Preparation of Fouling Resistant Nanofiltration and Reverse Osmosis Membranes and Their use for Dyeing Wastewater Effluent

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Abstract: To investigate the effect of surface charge and surface roughness on membrane fouling, the polyvinyl alcohol (PVA) with a neutral charge was coated on nanofiltration (NF) and reverse osmosis (RO) membranes. The coating of PVA on the NF membrane improved the salt rejection rate. With the coating of PVA on the RO membrane, the salt rejection rate was decreased. Our experiment revealed that the coating of PVA on the negative charged membranes has an influence on the fouling properties. By the coating of PVA, the surface negative charge of NF and RO membranes was decreased. In the case of RO membrane, the surface morphology became smooth. It also demonstrated that the extent of fouling is significantly influenced by the surface roughness and the surface charge. In our fouling experiment, a membrane with a smooth and neutral surface was fouled less. Although an RO membrane has a rough surface, the fouling on the membrane significantly decreased because of the reduced surface charge. When the PVA-coated NF membrane was applied to the dyeing wastewater effluent, it enabled us to recycle the permeate for washing water. With the PVA-coated RO membrane, the reuse of the permeate for dyeing was possible. Moreover, the membrane fouling was not severe except for the RO membrane.

Keywords: polyvinyl alcohol, nanofiltration, reverse osmosis, fouling, dyeing wastewater

Introduction

The wastewater in the textile dyeing process usually contains pollutants that are harmful to the environment. The effluent generated in the dyeing process provokes severe environmental problems. Discharging the effluents without appropriate treatment is a major problem in the textile industry. The effluent is a highly colored stream containing unfixed dyes along with salts and auxiliary chemicals such as emulsifying agents. Difficulties in the effluent treatment arise from its non-degradable property by aerobic digestion. Color removal by the conventional treatment process was found to be inadequate because most dyes have complex aromatic molecular structures that resist degradation. The stringent environmental regulations for discharge today are forcing the dyers and finishers in the textile industry to examine the potential for recycling the water from the waste stream by newer technologies.

Membrane filtration processes offer effective alternatives to effluent treatment. The membrane separation process can recover reusable water from the permeate stream, thus reducing water consumption and minimizing effluent discharge [1-5].

In recent years, the fouling of nanofiltration (NF) and reverse osmosis (RO) membranes has been widely investigated [6-8]. Vrijenhoek and coworkers reported that the extent of colloidal fouling was affected by the roughness of membrane surface [6]. Măntări and coworkers studied the fouling of membranes with different cut-off values and material properties. The hydrophobic membranes were fouled more. The rather loose NF membrane was fouled more than the tighter NF membrane [7]. Bouchard and coworkers studied humic acid adsorption onto the NF membranes coated with different materials. A polyamide NF membrane was less fouled than a cellulose acetate NF membrane [8].

A thin-film composite (TFC) polyamide membrane has been commercialized owing to its excellent membrane performance for NF and RO [9]. However, TFC membranes, especially RO membranes are sensitive to fouling.

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because of their rough surface morphology and highly negative surface charge. Most TFC membranes have negatively charged surfaces in the presence of water, which means that in the presence of positively charged solutes, the negatively charged membrane can be fouled heavily by the adsorption of counter-ionic solutes. To reduce the concentration of counter-ionic solutes near the membrane surface, the charge of the membrane surface should be blocked by coating the neutral material such as polyvinyl alcohol (PVA) or soluble cellulose.

PVA is a chemically and physically stable material. Moreover, PVA may be attractive owing to its hydrophilic and good film-forming properties. Because of its excellent properties PVA has been coated on the support membranes used for pervaporation [10-12] and RO membranes [13-14]. Lang and coworkers prepared TFC RO membrane with PVA and further cross-linking its surface [13]. Other researchers have also tried PVA-coating onto porous support membranes [15-16]. They used PVA for TFC NF or RO membrane preparation to increase the separation property and to decrease defect formations by a dip-coating method.

In this work, we investigated the possibility of water recycling for dyeing and washing by using the membrane processes (NF and RO) integrated in the dyeing wastewater treatment process. Membrane fouling was also taken into account.

Experimental

Commercial Membranes

Three types of flat-sheet membranes were kindly supplied by Sae-Han Corporation. The membranes are designated as CSM-NE and CSM-RO-HF. CSM-NE is a nanofiltration membrane with a negative surface charge. CSM-RO-HF with a highly rough skin layer and large surface area is designed to be operated at low pressure. It is reported that CSM-NE and CSM-RO-HF, composite membranes, are interfacially polymerized with piperazine and im-phenylene diamine as diamines of aqueous solutions, respectively.

Preparation of PVA-coated TFC Membranes

PVA of molecular weight of 35000-50000 g/mol (99% hydrolyzed) was supplied by Aldrich Chemicals (Milwaukee, WI). Aqueous PVA solution of 0.05 wt% was prepared by dissolving PVA in 90°C deionized water for 5 hrs. The support membranes (CSM-NE and CSM-RO-HF) were wetted in the PVA solution for 1 min. The membrane was then pressurized and dried for 2 h. The dried membrane was cross-linked by dipping into the glutaraldehyde solutions (GA, 25% aqueous solution, Tokyo Kasei Chemicals) for 30 sec. The GA solution was composed of H$_2$O/GA/HCl (87/10/3 wt%). The membrane was further cross-linked by drying at ambient temperature for 1 h. The dried PVA membrane was wetted in 50 wt% aqueous ethanol solution. The resulting PVA membranes coated onto the CSM-NE and CSM-RO-HF were designated as CSM-NE-PVA and CSM-RO-HF-PVA, respectively.

Membrane Performance

The membranes were tested in a flow cell at 25°C and supported in the cell by a porous stainless steel disk. The test unit consisted of circular plate-and-frame membrane cells, a back-pressure regulator, and a high pressure pump (Hydracell pump, Model-13, Wanner Engineering, USA). The active area of the membranes was 17.35 cm$^2$. The membranes were compressed at 300 psi for 2 hrs, then, pure water flux was measured at 200 psi. The rejection rate was determined at room temperature and 200 psi using aqueous solutions containing 2000 ppm of NaCl, CaCl$_2$, and MgSO$_4$. The flow rate of the feed was 1.0 L/min.

ζ-potential Measurements

Surface ζ-potentials of the membranes were measured using a ζ-potentiometer (electrophoretic method, Otsuka Electronics Co.). Polystyrene latex particles (diameter 520 nm, Otsuka Electronics, Japan) coated with hydroxy propyl cellulose (molecular weight of 300000 (Scientific Polymer Products, Japan)) were used as mobility-monitoring particles. These were dispersed in a 0.01 M NaCl solution to prevent the interactions on the quartz cell surface during measurement. In a cell consisting of membrane and quartz cells, asymmetric electroosmotic flow occurs due to the accumulation of ions on the membrane surface. The electrophoretic flow of a standard particle takes place due to the induced electroosmotic flow. The electrophoretic mobility of the particle can be measured, and exhibits a parabolic flow velocity profile. From determined electrophoretic mobility, the ζ-potentials can be calculated using the Smoluchowski’s equation (1).

$$\zeta_{EP} = 4\pi n U / \varepsilon \varepsilon_0$$  \hspace{1cm} (1)

Where $\zeta_{EP}$ is the ζ-potential by electrophoresis (mV), $n$ liquid viscosity ($0.89 \times 10^{-3}$ Pa · S), U the electrophoretic mobility of a particle (cm$^2$/V · S), $\varepsilon$ the liquid permittivity (78.38), and $\varepsilon_0$ the permittivity of free space ($8.854 \times 10^{-12}$ S · m$^{-1}$).

The concentration of the electrolyte solution was 0.01 M NaCl at different pH values (3, 5.5, and 10).

AFM Images

Membrane surface roughness was determined by AFM (Park Scientific Instruments, Korea). The horizontal X and Y scales are 10 μm × 10 μm, while the vertical Z-axis
is 0.5 μm. This distorted scale increases the peak to valley distances relative to the peak to peak separation in the AFM images.

**Fouling Experiments**

The membrane cell was a thin-channel rectangular type, providing a cross-flow over the membrane surface. The membrane, with an area of 35.36 cm² rested on a metal- porous support. 100 ppm of humic acid (Aldrich) was used as a foulant. The molar mass of the humic acid was 4100 g/mol. The complex of humic acid and calcium chloride was also used. Solution pH was controlled with NaOH and HCl. The concentration of calcium chloride was in the range of 20-300 ppm. The used membranes were CSM-NE, CSM-NE-PVA, CSM-RO-HF, and CSM-RO-HF-PVA. The experiments were conducted at a constant initial water flux of 1.0 m³/m²/day. The flux was normalized by dividing flux with time (J) by initial water flux of steady state ($J_0$). The temperature and the flow rate in the experiment were 25°C and 1.0 L/min, respectively.

**Nanofiltration and Reverse Osmosis of Dyeing Wastewater Effluent**

To investigate the possibility of reusing the dyeing wastewater, the dyeing wastewater effluent was filtered through several membranes for a long period. All experiments were conducted at a constant feed temperature of 25°C unless otherwise specified. The temperature and the flow rate in the experiment were 25°C and 1.0 L/min, respectively. Dyeing wastewater effluent was kindly supplied by the Sam-Yang Tex treatment plant (Daejeon, Korea). Conductivity and COD$_{TM}$ were performed according to the Standard Methods.

**Results and Discussion**

**Performance of PVA-coated NF and RO Membranes**

To investigate the effect of the membrane surface properties (surface roughness and surface charge) on the performance and the fouling of PVA-coated membranes, two support membranes (CSM-NE and CSM-RO-HF) with different surface properties were coated with 0.05 wt% PVA aqueous solution. GA was used for cross-linking the PVA. Table 1 shows the performance of the supports (CSM-NE and CSM-RO-HF) and the PVA-coated membranes (CSM-NE-PVA and CSM-RO-HF-PVA). By coating the support NF and RO membranes, fluxes decreased. The salt rejection rates were observed differently. In other words, the salt rejection rate of the CSM-NE-PVA membrane was higher than that of the CSM-NE membrane, while the salt rejection rate of the CSM-RO-HF membrane was lower than that of the CSM-RO-HF membrane. The salt rejection has been explained by the Donnan and size exclusion theory. The negative charge on the membrane surface can retain divalent anions, while divalent cations and monovalent ions can pass freely through the membrane. With the coating of neutral polymer on the negative membrane, the negative charge on the membrane surface decreased. By the theory of the Donnan exclusion, if the negative charge on the membrane surface decreased, the salt rejection rate might be decreased without the consideration of the size exclusion. In the case of the RO membrane, the Donnan exclusion may be more dominant than the size exclusion. However, in the case of the NF membrane which is much more porous than the RO membrane, the salt rejection can be more affected by the size exclusion than by the Donnan effect.

**Fouling by Humic Acid**

To investigate the effect of surface charge on the fouling, humic acid was chosen as a foulant, which has been widely used [7,17-23]. Figure 1(a) and 1(b) show the effect of pH of the humic acid solution on the membrane fouling. At a lower pH, membranes were fouled more easily. Especially, a CSM-RO-HF membrane with a negative surface charge and corrugated surface morphology was fouled more than other membranes. Humic acid is negatively charged at a higher pH than pH 3.5, which is the isoelectric point (IEP). The shape of the humic acids is changed with pH. In other words, at higher or lower pH, the humic macromolecules become extended and linear in shape because of the intramolecular repulsion forces, while at the IEP, the humic macromolecules become coiled and spherical owing to the interchain attraction. By coating the NF and RO membranes with PVA, the fouling of the NF membrane was almost unchanged. However, in the case of the RO membrane, the fouling decreased significantly. This fact explains that the surface
roughness is an important parameter affecting the membrane fouling. Figure 1 (c) shows that the complex of 20 ppm divalent cations (Ca²⁺) and 100 ppm humic acid is a significant foulant even at a neutral pH. Both divalent cations and humic acids are not significant foulants if they are present alone. Many researchers have shown that divalent cations such as Ca²⁺ and Mg²⁺ form complexes with the carboxylate groups of humic substances, thus the electrostatic repulsion of the humic acid molecule decreases [7]. The electrostatic repulsion between the humic acid and the membrane is reduced. As a result, the hydrophilicity of the humic acid decreases. The increase in the hydrophobicity of humic acid increases the fouling of the membrane. In addition, the hydrophilicity of the membrane would decrease owing to the bridge of the humic acid and the polyamide membrane by divalent cations. By coating a CSM-NE membrane with PVA, the carboxylic acid groups on the CSM-NE membrane are shielded. As a result, the effect of divalent cations on bridging the membrane and the humic acid can be reduced. By coating CSM-NE membrane with PVA, fouling by humic acid complex was less than CSM-NF membrane. This can be explained by the reduced surface charge caused by the shielding of the carboxylic acid group and by the shielding of the PVA/CSM-NE membrane.

The observed humic acid fouling behavior is related to the physical (surface morphology) and chemical (ζ-potential) membrane properties. It is reported that both the surface charge and the surface morphology on the membrane affect the membrane fouling. The AFM images of the four membranes shown in Figure 2 and Table 2 reveal the different extents of the surface roughness. Average roughness is defined as the average deviation of peaks and valleys from the mean plane. From the correlation between the membrane roughness and the fouling behavior, it becomes clear that membrane roughness is the influential membrane surface property. By PVA-coating on the CSM-RO-HF with the rough surface, its surface became smooth.
At a higher pH (pH 7), both the membrane and the humic acid are negatively charged. Because of the electrostatic repulsion between membrane and humic acid, humic acid cannot easily adsorb on the polyamide NF and RO membranes. By coating a CSM-NE or a CSM-RO-HF polyamide membrane with PVA, the acidic group (-COOH) is slightly shielded, as shown in $\zeta$-potential data of Figure 3. As shown in Figure 1 (b), the coated NF membrane was fouled more than the uncoated NF membrane. This is due to the shielded surface charge. The electrostatic repulsion force of the CSM-NE membrane becomes larger than the CSM-NE-PVA membrane. In other words the concentration of the humic acid around the CSM-NE-PVA membrane surface is higher than that of the humic acid around the CSM-NE membrane. According to the explanation, the CSM-RO-HF-PVA membrane should be fouled more than the CSM-RO-HF membrane. However, in this case, the coated RO membrane was fouled less than the uncoated RO membrane. It was revealed that in addition to the surface charge, surface roughness has to be considered. The decreased surface roughness was an important contributing factor in reducing the fouling.

In addition to AFM analysis, four membranes were characterized for $\zeta$-potential. The $\zeta$-potential versus pH curves for the four membranes are shown in Figure 3. At the fouling test condition (pH 7.0), the membrane surface $\zeta$-potentials were -68, -55, -42, and -33mV for CSM-RO-HF, CSM-NE, CSM-RO-HF-PVA, and CSM-NE-PVA,
Table 3. Typical Characteristics of Wastewater and Permeate

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<th>Content</th>
<th>Actual waste</th>
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Figure 4. Relative flux change with the operating time during the continuous filtration of wastewater effluent.

respectively. The $\zeta$-potential of CSM-NE membrane at a pH 7.0 is lower than that of CSM-RO-HF membranes. As a result, the CSM-RO-HF membrane was fouled more than the CSM-NE membrane. This phenomenon explains that in addition to surface roughness, the membrane with a higher surface charge is sensitive to the fouling. As shown in Figure 2, the surface roughnesses of CSM-NE and CMS-NE-PVA membranes are almost the same, while the CSM-NE-PVA membrane with a lower surface $\zeta$-potential value was fouled less than the CSM-NE membrane with a higher surface $\zeta$-potential. Now it has become clear that an increase in the surface $\zeta$-potential leads to more fouling. Compared to the CSM-NE and CSM-RO-HF-PVA membranes, the CSM-RO-HF-PVA was fouled less even though the surface roughness of the CSM-RO-HF-PVA is much higher than that of the CSM-NE. These findings led us to conclude that the surface $\zeta$-potential is also an important factor affecting the fouling.

Nanofiltration and Reverse Osmosis of Dyeing Wastewater Effluent

Figure 4 shows the relative flux change with the operating time during the continuous operation of the membranes. During the preliminary tests carried out on the NF and RO membranes, it was found that without MF filtration suspended solids induced a fouling of the membrane. Therefore, the effluent was filtered by the MF membrane with the pore size of 0.45$\mu$m. The same experiment was conducted with the feed filtered by the MF membrane. As can be seen in Figure 4, the CSM-NE, CSM-NE-PVA, and CSM-RO-HF-PVA membranes were slightly fouled, while the CSM-RO-HF membrane was significantly fouled. This fact explains that the surface roughness is one of the fouling factors when the feed contains organic materials and salts. After coating the CSM-RO-HF membrane with PVA, the fouling reduced significantly owing to the decrease in surface roughness and surface charge. It is expected that divalent cations (Mg$^{2+}$ and Ca$^{2+}$) are able to form complexes with the carboxylate groups of membranes or sulfonate groups of dyes as explained in the humic acid fouling behavior. The formation of complexes decreased the electrostatic repulsion between membranes and dyes. Instead of the electrostatic repulsion, the Vander Waals force may be dominant. To reduce a fouling, the negative charge of the membrane has to be blocked by coating the membrane with a neutral material to avoid the interaction between the membrane and the dye by salts. The results presented clearly demonstrate that the membranes with a lower negative charge were fouled less. The flux of the RO membrane is lower than that of the NF membrane because of a higher osmotic pressure. The RO membrane can retain almost all the salts, while the NF membrane in this experiment was able to retain only some of the salts.

Table 3 shows the quality of the permeate through the NF and RO membranes in addition to the quality of raw water and wastewater treated by the conventional treatment process. The quality of the permeate through the RO membrane was suitable for reuse in the dyeing process. The RO membrane can reject more than 99% of organic materials and salts. The conductivity of the permeate through the CSM-RO-HF membrane is lower than that of the permeate through the CSM-RO-HF-PVA membrane. It is not surprising because the CSM-RO-HF-PVA membrane has a lower surface charge than the CSM-RO-HF membrane as shown in Figure 3. By coating the CSM-RO-HF membrane with PVA, the surface charge became lower. For a charged membrane, the salt is retained through a combination of steric and Donnan effects. The Donnan effect may play a more important role in retaining salts in these RO membranes. The Donnan exclusion became less effective with a decrease in surface charge density on the membrane. However, in the case of NF membranes, the steric effects are more dominant than the Donnan effects. As can be expected from Table 1, by coating the
CSM-NE membrane with PVA, salts are retained more. If the Donnan exclusion effects are dominant, the rejections of salts become lower.

Conclusions

To investigate the performance and the fouling behavior of membranes with different chemical (ζ-potential) and physical (surface roughness) surface properties, commercial composite polyamide NF and RO membranes were coated with PVA. By coating the NF membrane with PVA, the flux decreased and the salt rejections increased. The increase in the salt rejection may be due to the steric effect rather than the Donnan exclusion. By coating the corrugated RO membrane with PVA, both the flux and salt rejections decreased. Our experiments revealed that the decrease in the salt rejection may be caused by the Donnan exclusion rather than the steric effect. The fouling experiment with the humic acid and calcium chloride solution showed that the PVA-coated membranes were fouled less than the uncoated membranes because of the decreased ζ-potential. Moreover, the decrease in the surface roughness of the corrugated RO membrane was one of the main factors that contributed to reducing the fouling. To study the possibility of wastewater recycling by the membrane process, the dyeing wastewater effluent was filtered with NF and RO membranes. By coating the NF and RO membranes with PVA, the fouling decreased significantly. The PVA-coated NF membranes and the uncoated NF membranes were suitable in terms of permeate quality and fouling for the reuse (washing) of the effluent. The uncoated RO membrane with a corrugated surface was not suitable for recycling because it was significantly fouled. However, the permeate through the PVA-coated RO membrane was able to be reused for the dyeing process.

References

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