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# Effect of Polyamine Flocculant Types on Dye Wastewater Treatment

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## ABSTRACT

Linear, branched, and grafted polyamine flocculants were synthesized and applied for dye wastewater treatment. The effect of polyamines on color removal was investigated by comparing two treatments: (i) alum alone and (ii) alum/polyamine in combination. Compared to alum alone treatment, the use of polyamine flocculants in combination with alum was highly efficient in color and turbidity removal. Addition of a small amount of polyamine (40 mg/L) reduced alum dosage by 50% while

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improving color removal efficiency by 20%. Branched polyamines were more efficient than grafted polyamines presumably because branched polyamine has higher charge density than grafted polyamine. Our results indicate that the use of alum/polyamine system is beneficial in dye wastewater treatment. The effects of polyamine flocculants on total organic carbon removal and zeta potential were also discussed.

*Key Words:* Dye wastewater; Color removal; Polyamine; Alum; Flocculant.

## INTRODUCTION

Wastewater from the fabric-dyeing industry is a considerable source of environmental contamination. Dye wastewater, especially the effluent from the dyeing stages of the dyeing and finishing processes contains strong color, high pH, temperature, and COD while biodegradability is low.[1] Unless coloring materials are properly removed, dye wastewater significantly affects photosynthetic activity in aquatic life due to reduced light penetration. Heavy metals and chlorides in the dye wastewater are also toxic to aquatic life.[2] Both biological and physicochemical methods have been used for the decoloration and the removal of organic compounds in dye wastewater. Typical dye wastewater treatment methods are coagulation/flocculation, adsorption, ozone, and photo/electrochemical oxidation in combination with biological treatments.[3–10] Among these methods, coagulation and flocculation processes that remove suspended particles and coloring materials have been used in pretreatment stage prior to biological treatment.[11,12]

Flocculating agents are mainly classified into inorganic coagulants and polymeric flocculants. The inorganic coagulants destabilize the suspended particles by compression of the electrical double layers surrounding the particles. In contrast, polymeric flocculants (polyelectrolytes) destabilize particles by adsorption and subsequent formation of a particle–polymer–particle bridge.[13] Polymeric flocculants are water-soluble polyelectrolytes carrying functional groups such as quaternary amine or carboxyl functionalities in the repeat units. The molecular weight of polymer ranges from a few thousands to millions.

The use of inorganic coagulants in dye wastewater is rather limited since a large amount of coagulant is required and subsequently a high volume of sludge is produced. In contrast, a proper use of polymeric flocculants (e.g., polyamines) can successfully remove suspended particles and coloring matters from the wastewater. Polyamines have been used as flocculants and charge neutralization agents in the pulping and mining industries. They are effective in wide pH ranges, easy to handle, and immediately soluble in aqueous solution. Another application of polyamine flocculants is color and turbidity removal in the pulp and dyeing wastewater treatment.[14] Our group has reported that polyamine flocculants are useful in drinking water treatment.[15–17] However, only a few studies have been investigated the applicability of polyamine flocculants in dye wastewater treatment.[18,19]

In this paper, polyamine flocculants with different molecular structure, charge density, and molecular weight were synthesized. The molecular weight of the polyamine flocculant was determined by measuring intrinsic viscosity. The applicability of the synthetic polyamines in dye wastewater treatment was evaluated via a jar test using water samples collected from dyeing industry near Taegu, Korea. Approximately 25% of the dye wastewater is from the scouring process (i.e., polyester processing) containing high pH (alkalinity), BOD, and suspended solids. The rest is from dyeing processes containing various dyes such as vat, direct, sulfur, and disperse dyes as well as suspended solids. The purpose of this study is to determine the applicability of the synthetic polyamines in combination with alum in dye wastewater treatment. The effect of polyamine addition on the removal of color, turbidity, and total organic carbon (TOC) is reported.



## MATERIALS AND METHODS

### Synthesis of Polyamine

Polyamine flocculants were synthesized in a 2-L glass reactor equipped with temperature controller, mechanical stirrer, and dropping funnel. Polyamine flocculants were synthesized by two-step polycondensation of dimethylamine (DMA, 50% aqueous solution) and epichlorohydrin (EPI, >99%).[19–21] In the first step, epichlorohydrin (0.98 mole) was reacted with mixture (1.0 mole) of dimethylamine and modifying agent by adding dropwise through a dropping funnel for 3 to 5 hr at 25°C–40°C to form oligomers. In the second step, polycondensation was conducted by stirring for 2 to 5 hr at 70°C–95°C. After the reaction was completed, aqueous polyamine solution was diluted with deionized water (DI water ≥ 16 MΩ-cm) to obtain 50% (wt.%) solid content.[15,19]

Branched polyamines with higher molecular weight were synthesized using hexamethylenediamine (HMDA, 1,6-diaminohexane, >70%) (Aldrich, Seoul, Korea) and trimethylhexane-diamine (TMHDA, trimethyl-1,6-hexanediamine, >99%) (Aldrich, Seoul, Korea) as modifying agents.[19] Grafted polyamines were synthesized by grafting copolymerization of acrylamide monomer (AAm, >99%) (Aldrich, Seoul, Korea) to the backbone of branched polyamine. After the second step of polyamine synthesis, polyamine solution was reacted with acrylamide monomer by adding dropwise through a dropping funnel. The acrylamide monomer concentration was varied to be approximately 10% to 50% of solid content of grafted polyamine. Ferric sulfate and potassium persulfate were added as redox initiators. After reaction completed (2 to 4 hours at 40°C–50°C), the obtained aqueous grafted polyamine solution was diluted with deionized water to obtain 50% of solid content.

### Viscosity Measurement

The relative viscosity of polyamine was measured using an Ubbelohde viscometer (Incheon, Korea) placed in a water bath (25°C). A solution of 1.0% NaCl was used as a solvent to remove the electric charge effect of polyamines in the viscosity measurement. The intrinsic viscosity of the polyamine sample was determined according to the Huggins' and Kramer's equation.[22]

### Charge Density Measurement

The charge density of synthetic polyamines was determined by colloid titration method.[23] Colloid titration is based on the reaction between oppositely charged polyelectrolytes. For the end-point detection, toluidine blue O (>80%) (Aldrich, Seoul, Korea) was used as cationic indicator with anionic polyelectrolyte PVSK (poly(vinyl sulfate, potassium salt)). (Aldrich, Seoul, Korea).

### Coagulation and Flocculation Experiment

A standard jar-test apparatus (Phipps & Bird Stirrer, Model 7790-400) equipped with stainless steel paddles and stirrer was used for the coagulation and flocculation tests. The dye wastewater samples were taken from a dye wastewater treatment facility near Taegu, Korea. Temperature, pH, color, and turbidity of raw wastewater were determined immediately after sampling. For the jar test, 1 L of wastewater sample was transferred into the jar. The pH of raw wastewater was adjusted by adding 2.25 N $H_2SO_4$ and 1 N NaOH. The jar tester was rapidly mixed at a paddle speed of 200 rpm. After addition of inorganic coagulant (alum, $Al_2O_3 = 8.0$ wt%), flocculants (polyamine) were added within 3–5 sec. The rapid mixing was conducted for 1 min, followed by 10 min of flocculation at 50 rpm, and 30 min of settling. After settling, 50 mL of the supernatant was subsampled to determine turbidity (Hach Turbidimeter, Model 9200N, Colorado, USA) and pH (Orion, Model 900A, Maliland, USA). Color (ADMI color units, C.U.) was determined following the standard methods.[24] Total organic carbon (TOC) was determined by TOC analyzer (Shimadzu, TOC-5000A, Tokyo, Japan). Zeta potential was determined using a zeta-meter (Malvern Instrument, Zetasizer Model 3000, Malvern, UK).

## RESULTS AND DISCUSSION

### Intrinsic Viscosity of Synthesized Polyamines

Linear polyamine with low molecular weight (MW $\leq$ 10,000 g/mol, $[\eta] \leq 0.1$ in 1.0 wt.% NaCl solution) was synthesized by polycondensation of N,N-dimethylamine (DMA) and epichlorohydrin (EPI). The linear polyamine was useful in drinking-water treatment[15,16]; however, no efficient color removal was observed in dye wastewater treatment (data not shown). This is presumably because the linear polyamine has short chain length, thereby bridging of the polyamine with coloring materials is not sufficient. To overcome this limitation of linear polyamine, we attempted to synthesize higher molecular weighted polyamines. The branched polyamines with higher molecular weight were synthesized using HMDA (AQfloc H series) or TMHDA (AQfloc T-1) as modifying agents. The polymerization was conducted by polycondensation reaction prior to the gel point where the polymer becomes rigid via three-dimensional crosslinking. The intrinsic viscosity of polyamine was dependent on the mole ratio of EPI and DMA, reaction temperature, and time. The intrinsic viscosity was used as a measure of molecular weight of the polymer. The graft polyamines (AQfloc A series) were also synthesized by grafting copolymerization of acrylamide to increase stability and molecular weight of the polymer. The graft polyamines become highly viscous when added acrylamide was over 40% (wt.%). The intrinsic viscosity of the synthetic polyamines was at the range of 0.13–0.65 dL/g (Table 1).

### Alum Alone Treatment

Alum coagulation processes are mainly affected by several factors such as alum concentration, pH, temperature, mixing conditions, nature of colloids, and size of particles.[25] Added alum in water and wastewater causes hydrolysis reactions that produce hydrogen ions and subsequently reduce the pH of treated water. The pH reduction depends on the alkalinity of the raw wastewater. Since the dye wastewater contains high pH and alkalinity, pH adjustment is required to

***Table 1.*** Intrinsic viscosities of synthesized polyamines.

| Polyamines | η (dL/g)[a] | Charge density (meq/g) |
|---|---|---|
| Branched polyamine | | |
| AQfloc T-1[b] | 0.15 | 8.75 |
| AQfloc H-1[b] | 0.20 | 8.75 |
| AQfloc H-2[c] | 0.25 | 8.75 |
| AQfloc H-3[c] | 0.25 | 8.75 |
| AQfloc H-4[c] | 0.30 | 8.75 |
| AQfloc H-5[c] | 0.32 | 8.75 |
| AQfloc H-6[c] | 0.36 | 8.75 |
| AQfloc H-7[c] | 0.40 | 8.75 |
| AQfloc H-8[c] | 0.57 | 8.75 |
| Grafted polyamine | | |
| AQfloc A-1 (10% AAm) | 0.13 | 7.88 |
| AQfloc A-2 (20% AAm) | 0.19 | 7.50 |
| AQfloc A-3 (30% AAm) | 0.20 | 7.00 |
| AQfloc A-4 (40% AAm) | 0.28 | 6.13 |
| AQfloc A-5 (50% AAm) | 0.65 | 5.13 |

[a] Intrinsic viscosity.
[b] THMDA was used as modifier.
[c] HMDA was used as modifier.

maintain the pH conditions where aluminum hydroxide precipitates can be formed and thereby optimum coagulation can occur. Effect of alum dosage on color removal and pH change was presented in Fig. 1. Initial pH of raw wastewater was adjusted to 7 and alum dosage was varied from 600 to 2400 mg/L. The color and pH of treated water gradually decreased as alum dosage increased. Alum dosage was 1500 mg/L, reducing color from 1325 C.U. to 400 C.U. for wastewater sample A, and 1800 mg/L, reducing 1285 C.U. to 600 C.U. for wastewater sample B, respectively (Table 2). The difference in optimum alum dosage is attributed to different characteristics of dye wastewater such as coloring materials, turbidity, COD, and alkalinity. Optimal pH (defined as pH of the treated wastewater) was observed in the range of pH 5–6 where color unit in the treated wastewater was low. Further increase on alum dose exhibited negative effect on color removal because the pH of treated water was dropped below optimal pH range. The effect of pH on color and turbidity removal was investigated (Fig. 2). The initial pH of raw wastewater was adjusted by adding 2.25 N $H_2SO_4$ and 1 N NaOH at 1500 (sample A) or 1800 mg/L (sample B) of alum dosage. The optimum pH ranges for efficient color and turbidity removal

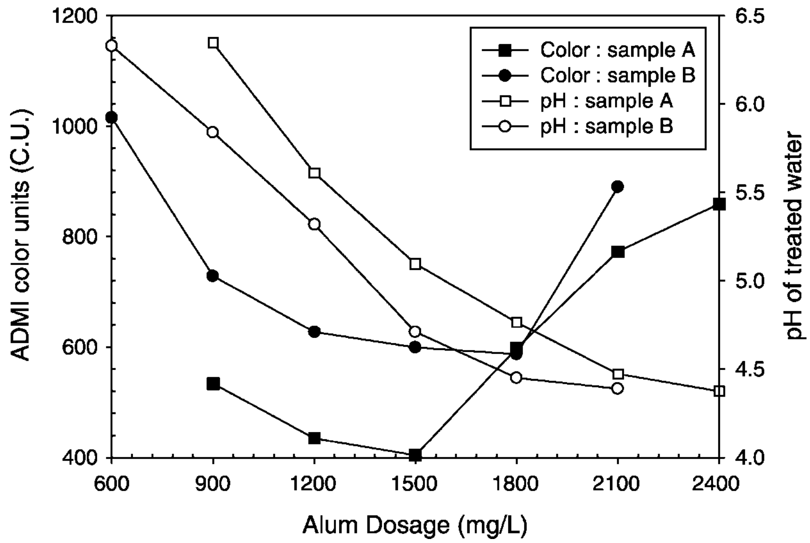


*Figure 1.* Effect of alum dosage on color removal.

was observed at treated water pH 5–6. In two dye wastewater treatments, turbidity was reduced to below 1.0 NTU (nephelometric turbidity unit) at optimum pH ranges.

## Effect of Polyamine Dosage

The effect of polyamine dosage on color removal was presented in Fig. 3. Two polyamines (AQfloc H-7 and A-2) were tested in

*Table 2.* Characteristics of dye wastewater used in this study.

| Sample | Color (C.U.) | Turbidity (NTU) | pH | TOC (mg/L) |
|---|---|---|---|---|
| A | 1325 | 173 | 11.82 | — |
| B | 1285 | 81 | 11.86 | 598 |
| C | 996 | 82 | 12.52 | 808 |
| D | 1403 | 78 | 12.23 | 655 |

Raw wastewater temperature: 35.5°C.

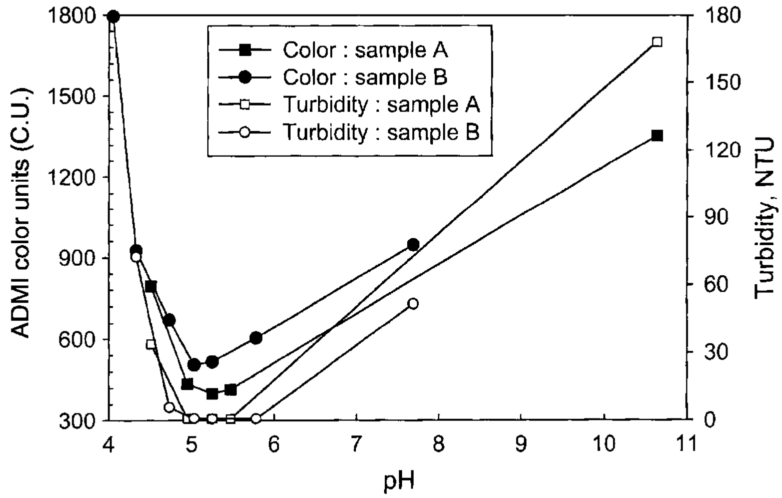


***Figure 2.*** Effect of final pH on color and turbidity removal.

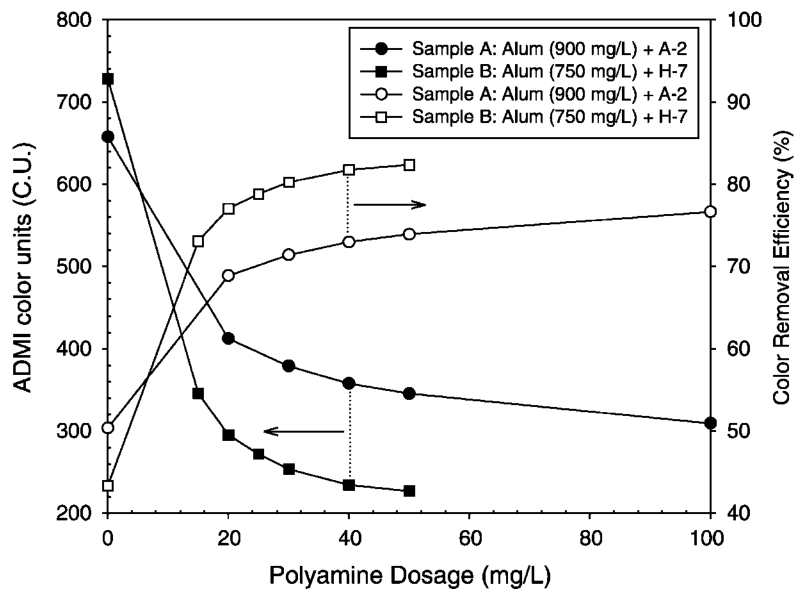


***Figure 3.*** Effects of polyamine dosage on color removal for different samples.

the alum/polyamine treatment. The color removal efficiency was dependent on the characteristics of raw wastewater. Addition of small amount of polyamine in addition to alum (50% of alum alone treatment) highly improved coloring removal. The color of treated water was successfully reduced to below 400 C.U. using 900 mg/L of alum and 30 mg/L of A-2 for sample A and 750 mg/L of alum and 15 mg/L of H-7 for sample B, respectively. Color removal was improved as polyamine dosage was increased up to 40 mg/L in both dye wastewater samples. This indicates that the use of alum/polyamine system is beneficial in color wastewater treatment while reducing alum dosage (half of alum alone treatment). However, approximately 20% to 25% of coloring materials were still persistent, indicating difficulty of color removal.

## Effect of Polyamine Types on Color Removal

Since our synthesized branched and grafted polyamines have widely different characteristics such as molecular weight (or intrinsic viscosity), structure, and charge density, the effects of polyamine types on color removal were investigated (Fig. 4). The effects of grafted polyamines on color removal for wastewater sample A were presented in Fig. 4a. Approximately 52% of color was removed (from 1325 C.U. to 632 C.U.) using 1500 mg/L of alum. In contrast, addition of 40 mg/L of grafted polyamine with 750 mg/L of alum achieved better color removal efficiency (69%–72%). However, color removal was no longer improved as the intrinsic viscosity or molecular weight of the grafted polyamine increased from A-1 ($[\eta] = 0.13$) to A-5 ($[\eta] = 0.65$). This is because the charge density within molecular structure of the polymer is reduced with the grafting of more acrylamide to the backbone of polyamine (Table 1). Both charge density and molecular weight of the polyamine flocculant are important in determining optimal dosage and flocculation efficiency.[26–28] Therefore, acrylamide concentration should be carefully selected since it is directly related to the intrinsic viscosity and charge density of the grafted polyamine. Among the grafted polyamines, AQfloc A-2 containing 20% of acrylamide was the most efficient flocculant in color removal (Fig. 4a).

The effects of branched polyamines on color removal were shown in Fig. 4b (wastewater sample B). In alum alone treatment, approximately 47% of color (from 1285 C.U. to 588 C.U.) was removed using 1800 mg/L of alum, while addition of 25 mg/L of polyamine achieved better color removal efficiency (72%–75%) while reducing alum dosage (900 mg/L, 50% of alum alone treatment). Color removal was improved as the intrinsic viscosity of

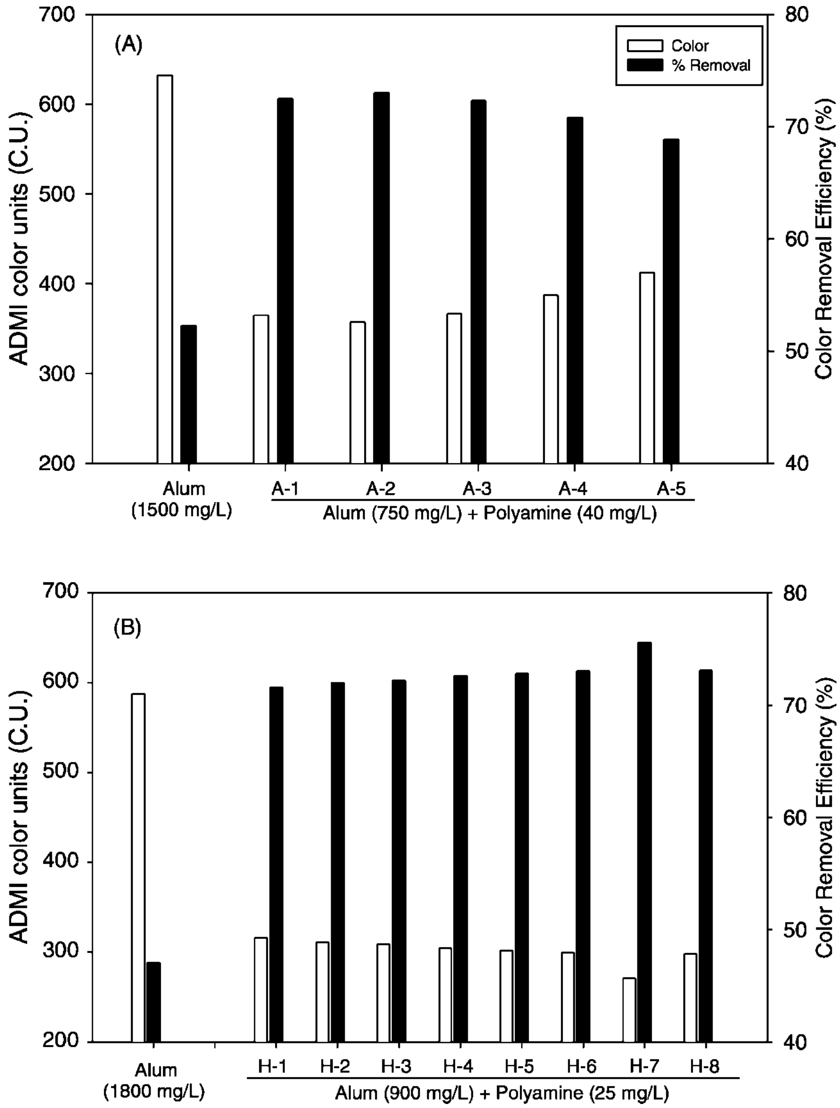


*Figure 4.* Comparison of polyamine types on color removal: (A) grafted and (B) branched polyamines.

the branched polyamines increased from AQfloc H-1 ($[\eta] = 0.20$) to H-8 ($[\eta] = 0.57$). Among the branched polyamines, the AQfloc H-7 ($[\eta] = 0.40$) was the most efficient in color removal.

## Comparison of Polyamine Types on Color Removal

Effect of polyamine types on color removal was investigated for wastewater sample C (Table 2). The color was reduced to 389 C.U. when 1800 mg/L of alum was added. Compared to alum alone treatment, the color was highly removed by adding 25 mg/L of polyamine and 900 mg/L of alum in combination. The color removal efficiency was improved up to 16% over alum alone treatment (61%). Addition of polyamine highly reduced the sludge volume over 20% while no significant differences in turbidity and TOC were observed between the polyamines. As summarized in Table 3, branched polyamine, AQfloc T-1 ($[\eta] = 0.15$) was more efficient than grafted polyamine, AQfloc A-2 ($[\eta] = 0.19$) in the treatment efficiency. The higher color removal by branched polyamine, even at lower intrinsic viscosity, is because the charge density of the branched polyamine (AQfloc T-1) is higher than that of grafted polyamine (AQfloc A-2). It appears that charge density rather than molecular weight of polymer flocculant determines the treatment efficiency.[25] When branched polyamines with same level of charge density are compared, AQfloc H-7 ($[\eta] = 0.40$) was more efficient than AQfloc T-1 ($[\eta] = 0.15$) in color removal due to higher intrinsic viscosity. The results indicate that both intrinsic viscosity and charge density should be considered in the selection of polyamine flocculants for the color removal from dye wastewater.

***Table 3.*** Quality of treated water on various flocculants.

| | Concentration | | Quality of treated water | | |
|---|---|---|---|---|---|
| Coagulant and flocculants | Alum (mg/L) | Polyamine (mg/L) | Color (C.U.) | Turbidity (NTU) | TOC (mg/L) |
| Alum alone | 1800 | 0 | 389 | 3.4 | 584 |
| Alum + AQfloc A-2 | 900 | 25 | 247 | 4.0 | 603 |
| Alum + AQfloc T-1 | 900 | 25 | 224 | 3.9 | 591 |
| Alum + AQfloc H-7 | 900 | 25 | 220 | 3.4 | 602 |

## Total Organic Carbon Removal

The effect of polyamine addition on TOC removal was investigated. The jar test was conducted for the wastewater sample D (Table 2). In alum alone treatment, the optimum alum dosage was 1800 mg/L, reducing the color to 807 C.U. at optimum pH condition (pH of treated water = pH 5–6). The effect of polyamine dosage on TOC removal was shown in Fig. 5a. Polyamine (AQfloc H-7) dosage was varied at the range of 5–50 mg/L while same amount of alum was used (1200 mg/L). Total organic carbon was decreasing as polyamine dosage was increasing. However, no further decrease in TOC was observed when polyamine concentration was increased to above 30 mg/L.

The effect of alum dosage on TOC removal was presented in Fig. 5b. Alum dosage was varied at the range of 900–2100 mg/L while polyamine dosage was fixed at 30 mg/L. In alum alone treatment, efficient TOC removal was observed at alum concentration higher than 1500 mg/L. In contrast, the use of 30 mg/L of H-7 branched polyamine in combination with alum (> 1000 mg/L) successfully removed TOC. Again, this indicates that the use of polyamine/alum treatment can highly reduce the amount of alum required for efficient TOC removal and subsequently reduces sludge production. However, less than 40% of TOC was removed in both alum alone and polyamine/alum treatments, indicating intrinsic difficulty of color removal.

## Effect of Zeta Potential and Charge Density

The effect of polyamine addition on zeta potential was investigated to explain higher color removal in alum/polyamine system. The zeta potential of the raw wastewater (sample D) was about −40.6 mV. The effect of polyamine (AQfloc H-7) dosage on zeta potential was represented in Fig. 6. The zeta potential was measured after the rapid-mixing and slow-mixing steps in jar test. In alum/polyamine treatment (alum = 1200 mg/L), zeta potential approached to the isoelectric point (zeta potential = 0 mV) as polyamine dosage increased. Color and turbidity removal were improved as the zeta potential approached to the isoelectric point. Optimum color removal (below effluent permit criteria, 400 C.U.) was observed when zeta potential was above −15 mV. This is due to increased adsorption of negatively charged particles onto the cationic polyamine flocculants at lower zeta potential. Similar results have been found in previous reports that zeta potential has a critical role in wastewater treatment.[29–31]

For better explanation, the effects of different polyamine species on zeta potential were investigated (Fig. 7). In alum alone treatment, addition

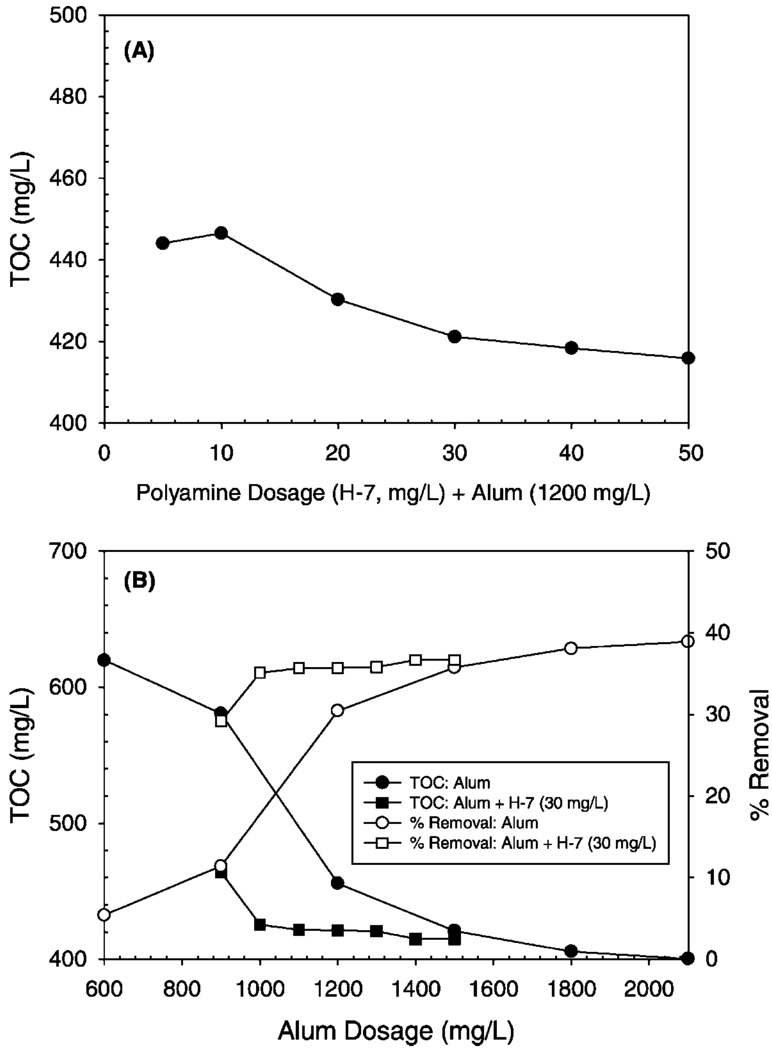


***Figure 5.*** Effect of polyamine on TOC removal: (A) effect of polyamine dosage (alum = 1200 mg/L) and (B) effect of alum dosage (H-7 = 30 mg/L).

of 1800 mg/L of alum lowered zeta potential to −17 mV, reducing color unit to 800 (C.U.). Less amount of alum (1200 mg/L) further lowered zeta potential to −22 mV. Addition of polyamine increased the zeta potential toward the isoelectric point (0 mV) using less amount of alum

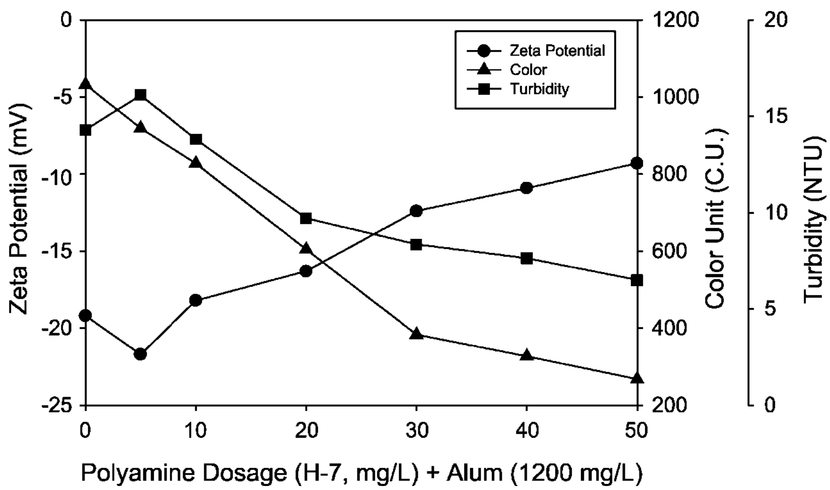


*Figure 6.* Effect of polyamine addition on zeta potential.

(1200 mg/L). The zeta potential of alum/A-2 grafted polyamine was lower than other alum/branched polyamines (T-1 and H-7). The higher zeta potential of the alum/branched polyamine is directly related to higher color removal. The higher color removal by alum/branched polyamine is also attributed to higher charge density of the branched polyamine. In Table 1, the intrinsic viscosity of the A-2 grafted polyamine ( = 0.19) was

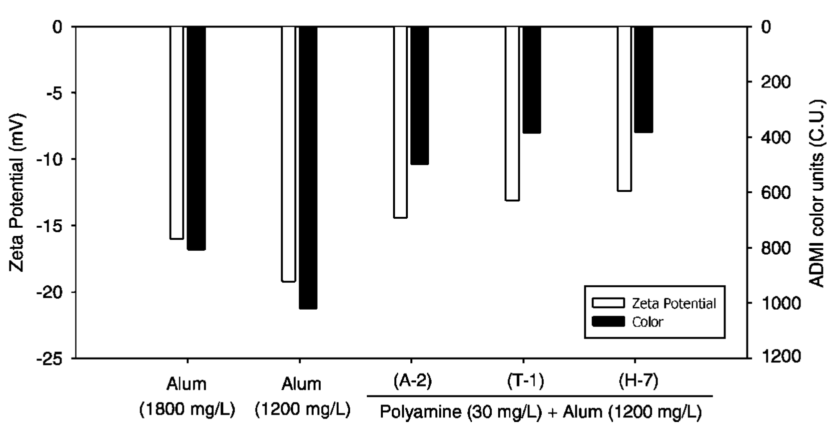


*Figure 7.* Effect of polyamine types on zeta potential.

between T-1 ( = 0.15) and H-7 ( = 0.40) branched polyamine, while the charge density of A-2 grafted polyamine ( = 7.50) was smaller than the T-1 and H-7 branched polyamines ( = 8.75). Since both intrinsic viscosity and charge density of H-7 polyamine were higher than those of A-2 grafted polyamine, higher color removal in alum/H-7 branched polyamine treatment was obtained. However, A-2 grafted polyamine with higher intrinsic viscosity was less efficient than alum/T-1 branched polyamine. This indicates that charge density rather than intrinsic viscosity is the key factor controlling color removal efficiency when intrinsic viscosity is near optimal level. Therefore, charge density as well as intrinsic viscosity of the polyamine flocculants should be considered in the design of color removal processes.

## CONCLUSIONS

Based on the results the following conclusions have been reached: The optimum pH ranges for color removal was observed at final pH 5–6. In alum alone treatment, higher amount of alum addition was required to lower the color of the treated wastewater. In contrast, addition of small amount of polyamine (40 mg/L) as flocculant aid reduced alum dosage by 50% while improving color removal efficiency up to 20%. In alum/polyamine system, branched polyamines were more efficient than grafted polyamines presumably due to their higher charge densities. Charge density of the polyamine flocculants was a controlling factor in determining color removal efficiency. Our results indicate that the use of alum/polyamine system is beneficial in dye wastewater treatment by reducing alum consumption as well as improving color removal efficiency.

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