Removal of Dyes by Aqueous Mixed Coagulants

Peik Yin Ooi Tjoon Tow Teng A. K. Mohd Omar

Environmental Technology Division School of Industrial Technology University Science of Malaysia 11800 Minden, Penang MALAYSIA Email: ttteng@usm.my

N. A. R. Nik Norulaini

School of Distance Education University Science of Malaysia

> Alum, MgCl,, and mixtures of alum and MgCl, have been used as coagulant to remove coloring matter in the reactive dye Levafix Brill Blue EBRA. The jar test was used to determine the effectiveness and the optimal condition of the coagulation process in terms of pH of the coagulation process, coagulant dosage, percentage color removal, and floc settling time. Coagulant dosages of 1,000-5,000 ppm were studied. The treatment of textile industry wastewater was done in the treatment plant of a printing mill. The results showed that coagulation by MgCl, and alum occurs at the removal pH ranges of 10.5-11.0 for MgCl, and 4.0-6.0 for alum. The mixtures of MgCl, and alum gave two distinct effective color-removal zones at pH 4-5.5 and pH 8-9.5. The addition of alum to MgCl, shifted the optimal pH of MgCl, from 10.5-11.0 to 8.0-9.5. The alum dose of 1,000-3,000 ppm in the coagulant mixture increased by 10-25 % the color removal in the alkaline zone. Floc settling time was found to (a) increase with coagulant dose and (b) take longer in the acidic color-removal zone than in the alkaline zone. The presence of alum increased the floc settling time in the alkaline zone. The study done at the treatment plant of a printing mill showed similar results. A mixture of 60% MgCl, and 40% alum at an average dosage of 2,800 ppm gave a color removal of 97% and reductions of 88% for COD and 69% for suspended solids.

Keywords: Chemical coagulation, color reduction, mixed coagulants, and textile waste.

INTRODUCTION

In Malaysia, textile wastewater remains a problem to be handled and solved carefully. The development of the textile industry, however, continues to generate massive volumes of colored wastewater. Textile wastewater is notorious for containing strong color dyes, large amounts of suspended solids (SS), and high concentrations of chemical oxygen demand (COD). In certain cases, this wastewater may even have fluctuating pH and high temperature (Gurnham 1965).

Dyes and chemical residue in wastewater undergo chemical and biological changes, consume dissolved oxygen from the stream and, as they are toxic in nature, even destroy aquatic life (Ajmal and Khan 1985). Therefore, wastewater that discharges directly into drains and rivers poses serious pollution problems.

Generally, industrial textile wastes that contain different dyes are treated using physicochemical methods. These methods include:

- Adsorption, with maximum adsorption capacities of 41.4–47.7 mg/g for acid dyes and 94.5–160 mg/g for basic dyes (El-Geundi 1991) and 80% removal for cationic dyes (Sun and Xu 1997);
- Oxidation by Fenton reagent with 97% color removal (Kuo 1992, Solozhenko et al. 1995);
- Ozonation with >70% COD reduction (Gould and Groff 1987, Lin and Lin 1993);
- Electrochemical treatment with >20 cm transparency (Lin and Peng 1994); and,
- Combined wet air oxidation and membrane technology with 90% color removal (Lei et al. 1998).

Biological treatment methods, such as aerated lagoons and conventional activated sludge processes, are also used to treat textile effluents (Judkins and Hornsby 1978, Grau 1991).

There are treatments, however, that use a combination of physicochemical methods. These methods include a combination of:

- Ozonation and coagulation with 62% color removal (Lin and Lin 1993, Sarasa et al. 1998);
- Electrochemical, coagulation, and ion exchange methods with 92% color removal (Lin and Chen 1997); and,
- Coagulation, electrochemical oxidation, and activated sludge process with over 20 cm transparency (Lin and Peng 1996).

These methods have significant differences in color removal, volume capability, operating speed, and capital cost (Cooper 1995).

Nevertheless, the coagulation-flocculation process is still more preferred than other novel technologies (Grau 1991). It involves chemical precipitation technique on color removal. The coagulation of dyestuff is achieved by adding coagulant to the dye wastewater to produce settable flocs. Often, a flocculant is added to facilitate the settling process. The flocs are then separated from the aqueous solution by physical sedimentation and filtration. Among the coagulants, alum $Al_2(SO_4)_3.16H_20$ is the most widely used. Its extensive use can be attributed to its (a) performance in treating water and wastewater of different characteristics and (b) low cost.

Recently, the polymerized form of aluminum, particularly polyaluminum chloride (PAC), has been increasingly used (Van Benschoten and Edzwald 1990). Likewise, other salts—such as ferric chloride, ferric sulphate, ferrous chloride, and ferrous sulphate—have also been used to treat textile wastewater. A magnesium salt like magnesium carbonate (Judkins and Hornsby 1978), for instance, has long been used as coagulant.

It was found that the treatment of vat dyes and sulphur dyes by both $MgCO_3$ and $Ca(OH)_2$ could effectively remove color and reduce chemical consumption. The treatment of textile wastewater with magnesium chloride was found more effective than treatment by alum and PAC (Tan et al. 2000). It had been shown that $MgCl_2$ could remove more than 90% of dyestuffs at a pH of 11 and a dose of 4 g of $MgCl_2/L$ aqueous solution. However, the final effluent had a pH value of 11. It had to be adjusted to pH values of 5.5–9.0 prior to discharge. This would increase chemical consumption as well as treatment cost.

An attempt to combine ferric chloride and alum as dual coagulants had been done (Johnson and Amirtharajah 1983). The results showed that by combining alum and ferric chloride as dual coagulants did not give encouraging removal efficiency.

The present work investigated the possibility of treating textile wastewater with a mixture of magnesium salt and alum. It involved the study of the effectiveness of this coagulant mixture on color removal, floc settling time, and coagulation pH of dye wastewater so that the optimal coagulation conditions for the mixtures could be determined.

EXPERIMENTAL

Magnesium chloride $MgCl_2.6H_2O$ (Macalai Tesque, analytical grade) and alum $Al(SO_4)_3.16H_2O$ (Fluka, analytical grade) were used as coagulants. Anionic polyelectrolyte, Koaret PA 3230 (Giulini Chemie, commercial grade) was used as flocculant. NaOH (R& Marketing, reagent grade) was used as pH adjusting agent. The reactive dye Levafix Brill Blue EBRA (Bayer) was used to prepare the aqueous dye solution of 1 g/L.

A six-beaker Jar test apparatus was used in this study. Each beaker contained 150 mL of dye solution. NaOH (1 N) was added to adjust the pH of the solution. The coagulant was then added into each beaker. The samples were mixed at 60–65 rpm for 3 minutes. Polyelectrolyte at a fixed concentration of 0.1 g/L was added and the samples were allowed to mix further at 60– 65 rpm for 1 minute. The solution was then allowed to settle and the time of settling (to reach half of the beaker height) was recorded. The supernatant was taken for analysis. The pH of the solution was measured as final pH by using ORION 410 pH meter.

The dye concentrations of the supernatant were measured at a wavelength corresponding to the maximum absorbance, λ_{max} , by means of a spectrophotometer (Shimadzu UV-160A). Distilled water was served as a reference. The concentration of the supernatant was obtained from the standard absorbance-concentration curve. The percentage of color removal was calculated by subtracting the concentration of the

supernatant from the concentration of the original untreated dye solution.

The treatment of industrial dye wastewater was carried out at the treatment plant of a printing mill at Kulim, Kedah, Malaysia. The dye wastewater was collected from the equalization tank of the plant. The treated effluent was collected from the discharge point for analysis. The color concentrations of both treated and untreated industrial wastewater were measured by spectrophotometer HACH DR 2000 in the unit of the PtCo. Analyses for both COD and SS were performed according to Standard Methods (APHA 1980).

RESULTS AND DISCUSSION

Coagulation with MgCl₂

The removal of EBRA aqueous dye solution of concentration 1.0 g/L by an aqueous MgCl₂ solution in the concentration range of 1,000--5,000 ppm was studied. The results of visible spectrometry showed that the concentration of the EBRA dye solutions was proportional to the absorbance at the wavelength of $\lambda_{max} = 590$ nm.



Figure 1. Treatment of 150 mL of 1.0 g/L Levafix Brill Blue EBRA with MgCl₂ at Concentrations of 1,000, 2,000, 3,000, 3,500, 4,000, and 5,000 ppm.

This suggests that the aqueous solution of dyes obeys Beer's law, which is expressed as:

$$A = abc \tag{1}$$

where, A is the absorbance of the dye solution, a is the absorptivity, b is the cell path length, and c is the concentration of the dye solution. The % color removal versus the final pH of the coagulation process of treatment with different MgCl₂ concentrations on reactive dye EBRA is shown in Figure 1.

It was observed that for each dosage, a curve with a maximum point was obtained. The maximum zone represents the optimal pH for the highest percentage color removal at the relevant $MgCl_2$ concentration. The optimal pH range for the coagulation process occured at 10.5–11.0, which agreed with the results in Tan et al. (2000).

Many researchers have suggested the mechanism of magnesium coagulation as a result of enmeshing particulates into large aggregates of $Mg(OH)_2$ by sweep floc coagulation (Folkman and Wachs 1973, Judkins and Hornsby 1978, Leentvaar and Rebhun 1982, Tan et al. 2000). Black and Christman (1961) found that $Mg(OH)_2$ particles were formed only at pH above 10.2. It is

evident in Figure 1 that before pH 10.2, the color removal of the dye is low because there are not enough Mg(OH)₂ precipitates to destabilize the dye particles. The optimal color removal occured at pH ~10.5. Further increase of pH beyond 11 will lead to a decrease in % color removal. This was probably due to the increase in solubility of the magnesium precipitate and the formation of hydrolysis products such as Mg(OH)⁺, Mg₂(OH)₄⁺, and Mg₄(OH)₄⁴⁺ (Beas and Mesmer 1976).

Figure 1 also shows that a minimum dosage of 3,500 ppm of MgCl₂ is required to achieve more than 95% color removal. This also agreed with the findings of Tan et al. (2000). However, further increase in MgCl₂ dosage could only achieve slight improvement in % color removal since almost all the dyes had been removed at this stage.

Coagulation with alum

Figure 2 shows the plot of % color removal of EBRA versus the final pH for the treatment by alum at various dosages. A plot similar to that in Figure 1, a curve with a maximum, was observed for each dosage of alum. The optimal pH for alum was in the range of 4.0–6.0.



Figure 2. Treatment of 150 mL of 1.0 g/L Levafix Brill Blue EBRA with Alum at Concentrations of 1,000, 2,000, 3,000, 4,000, and 5,000 ppm.

It was shown that a minimal dosage of 3,000 ppm was required to yield more than 92% color removal. The mechanism of color removal by alum is believed to be through adsorption-charge neutralization and/or enmeshment in the Al(OH)₃ precipitate (Edzwald 1986, Hundt and O'Melia 1988).

At low pH value, Al^{3+} ions exist in their simple free aqua-metal $Al(H_2O)_6^{3+}$ form. These ions are not readily adsorbed at colloid interfaces, hence, are not able to remove dye particles from the solution (Matijevic et al. 1961, O'Melia and Stumm 1967, Dentel and Gossett 1988). As the pH is raised, hydrolysis occurs and $Al(OH)_3$ is formed (Stephenson and Duff 1996). The hydrolysis products consist of soluble mononuclear species, polynuclear hydroxometal complexes, and $Al(OH)_3$ precipitates, which cause the % color removal to increase until it reaches its maximum.

The mononuclear species and polynuclear hydroxometal complexes destabilize the dye particles by adsorption and charge neutralization whereas the $Al(OH)_3$ precipitates by sweep coagulation. As the pH is further increased, the OH ions compete with the dye particles for metal adsorption sites (Randtke 1988) on Al hydrolysis

products to form soluble $Al(OH)_4$. Hence, lower % color removal is observed.

Coagulation with mixture of MgCl₂ and alum

The treatment of EBRA with a mixture of MgCl₂ and alum produces two distinct effective color removal zones, at pH 4–5.5 and 8–9.5, which can be shown using figures 3 to 7.

For each mixture of coagulants, a curve of two maximum zones is obtained, with one maximum zone in the acidic pH range and another in the alkaline pH range. The mechanism of color removal in the acidic zone was believed to be through the adsorptioncharge neutralization mechanism and enmeshment in Al(OH)₃ precipitate.

In the alkaline zone, color removal was believed to occur by enmeshment in both $Mg(OH)_2$ and $Al(OH)_3$ precipitates. Figure 3 shows that for 1,000 ppm $MgCl_2$ in the mixture, an average of 55% color removal is achieved at the alkaline zone. An increase in alum dose increases the % color removal in the acidic zone, but does not exert any effect in the alkaline zone. An



Figure 3. Treatment of 150 mL of 1.0 g/L Levafix Brill Blue EBRA with Mixtures of 1,000 ppm MgCl, and Various Concentrations of Alum



Figure 4. Treatment of 150 mL of 1.0 g/L Levafix Brill Blue EBRA with Mixtures of 2,000 ppm MgCl₂ and Various Concentrations of Alum





increase of alum dose from 1,000 to 2,000 ppm boosts the % color removal from 50 to 90 %. Further increase in alum dose leads to a slight improvement in color removal.

In the acidic zone, a similar increment trend in % color removal may be observed in Figures



Figure 5. Treatment of 150 mL of 1.0 g/L Levafix Brill Blue EBRA with Mixtures of 3,000 ppm MgCl₂ and Various Concentrations of Alum



Figure 7. Treatment of 150 mL of 1.0 g/L Levafix Brill Blue EBRA with Mixtures of 5,000 ppm MgCl, and Various Concentrations of Alum

4, 5, 6, and 7. Figure 4 gives an average of 97% color removal in the alkaline zone. Further increase in MgCl₂ dose in the mixture does not produce any significant increase in color removal due to the near completion of color removal achieved and shown in Figures 5 to 7.

In the acidic zone, the presence of MgCl₂ in the mixture does not significantly affect the color removal. Figure 8 shows the % optimal color removal in the acidic zone versus alum concentration at different dosages of MgCl_a. At an alum concentration of 1,000 ppm, the increase of MgCl₂ could only contribute a slight increase in % color removal. The % color removal for each point at 1,000 ppm alum for the different dosages of MgCl, was less than that at their relevant total dosage. At 2,000 ppm, alum with different dosages of MgCl₂ exhibited a similar pattern as that in 1,000 ppm alum for the mixtures observed. For alum concentrations from 3,000 to 5,000 ppm, the presence of MgCl, did not affect the color removal. This could be due to the existence of Mg in its simple ionic form, Mg²⁺, which did not participate in color removal at this acidic zone.

The optimal color removal in the alkaline zone versus concentration of $MgCl_2$ at different dosages of alum is shown in Figure 9. At 1,000 ppm $MgCl_2$, the presence of alum increases the % color removal by an average of 25–55 %.

A concentration of $1,000 \text{ ppm MgCl}_2$ is, thus, insufficient to treat the aqueous dye solution. At

2,000 ppm MgCl₂, however, the presence of alum boosted the % color removal by an average of 97%. The value of 97% color removal is higher than that produced by a total dose of 3,000 ppm of the mixtures (or 3,000 ppm MgCl₂ alone). This value though remains within the range of % color removal contributed by a total dose of either 4,000 ppm or 5,000 ppm. These observations indicate that the presence of Al(OH)₃ precipitates helps to increase the % color removal in the alkaline zone. Therefore, there was a significant increase in the % color removal compared to treatments by MgCl₂ alone.

On the one hand, the alum dose of 1,000-3,000 ppm in the coagulant mixture increased color removal by 10-25 % in the alkaline zone. On the other hand, the presence of alum in the mixture with 4,000 and 5,000 ppm of MgCl₂ did not significantly affect % color removal.

For coagulation with mixtures of $MgCl_2$ and alum, there was a shift in optimal pH at the alkaline zone when compared to treatment by $MgCl_2$ alone; that is, from pH 10.5–11.0 for $MgCl_2$ to pH 8.0–9.5 for the mixture. This shift could be due to the effects of the solubility



Alum Concentration, ppm

Figure 8. Optimal Color Removal Percentage in the Acidic pH Zone vs. Alum Concentration for Treatment of 150 mL of 1.0 g/L Levafix Brill Blue EBRA with Mixtures of MgCl₂ and Alum at Different MgCl₂ Conentrations

products, K_{sp} for Al(OH)₃ and Mg(OH)₂ (Skoog et al. 1994) as well as of the amphoteric behavior of Al(OH)₃ precipitate.

For Al(OH)₃, the solubility equilibrium is:

$$Al^{3+}(aq) + 3OH'(aq) \Leftrightarrow Al(OH)_{3}(s)$$
 (2)

The solubility product:

$$K_{\rm sp} = [\rm{Al}^{3+}] [\rm{OH}^{-}]^3 = 3.0 \times 10^{-34}$$
 (3)

For $Mg(OH)_2$, the solubility equilibrium is:

$$Mg^{2+}(aq) + 2OH(aq) \Leftrightarrow Mg(OH)_{2}(s)$$
 (4)

The solubility product expression:

$$K_{sp} = [Mg^{2+}] [OH^{-}]^2 = 7.1 \times 10^{-12}$$
 (5)

The solubility product is equal to the product of the concentrations of the ions involved in the equilibrium, each raised to the power of its coefficient in the equilibrium equation. As a general rule, if the product of the ion concentrations is greater than its K_{sp} , then precipitation occurs until the ion product and K_{sp} are in equilibrium. During the coagulation process, pH has to be maintained to ensure precipitation.

When the OH ions are in excess, the products of $[Al^{3+}]$ $[OH^{-}]^3$ and $[Mg^{2+}]$ $[OH^{-}]^2$ also exceed their respective K_{sp} values, and Al(OH)₃ and Mg(OH)₂ will precipitate. The formation of Mg(OH)₂ precipitates is more favored than that of Al(OH)₃. This can be attributed to the amphoterism of Al(OH)₃ (Skoog et al. 1994).

Amphoterism is often interpreted in terms of the behavior of the water molecules that surround the metal ion and are bounded to it by Lewis acid-base interactions. The $Al(H_2O)_3(OH)_3$ will dissolve in strongly basic solutions as a result of the formation of the complex anion $Al(H_2O)_2(OH)_4$. The reaction occurs as follows:

 $AI(H_2O)_3(OH)_3 (s) + OH (aq) \Leftrightarrow AI(H_2O)_2(OH)_4 (aq) + H_2O(l) (6)$

The OH⁻ ions have been used for the formation of $Al(OH)_3$ and $Mg(OH)_2$ precipitates as well as $Al(OH)_4^-$; hence, the optimal coagulation pH is lower than that for treatment with MgCl₂ alone.



MgCl, Concentration, ppm

Figure 9. Optimal Color Removal Percentage in the Alkaline pH Zone vs. MgCl₂ Concentration for Treatment of 150 mL of 1.0 g/L Levafix Brill Blue EBRA with Mixtures of MgCl₂ and Alum at Different Alum Dosages

The floc settling time

A comparison of the floc settling times by $MgCl_2$ and alum at their respective optimal color removal zones is shown in Figure 10. The floc settling time by $MgCl_2$ was shorter than that by alum for dosages between 1,000 and 5,000 ppm, with an average of 30% time reduction. A shorter settling time is preferred because this will help in handling a larger waste capacity. The floc settling time for treatment with $MgCl_2$ increased with

dosage. Treatment with 1,000 ppm alum gave an average of 40 seconds with 36% color removal. For concentrations of 2,000–5,000 ppm, however, floc settling time increased to an average of 22 minutes and 25 seconds with 95% color removal.

The floc settling time by mixtures of MgCl₂ and alum in the acidic optimal color removal zone is shown in Figure 11. For an alum dose of 1,000 ppm in the mixtures, a short settling time with an average of 4 minutes and 18 seconds was achieved. The corresponding color removal was



Figure 10. The Floc Settling Time for Treatment of MgCl₂ and Alum at 1,000–5,000 ppm Dosages



Figure 11. The Floc Settling Time of Treatment with Mixtures of MgCl₂ and Alum in the Acidic Optimal Color Removal Zone



Figure 12. The Floc Settling Time of Treatment with Mixtures of MgCl,

~53%, indicating that the dosage of the coagulant was insufficient to treat the dye; hence, little precipitate was produced. For treatment with concentrations of alum between 2,000 and 5,000 ppm in the mixtures, the floc settling time increased dramatically to an average of 22 minutes with a corresponding 94% color removal. This phenomenon was similar to that exhibited by alum alone. The long settling time was mainly due to the effect of alum.

Based on the empirical observation, the flocs formed by mixtures of coagulants in the acidic zone were similar to those formed by alum alone. They were relatively small and difficult to settle. The presence of $MgCl_2$ in the mixtures did not have any significant effect in floc settling time. This could be due to the existence of magnesium in its free ion form, Mg^{2+} , which did not participate in color removal.

The floc settling time by mixtures of $MgCl_2$ and alum in the alkaline optimal color removal zone is shown in Figure 12. Short settling time was obtained for the combination of 1,000–2,000 ppm $MgCl_2$ and 1,000–2,000 ppm alum. Increase in both $MgCl_2$ and alum doses would lead to an increase in floc settling time.

When compared to treatment by $MgCl_2$ in Figure 10, it can be observed that in the alkaline zone, the floc settling time for mixtures took longer than that by $MgCl_2$ alone. This was clearly seen for mixtures with $MgCl_2$ concentrations of 4,000 and 5,000 ppm. This observation indicated that the presence of alum in the mixtures affected the floc settling time in the alkaline zone.

THE TREATMENT OF INDUSTRIAL TEXTILE WASTEWATER

The samples of textile wastewater were treated in the treatment plant of a printing mill in Kulim, Kedah, Malaysia. Due to the mill's diverse daily operation, there was high variation in wastewater characteristics.

Treatment of wastewater was controlled so as to achieve optimal coagulation condition. Satisfactory flocs were formed in the coagulation-flocculation tank at their optimal pH ranges. The treated effluent was found to be clear and color-removed. Wastewater samples were taken from the equalization tank whereas the treated effluent was taken from the effluent discharge point. The dosage of the coagulant used was calculated from the flow rate of the wastewater and the dosing rate of coagulant. The results are summarized in Table 1.

Wastewater treated with an average dose of 850 ppm alum at a pH of 5.29 produced 89% in COD reduction, 68% in SS reduction, and 99% in color removal. Their initial values were 2,189 ppm for COD, 112 ppm for SS, and 11,833 PtCo unit for color.

With $MgCl_2$, an average dose of 1,200 ppm at pH 10.80 gave 81% COD reduction, 65% SS reduction, and 99% color removal. The treatment was done on wastewater with the following average initial characteristics: COD, 2,000 ppm; SS, 110 ppm; and, color, 12,300 PtCo unit.

Coagulant	Dosage ppm	COD, ppm			SS, ppm			Colour, PtCo Unit		
		Before	After	% Reduction	Before	After	% Reduction	Before	After	% Reduction
Alum	1333	2189	174	92.05	112	36	67.86	11833	40	99.66
Alum	1333	2189	214	90.31	112	29	74.11	11833	34	99.71
Alum*	667	2189	232	89.36	112	27	75.89	11833	44	99.63
Alum*	533	2189	207	90.54	112	39	65.18	11833	29	99.75
Alum*	400	2189	337	84.60	112	48	57.14	11833	27	99.77
MgCl ₂ *	1333	2189	390	82.18	112	35	68.75	11833	42	99.64
MgCl ₂ *	1066	1863	366	80.35	109	42	61.47	12750	88	99.31
M + A**	5054	6616	573	91.34	182	42	76.92	28000	360	98.71
M + A**	3580	5435	441	91.88	155	47	69.68	22800	431	98.11
M + A**	2889	3074	307	90.01	102	51	50.00	12400	174	98.60
M + A**	2278	3159	449	85.78	153	34	77.78	12400	479	96.14
M + A**	1492	3074	457	85.13	102	30	70.59	12400	800	93.55
M + A**	1333	3106	394	87.31	167	48	71.26	12250	132	98.92
Exporip	nent done	in labor	atoru	** $(6:4) = Proportion of 60-40\%$				$M = M \alpha C$	1	$\mathbf{A} = Alun$

 Table 1. Treatment of Industrial Textile Wastewater with MgCl₂, Alum, and Mixtures of MgCl₂ and Alum at Their Optimal Coagulation Conditions.

* Experiment done in laboratory ** (6:4) = Proportion of 60–40 % M = MgCl, A = Alum

The treatment with mixtures of 60% MgCl₂ and 40% alum at an average total dose of 2,800 ppm gave an average of 88% COD reduction, 69% SS reduction, and 97% color removal at an average pH of 7.21. This time, the wastewater had the following average initial characteristics: COD, 4,000 ppm; SS, 144 ppm; and, color, 16,700 PtCo unit. The final COD after treatment, however, was still higher than the regulatory limit; hence, further physical treatment by adsorption could be done to further reduce the COD.

CONCLUSIONS

The coagulation of 1 g/L of Levafix Brill Blue EBRA with $MgCl_2$ alone and alum alone both gave a one-color removal zone in their respective optimal pH ranges, namely at pH 10.5–11.0 for MgCl₂ and at pH 4.0–6.0 for alum.

A color removal of more than 96% was achieved for both coagulants with a concentration of 4,000 ppm. The floc settling time for treatment with MgCl₂ was shorter than that with alum.

The treatment of 1 g/L Levafix Brill Blue EBRA with mixtures of MgCl₂ and alum at dosages from 1,000 to 5, 000 ppm gave two distinct effective

color removal zones, namely: at pH 4.0–5.5 and 8.0–9.5. The addition of alum to MgCl₂ shifted the optimal coagulation pH range of MgCl₂ from 10.5–11.0 to 8.0–9.5. The floc settling time increased with the coagulant dosage in the mixtures. The floc settling time in the acidic color removal zone was longer than that in the alkaline zone. The presence of alum increased the floc settling time in the alkaline color removal zone.

The study on wastewater from the textile industry at the treatment plant of a printing mill showed similar results to those of the Jar test. The treatment of textile industrial wastewater with a mixture of 60% $MgCl_2$ and 40% alum at an average dosage of 2,800 ppm gave a color removal of 97% and reductions of 88% in COD and 69% in SS.

ACKNOWLEDGMENT

The authors express their gratitude to the University Science of Malaysia for providing a postgraduate fellowship.

REFERENCES

American Public Health Association. (1980). Standard methods for the examination of water and wastewater, 16th ed., APHA, Washington, D.C.

- Ajmal, M., and Khan, A. U. (1985). "Effect of factory effluent on soil and crop plant," J. Envir. Pollut. Ser. A., 37, 131–148.
- Beas, C. F., and Mesmer, R. E. (1976). *The hydrolisis of cations*, John Wiley & Sons, Inc., New York, 95.
- Black, A. P., and Christman, R. F. (1961). "Electrophoretic studies of sludge particles produced in lime-soda softening," J. Am. Wat. Wks. Assoc., 53, 737–747.
- Cooper, P. (1995). "Removing color from dyehouse waste waters," Asian Textile J., 3, 49–58.
- Dentel, S. K., and Gossett, J. M. (1988). "Mechanisms of coagulation with aluminum salts," *J. Am. Wat. Wks. Assoc.*, 80, 187–198.
- Dziubek, A. M., and Kowal, A. L. (1983). "Water treatment by coagulation-adsorption with dolomite," *Chemistry for protection of environment*. In: Proceedings of an International Conference, Toulouse, France, 205.
- Edzwald, J. K. (1986). "Conventional treatment and direct filtration, treatment and removal of total organic carbon and trihalomethane precursors." In N. M. Ram, E. J. Calabrese, and R. F. Christman, eds. *Carcinogens in drinking water*, John Wiley & Sons, New York.
- El-Geundi, M. S. (1991). "Color removal from textile effluents by adsorption techniques," *Wat. Res., 25,* 271–273.
- Folkman, Y., and Wachs, A. M. (1973). "Removal of algae from stabilization pond effluents by lime treatment," *Wat. Res.*, 7, 419–435.
- Gould, J. P., and Groff, K. A. (1987). "Kinetics of ozonolysis of synthetic dyes," *Ozone Sci. Eng.*, *9*, 153–167.
- Grau, P. (1991). "Textile industry wastewaters treatment," *Wat. Sci. Technol., 24,* 97–103.
- Gurnham, C. F. (1965). Industrial waste control, Academic Press, New York.
- Hundt, T. R., and O'Melia, C. R. (1988). "Aluminium fulvic acid interactions: Mechanisms and applications," J. Am. Wat. Wks. Assoc., 80, 176–186.
- Johnson, P. N., and Amirtharajah, A. (1983). "Ferric chloride and alum as single and

dual coagulants," J. Am. Wat. Wks. Assoc., 75, 232–239.

- Judkins, J. F., and Hornsby, J. J. S. (1978). "Color removal from textile dye waste using magnesium carbonate [J]," J. Water Pollution Control Federation, 50, 12, 2 446-456.
- Kuo, W. G. (1992). "Decolorizing dye wastewater with Fenton's reagent," *Wat. Res., 26,* 881–886.
- Leentvaar, J., and Rebhun, M. (1982). "Effect of magnesium and calcium precipitation on coagulation–flocculation with lime," *Wat. Res.*, *16*, 655–662.
- Lei, L., Hu, X., Chu, H. P., and Yue, P. L. (1998). "Improved wet oxidation for the treatment of dyeing wastewater concentrate from membrane separation process," *Wat. Res.*, *32*, 2753–2759.
- Liao, M. Y., and Randtke, S. J. (1986). "Predicting the removal of soluble organic contaminants by lime softening," *Wat. Res.*, 20, 27–35.
- Lin, S. H., and Chen, M. L. (1997). "Treatment of textile wastewater by chemical methods for reuse," *Wat. Res.*, *31*, 868–876.
- Lin, S. H., and Lin, C. M. (1993). "Treatment of textile waste effluents by ozonation and chemical coagulation," *Wat. Res.*, *27*, 1743–1748.
- Lin, S. H., and Peng, C. F. (1996). "Continuous treatment of textile wastewater by combined coagulation, electrochemical oxidation and activated sludge," *Wat. Res.*, 30, 587–592.
- Lin, S. H., and Peng, C. F. (1994). "Treatment of textile wastewater by electrochemical method," *Wat. Res.*, *28*, 277–282.
- Matijevic, E., Abramson, M. B., Ottewill, R. H., Schulz, K. F., and Kerker, M. (1961).
 "Adsorption of thorium ions on silver iodide sols," *J. Phys. Chem.*, 65, 1724–1729.
- O'Melia, C. R., and Stumm, W. (1967). "Aggregation of silica dispersions by iron (III)," J. Coll. Interface Sci., 23, 437–447.
- Randtke, S. J. (1988). "Organic contaminant removal by coagulation and related process combinations," J. Am. Wat. Wks. Assoc., 80, 40–56.
- Sarasa, J., Roche, M. P., Ormad, M. P., Gimeno, E., Puig, A., and Ovelleiro, J. L. (1998). "Treatment of a wastewater resulting from dyes manufacturing with ozone

and chemical coagulation," Wat. Res., 32, 2721–2727.

- Skoog, D. A., West, D. M., and Holler, F. J. (1994). Analytical chemistry: An introduction, 6th ed., Saunders College Publishing/ Publication, Philadelphia, USA.
- Solozhenko, E. G., Soboleva, N. M., and Goncharuk, V. V. (1995). "Decolorization of azodye solutions by Fenton's oxidation," *Wat. Res., 29*, 2206–2210.
- Stephenson, R. J., and Duff, S. J. B. (1996). "Coagulation and precipitation of a mechanical pulping effluent—I. Removal of carbon, color and turbidity," *Wat. Res.*, 30, 781–792.
- Sun, G., and Xu, X. (1997). "Sunflower stalks as adsorbents for color removal from textile wastewater," *Ind. Eng. Chem. Res.*, *36*, 808–812.
- Tan, B. H., Teng, T. T., and Mohd Omar, A. K. (2000). "Removal of dyes and industrial dye wastes by magnesium chloride," *Wat. Res.*, 34, 597–601.
- Van Benschoten, J. E., and Edzwald, J. K. (1990). "Chemical aspects of coagulation using aluminum salts: II. Coagulation of fulvic acid using alum and polyaluminum chloride," Wat. Res., 24, 1527–1535.
- Wang, S., and Chen, K. Y. (1983). "Bitterns as coagulants for treatment of color effluents," *Chemistry for protection of environment*. In: Proceedings of an International Conference, Toulouse, France, 193.