Study on the Effect of Membrane Active Surface Orientation in OMBR on Norfloxacin Wastewater Treatment

Xiaoqing Chen and Litong Cai

***Abstract*—The forward osmosis membrane bioreactor (OMBR) is a kind of new treatment technology which applied forward osmosis technology to the membrane bioreactor. In this paper, the OMBR was adopted to tackle with the typical antibiotic wastewater.The influence of orientation was investigated. The results showed that the magnesium chloride solution with high osmotic pressure is advantageous for OMBR due to its superior membrane flux and a better producing water quality and the membrane flux decreases with a rise of the concentration of sewage and sludge. In this condition, the removal rate of COD and norfloxacin is 84.21% and 93.70%, respectively.**

***Index Terms*—Forward osmosis technology, antibiotic wastewater, treatment technology, membrane flux.**

I. Introduction

With the continuous development of China's pharmaceutical industry and the increase in human demand for antibiotics, the discharge of pharmaceutical wastewater is also increasing day by day, and the discharge of antibiotic wastewater is also gradually increasing [1]. The pollution problem of antibiotics in water is serious. Antibiotics are often detected in different water samples and have high concentrations, which exert a serious impact on human health and environmental organisms.

At present, the main technologies for the removal of antibiotic wastewater at home and abroad include biological treatment, physical and chemical treatment, but they all have limitations. Therefore, how to treat antibiotic wastewater efficiently, reasonably and economically is a problem that needs to be solved urgently [2]-[5]. Forward osmosis (FO) refers to a membrane separation process that does not require external pressure and is driven only by the osmotic pressure of the solution [6]. The forward osmosis membrane bioreactor (OMBR) combines the retention effect of the forward osmosis membrane and the biodegradation of activated sludge to achieve high-efficiency treatment of wastewater. However, there are few studies on OMBR wastewater treatment effects and specific operating parameters.

This article applies the forward osmosis membrane bioreactor to the advanced treatment of the typical antibiotic norfloxacin wastewater [7]. Through single factor experiments to investigate the effect of membrane active surface orientation on forward osmosis membrane flux and wastewater treatment, optimize its process conditions, and provide theoretical basis and practical reference for antibiotic wastewater treatment.

Manuscript received October 25, 2021; revised November 5, 2021. Project supported by the Educational Research Projects for Middle-aged and Young Teacher of Fujian Province, China (Grant No. JT180454), and Research Support of Xiamen University of Technology (Grant No. E201300400).

The authors are with School of Environmental Science & Engineering, Xiamen University of Technology, Xiamen, 361024, China (e-mail: chenxq@xmut.edu.cn, 1260036772@qq.com).

II. Experiment

The device of the forward osmosis membrane bioreactor is shown in Fig. 1. This device mainly includes forward osmosis components, draw liquid and raw material liquid circulation system.

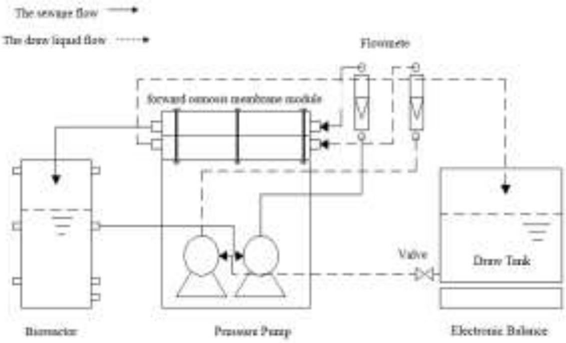

Fig. 1. Diagram of forward osmosis membrane bioreactor.

The forward osmosis laboratory test device includes a draw liquid pipeline system, a raw material liquid pipeline system and a forward osmosis bioreactor membrane module. The raw material liquid in the bioreactor is transported to the forward osmosis membrane module material liquid by a pressure pump, and then returned to the bioreactor after being intercepted by the membrane. The draw liquid is delivered to the draw liquid end of the forward osmosis membrane module by a pressure pump and then returned to the draw liquid tank. A membrane is placed in the middle of the bioreactor. This forward osmosis membrane is a CTA-ES composite membrane material produced by HIT in the United States. The active ingredient is asymmetric cellulose acetate, and polyester mesh is used as the support material, with a smooth dense layer and a relatively rough porous support layer. The effective membrane area is 0.0638 m2. In the forward osmosis membrane unit, the draw solution and the raw material liquid are cross-flowed on both sides of the forward osmosis bioreactor. The water flow channels on both sides of the membrane are the same, the channel length is 177 mm, the width is 18 mm, and the height is 13 mm. Two

doi: 10.18178/ijcea.2021.12.4.792

pumps are used to generate cross-flow velocity on both sides of the membrane in the reactor to ensure the normal operation of the draw liquid and the raw liquid circulation loop. The draw tank can be placed on an electronic balance to read the changes in the balance weight in real time to calculate the membrane flux. At room temperature 25°C, under low or no pressure, pure water flows from the raw material liquid to the draw liquid through the semi-permeable membrane.

A. Chemicals and Materials

DS (≥ 99.5%) was obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Acetonitrile (HPLC grade) was provided from Merck (Darmstadt, Germany). The chemicals including 4-nitroquinoline-N-oxide, dimethyl sulfoxide, o-nitrophenyl-β-D-galactopyranoside, sodium dodecyl sulfate (SDS) (≥ 95%) and humic acid (technical grade) were purchased from Sigma-Aldrich (Buchs, Switzerland). Nitrobenzene (NB, HPLC grade > 99%) was purchased from CNW (Dusseldorf, Germany). Sodium hypochlorite (NaClO) (active chlorine ≥ 5.2%) was acquired from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Salmonella typhimurium (TA1535/PSK1002) was purchased from Molecular Toxicology Inc. (Boone, NC, USA). The lyophilized Vibrio fischeri (strain NRRL-B-11177) was obtained from Macharey-Nagel (ref. 945 022) (Düren, Germany).

All chemicals used for solutions (NaCl, NaOH, HNO_3, Na_2HPO_4, NaH2PO4, etc.) were reagent grade. All solutions were prepared with ultrapure water produced from a Milli-Q® water purification system (Millipore Corp., Billerica, MA, USA).

B. Experimental Method

1) Experimental method

When you submit your final version, after your paper has been accepted, prepare it in two-column format, including figures and tables. Take 50L of sludge and place it in a bioreactor for cultivation. The inoculated sludge was taken from the secondary sedimentation tank of a sewage plant in Xiamen, and the sludge was inoculated into the bioreactor so that the nutrient element ratio C:N:P=100:5:1 is the most suitable for the growth of the sludge flora, respectively add a certain quality of glucose, ammonium chloride, and potassium dihydrogen phosphate. An aeration port is placed in the container to provide the organisms with the required oxygen. The sludge concentration in the culture tank is gradually increased by adding nutrients required by the sludge regularly and quantitatively, and the sludge concentration (MLSS) is controlled at 6-8 g/L changes within the range.

In order to adapt the inoculated sludge to the norfloxacin wastewater system, a solution of norfloxacin was added to the bioreactor every two days at the beginning of domestication. Then the dosage is gradually increased until 2 mg/L norfloxacin solution is added every day. When the activated sludge is adapted to the 2 mg/L norfloxacin wastewater environment, the sludge domestication is considered complete.

2) Simulated the proportion of antibiotic wastewater

The main components of artificial simulated antibiotic wastewater include: glucose 1000-5000 mg/L; NH4Cl 764mg/L; KH2PO4 175 mg/L; norfloxacin 2 mg/L.

C. Analysis Method

1) Measurement of membrane flux

Membrane flux is an indispensable index in the evaluation of forward osmosis performance. In this experiment by electronic balance real-time read on one side of the absorbing liquid to get the weight of the absorbing liquid quality difference ($\Delta \mathrm{m}$), when it began, namely control absorbing liquid flow velocity is constant, when the value and system stability on the electronic balance after the start time, running after a certain amount of time, record the added value of absorbing liquid on one side of the quality before and after the experiment. The calculation formula is as follows:

$$J_W = \frac{V}{S \cdot t} = \frac{\mathrm{V}m}{\rho \cdot A \cdot t} \tag{1}$$

where: V —through liquid product, L; t —Unit time, h ;

ρ —Density of water, $g \cdot L^{-1}$;

$\mathrm{V}m$ — Poor quality of the suction side within a certain time, g ;

A —Unit effective membrane area,m^2;

J_W — membrane flux, $L/\left(m^2 \cdot h\right)$.

2) Determination of ant permeability of salt

In the forward osmosis process, due to the different concentration of solution on both sides of the membrane, it is inevitable that the solute on one side of the suction solution diffused back into the feed solution, and this phenomenon is defined as the backmixing of the suction solution solute. Backmixing can reduce the total operation efficiency of forward osmosis process and affect the forward osmosis process to a certain extent. In this experiment, a portable conductivity meter was used to read the conductivity of the feed liquid side in real time, which was used as an index to detect the solute reverse permeability of the draw liquid side.

3) Determination of chemical oxygen demand (COD)

The determination method of COD in the experiment refers to the national standard GB11414-89 chemical oxygen demand (potassium dichromate method) determination, and the calculation formula is as shown in 2-2:

$$COD = \frac{C(V_1 - V_2)}{V_0} \times 8000 \tag{2}$$

where: COD —chemical oxygen demand in water sample, mg/L;

C — Concentration of ammonium ferrous sulfate standard titration solution, mol/L;

V_1—Volume of ammonium ferrous sulfate standard titration solution consumed in blank test, mL;

V_2—volume of ammonium ferrous sulfate standard titration solution consumed by water sample, mL;

V_0—Volume of water sample, mL.

4) Method for concentration analysis of norfloxacin

In the experiment, the concentration of Norfloxacin was used by HPLC, the detection wavelength was 278 nm, and the column was InertSustain C18. The chromatographic conditions were as follows: The mobile phase consisted of 50% ultrapure water (0.01 % formic acid) and 50% methanol at the flow rate of 1mL/min, the column temperature was 40 ℃, the injection volume was 10 μL, and the retention time of norfloxacin was 4 min.

Standard curve drawing and concentration calculation formula: the experiment prepared a concentration of 50 mg/L reserve liquid, and low temperature shading stored in the refrigerator. The prepared reserve solution was diluted to different concentrations of 1 mg/L, 5 mg/L, 10 mg/L, 15 mg/L and 20 mg/L, respectively. The determination results were analyzed, and the peak area of norfloxacin measured according to different concentrations was the ordinate and the concentration was the abscissa. The standard curve equation of this method is $y=1.16092 \times 10^{-5}x+0.14819$, and the correlation coefficient $R^2=0.999847$.

5) Other analysis methods

Free chlorine was analyzed using the N,N-diethyl-p-phenylenediamine (DPD) colorimetric method. An AQ4000 portable colorimeter (Thermo Scientific, Massachusetts, USA) was used to measure the concentration of free chlorine.

A high performance liquid chromatography system (LC-20AB, Shimadzu, Kyoto, Japan) equipped with a Shimadzu SPD-M20A diode array detector was employed to analyze the concentrations of DS and NB. The mobile phase solvent used for DS and NB analysis consisted of pure water and acetonitrile (50% pure water (0.05% trifluoroacetic acid) and 50% acetonitrile for DS, 65% pure water and 35% acetonitrile for NB) at a flow rate of 1.0 mL/min. The inertsil reverse-phase ODS-SP column (250 mm × 4.6 mm × 5 μm; GL Sciences, Inc., Tokyo, Japan) temperature was maintained at 40 °C. The detection wavelength of DS and NB were set at 275 and 262 nm, respectively, and the injected volume was 10 μL. The pH of the solution was measured with a pH/mV Meter (Ohaus, Changzhou, China).

The intermediates were identified using a Waters liquid phase-mass spectrometry system equipped with 2767 sample manager, 515 HPLC pump, 2489 UV/visible light detector and 3100 mass detector. The mass spectrometry conditions were set as follows: desolvation temperature and source temperate were 350 °C and 120 °C, respectively; desolvation gas flow and cone gas flow were 500 L/h and 50 L/h, respectively; capillary voltage was 3000 V and injection volume was 20 μL. Chromatographic conditions were set as follow. The mobile phase was consist of acetonitrile and water (65:35) with a flow rate of 1.0 mL·min-1, the working wavelength was 265 nm, the injection volume was 10 μL. Positive APCI mode was adopted for the identification of both DS and its transformation products.

Furthermore, we performed a DFT study to forecast the reactivity position of the DS molecule. DFT calculations were conducted by the hybrid Becke-3-Lee Yang Parr (B3LYP) density functional method on a Gaussian 09 package.

III. Results and Discussion

A. The Effect of Membrane Active Surface Orientation on the Removal Rate of COD and Norfloxacin

The asymmetric structure of the forward osmosis membrane and the nature of not requiring external pressure enable the forward osmosis process to have two different operating modes. Under the same operating conditions, the two membrane orientation modes of FO (active layer toward the raw material liquid) and PRO (active layer toward the draw liquid) were used to investigate the changes in wastewater treatment performance, membrane flux, and conductivity of salt back mixing. The results are shown in Fig. 2 and Table I.

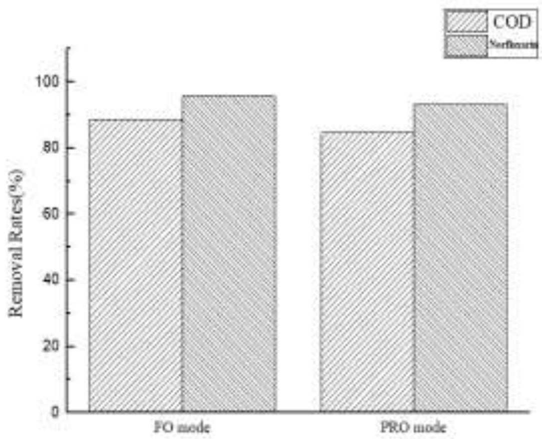

Fig. 2. Effects of different membrane orientations on COD and Norfloxacin removal.

TABLE I: COD in Inflow and Outflow Water under Different Membrane Orientations

Operating mode	Influent COD concentration (mg/L)	COD concentration of effluent (mg/L)
FO mode	2000	226.18
PRO mode	2000	308.15

TABLE II: Norfloxacin Concentrations in Inflow and Outflow Water under Different Membrane Orientations

Operating mode	Concentration of influent norfloxacin (mg/L)	Concentration of norfloxacin in effluent (mg/L)
FO mode	2	0.086
PRO mode	2	0.135

It can be seen from Fig. 2 that the removal rates of COD in FO and PRO modes are 88.7% and 84.6%, respectively, and the removal rates of norfloxacin are 94.68% and 93.25%, respectively. Compared with PRO mode, the removal of COD and norfloxacin in FO mode is higher. The reason may be that the active layer faces the raw material liquid in the FO mode. Compared with the support layer, the structure of the active layer is denser, and the resistance is larger. The water molecules carry COD and norfloxacin through the membrane to the draw solution. Therefore, COD and norfloxacin in FO mode have a higher removal rate.

B. The Effect of Membrane Active Surface Orientation on OMBR Flux

It can be seen from Fig. 3 that when the fixed draw solution is NaCl, in both FO and PRO modes, the conductivity of the raw material side continues to increase with the increase of time, analyze the linear relationship between the two (Table III) It can be seen that the conductivity change rate in the PRO mode is greater than that in the FO mode, which indicates that there is a certain degree of backmixing of the solute in the draw solution during the operation of OMBR, and the backmixing rate in the FO mode in this experiment is greater. The main reason for the solute back-mixing phenomenon in the draw solution is that part of the ions in the draw solution can penetrate the membrane and enter the side of the raw material solution, which causes the driving force to become smaller. By consulting relevant information and literature, the current methods to reduce solute reverse osmosis mainly include: (1) Change the characteristics of the extraction fluid, such as heating up and increasing the diffusion coefficient; (2) Change the characteristics of the membrane material, allowing only water molecules to pass through, but not ions; (3) Halophilia can be cultivated in the sewage treatment system Bacteria to reduce toxic effects, because halophilic bacteria can survive in higher salt solutions.

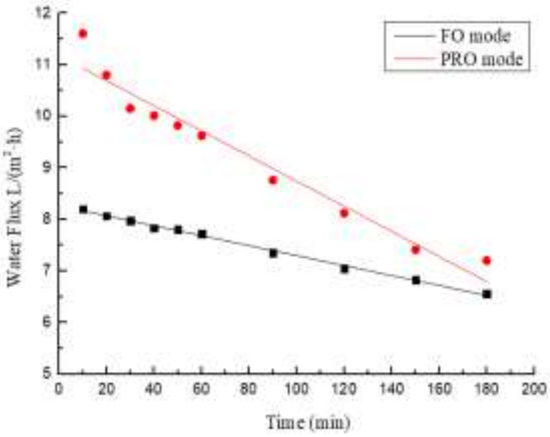

Fig. 3. Effects of membrane orientations on OMBR flux.

TABLE III: EFFECTS OF MEMBRANE ORIENTATIONS ON OMBR FLUX

Operating mode	Linear equation	R^2	Rate ms/cm·h
FO mode	y=0.0065x+2.9349	0.9779	0.39
PRO mode	y=0.0052x+3.1912	0.9576	0.31

Experiments show that when treating norfloxacin wastewater through a forward osmosis membrane bioreactor, the difference in COD and norfloxacin removal rates between PRO mode and FO mode is small. Compared with FO mode, PRO mode has a higher flux. It is more conducive to the following research and exploration. The analysis of the above indicators shows that it is more suitable for this system to adopt the PRO mode.

IV. CONCLUSION

This article mainly investigates the optimal wastewater treatment effect and OMBR flux of the forward osmosis membrane bioreactor under different membrane orientation operating conditions. The experimental conclusions are as follows:

While NaCl was used as the extraction solution to treat norfloxacin wastewater during the forward osmosis membrane bioreactor, the removal of COD and norfloxacin can achieve the same removal effect, the PRO mode has a larger flux than the FO mode, so it is suitable for norfloxacin wastewater treatment.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Xiaoqing Chen conducted the research and analyzed the data; Xiaoqing Chen and Litong Cai wrote the paper.

REFERENCES

[1] D. L. Cheng, H. H. Ngo, W. S. Guo *et al.*, "Bioprocessing for elimination antibiotics and hormones from swine wastewater," *Science of the Total Environment*, vol. 621, pp. 1664-1682, 2017.
[2] N. Li, G. P. Sheng, Y. Z. Lu *et al.*, "Removal of antibiotic resistance genes from wastewater treatment plant effluent by coagulation," *Water Research*, vol. 111, pp. 204-212, 2017.
[3] Y. G. Peng, Y. X. Zhang, H. L. Huang *et al.*, "Flexibility induced high-performance MOF-based adsorbent for nitroimidazole antibiotics capture," *Chemical Engineering Journal*, vol. 333, pp. 678-685, 2018.
[4] Y. G. Zhu, Y. Zhao, B. Li *et al.*, "Continental-scale pollution of estuaries with antibiotic resistance genes," *Nature Microbiology*, vol. 2, p. 16270, 2017.
[5] J. Wang, K. Li, Y. Wei *et al.*, "Performance and fate of organics in a pilot MBR-NF for treating antibiotic production wastewater with recycling NF concentrate," *Chemosphere*, vol. 121, pp. 92-100, 2015.
[6] V. L. Vilker and W. D. Burge, "Adsorption mass transfer model for virus transport in soils," *Water Research*, vol. 31, no. 2, pp. 335-339, 1985.
[7] D. S. S. Raghavan, G. L. Qiu, and Y. P. Ting, "Fate and removal of selected antibiotics in an osmotic membrane bioreactor," *Chemical Engineering Journal*, vol. 334, pp. 198-205, 2018.

Copyright © 2021 by the authors. This is an open access article distributed under the Creative Commons Attribution License which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited (CC BY 4.0).

Xiaoqing Chen was born in 1984, Xiamen, Fujian Province. She received master of engineering degree from College of Chemistry Engineering, Xiamen University in 2019. Her research interests is membrane technology.

She has been working in School of Environmental Science & Engineering, Xiamen University of Technology since graduation, engaged in membrane treatment and other related work. In recent years, she has published 5 papers in *Science and Technology* and other related journals.

Ms. Chen studies forward osmosis membrane bioreactor. This paper supported by the Educational Research Projects for Middle-aged and Young Teacher of Fujian Province, China (Grant No.JT180454), and Research Support of Xiamen University of Technology (Grant No. E201300400). She will continue to study the practical application of forward osmosis membrane bioreactors and promote it.

Litong Cai was born in 1997, Fuzhou, Fujian Province. He is pursuing master of engineering degree from College of School of Environmental Science and Engineering, Xiamen University of Technology. His research interests is formation and control of disinfection by-products.