Treatment of crystal violet and acid green 25 using Fenton process

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Abstract. The objective of this research was to investigate the application of the Fenton process for the degradation of cationic and anionic dyes, namely crystal violet (CV) and acid green 25 (AG 25), respectively. The operational parameters investigated were the effect of initial concentration of dye, effect of Fe²⁺ concentration, effect of H₂O₂ concentration, effect of solution pH and effect of solution matrix such as methanol (CH₃OH), ethanol (C₂H₅OH), oxalate (C₂O₄²⁻), chloride (Cl⁻), nitrate (NO₃⁻), sulfate (SO₄²⁻) and combined inorganic anion species. The mechanism for dyes removal was due to the generation of hydroxyl radicals (•OH) which are produced by the reaction of ferrous ion (Fe²⁺) and hydrogen peroxide (H₂O₂). The optimum conditions which achieved the highest degradation efficiency of 5 mg/L CV and 5 mg/L AG 25 were 5 mg/L Fe²⁺, 50 mg/L H₂O₂, initial solution pH 3 and room temperature. At 20 min of Fenton oxidative treatment, the degradation efficiencies of CV and AG 25 were 99.67% and 97.17%, respectively. Presence of CH₃OH, C₂H₅OH and C₂O₄²⁻ significantly decreased the degradation efficiency of CV as compared to presence of other solution matrix and combined species. Interestingly, the addition of organic solvent namely CH₃OH had resulted in increased degradation efficiency of AG 25 instead of inhibiting the degradation reaction. Kinetic rate constant of reaction (k) and coefficient of determination (R²) for the optimum experimental conditions for the degradation of CV and AG 25 were 0.1415 m⁻¹ and 0.9819 (first-order reaction) and 0.3517 L·mg⁻¹·min⁻¹ and 0.9756 (second-order reaction), respectively.

1. Introduction

Industrialization is important for the economic development in all countries in the world. However, in recent years, a lot of industries have been discharging wastewaters without adequate treatment and hence, the wastewaters contain various chemical constituents. Thus, this has resulted in severe environmental pollution and health problems. The wastewaters usually contain colour, chemical oxygen demand (COD), biochemical oxygen demand (BOD), recalcitrant organic compounds, and heavy metals such as chromium (Cr), zinc (Zn), arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg) and nickel (Ni). Among the different types of pollutants in water and wastewater, dye is a major type of pollutant which needs to be appropriately addressed.
Crystal violet (CV) (a cationic dye) is a type of triphenylmethane dye, which is widely employed in the textile processing industry for dying nylon, polyacrylonitrile modified nylon, wool, silk and cotton [1]. CV has been reported to be a mitotic poisoning agent, clastogen, and also a biohazard substance [2]. Furthermore, CV is a recalcitrant pollutant, i.e. it is difficult to be metabolized by microorganisms [3]. As a result, it is persistent in the environment. In addition, conventional biological wastewater treatment systems are found to be ineffective in treating CV, and thus, it may cause serious contamination in water.

Acid green 25 (AG 25) is an anthraquinonic anionic dye which is characterized by the two sulfonic groups and two azoic groups [4]. AG 25 is commonly used in the textile processing industry, hair dying formulation and cosmetic product. AG 25 is not easy to decompose in water at 20°C for up to 7 days [5]. Thus, this dye will potentially harm aquatic organisms and plants for a long period of time.

Fenton process is one of the advanced oxidation processes (AOPs) which can effectively oxidize non-biodegradable and toxic organic compounds. In Fenton reaction, the hydroxyl radical (•OH) can be produced when the ferrous ion (Fe²⁺) reacts with hydrogen peroxide (H₂O₂) [6]. The hydroxyl radical from Fenton reaction can effectively degrade many types of recalcitrant organic pollutants (including dyes) as it is non-selective and very reactive species which can completely oxidize the organic pollutants into carbon dioxide and water. In general, the main operating parameters in a Fenton process are pH, temperature, Fe²⁺ concentration, H₂O₂ concentration and the concentration of organic pollutants. The effects of these parameters may be affected by •OH scavengers, thus reducing the Fenton’s process degradation efficiency. In real wastewaters, effluents are likely to contain organic solvents and inorganic salts such as Cl⁻, NO₃⁻ and SO₄²⁻ ions. Thus, it is important to evaluate the effect of solution matrix.

In the present study, the main objective was to determine the degradation efficiency of CV (cationic dye) and AG 25 (anionic dye) by using the Fenton oxidation process. The influences of different operational parameters (dye concentration, Fe²⁺ concentration, H₂O₂ and initial solution pH) and solution matrix (CH₃OH, C₂H₅OH, C₂O₄²⁻, Cl⁻, NO₃⁻, SO₄²⁻, and combined ions) on the degradation efficiency of CV and AG 25 were investigated. Finally, the kinetic rate constants as determined from the zero-order kinetic model, first-order kinetic model and second-order kinetic model were compared.

2. Experimental

2.1. Chemicals

The dyes used were CV (Bendosen Limited) and AG 25 (Aldrich Chemistry). The chemicals used were FeSO₄•7H₂O (Bendosen Limited), H₂O₂ (30%) (ChemSoln), NaOH (R&M Chemicals), HCl (Friedemann Schmidt), methanol (ChemSoln), ethanol (John Kollin Chemicals), sodium oxalate (R&M chemicals), sodium chloride (Gene Chemical), sodium nitrate (Merck Millipore) and sodium sulfate (ChemSoln).

2.2. Analytical

The aqueous concentrations of CV and AG 25 were determined using the UV-Visible spectrophotometer. The wavelength of maximum absorbance for CV is 583 nm [7]. The wavelength of maximum absorbance for AG 25 is 642 nm [8]. A magnetic stirrer was used for stirring the dye solution. pH adjustment was carried out by using 0.1 M HCl and/or 0.1 M NaOH and the solution pH was analyzed using pH meter (Mettler Toledo). The degradation efficiency of the dyes was calculated according to Equation (1).

\[
\text{Degradation efficiency} = \left( \frac{C_o - C_t}{C_o} \right) \times 100 \%
\]  

(1)

where \( C_o \) is the initial concentration of dye (mg/L), and \( C_t \) is concentration of dye at reaction time \( t \) (mg/L).
2.3. Experimental procedures
All experiments were performed at room temperature using 500 mL of dye solutions. Appropriate amounts of Fe$^{2+}$ and H$_2$O$_2$ were added into the dye solutions. A magnetic stirrer provided continuous mixing for 20 min of reaction time. Samples were collected at pre-determined reaction time and were immediately added with small volumes of solutions containing high concentrations of methanol and oxalate (for the experiment of CV and AG 25, respectively) in order to stop Fenton reaction, prior to analyzing.

3. Results and discussion
3.1. Degradation of CV

3.1.1. Effect of initial dye concentration

Figure 1. Effect of initial dye concentration on the degradation of CV (Experimental details: solution volume = 500 mL, concentration of Fe$^{2+}$ = 5 mg/L, concentration of H$_2$O$_2$ = 50 mg/L, solution pH = 3 ± 0.2).

Figure 1 shows the effect of initial dye concentration on the degradation of CV. The degradation efficiency of CV decreased from 99.67% to 17.45% when the initial CV concentration was increased from 5 mg/L to 100 mg/L at the conditions of 5 mg/L Fe$^{2+}$ and 50 mg/L H$_2$O$_2$ at pH 3. Control studies (i.e. without Fe$^{2+}$ and without H$_2$O$_2$) confirmed that the degradation of CV was negligible. According to Jana et al. [9], 200 mg/L CV was reduced to 15 mg/L in 20 min of Fenton reaction at the conditions of 1000 mg/L H$_2$O$_2$ and 150 mg/L FeSO$_4$$\cdot$7H$_2$O. Hameed and Lee [10] studied the effect of initial concentration of malachite green (20, 45, 80, and 100 mg/L) using Fenton reaction. They found that the degradation efficiency was 96% at 35 min when the initial concentration was 20 mg/L. Meanwhile, when the initial concentration was 45, 80, and 100 mg/L, the degradation efficiencies were 47.23%, 32.07% and 10.02%, respectively, within 20 min of treatment. Theoretically, with increasing dye concentration (at fixed concentrations of H$_2$O$_2$ and Fe$^{2+}$), the efficiency of dye removal will decrease. This is because the •OH radicals in the solutions are insufficient to degrade higher concentrations of CV.
3.1.2. Effect of Fe$^{2+}$ concentration

Figure 2. Effect of Fe$^{2+}$ concentration on the degradation of CV (Experimental details: solution volume = 500 mL, initial concentration CV = 5 mg/L, concentration of H$_2$O$_2$ = 50 mg/L, solution pH = 3 ± 0.2).

Figure 2 depicts the effect of Fe$^{2+}$ concentration on the degradation of CV. Presence of 5 mg/L and 25 mg/L Fe$^{2+}$ had resulted in CV degradation of 99.67% and 100%, respectively. Meanwhile, addition of 1 mg/L of Fe$^{2+}$ concentration only resulted in 23.73% of CV removal in 20 min. Besides, when the concentration ratio of Fe$^{2+}$: H$_2$O$_2$ was 1:50, 1:10 and 1:2 (at the 4 min treatment time of Fenton oxidative treatment), the CV degradation efficiency was 15.49%, 87.01% and 92.63%, respectively. Similar trend on the effect of Fe$^{2+}$ concentration was reported whereby the removal efficiency of methyl orange was increased from 27.59% to 90.12%, when the concentration of FeSO$_4$ was increased from 0.035 mM to 0.19 mM (at the 15 min of Fenton treatment and initial solution pH 3) [11].

3.1.3. Effect of H$_2$O$_2$ concentration

Figure 3. Effect of H$_2$O$_2$ concentration on the degradation of CV (Experimental details: solution volume = 500 mL, initial concentration CV = 5 mg/L, concentration of Fe$^{2+}$ = 5 mg/L, solution pH = 3 ± 0.2).

Figure 3 shows the effect of H$_2$O$_2$ concentration on the degradation of CV. The degradation efficiencies of CV at the end of 20 min of Fenton treatment were 93.50%, 95.67% and 95.69%, for the conditions of 30 mg/L H$_2$O$_2$, 50 mg/L H$_2$O$_2$ and 70 mg/L H$_2$O$_2$, respectively. The result is attributed to the increase in •OH radicals as generated by the additional H$_2$O$_2$. However, there was no significant improvement in Fenton reaction by increasing the concentration of H$_2$O$_2$. This indicates that there should be an optimum H$_2$O$_2$ concentration. From the studies of Wang [12] and Sun et al. [13], the degradation efficiency of dye was increased with increasing concentration of H$_2$O$_2$ until the critical value of H$_2$O$_2$ was met for different types of dyes.
3.1.4. Effect of solution pH

![Figure 4](image)

**Figure 4.** Effect of solution pH on the degradation of CV (Experimental details: solution volume = 500 mL, initial concentration CV = 5 mg/L, concentration of Fe²⁺ = 5 mg/L, concentration of H₂O₂ = 50 mg/L).

Figure 4 depicts the effect of solution pH on the degradation of CV. Solution pH has a major effect on the efficiency of Fenton’s treatment as it can significantly affect the amount of •OH generation. The preferable condition for •OH generation is under acidic conditions [14]. At 20 min of Fenton treatment, the degradation efficiencies of CV were 99.67% (pH 3), 91.91% (pH 4) and 73.73% (pH 5). According to a study conducted by Saatci [15], the optimal pH value was pH 3 which yielded 96% degradation efficiency of 180 mg/L Remazol red F3B within 40 min of treatment time. At above pH 4, the degradation efficiency decreased as the catalyst would start to form hydroxide precipitates. In short, our results are in agreement with the other researchers, and the highest efficiency of CV removal was achieved at solution pH 3.

3.1.5. Effect of solution matrix

3.1.5.1. Effect of CH₃OH

![Figure 5](image)

**Figure 5.** Effect of CH₃OH on the degradation of CV (Experimental details: solution volume = 500 mL, initial concentration CV = 5 mg/L, concentration of Fe²⁺ = 5 mg/L, concentration of H₂O₂ = 50 mg/L, solution pH: 3 ± 0.2).

Figure 5 shows the effect of CH₃OH on the degradation of CV. It is evident that presence of 1 mg/L CH₃OH had less inhibiting effect on CV degradation as compared to the presence of 25 mg/L CH₃OH. Removal efficiencies of CV were 86.64% and 45.35%, respectively, when the concentration of CH₃OH was increased from 1 mg/L to 25 mg/L. Devi et al. [16] stated that methanol reacts with •OH and hydrogen radical, with second-order rate constants of 9.7 x 10⁸ mol⁻¹s⁻¹ and 2.6 x 10⁶ mol⁻¹s⁻¹, as shown in Equations (2) and (3). Thus, CH₃OH can act as a strong competitive species to inhibit the degradation efficiency of CV.
\[
\text{CH}_3\text{OH} + \cdot\text{OH} \rightarrow \text{CH}_3\text{O}• + \text{H}_2\text{O}
\]
\[
\text{CH}_3\text{OH} + \cdot\text{H} \rightarrow \text{CH}_3\text{O}• + \text{H}_2
\]

3.1.5.2. Effect of \(\text{C}_2\text{H}_5\text{OH}\)

![Figure 6](image)

Figure 6. Effect of \(\text{C}_2\text{H}_5\text{OH}\) on the degradation of CV (Experimental details: solution volume = 500 mL, initial concentration CV = 5 mg/L, concentration of \(\text{Fe}^{2+}\) = 5 mg/L, concentration of \(\text{H}_2\text{O}_2\) = 50 mg/L, solution pH: 3 ± 0.2).

Figure 6 shows the effect of \(\text{C}_2\text{H}_5\text{OH}\) on the degradation of CV. Overall, \(\text{C}_2\text{H}_5\text{OH}\) inhibited the degradation efficiency of CV. At low concentration (i.e. 1 mg/L), the degradation efficiency of CV was 72.17% and 85.03% at 4 min and 14 min, respectively. Meanwhile, presence of high concentration of \(\text{C}_2\text{H}_5\text{OH}\) (i.e. 25 mg/L) significantly inhibit the removal of CV, whereby the degradation efficiencies were only 14.99% (at 4 min) and 17.39% (at 14 min). At the end of the 20 min Fenton reaction, the degradation efficiency was 89.76% (presence of 1 mg/L \(\text{C}_2\text{H}_5\text{OH}\)) and 21.33% (presence of 25 mg/L \(\text{C}_2\text{H}_5\text{OH}\)). In the case without \(\text{C}_2\text{H}_5\text{OH}\), the final degradation efficiency was 99.67%. This shows that organic solvent can scavenge the •OH radicals and thus decrease the CV degradation.

3.1.5.3. Effect of oxalate

![Figure 7](image)

Figure 7. Effect of \(\text{C}_2\text{O}_4^{2–}\) on the degradation of CV (Experimental details: solution volume = 500 mL, initial concentration CV = 5 mg/L, concentration of \(\text{Fe}^{2+}\) = 5 mg/L, concentration of \(\text{H}_2\text{O}_2\) = 50 mg/L, solution pH = 3 ± 0.2).

Figure 7 shows the effect of \(\text{C}_2\text{O}_4^{2–}\) on the degradation of CV. In the presence of 1 mg/L of \(\text{C}_2\text{O}_4^{2–}\) and 25 mg/L of \(\text{C}_2\text{O}_4^{2–}\), 85.18% and 29.53% of CV degradation efficiencies were achieved, respectively, for a 20 min treatment time of Fenton reaction. In the case without oxalate, the degradation efficiency of CV was 99.67%. The oxalate species not only inhibit the initial degradation efficiency, but also throughout the whole degradation process. This shows that \(\text{C}_2\text{O}_4^{2–}\) acts a strong competitive species for •OH radicals during the Fenton reaction.
3.1.5.4. Effect of chloride

Figure 8. Effect of Cl$^-$ on the degradation of CV (Experimental details: solution volume = 500 mL, initial concentration CV = 5 mg/L, concentration of Fe$^{2+}$ = 5 mg/L, concentration of H$_2$O$_2$ = 50 mg/L, solution pH = 3 ± 0.2).

Figure 8 shows the effect of Cl$^-$ on the degradation of CV. 96.78% and 87.61% of CV degradation efficiencies were achieved when 1 mg/L and 25 mg/L of Cl$^-$ were present in the solution, respectively. According to Alshamsi et al. [17], around 50% of CV was degraded in 1 min, whereas the addition of Cl$^-$ negatively affected the degradation rate. Malik and Saha [18] reported that presence of Cl$^-$ can reduce the degradation efficiency of Blue 2B (B54) and Red 12B (R31) as Cl$^-$ can scavenge •OH according to Equation (4). Meanwhile, according to Equation (5), the formed ClOH$^-$ will react with Fe$^{2+}$ to form Cl$^-$, thus the scavenging of •OH will continue to further inhibit the degradation efficiency of CV.

\[
\text{Cl}^- + \cdot\text{OH} \rightarrow \text{ClOH}^- \tag{4}
\]

\[
\text{ClOH}^- + \text{Fe}^{2+} \rightarrow \text{Cl}^- + \text{OH}^- + \text{Fe}^{3+} \tag{5}
\]

3.1.5.5. Effect of nitrate

Figure 9. Effect of NO$_3^-$ on the degradation of CV (Experimental details: solution volume = 500 mL, initial concentration CV = 5 mg/L, concentration of Fe$^{2+}$ = 5 mg/L, concentration of H$_2$O$_2$ = 50 mg/L, solution pH = 3 ± 0.2).

Figure 9 depicts the effect of NO$_3^-$ on the degradation of CV. Presence of NO$_3^-$ ions had minor inhibitory effects on the degradation efficiency of CV by Fenton reaction when at low concentration (1 mg/L NO$_3^-$) and also at high concentration (25 mg/L NO$_3^-$). After 20 minutes of Fenton oxidation, presences of 1 mg/L and 25 mg/L NO$_3^-$ resulted in 97.33% and 96.11% degradation efficiencies of CV, respectively. As a comparison, the degradation efficiency of CV was 99.67% for the case without NO$_3^-$. The minor negative effect on the CV removal was likely to be due to the formation of inorganic radicals and the scavenging of •OH.
3.1.5.6. Effect of sulfate

![Figure 10](image)

**Figure 10.** Effect of SO$_4^{2-}$ on the degradation of CV (Experimental details: solution volume = 500 mL, initial concentration CV = 5 mg/L, concentration of Fe$^{2+}$ = 5 mg/L, concentration of H$_2$O$_2$ = 50 mg/L, solution pH = 3 ± 0.2).

Figure 10 shows the effect of SO$_4^{2-}$ on the degradation of CV. The degradation efficiency of CV after 20 min of Fenton reaction decreased from 99.67% (without SO$_4^{2-}$) to about 95.01% (in the presence of 1 mg/L SO$_4^{2-}$) and 95.56% (in the presence of 25 mg/L SO$_4^{2-}$). This corresponds to around 4-5% of lost in the degradation efficiency for CV. According to Alshamsi et al. [17], all the sodium salts such as Cl$^-$, SO$_4^{2-}$ and HPO$_4^{2-}$ had minor negative effect on degradation of CV. For complicated solution matrix, the efficiency of dye removal was decreased due to the formation of scavengers of •OH and less reactive inorganic radicals (such as •SO$_4^{2-}$) as shown in the Equations (6) to (8) [19].

\[
\begin{align*}
H^+ + SO_4^{2-} &\leftrightarrow HSO_4^- \quad (6) \\
H_2SO_4 + \cdot OH &\rightarrow \cdot SO_4^- + H^+ + H_2O \quad (7) \\
H_2SO_4^- + \cdot OH &\rightarrow \cdot SO_4^- + H_2O \quad (8)
\end{align*}
\]

3.1.5.7. Effect of combined anion species

![Figure 11](image)

**Figure 11.** Effect of combined species on the degradation of CV (Experimental detail: solution volume = 500 mL, initial concentration CV = 5 mg/L, concentration of Fe$^{2+}$ = 5 mg/L, concentration of H$_2$O$_2$ = 50 mg/L, solution pH = 3 ± 0.2).

Figure 11 shows the effect of combined species on the degradation of CV. The selected dual species were Cl$^-$ and NO$_3^-$, and the selected triple species were Cl$^-$, NO$_3^-$ and SO$_4^{2-}$. CV degradation efficiency was noticeably affected with the presence of dual species and triples species. In the case without inorganic ions, the degradation efficiency was 99.67%. Presence of dual species and triple species resulted in degradation efficiencies of 94.78% and 93.91%, respectively. In short, triple species demonstrated slightly more inhibitory effect on CV than dual species, as the effect of •OH scavenging was comparatively higher.
3.2. Degradation of AG 25

3.2.1. Effect of initial dye concentration

Figure 12. Effect of initial dye concentration on the degradation of AG 25 (Experimental details: solution volume = 500 mL, concentration of Fe$^{2+}$ = 5 mg/L, concentration of H$_2$O$_2$ = 50 mg/L, solution pH = 3 ± 0.2).

Figure 12 depicts the effect of initial dye concentration on the degradation of AG 25. The degradation efficiencies of AG 25 were 97.17%, 97.48%, 88.06% and 68.54% when the corresponding dye concentrations were 5, 10, 50 and 100 mg/L, respectively. Besides, the control study showed that reaction of Fenton oxidation did not occur when either one of the essential chemicals such as Fe$^{2+}$ or H$_2$O$_2$ was not added (i.e. the degradation efficiency was almost zero). When the concentration of AG 25 was increased, the degradation efficiency of AG 25 decreased as the amount of •OH radicals were not increased. Modirshahla et al. [20] reported that when the initial Acid Yellow 23 concentration was increased from 5 mg/L to 60 mg/L, the degradation efficiency in Fenton and photo-Fenton processes decreased. Importantly, comparison with the CV results yielded interesting findings. When 50 mg/L and 100 mg/L of AG 25 were used as the initial dye concentration, the degradation of AG 25 could proceed until 88% and 69% degradation efficiency, respectively. However, when CV was the target pollutant, the degradation efficiency was only about 17% and 28%, respectively. This seems to suggest that the degradation efficiency for AG 25 may be generally better as compared to CV, at higher concentration of dyes.

3.2.2. Effect of Fe$^{2+}$ concentration

Figure 13. Effect of Fe$^{2+}$ concentration on the degradation of AG 25 (Experimental details: solution volume = 500 mL, initial concentration AG 25 = 5 mg/L, concentration of H$_2$O$_2$ = 50 mg/L, solution pH = 3 ± 0.2).

Figure 13 shows the effect of Fe$^{2+}$ concentration on the degradation of AG 25. The degradation efficiencies of AG 25 were 94.63% and 97.42% when 1 mg/L and 25 mg/L of Fe$^{2+}$ were present in the
dye solution, respectively. As a comparison, the degradation efficiency was 97.17% in the presence of 5 mg/L of Fe$^{2+}$. This results clearly show the trend of increasing dye removal efficiency with increasing Fe$^{2+}$ concentration. Importantly, Fe$^{2+}$ catalyst concentration did not significantly affect the degradation efficiency of AG 25 as compared with CV. It was reported that the removal of Acid Green 1 was increased as the ratio of Fe:H$_2$O$_2$ was increased from 1:10 to 2:10 and to 3:10 (i.e. the quantity of Fe catalyst increased with constant H$_2$O$_2$) [21]. According to Ghaly et al. [22], 75 mg/L Fe$^{2+}$ resulted in the lowest dye removal compared with other larger quantities of Fe$^{2+}$ added because fewer •OH radicals were available for oxidation.

3.2.3. Effect of H$_2$O$_2$ concentration

Figure 14. Effect of H$_2$O$_2$ concentration on the degradation of AG 25 (Experimental details: solution volume = 500 mL, initial concentration AG 25 = 5 mg/L, concentration of Fe$^{2+}$ = 5 mg/L, solution pH = 3 ± 0.2).

Figure 14 depicts the effect of H$_2$O$_2$ concentration on the degradation of AG 25. When the H$_2$O$_2$ concentration were 50 mg/L and 70 mg/L, the degradation efficiencies AG 25 were 92.63% and 93.26%, respectively. This implies that 50 mg/L H$_2$O$_2$ was sufficient for AG 25 degradation in this study as the higher 70 mg/L did not yield significant difference in the oxidation of AG 25. Theoretically, the insignificant improvement at the higher concentration of H$_2$O$_2$ may likely be attributed to the recombination of •OH. Thasilu and Karthikeyan [21] revealed that the removal of CI Acid Green 1 could eventually increase to 84% as Fe: H$_2$O$_2$ ratio was increased from 2:5 to 2:50 (at constant concentration of Fe$^{2+}$). In general, the degradation efficiency of dyes will increase with the increase of H$_2$O$_2$ concentration, but there is usually an optimum H$_2$O$_2$ concentration.

3.2.4. Effect of solution pH

Figure 15. Effect of solution pH on the degradation of AG 25 (Experimental details: solution volume = 500 mL, initial concentration AG 25 = 5 mg/L, concentration of Fe$^{2+}$ = 5 mg/L, concentration of H$_2$O$_2$ = 50 mg/L).
Figure 15 shows the effect of solution pH on the degradation efficiency of AG 25. Degradation efficiency of AG 25 was significantly reduced from 97.17% to 35.47% and to 4.28% when the solution pH was 3, 4 and 5, respectively. Importantly, AG 25 degradation efficiency was predominantly lower at the solution pH of 4 and 5 as compared to the case of CV degradation. Thasilu and Karthikeyan [21] investigated the effect of solution pH from pH 3 to pH 12 and they found that the maximum degradation efficiency of AG 1 was 85% (occurred at pH 3) and the minimum degradation efficiency of AG 1 was 2% (occurred at pH 8). There are some reasons which account for the decrease of degradation efficiency with increasing pH (i.e. when solution pH is higher than 3). Firstly, at higher solution pH, the degradation activity of Fenton may be reduced due to the occurrence of relatively inactive iron oxohydroxides and of ferric hydroxide precipitate [23]. Due to the less available iron ions for Fenton reaction, thus hydroxyl radicals (•OH) are generated in less amount. Secondly, the oxidation potential of hydroxyl radicals decreases with increasing pH. It has been revealed that the oxidation potential for the redox couple •OH/H₂O to be 2.59 V vs. normal hydrogen electrode (NHE) at pH 0 and 1.64 V vs. NHE at pH 14 [24]. There are some reasons which led to significant reduction in degradation efficiency of AG 25 at pH 4 and almost complete inhibition of AG 25 removal at solution pH 5. One main reason is the characteristics of AG 25. As an anionic dye, AG 25 will tend to have higher electrostatic repulsion with the kaolin at higher solution pH. Another possible reason may be due to the fact that AG 25 used contained some amount of impurities (dye content ≥ 60%). Thus, more investigation could be conducted in the future to confirm the underlying oxidation mechanism.

3.2.5. Effect of solution matrix

3.2.5.1. Effect of CH₃OH

![Figure 16. Effect of CH₃OH on the degradation of AG 25 (Experimental details: solution volume = 500 mL, initial concentration AG 25 = 5 mg/L, concentration of Fe²⁺ = 5 mg/L, concentration of H₂O₂ = 50 mg/L, solution pH = 3 ± 0.2).](image)

Figure 16 depicts the effect of CH₃OH on the degradation of AG 25. At 1 min of Fenton reaction, the presence of 25 mg/L CH₃OH resulted in a higher degradation efficiency of AG 25 (93.91%) as compared to the case of solution without CH₃OH (86.4%). This may be due to the fact that the used chemical AG 25 contains impurities. CH₃OH is an organic molecule which is well known to be an effective •OH scavenger. Thus, it is anticipated that the presence of CH₃OH will result in a marked decrease in degradation efficiency of many organic pollutants. Our results therefore suggest that the unknown impurities in the CH₃OH may have participated in some form of chemical reactions which may somehow enhanced the Fenton reaction.
3.2.5.2. Effect of C$_2$H$_5$OH

Figure 17. Effect of C$_2$H$_5$OH on the degradation of AG 25 (Experimental details: solution volume = 500 mL, initial concentration AG 25 = 5 mg/L, concentration of Fe$^{2+}$ = 5 mg/L, concentration of H$_2$O$_2$ = 50 mg/L, solution pH = 3 ± 0.2).

Figure 17 shows the effect of C$_2$H$_5$OH on the degradation of AG 25. Presence of 1 mg/L and 25 mg/L of C$_2$H$_5$OH resulted in AG 25 degradation efficiency of 94.89% and 94.17%, respectively. In the earlier Fenton treatment time (i.e. below 5 min), it is evident that 25 mg/L of C$_2$H$_5$OH could decrease the degradation efficiency of AG 25 as compared to the case of without C$_2$H$_5$OH. The decrease in degradation efficiency of AG 25 is most likely be attributed to the fact that C$_2$H$_5$OH had scavenged some •OH radicals in the dye solution.

3.2.5.3. Effect of oxalate

Figure 18. Effect of C$_2$O$_4^{2-}$ on the degradation of AG 25 (Experimental details: solution volume = 500 mL, initial concentration AG 25 = 5 mg/L, concentration of Fe$^{2+}$ = 5 mg/L, concentration of H$_2$O$_2$ = 50 mg/L, solution pH = 3 ± 0.2).

Figure 18 shows the effect of C$_2$O$_4^{2-}$ on the degradation of AG 25. The degradation efficiency of AG 25 was significantly reduced to 24.98%, when high concentration of C$_2$O$_4^{2-}$ (i.e. 25 mg/L) was present in the dye solution. Interestingly, at lower concentration of C$_2$O$_4^{2-}$ (i.e. 1 mg/L), the inhibitory effect of C$_2$O$_4^{2-}$ only affected the degradation of AG 25 in the early treatment time of Fenton reaction (i.e. time less than 5 min). After 5 min, the degradation process of AG 25 could continue to almost completion. In comparison, the presence of 1 mg/L of C$_2$O$_4^{2-}$ noticeably decreased the overall degradation efficiency of CV. This suggests that the chemical properties of cationic and anionic dyes could have contributed to the difference in the initial Fenton reaction performance, as influenced by the presence of C$_2$O$_4^{2-}$. 

3.2.5.4. Effect of chloride

Figure 19. Effect of Cl$^-$ on the degradation of AG 25 (Experimental details: solution volume = 500 mL, initial concentration AG 25 = 5 mg/L, concentration of Fe$^{2+}$ = 5 mg/L, concentration of H$_2$O$_2$ = 50 mg/L, solution pH = 3 ± 0.2).

Figure 19 shows the effect of Cl$^-$ on the degradation of AG 25. At 20 min Fenton treatment time, the degradation efficiency of about 92-93% was achieved in the presence of low concentration and high concentration of Cl$^-$. In comparison, the degradation efficiency was 97.17% in the case without Cl$^-$. However, in the early stages of Fenton treatment (i.e. time less than 8 min), the effect of Cl$^-$ was generally more pronounced (especially for the case of 25 mg/L of Cl$^-$). This is due to the formation of inorganic radicals generated during Fenton reaction. Generally, our results suggest that sufficient time of Fenton treatment can overcome the detrimental effects of chloride in the dye solution. Meanwhile, other researchers have also revealed the effects of Cl$^-$ in inhibiting the dye degradation efficiency. According to Modirshahla et al. [20], presence of 250 mg/L of NaCl decreased the degradation efficiency of Acid Yellow 23 dye from 97% (without NaCl) to 95% within 60 min of reaction. Meanwhile, increasing the concentration of Cl$^-$ from 3 mM up to 600 mM had resulted in the degradation of Direct Red 81 dye to be reduced from 91% to 34% at 20 min of reaction [19].

3.2.5.5. Effect of nitrate

Figure 20. Effect of NO$_3^-$ on the degradation of AG 25 (Experimental details: solution volume = 500 mL, initial concentration AG 25 = 5 mg/L, concentration of Fe$^{2+}$ = 5 mg/L, concentration of H$_2$O$_2$ = 50 mg/L, solution pH = 3 ± 0.2).

Figure 20 depicts the effect of NO$_3^-$ on the degradation of AG 25. About 95-97% of AG 25 removal was achieved after 20 min of Fenton reaction. Apparently, NO$_3^-$ ions had little inhibitory effects on AG 25 degradation by Fenton reaction, for low concentration (1 mg/L NO$_3^-$) up to high concentration (25 mg/L NO$_3^-$). Interestingly, similar with the case of Cl$^-$, the initial degradation efficiency of AG 25 was reduced...
considerably, as this is due to the formation of inorganic radicals and scavenging of •OH. However, after 8 min of Fenton treatment, the effects of NO$_3^-$ was almost insignificant. Thus, the detrimental effect of NO$_3^-$ is not too much of concern in degradation of AG 25, as the Fenton reaction could still be occurring quite efficiently.

3.2.5.6. Effect of sulfate

Figure 21. Effect of SO$_4^{2-}$ on the degradation of AG 25 (Experimental details: solution volume = 500 mL, initial concentration AG 25 = 5 mg/L, concentration of Fe$^{2+}$ = 5 mg/L, concentration of H$_2$O$_2$ = 50 mg/L, solution pH = 3 ± 0.2).

Figure 21 shows the effect of SO$_4^{2-}$ on the degradation of AG 25. Presence of low and high concentration of SO$_4^{2-}$ resulted in AG 25 degradation efficiencies of 94.96% and 94.38%, respectively. In comparison, the degradation efficiency of AG 25 in the absence of SO$_4^{2-}$ was 97.17%. This reduction of about 2% on the degradation efficiency of AG 25 is not significant. Similarly with Cl$^-$ and NO$_3^-$, the presence of SO$_4^{2-}$ reduced the AG 25 degradation efficiency due to the generation of less reactive inorganic radicals and scavenger of •OH. It has been revealed that when the concentration of SO$_4^{2-}$ was increased to 30 mM, the negative effects on the degradation efficiency of Direct Red 81 were not too obvious [19]. However, when the SO$_4^{2-}$ was present in high concentration (100 mM to 200 mM), significant differences can be observed in the Direct Red 81 dye removal efficiency.

3.2.5.7. Effect of combined anion species

Figure 22. Effect of combined species on the degradation of AG 25 (Experimental details: solution volume = 500 mL, initial concentration AG 25 = 5 mg/L, concentration of Fe$^{2+}$ = 5 mg/L, concentration of H$_2$O$_2$ = 50 mg/L, solution pH = 3 ± 0.2).

Figure 22 shows the effect of combined species on the degradation of AG 25. The degradation efficiency of AG 25 was decreased from 95.90% to 93.78% when the inorganic species was increased from dual species (Cl$^-$ and NO$_3^-$) to triple species (Cl$^-$, NO$_3^-$ and SO$_4^{2-}$). In comparison, the effect of triple species was slightly more evident on the degradation efficiency of AG 25 as compared to CV. Inorganic ions may
impair the reactivity of Fe\textsuperscript{2+} catalyst [19]. This suggests that the effect of competitive inhibition may be potentially increased when there are more competitive species present in the solution.

3.3. Kinetic study

The results of the kinetic study can be analyzed using the zero-order reaction kinetics, first-order reaction kinetics and second-order reaction kinetics, as shown in Equations (9) to (11). The $k_0$, $k_1$, $k_2$, and $R^2$ were determined by fitting experimental data into the zero-order, first-order and second-order kinetic models.

\[
\frac{dc}{dt} = -k_0 \quad \text{(9)}
\]

\[
\frac{dc}{dt} = -k_1 C \quad \text{(10)}
\]

\[
\frac{dc}{dt} = -k_2 C^2 \quad \text{(11)}
\]

After integration, the following Equations (12) to (14) were obtained:

\[ C_t = C_o - k_0 t \quad \text{(12)} \]

\[ \ln \frac{C_t}{C_o} = k_1 t \quad \text{(13)} \]

\[ \frac{1}{C_t} = \frac{1}{C_o} + k_2 t \quad \text{(14)} \]

where $C_o$ is the initial concentration of dye (mg/L), $C_t$ is concentration of dye at reaction time $t$ (mg/L), $k_0$ is the kinetic rate constant of zero-order reaction (mgL\textsuperscript{-1}min\textsuperscript{-1}), $k_1$ is the kinetic rate constant of first-order reaction (min\textsuperscript{-1}), $k_2$ is the kinetic rate constant of second-order reaction (Lmg\textsuperscript{-1}min\textsuperscript{-1}), and $t$ is the reaction time (min).

Table 1 shows the kinetic rate constants for degradation of CV at different Fenton reaction conditions. In general, it appears that CV degradation is best fitted to first-order reaction. From previous literature studies, the degradation of cationic dyes using Fenton oxidation was well-fitted to first-order kinetic model [25, 26]. In terms of the effect of Fe\textsuperscript{2+} on CV degradation, our results revealed an increasing trend of $k_1$ with the increase in Fe\textsuperscript{2+} concentration. This result is in agreement with the findings of Wu et al. [27], whereby when the Fe\textsuperscript{2+} concentration was from increased from 0.024 mM to 0.064 mM, the corresponding kinetic rate constant also increased accordingly. In terms of the effect of H\textsubscript{2}O\textsubscript{2}, for the fitted first-order kinetics, it was found that the $k_1$ for 50 mg/L of H\textsubscript{2}O\textsubscript{2} was the highest (i.e. 0.1415 min\textsuperscript{-1}) as compared to the case of 30 mg/L (0.0910 min\textsuperscript{-1}) and 70 mg/L (0.0886 min\textsuperscript{-1}). This suggests that 50 mg/L of H\textsubscript{2}O\textsubscript{2} appears to be the optimum H\textsubscript{2}O\textsubscript{2} concentration. Meanwhile, for the effect of solution pH on CV degradation, the $k_1$ was the highest for the condition of solution pH 3 (i.e. 0.1415 min\textsuperscript{-1}) as compared to solution pH 4 (0.0658 min\textsuperscript{-1}) and solution pH 5 (0.0219 min\textsuperscript{-1}). This confirms that the Fenton oxidation is more efficient in solution pH 3 than solution pH 4 or 5. In terms of combined competitive inorganic ions species, the effect of dual species was quite close with that of the triple species, as shown by the considerably close kinetic rate constants. It is also noted that the fitting of the experimental data into the zero-order kinetic model was generally not promising as the $R^2$ values obtained for some cases were quite low ($R^2$ less than 0.5000).
Table 1. The kinetic rate constants for degradation of CV at different Fenton reaction conditions.

| No | CV (mg/L) | Fe²⁺ (mg/L) | H₂O₂ (mg/L) | pH | Solution matrix (mg/L) | Zero-order reaction kinetics \( k₀ (mg/L \cdot min^{-1}) \) | First-order reaction kinetics \( k_{1} (min^{-1}) \) | Second-order reaction kinetics \( k_{2} (L\cdot mg^{-1} \cdot min^{-1}) \) |
|----|-----------|-------------|-------------|----|------------------------|-----------------|-----------------|-----------------|
| 1  | 5         | 5           | 50          | 3  | 0 0 0 0                 | 0.0591 ± 0.0727 | 0.1601 ± 0.0634 | 0.0628 ± 0.0958 |
| 2  | 10        | 5           | 50          | 3  | 0 0 0 0                 | 0.0591 ± 0.0727 | 0.1601 ± 0.0634 | 0.0628 ± 0.0958 |
| 3  | 50        | 5           | 50          | 3  | 0 0 0 0                 | 0.0591 ± 0.0727 | 0.1601 ± 0.0634 | 0.0628 ± 0.0958 |
| 4  | 100       | 5           | 50          | 3  | 0 0 0 0                 | 0.0591 ± 0.0727 | 0.1601 ± 0.0634 | 0.0628 ± 0.0958 |
| 5  | 5         | 1           | 50          | 3  | 0 0 0 0                 | 0.0591 ± 0.0727 | 0.1601 ± 0.0634 | 0.0628 ± 0.0958 |
| 6  | 5         | 25          | 50          | 3  | 0 0 0 0                 | 0.0591 ± 0.0727 | 0.1601 ± 0.0634 | 0.0628 ± 0.0958 |
| 7  | 5         | 5           | 50          | 3  | 0 0 0 0                 | 0.0591 ± 0.0727 | 0.1601 ± 0.0634 | 0.0628 ± 0.0958 |
| 8  | 5         | 5           | 70          | 3  | 0 0 0 0                 | 0.0591 ± 0.0727 | 0.1601 ± 0.0634 | 0.0628 ± 0.0958 |
| 9  | 5         | 5           | 50          | 4  | 0 0 0 0                 | 0.0591 ± 0.0727 | 0.1601 ± 0.0634 | 0.0628 ± 0.0958 |
| 10 | 5         | 5           | 50          | 5  | 0 0 0 0                 | 0.0591 ± 0.0727 | 0.1601 ± 0.0634 | 0.0628 ± 0.0958 |

Table 2 depicts the kinetic rate constants for degradation of AG 25 at different Fenton reaction conditions. The AG 25 degradation was best fitted to second-order kinetic reaction for all the investigated parameters, i.e. effect of initial dye concentration, effect of Fe²⁺ concentration, effect of H₂O₂ concentration, effect of solution pH, and effect of solution matrix (due to higher \( R^2 \) values). In particular, the highest \( k_2 \) value was 0.9566 \( Lmg\cdot min^{-1} \), and it was obtained when 70 mg/L of H₂O₂ was present in the Fenton reaction. The second highest \( k_2 \) was 0.6930 \( Lmg\cdot min^{-1} \), and it was obtained from the presence of 25 mg/L of CH₃OH. Youssef et al. [11] also investigated methyl orange (an anionic dye) and they found that their degradation kinetic data were best fitted to second-order kinetic model. The \( R^2 \) as derived from their second-order kinetic result was 0.86785, and this value was more significant that the zero-order kinetics (\( R^2 = 0.48960 \)) and the first-order kinetics (\( R^2 = 0.69893 \)). In addition, the degradation of Orange G (an anionic dye) using Fenton reaction had been studied and it was found out that the experimental results were best-fitted to second-order kinetic model (\( R^2 = 0.9450 \)), followed by zero-order kinetic model (\( R^2 = 0.4784 \)) and first-order kinetic model (\( R^2 = 0.3905 \)) [28]. Trovó et al. [29] had found their experimental data were consistently best fitted to the second-order kinetic model, followed by first-order kinetic model, and zero-order model. In addition, El Haddad et al. [30] had reported that for their degradation of Reactive Yellow 84 using Fenton’s process, the second-order kinetic model (with \( R^2 \) ranging from 0.50 – 0.80) was better fitted than first-order kinetic model (with \( R^2 \) ranging from 0.30 to 0.70). Thus, our results are in agreement with many of the researchers’ findings, whereby it appears that the degradation of anionic dyes through Fenton reactions are usually best fitted to second-order reaction kinetic model. Similar to the findings of CV, the fitting of AG 25 experimental data to the zero-order kinetic model was not too suitable as the lowest \( R^2 \) yielded was less than 0.5000.
Table 2. The kinetic rate constants for degradation of AG 25 at different Fenton reaction conditions.

| No | AG 25 (mg/L) | Fe²⁺ (mg/L) | H₂O₂ (mg/L) | pH | Solution matrix (mg/L) | Zero-order reaction kinetics | First-order reaction kinetics | Second-order reaction kinetics |
|----|--------------|-------------|-------------|----|------------------------|-----------------------------|----------------------------|-------------------------------|
| 1  | 5            | 5           | 50          | 3  | 0                      | 0.0521                      | 0.5936                    | 0.1148                        |
| 2  | 10           | 5           | 50          | 3  | 0                      | 0.2011                      | 0.7607                    | 0.1549                        |
| 3  | 50           | 5           | 50          | 3  | 0                      | 1.8551                      | 8.5536                    | 0.1127                        |
| 4  | 100          | 5           | 50          | 3  | 0                      | 2.6309                      | 9.4611                    | 0.0560                        |
| 5  | 5            | 1           | 50          | 3  | 0                      | 0.1711                      | 0.8023                    | 0.1454                        |
| 6  | 5            | 25          | 50          | 3  | 0                      | 0.0215                      | 0.5017                    | 0.1028                        |
| 7  | 5            | 30          | 3           | 0  | 0                      | 0.1072                      | 0.7213                    | 0.1683                        |
| 8  | 5            | 70          | 3           | 0  | 0                      | 0.0551                      | 0.6555                    | 0.1703                        |
| 9  | 5            | 50          | 4           | 0  | 0                      | 0.0683                      | 0.9880                    | 0.0195                        |
| 10 | 5            | 50          | 5           | 0  | 0                      | 0.0071                      | 0.8659                    | 0.0016                        |
| 11 | 5            | 50          | 3           | 1  | 0                      | 0.0555                      | 0.5990                    | 0.1222                        |
| 12 | 5            | 50          | 3           | 25 | 0                      | 0.0425                      | 0.4150                    | 0.1486                        |
| 13 | 5            | 50          | 3           | 0  | 1                      | 0.0850                      | 0.5329                    | 0.0998                        |
| 14 | 5            | 50          | 3           | 0  | 25                     | 0.0837                      | 0.6068                    | 0.1148                        |
| 15 | 5            | 50          | 3           | 0  | 1                      | 0.0637                      | 0.6219                    | 0.1207                        |
| 16 | 5            | 50          | 3           | 0  | 25                     | 0.0095                      | 0.9420                    | 0.0030                        |
| 17 | 5            | 50          | 3           | 0  | 1                      | 0.0658                      | 0.6821                    | 0.1122                        |
| 18 | 5            | 50          | 3           | 0  | 25                     | 0.0748                      | 0.7224                    | 0.1301                        |
| 19 | 5            | 50          | 3           | 0  | 0                      | 0.0658                      | 0.6621                    | 0.1531                        |
| 20 | 5            | 50          | 3           | 0  | 0                      | 0.0748                      | 0.7224                    | 0.1697                        |
| 21 | 5            | 50          | 3           | 0  | 0                      | 0.0684                      | 0.6768                    | 0.1026                        |
| 22 | 5            | 50          | 3           | 0  | 0                      | 0.0727                      | 0.7361                    | 0.1055                        |
| 23 | 5            | 50          | 3           | 0  | 25                     | 0.1000                      | 0.7135                    | 0.1405                        |
| 24 | 5            | 50          | 3           | 0  | 25                     | 0.0862                      | 0.7030                    | 0.1037                        |

4. Conclusion
In this study, the effect of initial dye concentration, effect of Fe²⁺ concentration, effect of H₂O₂ concentration, effect of solution pH and the effect of solution matrix (such as CH₃OH, C₂H₅OH, C₂O₄²⁻, Cl⁻, NO₃⁻, SO₄²⁻ and combined anion species) on the degradation efficiencies of aqueous CV (cationic dye) and AG 25 (anionic dye) were investigated. At the conditions of Fe²⁺ concentration of 5 mg/L, H₂O₂ concentration of 50 mg/L, solution pH 3, reaction time of 20 min and room temperature, the degradation efficiencies of CV and AG 25 were 99.67% and 97.17%, respectively. In the presence of CH₃OH and C₂H₅OH, the degradation efficiencies of CV were considerably reduced due to the scavenging of •OH. Interestingly, the degradation efficiency of AG 25 was increased when CH₃OH was added. Meanwhile, presence of 25 mg/L of C₂O₄²⁻ markedly decreased the degradation efficiencies of CV and AG 25. The presence of inorganic anions and combined anion species resulted in slightly detrimental effect on the degradation efficiency of CV and AG 25, respectively. First-order kinetic model and second-order kinetic model were found to best fit the degradation kinetics of CV and AG 25, respectively.

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