DECOLORIZATION KINETICS OF ACID AZO DYE AND BASIC THIAZINE DYE IN AQUEOUS SOLUTION BY UV/H₂O₂ AND UV/FENTON: EFFECTS OF OPERATIONAL PARAMETERS

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Abstract:

The photochemical decolorization of two dyes, namely Acid Yellow 54 and Basic Blue 9, was studied using the UV/H₂O₂ and UV/Fenton processes. The effects of the amount of H₂O₂ and FeSO₄ as well as the initial pH solution on decolorization kinetics of both the dyes were investigated. The pseudo-first order kinetic model was applied to predict the decolorization of the selected dyes at the different operational conditions and results showed that this model fitted very well with the experimental data. The obtained results also showed the efficiency of UV/Fenton process to quickly degrade aqueous effluents polluted by Acid Yellow 54 and Basic Blue 9 compared to the UV/H₂O₂ process.

Keywords:

Advanced oxidation processes (AOP), decolorization, UV/H₂O₂, UV/Fenton, acid dye, basic dye

1. Introduction

The textile industry is characterized by its high water consumption and is considered to be one of the largest producers of industrial wastewater. Indeed, textile effluents contain a considerable amount of suspended solids and of weakly biodegradable substances such as additives, detergents, surfactants, and dyes. It displays highly fluctuating pH, high temperature, and COD concentration [1]. The wastewater, which is highly colored in the presence of various dyes, can block the penetration of sunlight and oxygen, which are both essential for various aquatic forms of life. Moreover, some dyes are toxic and mostly non-biodegradable and are consequently harmful to human beings and aquatic species. Thus, the removal of these pollutants from textile effluents is currently of great interest. In this field, a wide range of methods has been developed for the removal of synthetic dyes from wastewater. These involve adsorption [2], coagulation, ultrafiltration, sedimentation and the membrane process [3-5]. However, some of these mentioned techniques are fairly effective but they transfer the contaminants from wastewater to solid wastes, such that the secondary waste produced has to be either treated again or dumped as such.

One of the most effective methods for the elimination of many hazardous, toxic, organic pollutants from the environment is their photocatalytic degradation in the presence of catalytic particles [6]. In this context, advanced oxidation processes (AOPs) are a potential alternative to decolorize and to reduce recalcitrant wastewater loads from textile dyeing and finishing effluents [7-9]. Most investigations employing the

photo-assisted decomposition of dyes have utilized either H₂O₂, Fenton's reagent, ozonation, or TiO₂ in their treatment procedures, in order to generate highly oxidative species such as hydroxyl radicals, which are capable of oxidizing the pollutants to such an extent that the treated wastewater may be reintroduced into the receiving streams [10,11].

The purpose of this work is to conduct experimental investigation concerning the decolorization of an acid azo dye (CI Acid Yellow 54) and a thiazine basic dye (CI Basic Blue 9) using the photodegradation technique. The UV/H₂O₂ and UV/Fenton advanced oxidation processes were tested, and the effects of the key operating variables such as initial pH, H₂O₂, and FeSO₄ concentrations, chemical structure, and ionocity of the dye on the decolorization kinetics were evaluated in this study.

2. Experimental

2.1. Materials and methods

2.1.1. Reagents

Technical grade CI Yellow Acid 54 (AY54) and CI Basic Blue 9 (BB9) were purchased from Sigma Aldrich. The characteristics of the selected dyes and their molecular structures are given in Table 1 and Figure 1, respectively. Hydrogen peroxide solution (30%) of analytical grade, ferrous sulfate (FeSO₄), and all organic components were also supplied by Sigma Aldrich Company.

Table 1. Characteristics of the selected dyes.

Dye	Chemical Formula	Molecular weight (g.mol ⁻¹)	$\lambda_{\max}$ (nm)
CI Acid Yellow 54 (AY54)	C ₁₈ H ₁₄ N ₄ Na ₃ O ₉ S ₂	540.43	442
CI Basic Blue 9 (BB9)	C ₁₆ H ₁₈ N ₃ SCl	319.85	666

Figure 1. Chemical structures of the selected dyes

2.1.2. Procedures and analysis

The irradiation experiments were carried out in a glass crystallizer by means of two UV lamps (Philips TL 60 W) emitting radiation with a maximum wavelength at 365 nm. The exposed sample surface was 50 cm². The reaction temperature was kept at 21±2°C. During irradiation, the solution had a free contact with atmospheric air but, additionally, was not aerated.

For each experimental run, 50 mL of dye aqueous solution, having an initial concentration of 50 mg L⁻¹, was introduced in the UV reactor. Degradation of each dye was carried out at different H₂O₂ concentrations (4, 10, and 20 mL L⁻¹) as well as at various FeSO₄ concentrations (20 and 60 mg L⁻¹). The dye solutions were adjusted to the desired pH value by addition of HCl or NaOH solutions. The aqueous solutions were magnetically stirred, and at regular time intervals, samples were taken and analyzed by the Biochrom Libra S6 visible spectrophotometer to determine the residual dye concentration. For all photocatalytic tests, experiments were conducted at least twice in order to examine the reproducibility of the obtained results.

The efficiency of color removal was evaluated in this study by using the following equation:

$$\text{Decolorization Efficiency (\%)} = \left(1 - \frac{C}{C_0}\right) \times 100 \quad (1)$$

where C₀ and C (mg L⁻¹) are the dye solution concentrations at time 0 and t, respectively.

During the preliminary studies, it was found that the two dye solutions follow the Lambert–Beer law in the used concentration range. The absorbance of the dye solution is given by:

$$\text{abs} = \log \frac{I_0}{I} = \varepsilon \times l \times C \quad (2)$$

where abs is the absorbance of the dye solution, I_A (Einstein s⁻¹m⁻³) is the radiation intensity absorbed by the dye solution, I₀ (Einstein s⁻¹m⁻³) is the radiation intensity that reaches directly to exposed sample, ε (mmol⁻¹Lcm⁻¹) is the molar extinction coefficient, l (cm) is the path length of the sample and C (mg L⁻¹) is the concentration of the dye solution.

The values of the molar extinction coefficient (ε) determined based on calibration curves and the correlation coefficients (R²) obtained for the two dyes are presented in Table 2. In this case, the following relationship has been assumed:

$$\frac{\text{abs}_0}{\text{abs}} = \frac{C_0}{C} \quad (3)$$

where abs₀ and abs are the absorbance of the dye solution at time 0 and t respectively, C₀ and C (mg L⁻¹) are the dye solution concentrations at time 0 and t, respectively.

3 Results and discussion

3.1 Decolorization by the UV/H₂O₂ oxidation process

The combination of UV and H₂O₂ produces OH radicals by photolysis of the hydrogen peroxide [12]. This radical is

Table 2. The values of the molar extinction coefficient (ϵ) and the correlation coefficients (R^2) obtained for the two dyes

Dye	the molar extinction coefficient (ϵ)	the correlation coefficients (R^2)
CI Acid Yellow 54 (AY54)	0.014	0.998
CI Basic Blue 9 (BB9)	0.233	0.993

non-selective and very powerful oxidizer and can initiate the decolorization reactions by reacting with the dye molecules. The result of this reaction is the destruction of color according to the following reactions (4) and (5):

Figure 2 shows a typical set of decolorization curves for the selected dyes treated with 10 mL L⁻¹ of H₂O₂ solution at pH 7 and at a temperature of 21°C. As can be seen, the complete decolorization of AY54 and BB9 is achieved after 300 and 600 minutes, respectively.

When the kinetics of the photocatalytic decolorization reaction was studied, it was found that the correlation between $\ln C_0/C$ and the irradiation time was linear until 180 and 540 minutes for AY54 and BB9, respectively, as shown in Figure 3. This is typical of pseudo-first order reaction kinetics. The expression of the dye degradation kinetic can be presented as follows:

$$\ln\left(\frac{C_0}{C}\right) = K_{\text{app}} \times t \quad (6)$$

where k_{app} (min⁻¹) is the pseudo-first order rate constant for decolorization rate of the dye solution.

The efficiency of color removal was assessed using Eq. (1). The results revealed that after 180 minutes, the decolorization efficiency reached 94% for AY54 and 98% for BB9. Beyond these time intervals, the kinetics of the decolorization reaction decrease, reflecting a change in kinetic behavior. This can be

explained by the fact that: (1) much of the dye was degraded during the first reaction phase and (2) the competitive reaction between hydroxyl radical and dye on one hand and between OH[·] and oxidation products, on the other hand, can interfere in the decolorization reaction.

3.1.1 Effect of the pH

The impact of solution pH on the oxidation of target compounds and hydroxyl radical formation in the UV/H₂O₂ advanced oxidation process has been investigated in many studies [13,14]. In this field, the reactivity of hydrogen peroxide and the reaction rates of target compounds were found to depend on the solution pH. Since the dyes to be removed can be existing at different pH values in colored effluents, we have studied the effect of this parameter on the decolorization efficiency. pH values range between 3 and 11. The comparative irradiation experiments were performed following the evolution of the absorbance with time.

For the different concentrations of H₂O₂, the decolorization efficiency of AY54 solution increased from pH 3 to 7 and then remained almost constant up to pH 10. Beyond this limit, the efficiency decreased as the pH increased toward a value of 11 (Figure 4). In the case of BB9 solution, the decolorization efficiency increased with the increment of pH, reached a maximum value at around pH 7, and then decreased. When the concentration of H₂O₂ was fixed to 20 mL.L⁻¹, the maximum removal of this dye was obtained at pH 9 (Figure 5). Table 3 summarized the pH values corresponding to the optimal efficiency of decolorization.

Figure 2. The decolorization curves of AY54 and BB9 solutions in UV/H₂O₂ process. Experimental conditions: [Dye]= 50 mg.L⁻¹; [H₂O₂] = 10 mL.L⁻¹; pH=7

Figure 3. First order plot of dye decolorization in UV/H₂O₂ process. Experimental conditions: [Dye]= 50 mg.L⁻¹; [H₂O₂] = 10 mL.L⁻¹; pH=7

Figure 4. Effects of pH on the decolorization efficiency of AY54 solution in UV/H₂O₂ system, for different concentration of H₂O₂: a) [H₂O₂] = 4 mL.L⁻¹; b) [H₂O₂] = 10 mL.L⁻¹, c) [H₂O₂] = 20 mL.L⁻¹.

Figure 5. Effects of pH on the decolorization efficiency of BB9 solution in UV/H₂O₂ system, for different concentration of H₂O₂: d) [H₂O₂] = 4 mL.L⁻¹; e) [H₂O₂] = 10 mL.L⁻¹, f) [H₂O₂] = 20 mL.L⁻¹.

Table 3. pH values corresponding to the optimal efficiency of decolorization.

[H ₂ O ₂] (mL.L ⁻¹)	AY54		BB9	
	Optimal pH after one 1 hour of irradiation	Optimal pH after 2 hours of irradiation	Optimal pH after 1 hour of irradiation	Optimal pH after 3 hours of irradiation
4	7	7	7	7
10	7-10	7-10	7	4-7
20	10	7	9	9

The obtained results can be explained as follows:

In the acidic pH values, concomitant with acidification of the solution by HCl, increasing amounts of conjugated base were added to the solution. The anion Cl^- is able to react with hydroxyl radicals, leading to inorganic radical ions, as shown by the following reaction:

These inorganic radical anions exhibit a much lower reactivity than $\text{OH}^\bullet$, so that they do not take part in the decolorization of the dye. In addition to that, there is a drastic competition between the dye and the anions with respect to $\text{OH}^\bullet$. Similar results have been already reported in other works [15,16].

- At alkaline pH, the conjugate base of H_2O_2 increases.

In this case, HO_2^- has a higher cross-section, which favors the absorption of light by the reactive species and should normally increase the $\text{OH}^\bullet$ production.

But HO_2^- , the conjugate anion of H_2O_2 , reacts with a nondissociated molecule of H_2O_2 according to reaction (10), which leads to dioxygen and water, instead of producing hydroxyl radicals under UV radiation. Therefore, the instantaneous concentration of $\text{OH}^\bullet$ is lower than expected.

Furthermore, the deactivation of $\text{OH}^\bullet$ is more important when the pH of the solution is high. The reaction of $\text{OH}^\bullet$ with HO_2^- is approximately 100 times faster than its reaction with H_2O_2 .

The reactivity of $\text{O}_2^\bullet$ and $\text{HO}_2^\bullet$ with organic pollutants is very low [17].

The self-decomposition rate of hydrogen peroxide is strongly dependent on the pH value. In practice, H_2O_2 is supplied in slightly acid condition (pH = 5) because of its high self-decomposition rate at high pH. The first-order reaction rate constant of this self-decomposition was determined to be 2.29×10^{-2} and $7.40 \times 10^{-2} \text{ min}^{-1}$ at pH 7 and 10.5, respectively [18].

3.1.2 Effect of H_2O_2 concentration

The concentration of hydrogen peroxide is an important parameter in the advanced UV/ H_2O_2 oxidation process. Indeed, the $\text{OH}^\bullet$ free radicals produced upon photolysis of H_2O_2 can

react with dye molecules, particularly with an excess of H_2O_2 . However, a high excess of hydrogen peroxide and a high $\text{OH}^\bullet$ radical concentration result in competitive reactions, producing consequently an inhibitory effect on the decolorization. $\text{OH}^\bullet$ radicals are prone to react or to recombine according to the following schemes:

The reactions (14) and (17) involve the $\text{OH}^\bullet$ consumption, thus inducing a probable reduction of the substrate oxidation. Therefore, an important step in the optimization of the present method is the determination of the adequate concentration of H_2O_2 , in order to avoid an excess of reagent that can retard the decolorization process. For this, the effect of initial H_2O_2 concentration on the kinetics of decomposition of both dyes was investigated by varying the concentration of this product between 4, 10, and 20 mL L^{-1} . Experiments were carried out at the critical pH values of 4, 7, and 10. Figures 6 and 7 show the effect of hydrogen peroxide concentration on the decolorization rate.

At low H_2O_2 concentration, formation of $\text{OH}^\bullet$ is the rate determining step. In this case, H_2O_2 cannot generate enough hydroxyl radicals and the oxidation rate is logically slow. Further, most of the free radicals are directly consumed by the dye. In the presence of high concentration of H_2O_2 , we could expect that more $\text{OH}^\bullet$ radicals would be produced. However, these radicals preferentially react with the excess of H_2O_2 . This undesirable reaction competes with the degradation of the color.

For the AY54 solution, the optimal value of the decolorization rate was obtained for a hydrogen peroxide concentration of 4 mL L^{-1} and when the initial pH was about 7. Concerning the BB9 solution, the reaction rate is optimal for the following combination: 10 mL L^{-1} of hydrogen peroxide and pH 7.

Figure 6. Effects of H_2O_2 concentration on the decolorization rate of AY54 solution in UV/ H_2O_2 system, for different pH values

3.2. Decolorization by the UV/Fenton oxidation process

As described above, the photodegradation of AY54 and BB9 dyes was mainly initiated by the production of $\text{OH}^\cdot$ radicals, resulting from the direct photolysis of H_2O_2 . The photodegradation experiments using photo-Fenton conditions were therefore studied to investigate the effect of increased production of $\text{OH}^\cdot$ radicals by the catalytic decomposition of H_2O_2 in the presence of Fe^{2+} ions.

Figure 8 illustrates the photocatalytic degradation of AY54 and BB9 dye solutions (50 mg L^{-1}) in the presence of 10 mL L^{-1} of H_2O_2 and 60 mg L^{-1} of FeSO_4 . Experiments were performed at pH 4 and at a temperature of 21°C . The UV/Fenton decolorization of AY54 is completely achieved after 180 minutes. Concerning the BB9 dye, during the 15th minute, the degradation rate is very fast and the decolorization efficiency was around 72%. This rate of the reaction then decreased, and 98.5% of decolorization efficiency is obtained after 120 minutes of exposure to UV light.

The active species in the UV/Fenton decolorization can be generated by the inter-reaction of hydrogen peroxide with ferrous and ferric ions as shown below [19,20]:

Since the kinetic rate constant of reaction (19) is much lower than that of reaction (18), the transformation between the ferric ions and the ferrous ions, on one hand, and the production of active species (hydroxyl radicals and superoxide radicals), on the other hand, are clogged greatly by the reaction (19). In previous studies, it was found that UV illumination of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ or $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system significantly increased the Fenton degradation rate of many organic substances [21], [22]. The effect of UV light is attributed to the direct $\cdot\text{OH}$ radical formation and regeneration of Fe^{2+} from photolysis of the complex $[\text{Fe}(\text{OH})]^{2+}$ in solution as following mechanism [23], [24]:

The brief mechanism of the photo-Fenton reaction is shown below:

A typical first order plot of color degradation with time was obtained for the two dyes but at different intervals (Figure 9). The kinetic of decolorization was linear until 135 minutes for AY54, reaching a decolorization efficiency of about 89%. For BB9, the linearity of the degradation rate was observed during the first 45 minutes, at which time 93% of the dye was removed.

Figure 7. Effects of H_2O_2 concentration on the decolorization rate of BB9 solution in UV/ H_2O_2 system, for different pH values

Figure 8. The decolorization curves of AY54 and BB9 solution in UV/Fenton process. Experimental conditions: $[\text{Dye}] = 50\text{ mg.L}^{-1}$; $[\text{H}_2\text{O}_2] = 10\text{ mL.L}^{-1}$; $[\text{FeSO}_4] = 60\text{ mg.L}^{-1}$; pH=4.

Figure 9. First order plot of dye decolorization in UV/Fenton process. Experimental conditions: $[\text{Dye}] = 50\text{ mg.L}^{-1}$; $[\text{H}_2\text{O}_2] = 10\text{ mL.L}^{-1}$; $[\text{FeSO}_4] = 60\text{ mg.L}^{-1}$; pH=4.

Beyond these time intervals, the kinetics of the decolorization reaction decreased.

These results could be explained by the same reasons that were earlier enunciated in this paper. In addition to that, the catalytic power of ferrous ions, which depends on the oxidized form changes with time and during the reaction, which can influence the photocatalytic degradation.

Figure 10. Effects of pH on the decolorization efficiency of AY54 solution in UV/Fenton system, for different concentration of H_2O_2 : a) $[H_2O_2] = 4 \text{ mL.L}^{-1}$; b) $[H_2O_2] = 10 \text{ mL.L}^{-1}$; c) $[H_2O_2] = 20 \text{ mL.L}^{-1}$.

3.2.1. Effect of the pH

The effect of the initial pH solution on the decolorization efficiency of the selected dyes by the UV/Fenton oxidation process was investigated by varying the pH values between 1 and 11 (Figure 10 and 11).

Figure 11. Effects of pH on the decolorization efficiency of BB9 solution in UV/Fenton system, for different concentration of H_2O_2 : d) $[H_2O_2] = 4 \text{ mL.L}^{-1}$; e) $[H_2O_2] = 10 \text{ mL.L}^{-1}$; f) $[H_2O_2] = 20 \text{ mL.L}^{-1}$.

As can be seen, after 30 and 60 minutes of UV irradiation, the decolorization efficiency increased to a maximum value at pH 2 for AY54 and at pH 3 for BB9, and then decreased. This was observed for the different combinations of H_2O_2 and Fe_2SO_4 concentrations. When the pH exceeds a value of 4, the color removal capacity decreases. This behavior could be explained by the formation of ferric hydroxo complexes during the reaction, which blocks the decomposition of hydrogen peroxide catalyzed by the ferrous ions [25]. For pH 1, the decolorization percentage was low and this is probably due to the hydroxyl radical scavenging by the H^+ ions according to reaction (24) [26].

3.2.2. Effect of H_2O_2 and Fe_2SO_4 concentrations

Figures 12 and 13 show the relationship between the decolorization rate of the tested dyes and the initial dosage of H_2O_2 and Fe_2SO_4 in the UV/Fenton process. The objective of this evaluation is to select the best operational dosage. From Figure 12, it can be noted that when the H_2O_2 concentration ranged between 4 and 20 mL L^{-1} , the decolorization rate and efficiency of AY54 solution decrease. This phenomenon may be due to the scavenging of $\cdot\text{OH}$ radicals by H_2O_2 , which can be expressed by the following reactions [27,28]:

In the case of BB9 solution (Figure 13), the results indicate that increasing the initial H_2O_2 concentration from 4 and 10 mL L^{-1} had a positive effect on the decolorization of BB9 solution. This is because of the increase of the quantum yield of active $\cdot\text{OH}$. While H_2O_2 concentration was higher than 10 mL L^{-1} , the K_{app} value decreased with further increasing initial dosage of H_2O_2 . It means that the concentration of H_2O_2 is beyond the critical value, where the scavenging of $\cdot\text{OH}$ radicals by excessive H_2O_2 will occur.

The amount of iron is one of the main parameters that influence the Fenton/UV process. The obtained results indicate that the extent of decolorization increases with a higher initial iron concentration. In fact, when the concentration of Fe_2SO_4 is varied between 20 and 60 mg L^{-1} , the Fe^{2+} ions accelerate the kinetics of decolorization rate and enhance color removal. This may be attributed to the increase of the production of $\cdot\text{OH}$ radicals with the increase of iron dose.

3.3 Comparison of the decolorization processes

The experimental data demonstrate that both UV/ H_2O_2 and UV/Fenton processes are promising techniques for the degradation of AY 54 and BB 9 dyes from aqueous solutions. To compare the decolorization rates of the two processes, the reaction rates at the optimum conditions of each process are shown in Figure 14. It can be deduced from it that the UV/ H_2O_2 process was more efficient for the decolorization of AY54 than that of BB9. However, the inverse trend was observed by using the UV/

Figure 12. Effects of H_2O_2 and FeSO_4 concentration on the decolorization rate of AY54 solution by UV/Fenton process, at pH=2

Figure 13. Effects of H_2O_2 and FeSO_4 concentration on the decolorization rate of BB9 solution in UV/Fenton system, at pH=3

Figure 14. The decolorization curves of AY54 and BB9 solution in UV/ H_2O_2 and UV/Fenton process at the optimum conditions

Fenton process treatment. Indeed, the photodegradation of BB 9 under the photo-Fenton conditions is faster than that of AY54. This can be explained by the fact that the ionicity of the dye influences the decolorization kinetic. In fact, in the UV/Fenton process, Fe^{2+} ions are attracted by the acid dye AY54, which is negatively charged, thus affecting the catalyst efficiency. In the case of the basic dye BB9, there is rather repulsion between the dye molecules and the catalyst that will be invested entirely in the photodegradation reaction.

The optimal experimental conditions for the two studied techniques can be summarized in Table 4. As can be seen, the time required to remove both the dyes from aqueous solution is reduced by using the UV/Fenton process compared to the UV/ H_2O_2 process. These findings suggest that the Fe^{2+} ions play an important role in the enhancement of the decolorization rate of AY54 and BB9.

4. Conclusions

The photocatalytic degradation of an acid azo dye (CI Acid Yellow 54) and a thiazine basic dye (CI Basic Blue 9) was successfully achieved by applying two advanced photochemical processes: UV/ H_2O_2 and UV/Fenton. The studied processes are optimized by examining the reaction rate under various reaction conditions such as pH of the initial dye aqueous solution and the concentration of H_2O_2 as well as the one of FeSO_4 .

Based on the results, the following conclusions can be drawn:

The increase in H_2O_2 and FeSO_4 concentrations as well as the initial pH solution leads to a faster degradation of both the dyes up to a critical operational values beyond which the degradation process becomes slower and gradually decreased.

The pseudo-first order kinetic model is in good agreement with the experimental data.

The UV/ H_2O_2 process leads to more than 99% of the acid azo dye decolorization in 210 minutes, while the thiazine basic dye is decolorized after 500 minutes of exposure to UV light and in presence of H_2O_2 . The nature of chromophore group has, in this case, a great impact on the efficiency and photocatalytic degradation kinetics. This can be also valuable for the UV/

Fenton process, where the decolorization of more than 99% of the dye was reached after 1 hour of treatment for the acid azo dye, and after 45 minutes for the thiazine basic dye.

The UV/Fenton process allows a faster decolorization compared to the UV/ H_2O_2 process. However, it exhibited some disadvantages: (1) the obligation to work in acidic medium, (2) for pH values above 4, the formation of a precipitate can be observed and is accompanied by a sudden decrease in the decolorization rate, and (3) excessive concentration of iron sulfate causes turbidity, which can interfere in the colorimetric measurements.

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Table 4. The optimal experimental conditions for the two studied techniques

Procces	UV/ H_2O_2		UV/Fenton	
	AY54	BB9	AY54	BB9
Dye				
pH	7	7	2	3
$[\text{H}_2\text{O}_2]$ (mL/L)	4	10	4	10
$[\text{FeSO}_4]$ (mg/L)	-	-	60	60
Time (minutes)	210	500	60	45
K_{app} (min^{-1})	0.015	0.008	0.065	0.1

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