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Decolorization of reactive dyes using inorganic coagulants and synthetic polymer

Duk Jong Joo [a], Won Sik Shin [a], Jeong-Hak Choi [a], Sang June Choi [a], Myung-Chul Kim [b], Myung Ho Han [c], Tae Wook Ha [d], Young-Hun Kim [e,*]

[a] *Department of Environmental Engineering, Kyungpook National University, Taegu 702-701, South Korea*
[b] *School of General Education, Kyungil University, Gyeongsan-si, South Korea*
[c] *Department of Advanced Materials and Environment, Kyungil University, Gyeongsan-si, South Korea*
[d] *Taegu Science College, Taegu, South Korea*
[e] *Department of Environmental Engineering, Andong National University, Andong, Kyungpook 760-649, South Korea*

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Abstract

A coagulation/flocculation process was employed for the treatment of high concentration reactive dye wastewater. A polymer flocculant synthesized from cyanoguanidine and formaldehyde under acidic conditions was applied with inorganic coagulant (alum or ferric salt) for the dyeing wastewater. The flocculant was tested for synthetic wastewater containing four model reactive dyes (Black 5, Blue 2, Red 2 and Yellow 2) and real wastewater containing reactive dyes from a local dyeing industry. For the synthetic wastewater, the use of inorganic coagulant (1 g/L) alone achieved only 20% of color removal or less. However, with the aid of polymer flocculant, almost 100% of color removal was obtained. The dye removal efficiency increased as polymer dose increased and the efficiency was affected by solution pH and types of the used inorganic coagulant. The use of inorganic coagulant alone appeared little effective in the removal of reactive dyes from the real wastewater. However, alum/polymer and ferric salt/polymer combinations improved color removal up to 60% and 40%, respectively.

Keywords: Coagulation; Reactive dyes; Polymer flocculant; Decoloring; Wastewater

1. Introduction

Wastewater from fabric dyeing industry is a considerable source of environmental contamination. The effluent from the dyeing and finishing processes is characterized by strong color, high pH, high temperature, high COD, and low biodegradability [1]. In recent years, reactive dyes have been most commonly used due to their advantages such as better dyeing processing conditions and bright colors. Moreover, the use of reactive dyes is rapidly growing due to the increased use of cellulosic fibers. Generally reactive dyes contain functional groups such as azo, anthraquinone, phthalocyanine, formazin, and oxazine as chromophore. Among the reactive dyes, approximately 66% is unmetallized azo dye [2]. The reactive site of the dyes reacts with functional group on fiber under influence of heat and alkali. One of the major factors determining the release of a dye into environment is its degree of fixation on the fiber. Reactive dye is hydrolyzed to some extent during application processes; some of reactive dyestuff is inactivated by a competing hydrolysis reaction. Consequently, the release of reactive dyes into dyebath effluent is exacerbated by their relatively low fixation (50–90%) to cellulosic fibers, compared with other dyes such as acid, basic, disperse and direct dye [2,3]. Reactive dyes in dyeing wastewater have been identified as recalcitrant compounds since they contain high alkalinity, high concentration of organic materials and strong color in comparison with other dyes. Unless coloring materials are properly removed, dye wastewater significantly affects photosynthetic activity in aquatic life due to reduced light penetration [4].

* Corresponding author. Tel.: +82 54 820 5818; fax: +82 54 820 6187.
E-mail address: youngkim@andong.ac.kr (Y.-H. Kim).

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Both biological and physicochemical methods have been used for the decolorization and degradation of the organic compounds in dye wastewater. Typical dye wastewater treatment methods are coagulation/flocculation, adsorption and oxidation in combination with biological treatments [5–7]. Combined treatment methods such as adsorption processes by various adsorbents, advanced oxidation processes (using H_2O_2, ozone, UV, etc.) and biodegradation (aerobic and anaerobic) have been also proposed for the treatment of reactive dye wastewater [8,9]. Coagulation and flocculation processes have been widely used as pretreatments to remove suspended particles and coloring materials prior to biological treatment [10,11]. However, reactive dyes cannot be easily removed by conventional coagulation/sedimentation process and aerobic biological wastewater treatment systems have limitations in full scale application due to the poor biodegradability of the reactive dye [12]. Unless the reactive dyes are sufficiently removed in the pretreatment process, the subsequent activated sludge processes could not achieve the regulatory goals due to their low biodegradability.

In this paper, a polymeric flocculant was synthesized using cyanoguanidine and formaldehyde [13]. The synthetic polymer was tested for the synthetic reactive dye wastewater and real wastewater from a local dyeing industry via jar tests. The purpose of this study is to determine the applicability of the synthetic polymer as decolorization agent in combination with inorganic coagulants for the removal of reactive dye from dyeing wastewater. Optimum conditions of coagulation/flocculation such as pH, inorganic coagulant and polymer dosage were also determined.

2. Materials and methods

2.1. Polymer synthesis

A polymer coagulant was synthesized in a 2-L glass reactor equipped with temperature controller, mechanical stirrer and dropping funnel for formaldehyde solution. Paraformaldehyde was dissolved into HCl solutions (0.01–0.8 mol). The formaldehyde reacts with cyanoguanidine (dicyandiamide, industrial grade supplied in powder form) solution in HCl by adding dropwise through a dropping funnel for 2–12 h at 50–80 °C. After the reaction was complete, aqueous polymer solution was diluted with deionized water (DI water $\geq$ 16 MΩ) to obtain 50% (wt%) of polymer content. Viscosity of the synthetic polymer was measured using a viscometer (Brookfield, Model DV-II+).

2.2. Preparation of synthetic wastewaters

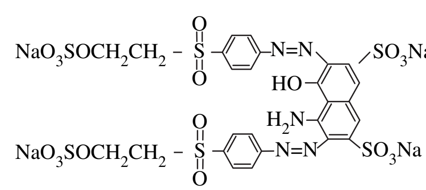
Synthetic wastewater was prepared by dissolving four anionic reactive dyes: Reactive Black 5 (Remazol Black B, RB5); Reactive Blue 2 (Procion Blue HB, RB2); Reactive Red 2 (Procion Red MX-5B, RR2); and Reactive Yellow 2 (Cibacron Brilliant Yellow 3G-P, RY2). All reactive dyes were purchased from Aldrich Chem. Co. and their characteristics and structures are shown in Table 1 and Fig. 1, respectively.

Table 1
Characteristics of reactive dyes

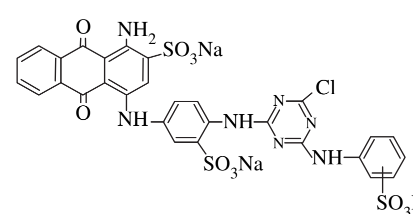
Dye	λ_{max} (nm)	Dyestuff (color index)	Purity (%)	M.W.
RB5	597	Remazol Black B	~55	991.82
RB2	607	Procion Blue HB	~60	840.12
RR2	538	Procion Red MX-5B	~50	615.34
RY2	404	Cibacron Brilliant Yellow 3G-P	–	872.97

λ_{max} = maximum wave length.

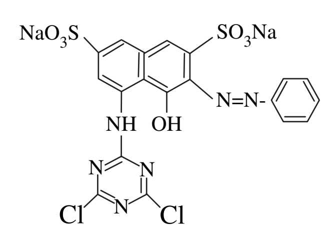
Reactive dyes required alkaline conditions for dyeing. In this condition, hydrolysis reaction competes with dyeing reaction and hydrolyzed non-reactive dyes will be found in the dyebath effluent. Therefore, synthetic reactive dye wastewaters were prepared by mimicking operating conditions of the dyeing processes. Each reactive dye (2 g, 2 N NaCl, 3.2 g of Na_2CO_3 and 3.2 g of NaOH were added into a sample basin and then 20 L of distilled water was added. The dye solution was hydrolyzed by heating at 50 °C for 1 h. The real dyeing wastewater samples were obtained from a local dyeing



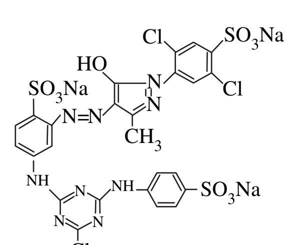
Reactive black 5 (597nm) Remazol Black B, ~55%



Reactive Blue 2 (607nm) Procion Blue HB, C.I. 61211, ~60%



Reactive Red 2 (538nm) Procion Red MX-5B, ~50%



Reactive Yellow 2 (404nm) Cibacron Brilliant Yellow 3G-P

Fig. 1. Chemical formula of reactive dyes.

Table 2
Characteristics of raw wastewater used in this study

Color (C.U.)	Turbidity (NTU)	pH	COD_{cr} (mg/L)	Alkalinity (mg/L as $CaCO_3$)
3586	120	13.56	2968	3110

Temperature = 40 °C.

company near Taegu, Korea. The obtained wastewater characteristics including temperature, pH, color, and turbidity were determined immediately after sampling and are summarized in Table 2.

2.3. 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. For the jar test, the synthetic or real wastewater of 1 L was transferred into the jar. The wastewater pH was adjusted with 2.25 N H_2SO_4 and 1 N NaOH. The sample in the jar was rapidly mixed at a paddle speed of 200 rpm and then inorganic coagulant (alum or ferric salt) and/or polymer were added. The rapid mixing was continued for 1 min followed by slow mixing for 10 min at 50 rpm and settling for 30 min. After settling, 50 mL of the supernatant was taken to measure turbidity (Hach Turbidimeter, Model 9200N) and pH (Orion, Model 900A). In the synthetic dye wastewater treatment, the dye concentrations were determined by measuring the absorbance at the λ_{max} (Table 1) of each reactive dye used. In the real wastewater treatment, color (ADMI color units, C.U.) and COD_{Cr} were determined by the standard methods [14].

3. Results and discussion

3.1. Synthesis of the polymer coagulant

The results of preliminary studies indicate that the degree of polymerization was highly dependent on the molar ratio of reactants (cyanoguanidine (CG) to formaldehyde (FA)), reaction temperature, reaction time, and acid concentration (data not shown). Inappropriate conditions often lead to gelation or solidification that causes poor coagulation. Preliminary results also showed that removal efficiency was improved by increasing polymer viscosity (data not included). After several trial and errors, the best condition was determined: reactant mole ratio (CG:FA:HCl = 1:2:0.8), reaction temperature (80 °C) and reaction time (4 h). Finally, stable polymer with 112.4 cps of viscosity and 1.97 of pH in 5% solution was obtained at the synthetic conditions.

3.2. Treatability test for synthetic wastewater

3.2.1. Effect of pH

In coagulation/flocculation processes using inorganic coagulant and/or polymer flocculant, pH plays an important role in determining coagulation efficiency. In wastewater treatment using inorganic coagulants, an optimum pH range in which metal hydroxide precipitates occur, should be determined, thereby efficient coagulation can be achieved. Previous studies on the removal of color from dye wastewater have reported that color removal was highly dependent on the pH [15–17]. The effect of pH on the reactive dye removal was investigated using fixed amount of inorganic coagulant (1.0 g/L) and synthetic polymer (0.25 g/L) in this study. In the ferric salt/polymer treatment, the removal of RB2 decreased as pH increased, while no considerable difference in the removal of RB5, RY2 and RR2 was observed over the pH range of 4–7 (Fig. 2a). However, RR2 removal was highly pH dependent over the alkaline condition in alum/polymer system (Fig. 2b). The optimum pH was observed near pH 5 and these result agrees with the known optimum coagulation pH of alum. The results indicate that pH should be properly controlled upon the characteristics of inorganic coagulant and the target dyes for efficient treatments.

3.2.2. Effect of polymer dosage

Combination of polymer and inorganic coagulants is applied for the synthetic wastewater. The effect of polymer dosage on the removal of hydrolyzed reactive dye was investigated. Polymer dosage was increased from 0 to 0.25 g/L with a fixed

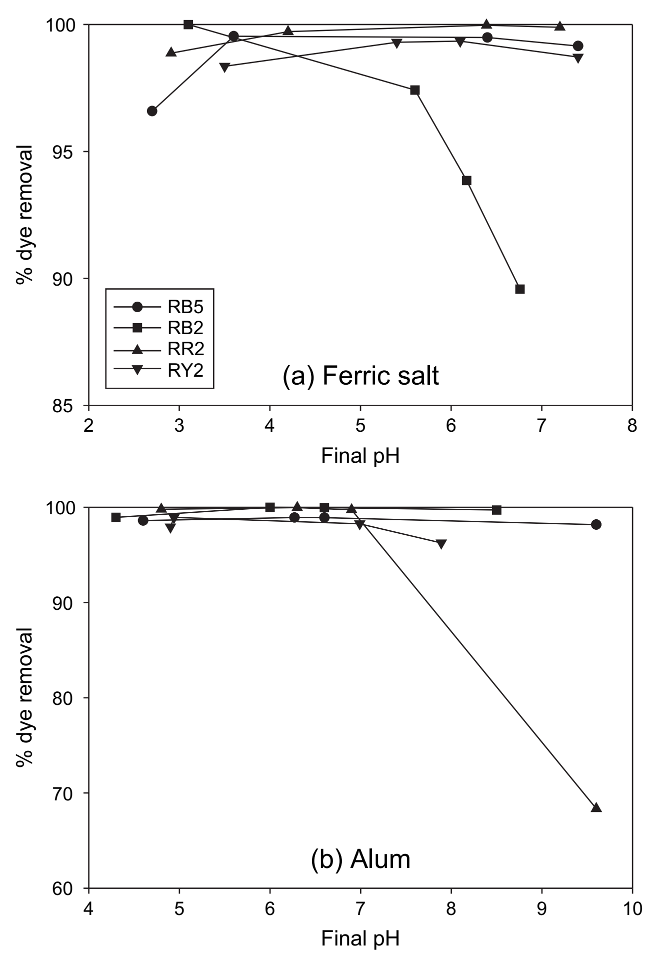


Fig. 2. Effect of pH on reactive dye removal: (a) alum; and (b) ferric salt.

amount of alum (1 g/L) dosage. The initial pH of wastewater was adjusted to pH 5.0. The dye removal efficiency was calculated from the dye concentration in the supernatant. The synthetic wastewater was tested with alum (1 g/L) alone or ferric salt (1 g/L) alone. The removal rates were 20% or less with the inorganic coagulant as shown in Fig. 2. The results showed that dye removal gradually improved with increasing polymer dosage. About 99% of decolorization was observed when polymer dosage was above 0.15 g/L, except RR2 that required additional polymer dosage (~0.25 g/L) (Fig. 3a).

Ferric salt was used instead of alum and polymer dosage was varied from 0 to 0.25 g/L. Similar trend was observed in ferric salt/polymer treatment (at pH 3.5) as shown in Fig. 3b. As polymer dosage increased, the dye removal efficiency increased. Compared to RR2 removal in alum/polymer treatment, higher removal efficiency was observed in ferric salt/polymer treatment.

3.2.3. Effect of inorganic coagulant dosage

Effect of inorganic coagulant dosage on reactive dye removal was examined. In the test with variable amounts of inorganic coagulants (0.4–1.0 g/L), the removal efficiency was not significantly changed (Fig. 4a and b). This indicates

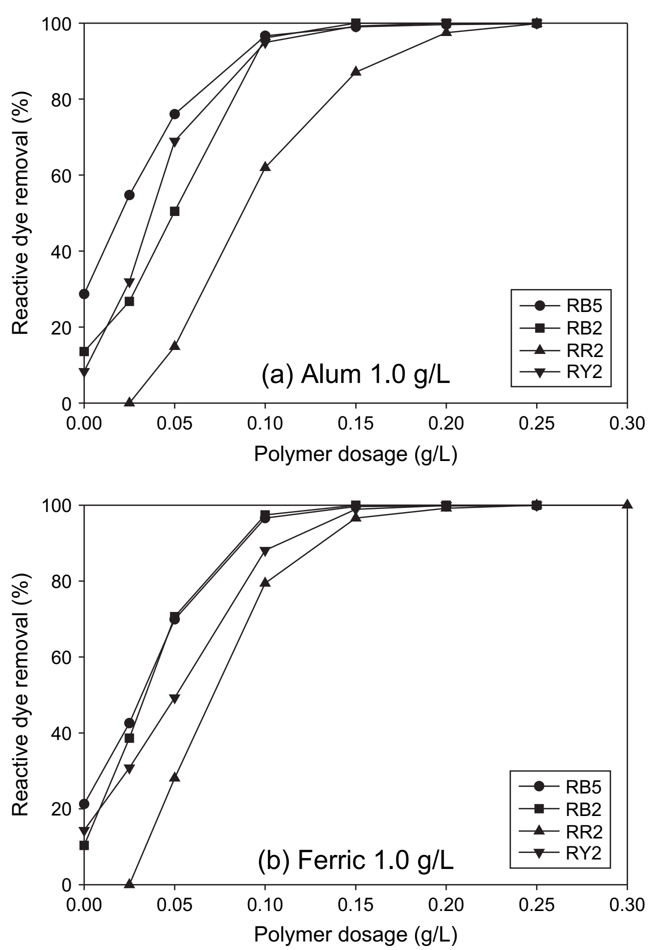


Fig. 3. Effect of polymer dosage on the reactive dye removal in polymer/alum and polymer/ferric salt treatment. Alum and ferric salt concentration = 1.0 g/L.

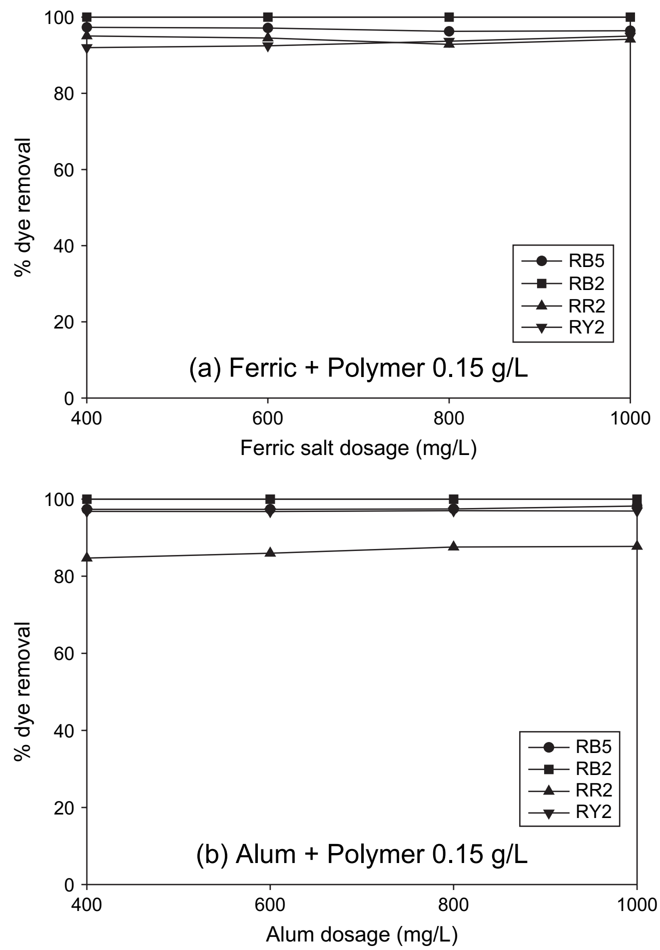


Fig. 4. Effect of inorganic coagulants dosage on dye removal.

that reduced inorganic coagulant dose with small amount of polymer coagulant gives pretty good performance in comparison with the use of inorganic coagulant only. The proper combination of polymer and inorganic coagulant resulted in reduction of sludge production by reducing the dose of inorganic coagulants. Previous studies for drinking water treatment showed similar results [18].

3.3. Treatability test for real dyeing wastewater

3.3.1. Inorganic coagulant alone

The real reactive dye wastewater was obtained from a local dyeing factory located in Taegu, Korea. The raw wastewater contains a high concentration of unknown reactive dyes as well as organic compounds (Table 2). The effect of initial pH on color, turbidity and COD was investigated when inorganic coagulants were used. At a fixed dosage of alum (2.0 g/L), the effect of initial pH on color removal and pH variation of treated water is shown in Fig. 5. However, as pH was decreased, the color removal efficiency increased up to 12%. The removal rates were very low in comparison with the rate for the synthetic dye wastewater. Similar trend was observed when ferric salt was used (Fig. 5). Effect of pH on turbidity and COD removal is depicted in Fig. 6. As pH

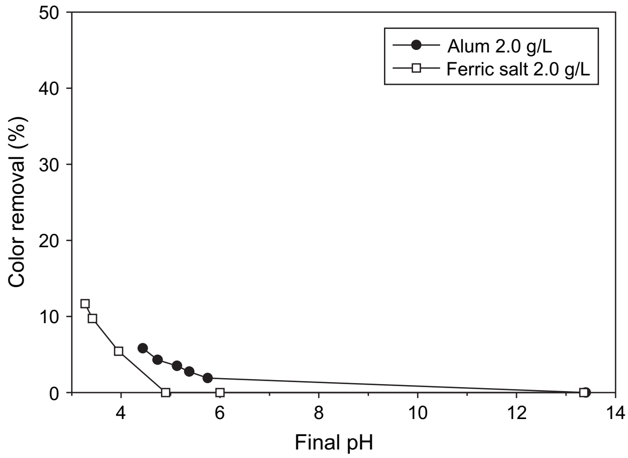


Fig. 5. Effect of pH on the removal of color from local dyeing wastewater.

increased above 10, turbidity rapidly increased due to inappropriate coagulation. Approximately 90% of turbidity and 35% of COD removal were observed at the optimum pH (final pH 5 for alum and 3.5 for ferric).

The synthetic wastewater showed high color removal rate at a wide pH range, but color removal rate of real wastewater was relatively low and affected by the pH using inorganic coagulants alone.

3.3.2. Addition of the polymer coagulant

In inorganic coagulants alone treatment, color removal efficiency was limited to only 5% for alum and 12% for ferric with fixed dosage (2 g/L) at optimum pH (Fig. 5). The effect of inorganic coagulant dosage on color removal was investigated at fixed amount of polymer (0.25 g/L). In alum/polymer treatment, the color removal efficiency gradually increased from 39% to 54% as alum dose increased from 2 to 5 g/L. In ferric salt/polymer treatment, the maximum removal rate (48%) was obtained by adding 3 g/L of ferric salt (Fig. 7). The COD removal rate also increased as inorganic coagulant dosage increased. Approximately 40% and 44% of COD removal was obtained for alum (5 g/L)/polymer and for ferric (4 g/L)/polymer system, respectively. Note that a high dose of inorganic coagulant can produce large amount sludge as secondary pollutant. The results indicate that more efficient reactive dye removal is expected when the polymer/inorganic coagulants are used together.

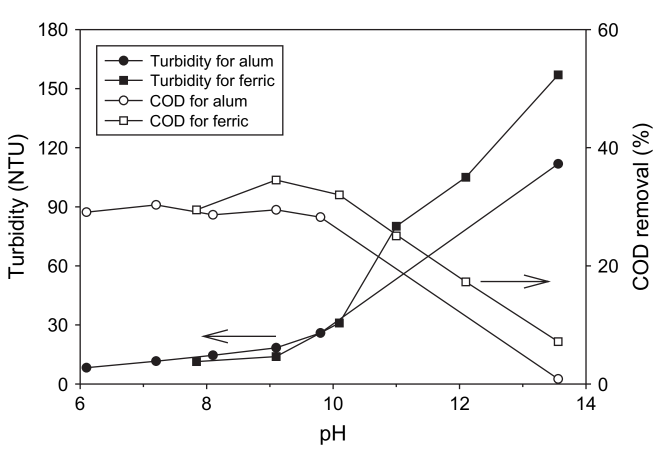


Fig. 6. Effect of pH on the removal of turbidity and COD removal from local dyeing wastewater.

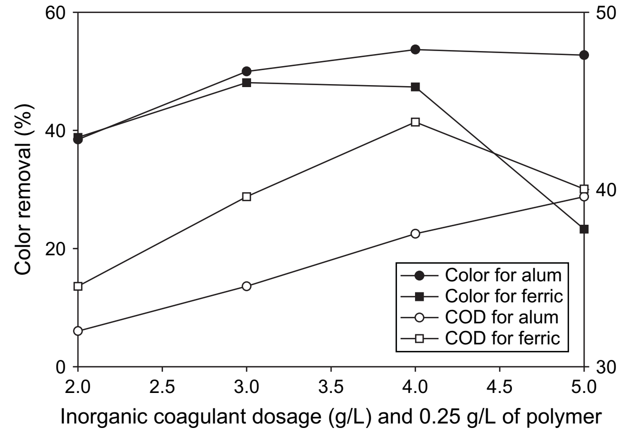


Fig. 7. Effect of inorganic coagulant dosage on color and COD removal.

3.3.3. Effect of polymer dosage

The effects of polymer dosage on color and turbidity removal are presented in Fig. 8. Polymer dosage was varied at the range of 0–0.5 g/L and fixed amounts of inorganic coagulants were

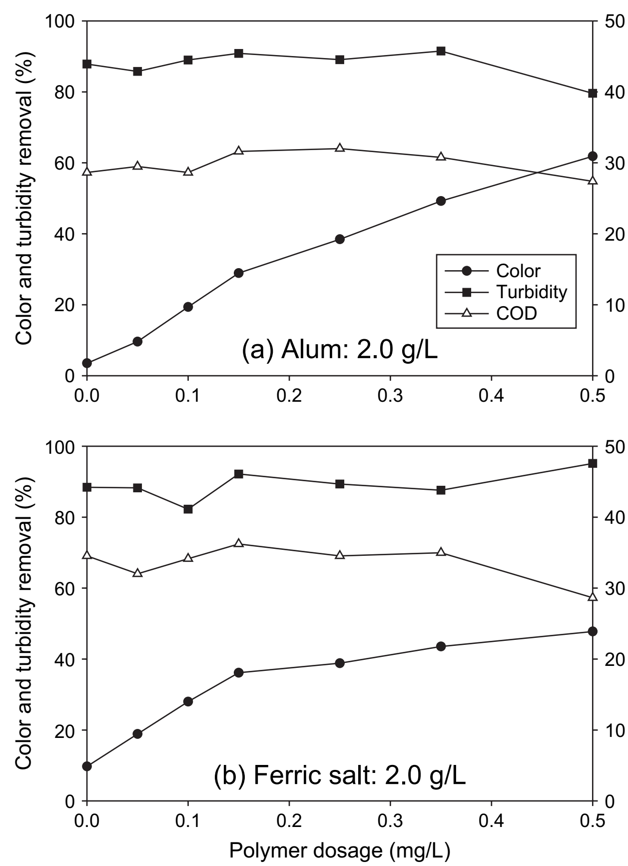


Fig. 8. Effect of polymer dosage on color, turbidity and COD removal: (a) alum; and (b) ferric salt.

used (2.0 g/L). Color removal gradually increased as polymer dosage increased. In alum/polymer treatment, color removal efficiency steadily increased up to 62% as polymer dosage was increased to 0.5 g/L (Fig. 8a). However, in ferric salt/polymer, rapid increase in color removal was observed up to 0.15 g/L of polymer and the increasing rate becomes small above 0.15 g/L of polymer dose (Fig. 8b). Generally alum/polymer was more efficient than ferric salt/polymer in color removal. However, polymer addition had no significant effect on turbidity and COD removal. Turbidity removal was about 90% in both treatments, and COD removal was 30% for alum/polymer and 35% for ferric salt/polymer treatment.

4. Conclusions

A cyanoguanidine–formaldehyde based polymer was synthesized and applied for the treatment of reactive dye wastewater. Synthetic wastewaters containing reactive dyes (RB5, RB2, RR2 and RY2) were nearly completely removed using inorganic and polymer coagulants in combination. Addition of decolorization agent (polymer) as well as inorganic coagulants was needed for the treatment of a high concentration and highly alkaline reactive dye wastewater. pH control in a proper range was required depending on the types of reactive dye and inorganic coagulants used. A combined system of inorganic coagulant and polymer resulted in much better color removal than inorganic coagulant alone system. Among the tested inorganic coagulants, alum was more efficient than ferric salt when used with polymer.

Color removal rate from real dyeing wastewater was not as high as in synthetic wastewater. Inorganic coagulant alone was not effective for the real wastewater. Addition of polymer increased the removal rate up to 62%.

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