Journal of Industrial and Engineering Chemistry 15 (2009) 784–790

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Modification of a hollow fiber membrane and its three-dimensional analysis of surface pores and internal structure for a water reclamation system

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ARTICLE INFO

Article history:
Received 16 September 2008
Accepted 31 May 2009

Keywords:
Hollow fiber
Modification
SEM and TEM images
Surface contamination
Water reclamation

ABSTRACT

A modified hollow fiber membrane with organic solvents was used for a membrane separation reactor to configure a water reclamation system. Changes in the surface and inner pores of the modified follow fiber membrane were analyzed three dimensionally. The results from the operation of the membrane separation reactor with MLSS of 7200 mg/l for 120 days were compared with those from pure water. Monitoring changes in permeate flux and separation efficiency, we made an effort to predict the possibility of back wash and the breakthrough point. During the initial operation, contamination of membrane surface was increased gradually without changes in inner pores whereas a long-term operation exhibited a decrease in inner pores and a change in microfibril, suggesting that there would be a rare possibility for backwashing. As the suction pressure was raised from 1 atm to greater than 2 atm due to the increased membrane surface contamination with 40 days of operation, the permeate flux and suction pressure were required to be continuously monitored. The results of more than 100 days of operation suggested that backwashing was not possible due to fouling.

1. Introduction

Worsening water quality has made difficult to secure various kinds of water in a current situation of ever-increasing water consumption with limited water resources. Thus securing water resources is an imperative task to take. The objectives of this study are to develop a water reclamation system as a measure to reuse discharged sewage/wastewater and to create demands by expanding the system applicability. First of all, the system basically consists of three reactors: (1) an electrolysis reactor which is very effective in oxidation of various organics and nitrification, (2) an activated carbon adsorber which can remove odor in the effluent of the electrolysis reactor and (3) a membrane separation reactor (MSR) which can improve the treated water quality. The feasibility of the water reclamation system will be demonstrated by providing the removal efficiency of each reactor.

Depending on the kind of membrane, the shape of membrane module and operating conditions, the MSR can give rise to very different removal efficiency. Thus it is necessary to consider various factors including the initial conditions of membrane when designing the MSR. Therefore, primary treatment is necessary to obtain steady filtrate by modifying the membrane surface to get optimum initial conditions for membrane. As the modification may lead to changes in membrane pores and its internal structure, this study will provide the design criteria for the MSR by three dimensionally analyzing fouling in the front section and the surface of membrane in terms of permeate flux change and operating period.

Firstly, as reported in the previous study [1], the membrane surface was pre-treated with 20–40% of ethanol in water to modify the surface pores. Accordingly, the results will be presented in terms of permeate flux change. Also Johnson and co-workers [2] studied the effects of pore size change on the removal of organic volatile matters in an osmotic distillation process with polyethylene and polypropylene type UF, suggesting that water surface tension forces to rearrange microfibril (which composes membrane), causing large surface pores to increase and small pores to decrease in size. When polysulfone type hollow fibers, which are manufactured with different non-solvents, are used in gas separation processes, the particle removal efficiency of cross-sectional pores decreases remarkably with an increase in permeation pressure due to overexpansion of large pores [3]. Kamo et al. [4] and other researchers [5,6] pointed out that solvent-treated hollow fiber can affect the change in pores because microfibril deformation shortens the length. As porous synthetic membranes are mainly used, such results indicate that the change

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1226-086X/$ – see front matter
doi:10.1016/j.jiec.2009.05.001

in membrane pores plays an important role in membrane separation processes.

Furthermore, since such porous synthetic membranes have asymmetric characteristics which can enhance the separation efficiency, the internal structure is different from that of the membrane surface. Therefore along with surface pore change mentioned above, a three-dimensional analysis of changes in internal structure or cross-sections can be used as most basic information for design, operation and back washing of membrane modules. For a long-term operation, in particular, concentration polarization or irreversible membrane fouling is inevitable, giving rise to a decline in the particle removal efficiency. The latter is a phenomenon that a flow rate is decreased by the irreversible accumulation of solutes on membrane surface with processes of adhesive layer formation and pore plugging [7].

From the previous study [1] that the optimum permeation flux was 32.7 l/m^2 h when the hollow fibers was placed diversely with 4 bundles and the packing density was 30.48 threads/cm^2, an intermediate aeration submerged type is used in this study. This study will provide selection criteria to optimize operational period, MLSS concentration range, suggesting the possibility of back washing by investigating changes in permeate flux throughout a three-dimensional analysis of changes in membrane surface, inner and cross-sections for the case of high-level MLSS.

2. Methods and experimental

2.1. Hollow fiber

To investigate the usability and performance of domestic membranes, hollow fiber from domestic S company was used and its specifications are listed in Table 1.

2.2. Composition of synthetic wastewater

To the feed for microorganisms cultivation, synthetic wastewater was made in the laboratory and listed in Table 2.

2.3. Operation conditions

The operating conditions of the submerged membrane bioreactor in this study are summarized in Table 3.

2.4. Pre-treatment of hollow fiber

The hollow fiber was submerged into a mixed solution of ethanol (20–40%) with water for 4 h, washed with distilled water, dried naturally and then used for membrane module setup.

2.5. Module design and set up

According to the results of our previous study on diverse placement module setup and optimum conditions, membrane modules were setup with 4 bundles of 30.48 threads/cm^2. A reactor with aeration lines was operated at the conditions: 25 °C, pH 6.5–7.2, MLSS 7200 ppm and suction pressure 1.0 atm. The schematic diagram of the membrane module and the reactor is shown in Fig. 1. The reactor was operated intermittently to reduce the membrane fouling with an interval of 5 min.

Table 1
Specifications of hollow fiber used.

Type	Hollow fiber
Pore size	0.01–0.02 μm
Material	Polysulfone
Outer diameter of fiber	0.7 mm
Membrane area	0.207 m^2
Number of fibers	400 threads

Table 2
Compositions of synthetic wastewater.

Chemicals	Concentration (mg/L)
Glucose ($C_6H_{12}O_6$)	1.000
KH_2PO_4	0.533
K_2HPO_4	0.640
$(NH_4)_2SO_4$	0.284
NH_4Cl	0.427
$CaCl_22H_2O$	0.013
$MgSO_47H_2O$	0.178
$MnSO_4H_2O$	0.018
KCl	0.025
$FeSO_47H_2O$	0.008

Table 3
Operation conditions of MBR.

Contents	Conditions
Temperature	20 ± 1 °C
pH	6–7
Volume	14 l
DO	6–7 mg/l
MLSS	About 6000 mg/l
Air flow	15 l/min

2.6. Identification of surface pore and cross-section

Depending on experimental conditions, the hollow fibers were separated and naturally dried. The surface and inner pores were cryogenically crushed in liquid nitrogen and measured with a scanning electron microscope (SEM: Quanta 200, Phillips). For the cross-sections, thin films of 10 μm in thickness were prepared and investigated with a transmission electron microscope (TEM: JEOL 1200EX). Fig. 2 depicts the positions of surface and inner pores.

2.7. Permeate and particle removal efficiency

Using latex solution having an average diameter of 0.1 μm, the permeate flux was measured with constant MLSS level, on the basis of the previous result [4] from the particle removal efficiency of hollow fiber membrane which was treated with organic solvent at suction pressure of 1.0 kgf/cm^2. The hollow fiber membrane was made of polysulfone type organic polymer and when mixed with radical solvents, its surface phenomena and internal structure get changed due to microfibril rearrangement. That is, the surface tension of water/ethanol, based on the mixing rate of radical solvent, is given by

$$\sigma_m = \frac{\sigma_1 + \sigma_2}{\sigma_1 X_2 + \sigma_2 X_1}$$

where σ is the surface tension and X is the mole fraction. The subscripts m, 1, and 2 are average, water and ethanol, respectively. In the case of 10% ethanol (σ_1: 72.58 dyn/cm, σ_2: 22.32 dyn/cm), for example, the average surface tension, σ_m, is 1.40. This indicates almost no flux taking place, which is consistent with the result of flux experiments (which will be discussed later).