

# Pretreatment of a dyeing wastewater using chemical coagulants

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## Abstract

For pretreatment of the feed water of membrane processes, chemical coagulants such as HOC-100A, alum, and ferric chloride were used. The feed water used in this experiment was a synthetic dyeing wastewater composed of Direct Red 75, polyvinyl alcohol (PVA), NaCl and Na<sub>2</sub>SO<sub>4</sub>. Total concentration of the materials in the feed water was 2500 ppm. The following optimum coagulation pretreatment conditions were sought using jar tests: for HOC-100A, the concentration of HOC-100A was 2000 ppm at the coagulation pH 7, for aluminum sulfate, 4000 ppm at pH 7, and for ferric chloride, 1500 ppm at pH 10. Under optimum conditions for all the coagulants used, about 90% of materials was removed from the solution when checked with the UV absorbance of the solution before and after treatment.

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## 1. Introduction

Automation and industrialization has resulted in rapid deterioration of water quality. The effluents released from different industries such as textile, leather, paint and so on comprise of hazardous and toxic compounds, which are known to be potential carcinogens. Considering both volume and composition, the wastewater produced by the textile industry is the most polluting among all industrial sectors [1]. Dye-house wastewater is the major source of the pollutants in the textile industry. Effluents from dye-houses contain high concentrations of both inorganic and organic chemicals.

Today more than 9000 types of dyes have been incorporated in the color index. Due to their low biodegradability, a conventional biological treatment process is not very effective in treating dye wastewaters, especially the reactive dyes. Physical or chemical processes have been usually used to treat them, however these processes are costly and cannot be used effectively to treat the wide range of dye wastewater. Of the

conventional chemical methods for removing color from wastewater, such as chemical coagulation, flotation, chemical oxidation and adsorption, adsorption is the most common technique because of its effectiveness, but it is an expensive process [2]. So a process that is economically favorable and easy to operate is needed.

Membrane separation process is one of the popular methods often being used in the textile industry. Although this technique requires relatively high initial setup cost, it is outweighed by the significant cost savings achieved through the reuse of salts and water. Operating costs are generally reduced by the use of pre-filters, regular cleaning to eliminate membrane-fouling problems, and choosing the most appropriate membrane system. Ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) have been widely used for the full-scale treatment and reuse of chemicals and water.

However, the membrane process has a problem of membrane fouling by the pollutants. The membrane surface can be contaminated and its pores can be clogged by the materials in the feed water, resulting in a decrease in the flux. Fouling behavior of different membranes differ by their cut-off values and their material properties, such as hydrophobicity. Solution chemistry is also an important factor in membrane fouling

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[3,4]. A pretreatment process is therefore needed before the solution is applied to the membrane process for removing the materials from the feed solution that give rise to the membrane fouling.

The coagulation and sedimentation process was used as a pretreatment process to remove colors and organics from the feed waters of the membrane process in this study. The effluents after precipitation were filtered using filter papers to get rid of the flocs that remained in the solution and used as feed solutions of the membrane process. This work was mainly focused on the determination of the optimum conditions for the pretreatment using coagulants such as HOC-100A, alum, and ferric chloride.

## 2. Experimental

### 2.1. Materials

Direct Red 75, polyvinyl alcohol (PVA, 88% hydrolyzed, MW 77,000), NaCl and Na<sub>2</sub>SO<sub>4</sub> 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, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) and ferric chloride (FeCl<sub>3</sub>) 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.

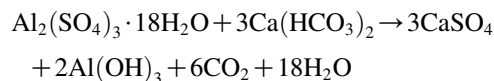
### 2.2. Preparation of an artificial dyeing wastewater

The characteristics of wastewater released from the dyeing plant, 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. Generally dyeing wastewater is composed of a 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 4000 ppm and the pH for the coagulation process was changed from 5 to 10. The chemical equation related to the coagulation by alum, for example, is as expressed below. Calcium bicarbonate should be added with alum for effective coagulation.



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

- (1) Dyeing wastewater of 2 L was filled into a round jar.
- (2) Dosing solutions were prepared by diluting the coagulant 10 times and by diluting the cationic polymer solution to 0.1% (in the case 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) Subsequently, 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 further tests.

### 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 the dye in the solutions before and after the coagulant pretreatment was determined by using an OPTIZEN UV–vis spectrophotometer (MECASYS Co., Korea). The absorbance of the dye was measured at 522 nm, which was the  $\lambda_{\text{max}}$  of the dye used (Direct Red 75). The COD of the solutions was measured using a COD meter (COD-10E, TOA Electronics, Japan).

## 3. Results and discussion

Of the methods that have been used for the treatment of dyeing wastewater, the membrane separation process has attracted considerable attention especially for the reuse of the

Table 1  
Characteristics of the artificial dye wastewater

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

wastewater, being known to be simple to use and economically favorable. However, the wastewater has to be pretreated not to cause a serious membrane fouling as the membrane process is applied to the treatment of 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. The characteristics and location of the deposited materials can play an important role in determining the extent and reversibility of permeate flux decline. A reduction in permeate flux that cannot be reversed is referred to as membrane fouling and materials in the water that produce reductions in permeate flux are collectively referred to as foulants.

To avoid such a membrane fouling, wastewater that contains large amount of foulants should be treated before its application to a membrane process. A coagulation and precipitation process using chemical coagulants is one of the easy and efficient ways to remove the foulant from the wastewater, though being unable to remove the foulants completely out of the solution. Therefore this method is good to be used as a pre-treatment process of the membrane separation process that has a purpose of reuse of the wastewater.

In this study, three different chemical coagulants, which have been widely used as typical chemical coagulants, such as HOC-100A, alum, and ferric chloride were selected and used to know which one is the best for the treatment of dyeing wastewater. The wastewater used was a synthetic one composed of dye (Direct Red 75), poly(vinyl alcohol) (PVA), NaCl, and Na<sub>2</sub>SO<sub>4</sub> as shown in Table 1. The reason for selecting those as materials of synthetic wastewater was that they are the major components of the dyeing wastewater. The total concentration of the materials of the synthetic wastewater was 2500 ppm.

Table 2 shows the characteristics of the coagulants and other coagulant aids used in this experiment (HOC-100A, alum, ferric chloride, anionic polymers and color removal agent) such as their ion concentrations, total dissolved solid (TDS) and COD, which can give some guidelines for optimizing the conditions to be used. The data shown in Table 2 were obtained from each aqueous solution of 1000 ppm of each chemical. Organic coagulants such as HOC-100A and color removal agent showed high CODs when they were dissolved in water, while inorganic coagulants such as alum and

Table 3

Characteristics of effluents after the coagulation and sedimentation process with HOC-100A at pH 5.0

Coagulant (ppm)	pH	Conductivity (μs)	TDS (ppt)	UVA (522 nm)	COD (ppm)
500 <sup>a</sup>	5.529	2.80	1.35	2.659	416
1000 <sup>a</sup>	5.158	3.64	1.78	0.061	392
1200 <sup>a</sup>	5.125	3.72	1.63	0.074	474
1500 <sup>a</sup>	5.105	3.87	1.96	0.077	502
1800 <sup>a</sup>	5.061	4.11	2.11	0.149	506
2000 <sup>a</sup>	4.961	4.46	2.23	0.114	504
500 <sup>b</sup>	5.698	2.81	1.36	2.860	400
1500 <sup>b</sup>	5.141	3.85	1.95	0.091	472
Raw water	7.510	2.93	1.48	21.90	1300

<sup>a</sup> Coagulant ratio: HOC-100A/anionic polymer = 1/1.

<sup>b</sup> Coagulant ratio: HOC-100A/anionic polymer = 1/2.

ferric chloride showed low CODs. These data suggest that using excess amount of the organic coagulants or color removal agent is not favorable for lowering the COD of the wastewater. However, the anionic polymer that was used with HOC-100A showed relatively low COD and TDS, even though it is an organic polymer.

### 3.1. HOC-100A

Tables 3 and 4 show the characteristics of the wastewater after treatment with a HOC-100A/anionic polymer mixture at two different pH values (5 and 7) by the coagulation and precipitation process. An anionic polymer was used together as a coagulant aid with HOC-100A. The ratio of the HOC-100A to anionic polymer used was mostly 1:1. When more anionic polymer was used, for instance two folds, the result was more or less the same as the case of 1:1 of HOC-100A and anionic polymer. Based on these data, it was found that the optimum amount of the coagulant was 1500 ppm when considering the UV absorbance and the COD of the wastewater after the treatment.

From Figs. 1 and 2 representing the UV absorbance and COD of the wastewater after the treatment at pH values 5 and 7, respectively, one can find that pH 7 is better for the treatment with HOC-100A to remove the organic components

Table 4

Characteristics of effluents after the coagulation and sedimentation process with HOC-100A at pH 7.0

Coagulant (ppm)	pH	Conductivity (μs)	TDS (ppt)	UVA (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 water	7.745	2.77	1.37	21.60	1000

Coagulant dose: HOC-100A/anionic polymer = 1/1.

Table 2

Characteristics of coagulants and coagulant aids of 1000 ppm

Coagulants (1000 ppm)	Conductivity (μs)	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

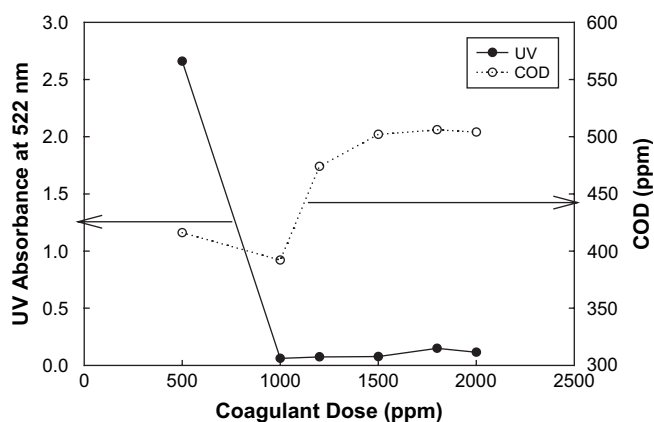


Fig. 1. UV absorbance and COD values with HOC-100A dose after the coagulation and sedimentation process at pH 5.

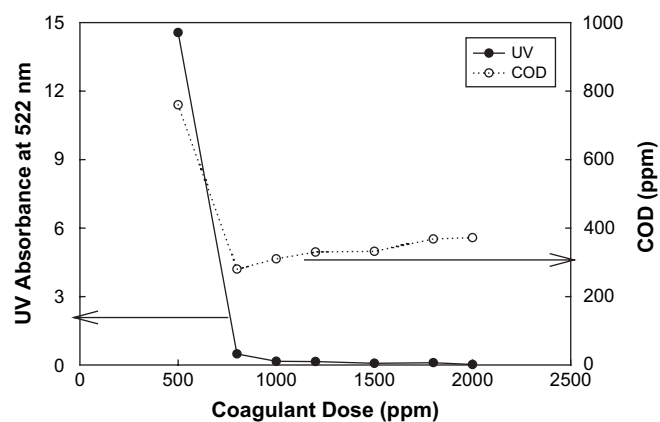


Fig. 2. UV absorbance and COD values with HOC-100A dose after the coagulation and sedimentation process at pH 7.

from the wastewater. From the decrease in the UV absorbance the removal of the dye in the wastewater can be estimated and from the decrease in COD the efficiency for the removal of the organic materials such as dye and PVA can be determined. For both pH values of the wastewater, when the concentration of the coagulant is more than 1000 ppm, the efficiency for the removal of the materials of the wastewater was satisfactory: more than 99% with respect to the UV absorbance and about 60% for COD.

### 3.2. Aluminum sulfate

In the case of HOC-100A, it was not necessary to use color removal agent together to remove the dye from the solution. However, alum without color removal agent could not remove the colorant in the water so the agent has been used together with alum in this experiment.

Table 5 shows the characteristics of the wastewater treated with alum under different conditions. The composition of the coagulation agent mixture used (alum/color removal agent/anionic polymer) was varied to find the optimum condition. The color removal agent and the anionic polymer were used together for the efficient removal of the foulants from the wastewater. The pH of the wastewater was controlled to be 7 during the coagulation and precipitation process.

As in the case of HOC-100A, the conductivity and the TDS of the wastewater treated were higher than those of the wastewater untreated. This phenomenon is generally known to be common in the wastewater treatment with chemical coagulants, due to the remaining chemical coagulants in the water. With increasing amount of the alum upto 6000 ppm, the UV absorbance decreased gradually indicating that the degree of the removal of the colorant in the wastewater increased. On the other hand, the COD of the wastewater after treatment varied, depending on the amount of color removal agent. As shown in Table 2, the COD caused by the color removal agent was very high as compared with that of alum so that as the larger amount of color removal agent was added, for instance 4000 ppm, the COD of the wastewater was larger (over 500 ppm), compared to that (less than 400 ppm) obtained from the use of the small amount of color removal agent, for example 2000 ppm. This high COD of the wastewater maybe due to the color removal agent that remained in the solution, not coagulated with the alum during the coagulation and precipitation process.

For the treatment of municipal wastewater, the typical process is as follows. For 500 ml of wastewater, after addition of 2000 ppm alum, controlling pH, and addition of 500 ppm color removal agent, the wastewater was agitated strongly. Then 0.5–1.0 ml of anionic polymer was added for the formation

Table 5

Characteristics of effluents after the coagulation and sedimentation process with alum at pH 7.0

Coagulant (ppm)			pH	Conductivity ( $\mu$ S)	TDS (ppt)	UVA (522 nm)	COD (ppm)
Alum	Color removal	Anionic polymer					
2000	1000	200	7.237	3.38	1.65	7.920	554
4000	1000	400	7.303	4.17	2.02	3.620	360
4000	2000	800	7.230	3.95	1.95	1.862	328
4000	4000	800	7.071	4.18	2.07	0.096	510
4000	4000	2000	7.105	4.21	2.09	0.091	524
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 water			7.754	2.91	1.42	22.08	1060

Table 6  
Characteristics of effluents after the coagulation and sedimentation process with ferric chloride at pH 5.0

Coagulant (ppm)			pH	Conductivity ( $\mu$ S)	TDS (ppt)	UVA (522 nm)	COD (ppm)
Ferric chloride	Color removal	Anionic polymer					
1000	500	1000	5.485	3.46	1.69	3.620	736
1500	500	1500	5.264	3.72	1.80	2.300	628
2000	1000	2000	5.475	4.01	1.98	0.128	378
2000	2000	2000	5.810	4.11	2.03	0.217	460
2000	1500	4000	5.666	3.96	1.96	0.122	426
1500	1500	1500	5.764	3.80	1.89	0.117	424
2000	1500	2000	5.523	4.04	2.00	0.124	402
2500	1500	2500	5.663	4.28	2.12	0.186	432
3000	1500	3000	5.685	4.47	2.21	0.246	400
4000	1500	4000	5.235	4.79	2.39	0.183	384
Raw water			7.886	2.97	1.47	4.200	1020

of floc to precipitate out the materials in the wastewater. However, for our synthetic dyeing wastewater, the general process did not work. In our case, however, as shown in Table 5, only when more than 2000 ppm of color removal agent and anionic polymer were added, that good floc formation and removal of colorant was possible. From the data given in Table 5, it can be concluded that for the effective removal of the materials from the wastewater using alum, alum dose should be more than 2000 ppm (its optimum amount is 4000 ppm), color removal agent should be more than 2000 ppm and anionic polymer more than 2000 ppm.

### 3.3. Ferric chloride

Treatment of the wastewater using ferric chloride as a coagulation agent was carried out at two pH values (5 and 10) of the solution. Table 6 exhibits the characteristics of the wastewater after treatment at pH 5 under various coagulation conditions. As in the case of wastewater treatment with alum, this treatment with ferric chloride also needed to use color removal agent together for effective removal of the colorants in water. Anionic polymer was also used to help coagulate the materials in the wastewater.

As one can see, with increasing concentration of the ferric chloride used from 1000 to 2000 ppm, the materials in the wastewater were removed more effectively. For example, the UV absorbance decreased from 4.2 (for raw wastewater) to about 0.12 (97% removal) when 2000 ppm ferric chloride was added. Beyond 2000 ppm of ferric chloride, however, further decrease in the UV absorbance was not noticeable. The COD

Table 7  
Characteristics of effluents after the coagulation and sedimentation process with ferric chloride at pH 10.0

Coagulant (ppm)	pH	Conductivity ( $\mu$ S)	TDS (ppt)	UVA (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 water	7.889	2.79	1.41	22.62	800

Color removal: 1500 ppm.

Anionic polymer: equal dosage of coagulant.

of the wastewater also decreased from 1020 to 378 ppm, depending on the dose of the color removal agent added. The decrease in COD of the wastewater was the largest when the concentration of the color removal agent was 1000 ppm.

Table 7 shows the characteristics of the wastewater treated with ferric chloride at pH 10. The concentration of the ferric chloride was varied from 2000 to 4000 ppm while that of the color removal agent was fixed at 1500 ppm and the concentration of the anionic polymer used together was the same as that of the ferric chloride. Compared with the data in Table 6 corresponding to the same composition of the coagulant mixtures, it was found that pH 10 is better than pH 7 in terms of the decrease in COD of the solution after treatment. The lowest COD of the solution treated at pH 10 was about 228 ppm, while that of the solution treated at pH 5 was 384 ppm. From these data it was found that ferric chloride shows better coagulation performance when the pH condition of the solution is higher than 7.

## 4. Conclusions

Organic and inorganic chemical coagulants such as HOC-100A, alum, and ferric chloride were effective for the removal of the materials from the synthetic dyeing wastewater composed of Direct Red 75, PVA, NaCl, and Na<sub>2</sub>SO<sub>4</sub>. Of the coagulants used, the HOC-100A appeared to be the best for the pretreatment of the synthetic wastewater. HOC-100A was capable of removing dye from water without using color removal agent, while alum and ferric chloride were not. The pH of the solution for good coagulation was dependent on the coagulants used; for HOC-100A, pH 7 was better than 5, for alum, pH 10, for ferric chloride, pH 10 was better than 5. Other conditions for the proper coagulation of the materials of the synthetic wastewater were dependent on the coagulants used.

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