



DECOLOURISATION OF REACTIVE BLUE 28 FROM AQUEOUS SOLUTION BY FENTON AND PHOTO-FENTON PROCESSES

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ABSTRACT

The decolorization of Reactive blue 28 (RB 28) in aqueous solution has been studied using Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and photo-Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$) processes. This investigation indicates that both these methods can remove the color of RB 28. The effects of different system variables namely initial concentration of Fe^{2+} , initial concentration of H_2O_2 , initial pH of solution and initial dye concentration were studied. The increase of initial dye concentration decreases the decolorization rate. Under optimum conditions, the photo-Fenton process was found to be more efficient than Fenton process.

Key words: Decolourisation, Reactive blue 28, Fenton process, Photo-Fenton process.

INTRODUCTION

Waste waters released from textile industries create problem for surrounding eco systems because of their toxicity and potentially carcinogenic nature¹⁻³. A part of the aesthetic problem related to coloured effluent is that the dyes strongly absorb sunlight and impeding the photosynthesis activity of aquatic plants and threatening to the whole eco system⁴. Hence, there is a need to treat dye waste water prior to discharge. The traditional treatment techniques such as coagulation/flocculation, membrane separation processes (ultra-filtration, reverse osmosis) and adsorption are applied for textile waste water. Those treatment processes only do a phase transfer of the pollutant, and the waste produced needs further treatment for disposal. Biological treatment method is still considered as an appropriate method for meeting discharge standard but it is not suitable for the dyes, which are bio refractory in nature.

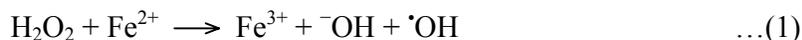
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The limitation of conventional wastewater treatment methods can be overcome by the application of the Advanced Oxidation Processes (AOPs), which present a potential alternative to decolourize and reduce recalcitrant coloured waste water loads. AOPs are able to oxidize a wide range of compounds that are otherwise difficult to degrade^{4,5}.

Among various AOPs, Fenton and photo-Fenton processes could be a good option to treat textile waste water. These processes appear to have the capacity to completely decolourize and mineralize the textile waste water in short reaction time⁴⁻⁷.

Azo dyes are synthetic organic compounds widely used in textile, leather, pharmaceutical, plastic, food, paint and other industries. They are characterized by having an azo group consisting of two nitrogen atoms (-N=N-) bearing aromatic rings and dominated the worldwide market of dye stuff with a share of about 70%⁸. Azo dyes are mainly classified into acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulphur dyes⁶. In these types, the most used ones are the reactive azo dyes. Additionally, these dyes are the most problematic pollutants of textile waste waters. This is due to the fact that about 15% of the textile dyes is lost in waste water stream during reactive dyeing operation⁹. Hence in this work, we have selected the dye Reactive blue 28 (RB 28), one of the most widely used reactive dyes for textile processing as representative dye pollutant of these industrial waste water. AOPs are based on the generation of very reactive species namely hydroxyl radicals ($\cdot\text{OH}$), which have a very strong oxidation potential ($E^\circ = + 2.8 \text{ eV}$). These radicals are capable of destroying wide range of organic pollutants in water and waste water¹⁰.

Fenton oxidation is a homogeneous catalytic oxidation process based on an electron transfer between hydrogen peroxide (H_2O_2) and homogeneous metal catalyst (Fe^{2+})¹¹. The main advantage of the Fenton's reagent is its simplicity. The chemicals are readily available at moderate cost and there is no need for special equipment⁶. In an acidic environment, if H_2O_2 is added to an organic solution with ferrous ion, a complex redox reaction will occur^{6,11-14}. The overall reaction is –



The hydroxyl radicals ($\cdot\text{OH}$) are generated due to the initiation reaction of ferrous ion and decomposition of H_2O_2 . They are capable of rapidly attacking organic substrates (RH) and cause chemical decomposition of the compounds in two ways namely, hydrogen abstraction and addition to C-C unsaturated bonds⁶ as shown in Eqs. (2-4).

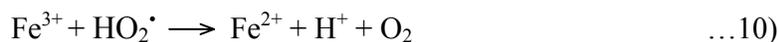
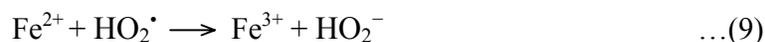
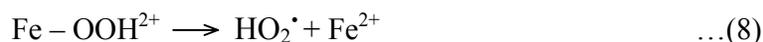
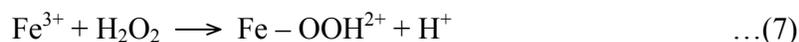




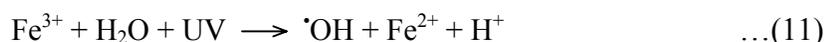
Hydroxyl radicals formed in Eq. (1) may be scavenged by reacting with Fe^{2+} or hydrogen peroxide as shown in Eqs. 5 and 6.



Ferrous ion (Fe^{3+}) formed through reactions (1) and (5) can react with H_2O_2 following a radical mechanism that involves hydroxyl and hydroperoxyl radicals, with regeneration of Fe^{2+} as shown in the following reactions¹⁵.



This reaction scheme is very attractive because Fe^{2+} or Fe^{3+} ions are inexpensive, while H_2O_2 is also relatively inexpensive and is environmentally safe. Moreover, Fe^{2+} ions are regenerated and can be utilized continuously. The two disadvantages of this method are: high acidic environment (pH 2-5) and recovery of Fe^{2+} or Fe^{3+} ions at the end of the treatment due to homogeneity⁴. Sludge problem at the end of the treatment is the major problem in this treatment. To avoid this problem, photolysis can be combined with Fenton process and sludge can be reduced to hydroxyl radicals and Fe^{2+} ions are regenerated as shown in Eq. (11).



Further, the formation of hydroxyl radicals also occurs by the following reaction.



The addition of UV to Fenton's process could be interesting in dye decolourisation due to its capacity to influence the direct formation of $\bullet OH$ radicals^{7,16}.

The main objective of this study is to analyse the feasibility of decolourization and mineralization of RB 28 by Fenton (F) and photo-Fenton (PF) process. The influence of different operational parameters (pH, H₂O₂ dosage, Fe²⁺ dosage and RB 28 concentration), which affects the efficiency of F and PF reaction in RB 28 was investigated and kinetic studies were carried out.

EXPERIMENTAL

Materials and methods

Commercial grade Reactive blue 28, a vinyl sulphone based reactive dye (CAS Number: 12225-45-5, λ_{max} 575 nm) was purchased from Micro Fine Chemicals, Chennai and used as received without further purification. Analytical grade of Na₂CO₃ (Reachem) and H₂SO₄ (Reachem) were used to adjust the solution pH. Initial pH of the solution was monitored using a pH Meter (Make : Elico). The dye solutions of desired concentration were prepared by dissolving requisite quantity of dye in deionized water. H₂O₂ (30% w/w) and FeSO₄.7H₂O (Merck) were used as received.

Photoreactor

Batch experiments were conducted at room temperature in a 1200 mL volume glass reactor (Inside diameter = 8 cm, Outside diameter = 10 cm and height = 25.8 cm). UV light source was provided by UV-lamp (11 Watts, 254 nm) and placed at the centre of the glass reactor. The solution was agitated using a magnetic stirrer. Temperature of the solution was maintained at room temperature using cooling water through jacket provided surrounding the reactor.

Analysis

A desired quantity of dye/Fe²⁺/H₂O₂ solution was freshly prepared from FeSO₄.7H₂O, H₂O₂ and the dye stock solution. The required amounts of Fe²⁺ and H₂O₂ were added simultaneously into the dye solution. In Fenton process, the solution mixtures were kept in dark and the reaction time started, when the H₂O₂ solution was added, whereas in photo-Fenton process, reaction time started, when UV light source and H₂O₂ was added simultaneously. Aliquot samples of the dye solution were withdrawn during the course of the reaction at periodic intervals and analysed for dye concentration by UV-visible Spectrophotometer (Make: Systronics 119). Na₂SO₃ solution was used to quench the oxidation before the spectrophotometer analyses. The concentration of the dye in the reaction mixture was obtained at a wavelength of 575 nm.

RESULTS AND DISCUSSION

Continuous absorption spectra of the dye solutions were recorded from the UV-Vis Spectrophotometer. From the observations it is clear that no new absorption peaks occurred near the original maximum wavelength. From this, it is evident that intermediate oxidation products do not disturb the original absorption band. The concentration of the residual dye in solution was calculated by Beer-Lambert's law at the characteristic wavelength ($\lambda_{\text{max}} = 575 \text{ nm}$). Percentage dye decolourization was calculated as follows:

$$\text{Dye decolourization} = \frac{(C_{\text{dye},0} - C_{\text{dye},t})}{C_{\text{dye},0}} \times 100\% \quad \dots(13)$$

Where $C_{\text{dye},t}$ and $C_{\text{dye},0}$ are the concentrations of dye at reaction time t and 0 , respectively.

Effect of pH

Fenton oxidation is known as a highly pH dependent process since pH plays an important role in the mechanism of hydroxyl radical production in the Fenton reaction¹⁷. The effect of pH on decolourization of RB 28 by Fenton and photo-Fenton process is shown in Figs. 1 and 2. The experiments were carried out at a pH range of 2-6 for the complete decolourization of dye. From the results, it is evident that the pH of the solution influences the decolourization significantly.

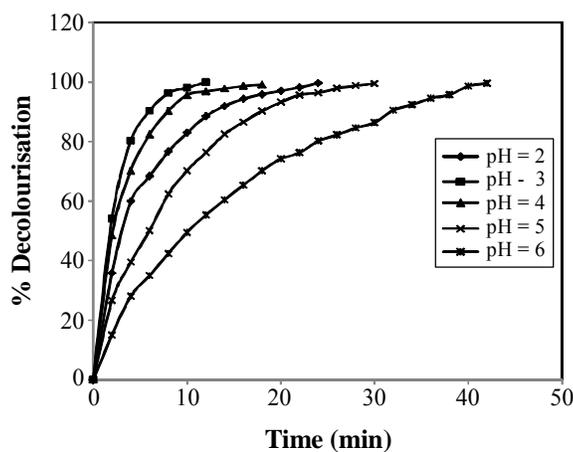


Fig. 1: Effect of pH on Fenton process
(Conditions: $\text{H}_2\text{O}_2 = 20 \text{ mM}$, $\text{Fe}^{2+} = 0.1 \text{ mM}$, Dye concentration = 200 mg/L)

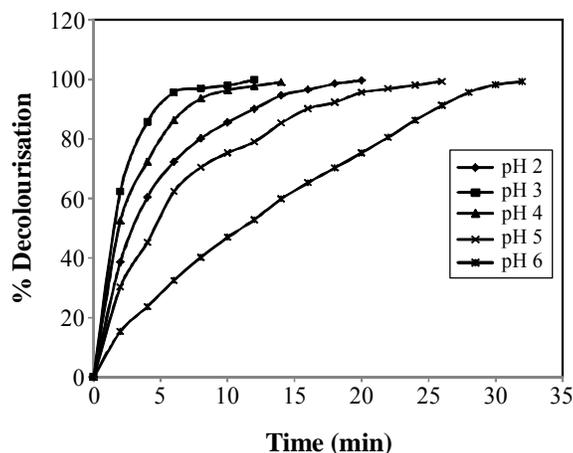


Fig. 2: Effect of pH on Photo-Fenton process
(Conditions: $\text{H}_2\text{O}_2 = 20 \text{ mM}$, $\text{Fe}^{2+} = 0.1 \text{ mM}$, Dye concentration = 200 mg/L)

The time required for complete decolourization of dye was reduced as the pH was increased from 2 to 3. From the results, it was observed that the minimum time required for complete decolourisation of dye is 12 min for Fenton process and 10 min for photo-Fenton process at pH 3. Further increase in pH did not favour the decolourization instead; the time required is increased for complete decolourization. This may be due to the following reasons. At higher pH ($\text{pH} > 4$), the generation of $\cdot\text{OH}$ radicals gets slower because of the formation of Fe^{3+} complexes. On the other hand, at very low pH values ($\text{pH} < 3$), hydrogen ion act as $\cdot\text{OH}$ radicals scavengers as shown in Eq. (14)¹⁶.



In addition, the reaction slowed down due to the formation of complex species $[\text{Fe}(\text{H}_2\text{O}_6)]^{2+}$, which reacts more slowly with peroxide compared to that of $[\text{Fe}_9\text{OH})(\text{H}_2\text{O})_5]^{2+}$. In addition, the peroxide get solvated in the presence of high concentration of H^+ ions to form stable oxonium ion $[\text{H}_3\text{O}_2]^+$. An oxonium ion makes peroxide electrophilic to enhance its stability and substantially reduces the reactivity with Fe^{2+} ions⁴. For photo-Fenton process, the decolourisation rate is higher, when compared to Fenton process. This may be due to the combined effect of photolysis and Fenton process. From the graph, it was observed that decolourization is possible even at pH 6 with the addition of UV light. The time required for complete decolourization of dye is 42 min for Fenton process and 32 min for photo-Fenton process, which is due to the regeneration of Fe^{2+} ions from Fe^{3+} by UV light source^{11,16}.

Effect of H₂O₂ dosage

Figs. 3 and 4 show the relationship between the decolourization of dye and initial concentration of H₂O₂ in Fenton and photo-Fenton processes. The objective of this study is to select the best operational dosage of H₂O₂ in Fenton and photo-Fenton process.

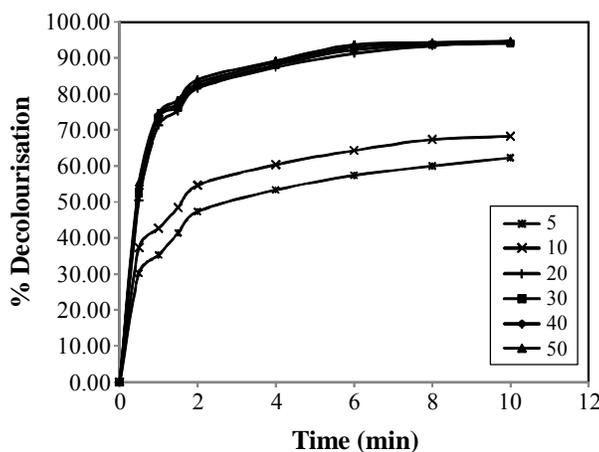


Fig. 3: Effect of H₂O₂ dosage on Fenton process
(Conditions: pH = 3, Fe²⁺ = 0.15 mM, Dye concentration = 200 mg/L)

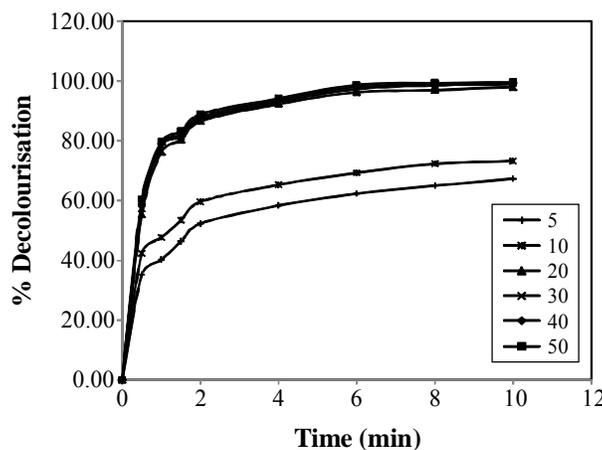


Fig. 4: Effect of H₂O₂ dosage on Photo-Fenton process
(Conditions: pH = 3, Fe²⁺ = 0.15 mM, Dye concentration = 200 mg/L)

The H₂O₂ dosage was varied from 5 mM to 50 mM. From the results, it was observed that in Fenton process, the addition of H₂O₂ from 5 mM to 20 mM increases the decolourisation from 62.28% to 94.68% at 10 min. In the photo-Fenton process, the addition

of H_2O_2 between 5 mM to 20 mM increases the decolourisation from 67.28% to 99.68%. Further increase in H_2O_2 dosage from 20 mM to 50 mM causes no significant change in decolourisation even for photo-Fenton process. This is due to the fact that at a higher H_2O_2 concentration, scavenging of $\cdot\text{OH}$ radicals will occur as shown in Eq. (6) and (15)^{4,6,11,16}.



The increase in decolourisation in photo-Fenton process is due to the additional formation of $\cdot\text{OH}$ radicals due to photolysis effect. Hence, 20 mM of H_2O_2 was used as optional dosage for Fenton and photo-Fenton process.

Effect of ferrous ion dosage

The effect of addition of Fe^{2+} ions on the decolourisation of RB 28 has been studied and results are shown in Figs. 5 and 6. Ferrous ion is one of the main parameter, which influences the Fenton and photo-Fenton processes. The results indicate that the extent of dye decolourization increases with the increase in initial Fe^{2+} concentration. In Fenton process, addition of Fe^{2+} from 0.05 mM to 0.15 mM increases the decolourization from 75.34 to 94.57% in 10 min and in photo-Fenton process, the increase is from 89.56 to 99.68% for the same time. It was observed that the decolourization efficiency increases with increasing initial Fe^{2+} concentration. Further increase in Fe^{2+} concentration from 0.15 mM to 0.3 mM did not show the improvement in decolourization, instead it decreases the percentage decolourization.

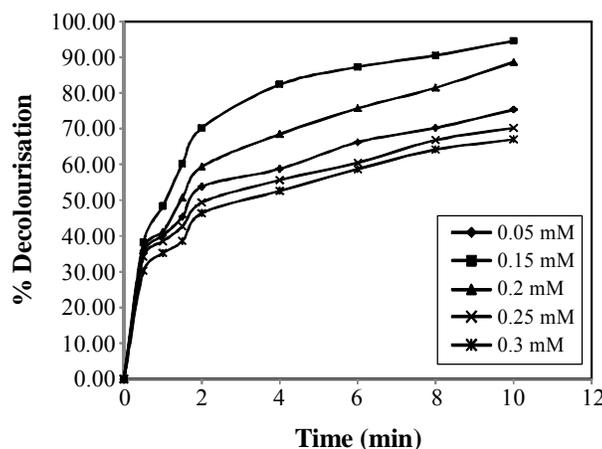


Fig. 5: Effect of ferrous ion dosage on Fenton process
(Conditions: pH = 3, $\text{H}_2\text{O}_2 = 20$ mM, Dye concentration = 200 mg/L)

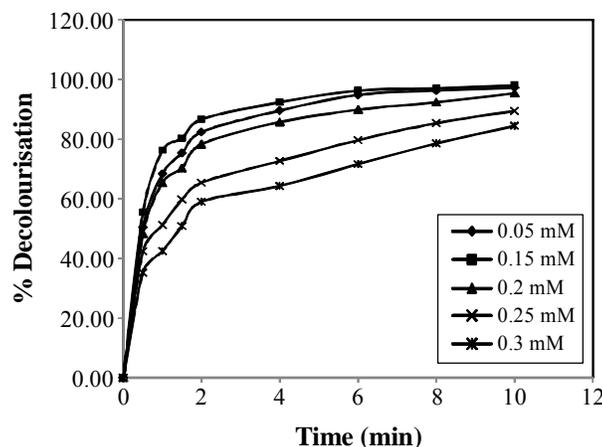
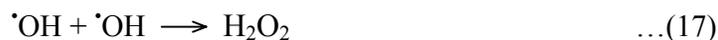


Fig. 6: Effect of ferrous ion dosage on Photo-Fenton process
(Conditions: pH = 3, H₂O₂ = 20 mM, Dye concentration = 200 mg/L)

This may be due to the scavenging of $\cdot\text{OH}$ radicals by H₂O₂ or excess Fe²⁺ ions^{5,18,19} as shown in Eq. (16). On the other hand, excess production of hydroxyl radicals may result self-scavenging effect as shown Eq. (17), which reduces the decolourization efficiency.



Effect of dye concentration

Since the pollutant concentration is an important parameter in waste water treatment, the effects of initial dye concentration on decolourization at optimum pH and Fenton reagent concentrations were studied in Fenton and photo-Fenton processes. The influence of concentration is shown in Figs. 7 and 8. From these results, it is possible to see that the extent of decolourization decreases with increase in initial dye concentration. Increase in dye concentration from 100 mg/L to 500 mg/L decreases the decolourization from 97.45% to 75.48% for Fenton and from 99.58 to 82.47% for photo-Fenton process in 10 min.

The increase in dye concentration increases the decolourisation as the number of dye molecules increases but not the hydroxyl radical concentration and hence, the decolourization rate diminishes. These results concur with the literature^{6,19,20}. In photo-Fenton process, the penetration of photons entering into the solution decreases due to the high dye concentration and therefore, hydroxyl radicals production rate is decreased¹⁶.

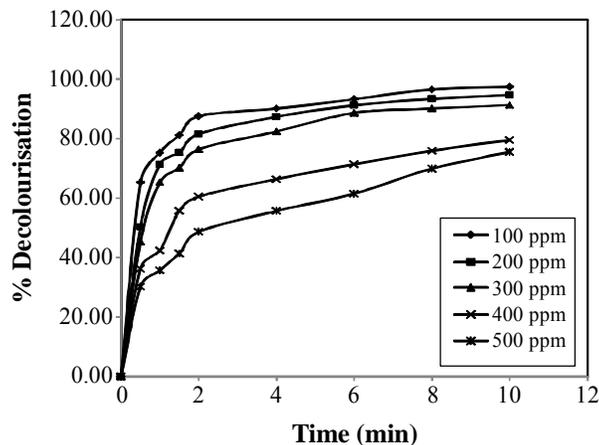


Fig. 7: Effect of dye concentration on Fenton process
(Conditions: pH = 3, H₂O₂ = 20 mM, Fe²⁺ = 0.15 mM)

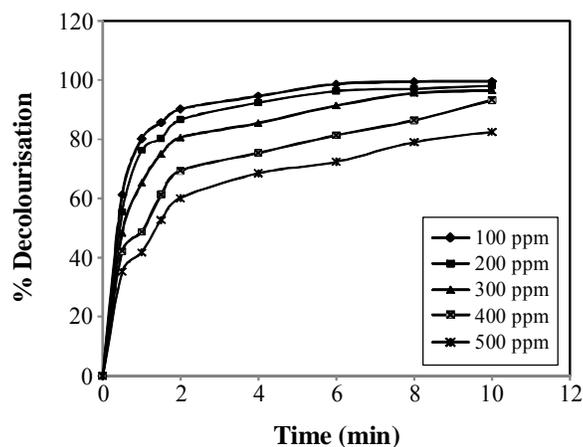


Fig. 8: Effect of dye concentration on Photo-Fenton process
(Conditions: pH = 3, H₂O₂ = 20 mM, Fe²⁺ = 0.15 mM)

From the Fig. 9, we can deduce that the contrary with degradation efficiency, concentration of degraded dye increases with increasing initial dye concentration. This may be due to the effect of H₂O₂ concentration at very low dye concentration. The concentration of H₂O₂ is in excess and it can trap hydroxyl radical easily as shown in Eq. (6). On the other hand, when the initial concentration was increased, all the produced hydroxyl radicals are used for dye degradation. So for the dye concentration between 100 to 500 g/L, the expression of the dye concentration gradient according to the initial concentration can be given as below for Fenton and photo-Fenton processes. The similar results were reported in the literature¹⁹.

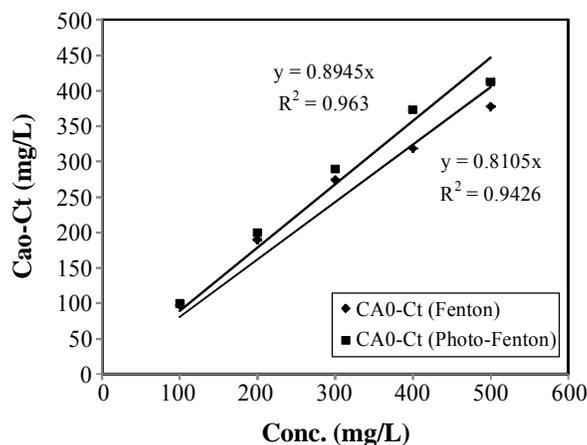


Fig. 9: Degradation efficiency of Fenton and Photo-Fenton process (pH = 3, H₂O₂ = 20 mM, Fe²⁺ = 0.15 mM time 10 min)

CONCLUSION

Based on the results, the following conclusions may be made.

The increase of initial dye concentration decreases the decolourization rate. The minimum time required for complete decolourisation of dye is 12 min for Fenton process and 10 min for photo-Fenton process at pH 3. The addition of H₂O₂ from 5 mM to 20 mM increases the decolourisation from 62.28% to 94.68% at 10 min in Fenton process and in the photo-Fenton process, the addition of H₂O₂ between 5 mM to 20 mM increases the decolourisation from 67.28% to 99.68%. The addition of Fe²⁺ from 0.05 mM to 0.15 mM increases the decolourization from 75.34 to 94.57% at 10 min in Fenton process and in photo-Fenton process, the increase is from 89.56 to 99.68% for the same time.

Thus, the results indicated that the degree of degradation of RB 28 was obviously affected by pH value and the dosage of Fe²⁺, and H₂O₂. Photo-Fenton showed higher treatment efficiency than that of Fenton process.

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