The removal of typical pollutants in secondary effluent by the combined process of powdered activated carbon–ultrafiltration

Lihua Sun, Ning He, Tianmin Yu, Xi Duan, Cuimin Feng and Yajun Zhang

ABSTRACT

This paper focused on the effects of powdered activated carbon (PAC) dosage on ultrafiltration (UF) membrane flux caused by natural organic matter (NOM). Three model foulants, humic acid (HA), bovine serum albumin (BSA) and sodium alginate (SA), were adopted to represent different NOM fractions in secondary effluent treated by the combined process of PAC-UF. Moreover, the membrane fouling resistance and fouling mechanism were also analyzed. The results indicated that the best PAC dosage for the membrane flux variation was 20 mg/L for HA and SA, and 10 mg/L for BSA. SA caused the most serious membrane fouling, which was mainly reversible fouling. The membrane fouling caused by HA and BSA was mainly irreversible membrane fouling. The membrane fouling caused by organics happened mainly at the initial stage of filtration. Because the filter cake layer formed by a moderate amount of PAC could intercept organics, the membrane fouling, especially the irreversible fouling, could be reduced.

Key words | cake layer, membrane flux, membrane fouling resistance, powdered activated carbon, ultrafiltration

INTRODUCTION

Ultrafiltration (UF) has been widely applied in drinking water or reclaimed water treatment due to its development of innovative materials and decreased costs in recent years (Shannon et al. 2008; Tian et al. 2015). Membrane fouling is one of the major impediments for the further development of UF technology. But some studies found that efficient combined processes can alleviate membrane fouling. Shon et al. found that powdered activated carbon (PAC) could adsorb a significant proportion of low molecular weight organics in secondary effluent and reduce membrane fouling (Shon et al. 2010). Research showed that PAC-UF could improve the filtration performance of UF (Zhang et al. 2012; Li et al. 2014). It has been reported that PAC could not only enhance the performance of organics removal but also control the membrane fouling efficiently (Campinas & Rosa 2010). Dong Bingzhi et al. found that PAC could alleviate the decline of membrane flux and mitigate membrane fouling by the adoption of the PAC-UF process to treat Huangpujiang River water (Dong et al. 2015). The preliminary studies mainly focused on the influence of organics on membrane flux. But the influence of varieties and components of organics on the adsorption efficiency of PAC and membrane flux were rarely studied.

In our experiment, humic acid (HA), bovine serum albumin (BSA) and sodium alginate (SA) were used to represent humus, proteins and polysaccharides in secondary effluent respectively. The influences of PAC dosage on membrane flux were investigated by the removal efficiency of three kinds of organics mentioned above, treated by the combined process of PAC-UF. Moreover, the synergistic effects of organics and PAC on membrane fouling were also investigated.

MATERIALS AND METHODS

Materials

Polyvinylidene fluoride flat-sheet UF membrane purchased from AMF (USA) with molecular weight cut-off of 100 kDa was used in this study. The chemical agents of HA, BSA and SA were used to represent humus, proteins
and polysaccharides, respectively. The mass concentration of each of the above three stock solutions was 20 mg/L. All solutions in the experiment were made up with ultrapure water. The ion strength was adjusted by 10 mmol/L NaCl and the pH value was adjusted to 7.5 ± 0.2 by 0.01 mol/L HCl and NaOH. Shell-based PAC was purchased from Heat-ton Environmental Protection Technology Co. Ltd (Shanghai, China). The main properties of PAC are listed in Table 1.

### Experimental setup

The schematic diagram of the UF experiment is shown in Figure 1. The volume of the UF filter bowl (Millipore, Amicon 8400, USA) was 400 mL. The operation pressure was controlled by a pressure gauge connected to a nitrogen-pressurized solution reservoir. The filtration experiment was performed in dead-end mode at room temperature with a constant pressure of 0.10 MPa. During the experiment, the permeate flux was recorded using an electronic scale connected to a computer, logging the data every 1 minute automatically.

During the experiment, the filtration time was set at three filtration cycles and every period lasting 60 minutes. A sample was taken in every period of filtration. At the end of every period, the UF was washed by adding 200 mL ultrapure water to the UF filter bowl, which was placed on a magnetic mixer with revolving speed 250 rpm for 5 minutes.

Adsorption tests were conducted to characterize the adsorption of the natural organic matter (NOM) fractions onto PAC. The concentrations of HA, BSA and SA employed in adsorption tests were 10–70 mg/L and the concentration of the adsorbent was 100 mg/L. The adsorbent was added to NOM solutions and the flasks were shaken in a rotary shaker at 200 rpm and 25 °C for 48 h. Finally, the samples were filtered with 0.45 μm blend cellulose membrane (CA-CN, Beihua Corp., China) to remove adsorbent particles, and the concentrations of HA, BSA and SA in the filtrate were measured. The retention of these NOM fractions by this filter has been proved to be negligible in preliminary tests. The adsorbed amounts of HA, BSA and SA onto the adsorbents were calculated by mass balance. Each sample was measured three times, and the average value was measured.

### Analytical methods

In this study, three classic adsorption isotherm models were used to fit the experiment results, that is, the Langmuir, Freundlich, and Temkin isotherm equations (Lou 2015). The equations are listed as follows:

- **Langmuir**: \( q_e = \frac{b q_m C_e}{1 + b C_e} \)  
- **Freundlich**: \( q_e = K_f C_e^{1/n} \)  
- **Temkin**: \( q_e = A + B \ln C_e \)

where \( q_e \) (mg/g) is the adsorption capacity or carbon load at equilibrium; \( C_e \) (mg/L) is the solute concentration of adsorbate at equilibrium; \( K_f \) and \( 1/n \) are the Freundlich equation constants; \( q_m \) (mg/g) is the maximum adsorption capacity of carbon load at the highest equilibrium concentration; \( b \) (L/mg) is the Langmuir constant; and \( A \) and \( B \) are the Temkin constants.

During the experiment, the permeate flux was described by using the normalized flux \((J/J_0)\). The membrane flux could be estimated by Equations (4).

\[ J = \frac{V}{At} \]  

where \( J \) is permeate flux (L/(m²·h)); \( V \) is filtration volume (m³); \( A \) is effective filtration area (m²); \( t \) is filtration time (h).

In this study, the analysis of fouling resistance distribution would favor the identification of fouling mechanisms. Total membrane resistance (\( R_t \)) was divided into membrane resistance (\( R_m \)) and total fouling resistance (\( R_f \)), which was the sum of reversible fouling resistance (\( R_r \)) and irreversible fouling resistance (\( R_i \)). The reversible and irreversible fouling resistance could be determined with the normalized flux after the membrane cleaning.

### Table 1 | Characteristics of PAC

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material</td>
<td>Apricot shell</td>
</tr>
<tr>
<td>Granularity (mesh)</td>
<td>200–300</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>587.38</td>
</tr>
<tr>
<td>Average pore diameter</td>
<td>3.351</td>
</tr>
<tr>
<td>Iodine number (mg/g)</td>
<td>700–1,000</td>
</tr>
<tr>
<td>Methylene blue (mg/g)</td>
<td>100–150</td>
</tr>
</tbody>
</table>
(Jermann et al. 2008).

\[ R_t = R_m + R_f = R_m + R_r + R_i \]  
\( (5) \)

Every kind of fouling resistance could be calculated as follows:

\[ R_m = \frac{(J_0 - J_{s1})}{J_0} = \frac{1 - J_{s1}}{J_0} \]  
\( (6) \)

\[ R_m = \frac{(J_{p1} - J_{pm})}{J_0} \]  
\( (7) \)

\[ R_m = \frac{(J_{pm} - J_m)}{J_0} \]  
\( (8) \)

where \( R_m \) is the irreversible fouling at the end of the \( n \) period, \( R_m \) is the reversible fouling at the end of the \( n \) period, \( J_0 \) is the flux of the new membrane \( (L/(m^2\cdot h)) \), \( J_{s1} \) is the initial flux in the first cycle \( (L/(m^2\cdot h)) \), \( J_{pm} \) is the flux at the end of the \( n \) period after backwashing \( (L/(m^2\cdot h)) \), \( J_{en} \) is the flux at the end of the \( n \) period \( (L/(m^2\cdot h)) \), \( n \) is filtration cycle \( (n = 1, 2, 3) \).

During the experiment, to investigate the fouling at different filtration stages, the filtration was divided into initial stage and later stage. Organics would be adhered on the membrane in the initial stage, and the interactions among organics would be occurring in the later stage. The formation of cake layer is an important symbol of the beginning of the cohesion stage. Therefore, the two phases were divided according to the cake layer filtration model \( (\text{Equation } (9)) \) \( (\text{Ye et al. } 2005; \text{Iritani } 2013) \):

\[ \frac{t}{V} = aV + b \]  
\( (9) \)

where \( t \) is filtration time \( (s) \), \( V \) is filtrate volume \( (mL) \), and \( a \) and \( b \) are model parameters.

In order to quantify the membrane fouling process, values of fouling potential \( (K) \) represent a quantitative index of fouling \( (\text{Gao } 2014) \). The cake layer formed by PAC particles had certain resistance. Therefore the decline in normalized flux caused by PAC particles and the unit mass of foulant which adsorbed on the membrane surface were defined as \( K \).

\[ K = \frac{\Delta f/J_0}{\Delta V \times C_b} \]  
\( (10) \)

where \( K \) is value of fouling potential \( (g^{-1}) \); \( C_b \) is the concentration of organics and PAC in raw solution \( (g/L) \).

**RESULTS AND DISCUSSION**

**Adsorption of NOM fractions onto PAC**

The adsorption isotherm curves of organic matter adsorption by PAC are shown in Figure 2. The parameters and correlation coefficients obtained from three isotherm models of different NOM fractions are summarized in Table 2.

The results showed that the Freundlich isotherm equation fitted the experiment data better than the Langmuir isotherm equation and the Temkin isotherm equation. The Freundlich model could well describe the PAC adsorption capacity of HA, BSA and SA. The Freundlich model assumes a heterogeneous adsorbent surface, where the stronger binding sites are occupied first.
The parameter of the Freundlich model, \( K_f \), is an approximate measure of adsorption capacity. Actually, \( K_f \) equals the adsorption capacity when the equilibrium adsorbent concentration is 1.0 (Tan et al. 2013). Additionally, the Freundlich \( 1/n \) values were less than 0.5 for PAC, suggesting the general adsorption affinities of the three organic matters on PAC (Wang et al. 2009). It was apparent that the adsorption of the organic matters on PAC was in the order of HA>BSA>SA.

**Effect of PAC dosage on membrane flux**

To understand the effect of PAC particles on the membrane flux, a series of UF filtration tests were performed by adding 10 mg/L, 20 mg/L and 25 mg/L PAC in ultrapure water. The flux decline curves in 60 minutes are shown in Figure 3.

It could be observed that the value of \( J/J_0 \) decreased a small extent with the final normalized flux being 0.94, 0.93, 0.92 and 0.90, respectively, which indicated that PAC particles by themselves played a minor role in the flux decline. It could be explained by the fact that PAC particles which are larger than membrane pores would not cause the pore blocking. Moreover, PAC particle deposition on the membrane surface would form a loose layer with higher porosity, leading to a slight flux decline, and would have slight influence on fouling resistance. A similar view was provided by Campinas and Rosa who concluded that the addition of PAC alone showed little influence on the flux decline (Campinas & Rosa 2010). Xia et al. found that a relatively loose structure and high porosity of PAC cake deposited on the membrane did not affect the process performance (Xia et al. 2007).

**Effect of PAC pre-adsorption on flux decline**

Some research pointed out that the PAC pre-adsorption is conducive to removal of organics, but whether it mitigates membrane fouling depended on the dosage of PAC. The lower dosage of PAC played a minor role in the membrane fouling, while the higher dosage would increase the membrane fouling (Zhao & Gu 2009; Jamal Khan et al. 2012). To understand the effect of different dosages of PAC on the membrane flux decline, a series of filtration tests were performed with the raw water pre-adsorbed with 10, 20 and 25 mg/L PAC, respectively. The flux decline with different PAC dosage during the filtration of three kinds of organics are shown in Figure 4.

As shown in Figure 4(a), the normalized flux decreased to be 0.55 at the end of filtration by direct UF when the organics was HA. By adding 10 mg/L or 20 mg/L PAC, the flux was improved and the value of \( J/J_0 \) was 0.62 and 0.63, respectively, whereas adding 25 mg/L PAC would intensify the flux decline and \( J/J_0 \) was 0.53, which indicated that the presence of PAC and...
HA would cause complex pollution on the membrane. It also indicated that the higher dosage of PAC obviously contributed to membrane fouling by HA. From the full cycle operation, when the PAC dosage was 20 mg/L, the permeate flux and its recovery degree after backwashing were the highest, indicating this dosage alleviated membrane fouling effectively.

As shown in Figure 4(b), adding 10 mg/L PAC displayed insignificant influence on flux, whereas adding 25 mg/L PAC would aggravate the decline of flux. When the dosage of PAC was 20 mg/L, the membrane flux was improved obviously and its recovery degree was high after backwashing. It illustrated that low or high dosage of PAC had disadvantage to improve membrane flux. To control the membrane fouling by SA, the best dosage of PAC was 20 mg/L.

The effect of PAC on membrane fouling by BSA is shown in Figure 4(c). The flux declined fast by direct UF filtration. After adding 10 mg/L or 20 mg/L PAC, the membrane flux improved and the recovery of flux was higher after backwashing. It indicated that PAC could improve the flux and control membrane fouling effectively. However, the flux decreased greatly with 25 mg/L PAC. These results showed that excessive PAC dosage would decrease the flux and have disadvantage to control membrane fouling.

From the above analysis, it could be concluded that the best dosage of PAC was different for diverse organics. For HA and SA, the best dosage was 20 mg/L PAC. And for BSA, 10 mg/L PAC would improve the flux and alleviate the membrane fouling.

The effect of pre-filtration by 0.45 μm membrane on flux decline

The main reasons for PAC affecting the membrane flux were as follows: PAC could absorb organic matter to reduce its concentration in the membrane influent and the interception performance of cake layer on organics (Tomaszewski & Mozia 2002; Wang et al. 2005; Thiruvennatakachari et al. 2006). In order to elucidate the effects of the presence of PAC in UF feed water on membrane fouling, prior to UF experiments, the adsorbent was added to HA, SA and BSA solutions at a dose of 20, 20 and 10 mg/L, respectively. The contact time was set at 30 minutes, and then the adsorbent particles were removed before UF by filtering through 0.45 μm membrane. The results are shown in Figure 5 and Table 3.

The results showed that PAC could adsorb some of the organics; the decrease of dissolved organic matters could improve the permeate flux. When adsorbent particles were removed before UF, the normalized flux of HA, SA and BSA could be increased 7.3%, 7.8% and 3.8%, respectively, under the best dosage of PAC. When PAC particles presented in UF feed water, the final membrane flux of HA, SA and BSA could be increased 12.3%, 18.5% and 11.8%, respectively. The result indicated that the cake layer formed by the proper amount of PAC could prevent the contact between organics and membrane, which efficiently controlled the membrane fouling and improved the flux. The result was consistent with previous researches. Dong et al. reported that the

<table>
<thead>
<tr>
<th>NOM</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
<th>Temkin model</th>
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<tbody>
<tr>
<td></td>
<td>( q_m )</td>
<td>( b )</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>HA</td>
<td>101</td>
<td>0.085</td>
<td>0.911</td>
</tr>
<tr>
<td>SA</td>
<td>28.3</td>
<td>0.242</td>
<td>0.884</td>
</tr>
<tr>
<td>BSA</td>
<td>40.8</td>
<td>0.096</td>
<td>0.939</td>
</tr>
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</table>
The effect of the decrease of dissolved organic matters on membrane flux was not larger than the effect of cake layer formed by PAC particles on membrane surface (Dong et al. 2013).

The distribution of membrane fouling resistance

The fouling resistance in the PAC-UF system might be derived from membrane pore narrowing, pore blocking or
the gel layer formed by cake layer and organics. In this experiment, the fouling resistance was characterized by the change of the normalized flux \( J/J_0 \). Prior to the filtration test, the membrane was used to filtrate a certain amount of pure water and achieve a stable flux to calculate membrane resistance \( R_m \). At the end of each filter cycle, recovered \( J/J_0 \) minus by membrane resistance was irreversible fouling resistance \( R_i \) after the membrane backwashing. The distribution of fouling resistance under different conditions is shown in Figure 6.

As shown in Figure 6, the total membrane fouling resistance was low for HA and BSA: 0.45 and 0.35, respectively, and the irreversible fouling of them was 0.30 and 0.23. The total fouling resistance caused by SA was 0.68, of which the irreversible fouling resistance was 0.32. The results demonstrated that HA and BSA mainly caused irreversible fouling and SA mainly caused reversible fouling. When there was no 0.45 \( \mu \)m membrane separation step before UF, in the best dosage of PAC, the permeate volume of the three kinds of organics, SA < HA < BSA at the beginning of the cake layer model stage. The formation of cake layer needed the membrane to be contacted with more organics. The greater permeate volume was achieved with lower membrane fouling, which was consistent with the seriousness of fouling caused by organics.

When PAC pre-adsorption was adopted before UF, the permeate volume of HA, SA and BSA was 77, 37 and 86 mL, respectively, at the stage of cake layer model. Compared with the direct UF filtration, the pre-adsorbent of PAC and cake layer could dramatically reduce the fouling and mainly controlled the irreversible fouling. When adsorbent particles removed by 0.45 \( \mu \)m membrane, the total fouling resistance caused by HA, BSA and SA was 0.43, 0.36 and 0.65, respectively. In addition, the irreversible fouling resistance was 0.28, 0.20 and 0.25, respectively. The absence of PAC particles obviously contributed to membrane fouling, demonstrating that the PAC-layer contributed to the fouling more efficiently than the decrease of organics concentration did.

**Analysis of the mechanisms of membrane fouling**

The segmentation of the filtration of HA, SA and BSA by direct UF filtration and PAC pre-adsorption with the best dosage is shown in Figure 7. As shown in Figure 7, when HA was filtrated by direct UF and the permeate volume increased to 92 mL, the cake layer model controlled the filtration. At the same stage, the permeate volume of SA and BSA was 52 mL and 107 mL, respectively. Comparing the permeate volume of the three kinds of organics, SA < HA < BSA at the beginning of the cake layer model stage. The formation of cake layer needed the membrane to be contacted with more organics. The greater permeate volume was achieved with lower membrane fouling, which was consistent with the seriousness of fouling caused by organics.

When PAC pre-adsorption was adopted before UF, the permeate volume of HA, SA and BSA was 77, 37 and 86 mL, respectively, at the stage of cake layer model. Compared with the direct UF filtration, the appropriate dosage of PAC accelerated the formation of cake layer. The flux decline and membrane fouling resistance distribution indicated that the PAC layer shortened the initial stage and reduced membrane fouling by rejecting organics. For better understanding of the effect of PAC on membrane fouling, the specific values of membrane fouling potential \( K \), represented membrane fouling, are shown in Table 4.

As shown in Table 4, when organics were filtrated by the combined PAC-UF process, the value of membrane fouling potential in the

<table>
<thead>
<tr>
<th>Operating condition</th>
<th>( J/J_0 )</th>
<th>Changing rate /%</th>
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<tbody>
<tr>
<td>HA</td>
<td>0.576</td>
<td>–</td>
</tr>
<tr>
<td>SA</td>
<td>0.312</td>
<td>–</td>
</tr>
<tr>
<td>BSA</td>
<td>0.656</td>
<td>–</td>
</tr>
<tr>
<td>HA + 20PAC</td>
<td>0.651</td>
<td>12.3</td>
</tr>
<tr>
<td>SA + 20PAC</td>
<td>0.37</td>
<td>18.5</td>
</tr>
<tr>
<td>BSA + 10PAC</td>
<td>0.731</td>
<td>11.8</td>
</tr>
<tr>
<td>HA + 20PAC + 0.45 ( \mu )m</td>
<td>0.600</td>
<td>7.3</td>
</tr>
<tr>
<td>SA + 20PAC + 0.45 ( \mu )m</td>
<td>0.337</td>
<td>7.8</td>
</tr>
<tr>
<td>BSA + 10PAC + 0.45 ( \mu )m</td>
<td>0.679</td>
<td>3.8</td>
</tr>
</tbody>
</table>
The initial stage was significantly larger than the value of the later stage \( (K_1/K_2 > 6) \), indicating that the same mass of organics in the initial stage which deposited on the membrane surface caused larger flux decline. It indicated that the membrane fouling in the initial stage was more serious than that in the later stage. The order of value of fouling potential in the initial stage was \( SA > HA > BSA \), and the SA fouling potential was much larger than HA and BSA. In other words, the same mass of SA severely caused the flux decline in the initial stage. When PAC pre-adsorption was adopted before UF, the decreased value of fouling potential in the initial stage was greater than that in the late stage, demonstrating that the flux decline caused by the same mass of PAC and organics was less than that caused by the same mass of organics. There were two probable interpretations for this phenomenon. Firstly, PAC adsorbed a fraction of organics to decrease the NOM concentration in the solution. Secondly, the cake layer formed by PAC particles could reject some proportion of organics and alleviate the flux decline to some extent. It could be observed from the \( K \) value in each stage (Table 4) that the pore blocking in the initial stage contributed to membrane fouling much more efficiently than the cake layer did. Lim and Bai found that pore blocking fouling prevailed in the early stage, which caused significant decline of permeation fluxes with time. Cake formation fouling dominated in the later stage after the initial pore blocking mechanism, which resulted in slower permeation flux decay over time (Lim & Bai 2003).

### CONCLUSIONS

Sequential filtration processes were performed to systematically investigate the effect of PAC particles on flux decline and membrane fouling. The following conclusions could be drawn.

1. The membrane fouling caused by different NOM fractions was in the order of \( SA > HA > BSA \). In addition, SA mainly caused reversible fouling, while HA and BSA mainly caused irreversible fouling.
2. PAC particles, by themselves, played a minor role in the flux decline, whereas HA and SA flux declines were...
exacerbated when the highest or lowest number of PAC particles was present in UF feed water. And the BSA flux decreased with the increase of PAC dosage. For HA and SA, the best dosage of PAC is 20 mg/L, whereas for BSA, the optimal dosage is 10 mg/L.

(3) The PAC layer mitigated the flux decline more efficiently than the decrease of dissolved organic matter did because the PAC layer would reject organic contributing to membrane fouling apparently. The interactions between PAC particles and NOM molecules exerted significant influence on fouling, which reduced irreversible fouling alleviating the flux decline efficiently.

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