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Short Communication

Enzymatic Cleaning of Ultrafiltration Membrane Fouled with a Semi-synthetic Type Cutting Oil

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Abstract : The effect of *Candida rugosa* and steapsin lipase cleaning was investigated for ultrafiltration polyethersulphone membrane (30,000 dalton MWCO) fouled with the semi-synthetic type cutting oil. The experimental apparatus for filtering and cleaning was a dead-end Amicon filtration cell controlled temperature by the water circulator. The enzyme cleaning effect was measured with respect to temperature, cleaning time and enzyme concentration. The optimum cleaning condition for the system was 25℃ and 2 hour cleaning with 1,000 units/mL steapsin solution. The pure water flux improvement by the steapsin solution cleaning was about 17% at the optimum cleaning condition.

1. Introduction

The membrane separation processes are widely used in many laboratories and industrial plants for the production of high purity or high performance materials. However, concentration polarization and membrane fouling including particleintrusion and adsorption in the pores are important factors that limit the performance of pressure driven membrane processes. Some researchers have attempted to alleviate fouling through various techniques including chemical modification of membrane surface, physical cleaning methods and hydrodynamic methods [1-3]. Membranes are normally cleaned by the combination of mechanical, chemical and/or biological methods. Recently, cleaning mixtures which contain bioactive agents such as enzymes or enzyme detergent, have been applied to enhance the removal of foulants. Enzymes are ideal cleaning agents for the purpose as they are highly specific for the reactions and the substrates with which they interact. In addition, enzymes act under mild cleaning conditions of pH, temperature and ionic strength and will not damage the membranes [4]. However, the cost of enzyme is usually very expensive. The development of the methods which can recycle the enzyme economically or immobilize the enzyme into the membrane, is required to apply enzyme cleaning for large-scale membrane system.

The purpose of this study is to investigate the effect of enzyme cleaning on the removal of foulants from polyethersulphone (PES) membranes fouled with oily waters. The nature of the membrane foulants present in the metal finishing oily water were mineral oils, fatty acids, emulsifiers and other additives. It was found that lipids such as mineral oils and fatty acids are the major foulants that can adsorb onto PES membrane surface or into the pores [5]. The fouled PES membrane after the filtration of oily water was cleaned by the lipase enzyme solution. The optimum

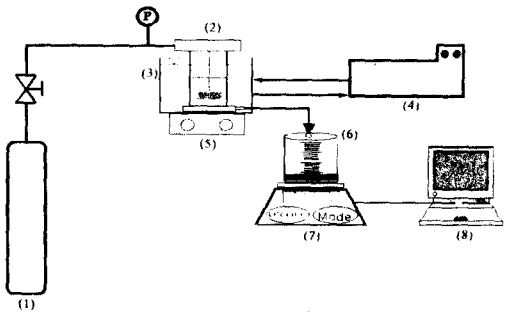
operating condition with respect to temperature, cleaning time and enzyme concentration was obtained.

2. Experimental

The experimental apparatus used in this study is shown schematically in Figure 1. The feed solution in a dead-end Amicon filtration cell (2) with capacity of 50 mL was pressurized by nitrogen gas (1). The effective membrane area was 13.4 cm^2. The cell was placed in the water bath (3) connected with a constant temperature water circulator (4) and a magnetic bar in the cell provided stirring (5). The membrane permeate was collected in a reservoir (6) placed on an electronic balance (7) interfaced to a computer (8) to collect data as a function of time.

2.1. Materials

The filtrations were performed on 30,000 dalton MWCO polyethersulphone membrane. The foulant oils used for the experiments were semi-synthetic type cutting oil (Hocut SSK, Korea Houghton Co.). All feed solutions (1 wt%) were prepared in ultra pure water (greater than 18.2 MΩ · cm) produced by Maxima system (Elga Co.). The enzyme cleaning solutions were prepared with the steapsin (Sigma Chemical Co.) and *Candida rugosa* (Sigma Chemical Co.) lipase. The pH of the enzyme solution was adjusted to 7.4 by adding a little amount of dilute NaOH or HCl.



(1) Nitrogen cylinder (2) Filtration cell
(3) Water bath (4) Constant temperature water circulator
(5) Magnetic stirrer (6) Permeate Reservoir
(7) Balance (8) Computer

Fig. 1. Schematic Flow Diagram for UF Filtration and Enzyme Cleaning.

2.2. Procedures

A new membrane was loaded in the cell and hydrophilized by the filtration of ethanol (Aldrich Co., HPLC grade) at 2.0 bar during 40 minutes. After then, the initial water flux (J_{w1}) was measured at 2 bar during 20 minutes. Fouling experiment for an oily water was carried out under the condition of 3 bar and 400 rpm during 90 minutes. After each run, the membrane and apparatus were thoroughly cleaned using pre-filtered and ultra-pure water, and the pure water flux (J_{w2}) was measured. In order to investigate the enzyme cleaning effect on the fouled membrane, the enzyme solution was introduced into the cell and permeated through the membrane under the various conditions of cleaning temperature, time and enzyme concentration at fixed 1 bar and 400 rpm. The membrane was rinsed using pre-filtered and ultra-pure waters, and then the pure water flux (J_{w3}) was measured again.

3. Results and Discussion

3.1. Effect of Cleaning Temperature

The pure water permeation fluxes (J_{w1}, J_{w2} and J_{w3}) were measured for cases of the *Candida rugosa* and steapsin cleanings of the membrane fouled with cutting oil as a function of temperatures. The enzyme concentrations were fixed at 1,000 units/mL. After the pure water filtration experiment, the flux improvement (FI) by enzyme cleaning method was calculated as follows:

$$FI = \frac{J_{w3} - J_{w2}}{J_{w2}} \times 100(\%) \quad (1)$$

The flux improvements for the *Candida rugosa* and steapsin enzymes were shown in Figure 2. The optimum temperature was about 35°C for *Candida rugosa* enzyme cleaning. The FI by the enzyme cleaning increased with respect to temperature up to 35°C, but the FI decreased

rapidly above 35°C. Moreover, the FI was only positive between 32 and 38°C. Below 32°C, operation temperature might be too low to react actively the enzyme with cutting oil. The enzyme could play as foulant rather than cleaning agent. Also, the enzyme might be degraded at high temperature (above 38°C), and the decomposed enzyme particles could play as foulant. The FI trend for steapsin cleaning was similar to that of *Candida rugosa*. However, the optimum temperature was 25°C and the value of FI was higher than that of *Candida rugosa*. Most of the enzymes are greater than average pore size 30,000 MWCO membrane. Hence, the enzyme cleaning method may be effective to reduce oil foulant on or just below the membrane surface. This may be a reason why the FI is no more than 20%.

3.2. Effect of Cleaning Time

The pure water permeation fluxes were measured for steapsin cleanings of the membrane fouled with cutting oil as a function of cleaning times. The operation temperature and the enzyme concentrations were fixed at 25°C and 1,000 units/mL, respectively. The optimum cleaning time was about 2 hours as shown in Figure 3. It might be required about more than 1.5 hours to degrade the fouled oils. The FI, however, decreased very rapidly, and then approached almost zero for the case of 3 hour enzyme cleaning. The excessively decomposed foulant oils and degraded enzyme might adsorb and/or foul the membrane, but it should be investigated in detail.

3.3. Effect of Enzyme Concentration

The membrane was fouled with 1 wt% cutting oil solution and the water permeation fluxes were measured as described above. The steapsin concentration in the cleaning solution was changed from 250 to 2,000 units/mL. The FI increased rapidly as the steapsin concentration increased up to 1,000 units/mL, and decreased slowly as shown in Figure 4. The optimum steapsin concentration was 1,000 units/mL. For the case of 2,000 units/mL,

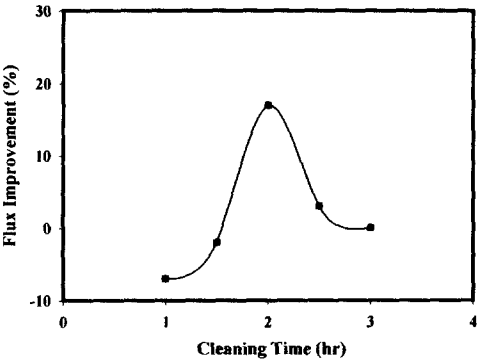


Fig. 3. Cleaning Time Effect on Flux Improvement for PES Membrane fouled with Cutting Oil after Steapsin Cleaning (1,000 units/mL) at 25°C.

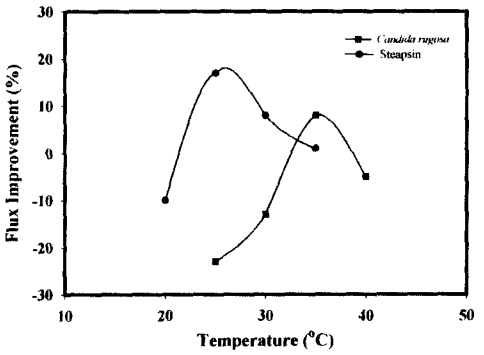


Fig. 2. Temperature Effect on Flux Improvements for PES Membrane fouled with Cutting Oil after 2 hour Enzyme Solution Cleanings (1,000 units/mL).

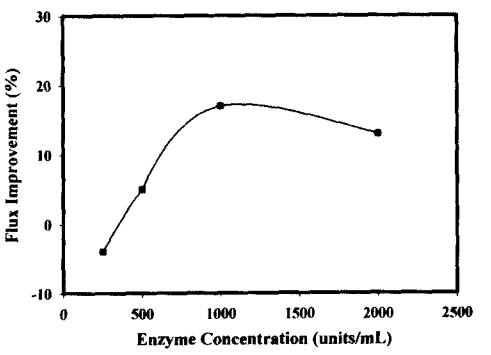


Fig. 4. Enzyme Concentration Effect on Flux Improvement for PES Membrane fouled with Cutting Oil after 2 hours Steapsin Cleaning at 25°C.

the excessive steapsin enzyme might be adsorded more on the membrane surface, and could play slightly as another foulant in addition to the oil foulant.

4. Conclusions

The optimum enzyme cleaning condition for membrane fouled with the cutting oil solution was investigated with respect to temperature, cleaning time and enzyme concentration. The enzyme cleaning might be effective to reduce oil foulant on or just below the membrane surface because most of the enzyme are greater than the membrane pore size. The flux improvements by *Candida rugosa* and steapsin enzyme cleaning were obtained positively between 32 and 38°C, 22 and 35°C, respectively. The optimum cleaning condition for the dead-end system was 25°C and 2 hour cleaning with 1,000 units/mL steapsin solution. The flux improvement was about 17% at the optimum cleaning condition. However, the oil defouling mechanism by the enzymes should be investigated in detail.

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