 | $q_e = 0.0296 C_e^{0.8978}$ | 0.9586 |

Figure 3 | Adsorption isotherms of OTC by m-PGMA at pH 6.8 ± 0.2 and room temperature.

Figure 4 | Influence of resin doses on OTC removal.
the fact that more m-PGMA provides more exchange sites. Of note, the removal rate dramatically increased within the first 5 min, but the increase in OTC removal became slow after that. This phenomenon probably occurred because there was a relatively higher concentration of OTC in the water in the initial stage of reaction, which results in a greater OTC concentration difference between the solution and the resin. Driven by the concentration difference, the ion exchange reaction is rapidly carried out. The reaction rate fell when the OTC concentration difference decreased as the trend of the curve shows in Figure 4.

Effects of inorganic anions

Effects of sulfate (SO₄²⁻) and chloride (Cl⁻) on m-PGMA removal of OTC are shown in Figures 5 and 6, respectively.

As can be seen from Figure 5, the removal rates of OTC by m-PGMA resin significantly decrease with increasing sulfate concentration. At the contact time of 10 min, the removal rates of OTC were 43%, 29%, 27% and 23% at concentrations of 0 mg/L, 50 mg/L, 100 mg/L and 200 mg/L sulfate, respectively. It should be noted that the removal rates of OTC were almost the same at 1 and 5 min, but the difference between the OTC removal rates in the presence of different sulfate concentrations at 10 min was not obvious. This observation is because sulfate has a stronger selectivity for m-PGMA than OTC, allowing sulfate to be preferentially removed. When the removal reached equilibrium, the difference in OTC removal at different concentrations of sulfate was not significant, as shown in Table 5.

The inhibiting effect of sulfate was because sulfate could compete with OTC for the exchange sites of m-PGMA. Furthermore, the sulfate molecule was smaller than OTC, and diffused more rapidly from the water to the attachment sites of the resin. Chloride could also inhibit the OTC removal by m-PGMA (as shown in Figure 6). Within 10 min, the OTC removal rates were 43%, 32%, 29% and 28% in the presence of chloride at concentrations of 0 mg/L, 50 mg/L, 100 mg/L and 200 mg/L, respectively. The role of chloride in OTC adsorption was mainly due to the presence of the exchange process. As a type of exchangeable ion on m-PGMA, the existence of chloride could influence the equilibrium point of the exchange reactions, thereby reducing the removal efficiency of m-PGMA for OTC.

Effect of solution pH

The effect of solution pH is shown in Figure 7.

Generally speaking, high pH favoured OTC removal. The removal efficiencies went up from 6 to 85% with increasing pH from 3.01 to 10.30. OTC dissociation is
strongly governed by pH (Pankaj et al. 2004). It exists predominantly as a cation, +00, at pH < 3.3 under which its dimethylammonium group is protonated; as a zwitterion, + 00, at pH 3.3–7.3 as a result of the loss of protons from the phenolic diketone moiety; and as an anion, + 00, at pH > 7.3 due to the loss of protons from the tricarbonyl system and phenolic diketone moiety. Owing to the strong base anion exchange characteristics of m-PGMA, OTC removal is better in alkaline conditions. While at pH 7.21 or 7.3, the OTC removal may be finished by the exchange between the chloride of m-PGMA and the negatively charged parts of OTC. In addition, this finding also validates the fact that OTC removal by m-PGMA is primarily due to ion exchange rather than adsorption.

Effect of organics

The effect of organics in the water is shown in Figure 8.

As can be seen from Figure 8, humic acid can interfere with the removal effects of OTC significantly; the removal rate decreased from 52 to 35% when the HA concentration was 1 mg/L. In addition, higher HA concentrations decreased the removal rate significantly. The reason lies in the competitive effect of HA and the OTC molecule.

Regeneration of saturated m-PGMA

It is desirable that a resin can be regenerated and reused so as to be put into another cycle of use and thus decrease the cost of application. Some studies on the regeneration of MIEX have been done to optimize the regeneration, during which certain concentrations of sodium chloride solutions were usually used (Liu et al. 2011). Owing to the special characteristics of m-PGMA and the OTC molecule, it was necessary to optimize the regeneration condition of saturated m-PGMA. Figure 9 shows the adsorption efficiency of the regenerated m-PGMA for OTC with 10 regeneration cycles.

In the first recycle study, the m-PGMA maintained a removal rate of more than 50% for OTC after one regeneration cycle. After 10 cycles of reuse, the regenerated m-PGMA still retained a removal rate of about 45% for OTC.

![Figure 7](image_url) | Influence of pH value on OTC removal.

![Figure 8](image_url) | Influence of humic acid on OTC removal.

![Figure 9](image_url) | Removal efficiency of the regenerated m-PGMA for OTC with initial concentration of 5 μg/L and resin dose of 10 mL/L at pH 7.0 ± 0.2 for 10 regeneration cycles.
and this changed little in the last several regeneration cycles. This indicated the m-PGMA could be readily regenerated by the sodium chloride solution and it was seldom that capacity decreased during the regeneration. Similar results were gained for the regeneration of magnetic ion exchange resins (MIEX) (Drikas et al. 2011). In all, m-PGMA showed better reusability for OTC removal.

Removal efficiency of OTC in raw water by m-PGMA

Considering the complexity of water sources, the presence of other ions and organics might compete with OTC for exchange sites and greatly degrade the removal performance by m-PGMA. To examine the ability of m-PGMA to remove OTC in the natural water environment, OTC removal studies were conducted using the natural water samples from Taihu Lake in Jiangsu province, China. Figures 10 and 11 show the kinetic study of OTC removal by m-PGMA in a natural water sample.

As can be seen from Figure 10, the coagulation process with poly aluminium chloride (PACl) could not remove OTC effectively, while the combined process with m-PGMA could enhance the removal effects significantly. In addition, m-PGMA pretreatment could enhance the coagulation as the MIEX pretreatment did, and the enhancing mechanism of m-PGMA was the same as that of MIEX.

CONCLUSIONS

Our experiments demonstrate that a new type of resin, m-PGMA, has a better performance than MIEX and PAC in terms of OTC removal. The better removal is due to the higher pore volume, larger specific surface area and unique molecular characteristics of m-PGMA. The removal of OTC by m-PGMA was significantly influenced by chemical dosage, the presence of inorganic anions, organics and solution pH. m-PGMA pretreatment could enhance the coagulation process during the treatment of natural water. Overall, m-PGMA is a promising water agent for the use of controlling antibiotic (e.g., OTC) induced water pollution.

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REFERENCES


Calamari, D., Zuccato, E., Castiglioni, S., Bagnati, R. & Fanelli, R.
2003 Strategic survey of therapeutic drugs in the rivers Po and Lambro in Northern Italy. Environ. Sci. Technol. 37 (7),
1241–1248.

Chen, W., Liu, Y. & Liu, C. 2013 Preparation and use of magnetic
poly (glycidyl methacrylate) resin in drinking water

Choi, K. J., Kim, S. G., Kim, C. W. & Kim, S. H. 2007
Determination of antibiotic compounds in water by on-line
SPE-LC/MSD. Chemosphere 66 (6), 977–984.

Comstock, S. E. H. & Boyer, T. H. 2014 Combined magnetic ion
exchange and cation exchange for removal of DOC and

Costanzo, S. D., Murby, J. & Bates, J. 2005 Ecosystem response to
antibiotics entering the aquatic environment. Marine Pollut.
Bull. 51 (1–4), 218–223.

Drikas, M., Dixon, M. & Morran, J. 2011 Long term case study of
MIEX pre-treatment in drinking water; understanding NOM

HPLC method for monitoring relevant residues of
pharmaceuticals products in environmental samples.

Gan, X., Karanfil, T., Kaplan Bekaroglu, S. S. & Shan, J. 2013 The
control of N-DBP and C-DBP precursors with MIEX®. Water

Heberer, T. 2002 Occurrence, fate, and removal of pharmaceutical
residues in the aquatic environment: a review of recent

of antibiotics in the aquatic environment. Sci. Total Environ.
225, 109–118.

Kim, H. & Dempsey, B. A. 2010 Removal of organic acids from
EfOM using anion exchange resins and consequent
reduction of fouling in UF and MF. J. Membrane Sci. 364
(1–2), 325–330.

Kolpin, D. W., Furlong, E. T., Meyer, M. T., Thurman, E. M.,
Zaugg, S. D. & Barber, L. B. 2002 Pharmaceuticals,
hormones, and other organic wastewater contaminants in US
Technol. 36 (6), 1202–1211.

Liu, C., Chen, W. & Cao, Z. 2010 Removal of algogenic organic
matter by MIEX® pre-treatment and its effect on fouling in

Liu, C., Chen, W., Hou, W. N., Cao, Z. & Robot, V. M. 2011
Performance of MIEX pre-treatment to treat AOM and
20 (4a), 1057–1062.

Liu, Y., Chen, W., Dong, C., Liu, C. & Liu, H. C. 2015 Mechanism
of pretreatment using magnetic poly(glycidyl methacrylate)
resin in an ultrafiltration membrane system used in algae-rich

Pharmaceuticals in the environment: good practice in predicting

Matilainen, A., Vepsäläinen, M. & Sillanpää, M. 2010 Natural
organic matter removal by coagulation during drinking water

Magnetic ion-exchange resin treatment: impact of water type

M. 2015 Size selected synthesis of magnetite nanoparticles in

Pankaj, K., Rossman, F. G. & Diana, S. A. 2004 Investigating the
molecular interactions of oxytetracycline in clay and organic
matter: insights on factors affecting its mobility in soil.

Pei, R., Cha, J., Carlson, K. H. & Amy, P. 2007 Response of antibiotic
resistance genes (ARG) to biological treatment in dairy lagoon

perspective on the use, sales, exposure pathways, occurrence,
fate and effects of veterinary antibiotics (VAs) in the

Ternes, T. A., Meisenheimer, M., McDowell, D. & Frank, S. 2002
Removal of pharmaceuticals during drinking water

antibiotics in conventional and advanced wastewater
treatment: implications for environmental discharge and

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