ELSEVIER

Separation and Purification Technology 32 (2003) 93–98

Separation and Purification Technology

www.elsevier.com/locate/seppur

Treatment of oily wastewater produced from refinery processes using flocculation and ceramic membrane filtration

Jing Zhong *, Xiaojuan Sun, Cheli Wang

Department of Chemical Engineering, Jiangsu Institute of Petrochemical Technology, Changzhou, Jiangsu 213016, People's Republic of China

Abstract

Treatment of oily wastewater produced from post-treatment unit of refinery processes using flocculation and micro-filtration with zirconia membrane was studied in this paper. The results show that the oil content and COD value were decreased dramatically by flocculation, and the optimum flocculent is 3530S which is a derivative of polyacrylamide. The influence of flocculation conditions on flocculation results is also investigated by orthogonal experiments, and the optimum conditions are dosage of 70 mg/l, temperature of 40 °C, stirring time of 90 min and holding time of 90 min. After flocculation, the effluents were treated with micro-filtration using zirconia membrane. The results of filtration tests show that the membrane fouling decreased and the permeate flux and permeate quality increased with flocculation as pretreatment. The permeate obtained from flocculation and micro-filtration can meet the National Discharge Standard and the recommended operation conditions for pilot and industrial application are transmembrane pressure of 0.11 MPa, and cross-flow velocity of 2.56 m/s.

Keywords: Oily wastewater containing sludge; Zirconia membranes; Micro-filtration; Flocculation; Operation conditions

1. Introduction

Large quantities of effluents containing oil, water and sludge were produced from the refinery processes. Draining of these effluents not only pollutes the environment but also reduces the yield of oil. The conventional method which including gravity settling, dewatering, and incineration performs poorly for emulsified oil and suspend particles [1]. Membrane filtration has emerged as a useful process for concentration and clarification of oily wastewater [2].

Investigation of the membrane separation process for oily wastewater was started around 1973. After that, there are many reports, particularly using ultra-filtration (UF) [3,4] and reverse osmosis (RO) [5], but the relatively low flux limits the large-scale applications of them. Recently, there are several reports using micro-filtration (MF) with polymer membranes and ceramic membranes [6–10]. Polymer membranes are sensitive to both polar and chlorinated solvents, as well as to high oil fractions, which limit the application range of them. The ceramic membranes, particularly the

* Corresponding author. Tel.: +86-519-3295-832; fax: +86-519-3290-011.

E-mail address: zjwyz@pub.cz.jsinfo.net (J. Zhong).

1383-5866/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1383-5866(03)00067-4

zirconia membranes show better separation performance such as higher flux, less fouling and higher oil rejection [7,10]. The reported investigations mainly focus on the filtration of oily wastewater from food industry, metal fabrication and allied industries, automotive industry, chemical manufacturing industry which including petroleum oils from tanker washers, spills, drilling, various processing steps, etc. [2,11], few focus on the oily wastewater with sludge from post-treatment unit of refinery processes.

Preliminary studies showed that the MF with zirconia (ZrO_2) membranes could decrease the oil content and chemical oxygen demand (COD) value of oily wastewater produced from refinery processes, but the oil content of permeate is not low enough to meet the discharge standard [12]. So, the scope of present work is to study the performance of MF using ZrO_2 membranes combined with traditional chemical method-flocculation as pretreatment. The effects of process parameters including flocculation conditions, filtration conditions, etc. on the quality of effluent are also investigated, and the optimum parameters for pilot plant and industrial application were determined.

2. Experimental

2.1. Materials

The wastewater used in this study was obtained from Refinery Plant of Yangtze Petrochemical Company (China), which including oil, water and sludge. The oil content of gray-colored wastewater is about 6 g/l, the COD of which is about 3 g/l, and the solid content is about 5 wt.%.

The asymmetric microporous ZrO_2 membranes were provided by Nanjing University of Chemical and Technology. The average membrane layer is about 30 μm thick and the nominal pore size is 0.2 μm. The membrane elements were placed in 20 cm-long stainless steel housing and sealed with silicon rubber gaskets on both ends.

All the reagents used in this experiment are analytical grade. The flocculants used in this study were shown in Table 1. The polymer flocculants used in this study were provided by Refinery Plant of Yangtze Petrochemical Company (China). The Poly1 and 3530S are derivative of polyacrylamide.

2.2. Experimental methods

The flocculation experiments were done in a 400 ml flask. First, put 200 ml oily wastewater into the flask, then add the flocculent and stir the mixture by an electronic stirrer which was maintained at a certain temperature. After a period of time, allow the mixture to stand for a certain time, then take the sample for characterization.

The optimum flocculation conditions were determined by orthogonal experiments of three levels and four factors. The four factors are dosage of flocculent, stirring time, holding time after flocculation, and flocculation temperature. The three levels of each factor were showed in Table 2. The arrangements of orthogonal experiments were listed in Table 3, which including nine sets of flocculation experiments.

The process flow schematic for MF is similar to that reported in published paper [10]. A mixture of oily wastewater and flocculent was run through the membrane for 120 min. The membranes were reused until the pure water flux after cleaning decreased about 20%.

2.3. Analytical methods

The oil contents of feed and solution after flocculation were analyzed by petroleum ether extraction test, but the oil contents of permeates were analyzed by UV spectrophotometry [13]. The COD values were determined by conventional potassium dichromate oxidation process.

3. Results and discussion

3.1. Selection of flocculants

In order to select the optimum flocculent for oily wastewater treatment, the flocculation tests were conducted with different inorganic and polymer flocculants. The selection bases on the oil contents and COD values of solution after floccu-

Table 1
Results of several flocculation tests with inorganic and polymer flocculent

Flocculent	Dosage (mg/l)	Stirring time (min)	Holding time (min)	COD (mg/l)	Oil content (mg/l)
Polyacrylamide	40	60	120	1165	760
Poly1	40	60	120	964	427
3530S	40	60	120	668	220
$Al_2(SO_4) \cdot 18H_2O$	80	60	120	1375	685
$FeSO_4 \cdot 7H_2O$	80	60	120	957	512
$FeCl_3 \cdot H_2O$	80	60	120	918	345

Volume of feed solution, 200 ml; flocculation temperature, 25 °C.

lation. The results listed in Table 1 show that the oil contents and COD values can be decreased dramatically by the addition of flocculants, and the optimum flocculent is polymer flocculent — 3530S that is a derivative of polyacrylamide. The decrease of oil content and COD value of feed after flocculation is perhaps because the flocculants broke the stability of colloid particles and emulsified oil in wastewater. The better performance of polymer flocculants —3530S is due that its long chain bridged between and/or absorbed the particles and emulsified oil in wastewater, then increased their sedimentation rate.

3.2. Effects of flocculation conditions

The flocculation results have close relation with flocculation conditions, such as: dosage of flocculent, stirring time, holing time after stirring, flocculation temperature etc. In order to determine the optimum flocculation conditions, the orthogonal experiments of three levels and four factors for 3530S were conducted. Because the values of oil contents are more important and more difficult be reduced than that of COD in this kind of wastewater, the selection of flocculation conditions is based on the oil contents. The optimum conditions are that can decrease the oil contents most. From the results obtained from analysis of orthogonal experiments (the last four lines of Table 3), the optimum flocculation conditions were determined, which are: dosage of 70 mg/l, temperature of 40 °C and stirring time of 90 min and holding time of 90 min.

3.3. MF tests with and without flocculation

Though the COD values and oil contents of feed effluents can be decreased dramatically after flocculation by 3530S, they have not met the National Discharge Standard yet (COD less than 120 mg/l, oil content less than 10 mg/l). The preliminary study showed that the oil contents of permeates after MF also could not meet the National Discharge Standard, though the color and solid content of wastewater are good enough [12]. So, the MF with flocculation as a pretreatment was done in this study. The results (Fig. 1 and Table 4) show that the flocculation could decrease the membrane fouling and increase the filtration flux, and the oil contents and COD values of permeates also decreased and could meet the National Discharge Standard.

Table 2
Levels and factors of orthogonal experiments

Factor	Dosage (mg/l)	Temperature (°C)	Stirring time (min)	Holding time (min)
Level 1	40	40	40	90
Level 2	70	25	70	150
Level 3	100	60	90	180

Table 3
Orthogonal experiments of flocculent-3530S

No.	Level				Result	
	Dosage	Temp.	Stirring time	Holding time	COD (mg/l)	Oil content (mg/l)
1	1	1	3	2	644	207.6
2	2	1	1	1	609	199.5
3	3	1	2	3	600	204.3
4	1	2	2	1	619	220.5
5	2	2	3	3	604	205.6
6	3	2	1	2	588	238.3
7	1	3	1	3	567	216.6
8	2	3	2	2	600	213.5
9	3	3	3	1	609	205.6
(1)	644.7	611.4	654.4	625.6		Based on oil content
(2)	618.6	664.4	638.3	659.4		
(3)	648.2	635.7	618.8	626.5		
R	29.6	53.0	35.6	33.8		

Volume of feed solution, 200 ml.

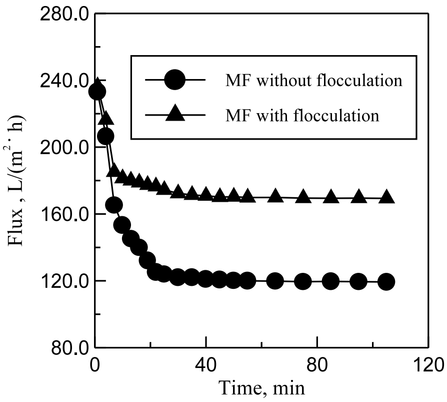

Fig. 1. Effect of pretreatment with flocculent on MF.

Table 4
MF results with and without flocculation pretreatment

	MF [12]	Flocculation+MF
Flux (l/m^2 h)	120	173.5
COD (mg/l)	154	108
Oil content (mg/l)	34.68	8.762

Permeate after MF 30 min used for COD and oil content analysis transmembrane pressure: 0.110 MPa, cross-flow velocity: 2.56 m/s, operation temperature: 25 °C.

The improvement of filtration flux after flocculation is because the size of emulsified oil droplets in wastewater increased by flocculation, then the extent of pore plugging decreased and the void of sedimentation layer on membrane surface increased after flocculation.

3.4. Effects of transmembrane pressure and cross-flow velocity

Selecting a set of optimum operation conditions is an important thing in membrane filtration which influence the filtration flux, the quality of permeate and the fouling extent of membrane [2]. In this study, the major operation conditions are transmembrane pressure and cross-flow velocity [12].

The effect of transmembrane pressure on filtration flux (Fig. 2) exhibits that the initial and pseudo-steady flux increased with pressure but the increase extent decrease, which was similar to the results obtained in former study [12]. This trend can be due to the competition of permeability and fouling potential that both of them increased with pressure. The effect of transmembrane pressure on permeate quality (Table 5) shows that the COD values almost unchanged with pressure, but the oil contents increased with pressure which consisted with the results reported by Ohya et al. [8] and exceeded the discharge standard at 0.155 MPa. These results are due that the oil droplets settled on the membrane permeated through membrane pores by the higher

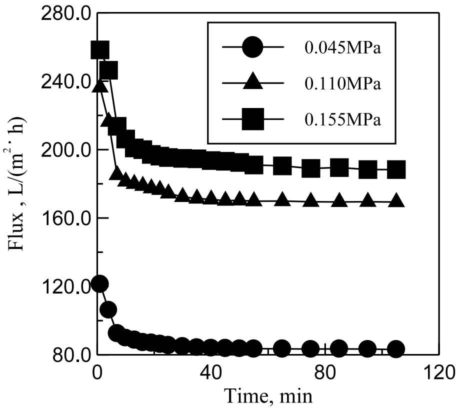

Fig. 2. Effect of transmembrane pressure on filtration flux.

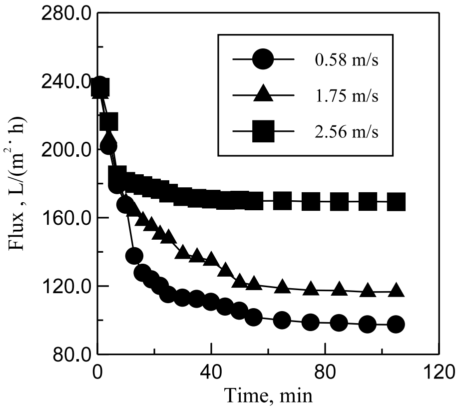

Fig. 3. Effect of cross-flow velocity on filtration flux.

Table 5
Effect of transmembrane pressure on permeate quality of MF

Pressure (MPa)	COD (mg/l)	Oil content (mg/l)
0.045	101	8.201
0.110	108	8.762
0.155	112	11.71

Permeate after MF 30 min used for COD and oil content analysis, cross-flow velocity: 2.56 m/s, operation temperature: 25 °C.

pressure, while the sizes of substances that influence the COD value almost unchanged with pressure. Based on these results, the transmembrane pressure of 0.11 MPa was recommended for pilot and industrial application.

Generally, the filtration flux increase with the increase of cross-flow velocity since the increase of cross-flow velocity leads to an increase of shear stress on membrane surface and decrease the height of sedimentation layer [2]. The results obtained in this study (Fig. 3) indicate that the permeate flux increased with cross-flow velocity as expected, but the increase extent is not proportional to the cross-flow velocity. The corresponding Reynolds numbers for these conditions are 4608, 13902 and 20338, respectively, which transferred from laminar flow to turbulent flow. These data showed that the flow pattern for this system must be complete turbulent flow, which would produce favorable effect on increasing the filtration flux. The effect of cross-flow velocity on quality of permeate (Table 6) shows that the COD values and oil contents of permeates decreased with the cross-flow velocity. The probable explanation for this phenomenon is that the large particles were removed more by shear stress when cross-flow velocity increase, then the void of sedimentation layer increased along with the cross-flow velocity and the rejections of emulsified oil and other substances increased. Based on these results, the cross-flow velocity of 2.56 m/s was recommended for pilot and industrial application.

4. Conclusion

The flocculation can decrease the oil content and COD value of oily wastewater containing sludge. The optimum flocculent is 3530S that is a derivative of polyacrylamide. The selective stan-

Table 6
Effect of cross-flow velocity on permeate quality of MF

Cross-flow velocity (m/s)	COD (mg/l)	Oil content (mg/l)
0.58	123	10.82
1.75	113	9.533
2.56	108	8.762

Permeate after MF 30 min used for COD and oil content analysis transmembrane pressure: 0.110MPa, operation temperature: 25 °C.

dard is the oil contents and COD values of the effluents after flocculation.

The flocculation conditions including flocculent dosage, temperature, stirring time and holding time after stirring were determined by orthogonal experiments, and the optimum conditions are dosage of 70 mg/l, temperature of 40 °C, stirring time of 90 min and holding time of 90 min.

The membrane fouling decreased and the filtration flux increased with flocculation as pretreatment. The quality of permeate after flocculation with 3530S and MF using 0.2 μm ZrO_2 membrane are better than that of only after MF, and can meet the National Discharge Standard.

The effects of transmembrane pressure and cross-flow velocity on flux and quality of permeate were also investigated, and the recommended parameters are transmembrane pressure of 0.11 MPa and cross-flow velocity of 2.56 m/s. The initial and pseudo-steady flux increased with pressure but the increase extent decrease. The COD values almost unchanged with pressure, but the oil contents increased with pressure and exceeded the discharge standard at 0.155 MPa; The permeate flux increased with cross-flow velocity, but the increase extent is not proportional to the cross-flow velocity. The calculation of corresponding Reynolds numbers showed that the flow pattern for this system must be complete turbulent flow. The COD values and oil contents of permeates decreased with the cross-flow velocity.

Acknowledgements

This research was supported by the Environmental Protection Bureau of Jiangsu Province, P. R. China. The authors wish to thank the Membrane Science and Technology Institute, Nanjing University of Chemical and Technology for providing the membranes used in this study.

References

[1] R. Sanjay Srivatsa, US 4383927, 1983.
[2] R.R. Bhave, Inorganic Membranes Synthesis, Characteristics and Applications, Van Nostrand Reinhold, New York, 1991.
[3] P.A. Bailey, Filtr. Sep. 14 (1977) 53.
[4] P. Lipp, C.H. Lee, A.G. Fane, C.J.D. Fell, J. Membr. Sci. 36 (1988) 161.
[5] O. Kutowy, W.L. Thayer, J. Tigner, S. Sourirajan, Ind. Eng. Chem. Prod. Res. Dev. 20 (1981) 354.
[6] J. Mueller, Y. Cen, R.H. Davis, J. Membr. Sci. 129 (1997) 221.
[7] R.J. Higgins, B.A. Bishop, R.L. Goldsmith, Proceedings of the 3rd International Conference on Inorganic Membranes, Worcester, MA, 10–14 July, 1994, p. 447.
[8] H. Ohya, J.J. Kim, A. Chinen, et al., J. Membr. Sci. 145 (1998) 1.
[9] R.L. Lahiere, K.P. Goodboy, Environ. Prog. 12 (1993) 86.
[10] C. Yang, G.S. Zhang, N.P. Xu, J. Shi, J. Membr. Sci. 142 (1998) 235.
[11] M. Cheryan, N. Rajagopalan, J. Membr. Sci. 151 (1998) 13.
[12] J. Zhong, P.H. Jiang, X.J. Sun, W. Dai, Mo Ke Xue Yu Ji Shu 22 (2002) 32 (in Chinese).
[13] L. Wang, J.J. Ge, Petrochem. Technol. 24 (1995) 645 (in Chinese).