



Degradation of crystal violet by an FeGAC/H₂O₂ process

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ABSTRACT

Because of the growing concern over highly contaminated crystal violet (CV) wastewater, an FeGAC/H₂O₂ process was employed in this research to treat CV-contaminated wastewater. The experimental results indicated that the presence of iron oxide-coated granular activated carbon (FeGAC) greatly improved the oxidative ability of H₂O₂ for the removal of CV. For instance, the removal efficiencies of H₂O₂, GAC, FeGAC, GAC/H₂O₂ and FeGAC/H₂O₂ processes were 10%, 44%, 40%, 43% and 71%, respectively, at test conditions of pH 3 and 7.4 mM H₂O₂. FeGAC/H₂O₂ combined both the advantages of FeGAC and H₂O₂. FeGAC had a good CV adsorption ability and could effectively catalyze the hydrogen peroxide oxidation reaction. Factors (including pH, FeGAC dosage and H₂O₂ dosage) affecting the removal of CV by FeGAC/H₂O₂ were investigated in this research as well. In addition, the reaction intermediates were separated and identified using HPLC-ESI-MS. The *N*-demethylation step might be the main reaction pathway for the removal of CV. The reaction mechanisms for the process proposed in this research might be useful for future application of this technology to the removal of triphenylmethane (TPM) dyes.

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1. Introduction

More than 10,000 different synthetic dyes and pigments are produced annually worldwide. The annual production of dyes and pigments is more than 7×10^5 tons, and it has been estimated that approximately 5–15% is lost in industrial effluents [1–3]. The large amount of wastewater generated in textile manufacturing processes represents an increasing environmental danger because of the refractory carcinogenic nature of the dyes [4–6]. For example, triphenylmethane (TPM) dyes are suitable for a large variety of technological applications. They are used extensively in the textile industry for dyeing nylon, wool, cotton, and silk, as well as for coloring oil, fats, waxes, varnish, and plastics. The paper, leather, cosmetic, and food industries are major consumers of various TPM dyes as well. A great deal of concern has arisen regarding the thyroid peroxidase-catalyzed oxidation of the TPM class of dyes because of the generation of *N*-dealkylated primary and secondary aromatic amines, which have structures similar to hazardous aromatic amine carcinogens [7,8]. Crystal violet (CV) is a typical triphenylmethane dye; it is toxic to mammalian cells and is a mutagen and a mitotic poison [9]. Therefore, CV was chosen as the model pollutant in this research.

A chemical coagulation process could remove dyes reasonably well, but it would produce a large amount of sludge, which causes another waste problem. Activated carbon processes can remove dyes in aqueous solution effectively, but activated carbon and the subsequent treatment of the spent carbon are costly [2,10–13]. Therefore, more efficient and economical technologies are needed for the treatment of dye-contaminated wastewater. Consequently, there are many researchers trying to explore processes that are more efficient to remove dye from wastewater. For example, both photolytic oxidation (TiO₂/UV or VIS [14–16], ZnO/UV [17], and H₂O₂/UV [18]), and Fenton's reagents (Fenton [12], Fe²⁺/H₂O₂/UV [18], and Fe³⁺/UV [19]) processes have been reported in literatures with promising results. In addition, Alshamsi et al. reported that Fenton's process had better CV degradation efficiency than that of photolytic process (H₂O₂/UV) [20]. However, the research also reported that the Fenton process was dramatically inhibited by the presence of hydrogen phosphate ions. In addition, one of the major limitations of the Fenton's process was that the process would produce a large amount of sludge, which caused another waste problem. Therefore, the purpose of this research is to develop an alternative oxidation process using FeGAC/H₂O₂ for the removal of CV in aqueous solutions. With the iron oxides coated on the surface of the GAC (granular activated carbon), the production of sludge can be minimized. The FeGAC/H₂O₂ processes combine both advantages of iron oxide coated granular activated carbon (FeGAC) and H₂O₂. FeGAC has high adsorption capacity of dyes due to GAC surface and the coating of iron oxides. In addition, the oxidation ability

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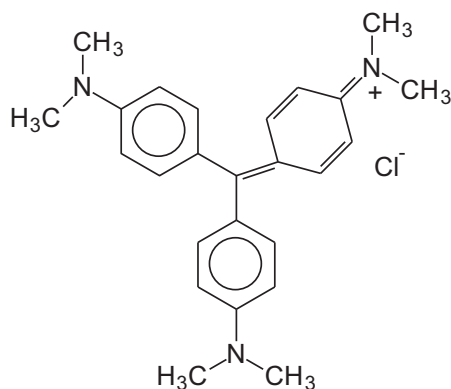


Fig. 1. Chemical structure of crystal violet (CV).

of H_2O_2 is enhanced by the catalytic properties of FeGAC. In previous study, the FeGAC/ H_2O_2 process could effectively remove acid black 24 [10] and humic acids [21], respectively. However, both studies did not identify the reaction intermediates and the reaction pathways. To obtain a better understanding of the mechanistic details of FeGAC/ H_2O_2 process for degradation of CV dye, the reaction intermediates of the process are identified in this research as well.

2. Materials and methods

CV was obtained from Tokyo Kasei Kogyo Co. and confirmed as a pure organic compound using HPLC analysis. The chemical structure of the CV is shown in Fig. 1. Stock solutions containing 2.69 mM (1000 mg/L) of CV in aqueous solution were prepared, protected from light, and stored at 4 °C. Hydrogen peroxide (35%) was purchased from Sigma–Aldrich Chemical Co. The granular activated carbon (GAC) employed herein was offered by Calgon Carbon Corporation (F400) and was provided courtesy of the manufacturer. All of the other chemicals used in this study were reagent grade.

FeGAC (iron oxide-coated granular activated carbon) was prepared as follows. A known amount of FeSO_4 solid was dissolved in deionized water and then mixed with GAC. The applied iron dosage in this research was approximately 40 mg Fe (II)/g GAC. This suspension was mixed for 12 h before being dried in an oven at 90 °C for 3 d. The resulting mixture was cooled to room temperature and washed several times with double-distilled water to remove detachable iron oxide. The resulting FeGAC composite adsorbent was dried in the oven at 105 °C for another 3 d and stored at room temperature in a covered glass container until needed.

The amount of Fe oxide coating on the FeGAC surface was measured by extracting the composite FeGAC in a boiling, concentrated

(10%) HNO_3 solution for 12 h. The total iron in the extraction solution was measured by flame atomic absorption spectrophotometry.

The BET specific surface areas of the samples (FeGAC and GAC) were measured with an automatic system (Micromeritics Gemini 2370C) with nitrogen gas as the adsorbate. The surface morphology of samples was examined by the scanning electron microscopy (SEM). The SEM analysis was carried out on the JSM-7401F model.

A Waters ZQ LC/MS system equipped with a Waters 1525 Binary HPLC pump, a Waters 2998 Photodiode Array Detector, a Waters 717 plus Auto sampler, and a Waters micromass-ZQ3100 Detector was used to identify CV and the reaction intermediates. Solvents A and B were used as the mobile phase. Solvent A was 25 mM aqueous ammonium acetate buffer, and solvent B was methanol. The mobile phase flow rate was 1.0 mL/min. An Atlantis™ dC18 column (250 mm × 4.6 mm i.d., dp = 5 μm) was used, and the column effluent was introduced into the ESI source of the mass spectrometer. The quadrupole mass spectrometer was equipped with an ESI interface with a heated nebulizer probe at 350 °C and an ion source temperature of 80 °C.

The removal efficiencies of five treatment processes (GAC, FeGAC, H_2O_2 , GAC/ H_2O_2 , and FeGAC/ H_2O_2) were studied in this research in a batch reactor. A known amount of adsorbent (GAC or FeGAC) and/or H_2O_2 was added into a sealed 1 L reactor filled with 10 mg/L CV and the pH adjusted to the desired value. Samples were collected and analyzed at predetermined time intervals. Blanks containing no GAC or FeGAC were used for each series of experiments as controls. All samples were filtered through filter paper prior to analysis and treatment. The samples were analyzed in triplicate within the accepted analytical error ($\pm 5\%$).

3. Results and discussion

3.1. Characteristics of FeGAC

SEM images of GAC and FeGAC are shown in Fig. 2. As shown in Fig. 2b, there were apparently some iron oxides coated on the surface of the GAC. The amount of iron oxides on FeGAC surfaces was approximately 38 mg Fe/g GAC. The BET surface areas for GAC and FeGAC were approximately 810 and 745 m^2/g , respectively. The lower surface area of FeGAC was another indicator of the coating of iron oxides on the GAC surface. The loss of iron oxide on the FeGAC after the treatment of CV was tested. The loss of iron oxide was less than 5%.

3.2. Treatment efficiency of FeGAC/ H_2O_2

One of the primary aims of this investigation was to study the removal efficiency of CV by the FeGAC/ H_2O_2 process. Five treatment processes (GAC, FeGAC, H_2O_2 , GAC/ H_2O_2 , and FeGAC/ H_2O_2) were

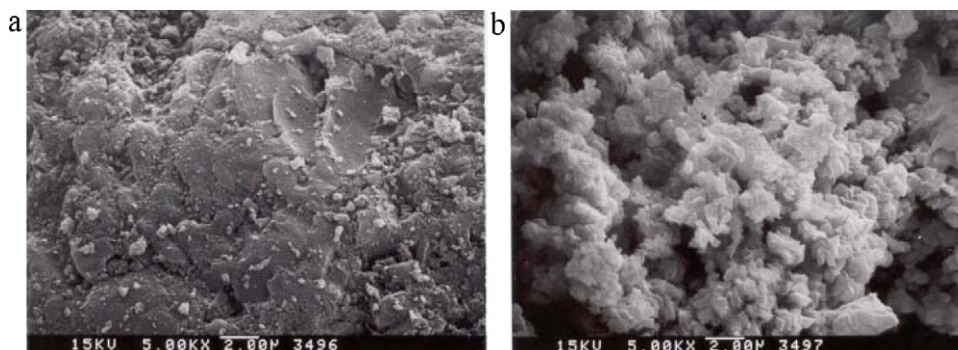


Fig. 2. SEM images of (a) GAC and (b) FeGAC.

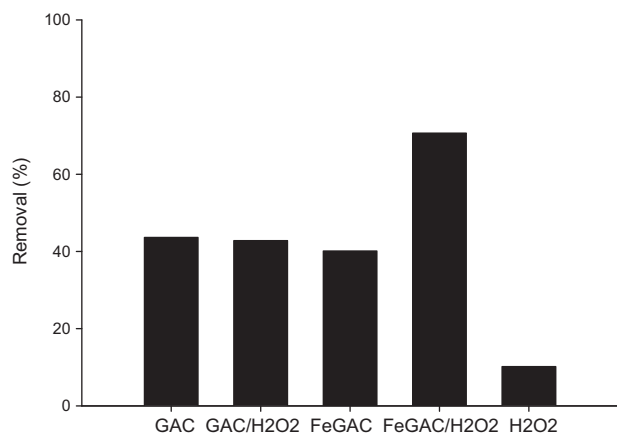


Fig. 3. CV removal efficiencies by various processes (CV = 10 mg/L, adsorbent 1.5 g/L, 7.4 mM H₂O₂, pH 3, 30 min).

conducted in this research to evaluate their CV removal efficiency. The removal efficiencies of the H₂O₂, GAC, FeGAC, GAC/H₂O₂ and FeGAC/H₂O₂ processes were approximately 10%, 44%, 40%, 43% and 71%, respectively (Fig. 3). H₂O₂ alone is not an effective process for the treatment of CV; FeGAC/H₂O₂ had the highest CV removal efficiency. The removal efficiency of FeGAC/H₂O₂ (71%) was 20% higher than that of the FeGAC (40%) and H₂O₂ (10%) processes combined. This result indicated that FeGAC could enhance the oxidation ability of H₂O₂. On the other hand, the removal efficiency of GAC/H₂O₂ was approximately the same as that of the GAC process. Therefore, the better removal efficiency of the FeGAC/H₂O₂ process was probably due to the catalytic reactions that occurred between coated iron oxides and H₂O₂. This result indicates that the presence of FeGAC greatly improved the oxidative ability of H₂O₂ for the removal of CV.

3.3. Factors affecting removal efficiency

The treatment efficiencies of these five treatment processes at initial pH values of 3 and 6 are shown in Figs. 4 and 5, respectively. In general, the sequence of the removal efficiencies of these five treatment processes was FeGAC/H₂O₂ > GAC/H₂O₂, FeGAC, GAC > H₂O₂. For instance, at pH 3, the removal efficiencies of the FeGAC/H₂O₂, GAC/H₂O₂, FeGAC, GAC and H₂O₂ processes were approximately 71%, 42%, 41%, 42% and 9%, respectively (Fig. 4a) at 1.5 g adsorbent/L and 11.4 mM H₂O₂. FeGAC/H₂O₂ had a better removal efficiency at pH 3 (Fig. 4) than at pH 6 (Fig. 5). In addition, a higher dosage of FeGAC or GAC had a higher CV removal rate as well. The removal efficiencies for FeGAC/H₂O₂ significantly increased from 37% to 70% as the FeGAC increased from 1.0 to 1.5 g/L (Fig. 4a). In contrast, for the FeGAC system, the removal efficiencies only increased from 31% to 44% as the FeGAC dosage increased from 1.0 to 1.5 g/L.

For the FeGAC/H₂O₂ system, it seems that there was a minimum dosage (critical dosage) requirement for FeGAC for the catalytic reaction to be dominant or effective. This result is further illustrated in Fig. 6. As shown in Fig. 6a (H₂O₂ dosage 3.5 mM), at dosages of FeGAC lower than 1.3 g/L, the higher removal efficiencies occurred at high pH values and high FeGAC dosages. However, at higher FeGAC dosages (>1.3 g/L), the better removal efficiencies occurred at low pH values and high FeGAC dosages. When the H₂O₂ dosage increased from 3.5 to 7.4 to 11.6 mM, the critical FeGAC dosages decreased from 1.3 to 1.22 to 0.78 g/L, as shown in Fig. 6a–c, respectively. These figures also indicate that if the FeGAC dosages were higher than the corresponding critical values, the use of H₂O₂ would be much more efficient.

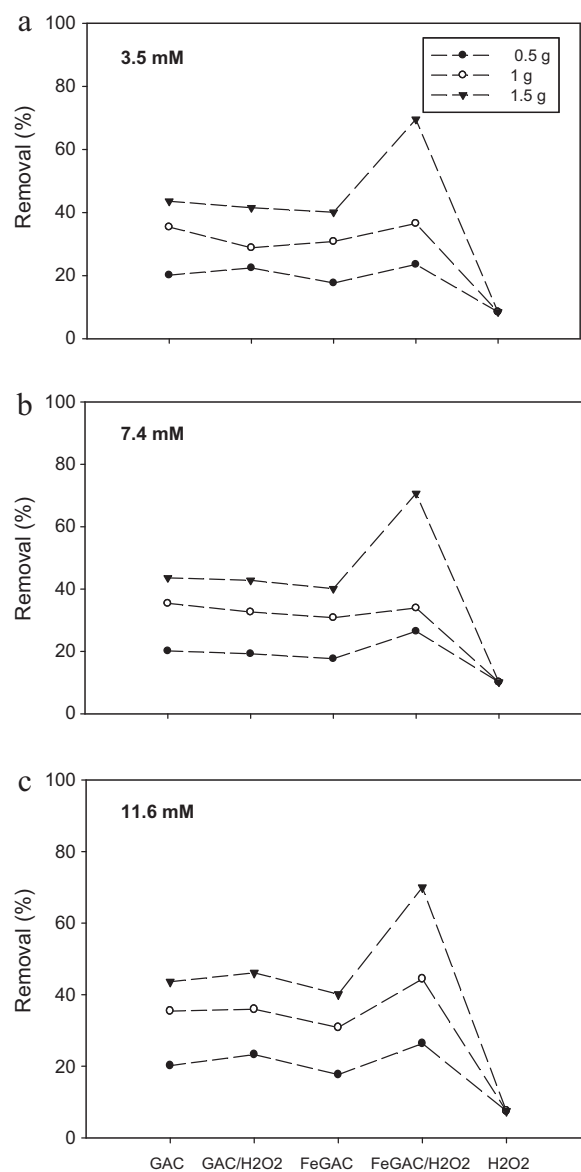


Fig. 4. CV removal efficiencies at pH 3 with various dosages of H₂O₂: (a) 3.5 mM, (b) 7.4 mM, and (c) 11.6 mM (CV = 10 mg/L, GAC or FeGAC dosage if added: ● 0.5 g/L, ○ 1.0 g/L, ▼ 1.5 g/L, 30 min).

It seems that there are two main different removal mechanisms. When the FeGAC dosage is lower than the critical value, the CV removal is mainly contributed by the adsorption process. The increased adsorption at the higher pH is due to the electrostatic attraction between the negatively charged sites of the adsorbents and the positively charged dye molecules. When the pH increased, the electrostatic attraction force of CV with FeGAC surface might increase as well. An increase of pH of the solution decreases the charge density, so the electrostatic repulsion between the positively charged dye and the surface of the adsorbent is lowered, which results in an increase in the extent of adsorption of CV. In addition, the decreased adsorption at the lower pH is probably due to the presence of excess H⁺ ions competing with the cation groups on the dye for adsorption sites on FeGAC surface. This result is in agreement with the findings of Monash and Pugazhenthii, Saeed et al. and Mittal et al., who have reported that MCM-41 [22], grapefruit peel [23] and bottom ash (BA) [24] had greater percentage adsorption of CV at the higher solution pH, respectively. On the other hand, when the FeGAC dosage is higher than the critical value,

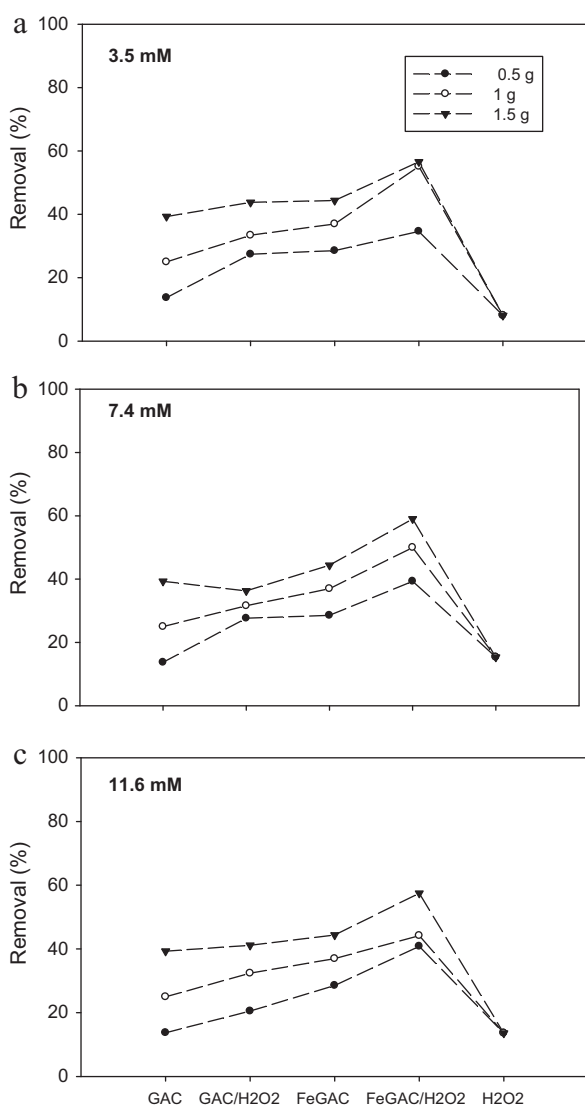


Fig. 5. CV removal efficiencies at pH 6 with various dosages of H₂O₂: (a) 3.5 mM, (b) 7.4 mM, and (c) 11.6 mM (CV = 10 mg/L, GAC or FeGAC dosage if added: ● 0.5 g/L, ○ 1.0 g/L, ▼ 1.5 g/L, 30 min).

the CV removal is mainly contributed by the catalytic reactions between FeGAC and H₂O₂. The better removal efficiencies occur at the lower solution pH. This result is in agreement with the removal of CV by Fenton and Fenton like processes [8].

3.4. Separation and identification of the intermediates

The experimental results indicated that CV could be removed efficiently by the FeGAC/H₂O₂ process, as shown in Fig. 7. The reaction intermediates were examined by HPLC using a photodiode array detector and ESI mass spectrometry. Six components (A–F) were observed and identified. The results of HPLC chromatograms, UV–vis spectra, and HPLC–ESI mass spectra are summarized in Table 1. Typical reaction intermediates observed by HPLC are shown in Fig. 8. Peak A is CV, and peaks B–F are reaction intermediates. The distributions of the intermediates are illustrated in Fig. 9. To minimize errors, the relative intensities of each intermediate were recorded at the maximum absorption wavelength of each intermediate.

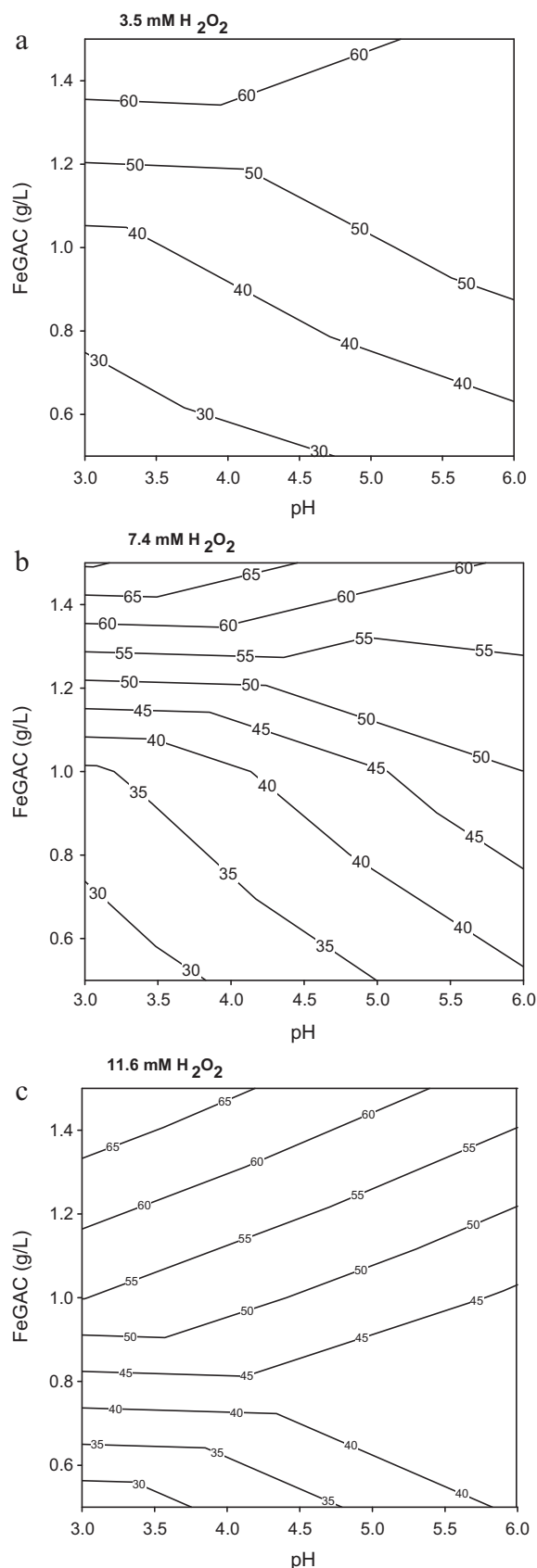


Fig. 6. CV removal efficiency contour map of pH and FeGAC dosages at (a) 3.5 mM, (b) 7.4 mM, and (c) 11.6 mM of H₂O₂.

Table 1
Reaction intermediates of CV by HPLC-ESI-MS.

HPLC peaks	De-methylation intermediates	ESI-MS spectrum ions (m/z)	Absorption maximum (nm)
A	<i>N,N,N',N',N'',N''</i> -hexaethylpararosaniline	372.18	588.5
B	<i>N,N</i> -dimethyl- <i>N',N'</i> -dimethyl- <i>N''</i> -methyl pararosaniline	358.14	581.2
C	<i>N,N</i> -dimethyl- <i>N'</i> -methyl- <i>N''</i> -methylpararosaniline	344.10	570.2
D	<i>N,N</i> -dimethyl- <i>N',N'</i> -dimethyl pararosaniline	334.09	579.8
E	<i>N</i> -methyl- <i>N'</i> -methyl- <i>N''</i> -methyl pararosaniline	336.36	566.3
F	<i>N,N</i> -dimethyl- <i>N'</i> -methylpararosaniline	336.10	570.0

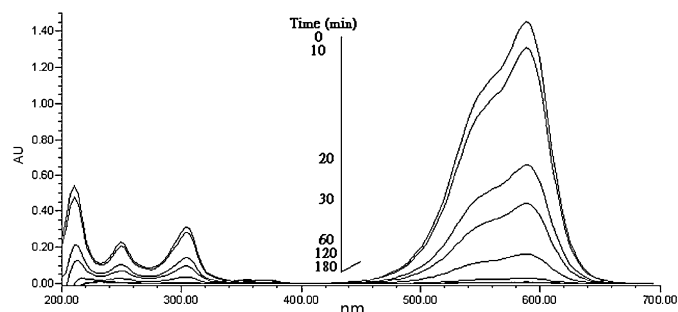


Fig. 7. The absorption spectra changes of CV by FeGAC/H₂O₂ as a function of time. Spectra from top to bottom correspond to a time of 0, 10, 20, 30, 60, 120, and 180 min, respectively.

3.5. Reaction pathways

There are two possible major competitive reaction pathways for degradation of TPM dyes: (1) *N*-demethylation and (2) cleavage of the CV chromophore ring structure [3,15,20]. Because compounds B–F were observed in this study, the *N*-demethylation might be the main degradation pathway for the FeGAC/H₂O₂ system, as shown in Fig. 10. In addition, there are two possible major competitive

reaction pathways for *N*-demethylation as well: (1) reaction with *N,N*-dimethyl groups (such as compounds D, F and H) and (2) reaction with *N*-methyl groups (compounds C, E and G) [6]. Considering that the *N,N*-dimethyl groups of compounds D, F and H are bulkier than those of the *N*-methyl groups of compounds C, E and G molecules, respectively, a nucleophilic attack by free radicals on the *N*-methyl groups might be favored over that on the *N,N*-dimethyl groups. However, considering that the attack probability on two *N,N*-dimethyl groups of compound D is higher than that on one *N,N*-dimethyl group in compound C molecules, the attack by free radicals on the *N,N*-dimethyl group might be favored over that on the *N*-methyl group. As shown in Fig. 9, compound C had a higher concentration and reached the maximum concentration sooner than that of compound D. This result indicates that the attack on the *N*-methyl groups (compound C) is significantly stronger than that on the *N,N*-dimethyl group (compound D).

This result suggests that the removal of CV was *N*-demethylated in a stepwise manner (i.e., methyl groups were removed one by one, as confirmed by the gradual peak wavelength shifts). This result is similar with Fenton and Fenton-like [8], and TiO₂/UV [9] processes for the removal of CV. Therefore, *N*-demethylation might be the dominating mechanism for the removal of CV by the FeGAC/H₂O₂ process. The cleavage of the CV chromophore ring structure is not the significant step. Based on these experimental results, reaction

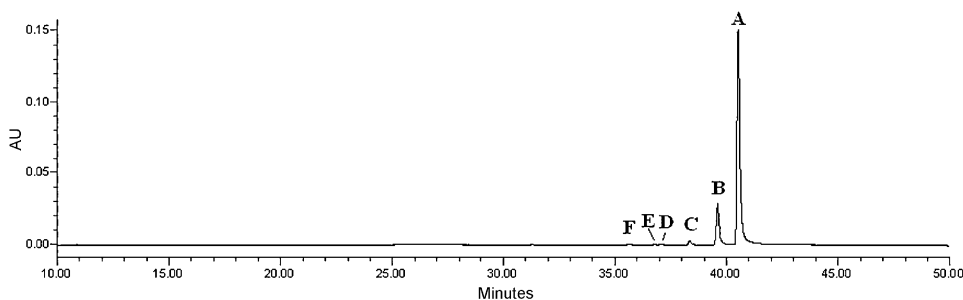


Fig. 8. HPLC chromatogram of the intermediates of the FeGAC/H₂O₂ reaction at pH 6, recorded at 580 nm.

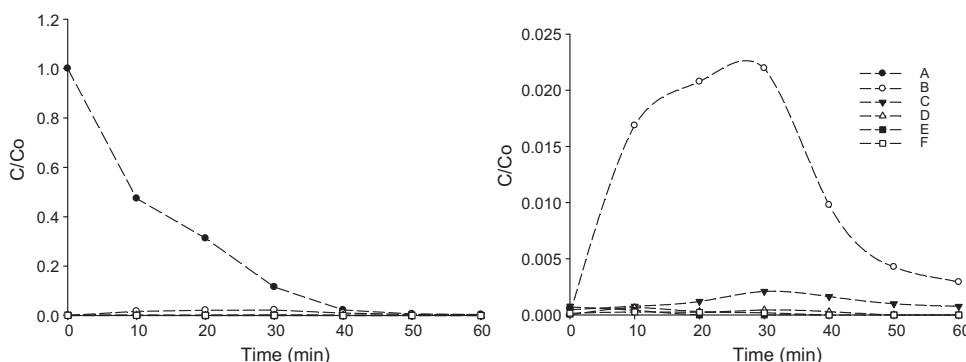


Fig. 9. Variations in the relative distribution of the intermediates for the FeGAC/H₂O₂ process.

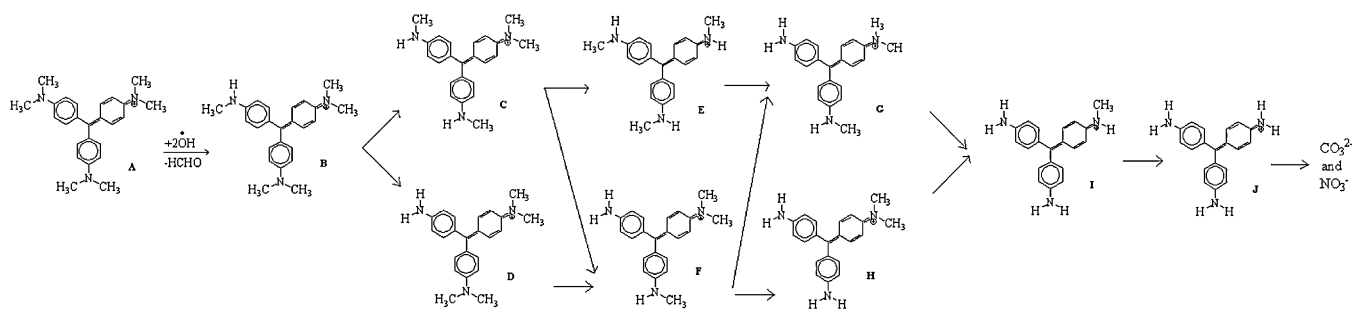


Fig. 10. Proposed pathways for the removal of CV by the FeGAC/H₂O₂ process.

pathways for the *N*-demethylation of CV are proposed and depicted in Fig. 10. This result is similar to the findings reported in literatures [8,9].

4. Conclusions

The FeGAC/H₂O₂ process could effectively remove CV in aqueous solutions. This process combined the advantages of both FeGAC and H₂O₂. In general, the removal efficiency sequence among the five processes tested was FeGAC/H₂O₂ > GAC/H₂O₂, FeGAC, and GAC > H₂O₂. The factors affecting the CV removal efficiencies included solution pH, FeGAC dosage, and H₂O₂ dosage. A minimum FeGAC dosage might be needed to sufficiently speed up the reaction process for the FeGAC/H₂O₂ processes. The reaction mechanisms of CV were proposed and discussed in this research. *N*-demethylation might be the main reaction pathway for the removal of CV from aqueous solutions.

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