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Ozonation pretreatment for ultrafiltration of the secondary effluent

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Abstract

In this study the effect of preozonization of the secondary effluent on the fouling of ultrafiltration membranes was investigated. The results showed that preozonization could effectively improve the biodegradability of secondary effluent, the apparent molecular weight distribution (AMWD) of organic substances in water was different in different ozone contact time, the AMWD of organic substances had great influence on membrane resistances, blocking and cake layer resistances had controlling force over fouling resistance. The following was the relationship between AMWD of organic substances and membrane resistances: (i) when $d/\varphi < 2/15$ (d: molecular weight of the organic substances in water, φ: membrane pore size), organic substances could easily permeate membrane pore, and when $2/15 < d/\varphi < 1/3$, organic substances tended to be adsorbed inside of membrane pore; (ii) when $1/3 < d/\varphi < 1$, organic substances mainly caused interior membrane pore blocking, and when $1 < d/\varphi < 5/3$, organic substances mainly caused the block in membrane surface; (iii) when $d/\varphi < 1$, especially when $d/\varphi < 5/3$, organic substances mainly formed membrane surface cake.

Keywords: Preozonization; Apparent molecular weight distribution; Membrane resistance; Fouling; Secondary effluent

1. Introduction

Membrane processes are widely considered for application in water and wastewater treatment, and show irreplaceable advantages, such as low energy cost, low capital investment, relatively uncritical scale-up and high throughput while maintaining product purity under ambient conditions [1–3]. Though membrane can effectively remove organic and inorganic pollutants in water, the low permeability caused by membrane fouling has become one of the central subjects in the wide application of membrane separation technology [4,5]. The previous study results showed that the organic substances are one of the main reasons causing membrane fouling, and cake layer on membrane surface is mainly produced by organic substances with high molecular weight (MW) [6–8]. Therefore, the characteristics of AMWD have great influence on the membrane filtration process that takes mechanical screening as a main mechanism [4–6].

Ozone is a powerful oxidant that preferentially oxidizes electron rich moieties containing carbon–carbon double bonds and aromatic alcohols [9]. It can break the structure of natural organic matter (NOM) and enhance the transformation of higher molecular weight compounds into lower MW ones, such as carboxylic acids, hydrophilic acids, carbohydrates, amino acids, etc. [10,11]. Upon ozonation of NOM, the total organic carbon (TOC) was either reduced, or unchanged [11]. It oxidizes the NOM that is believed to be largely responsible for the fouling of membranes [9,10].

In this study the secondary effluent was used as raw water, and the influence of AMWD of organic substances in water on membrane resistance was examined. Preozonization was carried out to vary AMWD in water and the optimal treatment time was investigated. Then, ultrafiltration was adopted as post-treatment process unit and the influence of AMWD of organic substances in water on membrane resistances was discussed.

2. Materials and methods

2.1. Raw water quality

Table 1 showed raw water quality, the water was from the secondary effluent of Bei-Shiqiao Wastewater Purification Center in Xi'an city.

Abbreviations: AMWD, apparent molecular weight distribution; MWCO, molecular weight cut-off; MW, molecular weight; NOM, natural organic matter; TOC, total organic carbon; UV_{254}, ultraviolet absorbance at 254 nm; COD, chemical oxygen demand; BOD, biochemical oxygen demand

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Table 1
The raw water quality

Item	Value
COD (mg/L)	10.8–41.2
BOD_5 (mg/L)	6–12
TOC (mg/L)	8–10
UV_{254} (cm^{-1})	0.106–0.163
Suspended solids (SS) (mg/L)	10–20
Turbidity (NTU)	4–20

2.2. Experimental apparatus

Fig. 1 showed the ozone pretreatment set-up in this study, consisting of an ozone generator (CF-G-3-005G, QingDao GuoLin), a static reactor (500 mL), an air pump and a tail gas absorption flask with potassium iodide inside. Air was used as material gas, the flux of air was 1 L/min, and the ozone production measured was 20 mg/min. The dose of ozone was controlled through adjusting ozone contact time, and the ozone contact time was 1, 5, 10 and 20 min, respectively.

Fig. 2 showed the UF experiment set-up, consisting of a N_2 pressure cylinder, membrane filtration equipment (SCM cup-shaped stirred cell, Institute of Physics, Chinese Academy of Sciences), an electronic balance, and a personal computer with data acquisition units. The effective membrane filtration area was 3.32×10^{-3} m^2, filtration pressure was 100 kPa, the flux was continuously measured by the electronic balance. By using this UF experiment set-up, polyethersulfone (PES) UF membranes whose molecular weight cut-off (MWCO), respectively, were 50, 30, 10 and 4 kDa were adopted to classify and separate AMWD of organic substances in water. Water samples were first filtrated through 0.45 μm filter whose material was cellulose acetate, the filtrates were then subject to membrane processing to be separated into several groups that contain organic substances of different AMWD ranges. Filtrates were analyzed for TOC and ultraviolet absorbance at 254 nm (UV_{254}). TOC was analyzed with a total organic carbon analyzer (TOC-5000A, Shimadzu). UV_{254} was measured with a spectrophotometer (UV 2100, Shimadzu).

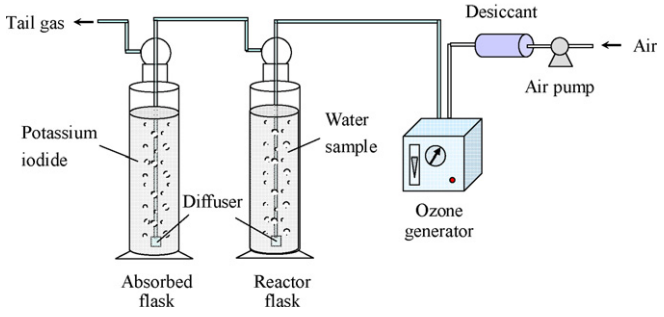

Fig. 1. Schematic diagram of the ozone pretreatment set-up.

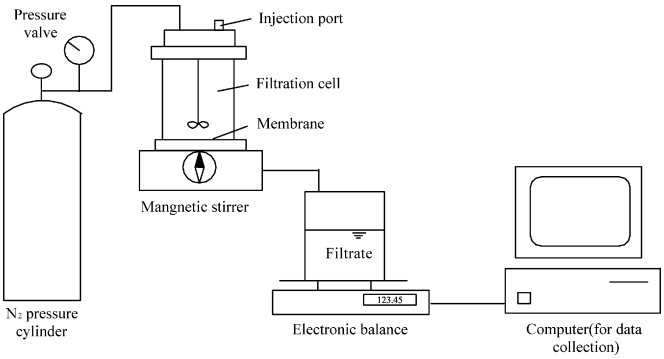

Fig. 2. Schematic diagram of the UF experiment set-up.

2.3. Methods to measure UF membrane resistances

In this study UF membrane resistances were divided into intrinsic resistance R_m, adsorption resistance R_a, surface cake layer resistance R_c, interior blocking resistance R_g, and concentration polarization resistance R_{cp}. The sum of R_a, R_c, R_g, and R_{cp} was defined as the fouling resistance marked R_f, that is, $R_f = R_a + R_c + R_g + R_{cp}$. The resistances were calculated by using Darcy's equation:

$$J = \frac{\Delta P}{\mu(R_m + R_f)} \quad (1)$$

where J is membrane flux (m^3/m^2 s); ΔP is the transmembrane pressure (Pa); μ is the water viscosity coefficient (Pa·s) and R_f is the membrane fouling resistance (m^{-1}).

In this experiment, the flat polyvinylidenefluoride (PVDF) UF membranes (MWCO was 30 kDa) were used to determine the resistances. The steps were stated as follows:

(1) Pure water flux of a membrane was determined, and R_m was calculated.
(2) Soak the above used membrane into water sample, 24 h later pure water flux of the membrane was determined, and $R_m + R_a$ was calculated.
(3) Soak the membrane into the water sample again, another 24 h later the membrane flux when filtrating water sample was determined and $R_m + R_a + R_c + R_g + R_{cp}$ was calculated.
(4) Then, the pure water flux of the membrane was determined, and $R_m + R_a + R_c + R_g$ was calculated.
(5) After the matter attached in membrane surface was washed, the pure water flux of the membrane was determined, and $R_m + R_a + R_g$ was calculated.
(6) Based on the above steps, R_m, R_a, R_c, R_g, R_{cp} and R_f could be calculated.

3. Results and discussion

3.1. Effect of ozonization on TOC content

Fig. 3 showed that TOC of secondary effluent changed with ozone contact time. The results indicated that TOC of secondary effluent was reduced with the increasing of ozone contact time. TOC concentration was from 9.44 to 4.7 mg/L, and the removal rate reached 50.2%. This was due to that ozone oxidized some organic substances into H_2O and CO_2. When ozone contact time was within 1 min and in the range of 1–5 min, the removal rates of