Insights into the generation of hydroxyl radicals from H$_2$O$_2$ decomposition by the combination of Fe$^{2+}$ and chloranilic acid

M. I. Ahmad$^1$ · N. Bensalah$^2$

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Abstract
In this work, the degradation of chloranilic acid (CAA) by chemical oxidation with H$_2$O$_2$ alone and in the presence of ferrous iron Fe$^{2+}$ catalyst was investigated in order to improve our understanding on the novel metal-independent approach. The interesting and efficient metal-independent hydroxyl radicals (OH) production by using halogenated quinones and H$_2$O$_2$ has been currently demonstrated. The results clearly confirmed the formation of OH radicals from the reaction of CAA with H$_2$O$_2$. CAA was slowly decayed by chemical oxidation with H$_2$O$_2$ and followed a pseudo-first kinetics. H$_2$O$_2$ doses ≥ 1000 mM were required to achieve complete CAA decay from 1 mM CAA. However, low total organic carbon (TOC) removal was measured with the accumulation of carboxylic acids. The addition of Fe$^{2+}$ enhanced the kinetics of CAA degradation and reduced the required dose of H$_2$O$_2$. High TOC removal was obtained, almost complete release of chloride ions, without accumulation of carboxylic acids. The decolorization of methylene blue (MB) aqueous solutions was performed using H$_2$O$_2$, H$_2$O$_2$/CAA, H$_2$O$_2$/Fe$^{2+}$, and H$_2$O$_2$/CAA/Fe$^{2+}$. H$_2$O$_2$/CAA/Fe$^{2+}$ was the most effective method in decolorizing MB solutions due to the accelerated Fe$^{2+}$ regeneration. Coupling Fenton reagent with CAA seems to be promising alternative to physical activation in water and soil treatment.

Keywords Hydrogen peroxide · Chloranilic acid · Chemical oxidation · Fenton reagent · Hydroxyl radicals

Introduction
Historically, Fenton reaction is based on the production of hydroxyl radicals by catalytic decomposition of hydrogen peroxide (H$_2$O$_2$) using a transition metal, mainly Fe$^{2+}$, as a catalyst (Eq. 1) (Babuponnusami and Muthukumar 2014; Pliego et al. 2015; M. hui Zhang et al. 2019; Oturan et al. 2012; Oliveira et al. 2014).

\[
H_2O_2(aq) + Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + OH(aq) + HO^-(aq) \quad (1)
\]

This reaction was recognized by its great success and high efficiency to remove many organic and inorganic recalcitrant compounds from soil and water (Telles and Granhen Tavares 2012; Nidheesh et al. 2013; Yue et al. 2015; Martínez-Costa et al. 2018; Giraldo-Aguirre et al. 2018; Verma and Chaudhari 2020). This is due to the intensive oxidative power, short lifetime, and high reactivity of the ‘OH radicals (Cheng et al. 2016; Buxton et al. 1988; García et al. 2013). These unique characteristics enable them to immediately react with the pollutant molecules in a non-selective way (Gligorovski et al. 2015; Keen et al. 2014). Generally, the degradation of pollutants by Fenton’s reagent ended with their transformation into harmless substances that pause little environmental concerns.

Nevertheless, this reaction is thermodynamically feasible at any pH; however, it is kinetically possible only at pH in the range 2–3 (Duesterberg et al. 2008; Jeong et al. 2010). This is limiting the utilization of Fenton process for the treatment to only acid streams. In addition, the slowness of the regeneration of the catalyst Fe$^{2+}$ (rate-determining step (Eqs. 2–3)) requires the addition of high amounts of Fe$^{2+}$ to
accelerate the degradation of pollutants by continuous feed up of \( \cdot \text{OH} \) radicals (Li et al. 2019; Qiang et al. 2003).

\[
\text{Fe}^{3+}(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \cdot \text{OH}(\text{aq}) + \text{H}^+(\text{aq}) \quad (2)
\]

\[
\text{Fe}^{3+}(\text{aq}) + \text{HO}_2 \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{O}_2 + \text{H}^+(\text{aq}) \quad (3)
\]

Furthermore, post-treatment including chemical reduction, acid–base reaction, and filtration is often needed to remove the excess of oxidant \( \text{H}_2\text{O}_2 \), neutralize the treated water, and remove the iron(III) hydroxide (\( \text{Fe(OH)}_3 \)) precipitate (Eq. 4) (Chen et al. 2011; Boonrattanakij et al. 2011). This post-treatment adds unnecessary costs to the whole treatment process.

\[
\text{Fe}^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq}) \rightarrow \text{Fe(OH)}_3(\text{s}) \downarrow \quad (4)
\]

Several attempts have been made to improve the performance of Fenton reaction in the treatment of natural waters and wastewaters (Babuponnusami and Muthukumar 2014; Pliego et al. 2015; M. hui Zhang et al. 2019; Thomas and Zdebik 2019; Thomas et al. 2017). The replacement of homogeneous \( \text{Fe}^{2+} \) catalyst with natural and synthetic heterogeneous catalysts reduced the costs of the process due to the possibility of recycling of the catalysts; however, it inhibited the pollutants degradation (Nidheesh 2015; Rahim Pouran et al. 2014). Combining Fenton with UV irradiation (known as photo-Fenton process) promoted the efficiency of pollutants degradation, enhanced the regeneration of the catalyst, and reduced its quantity (Ameta et al. 2018; Clarizia et al. 2017). Improved efficiency has been achieved with electro-Fenton, photo-electro-Fenton, and sono-electro-Fenton processes (Liu et al. 2018; Ganiyu et al. 2018). On the other hand, Chen et al. (Chen and Pignatello 1997) demonstrated the important role played by quinone intermediates as electron shuttles in Fenton and photo-Fenton oxidations of phenol derivatives. It was validated through experimental and simulation investigations that quinone intermediates transfer electrons to \( \text{Fe}^{3+} \), which facilitates the oxidation of the target compound. The conversion of quinone into semiquinone is complemented with the reduction of \( \text{Fe}^{3+} \) into \( \text{Fe}^{2+} \), thus accelerating the catalytic cycle of iron in the whole Fenton oxidation. Duesterberg and Waite (Duesterberg and Waite 2007) confirmed the results obtained by Chen et al. (Chen and Pignatello 1997) related to the role of quinones in the redox cycling of iron in Fenton process. These results implicated that the addition of co-oxidants such as quinones would solve the problems related to regeneration of \( \text{Fe}^{2+} \) catalyst in Fenton oxidation mechanisms, which reduces the required amounts of \( \text{Fe}^{2+} \), and thus that of the solid wastes. Furthermore, Zhu et al. (Zhu et al. 2002, 2012) demonstrated the metal-independent production of hydroxyl radicals from the reaction between hydrogen peroxide and tetrachloro-1,4-benzoquinone. Recently, Li et al. (Li et al. 2013) proved theoretically the possible production of OH radicals by the reaction between halogenated benzoquinone derivatives and hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) (Fig. 1).

This work aims to improve our understanding on the novel metal-independent approach and \( \text{Fe}^{2+} \)-catalyzed \( \text{H}_2\text{O}_2 \) decomposition and the combined system for the production of OH radicals and their application for removing organic pollutants in water. The efficiency of using quinone derivatives in producing in situ hydroxyl radicals by reaction with hydrogen peroxide in the absence of \( \text{Fe}^{2+} \) catalyst will be also demonstrated. The effect of addition of quinone derivatives on efficiency of Fenton reaction in

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**Fig. 1** Mechanism of production of OH radicals by nucleophilic attack of \( \text{H}_2\text{O}_2 \) onto tetrachloro-1,4-benzoquinone (Zhu et al. 2007)
decolorizing methylene blue solutions will be also evaluated. These findings will be important to explore and expand the implementation of H2O2-based methods in water treatment plants. Chloranilic acid (2,5-dichloro-3,6-dihydroxy-benzoquinone), CAA, was selected as quinone derivative to be reacted with H2O2. In the first part of this work, the degradation of CAA by H2O2 alone (to confirm the production of hydroxyl radicals by inter) and in the presence of ferrous iron Fe2+ catalyst was investigated. In fact, CAA was detected among others as stable halo-benzoquinone disinfection by-products in treated water (Wang et al. 2014, 2016). It has been detected in pulp mill bleaching effluents and polychlorophenols industrial wastewaters (Treviño-Quintanilla et al. 2011; Martínez-Huitl et al. 2004; Zhu et al. 2010). In the second part, the degradation of methylene blue dye was assessed by H2O2/CAA, H2O2/Fe2+, H2O2/CAA/Fe2+ systems. The experimental work was carried out at Central Lab Unit at Qatar University (October 2019-March 2020).

Materials and methods

Chemicals

Chloranilic acid (2,5-Dichloro-3,6-dihydroxy-benzoquinone) was received from Fluka (analytical grade, > 99%) and was used without further purification. Phenol, benzoic acid, and hydroquinone were bought from Sigma-Aldrich (> 99%). Hydrogen peroxide (30% H2O2 by mass) and ethanol (C2H5OH, > 99%) were VWR chemicals. Iron(II) sulfate hepta hydrate (FeSO4. 7H2O), sodium hydroxide (NaOH), sodium sulfite (Na2SO3), and sulfuric acid (H2SO4) were analytical grade Sigma-Aldrich chemicals. Deionized water received from Millipore Milli-Q equipment with resistivity ≥ 18.2 MΩ.cm and TOC content ≤ 5 ppb was used to prepare the aqueous solutions.

Experimental procedures

The degradation experiments were carried out in a 500-mL double-jacket glass reactor equipped with a magnetic stirrer and a thermometer. The temperature was maintained to room temperature (23–25 °C) by water circulation. The pH of 250 mL CAA (or MB) aqueous solution was adjusted to the desired value by addition of drops of 0.1 M NaOH or H2SO4. A precise amount hydrogen peroxide 30% was added to 250 mL of the solution to be treated. In Fenton experiments, an aliquot of 1000 mM Fe2+ aqueous solution was mixed with the CAA/MB aqueous solution before H2O2 is added. In all experiments, the degradation starts when H2O2 is added. All the experiments were performed in duplicate. 5 mL samples were periodically collected and immediately quenched with Na2SO3 or ethanol. All the samples withdrawn at desired times underwent a filtration through 0.2-μm membrane filters before analysis (three measurements for each sample).

Results and discussion

Degradation of CAA by chemical oxidation with H2O2

Figure 2 presents the effect of H2O2 dose on the changes of CAA concentration with time during the chemical oxidation of CAA (1 mM) by H2O2 in aqueous solution holding the other operating conditions unchanged (initial pH = 3.0, T = 23–25 °C, stirring: 300 rpm). The degradation of CAA

Analytical methods

TOC analysis was conducted using a Skalar FormacsHT TOC/TN analyzer. UV–visible spectrophotometer (Perkin Elmer Lambda 5) was used for UV–visible spectra plotting using a 1-cm quartz cells. The pH was monitored using a pH-meter (Seven Compact S210, METTLER TOLEDO®). The analysis of chloride ions was performed by ion chromatograph ( Dionex ICS 2000) using Ion Pac AS 19 column. DS6 conductometric cell was used as detector in parallel with ASRS 300 mm-4 mm suppressor. The limit of detection (LOD) of this method for chlorides was 0.025 mg/L. CAA concentrations were measured using HPLC using Shimadzu 20A Gradient LC System with UV–Vis Detector equipped with Shim-pack GWS C18 (150 x 4.6, 5 μm) column. A mixture of solvent A (1% CH3CO2H aqueous solution) and solvent B (methanol, CH3OH) was used as mobile phase with 1 mL/min flow rate. The temperature of the separation column was maintained at 30 °C during the analysis. The injection volume was fixed to 10 µL for all samples. Gradient elution mode was used as follows: 100% solvent A is eluted for 1 min, then the elution gradient of solvent B is linearly increased to reach 100% after 25 min, and finally 100% solvent B is eluted for 8 min. The wavelength of the UV detector was fixed at 248 nm. In these conditions, LOD for CAA was estimated to be 0.08 mg/L with 101% recovery. The same chromatograph was used to analyze phenol, benzoic, acid, and hydroquinone. The mobile phase is composed of a mixture of eluent C (0.1% HCO2H in H2O) and eluent D (0.1% HCO2H in CH3CN). The analysis of oxalic and maleic acids was performed using HPLC instrument equipped with Supelcogel H column. The mobile phase consists of 0.15% H3PO4 aqueous solution with a constant flow rate of 0.15 mL/min. The UV detector was set a wavelength of 210 nm. External standardization method was used for all the analytes in chromatography analysis (linear curves with regression coefficient r2 > 0.99).
was performed at pH = 3.0 to keep same pH conditions than Fenton reaction for sake of comparison. As it can be seen from Fig. 2.a, CAA concentration decreased with time for H$_2$O$_2$ doses in the range 100–2000 mM (the stoichiometric amount of H$_2$O$_2$, 1 mM, showed an observable change in CAA concentration after 24 h). The increase in H$_2$O$_2$ dose enhanced the rate and the yield of CAA depletion. CAA depletion yield (calculated after 420 min) increased from 51.7% at 100 mM H$_2$O$_2$ to 67.8, 92.2, 99.1, 99.9, 99.6, 99.9% at 200, 500, 1000, 1500, and 2000 mM H$_2$O$_2$, respectively. In addition, the graphs of CAA with time had an exponential trend for H$_2$O$_2$ doses indicating that the chemical oxidation of CAA by H$_2$O$_2$ follows a pseudo-first-order kinetics with rate constant $k_{obs}$. Thus, the rate law can be given by the equation:

$$r = -rac{d[CAA]}{dt} = k_{obs}[CAA]$$  \hspace{1cm} (5)
from the beginning of the experiment to reach a plateau at 29.2 mg Cl/L after 360 min. This result confirms the release of chloride ions during the chemical oxidation of CAA by H2O2 since the beginning of the reaction. The maximum of amount of chloride ions released was 84% of the total chlorine existing initially in the solution (no free chlorine was detected). This indicates that small portion of chlorine (16%) is still contained in chlorinated organic intermediates.

Figure 5 presents the changes of the concentrations of CAA, TOC, oxalic (OAA) and maleic (MAA) acids concentrations. Operational conditions: initial CAA concentration: 209 mg/L (1 mM), H2O2 dose: 1000 mM, initial pH = 3.0, T = 23–25 °C, stirring rate: 300 rpm
Degradation of CAA by Fenton oxidation (H₂O₂/Fe²⁺)

In order to accelerate the mineralization of CAA aqueous solutions and achieve high TOC depletion yield, the effect of the addition of small amounts of iron(II) (Fe²⁺) on the kinetics and efficiency of CAA degradation by H₂O₂/Fe²⁺ (Fenton oxidation) was evaluated. It was observed that the addition of Fe²⁺ to CAA aqueous solution changed the color of the solution from violet to dark brown indicating the formation of Fe²⁺-CAA stable complex (see Figure S2). The stoichiometry of Fe²⁺-CAA complex was determined by the method of continuous variations (also called Job’s method) (Long and Pfeffer 2015; Renny et al. 2013). The theory behind the Job’s method is that if the absorbance at a given wavelength of each solution is plotted against the mole fraction of the ligand, the maximum absorbance will occur at a mole fraction that corresponds to the composition. The illustration given in Figure S3 shows the continuous variations plot for the Fe²⁺-CAA complex. As shown from the Job’s method, Fe²⁺ and CAA form (1:2) complex, Fe(CAA)²⁺.

Figure 6 presents the effect of H₂O₂ dose on the changes of CAA concentration with time during Fenton oxidation of 1 mM CAA aqueous solution using 0.5 mM Fe²⁺ (stoichiometric Fe²⁺ dose to form Fe(CAA)²⁺) at pH 3.0 and room temperature under 300 rpm stirring. As shown in Fig. 6a, H₂O₂ dose affected the kinetics and efficiency Fenton oxidation of CAA. CAA depletion yields calculated after 60 min were 100, 99.9, 99.8, 96.1, 88.2, and 71.6% for 500, 200, 100, 75, 50, and 25 mM, respectively. Furthermore, as can be seen, CAA decay with time follows a pseudo-first-order kinetics for all H₂O₂ doses. Figure 6b shows a linear increase in pseudo-first-order rate constant (kₖobs) with H₂O₂ dose between 25 to 100 mM, and then the slope decreases for higher H₂O₂ doses than 100 mM. The increase in H₂O₂ dose accelerates the production of HO radicals by Fenton reaction, which explains the improvement in CAA depletion yield and the increase in the rate constant with H₂O₂ dose. However, higher doses of H₂O₂ result in the deceleration of the rate constant with H₂O₂ dose due to speeding up the secondary reactions of H₂O₂ auto-decomposition and its reaction with OH radicals (Eqs. 6–7) (Bensalah et al. 2011; Ghatak 2014).

\[
2H₂O₂ → O₂ + 2H₂O \tag{6}
\]

\[
H₂O₂ + \cdot OH → HO₂ + H₂O \tag{7}
\]

H₂O₂ dose of 100 mM is cost-effective and sufficient to achieve almost complete CAA decay within 60 min by Fenton oxidation. This optimal H₂O₂ dose is ten times lower than that required to achieve similar CAA depletion yield (1000 mM) during chemical oxidation of CAA by H₂O₂. This is due to the higher production of OH radicals by catalytic decomposition of H₂O₂ by Fe²⁺ (Fenton reaction, Eq. 1) than by chemical reaction between H₂O₂ and CAA.
Figure 7 presents the changes of CAA concentration with time during Fenton oxidation of CAA (1 mM) using 100 mM H₂O₂ and different Fe²⁺ doses at pH 3.0 and room temperature under 300 rpm stirring. The increase in Fe²⁺ dose from 0.0 to 2 mM enhanced the kinetics and the yield of CAA depletion. These results confirmed that Fenton oxidation is more effective than chemical oxidation using H₂O₂. It is well documented (Babuponnusami and Muthukumar 2014; Pliego et al. 2015; Hui Zhang, et al. 2019; Oturan et al. 2012; Oliveira et al. 2014) that the presence of Fe²⁺ catalyzes the decomposition of H₂O₂ resulting in the formation of OH radicals (Eq. 1) that are capable of destroying organics in water. All the kinetic results shown in Fig. 6a can be modeled using a pseudo-first-order kinetics model. The pseudo-first-order rate constant, k_{obs}, increased linearly with the increase in Fe²⁺ dose from 0.0 up to 1.0 mM, with decreasing slope for Fe²⁺ doses higher than 1.0 mM (Fig. 7b). CAA depletion yields after 30 min were 12.6, 73.0, 96.1, 99.1, and 99.4% for Fe²⁺ doses of 0.0, 0.2, 0.5, 1.0, and 2.0 mM, respectively. Higher Fe²⁺ doses than 1 mM are not cost-effective since they did not significantly enhance the kinetics of the reaction. This indicates that a catalytic dose of Fe²⁺ (molar ratio (H₂O₂/Fe²⁺) = 100) is required to achieve ≥ 99% CAA depletion within 30 min. It should be noted that generally smaller molar ratios (H₂O₂/Fe²⁺) than 100 (between 1 and 50) have been reported in the literature (Mitsika et al. 2013; Biglarijoo et al. 2016). Using 1 mM Fe²⁺, CAA/Fe²⁺ molar ratio is equal to 1, indicating that CAA ligand molecules were completely complexed with Fe²⁺ ions (considering a Fe(CAA)₂⁺ complex formula). Furthermore, it was found that, within the range 3.0 – 6.0, pH did not have a significant effect on CAA degradation and that Fe³⁺ and CAA form also stable complex Fe(CAA)₂³⁺ (see Figure S4). These results show the importance of Fe²⁺/Fe³⁺ organo-complexation in Fenton oxidation that might be related to the high solubility of Fe(CAA)₂⁺ complex enabling a rapid regeneration of the catalyst. In this case, CAA degradation by Fenton oxidation was less sensitive to pH due to the enhanced production of OH radicals by Fe²⁺/Fe³⁺ organo-complexation. It should be noted that similar results have been reported related to the presence of organic ligands susceptible to form complexes with Fe²⁺/Fe³⁺ ions (Messele et al. 2019). The results illustrated in Table 1 present the effect of initial pH on the degradation yield of some aromatic compounds including CAA, phenol, benzoic acid, and hydroquinone by Fenton oxidation. As it can be seen, Fenton oxidation achieved complete degradation of all aromatic compounds at pH 3.0 during 120 min. The initial pH affected the degradation yield of all compounds. Increasing pH to values higher than 3.0 decreased the pollutant degradation yield. It is markedly observed that CAA degradation was less affected by initial pH than the other compounds. More details about the effect of initial pH on CAA degradation by Fenton oxidation are given in Figure S5.

| Initial pH | CAA Yield (%) | Phenol Yield (%) | Benzoic Acid Yield (%) | Hydroquinone Yield (%) |
|-----------|---------------|-----------------|------------------------|------------------------|
| 3.0       | 99.1          | 98.7            | 98.5                   | 97.8                   |
| 4.0       | 98.9          | 98.2            | 98.1                   | 97.5                   |
| 5.0       | 97.7          | 97.1            | 96.7                   | 96.1                   |
| 6.0       | 96.2          | 95.7            | 95.2                   | 94.7                   |
| 7.0       | 94.5          | 93.7            | 93.3                   | 92.7                   |
| 8.0       | 92.7          | 91.9            | 91.5                   | 90.9                   |
| 9.0       | 90.5          | 90.1            | 89.7                   | 89.3                   |

Table 1 Effect of initial pH on the degradation yield of some aromatic compounds by Fenton oxidation. Experimental conditions: initial pollutant concentration: 1 mM, H₂O₂ dose: 100 mM, Fe²⁺: 1 mM, Time: 120 min, T = 23–25 °C, stirring: 300 rpm.
Figure 8 presents the results of CAA mineralization during Fenton oxidation of 1 mM CAA aqueous solution using 100 mM \( \text{H}_2\text{O}_2 \) and 1 mM \( \text{Fe}^{2+} \) at pH 3.0 and room temperature. As shown in Fig. 8a, CAA decay was too much more rapid than TOC depletion with pseudo-first-order rate constants of 0.173 and 0.014 min\(^{-1}\), respectively. CAA was completely depleted after 60 min; while 99% TOC was depleted after 300 min (see Fig. 8a). CAA decay was accompanied with a simultaneous formation of chloride ions, \( \text{CO}_2 \), OAA, and MAA from the beginning of photochemical treatment (Fig. 8b). It was found that 98% of organic chlorine was converted into chloride ions by Fenton oxidation after 300 min. No chlorate and perchlorate ions were detected, but small amount of free chlorine was formed based on N,N-dietethyl-p-phenylenediamine (DPD) rapid test (Rice et al. 2017). These results indicate that chloride ions and carbon dioxide are the major final products of CAA degradation using Fenton oxidation. OAA and MAA were formed as intermediate species that were converted into \( \text{CO}_2 \) and they were mostly depleted at the end of the treatment. These results reveal that the mechanism of CAA degradation by Fenton oxidation could involve similar steps than chemical oxidation using \( \text{H}_2\text{O}_2 \). During Fenton oxidation, both Fenton reaction and nucleophilic substitution of Cl with OOH followed by homolytic rupture of O – O bond produce more important amounts of hydroxyl radicals, which enhances CAA mineralization. It is remarkable that no accumulation of carboxylic acids was observed during CAA degradation by Fenton oxidation. This result confirms the importance of \( \text{Fe}^{2+/3+}-\text{CAA} \) complex formation that enables high solubility for iron(II)/iron(III) catalyst and accelerates the regeneration of \( \text{Fe}^{2+} \) catalyst, and thus large production of OH radicals occurs.

**Decolorization of MB aqueous solution by \( \text{H}_2\text{O}_2/\text{CAA}, \text{H}_2\text{O}_2/\text{Fe}^{2+}, \text{and H}_2\text{O}_2/\text{CAA/Fe}^{2+} \)**

The concentrations of reagents used to decolorize 0.025 mM MB solutions at pH = 3.0 and \( T = 23–25 \) °C

| \( \text{H}_2\text{O}_2 \) (mM) | CAA (mM) | \( \text{Fe}^{2+} \) (mM) | **Discoloration yield(%)** |
|---|---|---|---|
| 20 | 0 | 0 | 5.8 |
| 25 | 0 | 0 | 10.8 |
| 30 | 0 | 0 | 11.2 |
| 25 | 0.010 | 0 | 27.3 |
| 25 | 0.025 | 0 | 58.0 |
| 25 | 0.050 | 0 | 59.1 |
| 25 | 0 | 0.010 | 64.8 |
| 25 | 0 | 0.025 | 97.1 |
| 25 | 0 | 0.050 | 96.9 |
| 25 | 0.025 | 0.010 | 97.8 |
| 25 | 0.025 | 0.025 | 99.9 |
| 25 | 0.025 | 0.050 | 96.7 |

**Table 2** Optimization of experimental parameters on the discoloration yield of MB by \( \text{H}_2\text{O}_2 \)-based chemical methods. Experimental conditions: MB: 0.0125 mM (4 mg/L), pH = 3.0, \( T = 23–25 \) °C, Stirring rate: 300 rpm, Time: 120 min. **Discoloration yield(%)** = \( \frac{\text{Abs}_0 - \text{Abs}_{120}}{\text{Abs}_0} \times 100 \) (Abs\(_0\) and Abs\(_{120}\) are absorbance at 664 nm at time t = 0 min and t = 120 min)
under stirring rate of 300 rpm were optimized in preliminary experiments (see Table 2). The results of Table 2 demonstrate that the optimal conditions to reach the maximum discoloration yields were: 25 mM H$_2$O$_2$, 0.025 mM Fe$^{2+}$, and 0.025 mM CAA. Figure 9 presents the changes of the normalized absorbance (Abs$_t$/Abs$_0$) (with Abs$_t$ and Abs$_0$ are the absorbencies of MB at 664 at an instant t and at t = 0 s) of MB aqueous solutions with time during the degradation of MB (0.0125 mM) aqueous solution using different H$_2$O$_2$-based chemical oxidation methods (see Figure S6 for color differences). As it can be seen, H$_2$O$_2$/CAA/Fe$^{2+}$ was the most effective oxidation method to remove MB from water. Fenton oxidation (H$_2$O$_2$/Fe$^{2+}$) was more efficient than H$_2$O$_2$/CAA (Figure S7 shows the changes of UV–visible spectra with time for the different H$_2$O$_2$-based chemical oxidation methods). The chemical oxidation with H$_2$O$_2$ alone was the lowest effective method. The complete decolorization of MB aqueous solution was achieved after 75 min with H$_2$O$_2$/CAA/Fe$^{2+}$, while at this time, decolorization percent were 7.5, 42.0, and 90.6% for H$_2$O$_2$ alone, H$_2$O$_2$/CAA, and H$_2$O$_2$/Fe$^{2+}$, respectively. The rate constant calculated from the fitted data to pseudo-first-order kinetics model was 0.069, 0.031, 0.007, and 0.0007 min$^{-1}$ for H$_2$O$_2$/CAA/Fe$^{2+}$, H$_2$O$_2$/Fe$^{2+}$, H$_2$O$_2$/CAA, and H$_2$O$_2$ alone, respectively. Coupling H$_2$O$_2$ with CAA was able to partially decolorize the MB solution due to the small amount of OH radicals formed from the chemical oxidation of CAA by H$_2$O$_2$. H$_2$O$_2$/Fe$^{2+}$ (Fenton’s reagent) was more effective than H$_2$O$_2$/CAA due to larger amount of OH radicals produced by Fenton reaction. The cost of each process can be estimated based on the prices of chemicals. Considering that the same chemicals are used, it is obvious that H$_2$O$_2$/CAA/Fe$^{2+}$ is the most cost-effective compared to the other processes. Figure 10 shows the effect of initial pH on the changes of the normalized absorbance (Abs$_t$/Abs$_0$) with time during MB decolorization using H$_2$O$_2$/CAA/Fe$^{2+}$. As it can be seen, the increase in pH from 3.0 to 6.0 did not have a significant effect on the kinetics of MB decolorization; however, higher initial pH than 6.0 decelerated the MB decolorization. MB decolorization yield calculated after 60 min was 98.9, 98.4, 97.6, 95.4, 75.5, 49.3, and 32.6 for pH 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, and 9.0, respectively. CAA can also form stable complexes with Fe$^{2+}$/Fe$^{3+}$ that increases the solubility of Fe$^{3+}$ and then keep similar amount of catalyst available to decompose H$_2$O$_2$. The results of Fig. 10 confirm this hypothesis since the initial pH in the range 3.0 – 6.0 did not affect the MB decolorization by H$_2$O$_2$/CAA/Fe$^{2+}$ system.

Fig. 9 Decolorization of MB aqueous solutions using different H$_2$O$_2$-based chemical oxidation methods. Operational conditions: MB: 0.0125 mM (4 mg/L), H$_2$O$_2$: 25 mM, Fe$^{2+}$: 0.025 mM, CAA: 0.025 mM, pH = 3.0, T = 23–25 °C, stirring rate: 300 rpm

Fig. 10 Effect of initial pH on the decolorization of MB aqueous solution using different H$_2$O$_2$/CAA/Fe$^{2+}$ system. Experimental conditions: MB: 0.0125 mM (4 mg/L), H$_2$O$_2$: 25 mM, Fe$^{2+}$: 0.025 mM, CAA: 0.025 mM, pH= 3.0–9.0, T= 23–25 °C, stirring: 300 rpm
The higher effectiveness of \( \text{H}_2\text{O}_2/\text{CAA}/\text{Fe}^{2+} \) in decolorizing MB aqueous solution is due to the acceleration of iron(II) catalyst regeneration in Fenton oxidation mechanism. CAA (quinonoid substance) is capable of reducing \( \text{Fe}^{2+} \) into \( \text{Fe}^{3+} \) (Taran 2017; Sander et al. 2015) and then continuously feeds up the system with OH radicals. The estimated costs ($/m^3$) calculated based on the chemical costs (using technical grade chemicals) and the post-treatment costs (filtration, washing, and AC adsorption) are illustrated in Table 3. \( \text{H}_2\text{O}_2/\text{CAA}/\text{Fe}^{2+} \) costs are less than \( \text{H}_2\text{O}_2/\text{CAA} \) and \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) processes. \( \text{H}_2\text{O}_2/\text{CAA}/\text{Fe}^{2+} \) is the most cost-effective process due to cheaper post-treatment (AC adsorption).

### Conclusion

CAA can be slowly degraded by chemical oxidation with \( \text{H}_2\text{O}_2 \). The reaction required high amount of \( \text{H}_2\text{O}_2 \) (\( \text{H}_2\text{O}_2/\text{CAA} \) molar ratio = 1000) to achieve the almost complete removal of CAA within 420 min. The addition of ethanol (as OH radicals scavenger) confirmed the production of OH radicals. TOC analysis and chromatography results indicated that low organic carbon mineralization yield was achieved with accumulation of carboxylic acids intermediates and the release of 84% organic chlorine. The addition of \( \text{Fe}^{2+} \) enhanced CAA degradation and reduced the amount of \( \text{H}_2\text{O}_2 \) required to achieve complete CAA decay and 99% TOC removal. It seems that the formation of \( \text{Fe}^{2+3+} \cdot \text{CAA} \) complexes enables accelerates the regeneration of \( \text{Fe}^{2+} \) catalyst, and thus large production of OH radicals occurs. Furthermore, \( \text{H}_2\text{O}_2/\text{CAA}/\text{Fe}^{2+} \) system was more effective in decolorizing MB aqueous solution than \( \text{H}_2\text{O}_2/\text{CAA} \) and \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) systems. This might be due to larger OH radicals’ production and more rapid \( \text{Fe}^{2+} \) regeneration. This indicates that the addition of small amount of CAA (quinonoid compound) could be a promising method to enhance the effectiveness of Fenton oxidation without significant rise in costs compared to coupling Fenton oxidation with photolysis, sonolysis, or electrolysis.

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### Conflict of interest

The authors declare that they have no conflict of interest.

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