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Surface modification of polysulfone ultrafiltration membrane by oxygen plasma treatment

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Abstract

Oxygen plasma treatment was used to change the hydrophobic polysulfone ultrafiltration membrane to the hydrophilic membrane. The contact angle of water decreased with increasing the oxygen plasma treated time of polysulfone membrane and was saturated with 20 s of oxygen plasma treated time. Functional groups introduced by oxygen plasma treatment were examined using X-ray photoelectron spectroscopy (XPS) and zeta potential of oxygen plasma treated polysulfone membrane was measured using electrophoretic light scattering (ELS) spectrometer. O/C ratio increased from 33 to 50% and isoelectric point (IEP) of membrane surface increased from pH 3 to 4.5. For oxygen plasma treated polysulfone membrane, the flow rates of pure water and gelatin solution increased at all pH range and plasma treated membranes showed less fouling at membrane surface. The mechanisms of reduced fouling and improved cleaning efficiency of oxygen plasma treated polysulfone membrane were also studied.

Keywords: Surface modification; Polysulfone ultrafiltration membrane; Oxygen plasma; Fouling; Zeta potential

1. Introduction

Polysulfone is widely used as an ultrafiltration membrane and a supporting layer for pervaporation membranes since polysulfone has good thermal and chemical stabilities [1]. But hydrophobic surface of polysulfone membranes has a severe fouling during ultrafiltration of protein containing water solutions [2]. This fouling originates mainly from protein deposited onto membrane surface and the permeate flux of fouled membrane decreases up to less than 5% of initial flux with the increase of permeation time [3]. There are many factors contributing to fouling such as surface properties (chemistry, morphology, etc.), hydrodynamic conditions, ionic strength, and solute concentration [4]. And the extent of adsorption depends on the types of solute macromolecule–membrane interactions such as hydrogen bonding, dipole interaction, van der Waals interaction, and electrostatic effect [5].

One of the main factors enhancing the adsorption of the protein into the membrane surface is hydrophobic interaction between the surface of membranes and protein molecules [6–9]. Therefore, protein molecules adsorbed on the surface of membrane can be reduced by modifying hydrophobic membrane surface to hydrophilic membrane surface. And it is also easy to clean the hydrophilic surface of membranes because adsorbed protein molecules are more easily removed from the surface of membranes.

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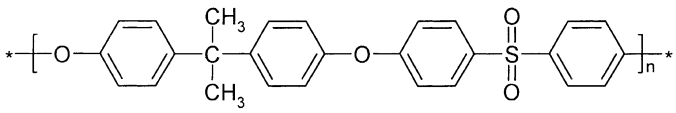


Fig. 1. Chemical structure of polysulfone membrane.

The other factor affecting the adsorption of the protein into the membrane surface is the charge interaction between the surface of membranes and protein molecules. According to the pH of feeding solution, the kind of charge of membrane surface and protein molecules is determined. If the kind of charge is the same, protein molecules cannot be adsorbed on membrane surface. Oxygen plasma treatment is a useful method modifying membrane surfaces from hydrophobic to hydrophilic: oxygen containing polar groups are introduced to membrane surfaces and the kind of charge of membrane can be changed [1,6,10,11]. As a result, the extent of fouling can be reduced and the flux of membrane can be increased.

2. Experimental

2.1. Material

Polysulfone ultrafiltration membrane (Fig. 1, molecular weight cut-off: 30,000 Da) was purchased from UOP Co. (USA). It is a flat sheet membrane and polysulfone is casted on polyethylene non-woven fabric. Gelatin (Aldrich, Type B, from bovine skin, isoelectric point (IEP) is pH 8) was chosen as a waste material and aqueous gelatin solution was used for ultrafiltration.

2.2. Plasma treatment of polysulfone membrane

Fig. 2 shows the homemade plasma equipment operating at radio frequency of 13.56 Mhz. It consisted of parallel plate reactor and rotary and diffusion pumps. 4 cm × 4 cm polysulfone membrane sheets was installed on the grounded electrode (diameter: 13 cm) and treated with oxygen plasma. The flow rate was 20 standard cubic cm per min (sccm), the pressure was 0.3–0.9 Torr, and the power was 60 W. Polysulfone membranes were treated for 5, 10, 20, 30, 60, and 120 s and contact angles of water were measured using goniometer to find out the optimum plasma treatment time. Contact angles decreased up to 20 s of plasma

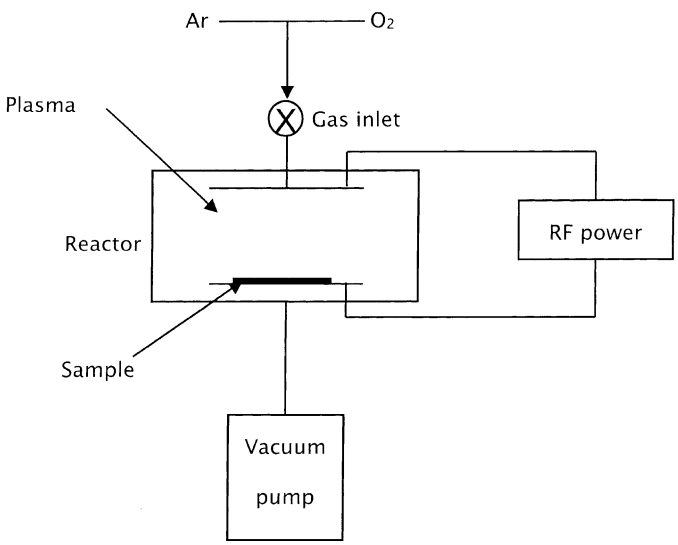


Fig. 2. Schematic diagram of plasma generator.

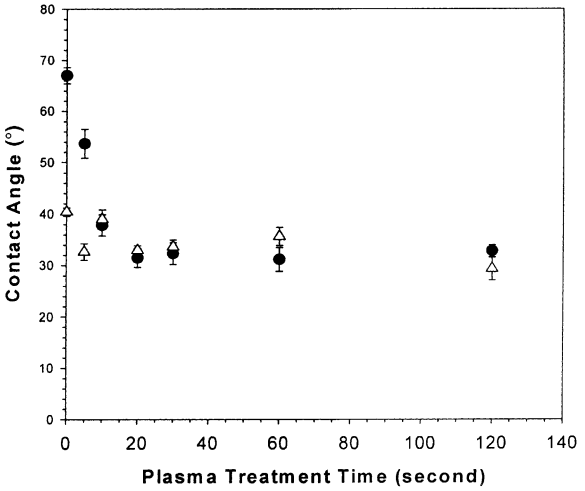


Fig. 3. Contact angle of water (●) and di-iodomethane (△) of oxygen plasma treated polysulfone membrane with the increase of plasma treatment time.

treatment and saturated after that (Fig. 3). Therefore, polysulfone membrane was oxygen plasma treated for 20 s in the experiment. After plasma treatment, membrane sheets were taken out under an argon atmosphere and stored in vacuum desiccators to prevent contamination of surface.

2.3. Contact angle

The surface properties of polysulfone membranes were examined by contact angle measurement. The advancing contact angles of water and di-iodomethane were measured with increasing the water drop volume by contact angle gonimeter (CA-A, Kyowa Surface Science, Tokyo, Japan). With the contact angles of water and di-iodomethane, the surface energy of polysulfone membrane was calculated from the following equations [1,11]:

$$\gamma = \gamma^{\mathrm{d}} + \gamma^{\mathrm{p}}$$

$$(1 + \cos\theta_1)\gamma_1 = 2(\gamma_{\mathrm{s}}^{\mathrm{d}}\gamma_1^{\mathrm{d}})^{1/2} + 2(\gamma_{\mathrm{s}}^{\mathrm{p}}\gamma_1^{\mathrm{p}})^{1/2} \quad (1)$$

$$(1 + \cos\theta_2)\gamma_2 = 2(\gamma_{\mathrm{s}}^{\mathrm{d}}\gamma_2^{\mathrm{d}})^{1/2} + 2(\gamma_{\mathrm{s}}^{\mathrm{p}}\gamma_2^{\mathrm{p}})^{1/2} \quad (2)$$

where γ is the surface free energy; γ^{d} the dispersive term of surface free energy; γ^{p} the polar term of surface free energy; γ_{s} the surface free energy of membrane; θ_1 the contact angle of water; θ_2 the contact angle of di-iodomethane; γ_1 the surface free energy of water and γ_2 is the surface free energy of di-iodomethane.

2.4. X-ray photoelectron spectroscopy (XPS)

The surface atomic compositions of plasma treated polysulfone were analyzed with a Perkin-Elmer Phi-5400 X-ray photoelectron spectrometer using a Mg Kα X-ray source (1253.6 eV, 350 W). The take off angle between the analyzer and the sample surface was 90°.

2.5. Zeta potential

Zeta potential of polysulfone membrane was measured by electrophoretic light scattering spectrometer (ELS 8000 Ostuka Electronic, Tokyo, Japan) equipped with a plated sample cell. Polysulfone membranes were cut squarely in 4 cm × 4 cm size plates. The measurement was carried out at 25 °C in NaOH solution with polystyrene latex monitor particles coated with hydroxypropylcellulose (particle diameter was about 520 nm). Zeta potentials were obtained at pH 3, 8 and 12, and pH was adjusted using 1N HCl and 0.1N NaOH solutions.

2.6. Flow rate

Flow rate measurement were carried out using homemade permeation cell. The cell were made of stainless steel and consisted of two detachable parts. The effective membrane area in the cell was 5.067 cm^2. Polysulfone ultrafiltration membrane was installed at the center of the cell and feed solution was cross-filtered. A high pressure gear pump was used for pumping the feed solution to the cell and pressure was maintained by a backpressure regulator. Before ultrafiltration of gelatin solution, deionized (DI) water was filtered for 1 h with a pressure of 3 kgf/cm^2 to densify the membrane, and then the flow rate of DI water (F_{w}, 0) was measured. Aqueous solution of 0.1 wt.% gelatin was ultrafiltered with a pressure of 3 kgf/cm^2 and a circulation pumping rate of 0.1 m^2/h at pH 3, 8, and 12. The pH of aqueous gelatin solution were adjusted with 1N NaOH and 0.1N HCl. The flow rate of gelatin solution was

measured every 30 min for 3 h. After ultrafiltration of gelatin solution, membrane was cleaned with DI water for 10 min without pressure to flush away the deposited gelatin on the membrane surface and the flow rate of DI water (F_w, 1) was measured again to observe the recovery of the flow rate. We got the flux recovery (%) of the membranes from the following equation:

$$\text{flux recovery (\%)} = \frac{\text{final pure water flux } (F_w,\ 1)}{\text{initial pure water flux } (F_w,\ 0)} \times 100$$

2.7. Deposited gelatin weight

The weight of deposited gelatin on the surface of polysulfone membrane was obtained by measuring the weight of dried membrane before and after ultrafiltration of the gelatin feed solution.

2.8. Field emission scanning electron microscope (FESEM)

FESEM was used to analyze how gelatin was deposited onto the surface of polysulfone membrane. After ultrafiltration of gelatin feed solution, the membrane was removed from the cell and it was rinsed for 1 min with DI water. Then the membrane was coated with platinum and examined by the FESEM (Hitachi, S4200, Japan) at 5 kV.

3. Results and discussion

3.1. Contact angles and surface free energies

Fig. 3 shows the contact angles of water and di-iodomethane for oxygen plasma treated polysulfone membranes as a function of oxygen treatment time. The contact angle of water decreased as plasma treatment time increased since hydrophilic functional groups were introduced on the surface of hydrophobic polysulfone membrane by oxygen plasma treatment [12,13]. On the other hand, the contact angle of di-iodomethane was constant.

Fig. 4 shows the surface free energy of oxygen plasma treated polysulfone membranes. The surface free energy increased mainly due to the increase of polar component and dispersive component was constant with the increase of plasma treatment time. The surface free energy increased rapidly within 20 s of plasma treatment time and then saturated. This indicates that the concentration of polar group within the depth of contact angle measurement (~0.5 nm) reached the saturation point within 20 s of plasma treatment time [13].

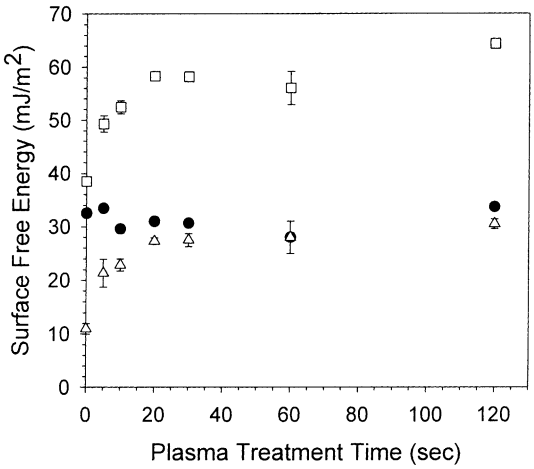


Fig. 4. Surface free energies of oxygen plasma treated polysulfone membrane with the increase of plasma treated time: dispersive component (●), polar component (△), and surface free energies (□).

3.2. XPS

Table 1 shows the atomic ratios of the surfaces of oxygen plasma treated polysulfone membrane measured by XPS depending on the plasma treatment time. Initial O/C ratio was 33% and increased up to about 50% with 5 s of plasma treatment time and then saturated. Hydroxyl, carbonyl, and carboxyl groups were introduced by oxygen plasma treatment. The concentration of hydroxyl, carbonyl, and carboxyl groups was measured by the deconvolution of the C1s peak. It appears that the concentration of hydroxyl group increased from 3 to 5 wt.% with 20 s of oxygen plasma treatment and the concentration of carbonyl and carboxyl groups were not changed with the increase of plasma treatment time.

Table 1
O/C ratio and functional groups of oxygen plasma treated polysulfone membranes

Functional group (%)	Chemical structure of C1s	Treatment time (s)					
		0	5	10	20	60	120
	–C–OH	–	3.97	3.07	5.36	5.56	4.83
	–C=O	–	2.64	0.98	5.21	3.66	2.65
	–C(=O)O	–	1.18	4.90	1.10	1.62	1.25
O/C (%)	–	33	54	49	49	53	48

3.3. Zeta potential of plasma treated polysulfone membranes

Fig. 5 shows the zeta potentials of polysulfone membranes as a function of pH. The zeta potential of untreated membranes was near zero at pH 3 and became more negative with increasing pH. That means that there was no surface charge on raw polysulfone membrane at pH 3 (IEP of untreated polysulfone was pH 3) and negative charge increased on the surface of untreated polysulfone membrane with the increase of pH from 3 to 12. Since the surface of oxygen plasma treated polysulfone membrane easily adsorbed and desorbed the proton due to the introduced hydrophilic functional groups, oxygen plasma treated polysulfone membrane showed a larger decline slope of zeta potential with increasing pH than untreated polysulfone membrane and its IEP was shifted from pH 3 to 4.5. Therefore, the surface of oxygen plasma treated membrane had positive charge at pH 3 and negative charge at higher pH than 4.5. Furthermore, oxygen plasma treated membranes was more negative than untreated membranes at pH 12. At pH lower than IEP of the membrane, membrane surface has an apparent positive charge due to proton adsorption, whereas at pH higher than IEP of the membrane, membrane surface has an apparent negative charge due to proton desorption and hydroxyl anion adsorption [14,15].

Since IEP of gelatin, filtering waste in this experiment, is pH 8, the charge of gelatin was positive at pH 3 and negative at pH 12. That represents that there was charge repulsion between the surface charge of oxygen plasma treated polysulfone membrane and that of gelatin at pH 3 and 12. Therefore, flow rate of gelatin

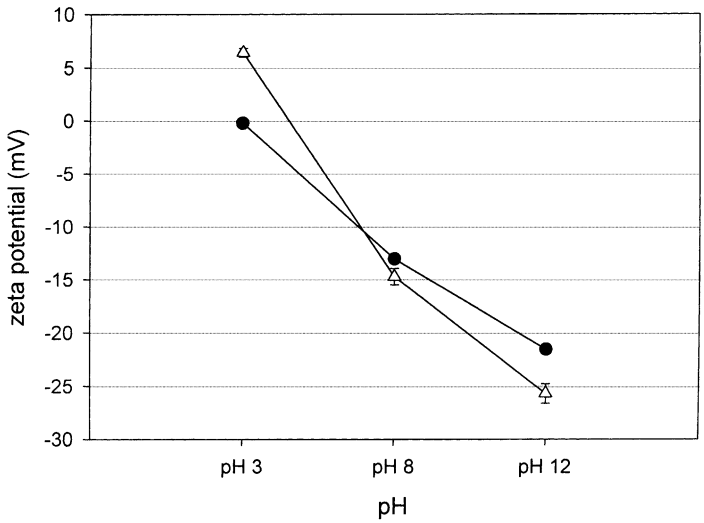


Fig. 5. Zeta potential of untreated polysulfone membrane (●) and oxygen plasma treated polysulfone membrane (△).

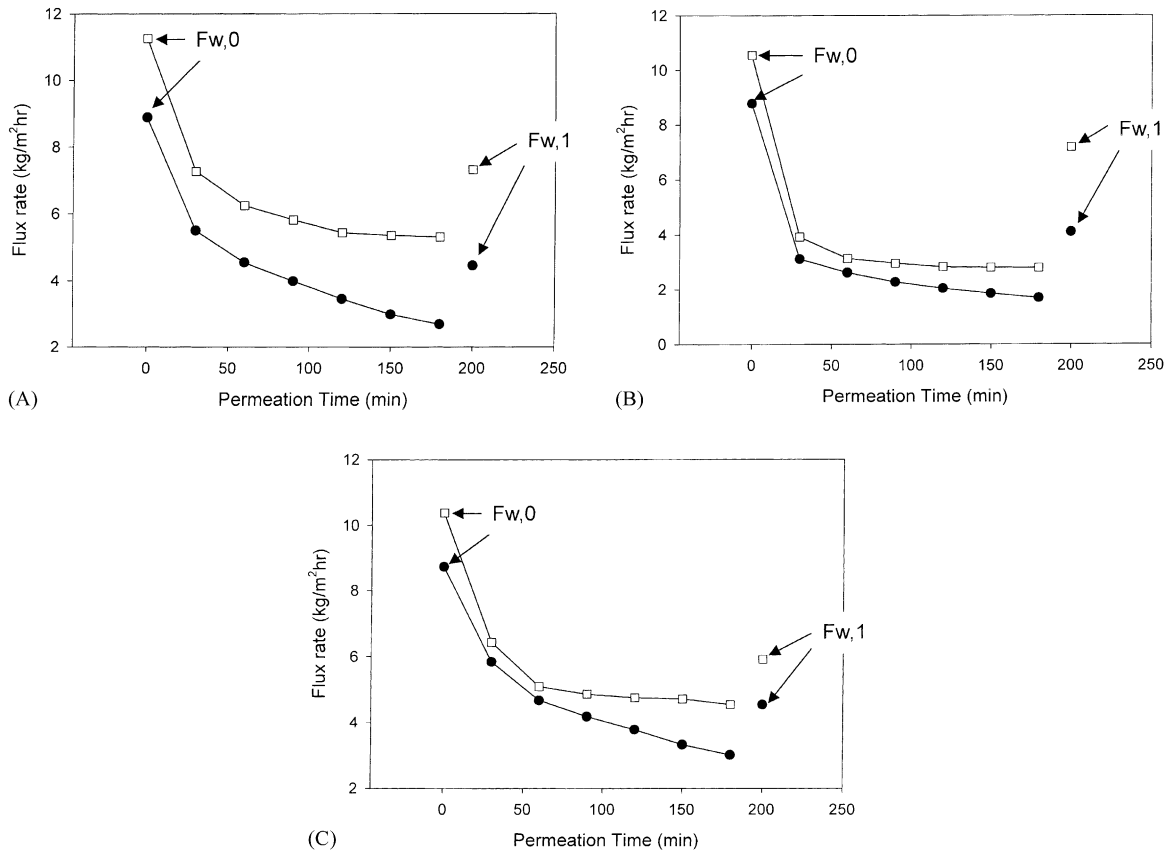


Fig. 6. Flux rate of aqueous gelatin solution at (A) pH 3, (B) pH 8, (C) pH 12: untreated polysulfone membrane (●) and oxygen plasma treated polysulfone membrane (□).

solution with plasma treated polysulfone membranes was higher than that of untreated membranes at pH 3 and 12 (Fig. 6A and C).

3.4. Flow rate and flux recovery

Fig. 6 shows the flow rate of pure water and gelatin solution with increasing the permeation time up to 3 h at pH 3, 8, and 12, respectively. Initial stiff flux decline was observed with both oxygen plasma treated polysulfone membranes and untreated membrane. But this stiff decline does not appear to come from fouling of the membrane but from concentration polarization [3]. The flow rate of pure water and gelatin solution with oxygen plasma treated polysulfone membrane kept greater than that of untreated membrane with increasing permeation time at all pH. This means that fouling of polysulfone membrane can be reduced by oxygen plasma treatment through formation of hydrophilic surface.

The effect of oxygen plasma treatment on the flow rate was the highest at pH 3 (Fig. 6A) due to charge repulsion between the positive charge of plasma treated membrane and the positive charge of gelatin, but the least at pH 8 (Fig. 6B) due to no charge repulsion between the plasma treated membrane and the gelatin.

The flux recovery ratio between the pure water flux before and after ultrafiltering of a gelatin solution (F_w, $1/F_w$, 0) is often used to estimate the fouling susceptibility of a membrane [16]. After flushing the membranes for 10 min, pure water flux was recovered

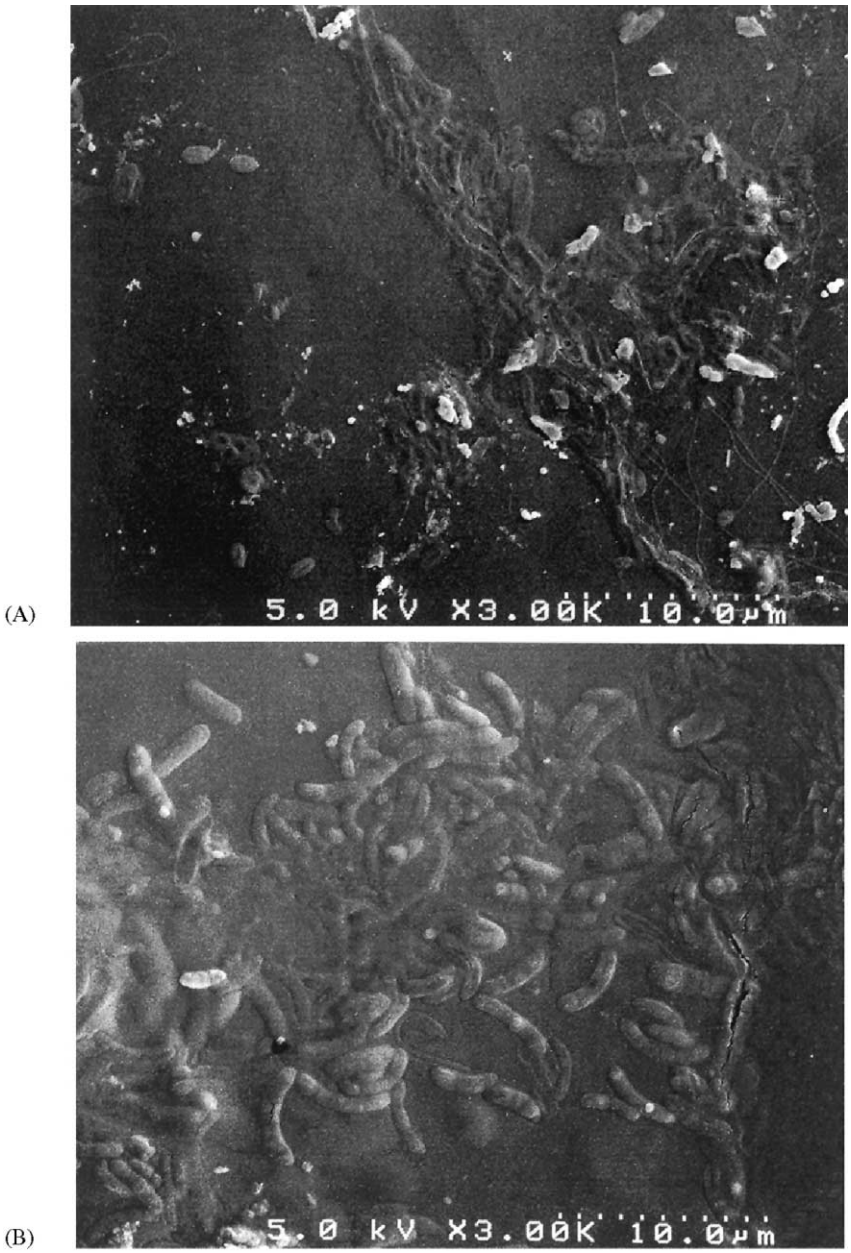
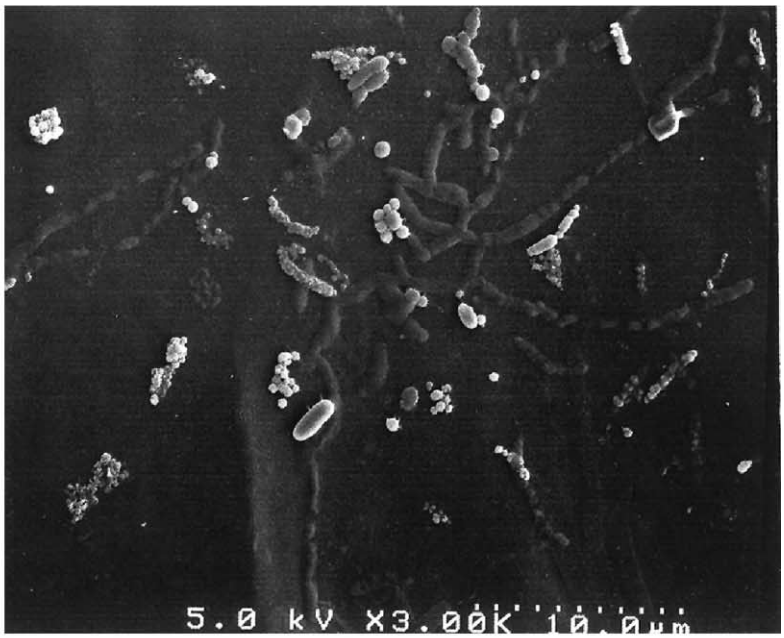


Fig. 7. SEM micrographs of untreated polysulfone membranes at (A) pH 3, (B) pH 8, (C) pH 12 and oxygen plasma treated polysulfone membranes, (D) pH 3, (E) pH 8 and (F) pH 12 after flux test of gelatin solution.

(C)



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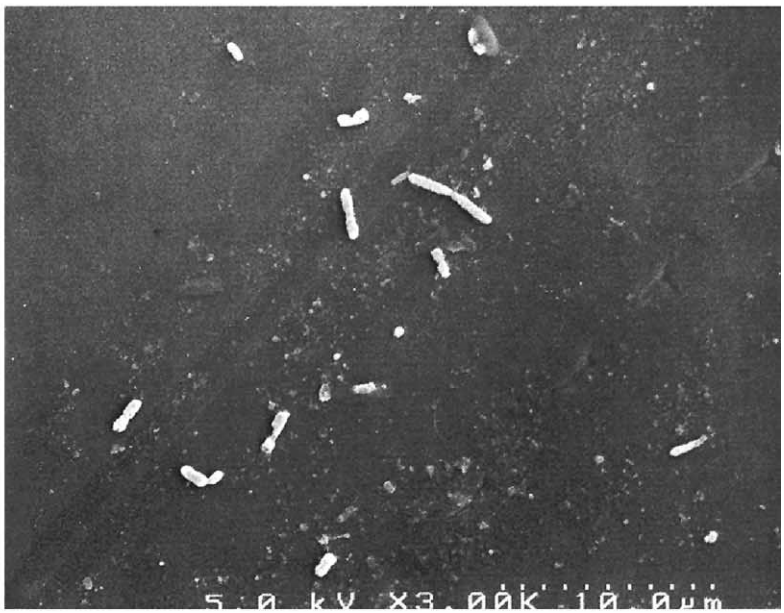
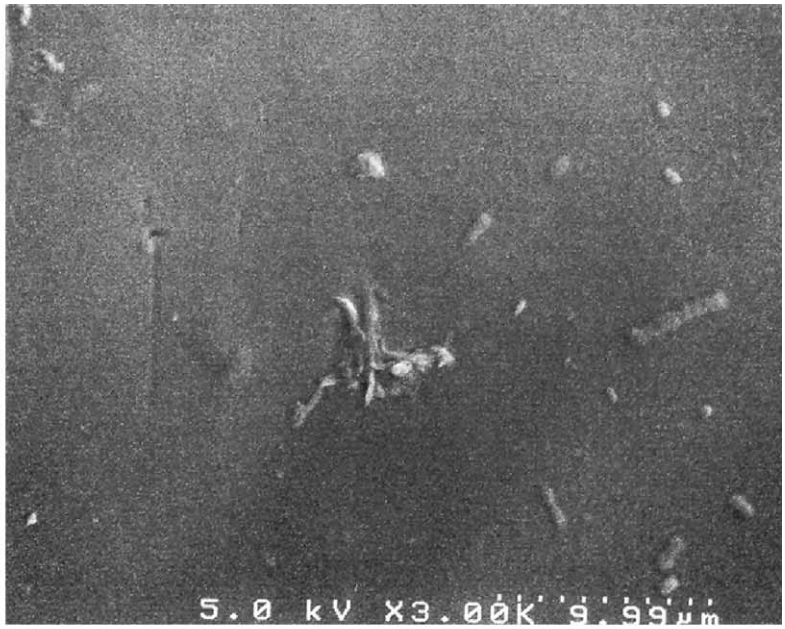


Fig. 7. (*Continued*).

(E)



(F)

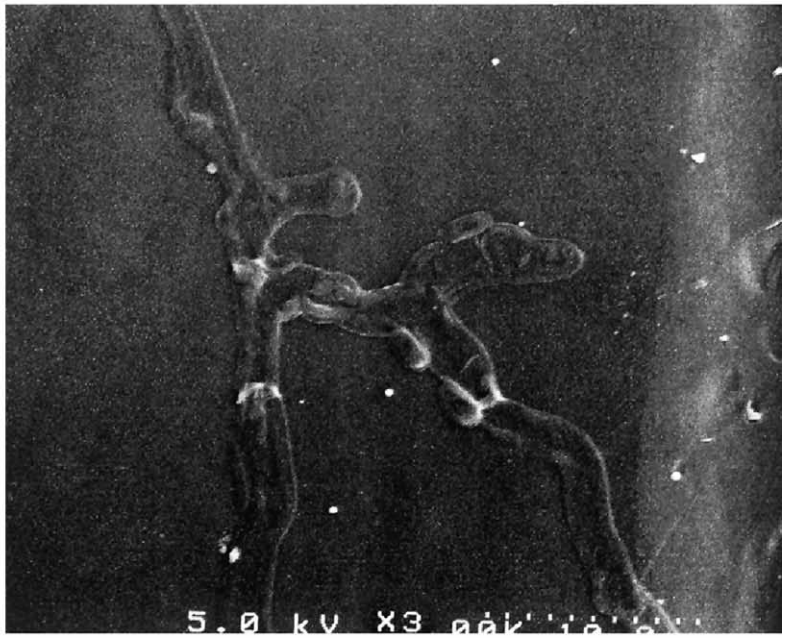


Fig. 7. (*Continued*).

Table 2
Flux recovery of untreated polysulfone membrane and oxygen plasma treated polysulfone membrane

pH	Sample	
	Untreated polysulfone membrane (%)	Oxygen plasma treated polysulfone membrane (%)
3	50	65
8	45	68
12	52	63

about 60% with oxygen plasma treated polysulfone membranes, while pure water flux was recovered about 50% with untreated membranes as shown in Table 2. This illustrated that the cleaning efficiency with oxygen plasma treated polysulfone membranes was better than that with untreated membranes.

3.5. Deposited gelatin weight

The weight of deposited gelatin on the plasma treated polysulfone membranes was lower than that on the untreated membranes as shown in Table 3. Reduced hydrophobic interactions and charge repulsion between the oxygen plasma treated membrane and the gelatin molecules interrupted the deposition of gelatin molecules into the oxygen plasma treated membrane surface.

Fig. 7 shows much more deposition of gelatin on the untreated polysulfone membrane than that on the oxygen plasma treated polysulfone membrane. Since gelatin molecules did not have charge repulsion between the untreated membrane and gelatin molecule at pH 8, gelatin was easily deposited on the untreated membrane (Fig. 7B).

Table 3
Gelatin adsorption weight of untreated polysulfone membrane and oxygen plasma treated polysulfone membrane

pH	Sample	
	Untreated polysulfone membrane ($\mu g/cm^2$)	Oxygen plasma treated polysulfone membrane ($\mu g/cm^2$)
3	0.09	0.06
8	0.14	0.11
12	0.09	0.06

4. Conclusions

The surface of polysulfone membrane was changed from hydrophobic to hydrophilic by oxygen plasma treatment. The optimum oxygen plasma treatment time was 20 s. Polar functional groups such as hydroxyl, carbonyl, and carboxyl group were introduced on the polysulfone membrane and confirmed by XPS and contact angle measurement. Since the hydrophilic polysulfone membrane could repel the hydrophobic gelatin molecules used as a waste, the fouling of polysulfone membrane was reduced. IEP of polysulfone membrane was also changed from pH 3 to 4.5. Therefore, oxygen plasma treated polysulfone membrane had positive charges at pH 3 and negative charges at pH 12. Since the gelatin molecules also had positive charge at pH 3 and negative charge at pH 12, there was charge repulsion between the oxygen plasma treated membrane and the gelatin molecules in the waste solution.

Consequently, oxygen plasma treatment of polysulfone membrane reduced the fouling and increased the flux of polysulfone membrane in the waste treatment, because of hydrophilicity of oxygen plasma treated membrane and charge repulsion between the oxygen plasma treated membrane and the gelatin molecules.

Acknowledgements

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