Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2019.23298

139 (2019) 105–110
January

Comparison of the micro-polluted surface water purification effect using two kinds of hybrid membrane systems

Rongrong Liu[a], Haichun Liu[a,b], Chundu Wu[a], Jiandong Zhou[a], Xujie Lu[b,*]

[a]*School of Resources and Environmental Engineering, Yangzhou Polytechnic University, Yangzhou 225127, China*
[b]*School of tropical eco-environment protection, Hainan tropical Ocean University, Sanya city 572022, China, Tel. +86 898 8865 1738 Fax +86 898 8865 1738, email: xujie_lu@163.com (X. Lu)*

Received 1 April 2018; Accepted 18 October 2018

ABSTRACT

In order to investigate treatment effects of ultra filtration membranes (UF) fouling by combined PAC treatment, two sets of processes were constructed: UF and powdered activated carbon (PAC) + UF. The efficiency of the treatment schemes was evaluated in terms of organic matter, ultraviolet absorbance at 254 nm (UV_{254}), turbidity removal as well as chemical oxygen demand (COD_{Mn}). The foulants were evaluated using Fourier transform infrared spectroscopy (FTIR) analysis. Micro-polluted surface water was treated using powdered activated carbon-ultra filtration membrane. The results showed that the removal rate of turbidity, UV_{254} and COD_{Mn} reached 91.7%, 84.9% and 77.5% respectively. Membrane fouling in ultra filtration membrane is attributable to proteins and humus. These materials deposit onto the membrane surface and into the membrane pores, clogging the pores, and leading to a decline in the permeability of the membrane. The trans-membrane pressure(TMP)can be recovered by chemical cleaning. It is evidenced that combined PAC technology could better enhance the rejection of contaminants and alleviate UF fouling.

Keywords: Micro-polluted water; Powdered activated carbon; Ultra filtration membrane; Membrane fouling

1. Introduction

As one of the most promising and attractive drinking water and wastewater treatment techniques, ultra filtration (UF) is widely applied in drinking water treatment [1–3], which has a wide application prospect in micro-polluted surface water treatment. Membrane fouling is one of the most important considerations in the design and operation of membrane systems as it affects pretreatment needs, cleaning requirements, operating conditions, cost and performance [4–11]. Membrane fouling is caused by particles, organic matter and microorganisms, resulting in decreased water production flux, increased cleaning costs, reduced life of ultra filtration membrane. Large molecular weight (MW) organic matter such as proteins and polysaccharides can induce significant membrane fouling [1,12]. Hydrophilic biopolymer is applied in drinking water supply, and a clear correlation between the concentrations of biopolymers and membrane fouling was observed for surface waters in Japan [13,14].

Powdered activated carbon (PAC) has been successfully used in conjunction with membrane ultra filtration (UF) to reduce taste, odour, colour and other concerns caused by organic material present in raw drinking water sources. PAC addition also typically significantly reduces the extent of fouling in hybrid PAC/UF systems [15–21].

Therefore, the objectives of this study were as follows: (1) to investigate treatment effects of two kinds of hybrid membrane systems; the efficiency of the treatment system was evaluated in terms of organic matter, UV_{254}, turbidity removal as well as COD_{Mn} and (2) to analyze

---

*Corresponding author.

preliminarily membrane fouling mechanism of combined process.

2. Materials and methods

2.1. Model raw water

Sample water was employed in the tests in order to simulate micro-polluted surface water and to provide sample consistency and reproducibility throughout the period of membrane operation (~60 d). The sample was prepared by adding an amount of domestic sewage effluent to tap water at a ratio of 1:50 (V/V), and 5 mg/L, Suwannee River Humic Acid (2S101H, International Humic Acid Substance Society, USA). The addition of domestic sewage effluent and humic acid provided organic matter and microorganisms which are expected to be representative of those found in surface waters. Prior to mixing with domestic sewage effluent and humic acid solution, the tap water was left over night to ensure the complete decay of residual chlorine. The characteristics of the model raw water are presented in Table 1. The temperature of sample water was maintained constant level of 20 ± 2°C during the experimental period.

2.2. Experimental process and materials

As shown in Fig. 1, a schematic of combination experimental process was as was followed: System-A for the traditional treatment process + ultra filtration, System-B for the traditional treatment process + PAC/UF.

Table 1
Water quality of raw water

Turbidity (NTU)	0.98–3.5
UV254 (cm^{-1})	0.031–0.071
COD Mn (mg/L)	3.11–5.95
pH	7.16–7.36
Temperature (°C)	22–28

The process includes a coagulation device, filter device, adsorption device, ultra filtration components, aeration device and other major components. Ultra filtration membrane transmembrane pressure (TMP) was collected and continuously recorded by the pressure sensor. In the combination experimental process, the effective volume of the coagulation tank was 60 L. The polymerization of aluminum chloride was used as a coagulant with a set optimum dosage of 5 mg/L, corresponding to a near zero zeta potential of the resulting floc. The aluminum chloride was added into the rapid mixing units for 30 s, after which model raw water pumped into slow mixing units for 30 s. The flow then passed into the adsorption pool of PAC, stirring for 40 min and precipitating for 4 h. The liquid level in the ultra filtration membrane filter remained constant by a liquid level controller. The effective volume of the ultra filtration membrane filter was 2.5 L. The aeration rate was 0.28 m^3/h. Membranes were operated at a pressure of 160 kPa. A constant flux of 150 L/(m^2 h) was maintained using a peristaltic pump during the filtration.

The hollow fiber membrane produced by Scinor Water Technology Co., Ltd. was used in this test, which is made of polyvinylidene fluoride (PVDF); the average pore size being 0.01 µm. The size of wood-based powder activated carbon was 200 meshes and the adsorption value of methylene blue was 9.8 mL, dosing 5 L each time.

2.3. Analytical methods

For the analytical protocol, Chinese State Environmental Protection Agency Standard Methods were followed [22]. Turbidity was measured using a commercial turbidimeter (Hach 2100, USA). Ultraviolet absorbance at 254 nm (UV_{254}) was determined by the colorimetric methods using the spectrophotometer (T6 New Century, Beijing, China). Chemical oxygen demand was measured by the potassium permanganate ($KMnO_4$) oxidation method. The TMP was measured by using a pressure sensor and was continuously recorded by the automatic control system. Ultra filtration membrane surface was analyzed by means of Fourier transform infrared spectroscopy (FTIR) technology.

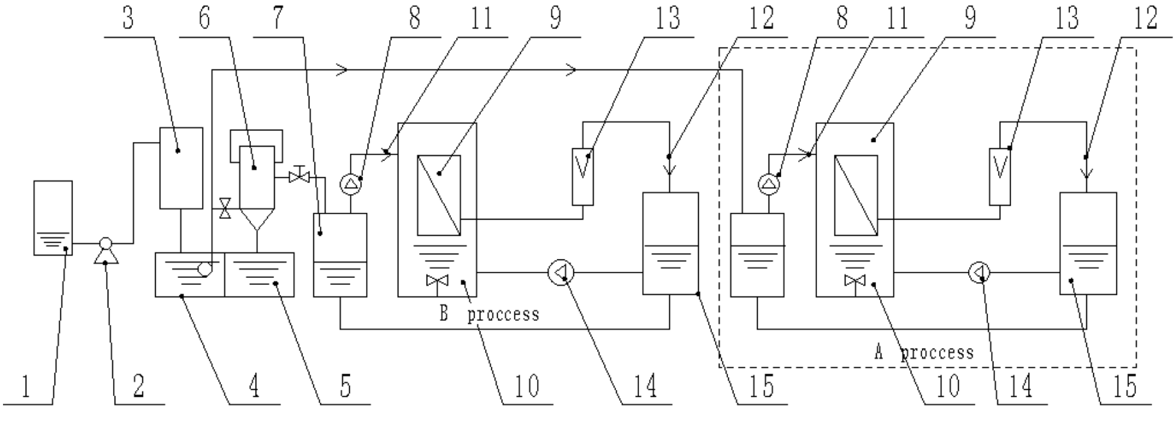

Fig 1. Schematic of combination experimental process. (1) Raw water tank (2) feed pump (3) traditional treatment process (4) water storage tank (5) water storage tank (6) PAC adsorption pool (7) water storage tank (8) pressure pump (9) ultra filtration membrane (10) air blower (11) influent of ultra filtration membrane (12) effluent (13) flow meter (14) backwash pump (15) producing water tank.

3. Results and discussion

3.1. Turbidity variation

The variation of turbidity within the two groups of combined processes was explored to understand removal efficiency of turbidity for micro-polluted surface water. The results are shown in Fig. 2. For the first phase, the lower initial turbidity removal and gradual decrease indicated that the particles were difficult to remove from the system. It is suggested the greater cohesiveness and adhesion to the membrane surface is partly caused by the existence of fouling materials. The average turbidity in the influent is 1.78 NTU in systems A and B, the turbidity of effluent fluctuated greatly and stabilized after a while. In A system, the average turbidity of the effluent was 0.31 NTU and the removal rate was 82.4%. In system B, the average turbidity in the effluent was 0.15 NTU, and the removal rate was 91.7%. The removal of turbidity in system B was slightly better than that of system A. Both of the average turbidities in the effluent were lower than the requirements of the "drinking water sanitary standard"(the water turbidity is less than 1.00 NTU). It was found that the turbidity of the effluent was almost not affected by the turbidity of raw water. It was evident that the removal of turbidity from micro-polluted water in the ultra filtration system was ideal, while a traditional process + ultra filtration combination process for the removal of organic matter is not ideal.

3.2. UV_{254} variation

As shown in Fig. 3, UV_{254} removal in each system is displayed. In the raw water, UV_{254} absorbance varied from 0.031–0.071 cm^{-1}, the average value being 0.048 cm^{-1}. In A system, the average UV_{254} of the effluent was 0.027 cm^{-1} and the removal rate was 43.1%. In B system, the average UV_{254} in the effluent was 0.007 cm^{-1} and the removal rate was 84.9%. UV_{254} removal showed a tendency to a relatively higher efficiency in B system. Because UV_{254} is an indicator of aromatic and unsaturated double-bond organic components [23], it is preferentially adsorbed by activated carbon but difficult to be removed by the ultra filtration membrane. It also explained that the removal effect of dissolved organic matter is not ideal by means of an ultra filtration membrane alone.

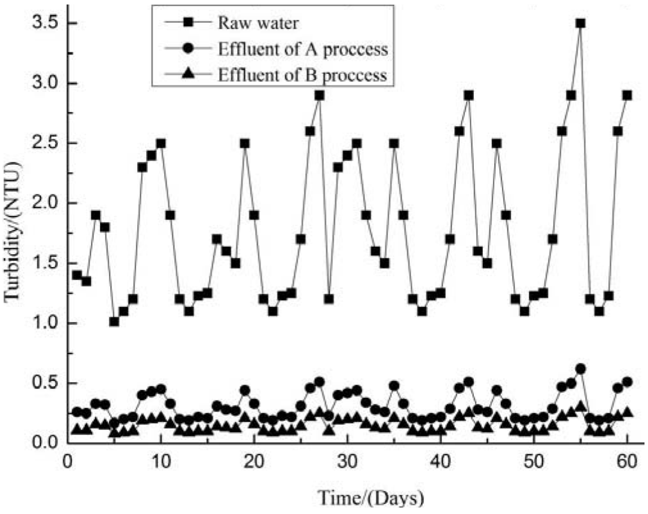

Fig. 2. Removal characteristics of turbidity.

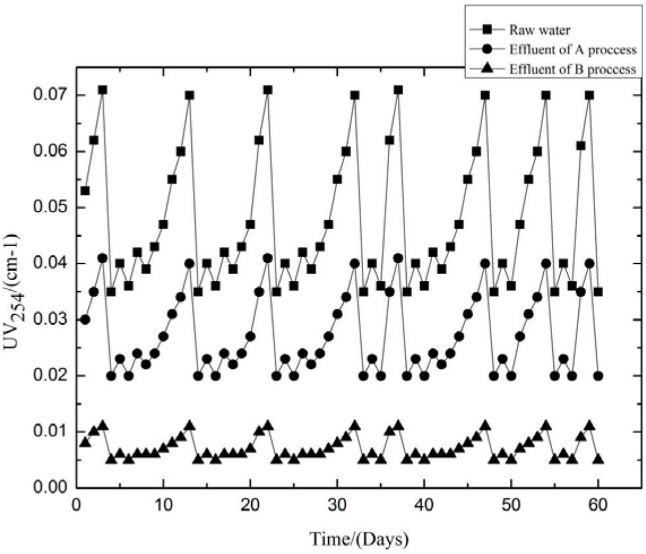

Fig. 3. Removal characteristics of UV_{254}.

3.3. Variation of COD_{Mn}

COD_{Mn} is a measure of the reductive substances which can be oxidized by $KMnO_4$, and it is widely accepted as a surrogate parameter for the total organic matter in the micro-polluted water. There was significantly COD_{Mn} removal difference between the two kinds of studied systems (Fig. 4.). In the raw water, COD_{Mn} concentration varied from 3.11 to 5.95 mg/L, the average value was 3.99 mg/L. In A system, the average COD_{Mn} value of the efflu-

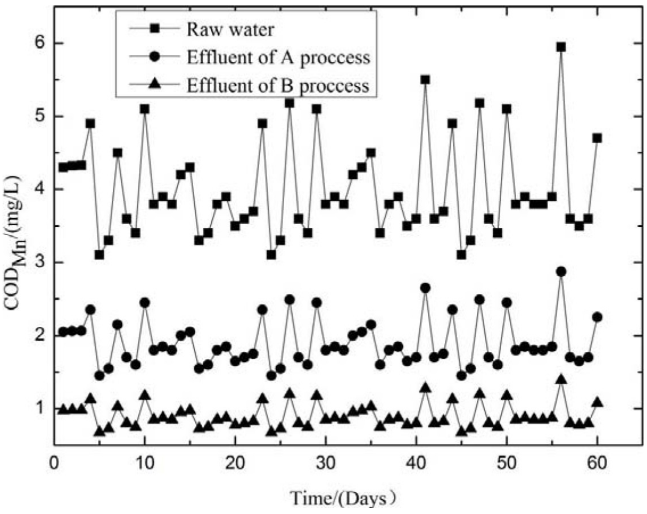

Fig. 4. Removal characteristics of COD_{Mn}.

ent was 1.89 mg/L and the removal rate was 52.5%. While in B systems, the average COD_{Mn} value of the effluent was 0.90 mg/L and the removal efficiency was as high as 77.5%. Both average COD_{Mn} in the effluent were relatively low, which is lower than requirements of the "drinking water sanitary standard" (the water COD_{Mn} is less than 3.00 mg/L). COD_{Mn} removal showed a similar tendency as that of UV_{254}, however, with a relatively lower efficiency in A system.

3.4. FTIR analysis of ultra filtration membrane

FTIR was used to investigate the internal foulants as well as the colloidal and dissolved matter in the external foulants.

In the paper, the mixed solution of 364.6 mg/LHCl+ 1000 mg/L NaClO was used as a cleaning agent to clean the polluted ultra filtration membrane in this study. FTIR analysis of the ultra filtration membrane is shown in Figs. 5a, b, c. Curves a, b and c represent the new membrane, fouling membrane and the membrane after cleaning, respectively. Fig. 5b shows a new absorption peak of humic acid at 3431 cm^{-1}, showing that the contaminants at this site are humic acids. At 2920 cm^{-1}, saturated hydrocarbon CH_2 anti-symmetrical vibration has been strengthened by means of cleaning, the peak almost recovered. The carbon-nitrogen double bond of the new amino compound appeared at 1645 cm^{-1}; Because the protein was hydrolyzed by the amino acid compound, the absorption peak at 1645 cm^{-1} should represent a protein or protein substances; By cleaning, the peak has been weakened. The absorption peak of humic acid appeared at 1404 cm^{-1}, indicating that the pollutant is also humic acid at 1404 cm^{-1}. The chloroaniline substances can be seen at 1182 cm^{-1} in Fig. 5. So, it could be concluded that proteins and humic substances played a major role in membrane fouling. Although the foulants consisting of proteins may also originate from natural organic matter (NOM) in the feed water, it is believed that a large proportion of these substances could be derived from microorganisms in the reactor. Proteins are reported to be important metabolic products of bacteria in both water and wastewater treatment systems. Therefore, the more severe membrane fouling observed in the UF can be associated with the proteins from biological resources and humic substances from NOM. Consequently, during the operation of the PAC-UF, the deposition of proteins and humic substances should be controlled by optimizing the operational conditions to minimize membrane fouling [24–30]. The results also indicated that chemical cleaning mainly removes organic pollutants, microbial pollution: such as humus, protein, etc. from membrane surface and membrane holes.

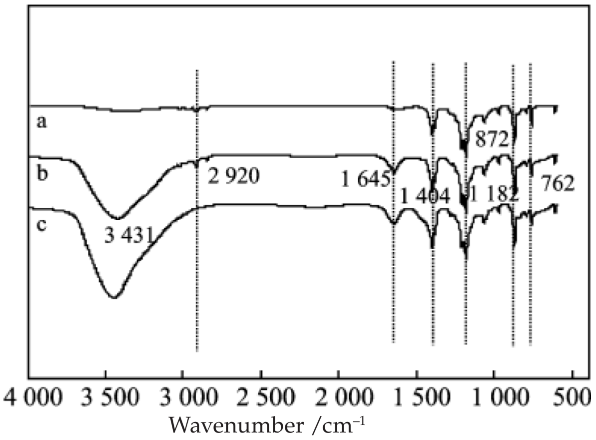

Fig. 5. FTIR analysis of ultra filtration membrane.

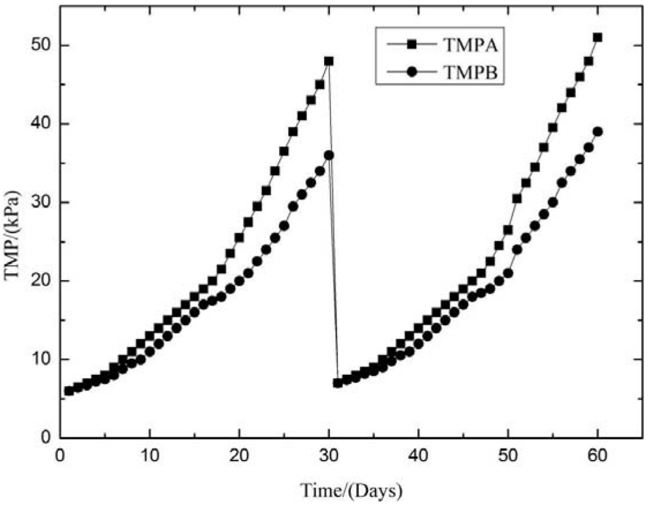

Fig. 6. Variation of TMP.

3.5. Variation of TMP

Membrane fouling was evidenced by the trans-membrane pressure (TMP) at a constant pumping flux. The increases in TMP during the membrane filtration are shown in Fig. 6. For the first phase of operation (up to 30 d), the TMP of the A system gradually increased to 48.3 kPa. The daily average growth rate was1.46 kPa/d. While the B system displayed less TMP increase, the daily average growth rate was 1.03 kPa/d. The results indicated that PAC prevented the development of membrane fouling that was observed in hybrid PAC/UF systems. This maybe a consequence of reduction of soluble protein and polysaccharide and delay increase of film filtration pressure. At the later running stage (up to 20 d), A sudden increase in the TMP (TMP jump) was observed (the slope of the transmembrane pressure became larger). This TMP jump could be ascribed to inhomogeneous fouling and cake compression during filtration. The TMP evolution of the hybrid PAC/UF systems was largely similar to that of UF for micro-polluted surface water treatment. Chemical cleaning was performed during the period of operation (by 364.6 mg/L + 1000 mg/L NaClO). At day 31, the TMP of the cleaned ultra filtration membrane was greater than that of the new membrane. The TMP basically can be restored, and the effect of cleaning is good. During the second phase of testing, the TMP increased in both systems as a consequence of irreversible contamination of the membrane surface. The results indicated that the combination of PAC adsorption in the hybrid UF process further enhanced the alleviation of total membrane fouling compared with the use of only UF process.

4. Conclusion

In this study, two sets of processes were constructed to investigate treatment effects of UF fouling by combined PAC treatment. Based on this study, the following conclusions may be drawn:

The values of effluent reach the requirements of the "Sanitary Standard for Drinking Water Plant ". The removal rates of turbidity, UV_{254} and COD_{Mn} reached 90.9%, 84.6% and 77.5%, respectively. It was evident that the removal of pollutants from micro-polluted water in hybrid PAC/UF systems is ideal, while a traditional process+ ultra filtration combination process for the removal of pollutants is not ideal. On the other hand, the main pollutants on the surface of the ultra filtration membrane are proteins and humic substances, which played a major role in membrane fouling. The TMP can be recovered by chemical cleaning. It is evidenced that combined PAC technology could better enhance the rejection of contaminants and alleviate UF fouling.

Overall results indicate that the hybrid PAC/UF systems is proved to be another promising option for the removal of pollutants from micro-polluted water.

Acknowledgements

This research was supported by 2017 middle-aged and young Academic Leaders of "Cyanine Engineering" in Jiangsu Province, 2016 Academic Leaders of "333 Project" in Jiangsu Province, the practice innovation training program projects for the Jiangsu College students in 2017 (NO: 201711462005Y), Natural science fund project of Yangzhou (NO: YZ2015102) and Yangzhou university-enterprise cooperation projects (NO: YZ201626B).

References

[1] J. Hu, R. Shang, H. Deng, S.G. Heijman, L.C. Rietveld, Effect of PAC dosage in a pilot-scale PAC-MBR treating micro-polluted surface water, Bioresour. Technol., 154 (2014) 290–296.

[2] S.-R. Chae, H. Yamamura, B. Choi, Y. Watanabe, Fouling characteristics of pressurized and submerged PVDF (polyvinylidene fluoride) micro filtration membranes in a pilot-scale drinking water treatment system under low and high turbidity conditions, Desalination, 244 (2009) 215–226.

[3] F. Chen, S. Peldszus, R.H. Peiris, A.S. Ruhl, R. Mehrez, M. Jekel, R.L. Legge, P.M. Huck, Pilot-scale investigation of drinking water ultra filtration membrane fouling rates using advanced data analysis techniques, Water Res., 48 (2014) 508–518.

[4] W. Yu, L. Xu, J. Qu, N. Graham, Investigation of pre-coagulation and powder activate carbon adsorption on ultra filtration membrane fouling, J. Membr. Sci., 459 (2014) 157–168.

[5] W. Yu, L.C. Campos, N. Graham, Application of pulsed UV-irradiation and pre-coagulation to control ultra filtration membrane fouling in the treatment of micro-polluted surface water, Water Res., 107 (2016) 83–92.

[6] Z. Ying, G. Ping, Effect of powdered activated carbon dosage on retarding membrane fouling in MBR, Separ. Purif. Technol., 52 (2006) 154–160.

[7] B. Wu, F. Zamani, W. Lim, D. Liao, Y. Wang, Y. Liu, J.W. Chew, A.G. Fane, Effect of mechanical scouring by granular activated carbon (GAC) on membrane fouling mitigation, Desalination, 403 (2017) 80–87.

[8] H. Wang, F. Qu, A. Ding, H. Liang, R. Jia, K. Li, L. Bai, H. Chang, G. Li, Combined effects of PAC adsorption and in situ chlorination on membrane fouling in a pilot-scale coagulation and ultra filtration process, Chem. Eng. J., 283 (2016) 1374–1383.

[9] T. Liu, Z.L. Chen, W.Z. Yu, S.J. You, Characterization of organic membrane foulants in a submerged membrane bioreactor with pre-ozonation using here dimensional excitation-emission matrix fluorescence spectroscopy, Water Res., 45 (2011) 2111–2121.

[10] C.N. Laabs, G.L. Amy, M. Jekel, Understanding the size and character of fouling-causing substances from effluent organic matter (EfOM) in low pressure membrane filtration, Environ. Sci. Technol., 40 (2006) 4495–4499.

[11] H. Huang, N. Lee, T. Young, A. Gary, J.C. Lozier, J.G. Jacangelo, Natural organic matter fouling of low-pressure, hollow-fiber membranes: effects of NOM source and hydrodynamic conditions, Water Res., 41 (2007) 3823–3832.

[12] M. Herzberg, T.Z. Rezene, C. Ziemba, O. Gillor, K. Mathee, Impact of higher alginate expression on deposition of pseudomonas aeruginosa in radial stagnation point flow and reverse osmosis systems, Environ. Sci. Technol., 43 (2009) 7376–7383.

[13] K. Kimura, T. Naruse, Y. Watanabe, Changes in characteristics of soluble microbial products in membrane bioreactors associated with different solid retention times: relation to membrane fouling, Water Res., 43 (2009) 1033–1039.

[14] K. Kimura, T. Naruse, Y. Watanabe, Micro filtration of different surface waters with/without coagulation: clear correlations between membrane fouling and hydrophilic biopolymers, Water Res., 49 (2014) 434–443.

[15] Y. Li, X. Zhang, W. Zhang, J. Wang, C. Che, Effect of powdered activated carbon on immersed hollow fiber ultra filtration membrane fouling caused by particles and natural organic matter, Desalination, 278 (2001) 443–446.

[16] H. Lin, F. Wang, L. Ding, H. Hong, J. Chen, X. Lu, Enhanced performance of a submerged membrane bioreactor with powdered activated carbon addition for municipal secondary effluent treatment, J. Hazard. Mater., 192 (2011) 1509–1514.

[17] G. Munz, R. Gori, G. Mori, C. Lubello, Powdered activated carbon and membrane bioreactors (MBRPAC) for tannery wastewater treatment long term effect on biological and filtration process performances, Desalination, 207 (2007) 349–360.

[18] C. Sheng, A.G.A. Nnanna, Y. Liu, J.D. Vargo, Removal of trace pharmaceuticals from water using coagulation and powdered activated carbon as pretreatment to ultra filtration membrane system, Sci. Total Environ., 550 (2016) 1075–1083.

[19] S. Shao, H. Liang, F. Qu, K. Li, H. Chang, H. Yu, G. Li, Combined influence by humic acid (HA) and powdered activated carbon (PAC) particles on ultra filtration membrane fouling, J. Membr. Sci., 500 (2016) 99–105.

[20] S. Shao, L. Cai, K. Li, J. Li, X. Du, G. Li, H. Liang, Deposition of powdered activated carbon (PAC) on ultra filtration (UF) membrane surface: influencing factors and mechanisms, J. Membr. Sci., 530 (2017) 104–111.

[21] A.B. Sengul, G. Ersan, N. Tufekci, Removal of intra- and extra-cellular micro cystin by submerged ultra filtration (UF) membrane combined with coagulation/flocculation and powdered activated carbon (PAC) adsorption, J. Hazard Mater., 343 (2018) 29–35.

[22] Chinese-EPA, 2002. Water and Wastewater Monitoring Methods, fourth ed. Chinese Environmental Science Publishing House, Beijing, China.

[23] Z.H. Pan, J.Y. Tian, G.R. Xu, J.J. Li, G.-B. Li, Characteristics of adsorbents made from biological, chemical and hybrid sludges and their effect on organics removal in wastewater treatment, Water Res., 45 (2011) 819–827.

[24] S. Shao, F. Qu, H. Liang, H. Chang, H. Yu, G. Li, Characterization of membrane foulants in a pilot-scale powdered activated carbon–membrane bioreactor for drinking water treatment, Process Biochem., 49 (2014) 1741–1746.

[25] J. Liu, Z. Wang, B. Dong, D. Zhao, Fouling behaviors correlating to water characteristics during the ultra filtration of micro-polluted water with and without the addition of powdered activated carbon, Colloids Surfaces A: Physicochem. Eng. Asp., 511 (2016) 320–328.

[26] Y. Li, X. Zhang, W. Zhang, J. Wang, C. Chen, Effect of powdered activated carbon on immersed hollow fiber ultra filtration membrane fouling caused by particles and natural organic matter, Desalination, 278 (2011) 443–446.

[27] K. Li, F. Qu, H. Liang, S. Shao, Z.-s. Han, H. Chang, X. Du, G. Li, Performance of mesoporous adsorbent resin and powdered activated carbon in mitigating ultra filtration membrane fouling caused by algal extracellular organic matter, Desalination, 336 (2014) 129–137.

[28] K. Li, H. Liang, F. Qu, S. Shao, H. Yu, Z.-s. Han, X. Du, G. Li, Control of natural organic matter fouling of ultra filtration membrane by adsorption pretreatment: Comparison of mesoporous adsorbent resin and powdered activated carbon, J. Membr. Sci., 471 (2014) 94–102.

[29] M.M.T. Khan, W. Jones, A. Camper, S. Takizawa, H. Katayama, F. Kurisu, S. Ohgaki, Powdered activated carbon and biofiltration improve MF performance: Part I, Membr. Technol., 2007 (2007) 7–10.

[30] W. Huang, L. Wang, W. Zhou, W. Lv, M. Hu, H. Chu, B. Dong, Effects of combined ozone and PAC pretreatment on ultra filtration membrane fouling control and mechanisms, J. Membr. Sci., 533 (2017) 378–389.