Highly efficient persulfate oxidation process activated with Fe⁰ aggregate for decolorization of reactive azo dye Remazol Golden Yellow

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Abstract The commercially available Fe⁰ aggregate has advantages of low-cost, fast-effective decontamination, reusability, and ease of operation. However, little study has been done on the performance of Fe⁰ aggregate as a catalyst in degradation of azo dyes, particularly used in persulfate (PS) oxidation process. This study investigated decolorization of a reactive azo dye, Remazol Golden Yellow (RGY, Reactive Orange 107), by persulfate oxidation activated with Fe⁰ aggregate. RGY decolorization was not effective in ultrasound-activated, heat-activated, and base-activated persulfate oxidation; however, a significant decolorization improvement was achieved by applying Fe⁰ aggregate to activated persulfate (PS/Fe⁰). Decolorization was strongly influenced by pH, Fe⁰, persulfate dosages and temperature. The suitable conditions for RGY decolorization were pH 6.0, PS 5×10⁻³ M, and Fe⁰ 0.5 g/L. This condition yields 98% color removal of 100 mg/L RGY solution within 20 min treatment; the azo bonds of RGY were completely broken down. RGY decolorization followed the first-order kinetics. Activation energy of the PS/Fe⁰ system was 0.479 kJ/mol, suggesting the temperature dependence of RGY decolorization is small. The presence of inorganic salt in RGY solution had an adverse effect on decolorization. The inhibitory effect of various inorganic salts on decolorization followed the sequence of Na₂HPO₄ > NaHCO₃ > NaClO₄ > NaCl > NaNO₃ > no salt. The Fe⁰ aggregate was reusable and a satisfactory decolorization efficiency was achieved with the repeated use of Fe⁰ for five times. The PS/Fe⁰ process provides an efficiency and effective technology for RGY decolorization.

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1. Introduction

Azo dyes, possessing a primary aromatic amino group, are the major colorants used in textile dyeing and printing industries. The effluents released from these industries are highly colored from the use of various dyes. If this effluent is treated inappropriately, it can cause adverse effects on aquatic environments.
Most azo dyes are refractory to biodegradation due to their complex structure and the stability. Thus, dye effluent treated by conventional biological treatment process may no longer meet stringent effluent discharge criteria. A broad range of physico-chemical decolorization methods are currently available, such as adsorption (Somasekhar Reddy and Nirmala, 2014; Pei et al., 2015; Ozbay and Yargic, 2015), membrane separation (Xing et al., 2012), sonophotocatalytic technique (Hemapriyamvadha and Sivasankar, 2015; Rasalingam et al., 2015), and electrochemical methods (Kobya et al., 2003; Raschitor et al., 2014); however, chemical sludge generation, adsorbent regeneration, and maintenance of fouled membranes may raise serious concerns (Pukdee-Asa et al., 2011; Weng et al., 2013).

Nowadays, persulfate oxidation (PS) has proven to be a promising technique for the removal of refractory organic pollutants (Liang and Lai, 2008; Oh et al., 2010; Li et al., 2013; Al-Shamsi and Thomson, 2013; Fang et al., 2013; Long et al., 2014) and decolorizing textile and printing industry wastewater (Wang et al., 2014; Li et al., 2014a,b; Cai et al., 2014). The PS process is generally associated with strong reactive sulfate radicals, $\text{SO}_4^\bullet^\bullet$ ($E^\circ = 2.6 \text{ V vs. normal hydrogen electrode (NHE)})$. The source of $\text{SO}_4^\bullet^\bullet$ is often from peroxodisulfate ($2\text{SO}_5^2^-$, PS, $E^\circ = 2.01 \text{ V vs. NHE}$), which is a strong and stable oxidizing agent and it has high aqueous solubility and high stability at room temperature as compared to hydrogen peroxide ($\text{H}_2\text{O}_2$, $E^\circ = 1.77 \text{ V vs. NHE}$) (Lin et al., 2013).

$\text{SO}_4^\bullet^\bullet$ can be generated in the reaction mixture by transition metals ($\text{Me}^{n+}$) reactive with persulfate anions ($2\text{SO}_5^2^-$).

$$\text{S}_8\text{O}_8^2^- + \text{Me}^{n+} \rightarrow \text{SO}_4^\bullet^\bullet + \text{Me}^{(n+1)+} + \text{SO}_5^2^-$$

$\text{SO}_4^\bullet^\bullet$ can also be generated though ultraviolet light, thermal energy, microwave, ultrasound, and strong basic solution (Yang et al., 2009; Furman et al., 2010; Xie et al., 2012; Lee et al., 2013; Ji et al., 2015).

$$\text{S}_8\text{O}_8^2^- + \text{hv} \rightarrow 2\text{SO}_4^\bullet^\bullet$$

$$\text{S}_8\text{O}_8^2^- \xrightarrow{\text{heat}} 2\text{SO}_4^\bullet^\bullet$$

$$\text{S}_8\text{O}_8^2^- \xrightarrow{\text{ultrasonic}} 2\text{SO}_4^\bullet^\bullet$$

where $\text{hv}$ refers to the application of ultrasound.

$$2\text{SO}_5^2^- + 2\text{H}_2\text{O} \xrightarrow{\text{OMF}} 3\text{SO}_4^\bullet^\bullet + \text{SO}_5^2^- + \text{O}_2^- + 4\text{H}^+$$

Because Fe is relatively nontoxic and inexpensive among various transition metal catalysts, it has been widely studied to activate persulfate oxidation for contaminant removal. Several types of Fe-based catalysts were used for the chemical activation of persulfate, including nano-sized zero-valent iron ($\text{Fe}^0$) (Wang et al., 2014), biochar supported nano-sized Fe$^0$ (Yan et al., 2015), zero-valent iron powder (Zhou et al., 2015; Li et al., 2014b), Fe-immobilized resin chars (Shi et al., 2015), Fe oxide-immobilized MnO$_2$ composite (Jo et al., 2014), Fe$_2$O$_3$ (Zhu et al., 2013), ferrous iron (Han et al., 2014), ferrous sulfide ore particles (Yuan et al., 2015), and Fe$_3$O$_4$ magnetic nanoparticles (Zhao et al., 2015). Influence of particle size of Fe$^0$ and comparison of various forms of Fe on the reactivity of activated persulfate oxidation have been studied (Li et al., 2014a; Rodriguez et al., 2014). In the past years, studies have focused on the synthesis of bimetallic-based catalysts and granular activated carbon supported metals as catalyst for heterogeneous activation of peroxydisulfate (Yang et al., 2011; Su et al., 2013; Lee et al., 2013; Cai et al., 2014). Possible leaching of cobalt from Co-containing catalysts and the high-cost of activated carbon and bimetallic catalysts have raised concerns.

In the PS process, oxidation efficiency is highly depending upon dye type, dye chemical structure, and the operating conditions. Operating conditions must be evaluated before applying any type of activators for persulfate. Reactive dyes is one of the most successful classes of modern synthetic dyes used in textile industry in dyeing wool, silk, cotton, and cellulosic fibers due to their shade versatility, application flexibility, and favorable fastness properties. Commercially available Fe$^0$ aggregate has long been applied in soil and groundwater remediation for reductive transformation of certain persistent organic and inorganic pollutants (Wilkin et al., 2005; Weng et al., 2007). In this study, an anionic reactive dye, Remazol® Golden Yellow RGB (RGY), a widely used dye in textile processing industries worldwide (Alvarenga et al., 2015) was used as model target compound to evaluate the decolorization efficiency of PS activated with Fe$^0$ aggregate (PS/Fe$^0$). To the best of our knowledge, there have been no studies of Fe$^0$ aggregate as an activator for PS oxidation of reactive dyes. The objectives were to: (a) examine the RGY decolorization efficiency achieved in the PS/Fe$^0$ system, (b) investigate key operating parameters such as initial pH, Fe$^0$ and PS dosages, reaction temperature, and salts on the RGY decolorization, and (c) evaluate the reusability of Fe$^0$ aggregate in the PS/Fe$^0$ system.

2. Materials and methods

2.1. Materials

RGY (C.I. Reactive Orange 107, C$_{16}$H$_{18}$N$_2$O$_{10}$S$_3$Na$_2$), an anionic fiber reactive dye, was obtained from DyStar (Germany) and used as received without further purification. While this sulfonated azo dye is widely used in the textile industry, the biodegradability of this dye is low (<10%). Fe$^0$ aggregate (Fig. 1) with particle size 0.297–2.380 mm and specific weight 2240–2560 kg/m$^3$ was obtained from Connelly-GPM (USA). Sodium persulfate (Na$_2$S$_2$O$_8$) was purchased from Nippon Shiyaku (Japan). All other reagents were of analytical grade.

![Figure 1](https://example.com/figure1.jpg) Fe$^0$ aggregate catalyst.

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2.2. Persulfate oxidation experiments

Persulfate decoloration experiments were performed in aluminum-foil-wrapped glass beakers containing 1000 mL of RGY solution prepared using distilled water. Unless otherwise stated, the experimental procedures were as follows. (1) The pH of RGY solution was adjusted with 0.01 M HCl/NaOH solution. (2) After adding Fe$^0$ aggregate and persulfate, RGY solution was immediately agitated with a mechanical stirrer (Shin-kwang, Taiwan) at 800 rpm for 30 min. (3) At preset time intervals, 10 mL of solution was taken by a syringe and filtered immediately through a 0.45-μm membrane filter (Advantec, Japan) to collect the supernatant. We confirmed that the filter and glass beaker could not adsorb the dye. (4) The residual RGY concentration in the supernatant was determined as described in Section 2.3.

The effect of temperature on PS decolorization was investigated under isothermal conditions by maintaining the dye solution in a water circulation bath. The detailed experimental procedures were as described above, except before adding Fe$^0$ and persulfate [step (2)], the dye solution was placed in the water bath for 0.5 h to reach the designated temperature. In the experiments of PS coupled with sonolysis, the dye solution was sonicated by an ultrasonic generator (S-450A, Branson, USA) equipped with a titanium horn-probe transducer. The sonication was administered in pulses with a 60% duty cycle at 60 kHz and 120 W for 10 min.

Each decolorization experiments were conducted in duplicate, and average values were used in analysis. Decolorization efficiency was calculated as follows:

$$\text{Efficiency (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100$$

(6)

where $C_0$ and $C_t$ were the RGY concentration at time 0 and reaction time $t$ (min), respectively. The rate of RGY decolorization was analyzed with pseudo-first-order (PFO) kinetic equation:

$$C_t = C_0 e^{-k_{obs} t}$$

(7)

where $k_{obs}$ is the observed rate constant (1/min).

2.3. Analysis

RGY concentration was analyzed by measuring the absorbance at 410 nm using a spectrophotometer (Thermo Scientific Evolution 201, USA). The concentration of Fe$^{2+}$ in the solution was analyzed by measuring absorption at 510 nm using HACH FerroVer iron reagent® (HACH, USA). Chemical oxygen demand (COD) was determined using the Reactor Digestion Method HACH (Method 8000) with a HACH DR/3900 spectrophotometer. This method is USEPA approved for wastewater analyses (Standard Method 5220D) (APHA et al., 2012). COD digestion reagents were obtained from HACH Co. The American Dye Manufacturers Institute (ADMI) Tristimulus Filter Method was used for analyzing the true color of the solution (APHA et al., 2012). The ADMI value was determined under three preset wavelengths (438, 540, and 590 nm). In Taiwan, environmental regulations prescribe a discharge COD limit of 140 mg/L and a true color limit of ADMI 550 for wastewater from dyeing, printing, and textile industries.

3. Results and discussion

3.1. Decolorization of RGY in different comparable systems

Fig. 2a shows a comparison of different decolorization systems, including Fe$^0$ only, Fe$^0$ assisted with ultrasound (Fe$^0$/US), ultrasound-activated PS system (PS/US), PS/Fe$^0$, and PS/Fe$^0$ assisted with ultrasound (PS/Fe$^0$/US). The insignificant color removal in both Fe$^0$ only and Fe$^0$/US systems indicates that adsorption and reduction reactions between Fe$^0$ and RGY could be neglected. In the PS/US system, despite generating SO$_4$$^{2-}$ radicals (Eq. (4)) (Li et al., 2013) is possible, RGY decolorization efficiency was not effective compared to the PS/Fe$^0$ system, which indicates only a small amount of SO$_4$$^{2-}$ was produced in the PS/US system.

Results of PS/US system also indicate that the RGY could not be oxidized by persulfate, even though persulfate is considered as a strong oxidant.

In the PS/Fe system, a notably decolorization efficiency (> 90%) was achieved within 10 min. The release of sufficient
amount Fe\textsuperscript{2+} from Fe\textsuperscript{0} aggregate is the key to generate SO\textsubscript{4}\textsuperscript{2-} and decolor RGY effectively. In this system, the initial pH decreased from 6.0 to 2.32 (inset table in Fig. 2a) resulted from the hydrolysis of persulfate (Eq. (8)). Consequently, the corrosion of Fe\textsuperscript{0} in acidic solution would produce Fe\textsuperscript{2+} (Eq. (9)). SO\textsubscript{4}\textsuperscript{2-} radicals were produced as S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} reacting with Fe\textsuperscript{2+} in the aqueous solution (Eq. (10)) (Fig. 3a) or directly contacting with Fe\textsuperscript{0} surface (Eq. (11)) via surface heterogeneous reaction (Fig. 3b).

\begin{equation}
\text{S}_2\text{O}_8^{2-} + 2\text{H}_2\text{O} \rightarrow \text{HO}_2^- + 2\text{SO}_4^{2-} + 3\text{H}^+ \tag{8}
\end{equation}

\begin{equation}
\text{Fe}^0 (s) \rightarrow \text{Fe}^{2+ (aq)} + 2e^- \tag{9}
\end{equation}

\begin{equation}
\text{Fe}^{2+ (aq)} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe}^{3+ (aq)} + \text{SO}_4^{2-} + \text{SO}_4^{2-} \tag{10}
\end{equation}

\begin{equation}
\text{Fe}^0 (s) + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe}^{2+ (aq)} + 2\text{SO}_4^{2-} + 2e^- \tag{11}
\end{equation}

Ultrasonic irradiation not only enhanced corrosion of Fe\textsuperscript{0} aggregate, but also produced more Fe\textsuperscript{2+} in the solution by refreshing the surface of Fe\textsuperscript{0} (Eq. (12)) (Weng et al., 2014).

\begin{equation}
\text{Fe}^0 \rightarrow \text{Fe}^{2+} + 2e^- \tag{12}
\end{equation}

In the PS/Fe\textsuperscript{0}/US process, the addition of 10 min ultrasound could not further increase the decolorization efficiency. Study (Wang et al., 2014) showed that decolorization of Acid Orange 7 could be significantly enhanced by the introduction of ultrasound; our results indicated that such enhancement by ultrasound on PS/Fe\textsuperscript{0} is minimal. The different results can be ascribed to different dye types (acid vs. reactive) and Fe\textsuperscript{0} forms (Fe\textsuperscript{0} powder vs. Fe\textsuperscript{0} aggregate) used in activating persulfate.

Fig. 2a shows that the RGY depletion by either PS/Fe\textsuperscript{0} or PS/Fe\textsuperscript{0}/US followed pseudo-first-order kinetics and the reaction could relate to fast homogeneous reaction occurring in the solution. The corresponding rate constant, $k_{\text{obs}}$, and regression coefficients ($r^2$) are shown in Fig. 2a (inset table). Because the value of $k_{\text{obs}}$ achieved in the Fe\textsuperscript{0}/PS system was nearly the same in the Fe\textsuperscript{0}/PS/US system, the introduction of ultrasound to the system is not necessary. The Fe\textsuperscript{0}/PS process is a fast and effective process for RGY decolorization and is selected for further evaluation.

The photographs (Fig. 2b) show that the solution changed from yellow to light yellow after 5 min and then became transparent after 10 min of PS/Fe\textsuperscript{0} treatment. This indicated that the destruction of the chromophore structure (−N==N−group) underwent persulfate oxidation easily. As shown, the true color decreased from ADI 3519 to 124 within 5 min treatment, which complies with Taiwan’s effluent criteria for true color (ADI 550) in textile, paper, and dyeing industries.

### 3.2. Effect of pH

Solution pH is a crucial factor affecting the decolorization because pH governs the speciation of iron and solubility of Fe\textsuperscript{0} aggregate. The effect of pH on RGY depletion in the PS/Fe\textsuperscript{0} system showed that a sharp depletion was observed at the initial pH between 4.0 and 10.0 (Fig. 4). At this pH region, satisfactory decolorization efficiency was achieved within 15 min of treatment. The depletion of dye and the variation of pH (inset graph in Fig. 4) were closely interrelated. When the initial pH was between 4.0 and 10.0, the solution pH decreased markedly to less than 3.0 within 5 min. In PS-driven oxidation reactions, the solution became sufficiently acidic (Eq. (8)). The strongly acidic solution favors Fe\textsuperscript{3+} releasing from the corrosion of Fe\textsuperscript{0} aggregate (Eq. (6)). The decolorization data at this pH range are well fitted by the PFO kinetics model with high regression coefficients (inset table in Fig. 4). The decolorization rate ($k_{\text{obs}}$) is proportionally correlated with a decrease in initial pH.

On the contrary, the solution pH remained nearly unchanged at an initial pH of 11.0, and insignificant dye depletion was observed. The insufficient of Fe\textsuperscript{2+} ion in the system would significantly hinder the activation of persulfate. Under basic conditions, although the generation of SO\textsubscript{4}\textsuperscript{2-}, superoxide radicals (O\textsubscript{2}\textsuperscript{•−}), and hydroxyl radicals (OH\textsuperscript{•−}, $E^o = 2.70 \text{V}$) is possible (Eqs. (5) and (13)) (Liang et al., 2007; Furman et al., 2010), results show that RGY decolorization is ineffective at initial pH of 11.0.

\begin{equation}
\text{SO}_4^{2-} + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \cdot \text{OH} \tag{13}
\end{equation}

### 3.3. Effect of persulfate concentration

Decolorization was also greatly enhanced by the increased addition of PS in the Fe\textsuperscript{0}/PS system (Fig. 5a). The PFO rate law (Eq. (7)) applied well to the data within the reaction period (inset table in Fig. 5a). In general, RGY decolorization proceeded in a satisfactory manner for PS dosage higher than $2.5 \times 10^{-3} \text{M}$. However, the system with a low PS concentration ($2 \times 10^{-4} \text{M}$) exhibited a slow reaction phenomenon. As the reaction proceeded, higher PS dosages led to lower the solution pH. The more acidic solution led to the release of greater amount of Fe\textsuperscript{2+} from the corrosion of Fe\textsuperscript{0} (Fig. 5b). Thereby, more SO\textsubscript{4}\textsuperscript{2-} radicals are produced for oxidizing RGY at a higher concentration of PS, which resulted in achieving a higher decolorization efficiency when sufficient Fe\textsuperscript{2+} was maintained in the system.

![Figure 3](image-url) Conceptual reaction scheme of persulfate radicals generation via (a) aqueous homogeneous reaction and (b) surface heterogeneous reaction in the PS/Fe\textsuperscript{0} system.
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3.4. Effect of Fe⁰ dosages

Fig. 6 shows that decolorization was greatly enhanced by increasing the addition of Fe⁰ in the Fe⁰/PS system. The introduction of a higher Fe⁰ dosage in the PS/Fe⁰ system resulted in higher decolorization efficiency. A fast decolorization efficiency (> 90%) was achieved within 15 min for Fe⁰ dosages higher than 0.5 g/L. However, system with low Fe⁰ dosage (< 0.3 g/L) exhibited slow decolorization kinetics. Fast decolorization data are best described by the PFO kinetics model. As shown in the inset table in Fig. 6, the observed decolorization rate (k⁰obs) is proportionally correlated with an increase in the Fe⁰ dosage. Increasing Fe⁰ dosage led to the release of a greater amount of Fe²⁺ for catalyzing the persulfate reaction, which produced more SO₄²⁻ radicals to oxidize RGY and resulted in accelerating the decolorization rate. Slow decolorization data are well fitted by the zero-order rate law (Eq. (14)) and can be mostly attributed to the insufficient Fe²⁺ in the solution.

\[ C_t = C_0 - k^{0}_{obs}t \]  

where \( k^{0}_{obs} \) is the observed zero-order oxidation rate constant (mg/L min). The \( k^{0}_{obs} \) achieved in the system with Fe⁰ dosage of 0.3 g/L and 0.1 g/L was 1.21 and 1.79 mg/L min, respectively (inset table in Fig. 6).

3.5. Effect of temperature on decolorization of RGY

Temperature plays a key role affecting RGY depletion for the PS and Fe⁰/PS systems. Although persulfate anions can be activated with thermal energy (Li et al., 2013; Deng et al., 2013) to generate sulfate radicals (Eq. (15)), RGY decolorization efficiency in the thermally activated persulfate system (PS/60 °C) is not promising (Fig. 7a).

\[ \text{SO}_4^{2-}_{(aq)} \xrightarrow{\text{heat}} \text{SO}_4^{2-} \]  

When the PS was activated with Fe⁰ at 60 °C (PS/Fe⁰/60 °C), a prominent decolorization efficiency was achieved at an elevated temperature. As shown in Fig. 7a, RGY depletion increased proportionally with increasing
treatment process because it may influence the activity of oxidation reaction, thus affecting the dye degradation. Fig. 8a shows a negative effect of RGY decolorization in the PS/Fe\(^0\) system when the solution contained salts (NaClO\(_4\), NaNO\(_3\), NaCl, NaHCO\(_3\), and Na\(_2\)HPO\(_4\)). The degree of decolorization behaved differently from the addition of these salts. The corresponding decolorization rate constants (\(k_{\text{obs}}\)) in inset table of Fig. 8a are in decreasing order: no salt (0.182 1/min) > NaClO\(_4\) (0.134 1/min) > NaNO\(_3\) (0.110 1/min) > NaCl (0.087 1/min) > NaHCO\(_3\) (0.016 1/min) > Na\(_2\)HPO\(_4\) (0.007 1/min). At initial pH of 6.0, the dominant anion would be ClO\(_4\)\(^-\), NO\(_3\)\(^-\), Cl\(^-\), HCO\(_3\)\(^-\), H\(_2\)PO\(_4\)\(^-\), and HPO\(_4\)\(^2-\). The presence of HCO\(_3\)\(^-\) or Cl\(^-\) species in activated persulfate systems could increase the concentration of active radicals (HCO\(_3\)\(^-\), CO\(_3\)\(^2-\), Cl\(^-\)) (Eqs. (17)–(20)) and possibly increase the oxidation efficiency of organic pollutants in wastewater (Yu et al., 2004; Bennedsen et al., 2012).

\[
\begin{align*}
SO_4^{2-} + HCO_3^- &\rightarrow SO_3^{2-} + HCO_3^- \\
HCO_3^- &\rightarrow H^+ + CO_3^{2-}, \quad pK_a = 9.5 \\
SO_4^{2-} + CO_3^{2-} &\rightarrow SO_3^{2-} + CO_3^{-} \\
SO_4^{2-} + Cl^- &\leftrightarrow SO_3^{2-} + Cl^-
\end{align*}
\]

3.6. Effect of salt

Effluents from textile and dyeing industries are often rich in color and contain variety of inorganic salts. The presence of high concentration salt is of great concern in the PS/Fe\(^0\) system. At higher temperatures, more energy is stored on the vibrational levels of the molecules, leading to an increase in molecular collision frequency, thereby accelerating the rate of decolorization. It appears that the catalytic activity of Fe\(^0\) aggregate remained high even the system was kept at elevated temperature of 60 °C.

Fig. 7a (inset table) shows the observed PFO rate constants (\(k_{\text{obs}}\)) for the PS only or PS/Fe\(^0\) processes. Based on the Arrhenius equation (Eq. (16)), the activation energy (\(E_a\)) of the PSS/Fe\(^0\) oxidation system was determined (Fig. 7b).

\[
\ln k_{\text{obs}}^1 = \ln A - E_a/RT
\]

where \(A = \) pre-exponential factor, \(E_a = \) the activation energy (kJ/mol), \(R = \) universal gas constant (1.987 cal/mol K), and \(T = \) absolute temperature (K). The \(E_a\) is 0.479 kJ/mol, which indicates the temperature dependence of RGY decolorization in the PS/Fe\(^0\) system is small.

3.6. Effect of salt

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However, inhibitory effect has been reported in a cobalt activated PS system for decolorization of Acid Orange 7 (Yuan et al., 2011) as solution contained concentration of NaCl less than 0.4 M; only hyper-concentration of NaCl (0.5 M) could enhance bleaching rate and NaCl higher than 5 × 10^{-3} M could decrease the inhibitory effect. Wang et al. (2011) have also found that Cl^{-} exhibited a significant inhibiting effect at low concentration (≤0.01 mol/L) in Co^{2+} activated peroxymonosulfate system for decolorization of Acid Orange 7. Our results clearly indicated that the dye oxidation was suppressed by the presence of these anions. The inhabitation of dye oxidation on the PS/Fe^{0} system was possible due to Cl^{-} served as SO_{4}^{2-} radicals scavengers to form less reactive less Cl^{-} radicals (Eq. (20)) (Yuan et al., 2011). The adverse effects of dye oxidation were by Cl^{-}, NO_{3}^{-}, and NaClO_{4}, and could also attributed to the fact that high concentration of salts would disturb the oxidation reaction due to the electronic interference resulted from the high ionic concentration (Weng et al., 2013), thereby decreasing the rate of decolorization. Particularly, the rate of RGY decolorization was inhibited significantly by the presence of NaHCO_{3} and Na_{2}HPO_{4}. Such effect is closely related to the pH variation during the treatment period (Fig. 8b). The pH was keeping at near neutral in the system containing NaHCO_{3} or Na_{2}HPO_{4}, which limited the corrosion of Fe^{0} aggregate. The formation of Fe(H_{2}PO_{4})_{3} and Fe(HCO_{3})_{3} under neutral pH condition is more stable than the complexes formed by NO_{3}^{-}, ClO_{4}^{-}, and Cl^{-}. The complexation formation also greatly affects the availability of Fe^{2+} and Fe^{3+} ions in the persulfate oxidation (Eqs. (9)–(11)) to generate SO_{4}^{2-} for RGY decolorization. Because the ionic strength of Na_{2}HPO_{4} (ca. as 1.5 × 10^{-2} M) is higher than that of NaHCO_{3} (ca. as 5 × 10^{-3} M) for a system with same salt concentration (5 × 10^{-4} M), the interference effect on the activity of persulfate reaction is higher. Consequently, decolorization rate was lower in the PS/Fe^{0} system containing Na_{2}HPO_{4} and NaHCO_{3}.

3.7. Decolorization mechanisms

To relate the changes in chemical structure of RGY and color depletion during PS/Fe^{0} treatment, the UV–vis spectra, dye concentration, and COD were measured during the treatment (Fig. 9). For an initial RGY concentration of 100 mg/L, approximately 98% decolorization efficiency was achieved within 20 min (inset graph in Fig. 9). Before the reaction, the spectra of RGY were characterized by one main band in the visible region with absorbance peak at 410 nm and a narrow absorbance peak at 295 nm in the ultraviolet region. After the reaction, the characteristic peak decreased quickly within 15 min and the peaks reduced to the minimum. This implies that the conjugate chromophore structure (≡N≡N= group) of RGY was destroyed and the color disappeared rapidly. Additionally, the increase of the absorbance with time at 295 nm was the evidence of the appearance of aromatic fragments as the reaction proceeded after breaking down RGY chromophore group.

A prominent COD removal was observed within 5 min reaction, indicating that RGY is easily oxidized by PS/Fe^{0} (inset graph in Fig. 9). A 55.6% of residual COD was found

![Figure 9](https://example.com/figure9.png)

**Figure 9** The variation of UV–vis spectra during the depletion of RGY in the PS/Fe^{0} system (RGY 100 mg/L, PS 5 × 10^{-3} M, Fe^{0} 0.5 g/L, initial pH 6.0, 25 °C). The graph insets are the COD, ADMI, and color depletion during the treatment.

![Figure 10](https://example.com/figure10.png)

**Figure 10** Effect of recycled Fe^{0} aggregate on RGY decolorization in the PS/Fe^{0} system (PS 5 × 10^{-3} M, initial pH 6.0, 25 °C).

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even though the color was completely disappeared within 30 min, which indicates all RGY in this process was not completely oxidized into carbon dioxide. The residual COD was mainly attributed to the formation of intermediate products of RGY, such as benzene, phenol, and carboxylic acids. The COD value decreased from the initial value of 97.5 to 54.2 mg/L, which was far below Taiwan’s discharge criterion (140 mg/L) for textile and dyeing industries.

The possible degradation pathway in the PS/Fe0 system for oxidation of RGY is proposed. SO42− radicals could remove electrons from RGY. When SO42− radicals added to the azo bonds, the azo bonds cleaved to form azobenzene. Azobenzene was oxidized by SO42− radicals to form phenol and benzene. SO42− could further attack on benzene ring because it is an electrophilic radical (Liang et al., 2008). Then phenol was further oxidized to hydroquinone and benzo-1,4-quinone. Benzene ring was cleaved to produce but-2-enedioic acid and then finally oxidized to carboxylic acids. Carboxylic acids, such as formic acid and acetic acid, are more difficult to be oxidized than their parent compounds (Ramirez et al., 2005; Wang et al., 2014; Weng and Huang, 2015). To improve COD removal, prolonging reaction time or employing more aggressive operating conditions, such as PS/Fe0 in conjunction with ultrasound/heat, could be considered in further study.

3.8. Reusability of Fe0 aggregate

The reusability of the Fe0 aggregate in the PS/Fe0 system is crucial for its practical application. The Fe0 aggregate was separated from the reaction mixture at the end of each cycle. Fig. 10 shows the performance of using recycled Fe0 aggregate in the PS/Fe0 system for five consecutive cycles. The mass of Fe0 decreased gradually from 0.5 g/L in the 1st cycle to 0.441 g/L after the 5th cycle. Based on a unit price of Fe0 aggregate (500 USD/ton), the average cost of Fe0 is only 5.9 × 10−3 USD/m3 for each cycle. The RGY decolorization efficiency and the rate of decolorization (kobs) are inversely proportional to the number of times Fe0 aggregate is recycled due to the gradual loss of Fe0 activity and the mass of Fe. Although a negative effect resulted from using the recycled Fe0 aggregate, decolorization occurred quickly without any delay of oxidation even when Fe0 aggregate was repeatedly used for five consecutive cycles. Because of its fast and effective azo-dye removal, and reusability, the Fe0 aggregate has potential applications in the PS/Fe0 system for dye laden wastewater treatment.

4. Conclusions

Persulfate oxidation activated by Fe0 aggregate for decolorization of reactive azo dye provides an effective technology for decolorization of Remazol Golden Yellow. Decolorization by PS/Fe0 process was favorable at initial pH < 10.0, high Fe0 and persulfate dosages, and high temperature. However, the rate of RGY decolorization was inhibited significantly by the addition of NaHCO3 and Na2HPO4. Further study may focus on minimizing such inhibitory effect by the addition of ultrasound or heat to the process. The Fe0 aggregate has advantages of low-cost (500 USD/ton), effective decolorization, reusability, and ease of operation (easy to be separated after use), which shows the practically feasible of Fe0 aggregate as an economic and efficient activator for the persulfate oxidation of reactive azo dye.

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