Assessing pre-adsorption time impact on ultrafiltration performance for surface water treatment

Bo Gui, Qingqing Zhao, Junxia Liu, Zhihong Wang, Huaqiang Chu, Bingzhi Dong, Chujun Bie, Fan Jia and Jing Tian

ABSTRACT

This study was to assess the effect of powdered activated carbon (PAC) pre-adsorption time on ultrafiltration performance for surface water treatment. Experimental results demonstrated that membrane fouling could be mitigated by extending the pre-adsorption time. The molecular weight (MW) distribution of water samples was determined by liquid chromatography – organic carbon detector (LC-OCD) and results showed that the mechanism of PAC controlling fouling was attributed to a decrease in the low molecular weight (LMW) fraction of raw water via extending the pre-adsorption time. Fouling indexes (FIs) were used to evaluate membrane fouling potential and the results showed that polysaccharides (PS) and proteins (PN) were greatly responsible for membrane fouling. Therefore, prolonging the PAC pre-adsorption time and decreasing the PS and PN content in raw water are the main measurement for the alleviation of membrane fouling when PAC is used as the pretreatment in waterworks.

Key words | FIs, membrane fouling, PAC, pre-adsorption time

INTRODUCTION

Nowadays, membrane fouling is still a severe issue limiting the potential of ultrafiltration (UF). It may be possible to prevent fouling before its occurrence by pre-treatment of the raw water or chemical modification of the membrane to improve the anti-fouling ability (Shi et al. 2014). Coagulation, adsorption and oxidation are regarded as common and useful pretreatment methods to prevent fouling (Sun et al. 2013). Powdered activated carbon (PAC) adsorption prior to membrane filtration is an optimistic technology to remove organic matter. Some studies suggested that PAC could enhance membrane performance (Gai & Kim 2008; Huang et al. 2009; Matsui et al. 2009). For instance, Gai & Kim (Gai & Kim 2008) reported that the filtrate quality and performance efficiency were enhanced when PAC was introduced into the filtration system. Li et al. (Li et al. 2014) suggested that PAC primarily removed the low molecular weight (MW) matter, and was proved to be valid in the control of irreversible fouling. Cai et al. (Cai et al. 2013) revealed that the formation of a cake layer by PAC particles could act as a profiler to prevent the foulants' direct contact with the membrane, thus alleviating the fouling. However, the influence of PAC pre-adsorption time on UF performance has not yet well been elucidated.

Since the reaction time is important for adsorption, the present study was therefore (1) to assess PAC pre-adsorption time impact on UF fouling, (2) to correlate the water qualities with fouling potential and (3) to explore the reason for PAC controlling fouling.

MATERIAL AND METHODS

Raw water and PAC

The raw water was collected from Sanhaowu water (Table 1), located in Tongji University, Shanghai city, China. A
commercially available wood-based carbon, supplied by Yuanli Active Carbon Co., Ltd, China, was used in this study, whose average Brunauer–Emmett–Teller (BET) specific area and mean particle size was 0.549 m²/g, 26.6 μm, respectively.

**UF experimental**

A polyvinylidene fluoride (PVDF) hollow-fiber UF membrane was used in this research, which was obtained from Toray. The surface area and nominal pore size were 0.016 m² and 0.01 μm respectively. PAC was directly added into the raw water (30 mg/L) and stirred at 0/1/4/7d, followed by a static settling period of about 1 hour, and the supernatant was fed into the feed tank. The feed water was then pumped by peristaltic pump into the UF process. A constant permeate flux of 100 L/square meter/hour (LMH) was applied. Five successive cycles were carried out with cyclic backwash. The process operated in the following way: filling water (2 min), filtering (56 min), rinsing and backwash (2 min). Then the process repeats. At the end of the UF filtration process, chemical cleaning of the fouled membrane was conducted using an acid solution (HCl, 0.1wt. %) and an oxidant solution (NaClO, 0.2wt. %), respectively. The cleaning process was finished when the flux was recovered.

**Fouling indexes**

Recently, Nguyen et al. (Nguyen et al. 2011) proposed the fouling indexes (FIs), including the total fouling index (TFI) and the hydraulically irreversible index (HIFI), on account of the resistance in-series model. Previous studies proved that TFI and HIFI were of use as indicators for bench, pilot and full-scale filtration processes (Ayache et al. 2013; Farias et al. 2014; Zupančič et al. 2014). In this study, TFI and HIFI were used to assess membrane fouling; these have been described in detail in previous studies (Nguyen et al. 2011; Zupančič et al. 2014).

**Analytical methods**

Total organic carbon (TOC) and UV254 were detected by a TOC detector (Shimadzu TOC-L, Japan) and a UV-spectrophotometer (Hach DR5000, USA) respectively. The molecular weight (MW) of organic matter was determined via liquid chromatography–organic carbon detector (LC-OCD) (Waters e2695, USA; Sievers 900 Turbo, USA). The polysaccharides (PS) and proteins (PN) were measured by the phenol–sulfuric acid method (Dubois et al. 1956) and the bicinchoninic acid (BCA) method (Smith et al. 1985).

**RESULTS AND DISCUSSION**

**UF performance**

Variations of TMP and specific flux during pre-adsorption/sedimentation followed by UF process for the Sanhaowu water treatment cycles are depicted in Figure 1.

It can be seen in Figure 1(a) that the TMP, at the initial 0.27 ± 0.01 bar in each experiment, generally increased as the operational time extended. And after the backwash, TMP dropped, and then gradually increased when the system started again. In the initial filtration cycles, there were no obvious differences between direct filtration of raw water and that after PAC adsorption. Nevertheless, as the running time extended to the third cycle, pre-adsorption gradually took effect, that is, the TMP with PAC pretreatment increased more slowly than that in raw water. Figure 1(b) exhibits specific flux variations under the addition of PAC with different pre-adsorption times. It seemed that as the pre-adsorption time increased, the specific flux decrease slowed slightly. Obviously, the mean specific flux decreases for raw water and 7d pre-adsorbed water were 37.8% and 27.6% respectively. The specific flux decline of each test was probably due to the fast pore blocking and particle deposition (Said et al.)
The FIs were calculated using the operational performance data. A comparison of TFI and HIFI for different adsorption times is illustrated in Table 2.

Basically, the value of TFI increased as the cycle proceeded, indicating that the rate of fouling speeded up as the filtration cycles continued, presumably due to irreversible foulants accumulating on/inside the membrane. The fouling rate observed with 7d water was much lower than the fouling rate observed with the raw water. It was worth noting that when the feed water was pre-adsorption for enough time, the TFI and HIFI of the raw water were twice as high compared to the 7d adsorption water, demonstrating that PAC adsorption could reduce both the total fouling and hydraulically-irreversible fouling.

Water characteristics

Figure 2 shows the removal of dissolved organic carbon (DOC) and UV254 by PAC adsorption with different reaction times.

It was found that pre-adsorptions was able to reduce DOC by 1.055 mg/L, 1.299 mg/L, 1.204 mg/L and 1.488 mg/L, corresponding to reaction time of 0 d, 1 d, 4 d and 7 d, respectively. The UV254 also exhibited a similar trend to that of DOC.
LC-OCD was applied to qualitatively analyze MW in raw water. Figure 3 plots the profile in the dissolved organic content with MW of the source water (Black curve).

Two major peaks were observed, i.e. 1,440 Da (Peak A) and 4,780 Da (Peak B). These could probably be associated with the low molecular weight matter (LMW, Peak A) and humic-like substances (HS) (Yu et al. 2012; Liu et al. 2014). Based on the above analysis, MW distribution of raw water was separated by peak-fitting into two peaks (color curves in Figure 3). Then quantitative information of isolated peaks could be calculated according to the peak-fitting. Figure 4 presents the removal of MW fractions by PAC adsorption with different time.

Figure 4 reveals that as the time increased, the removal of the LMW fraction clearly increased while the HS fraction was evenly increased, and slightly decreased at the pre-adsorption of 7d. The results suggested that pre-treatment increased the removal of the LMW fraction.

As is known to us all, PN and PS are regarded as the important components of organics. Therefore, the concentration of PS, as well as PN, should be taken into consideration. Figure 5 shows the removal of PN and PS by PAC adsorption with different reaction times (the samples were determined three times and the average values were applied).

It is interesting to note that the removal of PN was assumed to increase while that of PS was not expected to decrease with the extension of pre-adsorption time. But it was noted that as the adsorption time increased, the sum removal of PN and PS increased. The result supported the point that the reduction of fractions in feed water, i.e. PS and PN, could mitigate membrane fouling during UF performance for surface water treatment.

**Correlation between FIs and water qualities**

Table 3 shows the relationships ($R^2$) between the FIs and TOC concentration, UV 254, PS and PN concentration, MW distribution (LMW and HS).
As Table 3 clearly shows, no correlations between the HIFI values and UV254, DOC and HIFI could be observed. Very weak correlations of DOC and TFI/HIFI existed, probably because DOC only represents the total organic matter rather than the characteristic of raw water. Examination of the LC-OCD data also suggested that no clear correlation was found between HS and TFI/HIFI. In addition, UV absorbance in feed water could not be related to the HIFI values in the present study. Humic substances were related to UV254 due to the presence of the double/triple bonds and aromatic rings of their structures. These results implied that HS was not important in the formation of fouling, although it has been regarded as the main component causing membrane fouling (Sutzkover-Gutman et al. 2010; Hao et al. 2011). This could probably be explained by hydrophilic natural organic matter (NOM) being mainly responsible for membrane fouling (Kimura et al. 2014). A relatively remarkable correlation between PS, PN and the FIs was observed, suggesting that PS and PN were linked with UF fouling. Our results were also supported by the reports of Hallé et al. (Huck et al. 2009), Katsuki Kimura (Kimura et al. 2014) and Tian et al. (Tian et al. 2013). The above results revealed that the alleviation of TMP and FIs by long time pre-adsorption was mainly attributed to enhancing the removal of PN and PS in feed water.

**CONCLUSION**

Based on the analysis of pre-adsorption time on UF of surface water, the following conclusions may be drawn.

1. Pre-adsorption enhanced the removal of NOM in raw water. Membrane fouling could be reduced by extending the pre-adsorption time.
2. The results of LC-OCD suggested that the mechanism of PAC controlling fouling was attributed to a decrease in the LMW fraction of raw water via extending the pre-adsorption time.
3. Obvious correlations between PS, PN and FIs were observed.

Therefore, prolonging the PAC pre-adsorption time and decreasing the contents of PS and PN in raw water are the main measurement for the alleviation of membrane fouling when PAC is used as the pretreatment in full-scale waterworks.

**Table 3** Correlation between fouling potentials (TFI and HIFI) and water quality

<table>
<thead>
<tr>
<th></th>
<th>TFI</th>
<th>HIFI</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV254</td>
<td>0.4371</td>
<td>0.1566</td>
</tr>
<tr>
<td>DOC</td>
<td>0.4563</td>
<td>0.1671</td>
</tr>
<tr>
<td>PS</td>
<td>0.7806</td>
<td>0.6850</td>
</tr>
<tr>
<td>PN</td>
<td>0.7343</td>
<td>0.5022</td>
</tr>
<tr>
<td>LMW</td>
<td>0.5381</td>
<td>0.2396</td>
</tr>
<tr>
<td>HS</td>
<td>0.0025</td>
<td>0.0874</td>
</tr>
</tbody>
</table>

**Figure 4** The different values of MW fractions between raw water and water samples by PAC adsorption with different reaction time.

**Figure 5** The values of removed PN and PS by PAC adsorption with different reaction time.
ACKNOWLEDGEMENTS

This research was financially supported by the National Water Pollution Control and Treatment Key Technologies R&D Program (No. 2012ZX07403-001). The authors also thank the project funded by China Postdoctoral Science Foundation (No. 2017M612616).

REFERENCES


First received 9 May 2017; accepted in revised form 31 July 2017. Available online 14 August 2017.