Separation Science and Technology
Publication details, including instructions for authors and subscription information:
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Online publication date: 31 October 2001

To cite this Article Choi, Jeong-Hak , Shin, Won Sik , Lee, Seok-Hun , Joo, Duk-Jong , Lee, Ju-Dong , Choi, Sang June and Park, Lee Soon(2001) 'APPLICATION OF SYNTHETIC POLYAMINE FLOCCULANTS FOR DYE WASTEWATER TREATMENT', Separation Science and Technology, 36: 13, 2945 — 2958

To link to this Article: DOI: 10.1081/SS-100107638
URL: http://dx.doi.org/10.1081/SS-100107638

SEPARATION SCIENCE AND TECHNOLOGY, 36(13), 2945–2958 (2001)

APPLICATION OF SYNTHETIC POLYAMINE FLOCCULANTS FOR DYE WASTEWATER TREATMENT

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ABSTRACT

Polyamine flocculants were synthesized and applied for the removal of color, turbidity, and organic compounds from dye wastewater. The effect of polyamine on color removal was investigated by comparing 2 treatments: 1) alum alone and 2) alum/polyamine in combination. The effects of polyamine flocculant, concentration, types, and pH on the removal efficiency of colored materials were investigated. Polyamine flocculants were highly efficient in the removal of color and turbidity from dye wastewater. Compared with alum alone treatment, an addition of 25 mg/L of polyamine could reduce alum dosage by more than 50% and improve the color and turbidity removal efficiency. Highly efficient color removal was obtained by adding polyamine as a flocculant at widely different pH ranges. Results indicate that the use of polyamine flocculant is cost effective in dye wastewater treatment

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because it minimizes the amount of sludge produced as the dosage of inorganic coagulant is highly reduced. Effects of zeta potential and pH are also discussed in the paper.

INTRODUCTION

Wastewater from the fabric dyeing industry is a considerable source of environmental contamination. Dye wastewater often contains high levels of chemical and biochemical oxygen-demanding and residual color materials. Color removal is one of most difficult problems in dye wastewater treatment. Physical and chemical treatment methods, including coagulation, adsorption on activated carbon, polymer, and mineral sorbents; reverse osmosis; chemical oxidation; and biological treatments, have been extensively used in dye wastewater treatment (1–7). Coagulation and flocculation processes have been used as pretreatment steps for decolorization of dye wastewater (8–9). Coagulation and flocculation processes remove suspended particles and most of the coloring matters from wastewater.

Flocculating agents are mainly classified into inorganic coagulants and polymeric flocculants (10). The inorganic coagulants (metal salts) induce destabilization of suspended particles through compression of the electrical double layers surrounding the particles. In contrast, polymeric flocculants destabilize particles through the adsorption and subsequent formation of particle-polymer-particle bridges (11). Polymeric flocculants are water-soluble polymers carrying functional groups, such as quaternary amines or carboxyl functionalities, in the repeating units. The molecular weight of the polymer ranges from a few thousands to millions of grams per mole. According to the electric charge exhibited by the polymer flocculants in the aqueous phase, polymers are classified as cationic, anionic, and nonionic flocculants (12). The use of inorganic coagulants (e.g., alum) in dye wastewater is rather limited because a large amount of coagulating agents 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 in the wastewater from the dyeing industry. Polyamines have been used as flocculants and charge neutralization agents in the pulp and mining industries. They are effective in widely different pH ranges, easy to handle, and immediately soluble in aqueous systems. Polyamine flocculants are used to remove color and turbidity removal in pulp and dyeing wastewater treatment (13).

In this paper, we report on the synthesis of polyamine flocculants with different molecular structures, charge densities, and molecular weights. The characteristics of the polymers were determined by viscosity measurements. The applicability of the synthesized polyamines for the treatment of wastewater obtained from the dyeing industry near Taegu, Korea was investigated via a jar test. Our objective for this study was to determine the optimal conditions of polyamines for the physicochemical treatment of dye wastewater. Results indicated that the limitation created by inorganic flocculants that produce high volumes of sludge and residual aluminum concentration can be overcome by adding polyamine flocculants to the system.

EXPERIMENTAL

Synthesis of Polyamine

Polyamine flocculants were synthesized in a 2-L glass reactor equipped with temperature controller and mechanical stirrer. Polyamine flocculants were synthesized by a 2-step polycondensation of dimethylamine and epichlorohydrin (13–14). In the first step, 0.98 mol epichlorohydrin was reacted with a 1.0-mol mixture of dimethylamine and modifying agent that was added dropwise through a dropping funnel for 3–5 hours at 25–40°C to form oligomers. In the second step, polycondensation was conducted by stirring the oligomer mixture for 2–5 hours at 70–95°C. After the reaction was completed, the aqueous polyamine solution was diluted with deionized water, which has minimum resistivity of 16 MΩ-can to obtain solid content of 50% (wt). 1,2-Diaminoethane (1,2-DAE $>$ 99%) and 1,6-diaminohexane (1,6-DAH $>$ 99%) were purchased from Sigma-Aldrich Korea Ltd. (Seoul, Korea) and used as modifying agents to increase the molecular weight of polyamines.

Viscosity Measurement

The relative viscosity of polyamines was measured with an Ubbelohde viscometer placed in a water bath at 25°C. The intrinsic viscosity was determined through the application of both Huggins's and Kramer's equations (15). A 1.0%-NaCl solution was used as a solvent to remove the electric charge effect of polyamines in the viscosity measurement.

Coagulation and Flocculation Experiment

A 6-cube jar-test apparatus (Phipps & Bird Stirrer, model 7790-400) was used with each jar containing 1 L of a wastewater sample. Before conducting jar tests, temperature, pH, color, turbidity, biochemical oxygen demand, (BOD_5), chemical oxygen demand$_{Cr}$ (COD_{Cr}), total organic carbon (TOC), and zeta potential of raw wastewater were measured. The raw wastewater was pretreated with 2.25 N H_2SO_4 to obtain the final pH of of 5.7–5.9 after flocculant treatment. The

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rapid mixing was conducted for 1 minute at a paddle speed of 250 rpm. The flocculation was performed for 10 minutes at 70 rpm and was followed by a 30-minute sedimentation step. After flocculant settling, 50 mL of the supernatant was subsampled, and turbidity (Hach, Model 9200N) and pH (Orion, Model 900A) were measured immediately. TOC (Shimadzu, TOC-5000A), BOD_5, COD_{Cr}, and zeta potential (Malvern Instrument Zetasizer Model 3000) were measured and color was determined by a spectrophotometer (Varian UV-VIS-NIR Spectrophotometer, Model Cary 5G). The amount of sludge after sedimentation was determined by measuring total solids of the settled flocculant. Two treatments, alum (Al_2O_3 = 8.0% (wt)) alone and alum/polyamine (Kufloc) were used to compare the wastewater cleanup performances of the flocculation experiments.

RESULTS AND DISCUSSION

Intrinsic Viscosity of Synthesized Polyamines

Linear polyamine was synthesized from *N,N*-dimethylamine with epichlorohydrin by a polycondensation reaction (Fig. 1a). Linear polyamine with low molecular weight (M.W. $\leq$10 000 g/mol; viscosity (η) $\leq$0.1 in 1.0% (wt) NaCl solution) has been widely used in the flocculation process of potable water treatment. However, this linear polyamine was not efficient in dye wastewater treatment (data not shown) because its linear structure did not insufficiently create bridges with color material. Maximum flocculation and the subsequent, efficient removal of suspended solids, including color material, can be achieved by the bridging mechanism of polymeric flocculant. Therefore, synthesis of polyamine with higher molecular weights was attempted for more efficient dye wastewater treatment (Fig. 1b). The higher molecular weight polyfunctional amines were synthesized using 1,2-diaminoethane (1,2-DAE) and 1,6-diaminohexane (1,6-DAH) as modifying agents. The polymerization was conducted by a polycondensation reaction prior to the gel point where the polymer becomes rigid via three-dimensional cross-linking.

The intrinsic viscosity of the polyamine sample was determined by extrapolation of η_{sp}/c or ln $(\eta/\eta_0)/c$ values to the zero concentration according to the Huggins's (Eq. 1) and Kramer's (Eq. 2) equations, respectively (15):

$$\eta_{red} = \frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \qquad (1)$$

where η_{red} is the reduced viscosity (dL/g); η_{sp} is the specific viscosity (dimensionless); c is the concentration of polymer (g/dL); η is the intrinsic viscosity (dL/g); and k' is a constant.

$$\eta_{inh} = \frac{\ln(\eta/\eta_o)}{c} = [\eta] + k''[\eta]^2 c \qquad (2)$$

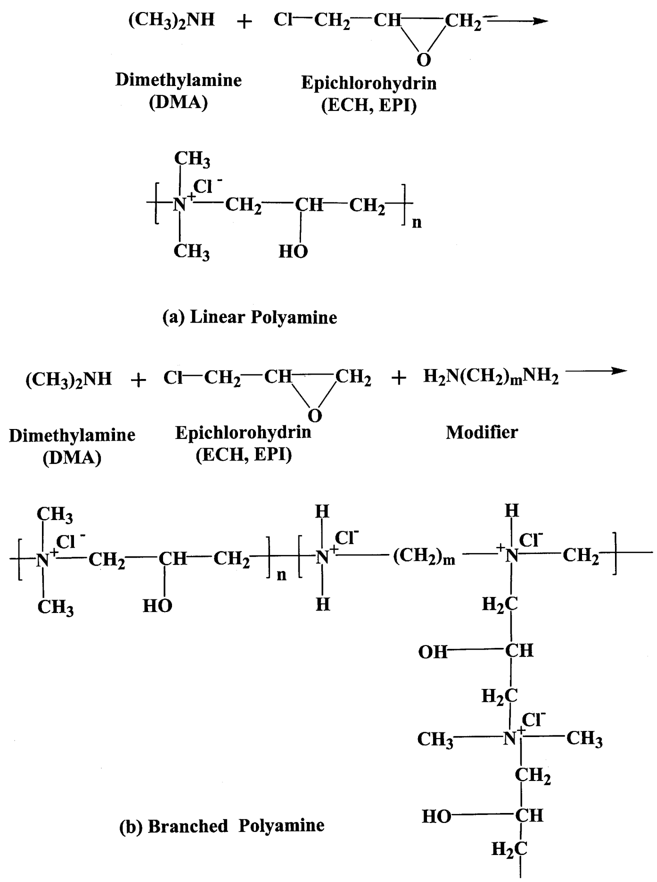

Figure 1. Synthesis of (a) linear polyamine and (b) branched polyamine.

where η_{inh} is the inherent viscosity (dL/g); η is the viscosity at the flow time of polymer solution, t; η_o is the viscosity at the flow time of solvent (1.0% NaCl solution), t_o in the Ubbelohde viscometer; and k'' is a constant. The specific viscosity, η_{sp} is often represented in terms of flow time:

$$\eta_{sp} = \frac{\eta}{\eta_o} - 1 = \frac{t}{t_o} = 1 \qquad (3)$$

A typical measurement of the intrinsic viscosity of a polyamine sample (Kufloc 601A) is shown in Fig. 2. The intrinsic viscosity is used as a measure of the molecular weight of the polymer. The synthesized polyamines exhibited intrinsic viscosity values at the range of 0.152–0.664 dL/g, which corresponds to a molar mass of 50 000–100 000 g/mol.

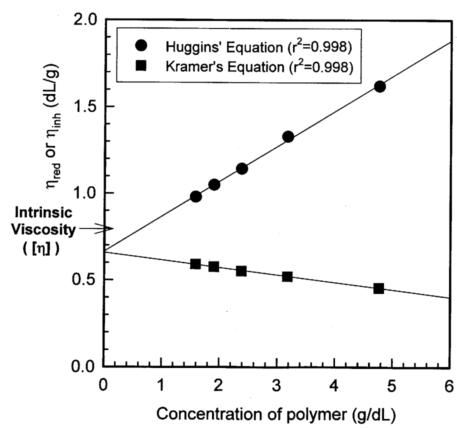

Figure 2. Intrinsic viscosity of Kufloc 601A by Huggins's and Kramer's equations.

The use of multifunctional diamines (1,2-DAE and 1,6-DAH) as modifying agents produced polyamines with relatively high intrinsic viscosity (Fig. 3). Polyamine synthesized with 1,6-DAH as modifying agent had higher intrinsic viscosity (i.e., higher molecular weight) than the one synthesized with 1,2-DAE. This outcome is presumably the result of the 6 methylene functional groups of 1,2-DAE while 1,6-DAH has only 2 reacting polymer chains. The reduced charge density between the 2 reacting polymer chains in the 1,6-DAH produces lower intrinsic viscosity. However, an overdose of modifier often leads to gelation during polymerization. Therefore, only a limited amount of modifier should be used. The intrinsic

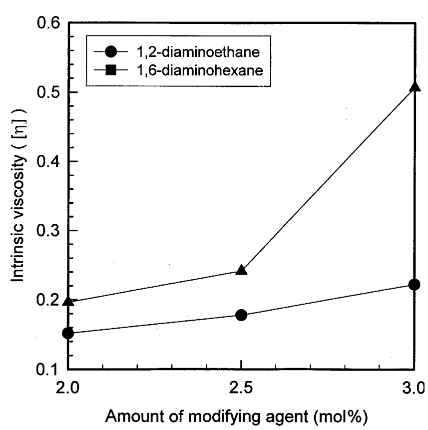

Figure 3. Change of intrinsic viscosity of polyamine with modifying agent concentration.

Table 1. Intrinsic Viscosities of Synthesized Polyamines

Polyamine	Intrinsic Viscosity (dL/g)
Kufloc 405A	0.475
Kufloc 407A	0.477
Kufloc 502A	0.530
Kufloc 601A	0.664
Superfloc 577C	0.442
Superfloc 581C	0.580

Superfloc 577C and 581C are commercial polyamine flocculants from Cytec, Inc, NJ, USA.

viscosities of the polyamines synthesized using 1,6-DAH as a modifier and commercial polyamine flocculants (Cytec, Inc, NJ, USA) are listed in Table 1.

Comparison of Alum and Alum/Polyamine System in Color Removal

The effect of polyamine on color removal was investigated by comparing treatments of alum alone and alum/polyamine in combination. Approximately 40% of the color material was removed when 900 mg/L of alum was added as coagulating agent (Fig. 4). Further increase in alum concentration above 900 mg/L

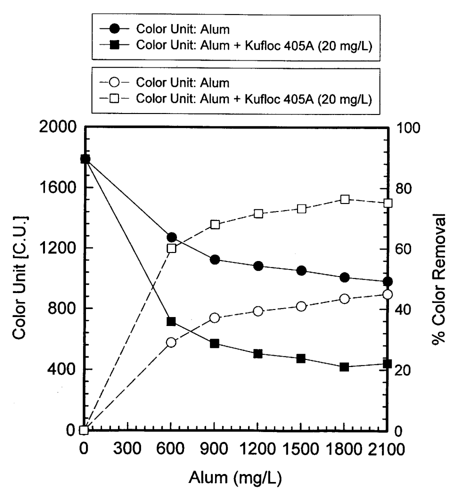

Figure 4. Effect of polyamine flocculant on color removal (raw water quality = 1787.0 C.U.).

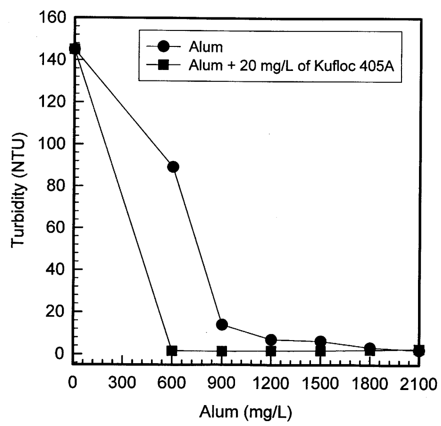

Figure 5. Effect of polyamine flocculant on turbidity removal (raw water quality = 145 NTU).

did not increase color removal efficiency. For comparison, 20 mg/L of polyamine flocculant was added while alum concentration (as 8.0% (wt) of Al_2O_3) was varied at the range of 600–2100 mg/L for the treatment of wastewater containing high color units (C.U.) (1787.0.) and turbidity (145 nephelometric turbidity unit (NTU)). The raw wastewater was sampled from the fiber-dyeing industry near Taegu, Korea. The color removal was improved to 70% when 20 mg/L of polyamine (Kufloc 405A) and 900 mg/L of alum were used in combination. No further increase in color removal was observed in alum/polyamine treatment at alum dosages higher than 900 mg/L).

The turbidity was reduced from 145 to 14 NTU by adding 900 mg/L of alum (Fig. 5). Turbidity removal was not efficient at alum concentrations lower than 900 mg/L. The turbidity removal was slightly improved as the alum concentration was increased above 900 mg/L. In contrast, addition of 20 mg/L of polyamine to 900 mg/L of alum removed turbidity to below 2.0 NTU. The results indicate that removal of color and turbidity can be successfully enhanced by adding a small amount of polyamine. The beneficial effect of using an alum/polyamine system was evident. However, an overdose of alum can produce higher residual aluminum ion concentrations in the water. Recent studies have shown that a high aluminum ion concentration, which may cause neurological diseases such as Alzheimer's disease and presenile dementia, is present in drinking water (10–11,16). The optimal concentration of alum/polyamine should be based on minimizing residual aluminum concentration.

Effect of Dosage and Type of Polyamine

Two polyamine samples (Kufloc 407A and 502A) were tested in the flocculation experiment. The effects of polyamine dosage on the color (Fig. 6) and tur-

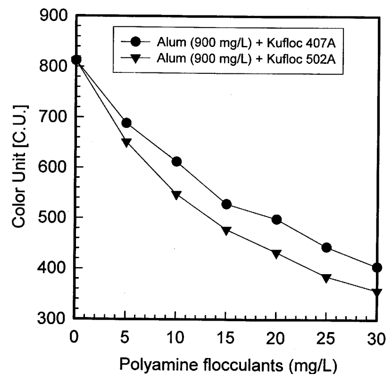

Figure 6. Effect of polyamine dosage on color removal. Color of raw water = 1217.7 C.U. Alum at concentration of 1800 mg/L reduced color to 716.6 NTU.

bidity removal (Fig. 7) were investigated for the treatment of raw wastewater containing 1217.7 C.U. and 135.0 NTU. The polyamine concentration was varied while the alum concentration was kept at 900 mg/L. The color of the wastewater was reduced to 716.6 C.U. when 1800 mg/L of alum was added (data not shown). Figure 6 shows the effect of polyamine concentration on color removal. Addition of polyamine flocculant improved color removal even when the alum dosage was 900 mg/L (50% of alum-alone treatment). The color was reduced from 1217.7 to 256.8 C.U. when 30 mg/L of polyamine was used with 900 mg/L of alum. How-

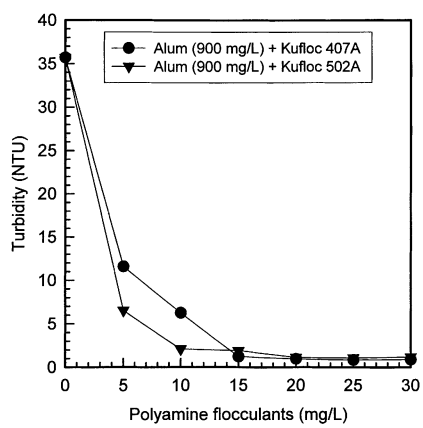

Figure 7. Effect of polyamine dosage on turbidity removal. Turbidity of raw water = 135.0 NTU. Alum at concentration of 1800 mg/L reduced turbidity to 9.15 NTU.

Table 2. Effect of Polyamine Species on the Removal of Color, Turbidity, Organic Compounds, and Amount of Sludge Produced

Coagulant and Flocculant Dosage (mg/L)			Quality of Treated Water						
Alum	Kufloc 502A	Kufloc 601A	pH	Color (C.U.)	Turbidity (NTU)	BOD_5 (mg/L)	COD_{Cr} (mg/L)	TOC (mg/L)	Sludge (mg/L of NTU removed)
1800	0	0	5.84	723.2	15.5	1277	2307	1109	11.9
900	0	0	5.81	884.1	70.6	1320	2469	1172	12.3
900	25	0	6.08	462.9	2.2	1277	2259	1062	10.1
900	0	25	6.08	432.9	1.6	1239	2225	1104	10.1

Raw water quality: $T = 35.5°C$; pH = 12.24; C.U. = 1535; turbidity = 148 NTU; BOD_5 = 1670 mg/L; COD_{Cr} = 3313 mg/L; and TOC = 1430 mg/L.

ever, approximately 35% of color was not removed indicating that the coloring matter is difficult to remove completely.

Polyamine was also highly efficient in turbidity removal. The color of the wastewater containing 135.0 NTU was reduced to 9.5 NTU using 1800 mg/L of alum (data not shown). Addition of 15 mg/L of polyamine flocculant with 900 mg/L of alum (one-half of alum-alone treatment) removed the turbidity to below 3.0 NTU. No more decrease in turbidity was observed at higher polyamine flocculant concentration (>15 mg/L). Kufloc 502A was more efficient than Kufloc 407A presumably due to its higher intrinsic viscosity. The intrinsic viscosity of the Kufloc polyamine flocculant was similar to that of commercial polyamine flocculant (Superfloc, Cytec, Inc, NJ, USA).

The effects of polyamine flocculants on the BOD_5, COD_{Cr}, TOC, and sludge production are summarized in Table 2. The wastewater containing 1535 C.U. and 148 NTU was treated with alum and alum/polyamine systems. Both treatments highly reduced BOD_5, COD_{Cr}, and TOC but no appreciable differences in removal efficiency were observed. By contrast, noticeable differences were observed in color and turbidity removal. Treatment with 900 mg/L of alum reduced color to 884.1 C.U. and turbidity to 70.6 NTU. A 2-fold increase in alum dosage (1800 mg/L) removed color to 723.2 C.U. and turbidity to 15.5 NTU. This lower removal by alum alone treatment was highly improved by adding 25 mg/L of polyamine flocculants. Addition of Kufloc 502A reduced color to 462.9 C.U. and turbidity to 2.15 NTU, while Kufloc 601A reduced color to 432.9 C.U. and turbidity to 1.6 NTU. The better removal with Kufloc 601A is due to its higher intrinsic viscosity.

Effect of Zeta Potential and pH

The effect of polyamine addition on zeta potential was investigated (Fig. 8). The wastewater treated with alum alone had more negative zeta potential than alum/polyamine systems. Alum/polyamine treatment reduced the negative zeta potential toward the isoelectric point (0 mV). The zeta potential is decreasing (approaching 0 mV) as the molecular weight of the polyamine is increased (see Table 1). This is presumably because charge density of the polyamine increases as the molecular weight of the polyamine increases (17). The higher charge density increases the adsorption of the suspended particles onto the polyamine flocculant. Polyamines with higher charge density have lower zeta potential and increasing adsorption capacity with the alum/polyamine treatment. Clearly, the zeta potential was a controlling factor in efficient flocculation.

Added alum for dye wastewater treatment can produce hydrogen ions via hydrolysis reactions that may subsequently reduce the pH of treated water. Because the dye wastewater contains high pH and alkalinity, pH adjustment is required to maintain conditions where aluminum hydroxide precipitates are formed so that optimum coagulation can be achieved. The pH of raw wastewater was preadjusted to 5–10 through the addition of 2.25 N H_2SO_4 so that the effect of pH on color removal could be determined (Fig. 9). Initial pH of the raw wastewater was 12.0, and the water contained 1491 C.U. The pH of the treated dye wastewater was lower than the initial pH. No significant difference between alum-alone treatment and alum/polyamine treatment was observed, indicating that pH reduction is mainly caused by alum.

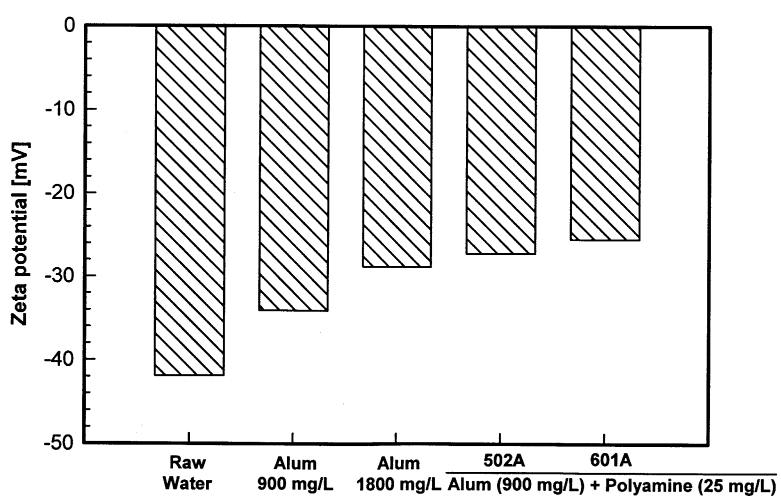

Figure 8. Effect of polyamine species on zeta potential.

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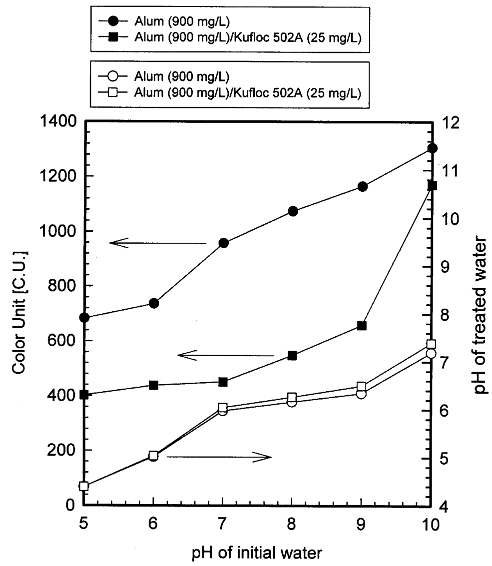

Figure 9. Effect of pH on color removal. Raw water quality: pH = 12.0 and color = 1491.3 C.U.

In alum-alone treatment, the color of treated water was approximately 680 C.U. at pH 5, which is well above the permit criteria of effluents (400 C.U.). Color removal decreased as pH increased. In contrast, consistently higher color removal was observed in alum/polyamine treatment at widely different pH ranges (pH 5–9). Similar to the observation in alum-alone treatment, the color removal decreased as pH increased. Addition of a small amount of polyamine (40 mg/L) as a flocculant aid was beneficial in dye wastewater treatment at widely different pH ranges.

CONCLUSIONS

Addition of a small amount of high molecular-weight polyamine as a flocculant aid was highly beneficial in dye wastewater treatment. Compared to alum-alone treatment, the alum/polyamine system was more efficient in the removal of color materials. Addition of polyamine (25 mg/L) reduced alum dosage of the alum-alone treatment by 50%, improving color removal efficiency. Results indicate that the use of polyamine flocculant is beneficial in dye wastewater treatment by reducing sludge production because the dosage of inorganic coagulant is reduced by 50%.

ACKNOWLEDGMENT

The authors thank the BK21 Project from the Ministry of Environment of Korea for the financial support of this research.

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Received August 2000
Revised November 2000