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Treatment of Fumaric Acid Wastewater Using Integrated Process of Hollow-Fiber Supported Liquid Membrane-Strip Dispersion with Reverse Osmosis

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In this paper, the integrated process of series connected hollow-fiber supported liquid membrane-strip dispersion (HFSLM-SD) with reverse osmosis (RO) was designed and used to recover fumaric acid (FA) from waste effluents and treat FA wastewater. The results showed that FA could be almost completely recovered by this integrated process, and TOC of wastewater finally decreased to the environment acceptable level. In addition, the continuous operation of wastewater treatment was implemented by the integrated process. After FA wastewater was extracted by six series connected HFSLM-SD modules, its TOC decreased from 35625 mg/L to 1000 mg/L, and the TOC removal rate reached 97.17%. Then the effluent from HFSLM-SD was further treated by RO, and TOC of permeate in RO was below 100 mg/L. The total TOC removal rate of the integrated process was as high as 99.7%. Furthermore, the effect of the osmotic pressure of RO process on TOC in the feed was obtained. The investigation of RO membrane fouling revealed that washing process was necessary because of the serious fouling in RO system.

Keywords fumaric acid; N_{7301}; organic wastewater; reverse osmosis; supported liquid membrane

INTRODUCTION

Fumaric acid (trans−butene diacid) is an important raw material of organic chemistry and has been applied in many fields including food, medicine, and light industry. Wastewater from the FA production process always exhibits low pH, high TOC value, high thiourea concentration, and low biodegradability. Much research has been done to treat FA wastewater, including microelectrolysis of iron and carbon, catalytic microwave oxidation, peroxide oxidation, bio−contact oxidation, and anaerobic hydrolysis (1–3). Although the TOC value of wastewater can be decreased greatly by these methods, FA is also degraded and cannot be reused.

Our previous work (4) revealed that FA could be efficiently recovered by complex extraction and stripping (CES) using N_{7301} as complexing agent. The overall COD_{cr} removal rate reached 88.16%, and the extraction efficiency of FA was 70.67%. In addition, the combination process of Reverse Osmosis (RO) with CES was designed to recover FA from wastewater by our group (5). After being treated by the combination process, TOC of FA wastewater decreased from $35625\,mg \cdot l^{-1}$ to $290\,mg \cdot l^{-1}$, and total TOC removal rate arrived at 99.2%. However, it was also found that the loss of the complexing agent N_{7301} in each extraction process was about 0.4%, which would increase the operation cost. Therefore, further work should be carried out to decrease the loss of the complexing agent.

Supported liquid membrane (SLM) is combined with extraction and stripping processes into one single step, which provides the maximum driving force for the separation of a target species. Because SLM works without the limitation of chemical equilibrium, it has been applied in many fields including the removal and recovery of metals (6–13), gas separation (14), separation of organic acids and amino acids (15–17), and sample enrichment for trace elements in chemical analysis (18). Hollow-fiber supported liquid membranes (HFSLMs) have been widely studied due to their high surface areas. However, the application of HFSLM was limited to an extent due to its instability. In recent years, Ho (10) and Teramoto (9) presented a new SLM operation module – SLM with strip dispersion, i.e., the strip solution was dispersed in the membrane organic phase. The new module can greatly improve the stability of SLM, and the loss of the organic phase in SLM is much less than that in complex extraction, thus, HFSLM with strip dispersion might be an alternative method to recover FA from its effluents.

The transport of fumaric acid from an aqueous feed solution through a hollow-fiber supported liquid membrane with

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TABLE 1
Physical and chemical characteristics of the FA wastewater

Appearance	pH	Color (multiple)	TOC (mg/l)	Fumaric acid (g/l)	Main components
Yellow, Opaque	1.73	1200	35625	6.47	Fumaric acid, Thiourea

strip dispersion (HFSLM-SD) containing trialkylamine (N_{7301}) as carrier was studied in detail by our group (19). The work depicted that at the optimum operating condition, the extraction of FA reached 89.5% and TOC removal rate was 96.5%. After HFSLM-SD treatment, TOC of the FA wastewater remained about 1000 mg/L, and 10.5% FA was still in the wastewater. And the HFSLM-SD process was a batch mode. Therefore, in this work, a further study was carried out, in order to recover residual FA and decrease TOC of wastewater.

MATERIALS AND METHODS

Chemicals and Materials

All chemicals used in these experiments were of analytical grade. The carrier and the diluent selected were trialkylamine (N_{7301}, Feixiang Chemicals Co., Ltd., Jiangsu, China) and kerosene (Fd-wzsh Co., Ltd., Zhejiang, China), respectively. The physical and chemical characteristics of FA wastewater from Ningbo Yuantai Fine Chemical Co., Ltd. (Zhejiang, China) are listed in Table 1.

Analytical Methods

The concentration of fumaric acid was measured by UV spectrophotometer S53/54 at 240 nm. pH values were measured by a Digital Acidimeter (pH/ISE 868, ORION, Shanghai, China). The TOC values were measured by TOC Analyzer (liquiTOC II) from Elementar, Germany.

Design of Integrated Process

Based on our previous work, an integrated process of hollow fiber supported liquid membrane-strip dispersion (HFSLM-SD) with reverse osmosis, shown in Fig. 1, was designed and used to recover FA from effluents and to further treat wastewater. FA wastewater was first treated by several series connected HFSLM-SD modules to extract and recover FA, and then was further treated by RO. When the FA concentration in the upstream of RO membrane came to a certain level, the retentate was circulated to the feed tank and entered the HSFLM-SD module to further extract FA. Therefore, most FA could be recovered by the integrated process, and TOC of FA wastewater finally decreased to the environment acceptable level. In addition, the integrated process realized the continuous operation. The experiment of HFSLM-SD was carried out as following: The feed solution was pumped through the HFSLM-SD module on the tube side, while the strip dispersion phase flowed on the shell side. The pressure on the feed solution was higher than that on the strip dispersion phase, and the low pressure difference between the feed solution side and the strip dispersion phase side was applied to prevent the organic solution passing through membrane pores from shell side to tube side. In the experiments, the volume ratio of the feed, strip and membrane solutions was of 2:2:1. The characteristics of the hollow-fiber membrane module used are listed in Table 2.

RO System

All RO membranes used were polyamide RO membranes from Development Center of Water Treatment Technology, Hangzhou, China. And the total membrane surface area was 40 cm^2. The pressure was kept constant

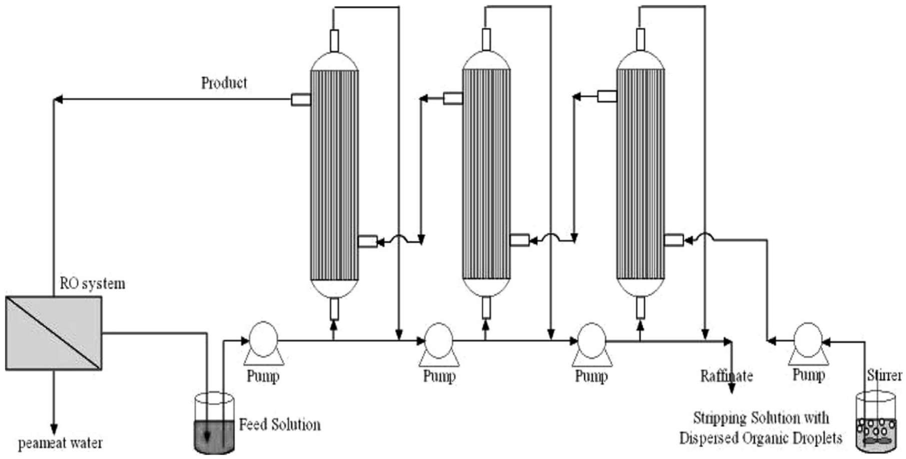

FIG. 1. Integration of HFSLM-SD with RO.

TABLE 2
Characteristics of HFSLM module

Fiber characteristics	
Material	Polypropylene
O.D. (μm)	470
δ (μm)	75
Length (cm)	35.8
Number	900
Pore size (nm)	143.7
Porosity ϵ	0.45
Total material surface area (cm^2)	3237
Shell characteristics	
Material	Polymethylmethacrylate
O.D. (cm)	5
I.D. (cm)	4.4
Length (cm)	39.6

at 1.0 MPa in all RO experiments. The RO system was similar to that reported in reference (5).

In RO system, flux (F), rejection (R'), and concentration ratio (β) are defined as the following:

$$F = V/(A \cdot t) \tag{1}$$

$$R' = (TOC_f - TOC_p)/TOC_f \times 100\% \tag{2}$$

$$\beta = V_0/V_t \tag{3}$$

RESULTS AND DISCUSSION

Water Permeability of RO Membrane

Pure water was used to investigate the dependence of pure water flux on the operating pressure at the range of 0.25~1.75 MPa, and the results were depicted in Fig. 2. Because there was no solute in the feed, the osmotic pressure difference was zero between the retentate and permeate sides of the membrane. Therefore, the pure water flux would be only dependent on the operating pressure. As shown in Fig. 2, the pure water flux was fairly linear to the operating pressure, which was greatly agreed upon with the theoretical result illustrated in Eq. (4):

$$L_p = (J_v/\Delta P)_{\Delta\pi=0} \tag{4}$$

Straight line with slope of 11.43 was obtained by fitting the scattering data in Fig. 2, and the fitting constant were R = 0.992. Thus the water permeability of the membrane obtained was $L_P = 1.143 \times 10^{-11}$ m s^{-1} Pa^{-1}.

The Effects of Concentration Ratio in RO System

Figures 3–4 depicts the effects of concentration ratio on the flux, rejection, and TOC in the retentate and permeate sides of the RO membrane. As shown in Fig. 3, it can be seen that both the flux and rejection decreased with increasing concentration ratio. When the concentration ratio was about 2.2, the flux and rejection were 12 L m^{-2} h^{-1} and above 90%, respectively. Figure 4 demonstrated that TOC in the permeate side of the membrane increased with increasing concentration ratio, and TOC in the retentate side of the membrane changed with the similar trend. At concentration ratio of 2.2, TOC in the permeate side of the membrane was about 150 mg/L, and the TOC removal rate arrived at 97.67%.

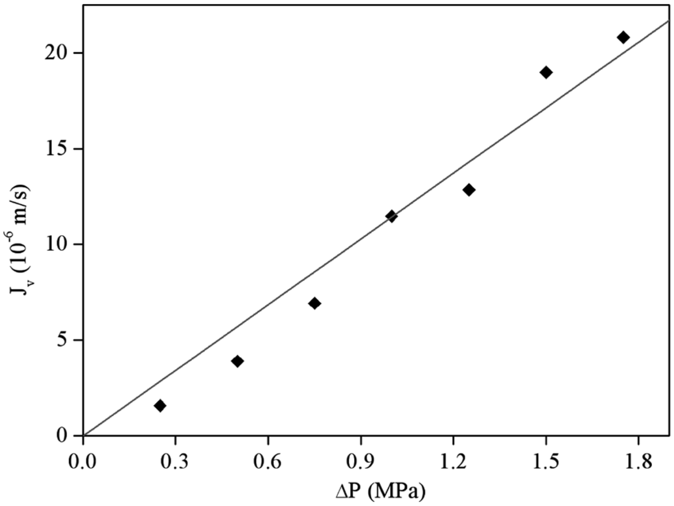

FIG. 2. Pure water flux as a function of operating pressure in RO.

Osmosis Pressure Between the Two Sides of Membrane

Figure 4 also revealed that when the concentration ratio increased largely, the TOC in the permeate side of the membrane increased, which means low TOC removal rate. One explanation is that the osmotic pressure of the

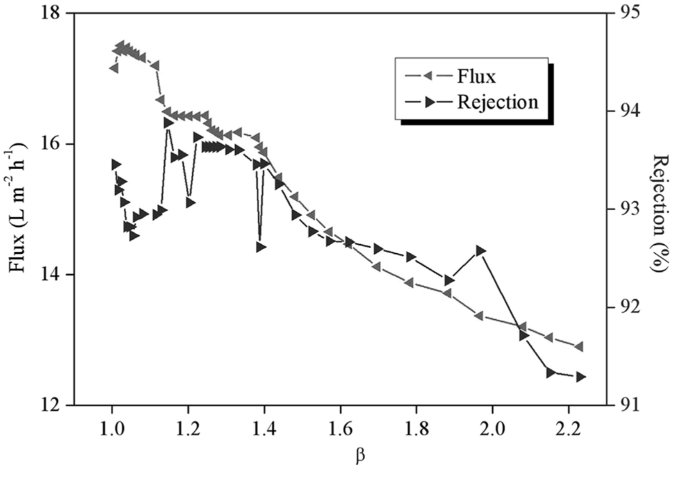

FIG. 3. Flux and rejection as a function of concentration ratio in RO.

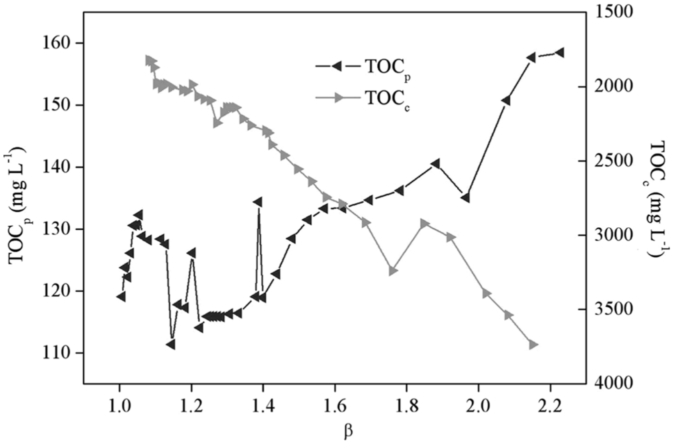

FIG. 4. The effects of concentration ratio on TOC in the concentrate and permeate sides of the membrane in RO.

membrane increases with increasing concentration ratio, therefore, when the concentration ratio comes to a certain level, the TOC removal rate will decrease at the present operating pressure. The osmotic pressure between the two sides of the membrane can be calculated according to the Van't-Hoff equation:

$$\Delta\pi = RT\Delta c \tag{5}$$

Thus, the osmotic pressure between the two sides of the membrane was calculated and investigated, and the results were illustrated in Fig. 5. It can be seen that the osmotic pressure of the membrane increases in the concentration process, while the water flux decreased. Therefore, TOC in the permeate side would increase correspondingly, which lead to low TOC removal rate. The variation of TOC in feed with the osmotic pressure between the two sides of the membrane was depicted in Fig. 6. By fitting the data, it can be seen that the osmotic pressure of the membrane was linear to the TOC in the feed solution. The relationship obtained can be described as: $\Delta\pi = 0.68 + 9.87 \times 10^{-5}$ TOC_f, the fitting constant $R = 0.97$.

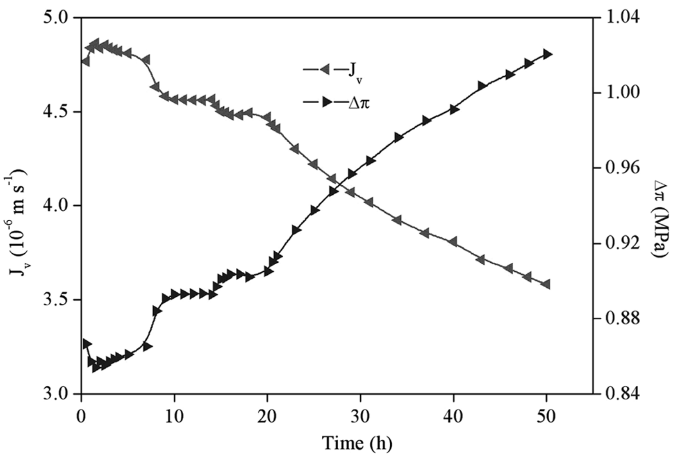

FIG. 5. Osmotic pressure and water flux in RO.

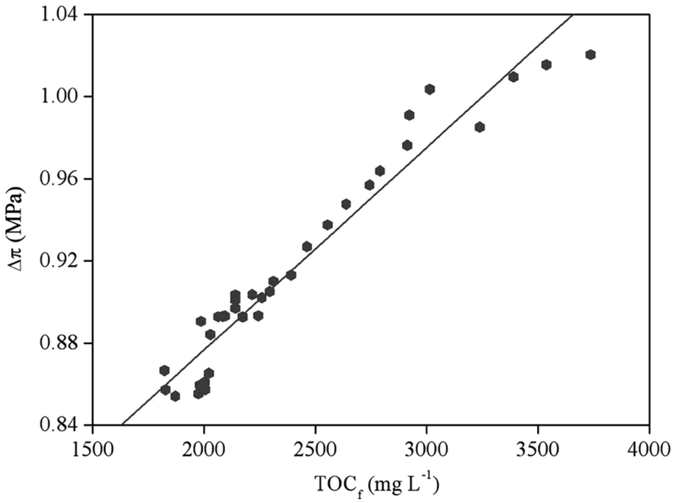

FIG. 6. Relationship between osmotic pressure and TOC in the feed solution TOC_f.

RO Membrane Fouling

In order to study the RO membrane fouling, the pure water flux in 35 h before and after FA wastewater treatment for 50 h was studied and compared, and the results were shown in Fig. 7. It can be seen that the pure water flux decreased by 33% after FA wastewater treatment for 50 h, which declared that the membrane fouling was serious. Other than the common causing, the membrane fouling mainly resulted from FA crystal. The FA concentration

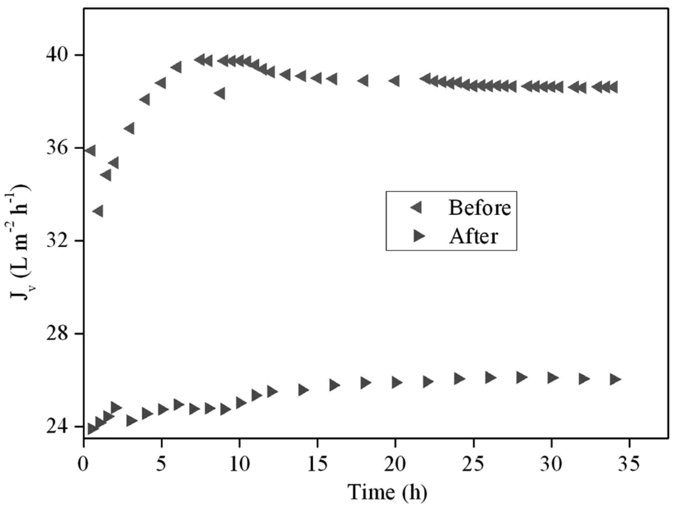

FIG. 7. Pure water flux of the membrane before and after FA wastewater treatment for 50 h.

TABLE 3
FA wastewater treatment results comparison among four methods

Method	FA extraction (%)	TOC removal (%)	Advantages	Disadvantages
CES	70.67	88.16	Easy to do; Maturity of the technology	Relatively large solvent loss
Combination of CES with RO	78.54	99.2	Much higher FA extraction and TOC removal obtained	Batch mode
HFSLM-SD	89.5	96.5	No significant solvent loss; Precious carrier feasible to use	Batch mode
Integration of HFSLM-SD with RO	96.38	99.7	Continuous operation; Environmentally acceptable level	

in the concentrate side increased with the operating time, and when the FA concentration come to the saturated concentration, FA crystal would form, which would lead to the FA precipitation on the membrane surface and result in membrane fouling. Therefore, the membrane needs be washed by alkali solution to alleviate the membrane fouling, following de-ionized water to recover the water flux of the membrane. After washing, the flux could be recovered about 92%.

Efficiency of the Integrated Process

The experiment results revealed that it's efficient to recover FA from waste effluents by integrating six series connected HFSLM-SD modules which characteristics were listed in Table 2, with reverse osmosis. After six series connected HFSLM-SD modules extraction, TOC of FA wastewater decreased from 35625 mg/L to 1000 mg/L, and the TOC removal rate came to 97.17%. Then the wastewater from HFSLM-SD was further treated by RO, and TOC of the permeate solution in RO was below 100 mg/L, and the total TOC removal rate by the integrated process was as high as 99.7%. Thus, the FA wastewater treated by the integrated process can be discharged to the environment safely.

The different FA wastewater treatment results were listed in Table 3 and the pros and cons of four different methods in our work were compared. The optimum treatment method and operating mode should be selected to meet the practical treating requirements.

CONCLUSION

It is effective to recover fumaric acid from effluents and to treat its wastewater to an environmentally acceptable level by a integrated process of hollow-fiber supported liquid membrane-strip dispersion with reverse osmosis. After the wastewater was treated by the integrated process, the TOC of the permeate in RO was below 100 mg/L. The total TOC removal rate by the integrated process was as high as 99.7%.

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NOMENCLATURE

A	Reverse osmosis membrane area, [m^2]
β	Concentration ratio
CES	Complex extraction and stripping
COD_{cr}	Chemical oxygen demand, [mg/L]
δ	Thickness, [μm]
Δc	Differential concentration between the two sides of membrane, [mol/m^3]
ΔP	Operating pressure, [MPa]
$\Delta\pi$	Osmotic pressure, [MPa]
F	Flux, [$L\ m^{-2}\ h^{-1}$]
FA	Fumaric acid
HFSLM	Hollow-fiber supported liquid membrane
HFSLM-SD	Hollow-fiber supported liquid membrane with strip dispersion
I.D.	Inside diameter, [cm]
L_P	Water permeability of RO membrane, [$m\ s^{-1}\ Pa^{-1}$]
N_{7301}	Carrier: trialkylamine
O.D.	Outside diameter, [cm]
R	Gas constant, [$KJ\ mol^{-1}\ K^{-1}$]
R'	Rejection, [%]
RO	Reverse osmosis
SLM	Supported liquid membrane
t	Time, [h]
T	Temperature, [K]
TOC	Total organic carbon, [mg/L]

TOC_c	Total organic carbon in the concentrate side in RO, [mg/L]
TOC_f	Total organic carbon in the feed side in RO, [mg/L]
TOC_p	Total organic carbon in the permeate side in RO, [mg/L]
V	Volume in the permeate side in RO, [L]
V_0	Volume in the concentrate side in RO at $t = 0$, [L]
V_t	Volume in the concentrate side in RO at $t = t$, [L]

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