정밀여과 공정에서의 파울링 현상 및 분리막 표면개질을 이용한 제어

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Membrane Fouling in Microfiltration Process and Its Control by Surface Modification of Membrane

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요 약: 나일론 분리막과 효모 현탁액을 모델 시스템으로 하여 정밀여과 공정시 일어나는 파울링 현상에 대하여 살펴보았다. 효모를 나일론 필름, 나일론 분리막, 개질된 나일론 필름, 개질된 나일론 분리막 등 여러 종류의 피흡착제에 흡착시킴으로써 파울링의 초기단계에서 분리막의 표면특성이 효모 입자들과 분리막 표면간의 상호작용에 미치는 영향을 살펴보았다. 효모의 흡착은 주로 피흡착제 표면의 친수성과 전기적 특성에 영향을 받았으며, 피흡착제를 산소 및 아크릴 산 플라스마를 이용하여 전기적으로 음성을 띈 친수성 표면을 갖도록 개질시켰을 때 가장 적은 흡착량을 보였다. 이에 따라, 파울링도 분리막을 산소 및 아크릴 산 플라스마로 개질시킴으로써 크게 줄일 수 있었다. 카세인 용액으로 시험한 결과, 이러한 플라스마들을 이용하면 분리막의 외부 표면뿐만 아니라 분리막 구멍들의 내부 표면까지도 개질시킬 수 있음을 알 수 있었다.

ABSTRACT: Membrane fouling phenomena ooccurring during microfiltration were studied for a nylon membrane with yeast (*Saccharomyces cerevisiae*) suspension as a model system. Yeast was adsorbed on various adsorbents (nylon film, nylon membrane, modified nylon film, and modified nylon membrane) for the examination of the effect of surface characteristics of a membrane on the interactions of yeast particles with membrane surface in the initial stage of fouling. The adsorption was mainly influenced by the hydrophilicity and the electrostatic charge of the adsorbent surface. The least amount of adsorption was observed on the modified adsorbents which have hydrophilic and negatively charged surface via oxygen or acrylic acid plasma treatment. As a consequence, the fouling could be reduced to a large extent by modifying the nylon membrane by oxygen or acrylic acid plasma treatment. Those plasma treatments modified not only the outer surface of the membrane but also the inner surface of membrane pores, which was tested with casein solution.

Keywords: *fouling, microfiltration, membrane, yeast, surface modification, low temperature plasma.*

INTRODUCTION

The membrane process is a highly attractive process for the separation of various materials, especially biological materials such as foods, beverages, and pharmaceuticals. It is a nonthermal energy-saving and highly efficient compact modular process. Because of these unique advantageous features, a lot of membrane processes have been developed since the preparation of a highly selective asymmetric polymer membrane in the early 1960s.[1] However, some of them could not be practically used because of one crucial problem, flux decline during the process which all the membrane processes suffer from.

There are three major phenomena which cause the flux decline: concentration polarization, membrane compaction, and fouling.[2-10] Concentration polarization occurs due to the selective transport characteristic of a membrane and reduces the flux by increasing the concentration of solutes in the vicinity of a membrane. Membrane compaction occurs due to the applied pressure and reduces the flux by densifying a membrane. These two phenomena occurs only in the beginning stage of the process, and thus may not be as critical as the last one, fouling. Fouling occurs due to the adsorption of materials from the feed stream and continuously accumulates solid deposits onto a membrane surface. The deposits create a growing new dense layer blocking pores in the membrane and resulting in the continuous flux decline. As a result, the process becomes less productive with shortened service-life of a membrane.

Efforts to reduce the fouling have been focused mainly to the treatment of a feed stream and the optimization of flow pattern in the early stage.[11-20] Prefiltration was used to remove large particles. Physico-chemical characteristics of the feed solution such as pH, temperature, and salt concentration were adjusted to control solubility, dispersion,

and confirmation of solutes. Cross flow with a high velocity in a small channel and pulsatile flow were used to increase the shear rate.[5,21] In recent years, more attention is given to the development of fouling-resistant membranes.[4] Since hydrophobic membranes are known to be more prone to fouling in an aqueous medium, major effort is given to the modification of a membrane surface to make more hydrophilic.[22-25]

In this work, membrane fouling during microfiltration was studied with a nylon membrane and yeast (*Saccharomyces cerevisiae*) as a model system. Yeast was adsorbed on various adsorbents for the examination of the effect of surface characteristics of a membrane on the interactions of yeast particles with membrane surface in the initial stage of fouling. Reduction of the fouling was tried by surface modification of a membrane using a low temperature plasma process.

Effect of Surface Characteristics of a Membrane on Fouling. Since fouling is initiated by the adsorption of materials from the feed stream although its overall mechanism is not well known yet, the effect of surface characteristics of a membrane on the fouling can be understood from the simple thermodynamic model of solid-solid adsorption in liquid.

According to the thermodynamic model, Gibbs energy should be decreased for particles in liquid to be adsorbed on a solid surface. Therefore,

$$\Delta G = \gamma sp - \gamma sl - \gamma pl < 0$$

where γsp refers to the interfacial energy between the solid surface (s) and the particle (p), γsl the interfacial energy between the solid surface and the liquid (l), γpl the interfacial energy between the particle and liquid. This equation implies that the adsorption and thus the fouling are favored as the interfacial energy between the solid surface and the liquid, γsl, increases for constant γpl.

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Therefore, fouling would be favored on a hydrophobic membrane surface than a hydrophilic membrane surface in aqueous system since γsl increases as hydrophobicity of a solid surface increases in aqueous system.

The above equation can also be expressed in terms of surface energies of each material. If the surface energy is divided into dispersive component (γ^d) and polar component (γ^p), it can be written as follows:
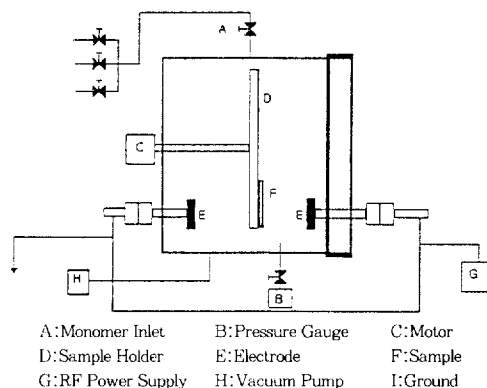
$$\Delta G = \gamma s p - \gamma s l - \gamma p l$$
$$= \{(\gamma s^d)^{1/2} - (\gamma p^d)^{1/2}\}^2 + [(\gamma s^p)^{1/2} - (\gamma p^p)^{1/2}]^2$$
$$- \{(\gamma s^d)^{1/2} - (\gamma l^d)^{1/2}\}^2 - [(\gamma s^p)^{1/2} - (\gamma l^p)^{1/2}]^2$$
$$- \{(\gamma p^d)^{1/2} - (\gamma l^d)^{1/2}\}^2 - [(\gamma p^p)^{1/2} - (\gamma l^p)^{1/2}]^2$$
$$= -2\gamma l^d - 2\gamma l^p + 2(\gamma p^d \, \gamma l^d)^{1/2} + 2(\gamma p^p \, \gamma l^p)^{1/2}$$
$$- 2(\gamma s^d \, \gamma p^d)^{1/2} + 2(\gamma s^d \, \gamma l^d)^{1/2} + 2(\gamma s^p \, \gamma l^p)^{1/2}$$
$$- 2(\gamma s^p \gamma p^p)^{1/2}$$

This equation shows that the Gibbs energy change increases as much as $2(\gamma s^p)^{1/2}[(\gamma l^p)^{1/2} - (\gamma p^p)^{1/2}]$ as the polar characteristic of the solid surface increases. This means that fouling can be reduced if a membrane surface is modified to be more polar as far as γl^p is greater than γp^p.

In addition to the surface or interfacial energy taken into account in the above thermodynamic model, forces between the particle and the solid surface, such as electrostatic force and hydrophobic force, play an important role in the adsorption of the particle.[26-28] Hydrophobic force may decrease as the solid surface becomes polar. However, electrostatic force does not always decrease. It decreases only when the particle and the solid surface have electrostatic charges of the same polarity.

EXPERIMENTAL

Membrane and Surface Modification. The membrane used in this study was a nylon micro-
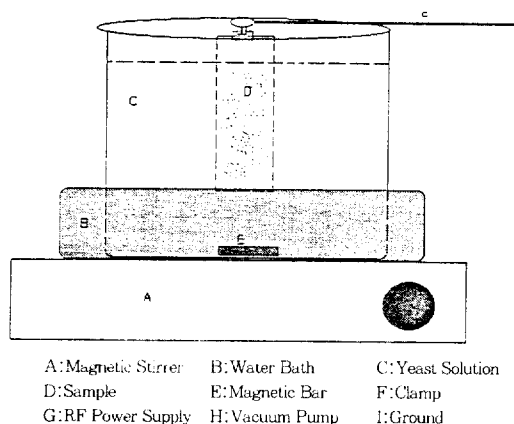

A:Monomer Inlet B:Pressure Gauge C:Motor
D:Sample Holder E:Electrode F:Sample
G:RF Power Supply H:Vacuum Pump I:Ground

Figure 1. Schematic diagram of a plasma reactor.

filtration membrane with a pore size of 0.2 μm. It was purchased from Aldrich (product of Schleicher & Schuell).
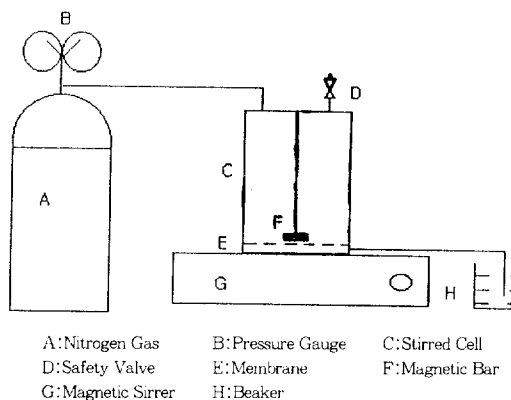
Surface modification of the membrane was carried out in a plasma reactor shown in Fig. 1. The membrane was attached on a rotating sample holder with a speed of 9.2 rpm for uniform treatment. Since the membrane moved in and out of plasma zone while rotating, real contact time of the membrane with plasma was approximately 1/4 of the treatment time.

Adsorption Experiment. Adsorption experiment was carried out at 15 ℃ by immersing a film or a membrane in a beaker which contained yeast suspension, as shown on Fig. 2. The suspension was stirred slowly with a magnetic stirrer to prevent sedimentation of yeast particles. Adsorbed amount of yeast was determined by measuring the dry weight of the film or the membrane before and after the adsorption, respectively.

Fouling Experiment. Fouling experiment was carried out at 15 ℃ for dead-end filtration with a stirred cell apparatus (purchased from Amicon) shown in Fig. 3. The cell was filled with 50 ml of yeast suspension and pressurized to 2.5 bars using a nitrogen gas while stirring the suspension with a magnetic stirrer to reduce the effect of concentration polarization.

A:Magnetic Stirrer	B:Water Bath	C:Yeast Solution
D:Sample	E:Magnetic Bar	F:Clamp
G:RF Power Supply	H:Vacuum Pump	I:Ground

Figure 2. Apparatus for adsorption experiment.

A:Nitrogen Gas	B:Pressure Gauge	C:Stirred Cell
D:Safety Valve	E:Membrane	F:Magnetic Bar
G:Magnetic Sirrer	H:Beaker	

Figure 3. Filtration apparatus for fouling experiment.

The filtration process was stopped when volume of the suspension was decreased to 30 ml and repeated with the same membrane after rinsing the membrane with a distilled water. The degree of fouling was determined based on the flux decline with repetition of the filtration. Total amount of foulants was calculated by measuring the dry weight of a membrane before and after the filtration respectively.

RESULTS AND DISCUSSION

Adsorption of Yeast. When yeast was
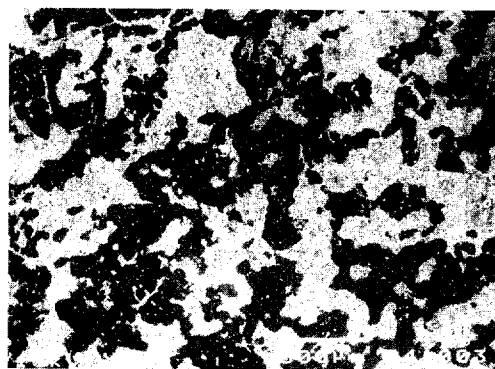
Figure 4. Scanning electron micrograph of nylon surface after the adsorption of yeast for 20 minutes.

adsorbed on a nylon film at pH 6.5 (distilled water), adsorbed yeast cells distributed non-uniformly on nylon surface forming small and large islands (Fig. 4) and the amount of adsorption fluctuated up and down rather than increasing steadily with time. The degree of fluctuation became higher as concentration increased. However, the average amount of adsorption was not much dependent on the concentration. This is shown in Fig. 5 for concentrations of 0.2, 0.3, and 0.5 wt.%. This seems to be due to shear force exerted on the islands while suspension is stirred to prevent sedimentation of yeast cells and weak adhesion of the adsorbed yeast cell islands. If the adhesion is not so strong to overcome the shear force, some islands will be detached while growing bigger resulting in the decreased amount of adsorption at that moment.
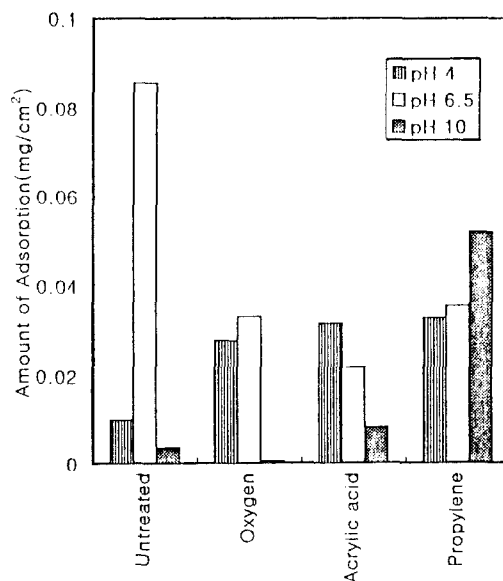
pH of 0.2 wt.% suspension was adjusted to 4 and 10 and adsorption was carried out for 2 hours to see the electrostatic charge effect of yeast cells and nylon surface. If yeast cells carry electrostatic charge, the amount of adsorption will be varied as pH changes. Electrostatically charged materials are known to show the highest adsorption at pH of their isoelectric point.[29] If both yeast cells and nylon surface carry electrostatic charge, adsorption will be promoted at pHs where they carry
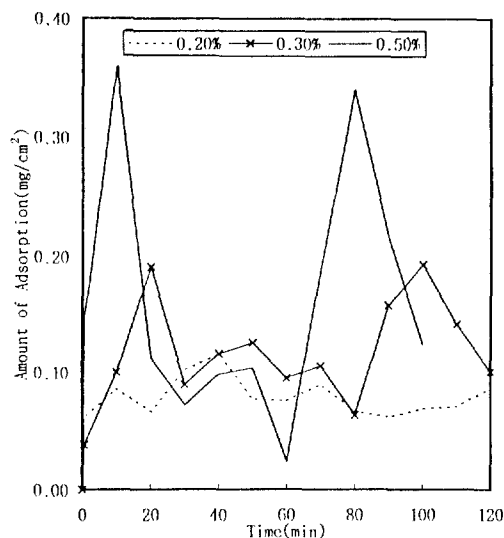
Figure 5. Amounts of adsorption as a function of time for 0.2, 0.3, and 0.5 wt.% yeast suspensions.

Figure 6. Amounts of adsorption on a nylon film and modified nylon films with propylene, oxygen, and acrylic acid plasmas after the adsorption for 2 hours in 0.2 wt.% yeast suspension at pH 4, 6.5, and 10.

the opposite charge and depressed at pHs where they carry the same charge.[30,31] The amount of adsorption decreased significantly as pH changed to 4 and 10 as shown in Fig. 6. This indicates that there surely was electrostatic interaction involved.

To investigate the electrostatic charge effect more in detail, the nylon film was modified first with propylene plasma. The propylene plasma treatment deposits an ultrathin nonpolar hydrocarbon film on nylon surface. The hydrocarbon film does not carry electrostatic charge at any pHs, the effect of electrostatic interaction between yeast cells and adsorbent surface can be eliminated if the modified film is used as an adsorbent. Amounts of adsorption on the modified film at three different pHs are also shown in Fig. 6. They are not much dependent on the pH. A little bit higher value at pH 10 seems to be due to the bridging effect by cations, which will be further discussed later. From this result, it can be concluded that the large difference between the amount of adsorption at pH 6.5 and those at pH 4 and 10 on a nylon surface was mainly attributed to electro-

static interaction between yeast cells and nylon surface. That is, yeast cells and nylon surface carried the opposite charge at pH 6.5 but the same charge at pH 4 (positive) and 10 (negative). Note that the amount of adsorption at pH 6.5 is smaller on the modified film than on the nylon film even though the modified film has more hydrophobic surface (water contact angle: 87°) than the nylon film (water contact angle: 70°).

Next, the nylon film was modified with oxygen and acrylic acid plasma. Since such films are negatively charged at pH 6.5 due to high concentrations of oxidized carbons and/or acid groups on the surface, as shown in Fig. 7, the amount of adsorption at pH 6.5 will decrease if yeast cells are negatively charged and increase if positively charged. Amounts of adsorption on the modified film with oxygen and acrylic acid at three different pHs are also shown in Fig. 6. It is shown that the modification decreased the amount of adsorption at pH 6.5 and 10 and increased the amount

Binding Energy (eV)

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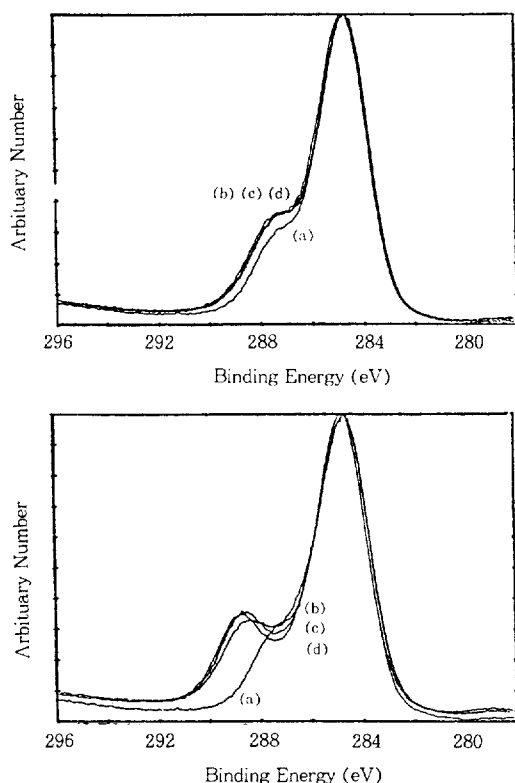
Figure 7. ESCA C_{1S} spectra of nylon surface and modified nylon surfaces with oxygen(above) and acrylic acid(below) plasmas: above; (a) unmodified, (b) 10 W, 15 min, (c) 20 W, 15 min, (d) 20 W, 20 min, below; (a) unmodified, (b) 30 W, 5 min, (c) 20 W, 5 min, and (d) 10 W, 5 min.

of adsorption at 4. This indicates that yeast cells are negatively charged at pH 6.5, which has been reported in the literature.[30] The reason why the amount of adsorption was increased at pH 4 may be that the modified film surfaces were still negative even at pH 4 (or neutral at least) while yeast cells became positive.

Finally, the adsorption experiments were repeated using a nylon membrane as an adsorbent. The same pattern of the adsorption was observed but the amount of adsorption was always smaller than the amount of adsorption on a nylon film as shown in Fig. 8. On a membrane modified with oxygen or acrylic acid plasma, the amount of
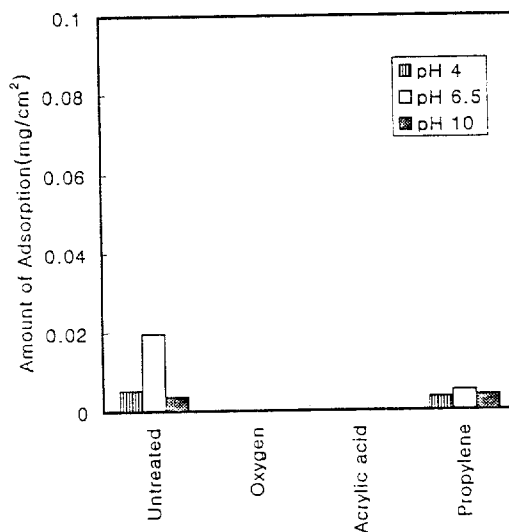

Figure 8. Amounts of adsorption on a nylon membrane and modified nylon membranes with propylene, oxygen, and acrylic acid plasmas after the adsorption for 2 hours in 0.2 wt.% yeast suspension at pH 4, 6.5, and 10.

adsorption could hardly be measured. This is because the membrane has much smaller contact area available for yeast cells. The membrane is porous and only the outer surface is available since the pore size of the membrane is smaller than the size of yeast cells.

Membrane Fouling and Its Control. When yeast suspension was filtrated with a nylon microfiltration membrane at pH 6.5, water flux continuously declined as the membrane was repeatedly used in a batch filtration unit indicating that the membrane was fouled by yeast cells in every run. As concentration increased, the flux decreased from the first run proportionally to the concentration. This is shown in Fig. 9 for concentrations of 0.2, 0.3, and 0.5 wt.%. However, the degree of fouling does not seem to be influenced by the concentration. Slopes of the flux decline are almost the same independently of the concentration.

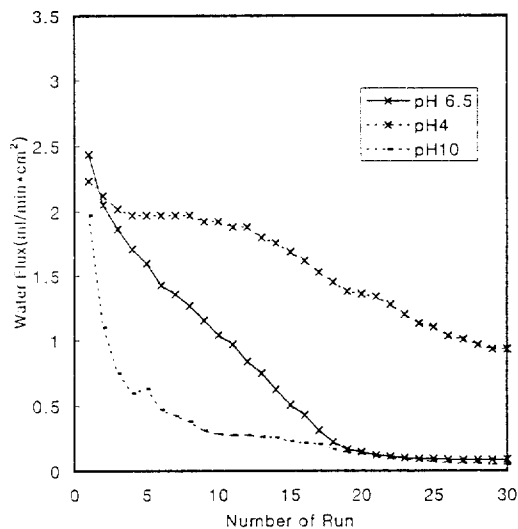Based on the results in the adsorption study, pHof suspension was adjusted to 4 and 10 to see
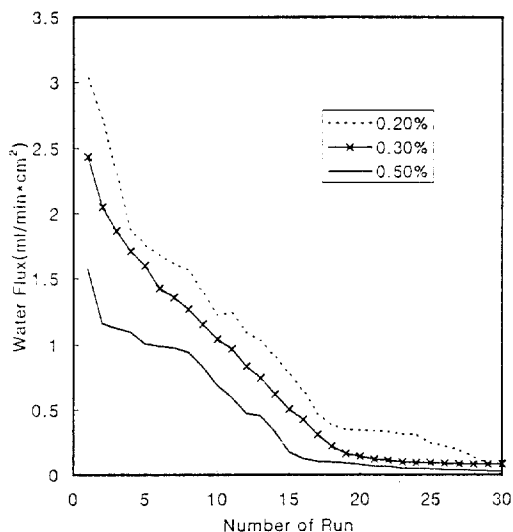
Figure 9. Water flux of a nylon membrane at pH 6.5 as a function of repeated number of filtration for 0.2, 0.3, 0.5 wt.% yeast suspensions.

Figure 10. Water flux of a nylon membrane at pH 4, 6.5, and 10 as a function of repeated number of filtration of 0.3 wt.% yeast suspension.

whether the fouling could be reduced. When tested for 0.3 wt.% suspension, less fouling was oberved at pH 4 as expected but even heavier fouling was observed at pH 10 on the contrary to the case of adsorption (see the flux decline in Fig. 10). This seems to be due to the bridging effect of Na^+ ions which was added in the form of NaOH to adjust the pH of suspension. The Na^+ ions coagulated yeast cells and enhanced the adhesion of yeast cells on nylon surface by acting as bridges among negatively charged yeast cells and between the yeast cells and negatively charged nylon surface.

The reason why the bridging effect which was not well observed in the adsorption study appeared so distinctly in the filtration may be that Na^+ ions were highly concentrated in the vicinity of the membrane surface due to concentration polarization and all the coagulated yeast cells were driven towards the membrane by the transmembrane pressure.

Since it has been reported in the literature that the addition of small amount of salt depressed the

adsorption of proteins and increased the flux,[32,33] pH adjustment to 10 was retried by adding NaOH and HCl together instead of NaOH alone. The result is shown in Fig. 11. The same trend is observed. The reason for this result is not explained in the literature but it is postulated that the bridging effect is screened by Cl^- ions. Fig. 11 also shows that the flux declines more rapidly when pH is adjusted with $Ca(OH)_2 + HCl$ than $NaOH + HCl$. This indicates that cations with higher valence has higher capability of bridging and are less screened with counter ions.

The membrane was modified with oxygen and acrylic acid plasma to reduce the fouling at pH 6.5. Oxygen plasma treatment was done at the discharge power of 20 W and at the gas pressure of 120 and 200 mtorr for 5, 15, and 30 minutes. Acrylic acid plasma treatment was done at the discharge power of 10, 20, and 30 W and at the gas pressure of 35 mtorr for 5 minutes. The results are shown in Figs. 12, 13, and 14. The figures show that the fouling can be reduced by the modifications. The reduction of fouling is attribut-
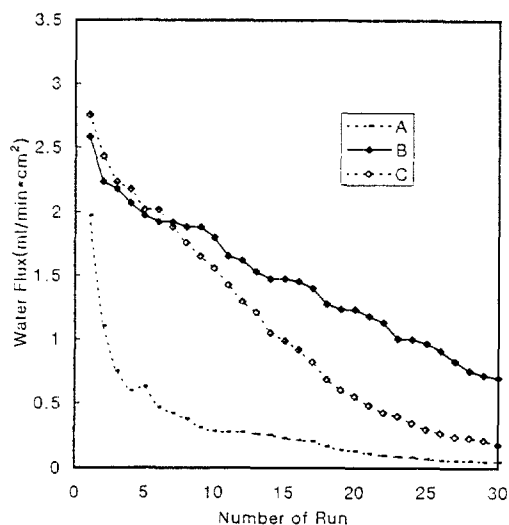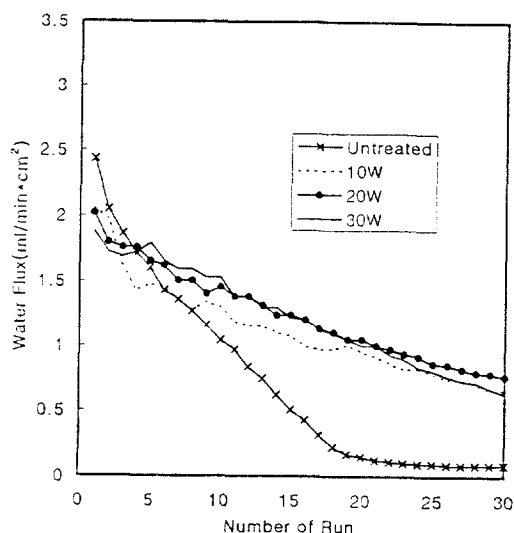
Figure 11. Water flux of a nylon membrane at pH 10 as a function of repeated number of filtration of 0.3 wt.% yeast suspension. The pH was adjusted in three different ways: A; with just NaOH, B; with NaOH and HCl, C; with Ca(OH)$_2$ and HCl.
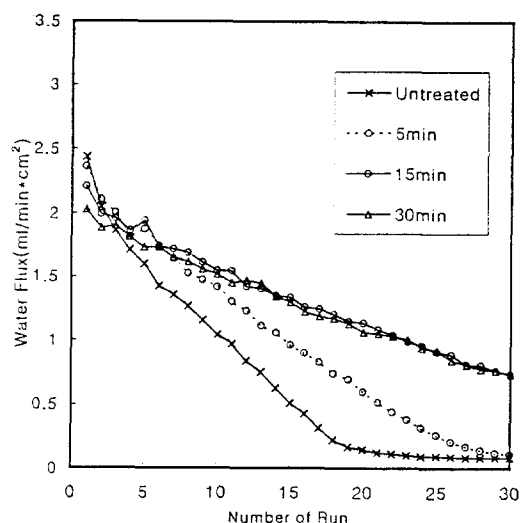
Figure 13. Water flux of modified nylon membranes with oxygen plasma at 20 W and 200 mtorr for 5, 15, and 30 minutes as a function of repeated number of filtration of 0.3 wt.% yeast suspension at pH 6.5.
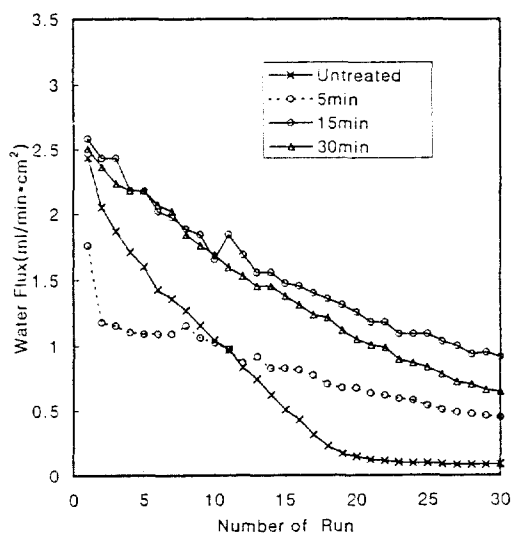
Figure 12. Water flux of modified nylon membranes with oxygen plasma at 20 W and 120 mtorr for 5, 15, and 30 minutes as a function of repeated number of filtration of 0.3 wt.% yeast suspension at pH 6.5.


Figure 14. Water flux of modified nylon membranes with acrylic acid plasma at 10, 20, and 30 W and 35 mtorr for 5 minutes as a function of repeated number of filtration of 0.3 wt.% yeast suspension at pH 6.5.

ed to the resistance of the modified surfaces against adsorption of yeast cells. Fig. 15 shows

fouled surfaces of a nylon membrane and a modified membrane with oxygen plasma which were
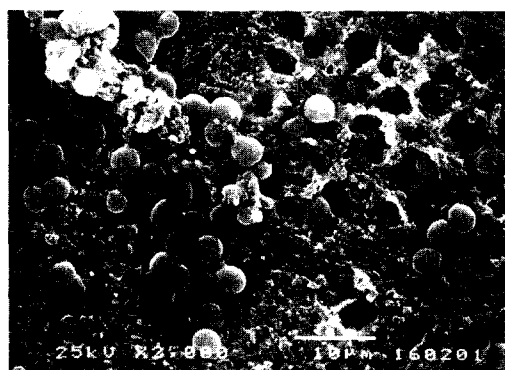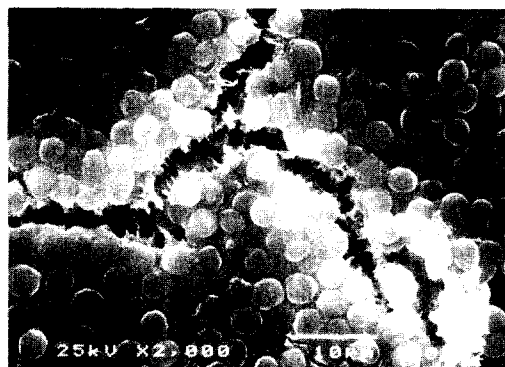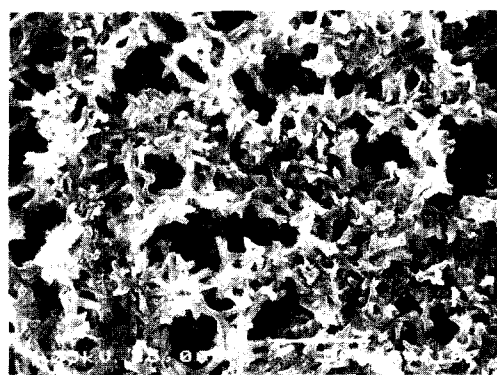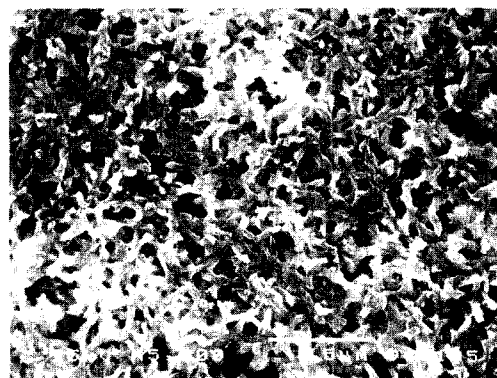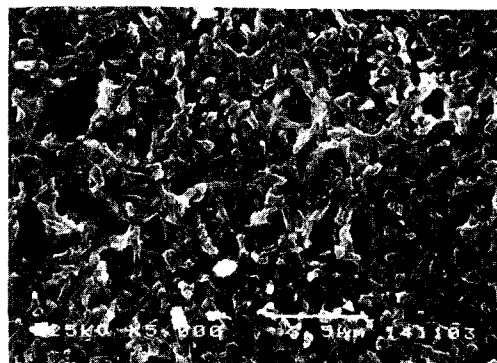
Figure 15. Scanning electron micrographs of fouled surfaces of a nylon membrane(above) and a modified nylon membrane with oxygen plasma (below) after being used for 30 times in the filtration of 0.3 wt.% yeast suspension.

used for 30 times in the filtration of 0.3 wt.% yeast suspension. The modified membrane is only partially covered with small number of yeast cells while the nylon membrane is entirely covered with a thick yeast layer.

In the case of oxygen plasma, the best result was obtained when treated for 15 minutes at any pressure. When treated longer, only the damage on the very surface of the membrane was resulted as shown in Fig. 16. In the case of acrylic acid plasma, the best result was obtained at 20 W and no change in the surface morphology of the membrane was observed at any discharge power although the modification resulted in the deposition of a thin film.

Figure 16. Scanning electron micrographs of nylon membrane surface and modified nylon membranes with oxygen plasma for 15 and 30 minutes: up; unmodified, middle; 15 min, below; 30 min.
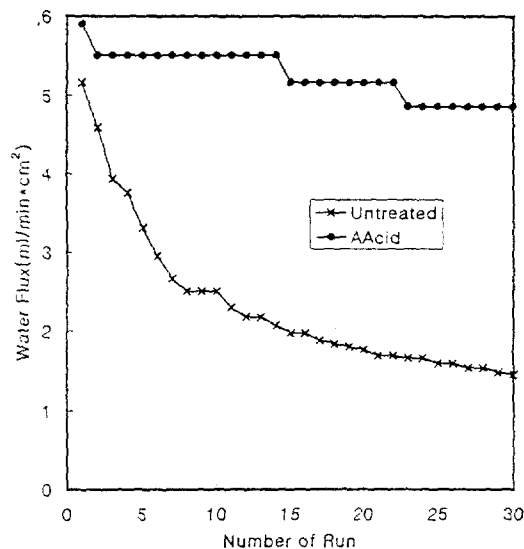
The membrane was also modified with propylene (20 W, 25 mtorr, 10 min), hexamethyldisiloxane (20 W, 100 mtorr, 10 min), and diaminocyclohexane (20 W, 100 mtorr, 5 min)lasmas for comparison. Hexamethyldisiloxane plasma makes
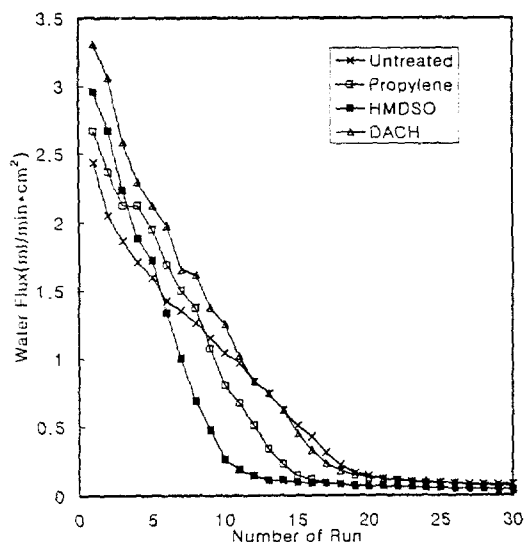
Figure 17. Water flux of a nylon membrane and modified nylon membranes with propylene, hexamethyldisiloxane (HMDSO), and diaminocyclohexane (DACH) plasmas as a function of repeated number of filtration of 0.3 wt% yeast suspension at pH 6.5.

Figure 18. Water flux of a nylon membrane and a modified membrane with acrylic acid (AAcid) plasma as a function of repeated number of filtration of 0.3 wt.% casein solution.

the membrane surface hydrophobic (water contact angle: approximately 105°) even more than propylene plasma. Diaminocyclohexane plasma makes the membrane surface hydrophilic (water contact angles: between 30° and 50° depending on the plasma conditions) but positively charged with high concentrations of primary amines.[34] The results are shown in Fig. 17. In all cases, the flux declines more rapidly after the modifications. These results show again the importance of the hydrophilicity and the electrostatic charge effect in the fouling.

Fouling can occur not only on the outer surface of a membrane but also on the inner surface of membrane pores if feed stream contains materials smaller than pore size of the membrane. In such case, the inner surface should also be modified for the membrane to be fouling-resistant. To check whether the plasma modifications can modify even the inner surface of membrane pores, 0.3 wt.% casein solution was passed through the membrane.

Since the size of casein is smaller than the pore size of the membrane, most of casein will deposit on the inner surface of pores which has much larger area than the outer surface if fouling occurs. The result is shown in Fig. 18. There is almost no flux decline for the modified membrane with acrylic acid plasma while flux declines rapidly as the filtration is repeated for the unmodified membrane. This indicates that plasma modification can modify the membrane surface all the way through the membrane pores.

CONCLUSIONS

Membrane fouling causes the flux decline in membrane filtration processes. The fouling is initiated by the adsorption of solid materials in feed stream on a membrane surface and thus highly influenced by surface characteristics. Therefore, the fouling can be reduced if the membrane surface is properly modified.

Less fouling occurs as interfacial energy between liquid medium and membrane surface decreases. Thus, the membrane should be modified to be hydrophilic to make it fouling-resistant in the filtration of aqueous feed stream.

When the feed stream contains electrostatically charged materials, however, just the hydrophilic modification is not enough. Electrostatic charge interaction between those materials and the membrane surface should be considered. Therefore, in such case, the membrane should be modified to be hydrophilic and electrostatically charged with the same polarity as the polarity of materials in the feed stream. The low temperature plasma process, plasma treatment or plasma polymerization, is a suitable process for such kind of modification. It modifies only the surface characteristics of the membrane without altering surface morphology of the membrane. And, it can modify not only the outer surface of membrane but also the inner surface of membrane pores.

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