

화학응집제에 의한 전처리 후 폴리아미드 RO-분리막에 의한 염색폐수처리

모 중 환* · 황 정 은 · 제갈중건[†] · 이 규 호 · 김 재 필*

한국화학연구원, 응용화학연구부, *서울대학교 공과대학 재료공학부

(2004년 8월 23일 접수, 2004년 9월 14일 채택)

Treatment of Dyeing Wastewater Using Polyamid Ro-Membranes After the Pretreatment with Chemical Coagulants

Joonghwan Mo*, Jeong-Eun Hwang, Jonggeon Jegal[†], Kew-Ho Lee, and Jaephil Kim*

Membrane and Separation Research Center, Korea Research Institute of Chemical Technology, Daejeon 305-606, Korea

*School of Materials Science & Engineering, Seoul National University, Seoul 151-1742, Korea

(Received August 23, 2004, Accepted September 14, 2004)

요 약: 폴리아미드 역삼투막을 이용하여 염색폐수를 처리하였다. 염색폐수를 멤브레인 공정에 적용하기 전에 알룸, 페릭 클로라이드, HOC-100와 같은 화학응집제를 이용하여 먼저 처리하였다. 이러한 전처리가 분리막에 의한 폐수처리 공정에 어떠한 영향을 주는지 알아보기 위하여 최적의 응집/침전 조건을 찾았다. 사용된 모든 응집제에 있어서, 전처리된 폐수의 COD와 UV-흡수도는 약 70% 정도의 감소를 보였다. 이렇게 전처리된 폐수를 다시 분리막 공정으로 처리하였다. 전처리 시 사용된 응집제들이 분리막 공정에서 어떻게 분리막 오염에 영향을 주는지를 조사하였으며, 그 결과 HOC-100가 폐수 내에 존재하는, 분리막 오염을 유발하는 물질 제거에 가장 좋은 효과를 나타내는 것을 알 수 있었다.

Abstract: Treatment of a dyeing wastewater was carried out using polyamide RO-membranes. Before applying the wastewater to the membrane process, it was pretreated with various chemical coagulants such as alum, ferric chloride and HOC-100A. In order to see the effect of the pretreatment on the membrane separation process, the optimum conditions for the coagulation and sedimentation process were sought. As a result, by the pretreatment, for all the coagulants used, the chemical oxygen demand (COD) and UV-absorbance of the wastewater were lowered by more than 70%. The pretreated wastewater was then applied to the membrane process. The effect of the coagulants used for the pretreatment on the membrane fouling was studied. From this study, it was found that the HOC-100A was the best out of the coagulants used for the removal of the materials that could cause membrane fouling.

Keywords: pretreatment, chemical coagulant, membrane process, dyeing wastewater, RO-membrane

1. Introduction

Growing concern about environmental issues has prompted the textile industry to investigate more appropriate and environmentally friendly treatment technologies to meet the discharge consents becoming stricter everyday. The textile industry is one that demands large quantities of water, producing large amounts of waste-

water. The wastewater is characterized by strong color and a high concentration of dissolved solids (organic and inorganic materials). Color has not been effectively removed by the conventional wastewater treatment, but mixed with rinse water to be diluted before discharging it to sewage systems. Of the conventional methods that have been used for removal of color from wastewater is chemical coagulation and flotation, chemical oxidation, and adsorption processes[1].

The most widely used treatment system is a con-

[†]주저자(e-mail : jggegal@pado.kRICT.re.kr)

ventional activated sludge. This system however poorly remove reactive dyes, the most widely used ones[2], clearly ineffective in decolorizing textile effluents even when mixed and treated together with sewage [3], leading to discharge the highly colored water, and earning complaints from the public. Powdered activated carbon (PAC) has been regarded as the most successful adsorbent. However, it is expensive and the level of color removal by it depends on the types of dye to be removed. Also, 100% color removal has rarely been achieved with it[4]. Ozone has shown to have the ability to breakdown the most dyes. However, even high doses of ozone were not able to mineralize the organic dye completely to carbon dioxide and water due to the decreasing decolorization rate with an increasing initial dye concentration[5].

Knowing the problems laid in front of the treatment of the wastewater from the dye industry, there is a definite need to find alternative treatment processes. Membrane technique, one of the popular treatment methods that has been used in textile industry, holds great promise in this field[6], as it has a great potential to either remove the dyestuff from the wastewater and allow reuse of the auxiliary chemicals used for dyeing or to concentrate the dyestuffs and auxiliaries and produce purified water. Microfiltration is especially suitable for removing colloidal dyes from the exhausted dye bath and the subsequent rinses. Ultrafiltration is effective as a single-step treatment of secondary textile wastewater. Nanofiltration (NF) allows the separation of low molecular weight (<1000) organic compounds and salts, with an appreciable softening effect. Reverse osmosis (RO) is suitable for removing ions and larger species from dye bath effluents. Permeate produced by the membrane process is usually colorless and low in total salinity. The Permeate produced by the RO process is good enough to be reused as wash-water[7]. It has been concluded that membrane based separation processes are technically, economically feasible to treat dye-containing effluent.

However, the membrane process has a problem. That

is the fouling of membranes by the materials of the wastewater. The rate and extent of the colloidal fouling is the most significantly influenced by the physical roughness of membranes regardless of physical, chemical operating conditions. More particles deposit on rough membranes than on smooth membranes[8]. Fouling behavior of different membranes differs by their cut-off values and their material properties, such as hydrophobicity. The adsorption fouling is dramatically more pronounced for the hydrophobic membrane. And high concentration polarization promotes the fouling, which means that the rather loose NF membrane fouled more than the tighter NF membrane. Solution chemistry is also an important factor for the membrane fouling[9].

Therefore, for the proper application of the membrane process to the wastewater treatment, a pretreatment process to remove the materials of the wastewater that can cause membrane fouling is needed. In this study, the coagulation and sedimentation process that is one of the conventional treatment processes for the water and wastewater was applied to the pretreatment for the removal of colors and organics from the wastewater.

2. Experimental

2.1. Materials

Direct Red 75, polyvinyl alcohol (PVA, 88% hydrolyzed, MW 77,000), NaCl and Na₂SO₄ bought from Aldrich Co. (Milwaukee, WI) were used for the preparation of a dyeing solution. The chemical coagulants such as HOC-100A, aluminum sulfate (alum, Al₂(SO₄)₃) and ferric chloride (FeCl₃) purchased from EFT Co. (Korea) were used for the coagulation-sedimentation process. HOC-100A was an integrated coagulant for the treatment of wastewater and a patent product made from polymerization reaction of aluminum salt as an inorganic part, chitosan as an organic part and other organics. The color removal agent used was YANGFLOC DC-400 (Eyang chemical Co., Korea). The anionic polymer purchased from EFT Co. (Korea) was used as a coagulant aid performed as a slow mixing procedure.

Table 1. Compositions of the Artificial Dyeing Wastewater

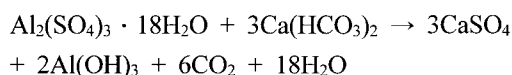
Materials		Concentrations (ppm)
Organic Materials	Direct Red 75	1000
	PVA	500
Inorganic Materials	NaCl	250
	Na ₂ SO ₄	750

2.2. Preparation of an Artificial Dyeing Wastewater

The characteristics of wastewater released from dyeing plants, in fact, vary by the wastewater plant and sampling time. Therefore it was required to prepare a dyeing wastewater with average concentrations of materials in the water for testing. Table 1 shows characteristics of the artificial dyeing wastewater. It has been general that a dyeing wastewater is composed of the mixture of organic materials such as dye, polyvinyl alcohol (PVA) and polyacrylic acid (PAA) and inorganic materials such as sodium chloride, sodium sulfate and magnesium sulfate.

2.3. Jar Test

A Jar tester was used for the coagulation and sedimentation process of the artificial dyeing wastewater. The concentration of coagulants was varied from 500 to 4,000 ppm and the pH for the coagulation process was changed from 5 to 10. The chemical equation related to the coagulation procedure by alum, for example, is as expressed below so that calcium bicarbonate should be added with alum for effective coagulation.



The jar test with various coagulants was performed with the artificial dyeing wastewaters whose characteristics are as shown in Table 1 and determined the optimum coagulant and coagulation conditions. The procedure of the jar test with three types of coagulants was

as follows.

- (1) 2 Liter of dyeing wastewater was filled into a round jar.
- (2) Prepared dosing solutions by diluting the coagulant 10 times and by diluting the cationic polymer solution to 0.1% (for the cases of aluminum sulfate and ferric chloride, color removal agent was specially prepared by diluting it 10 times).
- (3) By using 20% NaOH and HCl, pH of the dyeing wastewater was controlled: for the HOC-100A and aluminum sulfate, it was 7 and for the ferric chloride, it was 10.
- (4) After adding the coagulant (HOC-100A), whose amount was predetermined, the wastewater solution was stirred for 20 min at a speed of 200 rpm. When aluminum sulfate or ferric chloride was used, color removal agent was added together with the coagulant agent.
- (5) After which, the cationic polymer solution was added and stirred for another 20 min at a speed of 100 rpm.
- (6) After 30 min of precipitation, the clear solution located on top of the jar was taken for the further test.

2.4. Analysis Apparatus

A Jar test was performed using a SJ-10 jar-tester (Young Ji Co., Korea) that consisted of six paddles whose rotating speed was controlled by a tachometer attached. A pH-meter (SK-620PH, SATO KEIRYOKI MFG. Co., Japan) was used to control the pH of the solutions. 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. Permeation Test

Separation of the dyeing wastewater from its aqueous solution was carried out using CSM Reverse Osmosis membrane (RE1812-60GPD) purchased by SAEHAN (Korea). A typical set-up for membrane test was used for this test and operating pressure was controlled from 100 to 400 psi using backpressure regulators. Operating temperature was controlled at 25°C, using water bath circulator on feed tank and the flow rate passing through the membrane was 0.8 LPM (L/min). Flux and rejection were determined by a conventional method. Flux was determined from the weight of the permeate gathered for a certain period of time and rejection was calculated by the following equation:

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

Where, C_f and C_p are the concentrations of feed solutions and permeates, respectively.

3. Results and Discussion

Of the methods that have been used for the treatment of the wastewater from the textile industry, the membrane technology has been considered to be simple and economically favorable. However, for the successful treatment of the wastewater with membranes, it is important to consider how to avoid the membrane fouling by the materials contained in the wastewater. As materials accumulate near, on, and within the membrane, they may reduce the permeability of the membrane by blocking or constricting pores and by forming a layer of additional resistance to flow across the membrane. Reductions in permeate flux over time may be substantial and represent a loss in the capacity of a membrane facility. The reductions in permeate flux and procedures for maintaining permeate flux must be considered in the operation of membrane facilities.

To avoid such fouling problems, before applying the wastewater to the membrane process, the concentration of the materials of the wastewater should be controlled to some degree not to cause a serious membrane fouling.

Table 2. Conductivity, TDS and COD of the Water Caused when Chemical Coagulants of 1,000 ppm were Dissolved Into it

Coagulants (1,000 ppm)	Conductivity (μ S)	TDS (ppm)	COD (ppm)
HOC-100A	649	310	89
Alum	357	173	5
Anionic Polymer	31.2	14.8	2
Color Removal Agent	239	124	137

In this study, a coagulation and precipitation process using chemical coagulants, one of the easy and efficient ways to remove the excess amount of materials from the wastewater, was used to pretreat the wastewater. Three different coagulants were used: HOC-100A, alum and ferric chloride. The wastewater used was a synthetic one composed of dye (Direct Red 75), poly(vinyl alcohol) (PVA), NaCl, and Na₂SO₄, whose compositions were as shown in Table 1. The reason for selecting those materials for the formation of the synthetic wastewater was that they were the major components of the practical dyeing wastewater. The total concentration of the materials of the synthetic wastewater was 2,500 ppm.

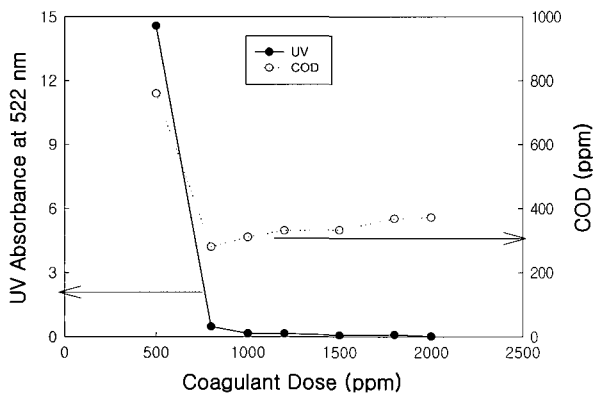
The wastewaters pretreated with different coagulants under different conditions were treated again with RO membranes for the further treatment to produce reusable water. By observing the flux decline with operation time, the effect of pretreatments with different coagulants on the membrane performance was studied.

3.1. Pretreatment with Coagulants

To help understand the jar test results obtained from using different coagulants, the features of the coagulants used affecting the quality of water when 1,000 ppm of each coagulant was dissolved in the distilled water were observed as shown in Table 2. The anionic polymer appeared to cause the least chemical oxygen demands (COD), total dissolved solids (TDS), and conductivity among the coagulants used, while the HOC-100A and color removal agent showed high COD and TDS values as well as conductivity as high as 649 μ S. These data might give a good guideline for the users who want to

Table 3. Characteristics of the Wastewaters Treated by the Coagulation and Sedimentation Process with HOC-100A at pH 7.0 Coagulant Dose: HOC-100A/Anionic Polymer = 1/1

Coagulant (ppm)	pH	Conductivity (ms)	TDS (ppt)	UVA (at 522 nm)	COD (ppm)
500	7.404	2.85	1.40	14.56	760
800	7.325	2.95	1.48	0.482	280
1000	6.894	3.06	1.51	0.159	310
1200	6.302	3.16	1.55	0.153	330
1500	6.665	3.16	1.56	0.076	332
1800	6.792	3.42	1.68	0.100	368
2000	7.867	3.49	1.72	0.024	372
Raw wastewater	7.745	2.77	1.37	21.60	1,000

**Fig. 1.** UV absorbance and COD values as a function of the coagulant dose of the wastewater pretreated by the coagulation and sedimentation process with HOC-100A at pH 7.

use these coagulants for the coagulation and sedimentation processes. From the Table 2, it was found that as less amounts of HOC-100A and color removal agent as possible should be used to produce good-treated waters.

3.1.1. HOC-100A Coagulant

To pretreat the wastewater using HOC-100A, the pH of the solution was controlled at 7. The data obtained from the wastewater pretreated with different amounts of HOC-100A are as shown in Table 3. The concentration of the HOC-100A was varied from 500 to 2,000 ppm. For the more effective removal of the materials from the wastewater, the same amounts of anionic polymer were used together with HOC-100A. Fig. 1 presenting the COD values and UV absorbance of the

pretreated wastewater as a function of coagulant doses indicates that the effective removal of the materials from the wastewater occurred for the coagulant dose more than 800 ppm. Beyond the 800 ppm of the coagulant dose, the COD value increased slightly with increasing coagulant doses, reflecting the features of the HOC-100A causing high COD when it was dissolved in water as shown in Table 2. However, the UV absorbance, from which dye concentration remained in the solution after the treatment can be estimated, decreased further.

By the treatment with HOC-100A, the COD and UV absorbance of the wastewater decreased drastically, but the TDS and conductivity were not changed much compared to the original wastewater. From this result it can be suggested that the organic materials of the wastewater such as dye and PVA were effectively removed from the wastewater by the pretreatment, but the inorganic components such as Na_2SO_4 and NaCl were not removed properly. When considering all the data obtained, it can be concluded that the best condition for the pretreatment with HOC-100A was 2,000 ppm of HOC-100A.

3.1.2. Aluminum Sulfate Coagulant

For the treatment of the dyeing wastewater with metal coagulants such as alum and ferric chloride, it has been known that for the effective removal of the color it's necessary to use color removal agent together with metal coagulants. Table 4 shows the characteristics

Table 4. Characteristics of the Wastewaters Treated by the Coagulation and Sedimentation Process with Alum at pH 7.0

Coagulant (ppm)			pH	Conduct-ivity (ms)	TDS (ppt)	UVA (at 522 nm)	COD (ppm)
Alum	Color Removal agent	Anionic Polymer					
3000	2000	2000	7.279	3.76	1.90	0.100	430
4000	2000	2000	7.189	4.05	2.00	0.044	376
5000	2000	2000	7.257	4.32	2.12	0.041	398
6000	2000	2000	7.090	4.60	2.24	0.066	422
Raw wastewater			7.754	2.91	1.42	22.08	1,060

Table 5. Characteristics of the Wastewaters Treated by the Coagulation and Sedimentation Process with Ferric Chloride at pH 10.0

Coagulant (ppm)	pH	Conductivity (ms)	TDS (ppt)	UVA (at 522 nm)	COD (ppm)
2000	8.332	4.36	2.15	0.138	276
3000	7.896	4.48	2.23	0.244	270
4000	8.687	4.86	2.41	0.150	228
Raw wastewater	7.889	2.79	1.41	22.62	800

* Color Removal Agent: 1,500 ppm, * Anionic Polymer: Equal Dosage of Coagulant

of the effluents after the pretreatment with alum at pH 7. The amount of alum varied from 3,000 to 6,000 ppm while the concentrations of the color removal agent and anionic polymer used together were all 2,000 ppm. As expected, by the pretreatment, the UV absorbance indicating the content of the colorant in the water and COD appeared to be drastically decreased by more than 90%, but conductivity and TDS became even higher. Based on these data, it can be concluded that the 4,000 ppm alum combined with 2,000 ppm of color removal agent and anionic polymer was the best condition for the treatment.

3.1.3. Ferric Chloride Coagulant

In the Table 5, the pretreatment data obtained by using ferric chloride as a coagulant were presented. The treatment condition was similar to the condition used for the case of alum: pH was 10, the concentration of color removal agent 1,500 ppm, the same amounts of anionic polymer as the ferric chloride were used for each case. As the case of alum, the treatment with ferric chloride also resulted in good reductions in UV absorbance and COD. The best condition for the treatment was seemed when 4,000 ppm ferric chloride was used.

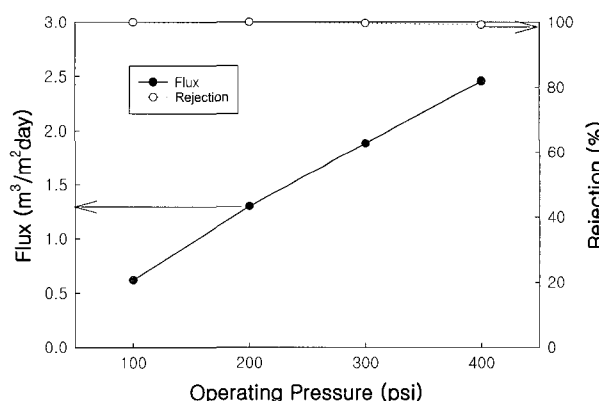


Fig. 2. Flux and rejection as a function of operating pressure through the TL RO membrane when 2,000 ppm aqueous NaCl solution was used as a feed.

3.2. Treatment with Membranes

For the further treatment to produce water good enough to be reused, the wastewaters pretreated by the coagulation-sedimentation process using different coagulants under different conditions were applied to the membrane process with a commercial RO-membrane purchased from the SacHan Co., whose trade name was TL-membrane. The basic permeation properties of the RO-membranes used in this experiment was as shown in Fig. 2 when tested with 2,000 ppm NaCl solution as a feed under operating pressures from 100 to 400 psi. Over all

Table 6. Optimum Treatment Conditions for Different Coagulants Used for the Preparation of Feed Solution of the Membrane Process

Dose (ppm)	Coagulant	Anionic polymer	Color removal agent	pH
HOC-100A	2,000	2,000	-	7.0
Alum	4,000	2,000	2,000	7.0
Ferric chloride	4,000	1,500	1,500	10.0

the operating pressures, the rejection was more than 99% and flux at 200 psi was about 1.3 m³/m²day, indicating this membrane was one of the high flux RO membranes.

For the treatment with a membrane process, three kinds of feed that were produced by treating the synthetic wastewater under different conditions such as different coagulants used as mentioned above were used. The feed solutions were prepared by filtering with a filter paper the wastewater after the pretreatments. Feed solution one was prepared by the pretreatment with HOC-100A, feed solution two by the pretreatment with alum and feed solution three by the pretreatment

with ferric chloride under the conditions shown in Table 6.

3.2.1. Effect of the Coagulants Used

Tables 7, 8, and 9 show the properties of the permeate obtained from the membrane separation process of the feed solution one, two, and three, respectively. Being compared to the properties of the feed solutions given together in the Tables 7, 8, and 9, all of the permeate was appeared to be good enough to be used again as a process water for dyeing processes. The CODs of the solutions were as low as 3.4 ppm and UVAs were as low as 0.000 (undetectable by the machine used in this experiment).

As one can see from the Tables 7, 8, and 9, the COD of the permeate produced from the feed solution one that was prepared by pretreating the wastewater with HOC-100A appeared to be the lowest, suggesting that HOC-100A was the best among the coagulants used in this experiment. That was as low as 3.4 ppm (about 99% rejection). The COD of the permeate from

Table 7. Characteristics of the Permeates of the Membrane Separation Process when HOC-100A was Used for the Pretreatment of the Wastewater to Prepare a Feed Solution

Operating Pressure (psi)	Conductivity (μ S)	TDS (ppm)	UVA (at 522 nm)	COD (ppm)
400	35.9	18.5	0.001	5.0
300	37.7	19.2	0.000	4.5
200	28.4	14.4	0.002	3.9
100	35.1	17.5	0.001	3.4
Feed solution	3,450	1,730	0.017	330
Raw wastewater (Average)	\approx 2,800	\approx 1,400	\approx 22	\approx 1,000

* Concentration of HOC-100A: 2,000 ppm, Concentration of Anionic polymer: 2,000 ppm

Table 8. Characteristics of the Permeates of the Membrane Separation Process when Alum was Used for the Pretreatment of the Wastewater to Prepare a Feed Solution

Operating Pressure (psi)	Conductivity (μ S)	TDS (ppm)	UVA (at 522 nm)	COD (ppm)
400	26.4	13.1	0.001	9.8
300	25.5	12.5	0.001	10.2
200	27.9	13.9	0.002	10.6
100	47.4	24.2	0.003	11.7
Feed solution	4,080	2,050	0.036	332
Raw wastewater (Average)	\approx 2,800	\approx 1,400	\approx 22	\approx 1,000

* Concentration of Alum: 4,000 ppm, Concentration of Color removal agent and Anionic polymer: 2,000 ppm

Table 9. Characteristics of the Permeates of the Membrane Separation Process when Ferric Chloride was Used for the Pretreatment of the Wastewater to Prepare a Feed Solution.

Operating Pressure (psi)	Conductivity (μ S)	TDS (ppm)	UVA (at 522 nm)	COD (ppm)
400	54.7	27.6	0.002	13.0
300	62.5	31.1	0.002	12.7
200	82.5	41.1	0.001	12.7
100	159.8	80.0	0.000	15.0
Feed solution	4,760	2,380	0.259	306
Raw wastewater (Average)	\approx 2,800	\approx 1,400	\approx 22	\approx 1,000

* Concentration of Alum: 4,000 ppm, Concentration of Color removal agent and Anionic polymer: 2,000 ppm

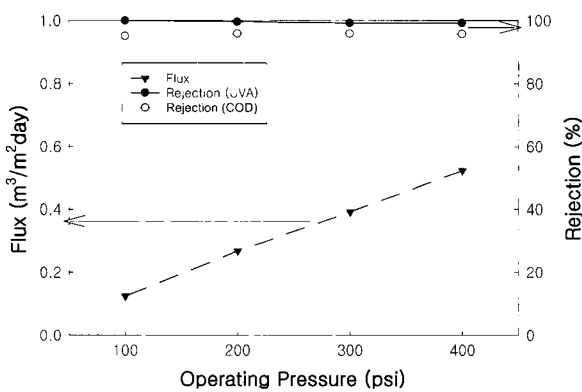


Fig. 3. Permselective properties of the TL-membrane when the feed solution prepared by the pretreatment of the wastewater with ferric chloride under the condition mentioned in Table 6 was used.

the feed solution three (ferric chloride was used for the pretreatment) was, however, 12.7 ppm (about 96% rejection). Considering the reduction in the COD and UVA of the wastewater by the membrane separation process, it was found that for the production of the feed solutions of RO-membrane process, HOC-100A was the best for the pretreatment of the dyeing wastewater, and the alum was the second and the ferric chloride the third.

The reason for this kind of result is not very clear yet, but it is likely that the COD and the UVA of the permeate are related to the membrane fouling behavior during the membrane separation of the wastewaters pretreated with the different coagulants as will be discussed in the following section.

Fig. 3 shows the permselective properties of the TL membrane used in this experiment when the feed solution was the wastewater pretreated with ferric chlo-

ride followed by the filtering with a filter paper. The flux increased to about $0.6 m^3/m^2/day$ at 400 psi with an increasing operating pressure. The rejection to the COD was appeared to be almost more than 98%. For the other two cases when HOC-100A and alum were used for the pretreatment of the wastewater, the permselective properties of the membrane were more or less the same as the Fig. 3.

From these results, considering the characteristic of the permeates and the performance of the membrane, it maybe suggested that it is feasible to recycle the dyeing wastewater by the coagulation treatment with chemical coagulants such as HOC-100A, alum and ferric chloride, followed by the membrane separation process using RO membranes.

3.2.2. Effect of the Coagulants on the Membrane Fouling

The permeate flux decline with operating time of the membrane separation process is as shown in Fig. 4. The feed solutions used for this experiment were the three different wastewaters pretreated with coagulants as explained above. There appear significant decreases in the permeate fluxes with operating time. Before 10 h of operation, most of the flux decline was occurred, and after that the rate of the flux decline was slow. There were also relatively large differences in the flux decline between the feed solutions used; depending on the methods through which the feed solutions were prepared. When HOC-100A was used for the pretreatment, the flux decline was the least and the wastewater pretreated with ferric chloride caused the highest flux

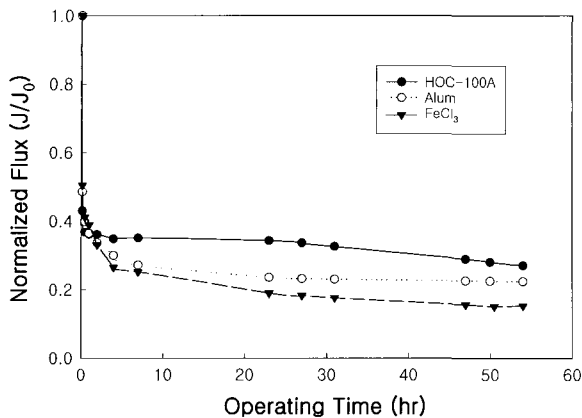


Fig. 4. Flux decline with the operating time through a TL membrane when the feed solutions prepared by the coagulation process with different coagulants followed by the filtration were used.

decline.

These results seemed to have some relationship with the characteristics of the feed solutions used shown in Tables 7, 8, and 9. The difference in the flux decline can be explained by some factors such as the interaction between the foulants in the feed and the membrane surface, and the floc size formed during the coagulation treatment process, via the formation of the foulant cake on the membrane surface whose resistance will be dependent of the physiochemical properties of the foulants. For instance when HOC-100A was used, the floc formed during the coagulation treatment of the wastewater was large in size and hard so that the COD and UVA of the resulting solution were as low as 330 ppm and 0.017, respectively. On the other hand, when the ferric chloride was used, the floc formed was small and soft, the COD and UVA of the treated wastewater were relatively high, 340 ppm and 0.259. Especially, the UVAs of the wastewater treated with ferric chloride were high; indicating a relatively large amount of dye was remained in the solution after the treatment. Probably, the large amount of the dye remained in the solution played a role to make a cake layer on the membrane surface, resulting in the large flux decline.

Fig. 5, presenting the effect of the filtration step for the preparation of feed solutions on the permeate flux

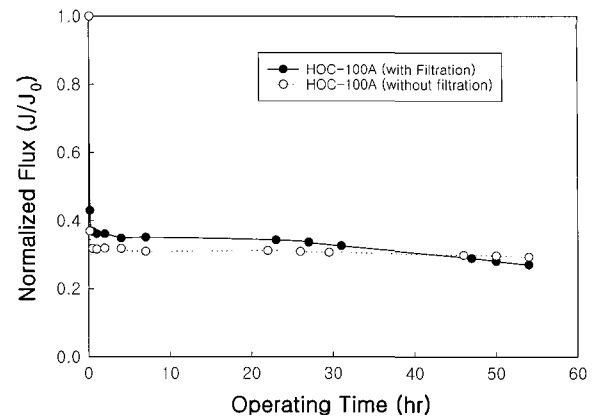


Fig. 5. Effect of the presence of the filtration process during the feed solutions were prepared from the wastewater by using HOC-100A as a coagulant on the flux decline behavior through the TL-membrane.

decline, supports the explanation mentioned above. In other words, when the feed solution of the membrane separation process was prepared by the coagulation and sedimentation process using HOC-100A without the following filtration step, the flux decline became even larger than when other feed solutions prepared by filtering after the pretreatment. There is possibility for the feed solution prepared without filtering step to have flocs in it that are small and soft enough not to be sediment, and the small, soft flocs may form on the membrane surface a more dense cake layer with higher resistance to water flux, causing more flux decline.

These results suggest that even for the RO separation, the proper selection of the chemical coagulant for the pretreatment of the dyeing wastewater is important.

4. Conclusions

Chemical coagulants such as HOC-100A, alum, and ferric chloride are effective for the production of the feed solutions of the RO-membrane process to produce reusable water out of the dyeing wastewater, when they are used under proper conditions. Among the coagulants used, HOC-100A seems to be the best for this purpose. The chemical coagulants remove the organic materials of the wastewater effectively, but they adversely affect on the TDS and conductivity of

the wastewater. To use alum and ferric chloride for the removal of the colorants in the water, color removal agent should be used together. The wastewater treated by the RO-membrane process after the pretreatment using coagulants is good enough to be reused. The membrane fouling behavior depends on the characteristics of the feed prepared by the pretreatment of the wastewater using different coagulants. The feed solution prepared by the coagulation process using HOC-100A, followed by the filtration with a filter paper was the best for the following RO-membrane process, when considered the quality of the water produced and membrane fouling.

Acknowledgement

This research was supported by a grant (code #: 04K1501-01210) from 'Center for Nanostructured Materials Technology' under '21st Century Frontier R&D Programs' of the Ministry of Science and Technology, Korea.

References

1. V. K. Gupta, D. Mohan, S. Sharma, and M. Sharma, Removal of basic dyes (Rhodamine B and Methylene blue) from aqueous solutions using bagasse fly ash, *Sep. Sci. Technol.*, **35**, 2097-2113 (2000).
2. U. Pagga and K. Taeger, Development of a method for adsorption of dyestuff on activated sludge, *Water Research*, **25**, 1051-1057 (1994).
3. P. C. Vandevivere, R. Bianchi, and W. Verstraete, Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies, *Journal of Chemical Technology and Biotechnology* **72**(4), 289-302 (1998).
4. A. Rozzi, F. Malpei, L. Bonomo, and R. Bianchi, Textile wastewater reuse in northern Italy (Como), *Water Science and Technology*, **39**(5), 121-128 (1999).
5. J. N. Wu, M. A. Eiteman, and S. E. Law, Evaluation of membrane filtration and ozonation processes for treatment of reactive dye wastewater, *Journal of Environmental Engineering ASC*, **124**(3), 272-277 (1998).
6. M. Marcucci, G. Nosenzo, G. Capannelli, I. Ciabatti, D. Corrieri, and G. Ciardelli, Treatment and reuse of effluents based on new ultrafiltration and other membrane technologies, *Desalination*, **138**, 75-82 (1970).
7. K. Treffry-Goatley, C. Buckley, and G. Groves, Reverse osmosis treatment and reuse of textile dye-house effluents, *Desalination*, **47**, 313-320 (1983).
8. E. M. Vrijenhoek, S. K. Hong, and M. Elimelech, Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes, *Journal of Membrane Science*, **188**(1), 115-128 (2001).
9. M. Manttari, L. Puro, J. Nuortila-Jokinen, and M. Nystrom, Fouling effects of polysaccharides and humic acid in nanofiltration, *Journal of Membrane Science*, **165**(1), 1-17 (2000).