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Treatment of dye aqueous solutions using nanofiltration polyamide composite membranes for the dye wastewater reuse

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Abstract

Five different kinds of dye aqueous solutions (Direct Red 75, 80 and 81, and Direct Yellow 8 and 27) were treated with nanofiltration (NF) polyamide (PA) composite membranes to obtain basic information on the dyeing wastewater reuse. The separation of dyes by the NF PA membrane appeared to be a good process for the effective removal of dyes from dyeing wastewater. The extent of the separation of dyes by the membrane was almost 100% for all of the dyes used, producing colorless water. When artificial dyeing wastewater containing Direct Red 75, PVA, NaCl and Na_2SO_4 as components of the wastewater was used as a feed solution for the membrane separation process, the separation efficiency turned out to be good, especially when one of the chemical coagulants, alum, was used for the pretreatment of the artificial dyeing wastewater. About 20% of improvement of flux was obtained by the pretreatment of the wastewater.

Keywords: Nanofiltration; Polyamide composite membranes; Dyeing wastewater; Reuse

1. Introduction

It is well known that in the textile industry a large amount of water has been used for the dyeing process and a large amount of wastewater is being produced, causing serious environmental problems. The wastewater produced by the textile industries has been known to have strong color and a high concentration of dissolved solids (organic and inorganic materials), and the color is hard to remove by the conventional methods. Among the conventional methods, chemical coagulation and flotation, chemical oxidation, and adsorption processes are the most popular ones [1].

Even though activated sludge is one of the most widely used treatment methods, it poorly removes dyes [2], clearly ineffective in decolorizing textile effluents, even when mixed and treated together with sewage [3], leading to the discharge of the highly colored water. Though powdered activated carbon (PAC) has been regarded as the most successful adsorbent, it is expensive, and 100% color removal has rarely been achieved with it [4]. Ozone that has been known to have the ability to breakdown most of the dyes is not very successful for the decolorization of high concentration of dyes [5].

A lot of attentions have been attracted on how to solve such problems in textile industries. And the membrane separation process using highly effective NF-membranes is considered as a competitive method for the treatment of the dyeing wastewater to make it possible to recycle the wastewater. Among the membrane processes frequently used for the wastewater treatment, NF-membranes that allow water and some extent of monovalent ions such as NaCl to penetrate freely through the membrane at a moderate operating pressure such as 100 or 200 psi are known to be the most useful ones for the recycle of the dyeing wastewater [6–10]. Considering the fact that to recycle the dyeing wastewater, all the materials dissolved in the dyeing wastewater except for the NaCl should be removed, the NF-membrane is found to be the proper membrane for this purpose.

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In this study, five different kinds of dyes and three other materials such as PVA, NaCl, and Na_2SO_4, most often found in the dyeing wastewater were used to make artificial dyeing wastewater. The NF polyamide composite membranes used were also prepared in our laboratory by using an interfacial polymerization technique [11–13]. The details of the membrane separation process of the dye aqueous solutions are elaborated as below.

2. Experimental

2.1. Materials

Direct Red 75, 80 and 81, and Direct Yellow 8 and 27, polyvinyl alcohol (PVA, 88% of hydrolysis, Mw: 77,000 g/mol), Na_2SO_4 were purchased from Aldrich Co. (Milwakee, WI) and used to make synthetic dyeing wastewater without further purification. For the formation of NF polyamide composite membranes, piperazine (PIP) and trimesoyl chloride (TMC) purchased from Tokyo Kasei Co. (Tokyo, Japan) were used as monomers of polyamide. Other chemicals used in this experiment were used as purchased without further purification.

2.2. Formation of artificial dyeing wastewater

In order to see the effect of the pretreatment of the dyeing solution on the membrane separation process, an artificial dyeing wastewater was prepared. The artificial dyeing wastewater was prepared by dissolving 1000 ppm of Direct Red 75, 500 ppm of PVA, 250 ppm of NaCl, and 750 ppm of Na_2SO_4 in distilled water at elevated temperature. The composition of the artificial dyeing wastewater was determined, considering the composition of real dyeing wastewater that is being produced in the dyeing industries.

2.3. Formation of NF PA composite membranes

The NF PA composite membrane was prepared by coating the surface of microporous PSf support with MWCO of 30,000 with crosslinked polyamide thin layers, using interfacial polymerization technique [11–13]. PIP and TMC were used as monomers to form the polyamide with the aid of triethylamine used together as a catalyst. After coating with the crosslinked polyamide layers, it was kept in distilled water to keep the membrane from drying.

2.4. Characterization

The cake layers of foulants accumulated on the surface of the membrane were observed with the field emission scanning electron microscope (FESEM, Model: XL 30, Philips Co., USA). A conductivity/TDS meter (RS-232, Cole–Palmer, USA) was used for the measurements of conductivity and TDS of the solutions. The color of dye in the solutions before and after the coagulant pretreatment was determined by using an Optizen UV/vis spectrophotometer (Mecasys Co., Korea). The absorbance measurement of the dye was measured at 522 nm, which was the λ_{max} of the dye used (Direct Red 75). The COD of the solutions was measured using a COD meter (COD-10E, TOA Electronics, Japan).

2.5. Membrane separation process

To test the separation behavior of dyes with an NF PA composite membrane employed as a tool for the dyeing wastewater treatment, a typical reverse osmosis (RO) membrane test set-up was used. The flux whose unit is m^3/m^2 day was determined from the amount of water penetrated through the membrane. The rejection that indicates the separation performance of the membrane was calculated from the solute concentrations of feed and permeate solutions obtained from the data from the high performance liquid chromatography (HPLC) using the following equation:

$$\text{Rejection}\ (\%) = 100 \times \left(C_f - C_p\right) / C_f$$

where C_f and C_p are the concentrations of the feed solution and permeate, respectively, calculated from the peak area of HPLC.

3. Results and discussion

3.1. Characterization of NF PA composite membrane

The NF PA composite membrane prepared by coating the surface of the microporous PSf support with crosslinked polyamide layers formed by interfacial polymerization of PIP and TMC was characterized in terms of its morphology and permselective properties. Fig. 1 shows the permselective performance of the membrane, when 1000 ppm aqueous solutions of PEG 600, Na_2SO_4 and NaCl were used as feed.

As one can see, the membrane shows a typical NF behavior of high flux at moderate operating pressure and high rejection of multivalent ions such as Na_2SO_4 and low molecular weight organics, PEG 600, but low rejection of monovalent ions such as NaCl. From the rejection behavior, it was found that the molecular weight cut off (MWCO) of the membrane was about 500 g/mol, since the rejection of PEG 600 at 200 psi was about over 95%.

3.2. Treatment of dye aqueous solutions with the membrane

Table 1 shows the molecular weights and chemical structures of the dyes used in this study. Aqueous solutions of the dyes (1000 ppm) prepared by dissolving them in distilled water were used for the membrane separation study without further pretreatment.

Fig. 2 shows the membrane performance as the five different dye solutions were treated with the membrane. One interesting point found in the separation of dyes by the membranes is that the rejection of dyes is almost 100%, indicating that the complete separation of dye compounds from the dye solutions

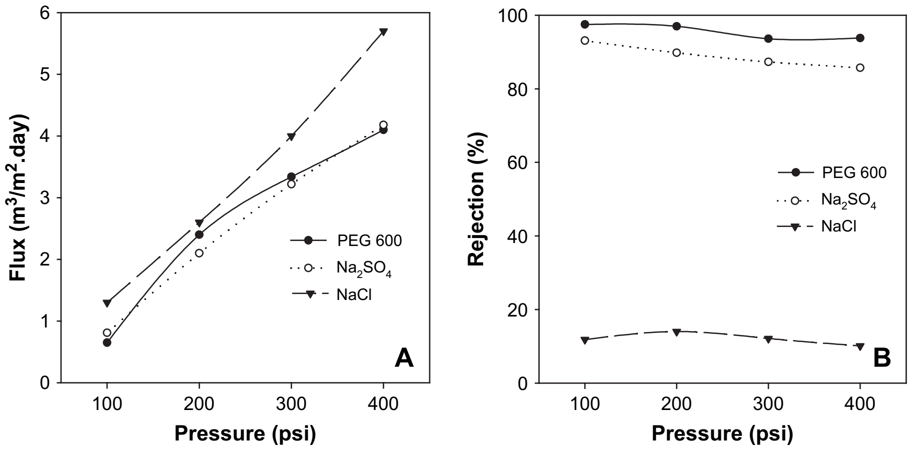
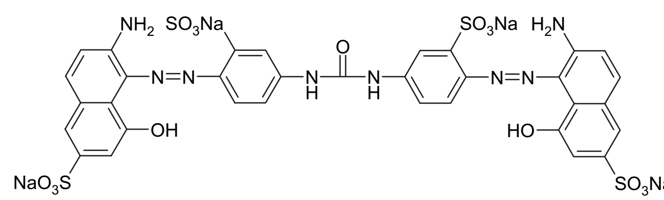
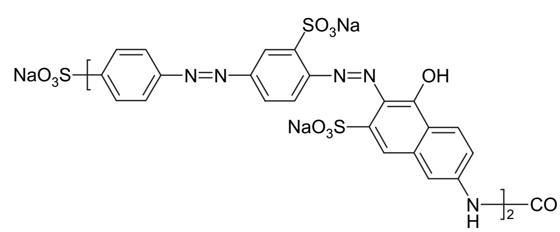
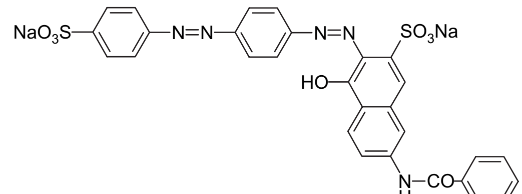
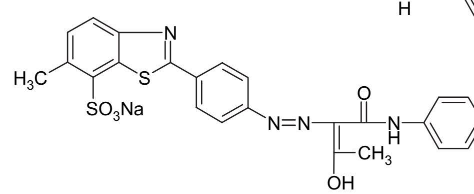
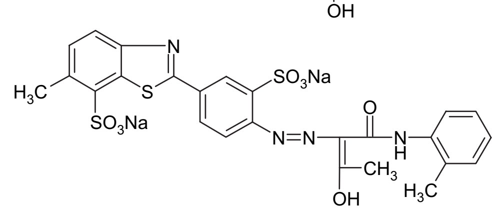


Fig. 1. Permselective properties of the NF PA composite membrane prepared by using PIP and TMC as monomers as 1000 ppm aqueous solutions of PEG 600, Na_2SO_4 and NaCl were used as feed: (A) flux and (B) solute rejection.

Table 1
Chemical structures and molecular weights of the dyes used in this study

Name	Molecular weight (g/mol)	Structure
Direct Red 75	990.8	
Direct Red 80	1373.1	
Direct Red 81	675.6	
Direct Yellow 8	518.6	
Direct Yellow 27	650.6	

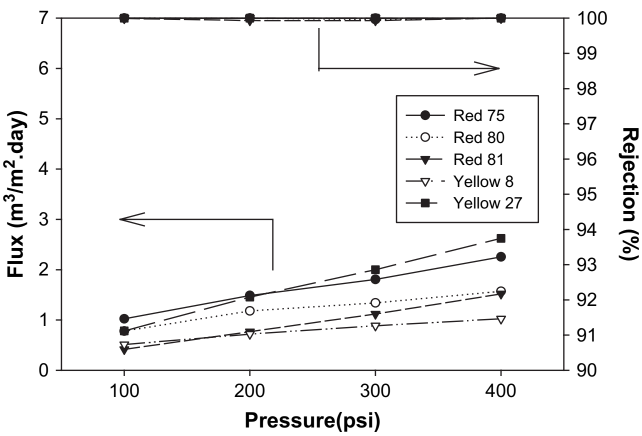


Fig. 2. The flux and rejection of the NF PA composite membrane as a function of operating pressure for the separation of five different dyes from their 1000 ppm aqueous solutions at room temperature.

is possible regardless of the kinds of dyes. In other words, only water penetrated through the membrane, not any of the dyes, and it seems that by using a membrane separation technique, there is possibility for the dyeing wastewater to be recycled.

However, the flux obtained from different dye solutions varied, depending on the chemical and physical properties of the dyes used. In other words, the amount of water penetrated through the membrane per unit time was changed according to the dye solutions used. The major factors affecting the flux of the membrane seemed to be the molecular size and shape of the dyes considering the properties of the dyes shown in Table 1, but there was no close relationship between the flux and molecular weight. Other factors should be considered together with molecular weight of the dyes, but they were not clear in this case.

The flux of the solutions of Direct Yellow 8 and Direct Red 81 was much lower than the solutions of Direct Red 75 and Direct Yellow 27. Generally speaking, when linear compounds with low molecular weight were used, they easily get into the pores of the NF PA membrane, blocking the pores, and reducing the flow of the water, and then causing the water flux through the membrane to decrease. On the other hand, when compounds with large molecular size were used, the nanometer pores are much smaller than the dyes, so it is less possibile for the dyes to get into the pores of the membrane, not inducing such flux decline as that of low molecular weight dyes.

It can be conclusively said from this result that the NF PA composite membrane with MWCO 500 is good enough to remove the dyes with molecular weights higher than 500 g/mol out of their aqueous solution for the purpose of wastewater recycle.

3.3. Membrane fouling by the dyes

Even though it was proved from Fig. 2 that the membrane separation process using NF PA composite membranes is effective for the removal of dyes from their water solutions, there is another thing to be considered. That is membrane fouling by the dyes, reducing the water flux, and making the membrane separation process less economically favorable.

Fig. 3 shows the dye layer accumulated on the surface of the membrane after 4 h of membrane operation for the separation of Direct Yellow 8 from its 1000 ppm aqueous solution. For the other dyes used in this study, though there was difference in the dye cake layers such as thickness and hardness of the cake, no dye was found that did not cause such membrane-fouling problem.

In order to avoid such membrane-fouling problem, pretreatment of the dye solution with chemical coagulant such as alum and ferric chloride is often needed. In this study, to see the effect of the pretreatment of the dyeing solution on the membrane separation process, an artificial dyeing wastewater was prepared and pretreated with chemical coagulant before applying this wastewater to the membrane. The artificial dyeing wastewater composed of 1000 ppm Direct Red 75, 500 ppm PVA, 250 ppm NaCl, and 750 ppm Na_2SO_4 was prepared and used. The reason for choosing such composition of dyeing wastewater was to make the artificial wastewater with very similar composition of real dyeing wastewater being produced in the dyeing industries. For dyeing textile, it is well known that salts such as NaCl and Na_2SO_4 are used together with dye. Also in the dyeing wastewater, no small amount of PVA is remained because before dyeing the textile, the PVA, used as a sizing agent, has to be removed from the textile.

The artificial wastewater was pretreated with alum that has been known to be effective for the removal of dyes. For the pretreatment, certain amounts of alum, color removal agent and anionic polymer as shown in Table 2 were added into the wastewater, and stirred for 20 min at 200 rpm with a stirrer. After that, the solution was allowed to be still for another 30 min and flocs formed by the alum were precipitated. The precipitants were then removed out of the solution by decanting the upper clear solution and filtering with a filter paper.

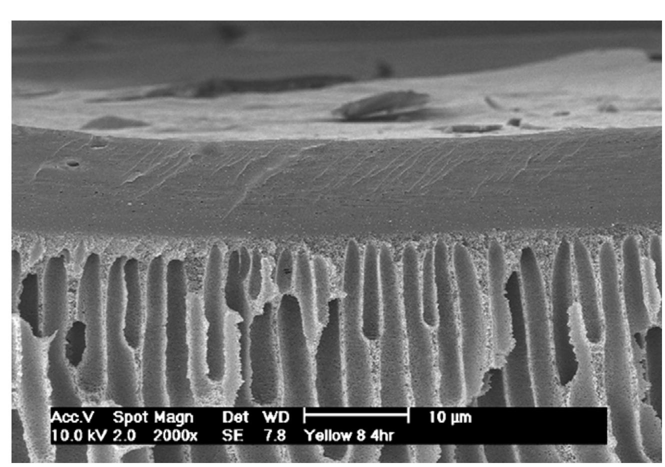


Fig. 3. A dye cake layer accumulated on the surface of the membrane after 4 h of membrane operation for the separation of Direct Yellow 8 from its 1000 ppm aqueous solution.

Table 2
Chemical properties of the wastewater according to the compositions and concentrations of the chemical coagulants used for the treatment

Coagulant (ppm)			Conductivity (mS)	TDS (ppt)	UVA (522 nm)	COD (ppm)
Alum	Color removal	Anionic polymer				
4000	1000	400	4.17	2.02	3.620	360
4000	2000	800	3.95	1.95	1.862	328
4000	4000	800	4.18	2.07	0.096	510
4000	4000	2000	4.21	2.09	0.091	524
4000	2000	2000	4.05	2.00	0.044	376
5000	2000	2000	4.32	2.12	0.041	398
6000	2000	2000	4.60	2.24	0.066	422
Raw water			2.91	1.42	22.08	1060

Table 2 shows the concentrations of the chemical coagulants used and the chemical properties of the wastewater after the treatment.

As one can see from Table 2, pretreatment of the dyeing wastewater with alum effectively removed the dye from the solution. The UV absorbance of the dye wastewater containing 1000 ppm of Direct Red 75 at 522 nm was 22.08. However, this value reduced to less than 0.1 when 5000 ppm of alum was used with 2000 ppm of color removal agent and 2000 ppm of anionic polymer together, indicating more than 99% removal efficiency. The COD of the wastewater was also reduced effectively by using alum, more than 60% decrease in the COD of the wastewater being noted.

However, the TDS of the wastewater increased by the pretreatment with alum. After treatment with alum, 150% of TDS was observed from the wastewater and this kind of phenomenon can be explained by the remaining alum. Even though, most of the alum added into the wastewater was used for the formation of flocs with dye compounds, some of it remained in the water, causing increase in the TDS of the wastewater. This kind of behavior of the chemical coagulant such as alum and ferric chloride is something well accepted among the people involved in the treatment of wastewater with chemical coagulants.

3.4. Membrane separation after pretreatment

Fig. 4 shows the effect of the pretreatment of wastewater on the flux of the membrane. Normalized flux (J/J_0) calculated by dividing the flux along the operation time by the initial flux was plotted according to the operation time when two kinds of wastewater, original wastewater and pretreated one, were used. For this experiment, the wastewater that was pretreated with a mixture of 4000 ppm of alum, 2000 ppm of color removal agent and 2000 ppm of anionic polymer was used.

This result indicates that the pretreatment with chemical coagulant, alum, is effective for the decrease in the extent of membrane fouling. In other words, when pretreated wastewater was used for the membrane separation process, the degree of flux decline along the operation time became smaller than when original wastewater was used. About 20% of improvement of flux was obtained by using the pretreated wastewater. Even though the TDS of the wastewater increased by the pretreatment with alum, the decrease in both the COD and dye concentration acted positively for the membrane separation performance, increasing the separation efficiency of the membrane by decreasing the extent of membrane fouling.

4. Conclusions

Dyes can be separated from their aqueous solutions effectively by the membrane separation process using NF PA composite membranes. NF-membranes with MWCO 500 are good enough to separate several different dyes such as Direct Red 75, 80 and 81, and Direct Yellow 8 and 27 whose molecular weight is over 500 g/mol. The rejection ratio for the all dyes used in this study was almost over 99.5%. The efficiency of the membrane in the treatment of dyeing wastewater containing dyes, PVA and salts can be improved by the pretreatment of wastewater with chemical coagulants such as alum and ferric chloride, before applying the wastewater to the membrane process.

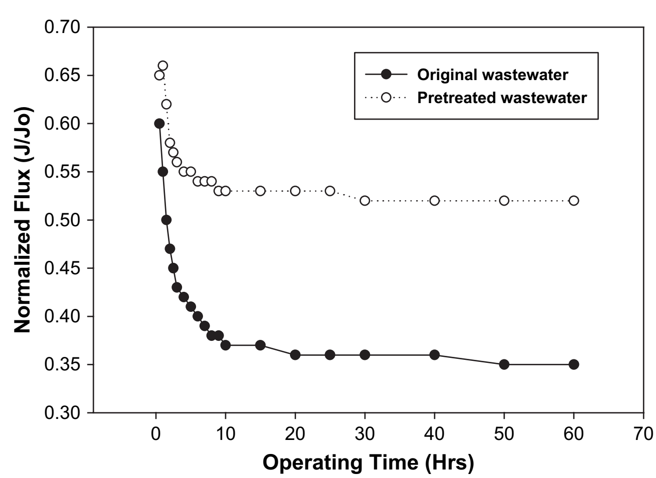


Fig. 4. Effect of the pretreatment with alum on the flux decline along the operating time when the artificial dyeing wastewater was treated with the NF PA composite membrane: for the pretreatment of the wastewater, the mixture of chemical coagulant (4000 ppm of alum, 2000 ppm of color removal agent and 2000 ppm of anionic polymer) was used.

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