Chemical Engineering Journal xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

New insight into the effect of mixed liquor properties changed by pre-ozonation on ceramic UF membrane fouling in wastewater treatment

Shengyin Tang [a,b,1], Zhenghua Zhang [a,b,1,*], Xihui Zhang [a,b,c]

[a] Tsinghua-Kangda Research Institute of Environmental Nano-Engineering & Technology, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, Guangdong, China
[b] School of Environment, Tsinghua University, Beijing 100084, China
[c] Environmental Science and Technology Laboratory, Tsinghua-Berkeley Shenzhen Institute, Shenzhen 518055, Guangdong, China

HIGHLIGHTS

- The mixed liquor membrane filterability is enhanced by pre-ozonation (⩽5 mg/L).
- Intermediate blocking is the main membrane fouling during filtration.
- The maximum TMP reduction is achieved at an intermediate ozone dosage of 5 mg/L.
- Severe cell lysis and membrane fouling happen at high ozone dosages (⩾10 mg/L).
- The permeate water quality is better after pre-ozonation (⩽5 mg/L).

ARTICLE INFO

Article history:
Received 22 October 2016
Received in revised form 6 December 2016
Accepted 8 December 2016
Available online xxxx

Keywords:
Mixed liquor
Wastewater treatment
Pre-ozonation
Ceramic membrane
Membrane fouling

ABSTRACT

The effect of mixed liquor properties changed by ozonation especially with high dosages on membrane fouling is very complex and remains unclear. In this study, the effect of mixed liquor properties changed by ozonation especially with high dosages on ceramic ultrafiltration (UF) membrane fouling in wastewater treatment and the corresponding mechanism were systematically studied by characterization of the mixed liquor properties, hydraulic performance, the fouling layers and modeling at different ozone dosages (0, 2, 5, 10 mg/L). The membrane filterability of the mixed liquor after pre-ozonation (⩽5 mg/L) was enhanced and the corresponding membrane fouling was mitigated. After pre-ozonation, activated sludge had the better settleability and larger floc size. Meanwhile, there was a remarkable reduction of dissolved organic carbon (DOC), soluble microbial products (SMP) and extractable extra-cellular polymeric substances (EPS) after pre-ozonation and the removed organics were mainly belonged to the high molecular weight (MW) (1–10 kDa) and very high MW (10–200 kDa) substances. Intermediate blocking was the main membrane fouling during the mixed liquor filtration process and the best fouling mitigation performance was achieved for the sample with an intermediate ozone dosage of 5 mg/L (1.7 mg-ozone/g-mixed liquor suspended solids (MLSS)). Meanwhile, the water quality of permeate was even better after pre-ozonation (⩽5 mg/L) with the lower DOC and total nitrogen (TN) concentrations. Severe cell lysis occurred with the significant increase of the released organics in the mixed liquor and the activated sludge had smaller floc size and worse settleability when the pre-ozonation dosage was above 10 mg/L, which in turn resulted in the deteriorated membrane fouling control performance.

1. Introduction

Ultrafiltration (UF) membrane is increasingly utilized as an advanced tertiary process to continuously separate the activated sludge from the secondary biological treated effluent in wastewater treatment plants, especially the state-of-the-art membrane bioreactor (MBR) technology [1]. Even though UF membrane has several advantages such as high performance of contaminant removal, small footprint, membrane fouling is still a big concern during the applications especially in wastewater treatment [2]. Cake layer, gel layer and pore blocking are the three typically contributors to membrane fouling in wastewater treatment [3] with major foulants of biomass flocs mainly responsible for cake layer formation, soluble microbial products (SMP) and extractable

* Corresponding author at: Tsinghua-Kangda Research Institute of Environmental Nano-Engineering & Technology, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, Guangdong, China.
E-mail address: zhenghua.zhang@sz.tsinghua.edu.cn (Z. Zhang).
[1] These are the co-first authors.

http://dx.doi.org/10.1016/j.cej.2016.12.032
1385-8947/

Please cite this article in press as: S. Tang et al., New insight into the effect of mixed liquor properties changed by pre-ozonation on ceramic UF membrane fouling in wastewater treatment, Chem. Eng. J. (2016), http://dx.doi.org/10.1016/j.cej.2016.12.032

Nomenclature

DOC	dissolved organic carbon	SYBR	N′,N′-dimethyl-N-[4-[(E)-(3-methyl-1,3-benzothiazol-2-ylidene)methyl]-1-phenylquinolin-1-ium-2-yl]-N-propylpropane-1,3-diamine
EEM	fluorescence excitation-emission matrix spectra	SV_{30}	sludge volume after 30 min sedimentation
EPS	extractable extra-cellular polymeric substances	SVI_{30}	sludge volume index after 30 min sedimentation
HMWS	high molecular weight substances	TMP	transmembrane pressure
MW	molecular weight	TN	total nitrogen
MLSS	mixed liquid suspended solids	UF	ultrafiltration
MLVSS	mixed liquid volatile suspended solids	ΔTMP	normalized TMP increase
PI	propidium iodide		
SMP	soluble microbial products		

extra-cellular polymeric substances (EPS) mainly responsible for gel layer formation and pore blocking [4–10].

In order to effectively control membrane fouling in wastewater treatment, various approaches have been adopted such as coagulation [11–17], flocculation [18,19], adsorption [20,21], stabilization [22,23]. As a powerful oxidant, ozone can efficiently break down and/or minimize the high molecular weight (MW) organics and thus mitigate membrane fouling [24]. For instance, ozonation with low dosage (0.25 mg-ozone/g-MLSS ~ 2.5–3.1 mg/L ozone) has been used to improve the polymeric membrane filterability of the mixed liquor and mitigate membrane fouling in a long-term MBR [25,26]. However, there is a high risk for the combined process of polymeric membrane and ozonation as the dissolved ozone and the resultant hydroxyl radicals would oxidize and destroy the polymeric membrane. As such, low ozone dosage was usually used in the integration process of ozonation and polymeric membrane. Ceramic membrane, however, can withstand the presence of ozone and the resultant hydroxyl radicals in the same tank even at high ozone dosage with its robust chemical stability. In our previous studies, we have successfully applied an integrated process of ozonation (2–15 mg/L) and ceramic UF membrane in the treatment of drinking water [27,28] and algal-rich water [29,30] with the results showing that ozonation could effectively mitigate membrane fouling under certain conditions.

Meanwhile, the effect of mixed liquor properties changed by ozonation especially with high dosages on membrane fouling is more complex and remains unclear. Ozonation may change the size and structure of the biological flocs resulting in membrane fouling mitigation, while it may also convert cell bound EPS to free/dissolved EPS leading more severe membrane fouling. For instance, the re-flocculation of flocs occurred after ozonation and the membrane filterability of the mixed liquor was enhanced, which facilitated membrane fouling mitigation in a long-term MBR [25,26]. However, ozonation also inactivated bacterial and/or caused cell lysis with the release of EPS into the mixed liquor and thus leading more severe membrane fouling during filtration [29,30].

In this study, the effect of mixed liquor properties changed by ozonation especially with high dosages on ceramic UF membrane fouling in wastewater treatment and the corresponding mechanism were systematically studied by characterization of the mixed liquor properties, hydraulic performance, the fouling layers and modeling at different ozone dosages (0, 2, 5, 10 mg/L).

2. Materials and methods

2.1. Pre-ozonation treatment

In this study, the mixed liquor was sampled from the aerobic tank of Luofang Wastewater Treatment Plant in Shenzhen with its mixed liquid suspended solids (MLSS) concentration of 2.9 ± 0.5 g/L. Ozone was produced from ultra-pure oxygen by an ozone generator and more details can be found in our very recent papers [29,30]. Pre-ozonation of 30 L mixed liquor was conducted before the filtration tests with different gaseous ozone concentrations of 0, 2 (0.68 mg-ozone/g-MLSS), 5 (1.7 mg-ozone/g-MLSS) and 10 mg/L (3.4 mg-ozone/g-MLSS).

2.2. UF filtration tests

Fig. 1 shows the schematic diagram of the filtration experiment with the integrated process of pre-ozonation and ceramic UF membrane. The cubic plexiglass membrane tank has an inner dimension of 250 mm × 80 mm × 500 mm (length × width × height) with a flat sheet Al_2O_3 ceramic membrane (active area of 0.0425 m^2, average pore size of 100 nm and the dimension of 120 mm (length) × 9 mm (width) × 280 mm (height) (Fig. S1) (Meidensha Corporation, Japan) vertically fixed in the membrane tank. More details about the setup of the filtration experiment can be found in our very recent papers [29,30]. Normalized TMP (ΔTMP) (the gap between the final TMP and the initial baseline) was used here to indicate the fouling control performance.

To facilitate a meaningful comparison of the effect of pre-ozonation (0, 2, 5 and 10 mg/L) on membrane fouling control, four filtration experiments with the identical setup and operating conditions were run at the same time. Four membrane tanks were respectively seeded with 8 L mixed liquor from the pre-ozonation treated 30 L mixed liquor with four different ozone dosages and the pre-ozonation treated mixed liquor were fed continuously to the corresponding tank during the filtration experiment. Each membrane tank was equipped with a stirrer with the same stirring speed (1800 rpm) to distribute the mixed liquor homogeneously. No aeration was performed for each membrane tank as aeration would change the properties of mixed liquor [25] and thus affect the comparison of membrane fouling control performance by pre-ozonation. All experiments were conducted at a same protocol with a constant filtration flux of 30 L/m^2·h (subcritical flux), an intermittent mode for pump with on/off ratio of 9 min: 1 min, and a running period of 3.08 h. After the filtration experiment, the fouled membrane was then cleaned following two steps: 1) rinsed by 100 mL Milli-Q water (physical cleaning for hydraulically reversible fouling); and 2) soaked in 500 mL NaClO solution (1000 ppm available chlorine) for 12 h followed by soaking in 500 mL citric acid solution (1000 ppm) for 12 h (chemical cleaning for hydraulically irreversible fouling). The size fractionated (⩽0.45 μm) physical cleaning solution was analyzed for dissolved organic carbon (DOC), protein, polysaccharide, fluorescence excitation–emission matrix (EEM) and MW distribution. The size fractionated (⩽0.45 μm) chemical cleaning solution was analyzed for DOC only (as NaClO has the effect on the other tests). All experiments were operated at room temperature of 18-20 °C and run in duplicate.