Impact of magnetic ion exchange resin pretreatment on alleviating UF membrane fouling
H. Xu, W. Chen, J. Sun and Z. Yuan

ABSTRACT
The purpose of this study is to understand the effect and mechanism of preventing ultrafiltration (UF) membrane fouling by using magnetic ion exchange resin (MIEX®) in terms of fractional content and molecular weight of NOM. In the experiment, pretreatment decreasing trans-membrane pressure and preventing membrane fouling were studied. The result showed: when the MIEX® dosage reached 800 bed volume (BV), the polymeric aluminium chloride (PAC) dosage could be reduced to 14 mg/L, and the Trans-Membrane Pressure (TMP) could be recovered effectively after hydraulic flush. This pretreatment could remove most of the hydrophobic and hydrophilic charged organics as well as some neutral organics. Foulants of molecular weight (MW) < 1000 dalton (Da) and 3000 Da < MW < 100,000 Da organics could be removed by 40.7% and 96.0%, respectively. By reducing pore blocking and membrane cake resistance, the ultrafiltration (UF) membrane reduced the total resistance of membrane. As a result, membrane fouling was alleviated and the water production ratio was enhanced.
Key words | drinking water, membrane fouling, magnetic ion exchange resin (MIEX®), NOM, trans-membrane pressure, ultrafiltration

INTRODUCTION
Ultrafiltration (UF) is an effective way to remove suspended solids and colloid. However, the UF membrane can only remove macromolecular organics, and most dissolved organics are difficult to be removed. In addition, membrane fouling is another important barrier to the development of membrane technology. Hao (1999) and Lin et al. (2000) found molecular weight (MW) has some connection with membrane fouling. According to their research, macromolecular organics brought a great decrease of membrane flux. Yuan (2000) identified that the membrane fouling generated by small MW particles was slighter. Dong et al. (2005) determined that the organics with a molecular weight of more than 1,000 Da was an important factor to cause membrane fouling, and Carroll et al. (2000) found the main substance causing membrane fouling was neutral hydrophilic organics. Therefore, it can be considered that the dissolved organics is the primary cause of increased membrane fouling, and one important way to avoid membrane fouling is to reduce the organics flowing into the membrane module.

Bian et al. (1998) considered that coagulation could remove macromolecular humic acid and therefore it could avoid membrane from fouling. However, Lahoussine-Turcaud et al. (1990) made a comparison of treating Seine River water with a process including pre-coagulation and membrane treatment and another with only membrane treatment. They found that coagulation could remove DOC effectively and reduce the resistance pressure, but it could not slow down the pollution process or restrict the pollutant to a low degree.

More recently a new technology (the MIEX® process) has been developed that can effectively remove NOM, especially at MW < 3,000 Da (Boyer & Singer 2005). The small particle size of the resin, around 180 m, provides a high surface area allowing rapid adsorption of NOM. Some research showed that this resin could reduce the dosage of
coagulants when it was used as a pretreatment process. Kitis et al. (2007) found that compared to the process of direct coagulation with aluminium, pretreatment by MIEX gave a 25% to 60% aluminum coagulant reduction, while reaching about the same turbidity or DOC removal rate level.

In this research, MIEX was considered as a pretreatment process, and in this paper its impact on NOM removal was discussed, as well as its alleviation effect on the transmembrane pressure increasing and membrane fouling.

**METHODS**

**Quality of raw water**

The raw water was taken from a tributary of Huai River. The concentration of CODMn was 3.5–4.8 mg/L (the average was 4.37 mg/L). The concentration of DOC was 3.7–5.3 mg/L (the average was 4.54 mg/L). The average concentration of UV254 was 0.076 cm−1.T he turbidity was 19–88 NTU (the average was 38 NTU), and the water temperature was 24.2°C.

**Experiment device and membrane**

The experiment flow chart is shown in Figure 1. The pilot plant was set up at the water treatment plant in Huai-an, China. Magnetic ion exchange resin was provided by Orica Watercare of Watkins Company, and UF membrane was provided by Litree Company respectively. In process 1, the raw water was pumped into a MIEX reactor and then to a coagulation reactor after adding the coagulant through a gravitational dosing system. The effluent of the coagulation reactor flowed into inclined tube settling tank and finally pumped into the membrane module. The MIEX reactor was composed of an agitated reaction part and a plated sedimentation part. At the reaction part, the resin particles mixed sufficiently with water and pollutants and reacted with pollutants through iron exchange. At the upper settling part, high efficiency of solid-liquid separation could be achieved. In process 2, the raw water flowed into a coagulation reactor directly. In the experiment, poly-aluminium chloride (PAC) was used as a coagulant, and the dosage in process 1 and process 2 were 14 mg/L and 32 mg/L, respectively.

The UF system was running dead-end. The filtration flux was 75 L/m² h, and the backwash water was filtered water. PVC alloy membrane was used in the experiment, and the cut-off molecular weight of the membrane was 100,000 Da. The detailed parameters is shown in Table 1.

**Table 1** | UF membrane parameters

<table>
<thead>
<tr>
<th>Parameter names</th>
<th>Parameter</th>
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<tbody>
<tr>
<td>Hollow Fiber Membrane Material</td>
<td>PVC alloy</td>
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<tr>
<td>Filter length (mm)</td>
<td>200</td>
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<tr>
<td>Filter diameter (mm)</td>
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<tr>
<td>The average pore diameter of UF (µm)</td>
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<td>Design flux (L/h)</td>
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<tr>
<td>Max trans-membrane (MPa)</td>
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<td></td>
</tr>
<tr>
<td>The influent pH</td>
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<td></td>
</tr>
<tr>
<td>The influent temperature (°C)</td>
<td>5–45</td>
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</table>
Analyze Methods

UV$_{254}$ was measured by UV-V spectrophotometer. DOC was performed by the high temperature combustion method using a MultiN/C2100 TOC analyzer. Turbidity was determined by 2100 P portable Turbidimeter (Hach, USA). The microstructure was observed by EVO-MA-10 Scanning electron microscope (ZEISS Co Ltd, Germany).

The fractionation procedure was based on adsorption by different adsorbent resin according to the method published by Croue et al. (1994) and Bolto et al. (1999) and resulted in four fractions: VHA (adsorbed by DAX-8), SHA (adsorbed by XAD-4), CHA (adsorbed by IRA-958) and NEU, which was not adsorbed on any of the ion exchange resin. The sample of 500 mL filtered through a 0.45 μm cellulose nitrate membrane, was acidified to pH 2 with HCl and was passed through the DAX-8 column at $3.0 \text{ mL min}^{-1}$ (0.2 bed volumes min$^{-1}$). The first two bed volumes were discarded and the remaining effluent was collected. A sub sample of 100 mL was collected for DOC analysis. The remaining effluent (360 mL) was passed through the XAD-4 column, and the first two bed volumes (30 mL) was discarded. After sampling 100 mL for DOC analysis, the effluent from the XAD-4 column was adjusted to pH 8 by NaOH and was pumped through the IRA-958 column, the first two bed volumes (30 mL) again being discarded. All pH adjustments were performed using concentrated solutions to minimise dilution of the sample. The analytical procedure was based on measuring the organic carbon concentrations of the raw, DAX-8 effluent, XAD-4 effluent and IRA-958 effluent. The organic carbon concentration of each fraction was calculated based on the subtraction of the organic carbon concentration before and after contact with the resin. The detail of the calculation is shown below:

- Very Hydrophobic Acids (VHA) = Raw – (DAX – 8 effluent)
- Slightly Hydrophobic Acids (SHA) = (DAX – 8 effluent) – (XAD – 4 effluent)
- Hydrophilic Charged Acids (CHA) = (XAD – 4 effluent) – (IRA – 958 effluent)
- Hydrophilic Neutral (NEU) = (IRA – 958 effluent)

The organic molecular weight distribution was determined by Millipore UF membrane. The sample, first filtered through a 0.45 μm cellulose nitrate membrane, and then passed through the UF membrane with 100,000 Da, 10,000 Da, 3,000 Da, 1,000 Da molecular weight cut-off. The filtration of DOC was measured and each MW section was calculated by subtraction.

RESULTS AND DISCUSSION

Impact of pretreatment on coagulation effect

Much literature shows that a combination of magnetic ion exchange resin and coagulation can reduce coagulant demand by 25–60% compared to coagulation alone when targeting NOM and turbidity removal (Fearing et al. 2004; Boyer & Singer 2006; Chen et al. 2009). As seen in Figure 2, the pre-treatment process not only improved the removal effect of NOM but also enhanced the coagulation process. When the MIEX® reached 800 BV, in Process 1, the turbidity decreased from 44 NTU to 2.3 NTU with the PAC dosage of 14 mg/L (the removal rate is 95%). The same removal rate could be reached in Process 2 with the PAC dosage of 32 mg/L. It could be concluded that MIEX® could save 56% coagulant dosage to achieve the same removal effect of turbidity, and that the pretreatment could greatly improve the turbidity removal effect in the following procedure of coagulation and sedimentation treatment. It was observed that in MIEX-coagulation trials the flocs formed were bigger than in coagulation trails. That was because the NOM in the water consumed a large amount of the coagulant and moreover hydrophilic NOM adhered to the coagulant which had adverse effect on coagulation. The pretreatment could remove most of the NOM, and therefore weakened the disturbance on coagulation, which was favorable for enhanced removal of turbidity. The experimental result showed with the rise of bed volume of magnetic ion exchange resin, the removal effect of turbidity decreased slightly.

NOM removal

Figure 3 shows the changes of NOM concentration in the two processes. The average DOC and UV$_{254}$ was 4.54 mg/L and 0.076 cm$^{-1}$ in the raw water, but the difference of the NOM concentration in the UF effluent was large.
pretreatment exhibited greater NOM removal than coagulation alone. When magnetic ion exchange resin was employed alone, approximately 54.1% UV254 absorbing material was removed and 73.1% DOC was removed. When 14 mg/L PAC was added, the UV254 and DOC removal was improved to 78.2% and 67.7%, respectively. In the process 2, when 32 mg/L PAC was added, the UV254 and DOC removal was improved to 20.6% and 25.4% in the effluent of the settling tank. 69.5% of the DOC and 80.7% of the UV254 was removed in the process 1, while 23.2% of the DOC and 26.7% of the UV254 was removed in the process 2. It was indicated that MIEX® has the potential to remove more DOC and UV254 than coagulation, and removed a wider range of molecular weight and organic acid fractions of NOM than coagulation. Thus the pretreatment could alleviate the membrane fouling caused by NOM.

Figure 4 showed that, hydrophobic NOM accounted for 49.9% of all the NOM in the raw water, among which, VHA and SHA accounted for 37.8% and 12.1%, respectively. Besides, CHA and NEU accounted for 23.1% and 27.0% respectively. In process 1, the removal rate of hydrophobic NOM, CHA and NEU were 65.0%, 83.8% and 7.3%, respectively, through the pretreatment. The corresponding removal rates of the above NOM through coagulation were 58.4%, 47.0% and 8.8%. While in UF process, most of NEU was removed (the removal rate was 39.4%), and CHA increased slightly. In process 2, the removal rate of hydrophobic NOM and NEU were 41.9% and 4.9%, respectively, after
coagulation and sedimentation treatment. The removal rate of the above two NOM were 15.2% and 12.0% through UF membrane, while the CHA were not removed during the whole process. From the above results, it could be considered that, UF mainly removed NEU and hydrophobic NOM, and was less effective for the removal of hydrophilic NOM. The cutting-off efficiency order of NOM by UF membrane was: NEU > VHA > SHA > CHA. The MIEX® pretreatment mainly removed hydrophobic NOM and CHA, and it also had some effect on the removal of NEU, while coagulation and sedimentation mainly removes hydrophobic NOM and NEU. The removal of hydrophobic NOM and NEU in the MIEX® process alleviated the following coagulant dosage and thus relieved the membrane fouling effectively.

NOM in the raw water are mainly of low molecular weight. Figure 5 showed that, the NOM with MW <1,000 Da accounted for 67.8% of the whole, and NOM with MW >3,000 Da accounted for 30.8%. In process 2, 29.5% NOM with MW <1,000 Da and 54% NOM with MW >10,000 Da were removed through coagulation and sedimentation, while the NOM contents with MW of 1000~3000 Da increased largely after the treatment. It was because this kind of NOM was less in the raw water, while the PAC was added as a kind of macromolecule polymer, which could produce NOM with MW of 1,000~5,000 Da during coagulation hydrolysis process. The results also showed that UF membrane mainly cuts off NOM with MW >3,000 Da, among which, the removal rate of NOM were 54.5% (3,000 Da < MW < 10,000 Da) and 56.6% (MW >10,000 Da), and the NOM with MW <1,000 Da increased by 12%. In UF process, aluminium and other metal ions deposit on the membrane surface and react with NOM (forming complex). Because the function groups of NOM were masked by inorganic ions in the reaction, the molecular chains of NOM began to shrink, leading to the superficial size reduction of complex (Dong et al. 2006). In addition, it could be concluded that pretreatment mainly removed NOM with MW <1,000 Da (the removal rate was 40.7%) and MW of 3,000~100,000 Da (the removal rate was 96.0%). The following coagulation and sedimentation treatment mainly removed NOM with MW <1,000 Da (the removal rate was 55.5%) and MW >10,000 Da (the removal rate is 73%). The concentration of organic contents in the effluent of sedimentation tank was low, and most of them are NOM with MW <1,000 Da, which could not be cut off by UF membrane and thus accounted for 86.3% of the whole NOM in the effluent. The NOM with MW <1,000 Da had a high concentration in the raw water, and they could not be removed effectively by traditional coagulation and sedimentation, while the pretreatment removed 40.7% of them and reduced the following coagulant dosage. The results showed that, NOM with MW >3,000 Da was the main substances causing membrane fouling, and the pretreatment could remove as much as 96.0% of NOM with MW of 3,000~100,000 Da, which could control the membrane fouling effectively.

Impact of magnetic ion exchange resin pretreatment on trans-membrane pressure

Figure 6 presented the trans-membrane pressure of two processes. In process 1, the initial pressure of a new membrane was 0.025 MPa, which rose straightly to 0.051 Mpa within 3 minutes. On the whole, the pressure curve increased rapidly during the first 9 minutes, and presents an inflection point.
point at the 9th minute, then rising gradually. The pressure increased by 24% after the first time backwashing. In process 2, the pressure rose rapidly to 0.062 MPa within 3 minutes, and at the 9th minute, it reached 0.076 MPa, then it increasing slowly to 0.080 MPa. After backwashing, the pressure alleviated to 0.038 MPa. Therefore, the final pressure was generally 52.0% higher than the initial pressure in process 1. The experiment result indicated that, with the alternate performance of filtration and backwashing, the trans-membrane pressure presented an increasing trend on the whole. In addition, the pressure at the inflection point as well as the pressure difference between the final and the initial filtration period of process 1 was lower than that of process 2.

As seen from Figure 7, in process 1, when the BV of the resin varied, the alterations of trans-membrane pressure were different. As the BV increased, the trans-membrane pressure rose gradually. MIEX pretreatment and coagulation are complementary treatment processes, so that most of the NOM were removed. It is indicated that the pretreatment improved the permeability of the membranes and reduced the fouling of the membranes. When the magnetic ion exchange resin reached 800 BV, the trans-membrane pressure could recover effectively after backwashing. Considering both the quality of effluent and the economic efficiency of the process, the appropriate BV of the magnetic ion exchange resin was 800 BV.

**SEM images of membrane surface**

SEM images are shown in Figures 8–10. Figure 8 shows the surface of a new membrane; the membrane pore could be observed easily. Figures 9 and 10. presented the surface of the backwashed membrane used in process 1 and process 2, respectively. Figures 9 and 10 indicate that neither in process 1 (membrane 1) nor in process 2 (membrane 2) could the membrane be backwashed cleanly. However, the cake layer on membrane 2 had higher density and lower porosity than that of membrane 1, because the coagulant dosage in process 2 was higher, and the residual coagulant decreases the repulsing force between organic molecules, further causing the deposition of some colloid and molecules on the membrane surface. While in process 1, the cake layer had a looser structure, with higher porosity, and thus it was easy to be destroyed and washed away.
Mechanisms of membrane fouling

The trans-membrane pressure was usually described by Dancy equation:

$$\Delta P = \mu \cdot J \cdot R_t$$ (1)

where \(\Delta P\) is the trans-membrane pressure (Pa), \(\mu\) is the fluid viscosity (PaS), \(J\) is the water flux (m/s), \(R_t\) is the total resistance of membrane (1/m).

Equation 1 showed that, when dead-end constant flow filtration was adopted, the main factor impacting the trans-membrane pressure is the total resistance of membrane, which was achieved by:

$$R_t = R_m + R_a + R_g + R_c + R_{cp}$$ (2)

where \(R_m\) is the structure resistance (1/m), \(R_a\) is the membrane adsorption resistance (1/m), \(R_g\) is the membrane pore resistance (1/m), \(R_c\) is the membrane cake resistance (1/m), \(R_{cp}\) is the concentration polarization resistance (1/m).

Previous research showed that (Dun & Wang 1997), adsorption resistance was mainly generated by small hydrophilic NOM. The organic matters with MWs less than 3000 Da could permeate through the membrane pore, thus the adsorption resistance did not account for the increase of trans-membrane pressure. However, these organic matters in effluence influenced the water quality (Figures 4 and 5).

Generally, membrane pore resistance was generated by NOM which had a similar size with membrane pore. The organic matters with MW ranged between 3,000 and 100,000 Da could block the membrane pore where smaller-molecular matters have been adsorbed in. Although the concentration of this part of NOM was low, their impact was greater. Furthermore, it was difficult to remove them through backwashing, unless chemical rinse was adopted in the following process In this research, the experiment result showed that, coagulation and sedimentation only removed a small part of NOM with MW of 3,000–100,000 Da, while 96.0% of them could be eliminated by magnetic ion exchange resin pretreatment. Figure 2 shows that the trans-membrane pressure after backwashing of process 1 was 13.6–18.4% lower than that of process 2, and the average pressure value at the inflection point was about 20% lower than that of the latter. Therefore, the difference of membrane pore resistance between process 1 and process 2 was the main reason causing the diversity of their whole trans-membrane pressure.

In this research, the membrane cake resistance was mainly generated by hydrophobic NOM, dissolved NOM with MW > 100,000 Da and organic particles with grain...
size > 0.45 μm. The result showed that, these NOM could be removed effectively through coagulation, and some of them could be removed by backwashing. The other part which was hard to be washed out began to form the dense cake layer, leading to the increase of trans-membrane pressure. Similar to membrane pore blocking, membrane cake resistance was also the main reason causing the difference of the whole trans-membrane pressure in process 1 and process 2.

The concentration polarization resistance was usually formed by the concentration gradient between membrane surface and the bulk solution. In the two processes, the content of dissolved NOM with MW > 100,000 Da in the UF membrane influent was very low. Therefore, the concentration polarization resistance could be neglected.

Most NOM with MW of 5,000–100,000 Da was removed during the pretreatment. Therefore, the content of hydrophobic NOM, the membrane pore blocking and membrane cake resistance were alleviated. This implies that, magnetic ion exchange resin treatment could control the whole resistance of membrane operation and consequently alleviate the membrane fouling.

CONCLUSIONS

The trans-membrane pressure was alleviated with the increase of MIEX® dosage. The pretreatment could remove most SHA and CHA, as well as some NEU. The molecular weight of the removed NOM was identified in the range of <1,000 Da (the removal rate is 40.7%) and 3,000 ~ 100,000 Da (the removal rate was 96.0%). In addition, MIEX® pretreatment could reduce the dosage of coagulant and alleviated the membrane pore blocking and membrane cake resistance, which could alleviate the UF membrane fouling.

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