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COLOR AND COD REMOVAL OF DYEING WASTEWATER BY COMBINATION TREATMENT OF COAGULATION AND FENTON OXIDATION

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Abstract

Color and COD removal of dyeing wastewater containing green vat dye from Minh Khai Textile Company by the combination treatment of coagulation and Fenton oxidation was studied. $\text{Al}_2(\text{SO}_4)_3$ and FeSO_4 were used as coagulants. Effects of operating conditions, including pH, content of coagulants and reactants on the color and COD removal efficiencies were investigated, and optimum operating conditions were experimentally determined. Observation of changes in content and structure of dye before and after treatment was carried out by using UV - visible spectral analysis. The results indicated that FeSO_4 coagulant was more effective than $\text{Al}_2(\text{SO}_4)_3$ in reduction of color as well as COD. At optimum conditions, total removal efficiencies of color and COD in the combination treatment were 94% and 92%, respectively.

Key words: Coagulation, fenton oxidation, aluminum sulfate, ferrous sulfate, fenton

Introduction

The environmental concern of textile wastewater discharge is mainly on their high chemical oxygen demand (COD) as well as high color. These pollutants must be removed from discharge to avoid a damaging effect on the aquatic life [4]. Among numerous textile wastewater streams, the one from dyeing operation deserves special attention. The dyes are highly structured organic substance, strongly colorful and hard to decompose biologically. Hence, biological processes are not effective for treatment of such type of wastewater [4].

Oxidation by using Fenton's reagent, one of the most advanced oxidation processes is able to deal with the textile wastewater treatment. Previous investigations showed that Fenton's reagent, a mixture of H_2O_2 and Fe^{2+} is effective in decoloration and COD removal of the wastewater that contains various types of reactive, direct, base, acid and disperse dyes [5].

The object of this study was to determine the efficiency of color and COD removal from dyeing wastewater containing vat dye (from Minh Khai Textile Company) by a combination treatment of chemical coagulation and Fenton oxidation. Effects of treatment conditions were investigated, and the optimum operating conditions were determined.

Experimental

Materials

Wastewater sample used in coagulation experiments was dyeing wastewater containing green vat dye from Minh Khai Textile Company with an initial COD content of 1066 mg/l, collected directly from a dyeing machine after dyeing. Wastewater for Fenton treatment studies was wastewater pre-treated by coagulation. Coagulants ($\text{Al}_2(\text{SO}_4)_3$, FeSO_4) and pH - adjusting agents were pour grade.

Experiments

Coagulation

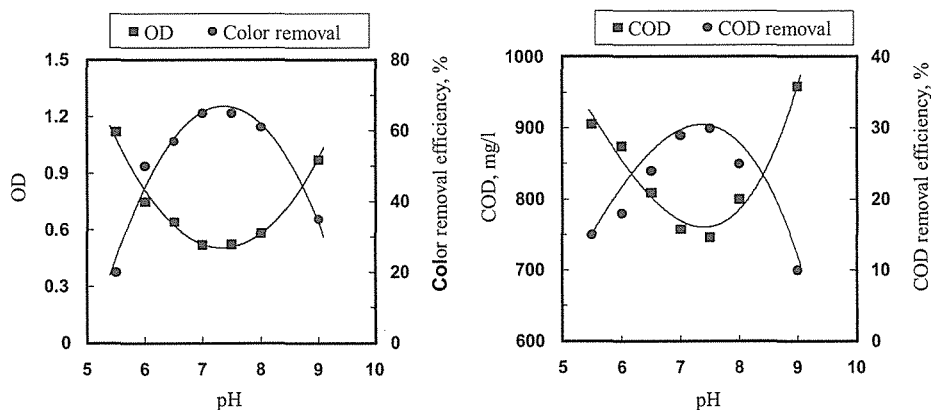
Coagulation experiments were carried out at conditions showed in Table 1 as follows. 200 ml of wastewater sample in a glass beaker was added with coagulant solution, then adjusted to the study pH and agitated at 200 rpm for 3 minutes. The solution was then continuously agitated at 50 rpm for 10 minutes. After standing for 60 minutes to settle out the flocculates, the sample was taken for measurements of COD and optical density (OD).

Table 1: Experimental conditions for coagulation treatment

Experimental conditions	Aluminum sulfate	Ferrous sulfate
Amount of coagulants (g/l)	0.15 – 0.8	0.05 – 0.4
pH	5 – 9	6 – 11
Temperature (°C)	Room temperature	Room temperature

Fenton oxidation

According to previous studies [1, 3], Fenton's reagent is most effective at a pH between 2 and 4, with an optimum pH of approximately 3. In this study, Fenton treatment experiments were conducted at room temperature and pH of 3 in a transparent glass reactor equipped with a speed-adjustable agitator. 200 ml of pre-coagulated wastewater sample was adjusted to pH 3, then added with reactants and agitated at 200 rpm. After 1 hour of reaction, the solution was adjusted to pH 9 (optimum pH for coagulation by ferrous sulfate), and agitated at 50 rpm for 10 minutes. After settling for 60 minutes, the sample was then taken for measurements of required parameters.

Figure 1: Effect of pH on the color and COD removal Coagulant: $\text{Al}_2(\text{SO}_4)_3$ 0.5 g/l

Analysis

OD was determined by a spectrophotometer DR/2000 (HATCH, America) at the wavelength of 470 nm. UV-visible spectral analyses were performed in a Cintra 40 spectrometer (GBC, America - Australia). COD was analyzed by a titration method according to the Vietnamese Standard TCVN 4565 - 88.

Results and discussion

Coagulation studies

Effect of pH on the color and COD removal

The experiments were performed with the fixed amounts of 0.5 g/l $\text{Al}_2(\text{SO}_4)_3$ and 0.4 g/l FeSO_4 , respectively. Color and COD removal efficiencies were calculated by equations (1) and (2):

$$\eta_{\text{color}} = \frac{\text{OD}_0 - \text{OD}}{\text{OD}_0} \times 100 \quad (1)$$

$$\eta_{\text{COD}} = \frac{\text{COD}_o - \text{COD}}{\text{COD}_o} \times 100 \quad (2)$$

where, color and COD are color and COD removal efficiencies, respectively; ODo and OD are optical densities before and after treatment, respectively; COD_o and COD are chemical oxygen demands before and after treatment, respectively.

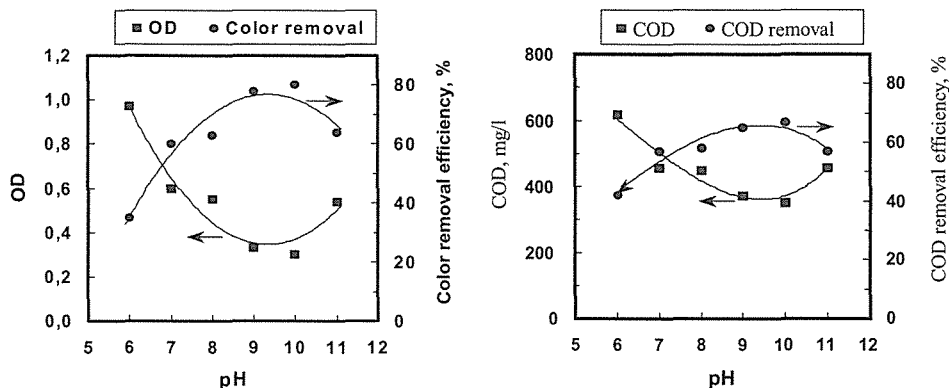


Fig. 2 Effect of pH on the color and COD removal Coagulant: FeSO₄ 0.4 g/l

Figures 1 and 2 demonstrate the effect of pH on the color and COD removal. Coagulation with Al₂(SO₄)₃ was effective in neutral environment, pH = 7.0 - 7.5, while with FeSO₄ was in alkaline environment, pH = 9 - 10. These results were in agreement with theoretical expectation.

Effect of coagulant content on the color and COD removal

The effect of coagulant content on the color and COD removal is shown in Figures 3 and 4.

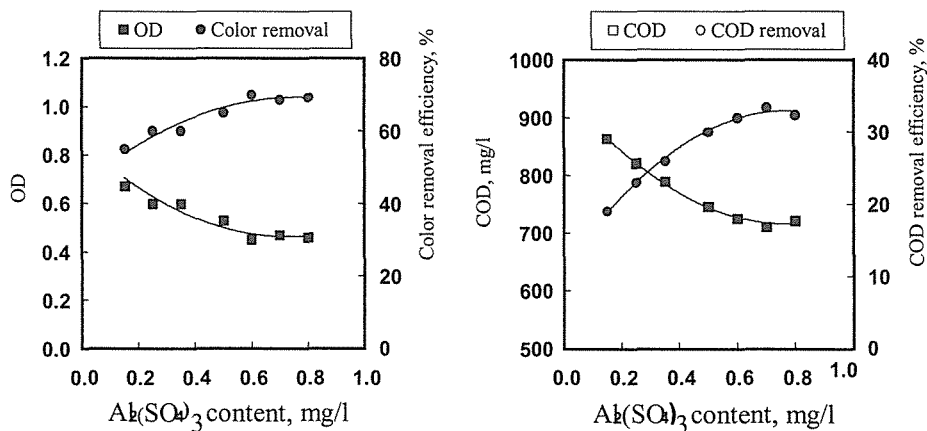


Fig. 3 Effect of Al₂(SO₄)₃ content on the color and COD removal (pH = 7.0)

With increasing coagulant content, color and COD removal efficiencies tended to increase to constant values for both cases of Al₂(SO₄)₃ and FeSO₄. FeSO₄ showed higher removal efficiencies of both color and COD in comparison with Al₂(SO₄)₃.

In coagulation using $\text{Al}_2(\text{SO}_4)_3$ coagulant, the maximum color and COD removal efficiencies of approximately 70% and 32%, respectively were obtained at the values above 0.6 g/l $\text{Al}_2(\text{SO}_4)_3$.

While for the case of FeSO_4 , maximum color and COD removal efficiencies of approximately 80% and 67%, respectively, were achieved at the values above 0.3 g/l FeSO_4 . It can be also seen from the Figures 2 and 3 that the removal efficiency of color was higher than that of COD for both cases of $\text{Al}_2(\text{SO}_4)_3$ and FeSO_4 .

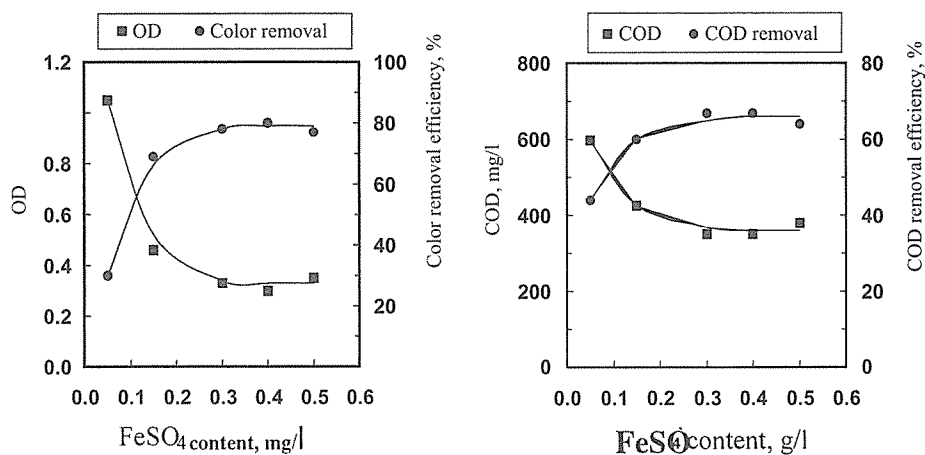
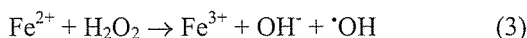


Fig. 4 Effect of FeSO_4 content on the color and COD removal (pH = 10)

Fenton oxidation studies

Oxidation by Fenton's reagent is attributed to the generation of hydroxyl radical, HO^\bullet via the following reaction:



The generated hydroxyl radical, which is a strong oxidant, can either react with Fe^{2+} producing Fe^{3+} (4) or attack organic pollutants present in solution thus causes chemical decomposition of these compounds (5):

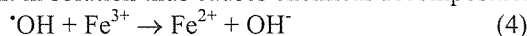
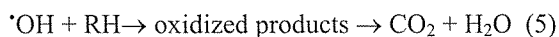


Table 2: Effect of FeSO_4 content on the color and COD removal ($\text{OD}_0 = 0.30$; $\text{COD}_0 = 352$ mg/l)

FeSO_4 content, g/l	H_2O_2 0,5 mg/l				H_2O_2 0,7 mg/l			
	Color		COD		Color		COD	
	OD	η_m , %	COD, mg/l	η_{COD} , %	OD	η_m , %	COD, mg/l	η_{COD} , %
0.1	0.15	50	245	30	0.14	53	214	39
0.2	0.13	57	213	40	0.11	63	173	51
0.3	0.10	67	162	54	0.10	67	105	70
0.4	0.11	63	151	57	0.09	70	85	76
0.5	0.10	67	150	57	0.09	70	87	75



On the other hand, after reaction, iron ions present in solution can act as a coagulant when adjusting pH of the solution to the suitable region.

The decomposed organic molecules and/or other dissolved suspended solids are captured and precipitate out. Such a coagulation - precipitation action may contribute an important part of COD reduction of the Fenton treatment process.

Effect of FeSO₄ content on the color and COD removal

Effect of FeSO₄ content on the color and COD removal was investigated at the fixed H₂O₂ amounts of 0,5 g/l and 0,7 g/l. Wastewater sample for the experiments was pre-coagulated with FeSO₄ coagulant.

The results in Table 2 indicated that the color removal efficiency increased as FeSO₄ content increased, and reached a maximum value of approximately 67% when FeSO₄ content was higher than 0.3 g/l. Similar tendency was also observed with the change of COD. A maximum COD removal efficiency of approximately 76% was obtained at FeSO₄ content of 0.4 - 0.5 g/l for the case of using 0.7 mg/l H₂O₂.

Table 3 Effect of H₂O₂ content on the color and COD removal

H ₂ O ₂ content, (g/l)	Color (OD ₀ = 0,30)		COD (COD ₀ = 352 mg/l)	
	OD	η _m , %	COD mg/l	η _{COD} , %
0.1	0.15	50	320	10
0.3	0.12	60	181	49
0.5	0.11	63	151	57
0.6	0.10	67	105	70
0.7	0.09	70	85	76
0.8	0.09	70	97	72
0.9	0.09	70	129	63

Effect of H₂O₂ content on the color and COD removal

The effect of H₂O₂ content on the color and COD removal was investigated in the range of 0.1 - 0.9 g/l H₂O₂ with the fixed FeSO₄ content of 0.4 g/l. It was clear from the results in Table 2 that, when H₂O₂ content increased from 0.1 g/l to 0.7 g/l, the removal efficiencies of color, especially of COD were evidently improved, from 50 % to 70 % and from 10 % to 76 %, respectively. As H₂O₂ content exceeded 0.7 g/l, a remarkable change in color removal efficiency was not observed, however the COD removal efficiency decreased slightly. The reason for this decrease in COD efficiency is due to the excess amount of H₂O₂, which was not completely consumed in the reaction, remaining in the solution and causing an increase in COD of the solution. This phenomenon was also previously reported [5]. The above results indicated that the most effective H₂O₂ content for the treatment was 0.7 mg/l. At this optimum condition, the color of wastewater was practically eliminated, and a reduction of COD from 352 mg/l to below 85 mg/l was achieved.

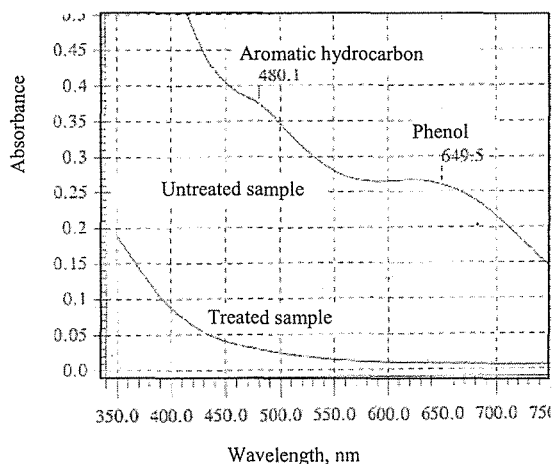


Figure 5: UV-visible spectra in the wavelength of 350 - 900 nm

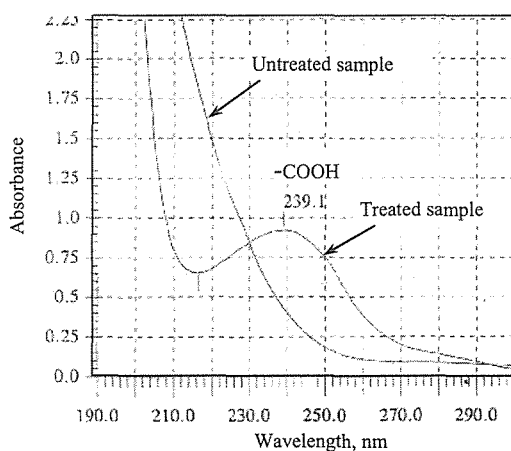
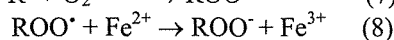
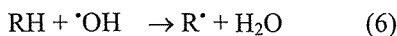


Figure 6: UV-visible spectra in the wavelength of 190 - 350 nm

UV-visible spectral analysis

Figure 5 shows UV-visible spectra of wastewater sample before and after treatment in the wavelength range of 350 – 900 nm. Absorbance peaks of aromatic hydrocarbon group and phenol group were observed at the wavelengths of 480 nm and 649 nm, respectively for the untreated wastewater sample. However, there was no appearance of these peaks for the treated wastewater sample. UV-visible spectra in the wavelength range of 190 - 350 nm in Figure 6 showed that acid (-COOH, at the wavelength of 239 nm) was an intermediate product of the dye oxidation by Fenton's reagent. This product may be formed via following pathway [6, 8]:



These above results suggested that content and structure of the dye had changed obviously by the Fenton treatment.

Conclusions

The results of treatment of dyeing wastewater containing vat dye from Minh Khai Textile by a combination process of coagulation and Fenton oxidation lead to the following conclusions:

- FeSO_4 coagulant was more effective than $\text{Al}_2(\text{SO}_4)_3$ in reduction of color as well as COD. Optimum coagulation conditions for $\text{Al}_2(\text{SO}_4)_3$ were in the pH range of 7,0 - 7,5 and $\text{Al}_2(\text{SO}_4)_3$ content range of 0.6 - 0.7 g/l. Those for FeSO_4 were in the pH range of 9 - 10 and FeSO_4 content range of 0.4 - 0.5 g/l. At optimum conditions, color and COD removal efficiencies of $\text{Al}_2(\text{SO}_4)_3$ were 70% and 32%, respectively, and those of FeSO_4 were 80% and 67%, respectively. The removal efficiency of color was higher than that of COD for both cases of $\text{Al}_2(\text{SO}_4)_3$ and FeSO_4 .
- Fenton's reagent was effective for reducing color and COD of dyeing wastewater containing vat dye. The effective content ranges of FeSO_4 and H_2O_2 for the Fenton treatment were in 0.7 - 0.8 g/l and 0.3 - 0.4, respectively. At these conditions, color and COD removal efficiencies for pre-coagulated wastewater were 70% and 76%, respectively.
- Total removal efficiencies of color and COD in the combination treatment of coagulation and Fenton oxidation were 94% and 92%, respectively. The color of wastewater treated by the combination process was practically eliminated, and a reduction of COD from 1066 mg/l to below 85 mg/l was achieved.

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