Comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation

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Abstract

The composition of wastewater from the dyeing and textile processes is highly variable depending on the dyestuff type and typically has high COD and color. This study examined the decolorization of some of the most commonly used disperse and reactive dyestuffs by combination of chemical coagulation and Fenton oxidation. In addition, performances between Fe^{3+} coagulation and Fenton oxidation of dye solutions were compared by measuring COD and dye removals, distributions of zeta potential, concentration of suspended solid were investigated. Fenton oxidation in combination with Fe^{3+} coagulation has shown to effectively remove COD and dye. About 90% of COD and 99% of dye removals were obtained at the optimum conditions. Compared to reactive dyes, disperse dyes have lower solubility, higher suspended solids concentrations and lower SCOD/TCOD ratios. The COD and dye removed per unit Fe^{3+} coagulant added for disperse dye solutions were higher than those for reactive dye solutions. Therefore, the disperse dye solutions are more easily decolorized by chemical coagulation than reactive dye solutions. Conversely, reactive dye solutions have higher applicability of Fenton oxidation than disperse dye solutions due to their higher solubility, lower suspended solids concentrations and higher SCOD/TCOD ratios. The COD and dye removed per Fe^{2+} Fenton reagent added for reactive dye solutions are respectively higher than those for disperse dye solutions.
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1. Introduction

Dyeing wastewater contains large amounts of dyestuff together with significant amounts of suspended solids, dispersing agents, salts and trace metals. This dyeing wastewater can cause serious environmental problems due to their high color, large amount of suspended solids (SS) and high chemical oxygen demand (COD). Furthermore, the composition of wastewater from the dyeing and textile processes varies greatly from day to day and hour to hour, depending on the dyestuff type, the fabric type and the concentration of fixing compounds which are added [1]. Unfixed dye releases high doses of color to effluent. The dye is visible even at low concentrations and causes an aesthetic problem in the receiving waters [2].

The conventional treatments of wastewater containing dyestuff include biological oxidation, chemical coagulation and adsorption. Biological methods are generally cheap and simple to apply and are currently used to remove organics and color from dyeing and textile wastewater. However, this dyeing wastewater cannot be readily degraded by the conventional biological processes, e.g., activated sludge process, because the structures of most commercial dye compounds are generally very complex and many dyes are non-biodegradable due to their chemical nature, molecular size and result in sludge bulking [3–5]. Although dyestuffs and color materials in wastewater can be effectively destroyed by wet oxidation [6], advanced chemical oxidation such as H_2O_2/UV, O_3 [7–9], adsorption using activated carbon [10,11] and electrocoagulation using Al or Fe soluble electrodes [12], the costs of these methods are relatively high.

Destabilization of colloidal or suspended particles is usually brought about by changing the solutions pH value or by adding chemicals high molecular weight polymers of cationic, anionic or non-ionic character. Two principal in-

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organic coagulants used in water treatment are salts of aluminum and ferric ions. These hydrolysable cations are readily available as sulfate or chloride salts in both liquid and solid form. However, ferric species are more insoluble than aluminum species and are also insoluble over a wider pH range. Thus, ferric ions are often the coagulant of choice to destabilize the colloidal and suspended solids.

Recently, advanced oxidation process (AOP) has been successfully used to treat industrial wastewaters that are non-biodegradable and toxic to microorganisms. Especially, Fenton oxidation has been applied for the decolorization of effluents from textile dyeing process and dye manufacturing process. Compared to other oxidation processes, such as UV/H_2O_2 process, costs of Fenton oxidation are quite low [13]. Fenton oxidation has been lately used for different treatment processes because of its ease of operation, the simple system and the possibility to work in a wide range of temperatures [14]. Fenton oxidation can be carried at normal temperature and at atmospheric pressure. Fenton reactions exploit the reactivity of the hydroxyl radical ($OH^\bullet$), which has a very high oxidation potential and is able to oxidize almost all organic pollutants quickly and non-selectively, produced in acidic solution by the catalytic decomposition of H_2O_2. Its position is second in the oxidation potential series next to fluorine and it is twice as reactive as chlorine [15].

A few studies for pretreatment of organic compounds using Fenton oxidation to reduce the toxicity and to improve the biodegradability prior to biological treatment have also been reported [16,17]. Recently, a large number of studies have shown that textile and dyeing wastewater, commercial dye solutions [13–15,18,19], 1-amino-8-naphthol-3,6-disulfonic acid (H-acid) [20,21], desizing wastewater [22] and ethylene glycol [23] can be successfully treated by Fenton oxidation process. The oxidation efficiencies of disperse dyes by electrochemical process, ozone, hypochlorite and Fenton reagent were compared [18] and the heterogeneous and homogeneous advanced oxidation processes were investigated [15,19]. An extensively review of Fenton oxidation process has been presented elsewhere.

However, all the oxidation processes, especially Fenton oxidation, have their limitations when wastewater contains high concentration of suspended solids. To solve this problem, the combination of chemical coagulation and Fenton oxidation can be effective methods to treat dyeing wastewater. Among the commercial textile dyes, disperse and reactive dyestuffs are of great environmental concern because of their widespread use. In this study, chemical coagulation and Fenton oxidation were used to remove disperse dyes and reactive dyes. The optimal coagulation conditions (pH and coagulant dose) and Fenton oxidation conditions (Fe^{2+}:H_2O_2 ratio and dose) were determined. The characteristics of dye removal of disperse dye and reactive dye solutions by chemical coagulation and Fenton oxidation were also investigated. Finally, the effectiveness of the combination of chemical coagulation with Fenton oxidation for treatment of dye solutions was studied.

2. Materials and methods

The commercially available disperse and reactive dyes, Suncron Blue RD-400, Suncron Yellow 3GE-200, Suncion Blue P-3R, Suncion Yellow H-E4R, were obtained from Oh-Young Ind. Ltd., Korea. Their color index (CI) numbers are disperse blue 106, disperse yellow 54, reactive blue 49 and reactive yellow 84, respectively. The CI number, commercial name and chemical structure of the dyestuffs are shown in Fig. 1. Distilled water was used to prepare the desired concentration of dyestuff solutions.

The optimal pH and the amount of $FeCl_3 \cdot 6H_2O$ to be used as chemical coagulant were determined by jar-tester. Diluted solutions of H_2SO_4 and NaOH were added to adjust the pH of the solution to the desired value. Chemical coagulant was added and mixed for 2 min under rapid mixing condition (250 rpm). The solution was mixed at slow flocculation (40 rpm) for 15 min after rapid mixing. Residual dye concentration, COD, SS and pH of supernatant were measured after settling for 30 min. The coagulations were conducted by varying the initial pH (4–9) and the coagulant concentration (0.09–7.40 mM). After treatment, the optimum pH and coagulant concentration were determined on the basis of dye removal efficiency.
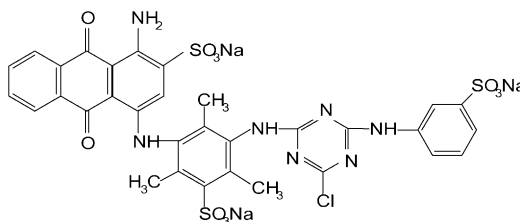
Disperse Blue 106 (Suncron Blue RD-400)
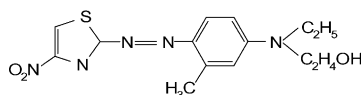
Disperse Yellow 54 (Suncron Yellow 3GE-200)
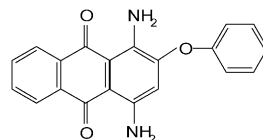
Reactive Blue 49 (Suncion Blue P-3R)
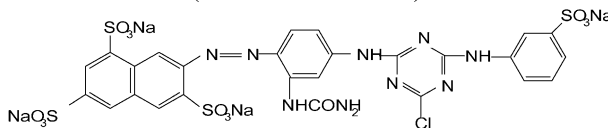

Reactive Yellow 84 (Suncion Yellow H-E4R)

Fig. 1. CI number, commercial name and chemical structure of disperse dyes and reactive dyes.

$FeCl_2 \cdot 4H_2O$ (MERCK, purity 98%) was prepared at a predetermined concentration of 200 g/l for Fenton oxidation. H_2O_2 (MERCK, purity 30%) and other chemicals used in the experiment were of analytical grade. The optimal amounts of $FeCl_2 \cdot 4H_2O$ and H_2O_2 for Fenton oxidation were determined by jar-tester. A digital pH-meter (model 420A, Orion Co., USA), thermometer were used for pH and temperature measurements. All experiments were carried out at 293 K and samples were taken at 30 min to determine the residual concentrations of COD and dye. The required amount of Fe^{2+} and H_2O_2 were added simultaneously into the solution.

A UV-Vis spectrophotometer (UNVIKON XS, BIO-TEK Instruments, Italy) was employed to measure the maximum wavelength, and the concentration of the dyestuff was also measured at this maximum wavelength. The decrease of the absorbance peaks was directly proportional to the reduction of the dye concentration. The COD was analyzed using a colorimetric method after digestion of the samples in a COD reactor (model 45600, HACH Co., USA), according to Standard Method [24]. In order to elucidate the effects of SS on chemical coagulation, TCOD (total COD) and SCOD (soluble COD) were determined. TCOD was measured without any pretreatment, and SCOD was measured after centrifuging the supernatant at 10,000 rpm for 10 min. Zeta potential measurements were also performed in order to interpret the obtained results. The determinations of zeta potential and conductivity were carried out using zeta potential meter (Zeta-meter 3+, AST Co., USA).

3. Results and discussion

3.1. Characterizations of disperse and reactive dye

Four kinds of reactive and disperse dyes (Fig. 1) were selected and the CI number, λ_{max} and SS of selected dye solutions are shown in Table 1. The COD loadings according to the dyestuff types are shown in Fig. 2. The SS of disperse dyes were much higher than those of reactive dyes. The COD loading results were similar. The TCOD loadings of disperse dyes were 1.54, 1.40 g TCOD/g dye, those of reactive dyes were 0.68, 0.49 g TCOD/g dye. However, the SCOD loadings of disperse dyes were significantly lower at 1.07, 0.88 g SCOD/g dye, whereas those of reactive dyes were still 0.66, 0.46 g SCOD/g dye, as shown in Fig. 2(b).

The distributions of zeta potential and conductivity values of different dyestuff type, i.e., disperse dye and reactive dye, as a function of concentrations are shown in Fig. 3. In all the cases, the zeta potentials were negative. The dyestuff solutions in water have a negative charge on their surfaces. In general, most particles in natural waters are also negatively charged (clays, humic acids, bacteria and dyes) in the neutral pH range (pH 6–8) [25]. The reactive dyes are more strongly charged than disperse dyes and the conductivities of reactive dyes are much higher than those of disperse dyes. Zeta potential is a controlling parameter of double layer repulsion for individual particles and can usually be used to interpret the trend of coagulation efficiency. Ideally, colloidal

Table 1
λ_{max}, COD loading and SS of disperse dyes and reactive dyes solutions

	Commercial name	CI number[a]	λ_{max} (nm)	SS (mg/L)[b]
Disperse dye	Suncron Blue RD-400	DB 106	625	23
	Suncron Yellow 3GE-200	DY 54	420	42
Reactive dye	Suncion Blue P-3R	RB 49	586	6
	Suncion Yellow H-E4R	RY 84	226	3

[a] DB: disperse blue; DY: disperse yellow; RB: reactive blue; RY: reactive yellow.
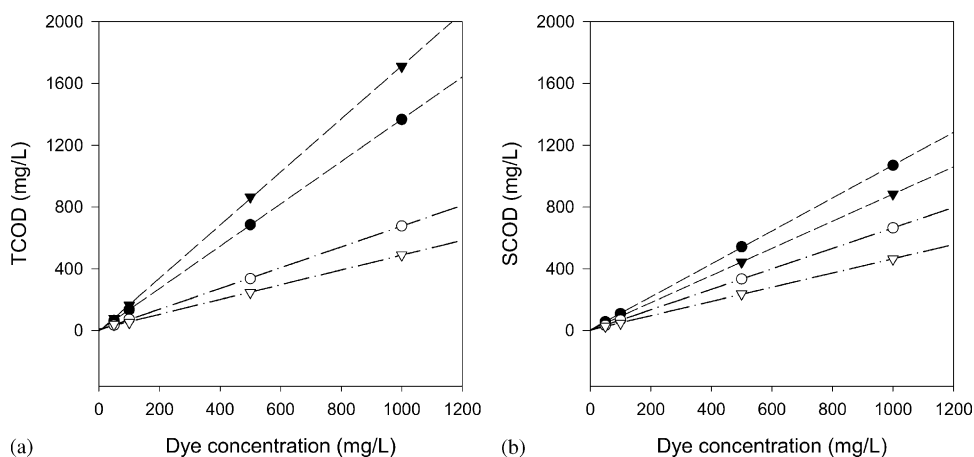[b] SS data at 500 mg/L dye solutions.

Fig. 2. Distributions of COD loadings according to dyestuff types and concentrations: (a) TCOD; (b) SCOD.
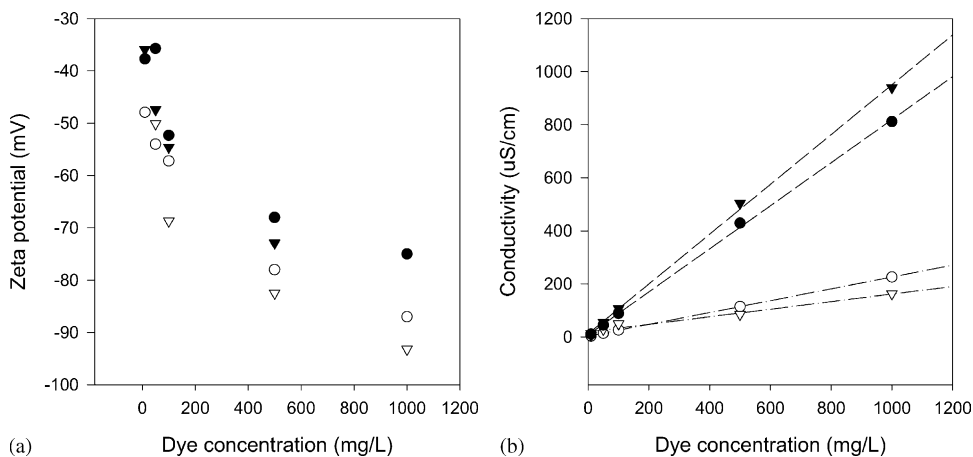
Fig. 3. Distributions of zeta potential (a) and conductivity (b) according to dyestuff type: disperse blue 106 (●); disperse yellow 54 (▼); reactive blue 49 (○); reactive yellow 84 (▽).

particles should have zero net surface charge (iso-electric point; IEP) for agglomeration. This can be achieved by the adsorption of H^+ ions or positively charged ions, such as ferric ions, on negatively charged surfaces. When the zeta potential of particles is reduced towards zero, coagulation efficiency is improved. The data in Fig. 3 also shows that reactive dyes are soluble in solution, whereas disperse dyes are not. Most of disperse dye are suspended or colloidal solids in solutions.

3.2. Chemical coagulation of dye solutions

The subsequent experiments were designed to find the optimal conditions of pH and concentration of coagulant that allows for maximum dye removal. Destabilization of the disperse and reactive dye solutions were examined at pH 4–9 at ferric chloride doses of 0.15 mM for disperse dyes, 0.50 mM for reactive dyes, respectively. The influence of pH was subsequently investigated by simultaneously adding H_2SO_4 and NaOH to achieve desired initial pH values. The

results are shown in Fig. 4. The maximum COD and dye removals of disperse dyes were 59.1% of COD, 71.7% of dye at pH 6 for disperse blue 106, 77.8% of COD, 93.9% of dye at pH 5 for disperse yellow 54, respectively. Small changes in the removal efficiencies were observed in the pH range 5–8. Between pH 4 and 5, pH 8 and 9, the differences of COD and dye removal efficiencies were relatively significant. However, for reactive dyes, the maximum removals were 22.9% of COD, 40.6% of dye at pH 7 for reactive blue 49, 63.3% of COD, 43.9% of dye at pH 6 for reactive yellow 84, respectively. In all pH ranges, small changes in the removal efficiencies were observed. As shown in Fig. 4, the removal of disperse dyes were higher than those of reactive dyes. Ferric species in the pH range between 4 and 8 are almost completely insoluble. The hydrolysis of ferric chloride generates ferric hydroxide particles. These particles agglomerate forming macroscopic flocs and are apparently readily adsorbed onto colloids [26].

For all dyestuff types, dye solutions retained a net negative charge (Fig. 5). For disperse blue 106, the zeta potential of
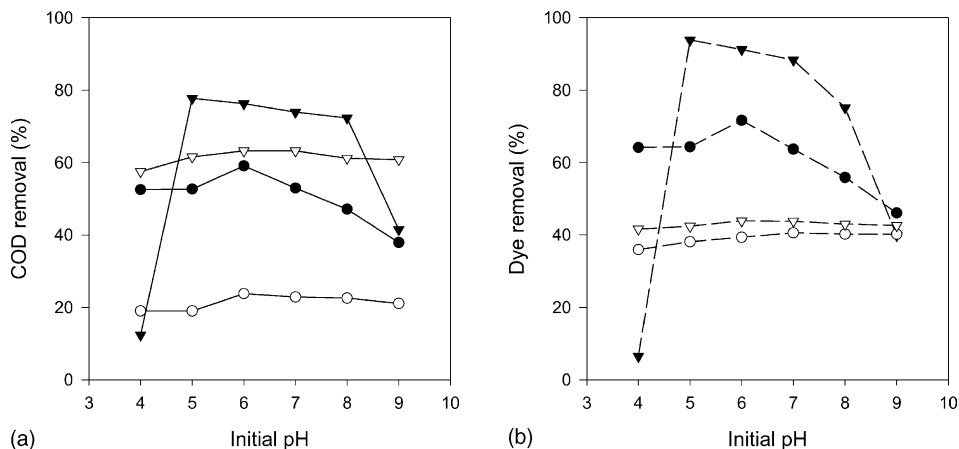

Fig. 4. COD (a) and dye (b) removals by ferric chloride coagulation according to initial pH: disperse blue 106 (●); disperse yellow 54 (▼); reactive blue 49 (○); reactive yellow 84 (▽).
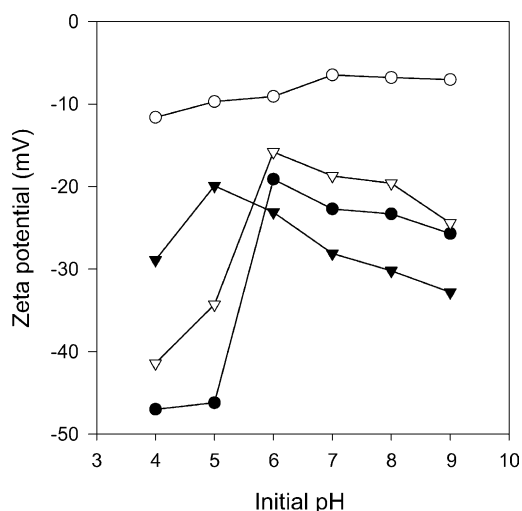
Fig. 5. Distributions of zeta potential according to initial pH: disperse blue 106 (●); disperse yellow 54 (▼); reactive blue 49 (○); reactive yellow 84 (▽).

the dye solution increased from −47.0 to −19.1 mV as the pH was increased from 4 to 6, but decreased to −25.7 mV at pH 9. Similarly, the zeta potential nearest to the IEP was observed at pH 5 for disperse yellow 54, pH 7 for reactive blue 49 and pH 6 for reactive yellow 84. Although the zero net zeta potential values of solutions were not found for all solutions and zeta potentials varied from −6.48 to −47.0 mV, the optimal pH conditions for chemical coagulation appeared when the zeta potential values were close to zero. At pH values above 7, the disperse dye and reactive dye solutions were more negatively charged, and dye removal efficiencies decreased. This was probably due to the increasing concentration of $Fe(OH)_4^-$ that occurs at these pH values [25]. If the pH of the solution is below the IEP of the respective metal hydroxide, then positively charged polymers will predominate and the adsorption of these can destabilize the negatively charged colloids through charge neutralization.

Above the IEP, anionic polymers will prevail and the destabilization of particles may take place by the mechanisms of adsorption and bridge formation [27]. When ferric salts are used as coagulants, monomeric and polymeric ferric species are formed, which are highly dependent on pH.

The optimal concentrations of ferric chloride coagulant for disperse and reactive dyes were determined by varying the coagulant dose at the optimal pH for each solution: pH 5 for disperse blue 106, pH 6 for disperse yellow 54 and reactive yellow 84, pH 7 for reactive blue 49. COD and dye removals as a function of coagulant dose are shown in Fig. 6. The COD and dye removal efficiencies of the disperse dyes were higher than those of the reactive dyes, and the coagulant concentrations needed to achieve the maximum removal efficiency were lower for the disperse dyes than for the reactive dyes. The maximum removal efficiencies for the disperse blue 106 and disperse yellow 54 dyes were 84.0% of COD, 97.7% of dye and 88.0% of COD, 99.6% of dye, respectively, and these were achieved at coagulant concentrations of 0.93 and 0.74 mM ferric chloride. The maximum removal efficiencies for reactive blue 49 and reactive yellow 84 dyes were 25.0% of COD, 60.9% of dye and 66.5% of COD, 71.3% of dye, respectively, at coagulant concentrations of 2.78 and 1.85 mM ferric chloride.

Distributions of zeta potential as a function of coagulant dose are shown in Fig. 7. The zeta potentials of dye solutions were highly affected by the ferric chloride dose. An increase in coagulant concentration resulted in an increase of the zeta potential values. Adequate addition of chemical coagulant yields zeta potential values close to zero. A charge reversal was observed with increasing coagulant concentration. The dyestuff particles were positively charged and the zeta potential became positive, indicating that the stability progressively increased in the aqueous environment. In this case, the electrostatic repulsion forces clearly dominate the dispersion forces of attraction in the system. In this system, Fe(III) is the potential determining ion since it controls the surface charge and IEP. The results of chemical coagulation
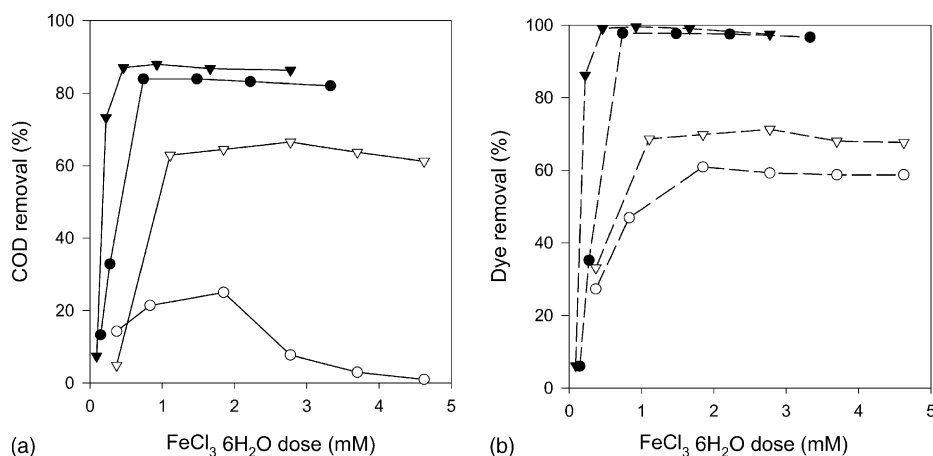

Fig. 6. COD (a) and dye (b) removals by ferric chloride coagulation according to coagulant dose: disperse blue 106 (●); disperse yellow 54 (▼); reactive blue 49 (○); reactive yellow 84 (▽).
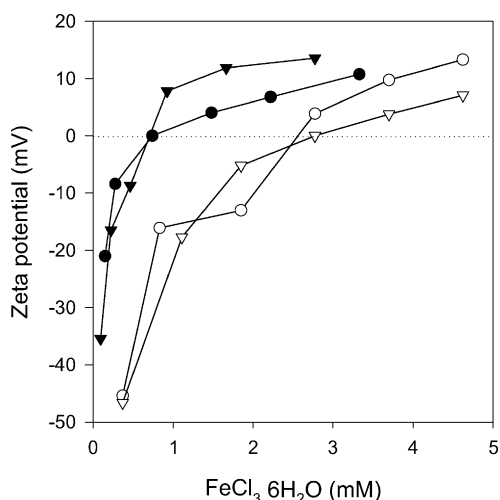
Fig. 7. Distributions of zeta potential according to ferric chloride coagulant dose: disperse blue 106 (●); disperse yellow 54 (▼); reactive blue 49 (○); reactive yellow 84 (▽).

efficiency are in good agreement with zeta potential measurements. The maximum COD and dye removal efficiencies appeared when the zeta potential values were close to zero.

From Fig. 7, it is clear that the quantity of chemical coagulant needed to obtain the IEP for the reactive dyes was higher than that for disperse dyes. For the reactive dyes, about 2.78 mM ferric chloride was needed to reach the IEP, however, only 0.74 mM ferric chloride was needed to reach the IEP for disperse dyes. The reversal of the zeta potential of the dye solutions was observed when the ferric chloride coagulant concentration was greater than the IEP. These results indicate that dispersed dyes were more easily removed than reactive dyes by chemical coagulation using ferric chloride.

3.3. Fenton oxidation of dye solutions

It is known that the dye removal efficiency by Fenton oxidation is not affected by pH changes in the range of 2–7. However, the Fenton oxidation is not applicable to alkaline solutions, when pH > 8, Fe^{2+} ion begins to form floc and precipitates and H_2O_2 is also unstable and may decompose to give oxygen and water, and finally loses its oxidation ability. Most studies show that pH between 2 and 3 is the most effective in the degradation reactions [28]. Therefore, the dye solution was adjusted to pH 3 prior to Fenton reagent adding in this study. The Fenton oxidation time was also set at 30 min, because the majority of color was generally removed at a rather short oxidation time, such as 1 min [29], 10 min [19], and 15 min [30], and most of H_2O_2 added must be consumed during the Fenton oxidation.

The effects of Fe^{2+}, H_2O_2 dose were investigated and the molar ratios of Fe^{2+} and H_2O_2 were optimized. Firstly, in order to investigate the effect of Fe^{2+} concentration on the dye degradation, experiments were conducted at different Fe^{2+} concentration and at fixed H_2O_2 concentrations of 1.91, 1.47, 4.41 and 1.15 mM for disperse blue 106, disperse yellow 54, reactive blue 49 and reactive yellow 84, respectively. Fig. 8 shows the COD and dye removals as a function of the concentration of Fe^{2+}. The trends of COD removal according to Fe^{2+} dose were similar with those of dye removal as shown in Fig. 8. The highest COD and dye removals were showed at 0.38, 0.41, 1.61 and 0.23 mM of Fe^{2+} concentration for disperse blue 106, disperse yellow 54, reactive blue 49 and reactive yellow 84, respectively, which corresponds to the $[Fe^{2+}]:[H_2O_2]$ molar ratio of 1:0.20, 1:0.28, 1:0.37 and 1:0.20, respectively.

The COD and dye removal efficiencies of disperse dyes are 48.0–56.2 and 83.3–85.0%, respectively, however, those of reactive dyes are 70–80.3 and 92.0–95.8%, respectively. Thus, reactive dyes were more easily removed by Fenton oxidation than disperse dyes. After the optimal Fe^{2+} addition,
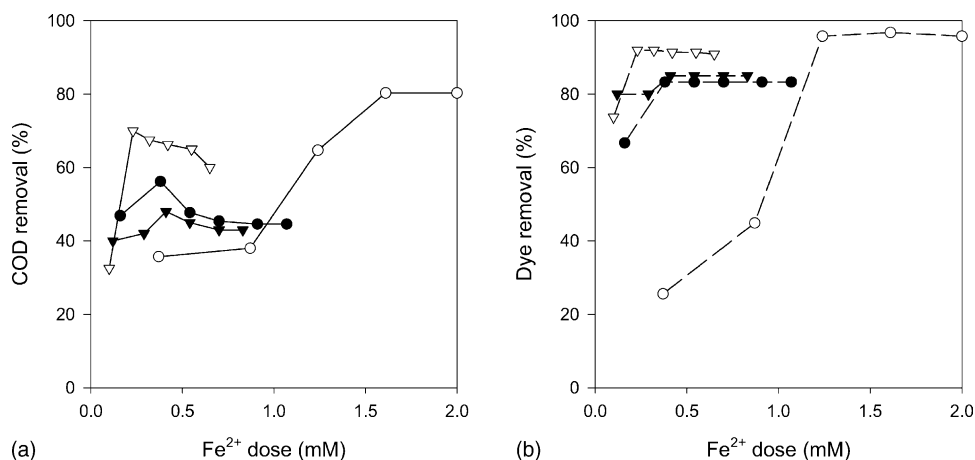

(a)

(b)

Fig. 8. COD (a) and dye (b) removals by Fenton oxidation according to Fe^{2+} dose: disperse blue 106 (●); disperse yellow 54 (▼); reactive blue 49 (○); reactive yellow 84 (▽).

the higher addition of Fe^{2+} resulted in a brown turbidity that causes the recombination of hydroxyl radicals and Fe^{2+} reacts with hydroxyl radicals as a scavenger. Therefore, the COD removal could decrease [28].

The main cost of Fenton reaction process is the cost of H_2O_2. So, it is important to optimize the amount of H_2O_2 in the Fenton oxidation. To determine the optimum H_2O_2 concentration on dye degradation, experiments were conducted by varying the Fe^{2+} and H_2O_2 concentrations, keeping the ratios of $[Fe^{2+}]$:$[H_2O_2]$ fixed at optimal ratio as determined above. The COD and dye removals as a function of $[H_2O_2]$ were presented in Fig. 9. The results indicate that the removals of COD and dye increase with the increase in the $[Fe^{2+}]$ and $[H_2O_2]$ concentrations. Then, it shows that the fractional degradations of the COD were maximum at 2.48, 1.91, 4.41 and 1.15 mM of $[H_2O_2]$ for disperse blue 106, disperse yellow 54, reactive blue 49 and reactive yellow 84, respectively. The optimum $[H_2O_2]$ doses for dye removals are also found to be around 2.48, 1.91, 4.41 and 1.15 mM of $[H_2O_2]$, respectively. These values are in agreement with the dose values of $[H_2O_2]$ for COD removals. The highest removal efficiencies of the COD at a fixed $[Fe^{2+}]$:$[H_2O_2]$ molar ratio for disperse blue 106, disperse yellow 54, reactive blue 49 and reactive yellow 84 were 60.0, 48.0, 80.3 and 70.0%, respectively, at the optimal $[H_2O_2]$ doses as aforementioned. The maximum dye removal efficiencies for four types of dye solutions were 91.6, 90.0, 97.9 and 92.0%, respectively. However, further increase in $[H_2O_2]$ has negligible effects. At higher H_2O_2 concentration, there is a competition between the substrate and H_2O_2. H_2O_2 in high concentration acts as a scavenger of the hydroxyl radical ($HO^\bullet$) to produce perhydroxyl radical ($HO_2^\bullet$) which has much lower oxidation capacities than hydroxyl radical.

Fig. 9 also shows that the COD and dye removals of reactive dye solutions were higher than those of disperse dye solutions. This is due to the fact that reactive dyes are soluble in solution, whereas disperse dyes are not. Most disperse dyes are suspended or colloidal solids in solutions. (They are also more difficult to treat by Fenton oxidation than reactive dyes.) These results indicate that the efficiencies of Fenton oxidation of reactive dye solutions are higher than those of disperse dye solutions.

In addition, the dye removals by Fenton oxidation were noticeably higher than the COD removal. This can be attributable to fact that the organics, which were decomposed to the smaller organics, still have COD, although the dye solutions were decolorized by the cleavage of critical dye bonds, for example azo double bonds or aromatic ring linkages, as a result of Fenton oxidation [31].

3.4. Comparison of chemical coagulation and Fenton oxidation of dye solutions

In order to evaluate the characteristics of chemical coagulation and Fenton oxidation of dye solutions according to dye type, the COD and dye amounts removed per chemicals added (Fe^{3+} for chemical coagulation, Fe^{2+} for Fenton oxidation) were determined and compared. The results are showed in Fig. 10.

With regard to chemical coagulation, 460.2–477.0 g COD and 525.7–672.7 g dye were removed per mol Fe^{3+} for disperse dye solutions, whereas only 37.4–86.5 g COD and 109.5–192.7 g dye were removed per mol Fe^{3+} for reactive dye solutions. Accordingly, disperse dyes are more easily removed by chemical oxidation than reactive dyes. In contrast, the efficiencies of Fenton oxidation of disperse dye solutions were lower than those of reactive dye solutions. Although 14.0–80.0 g COD and 3.7–20.8 g dye were removed per mol Fe^{2+} for disperse dye solutions, 114.2–199.6 g COD and 118.9–489.2 g dye were removed per mol Fe^{3+} for reactive dye solutions.

The performance of dye removal using chemical treatment, such as chemical coagulation and Fenton oxidation, depends upon the solubility of the dyes as well as chemical structures. Dye with low solubility such as disperse dyes, can be easily adsorbed and flocculated by coagulants. How-
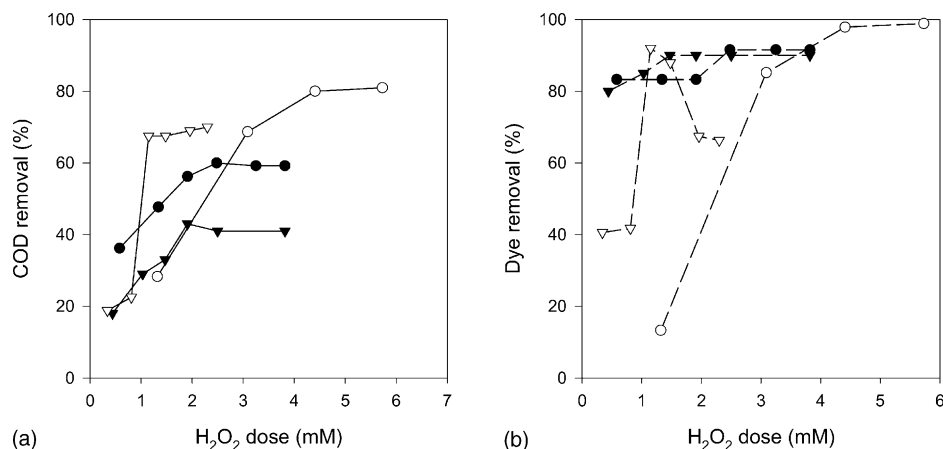

Fig. 9. COD (a) and dye (b) removals by Fenton oxidation according to H_2O_2 dose: disperse blue 106 (●); disperse yellow 54 (▼); reactive blue 49 (○); reactive yellow 84 (▽).
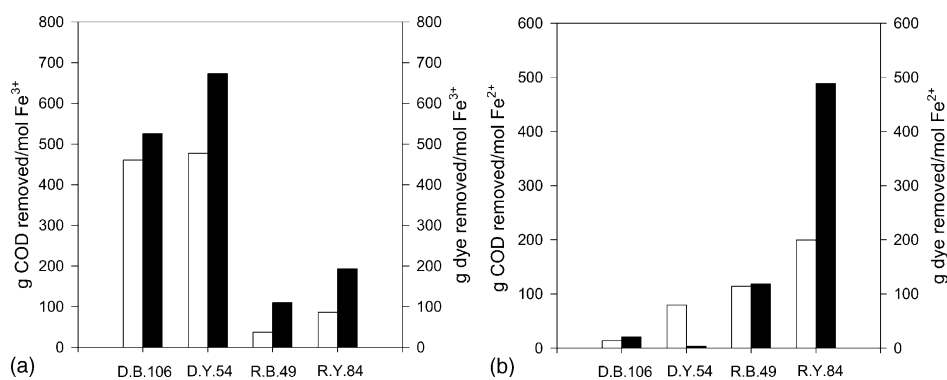
Fig. 10. Comparison of chemical coagulation (a) and Fenton oxidation (b) efficiencies according to dyestuff type: (□) COD removal; (■) dye removal.

ever, soluble dyes cannot be well removed by coagulation. Solubility differences are attributed to different chemical structures. Disperse dyes are often of anthraquinone and sulfide structures. They have many –C=O, –NH– and aromatic groups. Therefore, they tend to be adsorbed by $Fe(OH)_x$ particles and have high TOC/color values. Reactive dyes are characterized by azo bonds (N=N). Reactive dyes have also –SO_3^-, –COO–, –OH groups. This indicates that reactive dyes are more stable than disperse dyes. These reactive dyes have high solubility and they are not prone to be adsorbed [1,32], but can be more easily removed by oxidation process such as Fenton oxidation. Therefore, for disperse dye solutions, the applicability of chemical coagulation is higher than that of Fenton oxidation, whereas for reactive dye solutions, the applicability of Fenton oxidation is higher than that of chemical coagulation.

4. Conclusions

In this study, our aim was to identify any apparent differences between the chemical coagulation and Fenton oxidations of the two most common dye types, i.e., disperse dye and reactive dye, used in the commercial dyeing process. The optimal coagulation conditions (pH and coagulant dose) and Fenton oxidation conditions (Fe^{2+}:H_2O_2 molar ratio and dose) for each dyestuff type were determined using COD and dye removal efficiencies. The performances of chemical coagulation and Fenton oxidation of dye solutions were also investigated. In addition, the COD and dye removal effectiveness per chemical added (Fe^{3+} for chemical coagulation and Fe^{2+} for Fenton oxidation) were compared.

After chemical coagulation of disperse dye solutions, the concentration of the dyestuff compound present was reduced to acceptable percentages. The disperse dyes had a high SS concentration, low SCOD/TCOD ratio and low zeta potential distributions due to low solubility. The disperse dyes are more easily removed by chemical coagulation than the reactive dyes due to not only to their low solubility but also the characteristics of chemical structures However, COD and dye removals of reactive dye solutions by Fenton oxidation

were higher than those of disperse dye solutions due to their high solubility, low SS concentration comparing with disperse dye.

Conclusively, the probability of successful chemical coagulation of disperse dye solutions is higher than that of reactive dye solutions, whereas the probability of successful Fenton oxidation of reactive dye solutions is lower for than that of disperse dye solutions.

Both disperse dyes and reactive dyes were effectively removed by the combination of chemical coagulation and Fenton oxidation. The Fenton oxidation in combination with Fe^{3+} coagulation process showed about 90% of COD and 99% of dye removals efficiencies at the optimum conditions.

References

[1] Y. Al-Degs, M.A.M. Khraishen, S.J. Allen, M.N. Ahmad, Water Res. 34 (3) (2000) 927.
[2] J. Sarasa, M.P. Roche, M.P. Ormad, E. Gimeno, A. Puig, J.L. Ovelleiro, Water Res. 32 (9) (1998) 2721.
[3] S.H. Lin, C.F. Peng, Water Res. 30 (1996) 587.
[4] T.-H. Hsu, C.-S. Chiang, J. Environ. Sci. Health 32 (1997) 1921.
[5] D.-H. Ahn, W.-S. Chang, T.-I. Yoon, Process Biochem. 34 (1999) 429.
[6] A.D. Dhale, V.V. Mahajani, Waste Manage. 20 (2000) 85–92.
[7] G. Chen, L. Lei, P.L. Yue, Ind. Eng. Chem. Res. 38 (1999) 1837.
[8] I. Arslan, I.A. Balcioglu, Desalination 130 (2000) 61.
[9] W. Chu, C.-W. Ma, Water Res. 34 (12) (2000) 3153.
[10] S.H. Lin, C.H. Lai, Water Res. 34 (3) (2000) 763.
[11] G. Sun, X. Xu, Ind. Eng. Chem. Res. 36 (1997) 808.
[12] T.-H. Kim, C. Park, E.-B. Shin, S. Kim, Desalination 150 (2002) 165.
[13] K. Dutta, S. Mukhopadhyay, S. Bhattacharjee, B. Chaudhuri, J. Hazard. Mater. B 84 (2001) 57.
[14] E.G. Solozhenko, N.M. Soboleva, V.V. Goncharuk, Water Res. 29 (9) (1995) 2206.
[15] I. Arslan, I.A. Balcioglu, Dyes and Pigments 43 (1999) 95.
[16] V. Sarria, M. Deront, P. Peringer, C. Pulgarin, Appl. Catal. B: Environ. 1251 (2002) 1.

[17] W. Zhu, Z. Yang, L. Wang, Water Res. 35 (8) (2001) 2087.
[18] L. Szpyrkowicz, C. Juzzolino, S.N. Kaul, Water Res. 35 (9) (2001) 2129.
[19] W.Z. Tang, R.Z. Chen, Chemosphere 32 (5) (1996) 947.
[20] K. Swaminathan, S. Sandhya, A.C. Sophia, K. Pachhade, Y.V. Subrahmanyam, Chemosphere 50 (2003) 619.
[21] W. Zhu, Z. Yang, L. Wang, Water Res. 30 (12) (1996) 2949.
[22] S.H. Lin, C.C. Lo, Water Res. 31 (8) (1997) 2050.
[23] D. Mcginnis, V.D. Adams, E.J. Middlebrooks, Water Res. 34 (8) (2000) 2346.
[24] APHA/AWWA/WEF, Standard Methods for Examination of Water and Wastewater, 19th ed., APHA/AWWA/WEF, Washington, DC, 1995.
[25] J.H. Montgomery, Water Treatment Principles and Design, Wiley/Interscience, New York, 1985.
[26] H.A. Bustamante, S.R. Shanker, R.M. Pashley, M.E. Karaman, Water Res. 35 (13) (2001) 3179.
[27] A.I. Zouboulis, A. Avranas, Colloids Surf. 172 (2000) 153.
[28] G. Yu, W. Zhu, Z. Yang, Chemosphere 37 (3) (1998) 487.
[29] S.-F. Kang, C.-H. Liao, M.-C. Chen, Chemosphere 46 (2002) 923.
[30] S.F. Kang, H.M. Chang, Water Sci. Technol. 36 (1997) 215.
[31] C. Raghavacharya, Chem. Eng. World 32 (7) (1997) 53.
[32] Z. Shen, W. Wang, J. Jia, J. Ye, X. Feng, A. Peng, J. Hazard. Mater. B 84 (2001) 107.