JOURNAL OF ENVIRONMENTAL SCIENCES XX (2016) XXX–XXX

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JES JOURNAL OF ENVIRONMENTAL SCIENCES

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Drinking water treatment using a submerged internal-circulation membrane coagulation reactor coupled with permanganate oxidation

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ARTICLE INFO

Article history:
Received 30 January 2016
Revised 22 August 2016
Accepted 6 September 2016
Available online xxxx

Keywords:
Membrane coagulation reactor (MCR)
Polyaluminum chloride (PACl)
Hybrid membrane process
Potassium permanganate ($KMnO_4$)
Drinking water

ABSTRACT

A submerged internal circulating membrane coagulation reactor (MCR) was used to treat surface water to produce drinking water. Polyaluminum chloride (PACl) was used as coagulant, and a hydrophilic polyvinylidene fluoride (PVDF) submerged hollow fiber microfiltration membrane was employed. The influences of trans-membrane pressure (TMP), zeta potential (ZP) of the suspended particles in raw water, and $KMnO_4$ dosing on water flux and the removal of turbidity and organic matter were systematically investigated. Continuous bench-scale experiments showed that the permeate quality of the MCR satisfied the requirement for a centralized water supply, according to the Standards for Drinking Water Quality of China (GB 5749-2006), as evaluated by turbidity (<1 NTU) and total organic carbon (TOC) (<5 mg/L) measurements. Besides water flux, the removal of turbidity, TOC and dissolved organic carbon (DOC) in the raw water also increased with increasing TMP in the range of 0.01–0.05 MPa. High ZP induced by PACl, such as 5–9 mV, led to an increase in the number of fine and total particles in the MCR, and consequently caused serious membrane fouling and high permeate turbidity. However, the removal of TOC and DOC increased with increasing ZP. A slightly positive ZP, such as 1–2 mV, corresponding to charge neutralization coagulation, was favorable for membrane fouling control. Moreover, dosing with $KMnO_4$ could further improve the removal of turbidity and DOC, thereby mitigating membrane fouling. The results are helpful for the application of the MCR in producing drinking water and also beneficial to the research and application of other coagulation and membrane separation hybrid processes.

Introduction

The deterioration of water quality is a great challenge for traditional purification processes of drinking water in achieving adequate removal of trace organic matters, toxic microbes such as *Giardia lamblia* and *Cryptosporidium tyzzer*, and the toxic organic halides produced by chlorination.

Membrane filtration has been believed to be the water treatment technique of the 21st century, and is widely applied in water treatment processes (Ang et al., 2015). Ultrafiltration

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http://dx.doi.org/10.1016/j.jes.2016.09.011
1001-0742/

Please cite this article as: Zhang, Z., et al., Drinking water treatment using a submerged internal-circulation membrane coagulation reactor coupled with permanganate oxidation, J. Environ. Sci. (2016), http://dx.doi.org/10.1016/j.jes.2016.09.011

or microfiltration can remove the microbes that are difficult to inactivate by conventional disinfection processes, such as *G. lamblia* and *C. tyzzer*, to concentrations below the specified levels (Fu et al., 2010). Additionally, these two techniques can efficiently remove natural organic matters (NOMs) and the disinfection by-product precursors of chlorination (Ang et al., 2015). The removal of turbidity and bacteria is close to 100% (Bergamasco et al., 2011; Sadr Ghayeni et al., 1999; Wang et al., 2013). The advantages of membrane filtration include low construction cost, simple operation and management, small footprint, stable permeate quality, and ease of automation. Therefore, membrane separation processes, especially ultrafiltration and microfiltration, have been considered as the best alternatives to conventional processes for drinking water purification (Doyen et al., 1998; Schäfer et al., 2001).

To improve separation efficiency and mitigate membrane fouling, membrane filtration is commonly integrated with other techniques (Ang et al., 2015; Huang et al., 2009; Jeong et al., 2014). The membrane coagulation reactor (MCR), which is a hybrid process of membrane filtration and coagulation, is a successful example (Zhang et al., 2005; Zularisam et al., 2009). Coagulation can effectively remove higher-molecular-weight fractions (>1 kDa) of organic matter such as biopolymers and humic substances (Haberkamp et al., 2007) that are membrane foulants (Huang et al., 2007; Zheng et al., 2009). Consequently, coagulation can significantly mitigate membrane fouling and improve permeate quality (Huang et al., 2009; Wray et al., 2014). Thus, the MCR has been a focus of research and application in the field of membrane filtration in recent years (Ang et al., 2015; Konieczny et al., 2006; Li et al., 2014, 2015).

Membrane material has a significant influence on the coagulation-membrane separation process. Compared to hydrophobic polypropylene, the membrane fouling of a hydrophilic polyvinylidene fluoride (PVDF) membrane was mitigated with polyaluminum chloride (PACl) as coagulant (Myat et al., 2014). Chen et al. (2015) reported that a hydrophilic PVDF membrane had a negative zeta potential (ZP) identical in electrical properties to that of the sludge foulant, which can prevent the sludge foulant from adhering to the membrane surface. Furthermore, a hydrophilic membrane is less prone to become blocked than a hydrophobic membrane in treating surface water (Jung et al., 2006).

Dosing with coagulant in a MCR will induce a change of the zeta potential of the particles in raw water. It was found that in the hollow fiber ultrafiltration (UF) process, there is a strong correlation between fouling resistance and the zeta potential of the particles in raw water, and a more negative charge density for the particles will lead to more serious fouling (Xiao et al., 2013). Therefore, it can be speculated that the zeta potential of the flocs in raw water would affect the membrane fouling in a MCR. Furthermore, the trans-membrane pressure (TMP) is a vital important operating parameter for microfiltration or ultrafiltration processes. A high TMP will lead to high water flux as well as serious membrane fouling in some cases. In addition, some studies showed that dosing with permanganate ($KMnO_4$) can mitigate membrane fouling by the pre-oxidation of organic matter (Tian et al., 2013; Yu et al., 2011). Moreover, the insoluble MnO_2 formed in the process of $KMnO_4$ reduction can also mitigate membrane fouling by adsorbing organic matter (Tian et al., 2013; Yu et al., 2011). With regard to cell-related fouling, MnO_2 particles even show a superior ability in reducing fouling than $KMnO_4$ (Qu et al., 2015). However, no report has appeared on the effects of $KMnO_4$ on the separation performance and membrane fouling in a MCR, although it can be speculated that $KMnO_4$ will play an important role.

In our previous work (Liu et al., 2016), a novel submerged internal-circulation membrane coagulation reactor was developed in order to further improve the separation performance, mitigate membrane fouling, and reduce the footprint of a conventional MCR. The submerged MCR was designed based on the theory and technology of micro-eddy vortex flocculation (Casson and Lawler, 1990; Dharmappa et al., 1993), non-linear flocculation dynamics (Adler, 1981; Han and Lawler, 1991), swirl flocculation technology (Menezes et al., 1996), and secondary flow mixing technology (Liang and Zhang, 2014; Liu et al., 2011). Its principles and application prospect have already been reported in our previous studies (Liu et al., 2016).

Aimed at promoting engineering application of the novel MCR in drinking water treatment with surface water as raw water, a systematic bench-scale study was conducted in a continuous experimental apparatus, focusing on the impacts of TMP and the zeta potentials of flocs on the water flux and the removal of turbidity and organic matter, and especially the enhancing effect of permanganate oxidation. Polyaluminum chloride (PACl) was used as coagulant and a hydrophilic polyvinylidene fluoride (PVDF) submerged hollow fiber microfiltration membrane was employed in the MCR. Some useful results were obtained for the practical application of the MCR in producing drinking water and better understanding its performance.

1. Materials and methods

1.1. Experimental materials

The raw water was drawn from the Chang River in Beijing. The Chang River is classified as a protected area for a first-class water source, with the water quality meeting the requirements for category II drinking water, as specified in the Environmental Quality Standards for Surface Water of China (GB 3838-2002). The raw water had pH of 7.70–8.56, turbidity of 11.3–53.0 NTU, ZP of −11.0 to −6.90 mV, total organic carbon (TOC) of 2.53–3.92 mg/L, dissolved organic carbon (DOC) of 1.97–3.78 mg/L and UV_{254} of 0.028–0.067 cm^{-1}. During the study period, the raw water was taken once a day and stored in the tank shown in Fig. 4 for the tests of a whole day. The quality of raw water was measured one time each day because the fluctuation of water quality was negligible.

A commercially available PACl was used as coagulant in this work. The PACl was in powdered form, with a basicity (OH/Al) of 1.44 and an Al_2O_3 content of 30%. The stock solution was obtained by dissolving PACl into deionized water, with the Al concentration of 2 mol/L. The fresh PACl solution for the tests had the Al concentration of 0.1 mol/L, obtained by diluting the stock solution one day before each batch of tests to avoid aging and maximize repeatability.

The $KMnO_4$ (AR) used in the work was produced by Sinopharm Chemical Reagent Beijing Co., Ltd.

A hydrophilic PVDF submerged hollow fiber membrane with a contact angle of 25.3° was used in the work. The membrane