

Development of new homogeneous photo-Fenton catalytic systems using oxalic acid and ferric ions in very low concentrations

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Abstract:

Despite its contribution to the economic development of many countries over the last few decades, the rapidly growing global textile industry has raised a wide range of environmental problems via the discharge of high amounts of toxic and non-biodegradable dye molecules into the wastewater. In this work, we proposed to combine oxalic acid and ferric ions in very low concentrations to create new, economic, and effective homogeneous photo-Fenton catalytic systems for the degradation of methylene blue. The effects of ferric concentration, $\text{H}_2\text{C}_2\text{O}_4$ concentration, pH, and tert-butanol on the catalytic activity were also investigated. According to the experimental results, Fe^{3+} ions exhibited impressive catalytic performances in the presence of $\text{H}_2\text{C}_2\text{O}_4$ at concentrations below type B (5.0 mg.l⁻¹) from the Vietnam National Technical Regulation on Industrial Wastewater. Specifically, a ferric concentration of 3.0 mg.l⁻¹, $\text{H}_2\text{C}_2\text{O}_4$ concentration of 10–3 mol.l⁻¹, and pH value of 3 were found to be the best conditions for MB degradation under UVA light. Furthermore, owing to a very low concentration of ferric ions, iron sludge formation can be avoided after wastewater treatment, which makes the photo-Fenton process suitable for practical applications.

Keywords: ferric ions, homogeneous photo-Fenton activity, methylene blue, oxalic acid, very low concentration.

Classification number: 2.2

1. Introduction

Despite its contribution to the economic development of many countries over the last few decades, the rapidly growing global textile industry has raised a wide range of environmental problems via the discharge of high amounts of toxic and non-biodegradable dye molecules into the wastewater. This kind of wastewater represents a severe threat to surrounding ecosystems and thus has stimulated the need for effective wastewater treatment technologies. Since the 1990s, homogeneous Fenton reagents that rely on $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions and hydrogen peroxide have been proposed as a powerful method to completely mineralize dye molecules owing to the generation of highly reactive oxygen radicals such as hydroxyl and superoxide anion radicals [1, 2]. Moreover, it has been universally acknowledged that the combination of Fenton's reagents and UV-visible light illumination greatly improves the efficiency of organic compound decomposition [2, 3]. In fact, UV-visible irradiation accelerates the regeneration of Fe^{2+} ions via the photoreduction of Fe^{3+} ions, which ameliorates the production of reactive oxygen species.

Nevertheless, the practical application of the classical homogeneous Fenton technique is still restricted mainly by the enormous quantity of ferric sludge produced during the post-neutralisation process [4]. It is almost impossible to retain these homogeneous catalysts in a continuous system of wastewater treatment since $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions are completely dissolved in the solution. Therefore, large amounts of iron salts must be continuously added to the solution to maintain Fenton reactions that not only increases the content of catalysts, but causes the rise of treatment cost and the formation of ferric sludge as a secondary pollution source [5]. Due to its hazardous features, this solid waste sludge also requires further treatment and thus is considered as a major obstacle blocking the application of Fenton processes on an industrial scale.

To overcome this drawback, numerous efforts have been made to impregnate iron ions into clay [6, 7], porous zeolite [8], and activated carbon [9, 10] or to develop other Fenton-like heterogeneous catalysts such as iron oxides [11, 12] and zero-valent iron [13]. Unfortunately, these

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heterogeneous catalytic systems show lower activity than classical homogeneous $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions. Moreover, most of heterogeneous Fenton-like or photo-Fenton-like catalysts were found to be well dispersed in water due to their nanoscale particle size, which makes the catalyst recovery strenuous in real applications. On the other hand, H_2O_2 , which is traditionally used as the oxidant in photo-Fenton reactions, is found to be unstable and thus able to be decomposed during storage before use.

Therefore, in this work, we proposed to develop a new homogeneous photo-Fenton catalytic system based on the combination of ferric ions in very low concentration and $\text{H}_2\text{C}_2\text{O}_4$ as a radical producing source. Specifically, ferric ions were provided into a solution with concentration below type B (5.0 mg.l^{-1}) from the Vietnam National Technical Regulation on Industrial Wastewater (QCVN 40:2011/BTNMT). Thanks to the very low concentration of Fe^{3+} ions, treatment costs can be reduced and ferric sludge is nearly impossible to form. In addition, according to some previous reports [14, 15], the presence of ferrioxalate complexes produced from the reaction of iron ions and oxalate species can enhance the light absorption and consequently ameliorate catalyst performance. Thus, the replacement of H_2O_2 by $\text{H}_2\text{C}_2\text{O}_4$ in our work may allow us to not only improve the photo-Fenton catalytic activity of ferric ions but also easily store chemicals in the long term due to the high stability of oxalic acid. The influences of ferric concentration, $\text{H}_2\text{C}_2\text{O}_4$ concentration, and pH of solution on the performance of the catalytic system were also investigated.

2. Experimental

2.1. Preliminary tests

The starting materials $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, H_2O_2 , $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (>98%, ACS reagent), and methylene blue (MB) as the model pollutant were purchased from Sigma Aldrich (USA). In addition, H_2SO_4 , NaOH and tert-butanol ($\geq 99.5\%$) were obtained from Merck.

To ensure that our hypothesis of the combination of ferric ions in very low concentration and $\text{H}_2\text{C}_2\text{O}_4$ can work as reagents, photo-Fenton tests for MB degradation under ultraviolet A (UVA) light were carried out with two ferric concentrations in the presence of H_2O_2 or $\text{H}_2\text{C}_2\text{O}_4$: a high concentration, 0.1 mol.l^{-1} , and a very low concentration, $9.0 \times 10^{-5} \text{ mol.l}^{-1}$ corresponding to the type B (5.0 mg.l^{-1}) of QCVN 40:2011/BTNMT. In a typical run for the high concentration of ferric ions, an amount

of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in water acidified with a diluted sulphuric acid solution. This ferric solution was poured into a stock solution containing both MB and H_2O_2 or $\text{H}_2\text{C}_2\text{O}_4$. Deionized water was quickly added to obtain a final solution with the volume of 250 ml. The concentrations of Fe^{3+} , MB, and $\text{H}_2\text{O}_2/\text{H}_2\text{C}_2\text{O}_4$ are, respectively, 0.1 , 3×10^{-5} , and $10^{-3} \text{ mol.l}^{-1}$. Then, the final solution was constantly stirred by a mechanic agitator and irradiated by a 9-W Radium 78 light lamp (UVA light), which was hung above the solution. The distance between the UVA light lamp and the solution surface was about 10 cm. During the reaction, the solution temperature was kept at $29\text{--}31^\circ\text{C}$ using a water circulation system. At regular time intervals, 5-ml aliquots of dye solution were taken out and their MB concentration was analysed by an Optima UV/VIS SP-300 spectrophotometer (Optima, Japan) at 664 nm. For the low concentration of ferric ions, the test was carried out in the same procedure but using ferric solution with the concentration of 5 mg.l^{-1} instead of 0.1 mol.l^{-1} .

To preliminarily investigate the mechanism of our catalytic system, three blank tests were effectuated: (i) a test for the photo-degradation of MB in the presence of $\text{H}_2\text{C}_2\text{O}_4$ without ferric ions, (ii) a test for the photo-degradation of MB in the presence of ferric ions without $\text{H}_2\text{C}_2\text{O}_4$, and (iii) a test for the catalytic degradation of MB in the presence of both $\text{H}_2\text{C}_2\text{O}_4$ and ferric ions without light illumination. Moreover, as a scavenger of hydroxyl radicals, tert-butanol was added into the solution containing MB, $\text{H}_2\text{C}_2\text{O}_4$, and ferric ions (5 mg.l^{-1}) to study the role of hydroxyl radicals.

2.2. Investigation of factors affecting the photo-Fenton process

The influences of ferric concentration, $\text{H}_2\text{C}_2\text{O}_4$ concentration, and pH on the photo-Fenton performance of our homogeneous catalytic system were studied via the same MB degradation procedure with different ferric concentrations (0.3 , 0.5 , 1.0 , 3.0 , 5.0 , 10.0 mg.l^{-1}), $\text{H}_2\text{C}_2\text{O}_4$ concentrations (10^{-4} , 5×10^{-4} , $10^{-3} \text{ mol.l}^{-1}$), and pH values (1 , 3 , 5 , 7 , 9 , 11), respectively. H_2SO_4 (1.0 mol.l^{-1}) and NaOH (1.0 mol.l^{-1}) solutions were used to adjust pH.

3. Results and discussion

3.1. Preliminary tests

As mentioned above, preliminary tests were carried out to verify whether the combination of ferric ions in very

low concentration and $\text{H}_2\text{C}_2\text{O}_4$ can effectively degrade MB under UVA light. Fig. 1 compares the $\text{Ln}(C_0/C)$ versus time plots of MB degradation (C_0 and C are the MB concentrations (mol.l^{-1}) at the beginning and at time t , respectively) under 3 different experimental conditions: (i) H_2O_2 ($10^{-3} \text{ mol.l}^{-1}$), Fe^{3+} ions (0.1 mol.l^{-1}); (ii) $\text{H}_2\text{C}_2\text{O}_4$ ($10^{-3} \text{ mol.l}^{-1}$), Fe^{3+} ions (0.1 mol.l^{-1}), and (iii) $\text{H}_2\text{C}_2\text{O}_4$ ($10^{-3} \text{ mol.l}^{-1}$) and Fe^{3+} ions (5.0 mg.l^{-1}). All the plots are quasi-perfectly linear, which proves that MB degradation over all our catalytic systems fits to a pseudo-first-order kinetic model. Hence, the photo-Fenton activity of the three different catalytic systems can be evaluated through an apparent rate constant (k , Table 1). At high ferric concentration (0.1 mol.l^{-1}), the combination of H_2O_2 and

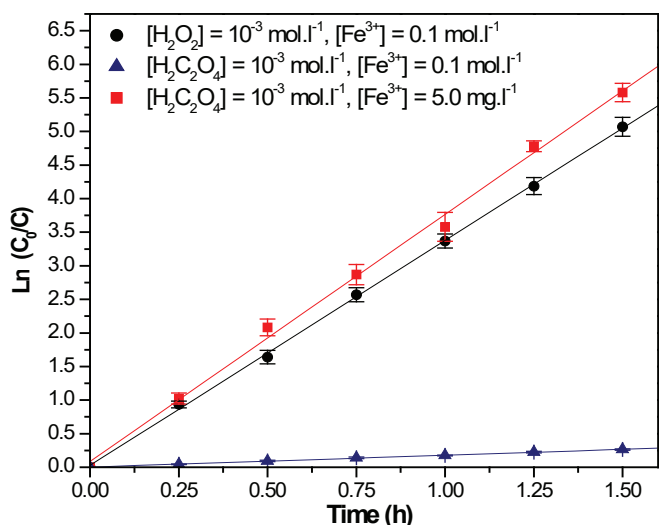


Fig. 1. Kinetic plot of UVA-induced MB degradation in different catalytic solutions.

Table 1. Rate constants (k) of UVA-induced MB degradation in different catalytic solutions.

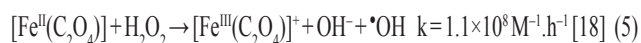
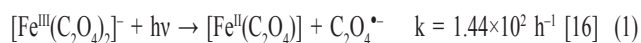
Ferric concentration	0.1 mol.l^{-1}	0.1 mol.l^{-1}	$9.0 \times 10^{-5} \text{ mol.l}^{-1}$ (5.0 mg.l^{-1})
Radical producing source	$[\text{H}_2\text{O}_2] = 10^{-3} \text{ mol.l}^{-1}$	$[\text{H}_2\text{C}_2\text{O}_4] = 10^{-3} \text{ mol.l}^{-1}$	$[\text{H}_2\text{C}_2\text{O}_4] = 10^{-3} \text{ mol.l}^{-1}$
$k \text{ (h}^{-1}\text{)}$	3.35	0.18	3.68

Table 2. Evolution of MB concentration versus time in three blank tests.

Experimental conditions	Time (h)	0	0.25	0.5	0.75	1.0
Blank test 1 $[\text{H}_2\text{C}_2\text{O}_4] = 10^{-3} \text{ mol.l}^{-1}$; UVA without Fe^{3+} ions	[MB] (mol.l^{-1})	2.62×10^{-5}	2.68×10^{-5}	2.65×10^{-5}	2.67×10^{-5}	2.67×10^{-5}
Blank test 2 $[\text{Fe}^{3+}] = 5.0 \text{ mg.l}^{-1}$; UVA without $\text{H}_2\text{C}_2\text{O}_4$	[MB] (mol.l^{-1})	2.41×10^{-5}	2.54×10^{-5}	2.24×10^{-5}	2.25×10^{-5}	2.13×10^{-5}
Blank test 3 $[\text{H}_2\text{C}_2\text{O}_4] = 10^{-3} \text{ mol.l}^{-1}$; $[\text{Fe}^{3+}] = 5.0 \text{ mg.l}^{-1}$ without UVA light	[MB] (mol.l^{-1})	2.70×10^{-5}	2.74×10^{-5}	2.83×10^{-5}	2.67×10^{-5}	2.69×10^{-5}

Fe^{3+} ions ($k=3.35 \text{ h}^{-1}$) had a much higher performance than that of $\text{H}_2\text{C}_2\text{O}_4$ and Fe^{3+} ions ($k=0.18 \text{ h}^{-1}$) proving that H_2O_2 is the better radical producing source than $\text{H}_2\text{C}_2\text{O}_4$ in the photo-Fenton process. However, in practical applications, the recovery of ferric ions at high concentration is very difficult. Furthermore, using a large amount of Fe^{3+} ions may cause ferric sludge as a secondary pollution source. Interestingly, in the presence of $\text{H}_2\text{C}_2\text{O}_4$, when the ferric concentration was decreased to type B of QCVN 40:2011/BTNMT (5 mg.l^{-1} , which is about 1120 times lower than a ferric concentration of 0.1 mol.l^{-1}), the MB rate constant was enhanced by a factor of 20.6 ($k=3.68 \text{ h}^{-1}$) in comparison with the rate constant for a ferric concentration of 0.1 mol.l^{-1} ($k=0.18 \text{ h}^{-1}$). This result demonstrates that a very low amount of ferric ions can effectively play as a photo-Fenton catalyst. Especially, since the ferric concentration is equal to type B of QCVN 40: 2011/BTNMT, the solution after reactions does not require any post-treatment and does not cause sludge.

Table 2 presents the results of the 3 blank tests used to preliminarily investigate the catalytic nature of Fe^{3+} ions in low concentration in the presence of $\text{H}_2\text{C}_2\text{O}_4$. Without Fe^{3+} ions or $\text{H}_2\text{C}_2\text{O}_4$ or light illumination, the MB concentration remained unchanged after 1 h. This confirms that the ferric ions, $\text{H}_2\text{C}_2\text{O}_4$, and UVA light must be involved in a catalytic mechanism for a methylene blue decomposition reaction. According to some previous reports [16-20], when ferrioxalate complexes are dispersed in a solution, UVA light can transform these complexes into many radicals like hydroxyl radicals through the following reactions (Eqs. 1-5):



Then, the generated hydroxyl radicals as highly oxidative reagents cause the complete mineralization of MB molecules. From the suggested mechanism, it was observed that the MB decomposition only takes place in the presence of all three agents, namely, the Fe(III) component, the oxalate species, and UV light, which is consistent with the results of our three blank tests. In our work, although we did not use ferrioxalate complexes, the addition of ferric ions (in very low concentration) into the solution containing $\text{H}_2\text{C}_2\text{O}_4$ is likely to form these complexes and then promote the above reactions to occur.

Moreover, when we added tert-butanol with the increasing concentration into the reaction mixture, we noticed that the performance of our photo-Fenton catalytic system gradually reduced (Fig. 2 and Table 3). Generally, tert-butanol has been widely acknowledged as a $\text{OH}^{\bullet}$ scavenger [21, 22], thus the decline in catalytic activity of MB degradation after adding tert-butanol proves that the hydroxyl radicals are the main agent for the degradation of organic molecules.

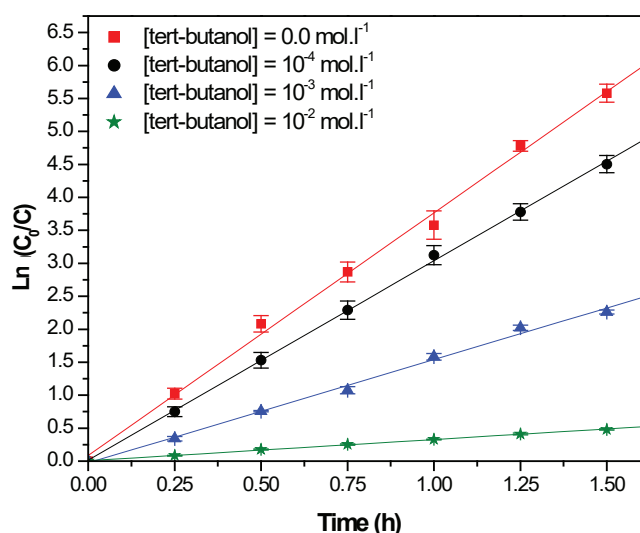


Fig. 2. Kinetic plot of UVA-induced MB degradation in the presence of Fe^{3+} ions (5.0 mg.l^{-1}), $\text{H}_2\text{C}_2\text{O}_4$ ($10^{-3} \text{ mol.l}^{-1}$) and tert-butanol with different concentrations.

Table 3. Rate constants (k) of UVA-induced MB degradation in the presence of Fe^{3+} ions (5.0 mg.l^{-1}), $\text{H}_2\text{C}_2\text{O}_4$ ($10^{-3} \text{ mol.l}^{-1}$) and tert-butanol with different concentrations.

[tert-butanol] (mol.l ⁻¹)	0.0	10 ⁻⁴	10 ⁻³	10 ⁻²
k (h ⁻¹)	3.68	3.02	1.57	0.32

3.2. Investigation of factors affecting the photo-Fenton process

To better understand the possibility of using ferric ions in low concentrations as a homogeneous photo-Fenton catalyst, we sequentially investigated the influence of ferric concentration, $\text{H}_2\text{C}_2\text{O}_4$ concentration, and pH on the catalytic performance of MB degradation.

3.3. Influence of ferric concentration

Figure 3 and Table 4 show the MB degradation profiles over our catalytic systems with different ferric concentrations (0.3, 0.5, 1.0, 3.0, 5.0, 10.0 mg.l^{-1}) in the presence of $\text{H}_2\text{C}_2\text{O}_4$ ($10^{-3} \text{ mol.l}^{-1}$). At the lowest concentration, the ferric ions exhibited the lowest photo-Fenton catalytic activity for MB degradation ($k=0.87 \text{ h}^{-1}$). This can be explained by the fact that when the concentration of Fe^{3+} ions is only 0.3 mg.l^{-1} , these ions hardly react with $\text{H}_2\text{C}_2\text{O}_4$. As a result, very few ferrioxalate complexes were formed, which leads to a small number of hydroxyl radicals generated by illumination with UVA light. In contrast, when the ferric concentration was up to 3.0 mg.l^{-1} , the rate constant quickly increased to 3.87 h^{-1} due to the facile formation of ferrioxalate complexes. However, for ferric concentrations ranging from 5.0 to 10.0 mg.l^{-1} , the catalytic performance slightly declined. It should be reminded that the catalytic performance was dramatically reduced to 0.18 h^{-1} at a ferric concentration of 0.1 mol.l^{-1} . The decrease in photo-Fenton catalytic activity may be related to the self-scavenging of $\text{OH}^{\bullet}$ radicals by Fe^{2+} . In fact, it was reported that radicals such as $\text{COO}^{\bullet}$, $\text{O}_2^{\bullet-}$, and $\text{HO}_2^{\bullet-}$ can act as both oxidants and reductants [23]. At the high ferric concentration (0.1 mol.l^{-1}), after the formation of ferrioxalate complexes, Fe^{3+} ions were still abundant and able to react with many radicals such as $\text{COO}^{\bullet}$, $\text{O}_2^{\bullet-}$, $\text{HO}_2^{\bullet-}$, and even H_2O_2 to form Fe^{2+} ions (Eqs. 6-7) [23, 24]. Then, according to several works [25, 26], these ferrous ions can consume hydroxyl radicals (Eq. 8), which leads to the slow decrease in MB concentration.

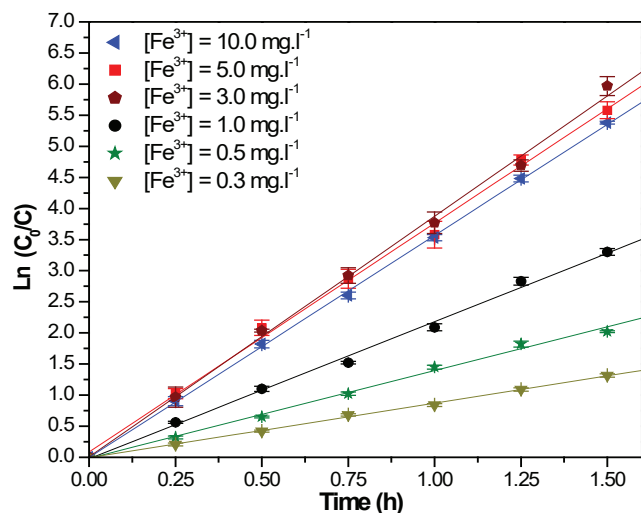


Fig. 3. Kinetic plot of UVA-induced MB degradation with different ferric concentrations in the presence of $\text{H}_2\text{C}_2\text{O}_4$ ($10^{-3} \text{ mol.l}^{-1}$).

Table 4. Rate constants (k) of UVA-induced MB degradation with different ferric concentrations in the presence of $\text{H}_2\text{C}_2\text{O}_4$ ($10^{-3} \text{ mol.l}^{-1}$).

$[\text{Fe}^{3+}]$ (mg.l^{-1})	0.3	0.5	1.0	3.0	5.0	10.0
k (h^{-1})	0.87	1.40	2.19	3.87	3.68	3.58

3.4. Influence of $\text{H}_2\text{C}_2\text{O}_4$ concentration

Besides the ferric concentration, the concentration of $\text{H}_2\text{C}_2\text{O}_4$ is also a factor affecting the photo-Fenton activity of our homogeneous catalytic systems. Therefore, we also investigated MB degradation in a solution containing Fe^{3+} ions (3.0 mg.l^{-1}) and $\text{H}_2\text{C}_2\text{O}_4$ with different concentrations (10^{-4} , 5×10^{-4} , 10^{-3} , $5 \times 10^{-3} \text{ mol.l}^{-1}$) (Fig. 4 and Table 5). The pH values of these solutions are also shown in Table 5. The rate constant of MB degradation strongly rose when the $\text{H}_2\text{C}_2\text{O}_4$ concentration varied from $10^{-4} \text{ mol.l}^{-1}$ to $5 \times 10^{-4} \text{ mol.l}^{-1}$ but slightly increased at a $\text{H}_2\text{C}_2\text{O}_4$ concentration of $10^{-3} \text{ mol.l}^{-1}$ and then decreased when the $\text{H}_2\text{C}_2\text{O}_4$ concentration was upped to $5 \times 10^{-3} \text{ mol.l}^{-1}$. This evolution can be partly explained by the dependence of the formation of ferrioxalate complexes on $\text{H}_2\text{C}_2\text{O}_4$ concentration. At a concentration of $10^{-4} \text{ mol.l}^{-1}$, the quantity of $\text{H}_2\text{C}_2\text{O}_4$ molecules is not sufficient to produce a significant amount of ferrioxalate complexes, resulting in a very low photo-Fenton activity. When the $\text{H}_2\text{C}_2\text{O}_4$ concentration increased to $5 \times 10^{-3} \text{ mol.l}^{-1}$ and $10^{-3} \text{ mol.l}^{-1}$, more Fe^{3+} ions were transformed into ferrioxalate

complexes, which effectively enhanced the catalytic performance. However, at a higher $\text{H}_2\text{C}_2\text{O}_4$ concentration ($5 \times 10^{-3} \text{ mol.l}^{-1}$), $\text{H}_2\text{C}_2\text{O}_4$ molecules may compete with MB molecules for the consumption of $\text{OH}^{\bullet-}$ radicals leading to the decrease in MB degradation rate. It should be noted that oxalate species may be related to kidney stone formation [27]. Therefore, in all our experiments, $\text{H}_2\text{C}_2\text{O}_4$ was always used in low concentration (from 5×10^{-4} to $5 \times 10^{-3} \text{ mol.l}^{-1}$). Besides, according to Eqs. 1-5, the oxalate species will be consumed during the photo-Fenton reactions, which lowers the risk of oxalate pollution. However, any remaining oxalate species must still be controlled and the post-treatment of the solution after the photo-Fenton reactions also needs to be investigated in the near future.

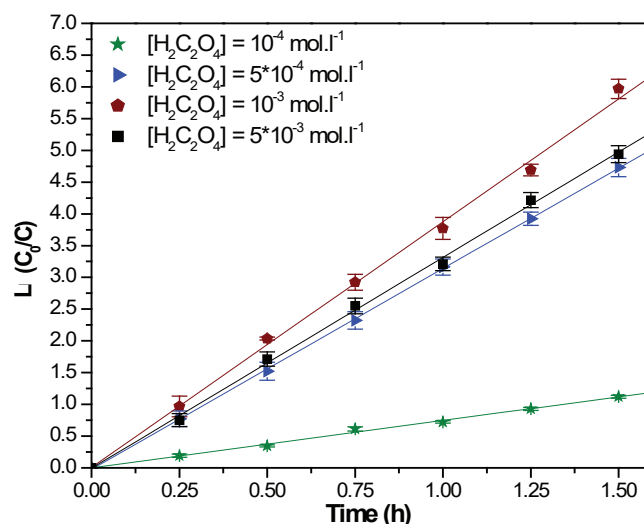


Fig. 4. Kinetic plot of UVA-induced MB degradation with Fe^{3+} ions (3.0 mg.l^{-1}) and $\text{H}_2\text{C}_2\text{O}_4$ at different concentrations.

Table 5. Rate constants (k) of UVA-induced MB degradation with Fe^{3+} ions (3.0 mg.l^{-1}) and $\text{H}_2\text{C}_2\text{O}_4$ at different concentrations.

$[\text{H}_2\text{C}_2\text{O}_4]$ (mol.l^{-1})	10^{-4}	5×10^{-4}	10^{-3}	5×10^{-3}
pH	3.9	3.6	3.2	2.6
k (h^{-1})	0.74	3.13	3.87	3.32

3.5. Influence of pH

Figure 5 and Table 6 display the MB degradation profiles at various pH (1, 3, 5, 7, 9, 11) in the presence of Fe^{3+} ions (3.0 mg.l^{-1}) and $\text{H}_2\text{C}_2\text{O}_4$ ($10^{-3} \text{ mol.l}^{-1}$). In the literature, it was reported that the optimal pH for classical Fenton reactions with H_2O_2 as an oxidant is about 2.8-3.0 [12, 28]. Our study exhibited the same results with

the highest efficiency ($k=3.70 \text{ h}^{-1}$) at pH 3. According to the proposed photo-Fenton mechanism of ferrioxalate complexes (Eqs. 1-5), H^+ ions are necessary to promote the formation of hydroxyl radicals, which is the main reagent for the oxidation of MB molecules. Thus, at pH values greater than 3, catalytic activity was quickly suppressed. However, at pH below 3, the catalytic performance of our system also reduced. This may be attributed to the stability of oxonium ions produced from the reaction between H_2O_2 and H^+ ions (Eq. 9) [29]. In fact, H_2O_2 can be generated by the interactions of ferrioxalate complexes, oxygen molecules, and H^+ ions under UVA light. If the pH is too low, a large amount of H^+ ions can easily react with H_2O_2 to form stable oxonium ions (H_3O_2^+), which makes the conversion of H_2O_2 to hydroxyl radicals more difficult.

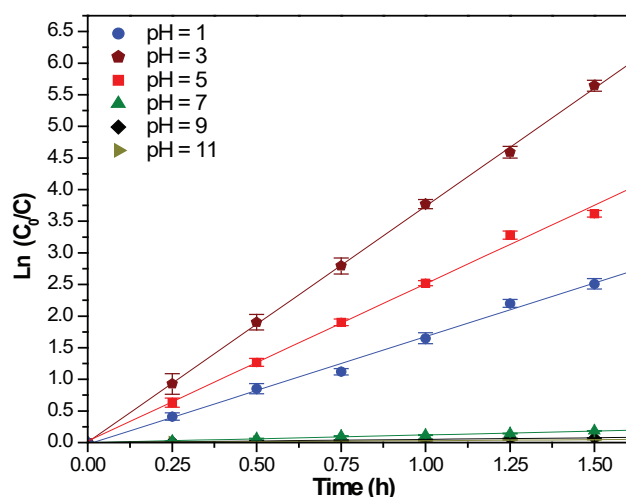


Fig. 5. Kinetic plot of UVA-induced MB degradation in the presence of Fe^{3+} ions (3.0 mg.l^{-1}) and $\text{H}_2\text{C}_2\text{O}_4$ ($10^{-3} \text{ mol.l}^{-1}$) at different pH values.

Table 6. Rate constants (k) of UVA-induced MB degradation in the presence of Fe^{3+} ions (3.0 mg.l^{-1}) and $\text{H}_2\text{C}_2\text{O}_4$ ($10^{-3} \text{ mol.l}^{-1}$) at different pH values.

pH	1	3	5	7	9	11
$k \text{ (h}^{-1}\text{)}$	1.68	3.71	2.49	0.12	0.05	0.03

4. Conclusions

In summary, we successfully developed a new and effective homogeneous photo-Fenton catalytic system for the degradation of dye molecules based on a mixture of $\text{H}_2\text{C}_2\text{O}_4$ and ferric ions in very low concentration (below the type B (5.0 mg.l^{-1}) of QCVN 40:2011/BTNMT). The very low concentration of ferric ions allows us to reduce

the cost of treatment and nearly avoid the formation of sludge as a secondary pollution source. Moreover, using $\text{H}_2\text{C}_2\text{O}_4$ instead of classical H_2O_2 permits long-time storage of chemicals owing to the stability of $\text{H}_2\text{C}_2\text{O}_4$. The influences of ferric concentration, $\text{H}_2\text{C}_2\text{O}_4$ concentration, and pH on the photo-Fenton performance of our catalytic system were also investigated. Among different experimental conditions, the ferric concentration of 3.0 mg.l^{-1} , the $\text{H}_2\text{C}_2\text{O}_4$ concentration of $10^{-3} \text{ mol.l}^{-1}$, and pH 3 were found to be the best conditions for efficient catalytic MB degradation.

CRedit author statement

Quoc Viet Bui: Data analysis and interpretation, Writing and manuscript revising; Thuy Vy Phan, Tien Khoa Le: Method, Data analysis and Writing.

COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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