

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Comparison of UV/H₂O₂ and Photo-Fenton Processes

Figures 4.1 (a)-(d) show the results obtained from the experiments; they are the remaining ratio of formaldehyde versus time, remaining ratio of methanol versus time, remaining ratio of hydrogen peroxide versus time, and a profile of pH variation versus time. In this study, the concentration of formaldehyde of 0.333 M was applied in all experiments. At this concentration, 0.0796 M of methanol was already added in a commercial product of formaldehyde. Therefore, methanol oxidation was also investigated in this research. From our observation, it is an obvious three-stage reaction, the oxidation reactions of formaldehyde and methanol were very fast during the first 5 min (the first stage) then they gradually slowed down (the second stage), and got slower after 20 min (the third stage) as shown in Figure (4.2). The main reason for the three stages of the reaction is because ferrous ion reacted with hydrogen peroxide very quickly, producing a large amount of hydroxyl radicals. The generated hydroxyl radicals can react rapidly with organic matters, and thus in the first stage, formaldehyde and methanol were decomposed quickly; this is referred to the Fe²⁺/H₂O₂ stage. In the second and the third stages, the rate of formaldehyde and methanol decomposition was slower than that in the first stage. Since the reaction rate constant (M⁻¹ s⁻¹) of ferrous ions reacting with hydrogen peroxide to produce hydroxyl radicals is 53 and the reaction rate constant of ferric ions with hydrogen peroxide to form ferrous ions is 0.02 (Sun and Pignatello, 1993). Therefore, it can be derived that the former reaction is far swifter than the latter, resulting in a higher rate of hydroxyl radical formation in the first stage reaction than those in the second and the third stages. Hence, UV light was used to regenerate Fe²⁺ from Fe³⁺ in order to increase the concentration of hydroxyl radicals, which can promote the oxidation efficiencies of formaldehyde and methanol.

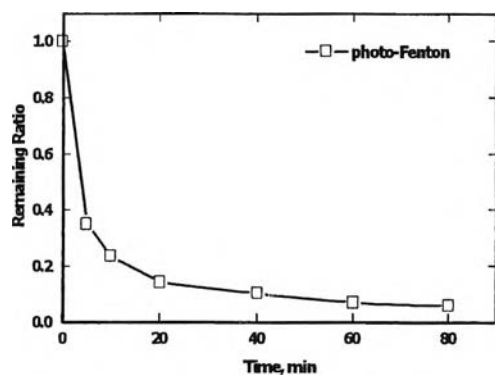


Figure 4.1 (a) Remaining ratio of formaldehyde with reaction time

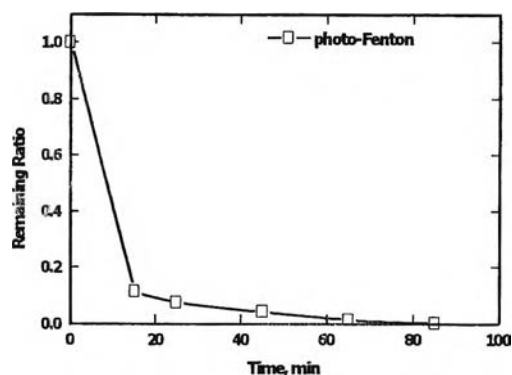


Figure 4.1 (c) Remaining ratio of H_2O_2 with reaction time

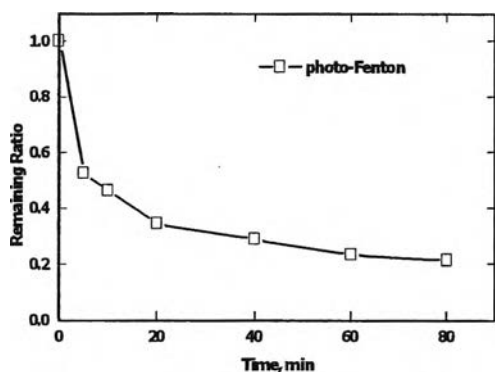


Figure 4.1 (b) Remaining ratio of methanol with reaction time

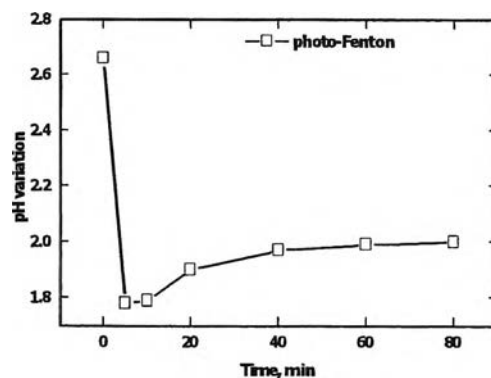


Figure 4.1 (d) pH variation with reaction time

In this study, the oxidation rates of formaldehyde and methanol were divided into a three-stage reaction. However, only the first- and the third-stage of the oxidation reaction are discussed here. The first stage of the oxidation reaction was discussed by the initial average rate at the first 5 min and the third stage was discussed by mean of the first order rate constant (k). For the second stage, the reaction rate could not be described by a first order rate constant due to its variation. Thus, the second stage is ignored here. Moreover, the competition between formaldehyde and

methanol will be described as r_m/r_f , where r_m and r_f were the initial rate of methanol and formaldehyde, respectively.

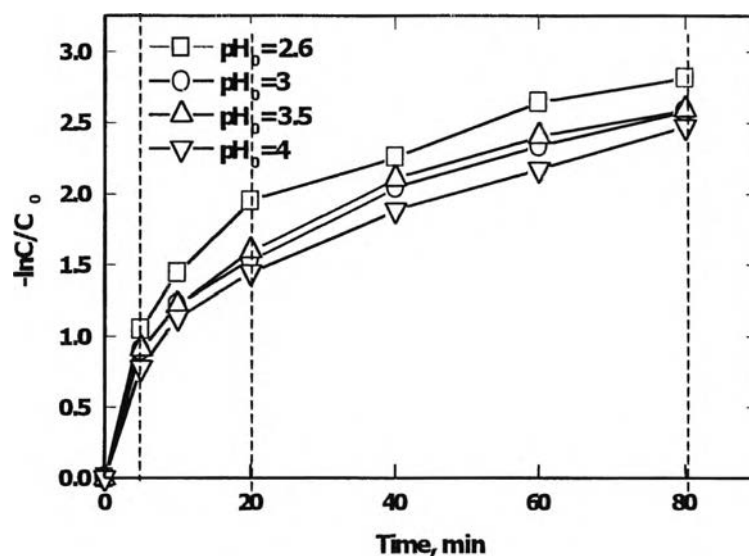


Figure 4.2 Three stages of formaldehyde oxidation

Since photo-Fenton process is initiated by the combination of UV/H₂O₂ and Fe²⁺, the oxidation efficiency of UV/H₂O₂ should be studied first and then compared with photo-Fenton process. In UV/H₂O₂ process, hydroxyl radicals are formed according to equation (4.1):



In photo-Fenton process, Fe²⁺ can catalyze H₂O₂ to produce OH[•] as shown in equation (4.2):





The role of UV irradiation leads not only to the formation of additional hydroxyl radicals as shown in equation (4.1), but also to a recycling of the Fe^{2+} catalyst by the reduction of Fe^{3+} as expressed in Equation (4.3) and (4.4). By this way, the concentration of Fe^{2+} increases and therefore the oxidation reaction is accelerated because much more hydroxyl radicals are generated (Ghaly et al., 2001). With this reason, photo-Fenton could be more efficient than the UV/ H_2O_2 process for treating formaldehyde and methanol.

In order to compare the efficiencies of the UV/ H_2O_2 and photo-Fenton processes, both of these experiments were conducted. Initial conditions were as follows: 0.333 M of CH_2O , 0.0796 M of CH_3OH , 0.667 M of H_2O_2 , 6.67×10^{-2} M of Fe^{2+} and an initial pH of 2.6 ± 0.1 . Results are depicted in Figures 4.3 (a) to (d). As seen in Figures 4.3 (a) and (b), the decomposition rates of formaldehyde and methanol by UV/ H_2O_2 process were slow when compared with those by photo-Fenton. In UV/ H_2O_2 process, the removal ratios of formaldehyde and methanol at 5 min were 5% and 0.2%, and at 80 minutes, they were 48% and 32%, respectively. When Fe^{2+} was introduced into UV/ H_2O_2 process, the removal ratios of formaldehyde and methanol at 5 min were 65% and 47%, and after 80 min, they were 94% and 78%, respectively.

Figure 4.3(c) shows the remaining ratio of H_2O_2 with time. In photo-Fenton process, hydrogen peroxide reduced faster than in UV/ H_2O_2 process at the beginning of the oxidation reaction. Then after 15 min, in UV/ H_2O_2 process, H_2O_2 was decomposed quite slowly in the same tendency as in photo-Fenton. Furthermore, after 80 min., in photo-Fenton process formaldehyde and methanol could not be reduced further because almost all of the hydrogen peroxide concentration was decomposed. While in UV/ H_2O_2 process, 42% of H_2O_2 still remained in the system at 85 min.

As presented in Figure 4.3 (d), after the reaction of UV/H₂O₂ process had begun for 5 min, the pH value reduced gradually from an initial pH of 2.64 to 2.21 at the 80-min mark. On contrary, the pH value sharply reduced from a pH of 2.66 initially to a pH of 1.78 at 5 min in photo-Fenton. After that, the pH value started to increase gradually and reached 2.0 at the end of 80 min. The role of pH reduction at the beginning stage may be caused by the three factors; they are (1) the pH of H₂O₂ itself, (2) the decomposition of H₂O₂ to O₂ and H⁺; Fe³⁺ acts as a catalyst as illustrated in Equation (4.5), and (3) the appearance of organic acid intermediate. There are some literatures reporting that formic acid is an oxidation intermediate of formaldehyde (Stefan and Bolton, 1998; Heit et al., 1998; Gonzalez and Braun, 1996); the oxidation pathway of formaldehyde is depicted in Figure 2.3. The occurrence of formic acid during the oxidation reaction may result in the reduction of pH.

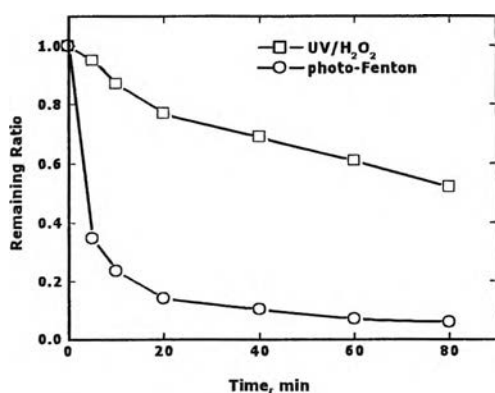


Figure 4.3 (a) Remaining ratio of formaldehyde with reaction time

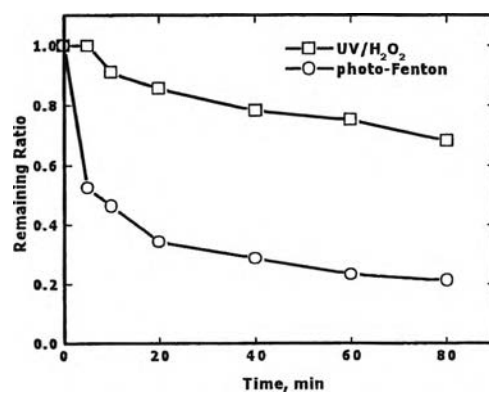


Figure 4.3 (b) Remaining ratio of methanol with reaction time

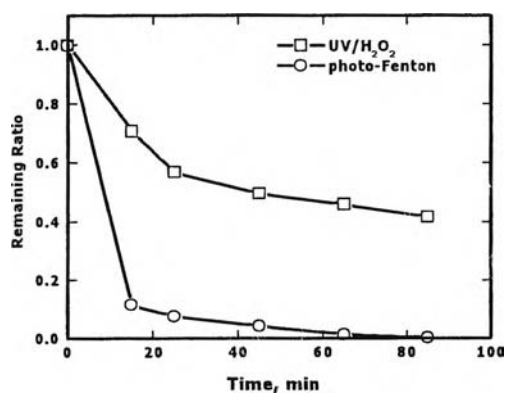


Figure 4.3 (c) Remaining ratio of H₂O₂ with reaction time

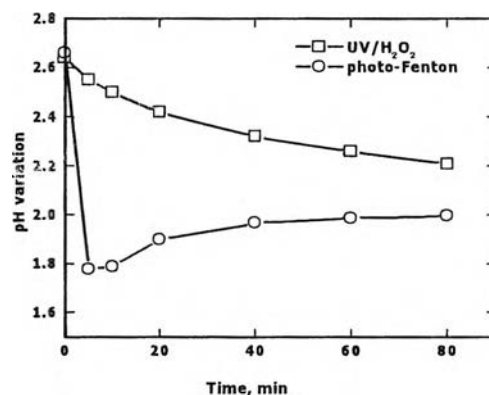


Figure 4.3 (d) pH variation with reaction time

As presented in Table 4.1, the initial rates of formaldehyde degradation increased from $3.33 \times 10^{-3} \text{ M min}^{-1}$ to $4.33 \times 10^{-2} \text{ M min}^{-1}$ and $3.18 \times 10^{-5} \text{ M min}^{-1}$ to $7.55 \times 10^{-3} \text{ M min}^{-1}$ for methanol degradation by applying photo-Fenton process. For the third stage, the k values of formaldehyde and methanol changed from $6.5 \times 10^{-3} \text{ min}^{-1}$ to $1.49 \times 10^{-2} \text{ min}^{-1}$ and $3.66 \times 10^{-3} \text{ min}^{-1}$ to $8.25 \times 10^{-3} \text{ min}^{-1}$, respectively.

From the experiments, it can be concluded that photo-Fenton process can significantly increase the efficiency of formaldehyde and methanol oxidation in an aqueous solution. However, the oxidation rate of formaldehyde and methanol changed slightly in the last stage of the oxidation reaction; this may be caused by the slow rate of $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ reaction and almost all of the hydrogen peroxide disappearance in the last stage. Moreover, formic acid may be an oxidation intermediate of formaldehyde, and may result in the reduction of the solution pH.

Table 4.1 Comparison of UV/H₂O₂ and photo-Fenton processes

| | UV/H ₂ O ₂ | | photo-Fenton | |
|------------------------------------|----------------------------------|-----------------------|-----------------------|-----------------------|
| | CH ₂ O | CH ₃ OH | CH ₂ O | CH ₃ OH |
| % removal at 5 min | 5 | 0.2 | 65 | 47 |
| % removal at 80 min | 48 | 32 | 94 | 79 |
| initial rate(M min ⁻¹) | 3.33x10 ⁻³ | 3.18x10 ⁻⁵ | 4.33x10 ⁻² | 7.55x10 ⁻³ |
| k (min ⁻¹) | 6.5x10 ⁻³ | 3.66x10 ⁻³ | 1.49x10 ⁻² | 8.25x10 ⁻³ |
| r ² | 0.9962 | 0.9885 | 0.9899 | 0.9887 |
| r _m /r _f | 0.0095 | | 0.1740 | |

4.2 Effect of Initial pH on Photodecomposition of Formaldehyde and Methanol

According to many literature reviews, photo-Fenton is strongly affected by the pH value. Many studies reported that the effective pH for the photo-Fenton process is an acidic pH. For pH values above 4, the efficiency strongly decreases because iron precipitates as hydroxide that reduces the transmission of the radiation at higher pH values (Ghaly et al., 2001; Faust and Hoigne, 1990). Whereas, at relatively low pH, the regeneration of Fe²⁺ may reduce due to the high concentration of H⁺ in the system (Equation (4.5)). Many researches have studied the influence of pH on the oxidation efficiency of photo-Fenton reaction; for example, in 2001, Ghaly et al. studied the oxidation of p-chlorophenol by applying photo-Fenton process. The result showed that the maximum degradation of 96.5% was obtained at pH 3. Oliveros et al. (1997) studied the feasibility of a large scale development of a light-enhanced Fenton reaction for the treatment of highly contaminated industrial wastewater containing toxic aromatic amines (dimethyl anilines or xylidines). They concluded that the initial pH of the wastewater to be treated is the major operating parameter of the Fenton reaction, an initial acidic pH between 2 and 3 yielding the optimal result. And, in 2000, Kang et al. studied the decolorization of textile wastewater by photo-Fenton oxidation technology. This study indicated that the generating amount of OH[•] appears

to be no difference at pH 3-5. Such a result is consistent with the optimum pH of 3-5 for color removal.

There is no report about the optimum pH for formaldehyde and methanol oxidation. In order to investigate the effect pH on the oxidation of formaldehyde and methanol by photo-Fenton process in this study, the initial pH values of 2.6 ± 0.1 , 3 ± 0.1 , 3.5 ± 0.1 , and 4 ± 0.1 , along with 0.333 M of CH_2O , 0.0796 M of CH_3OH , and 0.667 M of H_2O_2 , were applied as the experimental conditions. The experiments were conducted with two concentrations of Fe^{2+} ; they were 6.67×10^{-2} M and 6.67×10^{-3} M of Fe^{2+} and the results are expressed in Figures 4.4 (a) to (d) and Figures 4.5 (a) to (d), respectively. In the reaction of formaldehyde and methanol decomposition by photo-Fenton process, the pH changed with the reaction time. Nevertheless, only the effects of the initial pH on formaldehyde and methanol oxidation will be discussed here.

4.2.1 Influence of pH on Formaldehyde and Methanol Oxidation with High Concentration of Fe^{2+}

Figure 4.4 (a) shows the relationship between the remaining ratios of formaldehyde with time. It can be observed that the differences of formaldehyde decomposition at 80 min among the different pH values were not obvious; at the pH values of 2.6, 3.0, 3.5, and 4.0, removal percentages of formaldehyde at all initial pH values fell from 92%-94%. It can be derived that the initial pH does not have a significant influence on the decomposition of formaldehyde; however, the highest oxidation efficiency was obtained at an initial pH 2.6, as shown in Figure 4.4 (a). This result agrees with Kang et al. (2000). They indicated that the generating amount of hydroxyl radicals appears to be no difference at initial pH 3-5 for color removal. While considering each stage separately, it is seen that initial pH plays a more apparent effect on the initial stage than the removal ratio of formaldehyde at 80 min; all formaldehyde removal fell from 54%-65%.

The remaining ratios of methanol with time under the same experimental conditions are shown in Figure 4.4 (b). It is noticeable that the initial pH has a more

obvious effect on methanol oxidation than on formaldehyde. As the initial pH changed from 2.6 to 3 to 3.5 and finally 4, the removal percentages of methanol at 5 min were 48%, 14%, 38%, and 31%, respectively, and at 80 min, they were 79%, 69%, 74%, and 71%, respectively. Figure 4.4 (b) indicates that the highest oxidation efficiency of methanol was achieved at initial pH 2.6. This result agrees with that depicted in Figure 4.4 (a); the highest formaldehyde oxidation was obtained at initial pH 2.6.

The remaining ratios of H_2O_2 with reaction time are presented in Figure 4.4 (c). It was observed that H_2O_2 swiftly decomposed in the first 15 min due to the fast reaction between Fe^{2+} and H_2O_2 . After that, the decomposition rate of H_2O_2 slowed down. The remaining ratios at 15 min were 11%, 18%, 17%, and 19% as the initial pH changed from 2.6 to 3.0 to 3.5 and finally 4, respectively. It is noticeable that at an initial pH of 2.6, H_2O_2 was used more than at other pHs. This may result in the highest efficiency that was observed at initial pH 2.6. However, at 80 min, almost all of the H_2O_2 decomposed at all initial pH values.

Figure 4.4 (d) indicates that although the initial pH value was adjusted to 2.6 ± 0.1 , 3.0 ± 0.1 , 3.5 ± 0.1 , and 4.0 ± 0.1 , the solution pH sharply reduced to almost the same value within 5 min. At 5 min of the oxidation reaction, pH values dropped to 1.78, 1.92, 1.86, and 1.92 as the initial pH values were set at 2.6, 3, 3.5, and 4, respectively. At initial pH 2.6, the pH value started to increase after 5 min. For the other initial pH values, they continued to reduce after 5 min and only started to increase after 10 min.

The relationship between the initial rate and rate constant of formaldehyde and methanol with different initial pHs are demonstrated in Figures 4.4 (e) and (f). (see the initial rates and k values from Table 4.2). Figures 4.4 (e) and (f) indicated that in both formaldehyde and methanol oxidation, k changed slightly when compared with the initial rate. It might conclude that the initial pH plays an obvious effect in some extent on the first stage than it does on the last stage.

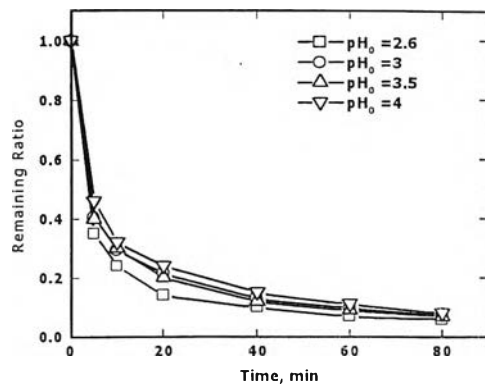


Figure 4.4 (a) Remaining ratio of formaldehyde with reaction time

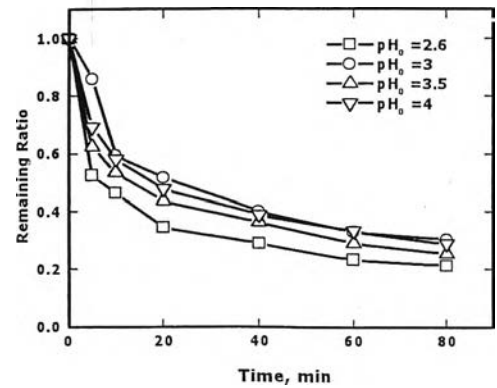


Figure 4.4 (b) Remaining ratio of methanol with reaction time

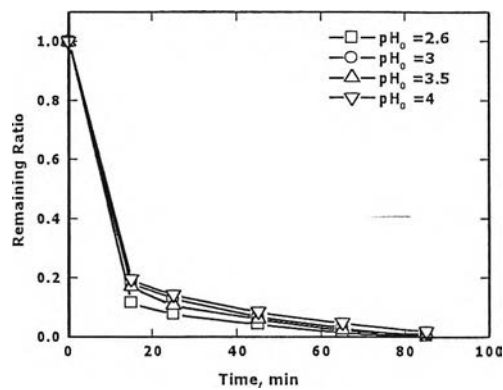


Figure 4.4 (c) Remaining ratio of H_2O_2 with reaction time

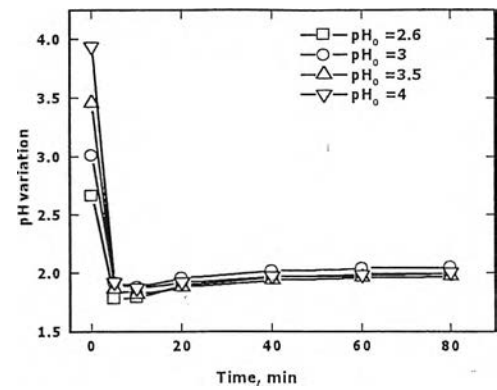


Figure 4.4 (d) pH variation with reaction time

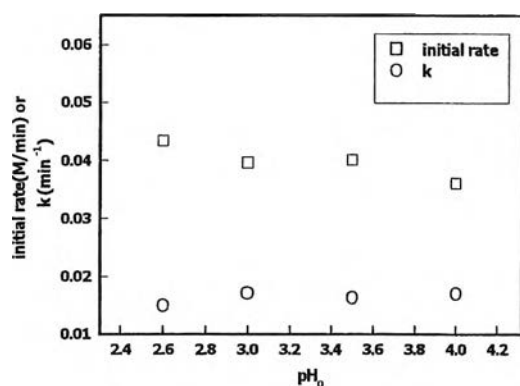


Figure 4.4 (e) Effect of pH on initial rate and rate constant of formaldehyde oxidation

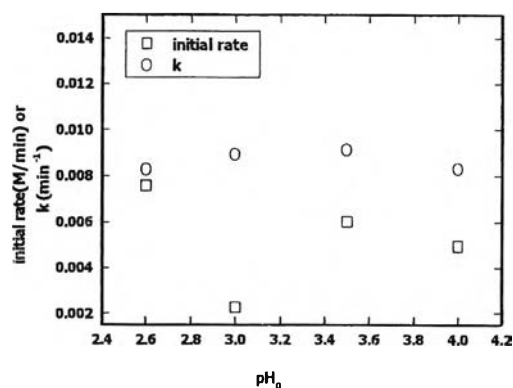


Figure 4.4 (f) Effect of pH on initial rate and rate constant of methanol oxidation

Table 4.2 Effect of initial pH on photodecomposition of formaldehyde and methanol with 6.67×10^{-2} M of Fe^{2+}

| Parameters | pH 2.6 | | pH 3 | | pH 3.5 | | pH 4 | |
|-------------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| | CH ₂ O | CH ₃ OH | CH ₂ O | CH ₃ OH | CH ₂ O | CH ₃ OH | CH ₂ O | CH ₃ OH |
| % removal at 5 min | 65 | 47.5 | 59.4 | 13.9 | 60 | 37.6 | 54 | 30.9 |
| % removal at 80 min | 94 | 78.6 | 92.4 | 69.5 | 93 | 74.4 | 92 | 71.1 |
| initial rate (M min ⁻¹) | 4.33 $\times 10^{-2}$ | 7.55 $\times 10^{-3}$ | 3.95 $\times 10^{-2}$ | 2.23 $\times 10^{-3}$ | 4.00 $\times 10^{-2}$ | 5.99 $\times 10^{-3}$ | 3.60 $\times 10^{-2}$ | 4.92 $\times 10^{-3}$ |
| k (min ⁻¹) | 1.49 $\times 10^{-2}$ | 8.25 $\times 10^{-3}$ | 1.71 $\times 10^{-2}$ | 8.91 $\times 10^{-3}$ | 1.63 $\times 10^{-2}$ | 9.09 $\times 10^{-3}$ | 1.69 $\times 10^{-2}$ | 8.29 $\times 10^{-3}$ |
| r ² | 0.9799 | 0.9776 | 0.9691 | 0.9530 | 0.9530 | 0.9912 | 0.9886 | 0.9911 |
| r _m /r _f | 0.174 | | 0.056 | | 0.150 | | 0.137 | |

4.2.2 Influence of pH on Formaldehyde and Methanol Oxidation with Low Concentration of Fe^{2+}

Figures 4.5 (a) to (d) express the effect of pH on formaldehyde and methanol degradation at the initial concentration of Fe^{2+} of 6.67×10^{-3} M. Other experimental conditions used in this set of the experiment were as follows: $[\text{CH}_2\text{O}] = 0.333$ M, $[\text{CH}_3\text{OH}] = 0.0796$ M, and $[\text{H}_2\text{O}_2] = 0.667$ M. Initial pHs were 2.6 ± 0.1 , 3.0 ± 0.1 , 3.5 ± 0.1 , and 4.0 ± 0.1 . Results show that, with different the initial pH values of 2.6, 3.0, 3.5 and 4.0, the decomposition ratios of formaldehyde at 5 min were 22%, 23%, 24%, and 24%, and at 80 min were 62%, 54%, 55%, and 57%, respectively (Figure 4.5 (a)). As seen in Figure 4.5 (a) that initial pH plays an insignificant effect on the oxidation of formaldehyde. However, the most efficient pH that yielded the highest removal ratio of formaldehyde was 2.6. This result is similar to the result depicted in Figure 4.4 (a); the most effective initial pH for formaldehyde oxidation was obtained at pH 2.6 with the concentration of Fe^{2+} of 6.67×10^{-2} M

The remaining ratios of methanol versus time are presented in Figure 4.5 (b). At the initial pH value of 2.6, 3.0, 3.5, and 4.0, the removal percentages of methanol at 5 min were 2.5%, 27%, 23%, and 21% and reached 44%, 46%, 46%, and 44.2% at the end of the 80-min reaction period. Figure 4.5 (b) shows that the highest efficiency was not achieved at pH 2.6. This result is different from the result obtained from Figure 4.4 (b); the most effective pH for methanol degradation is obtained at initial pH 2.6 with the initial dose of Fe^{2+} of 6.67×10^{-2} M.

The profile of H_2O_2 residual versus time is showed in Figure 4.5 (c). At all initial pHs, there was no obvious effect for H_2O_2 decomposition. At the end of 80 min, all remaining ratios of H_2O_2 in the system fell in 31-33% region. Figure 4.5 (d) presents the profile of pH variations versus time. At the initial pH values of 2.6, 3, 3.5 and 4, pH values swiftly reduced within 5 min to 2.24, 2.35, 2.43, and 2.39, respectively. After 5 min, the pH of the solution reduced continuously to 2.06, 2.09, 2.08, and 2.09, by the end of 80-min reaction period (Figure 4.5 (d)). Figure 4.5 (d) shows a different tendency from earlier experiments with 6.67×10^{-2} M of Fe^{2+} (Figure 4.4 (d)) where the pH sharply decreased and then increased after approximately 10 min of the oxidation reaction.

The initial rates and k of formaldehyde and methanol are listed in Table 4.3. From the table, it is seen that k values of formaldehyde are higher than those of methanol at all initial pHs. Consequently, the rate of methanol degradation at the last stage was slower than that of formaldehyde.

From this part of the experiments, it can be concluded that the initial pH plays an insignificant effect on formaldehyde and methanol oxidation in both the experiments of $6.67 \times 10^{-2} \text{ M}$ and $6.67 \times 10^{-3} \text{ M}$ of Fe^{2+} . For formaldehyde oxidation, the most effective initial pH was 2.6, which it provided the highest removal efficiency.

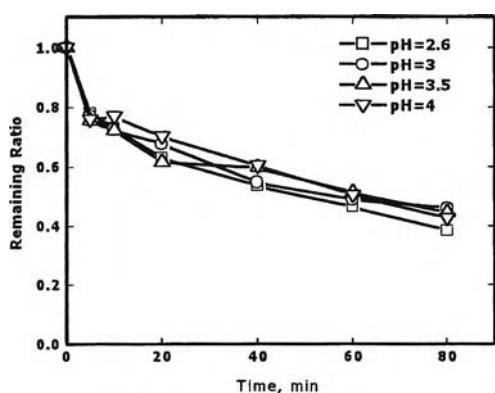


Figure 4.5 (a) Remaining ratio of formaldehyde with reaction time

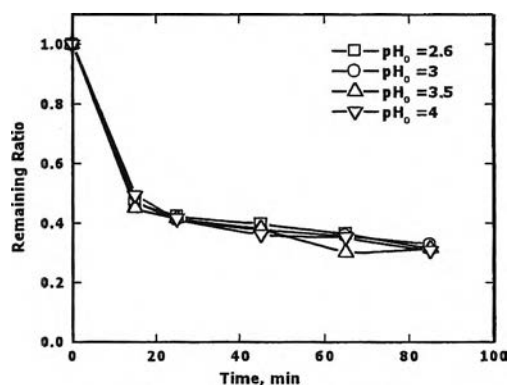


Figure 4.5 (c) Remaining ratio of H_2O_2 with reaction time

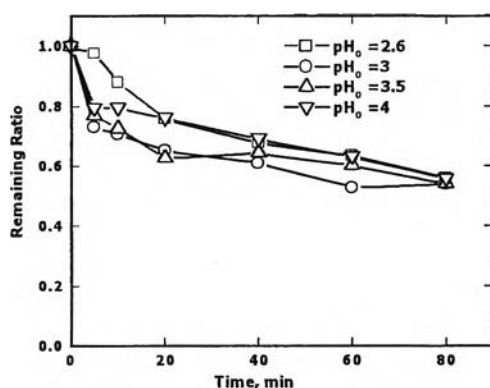


Figure 4.5 (b) Remaining ratio of methanol with reaction time

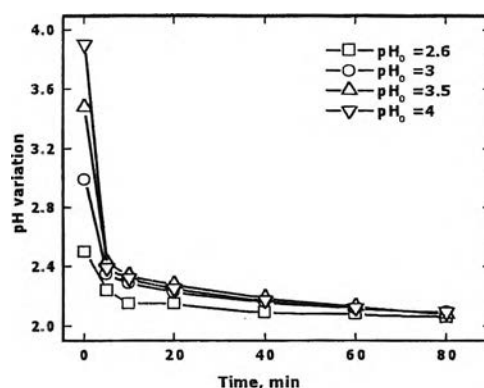


Figure 4.5 (d) pH variation with reaction time

Table 4.3 Influences of initial pH on photodecomposition of formaldehyde and methanol with 6.67×10^{-3} M of Fe^{2+}

| Initial pH | pH 2.6 | | pH 3 | | pH 3.5 | | pH 4 | |
|--------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| | CH ₂ O | CH ₃ OH | CH ₂ O | CH ₃ OH | CH ₂ O | CH ₃ OH | CH ₂ O | CH ₃ OH |
| Removal ratio at 5 min (%) | 22 | 2 | 23 | 27 | 24 | 23 | 24 | 21 |
| Removal ratio at 80 min (%) | 62 | 44 | 54 | 46 | 55 | 46 | 57 | 44 |
| Initial rate (M/min) | 1.46 $\times 10^{-2}$ | 3.98 $\times 10^{-4}$ | 1.53 $\times 10^{-2}$ | 4.28 $\times 10^{-3}$ | 1.63 $\times 10^{-2}$ | 3.69 $\times 10^{-3}$ | 1.6 $\times 10^{-2}$ | 3.28 $\times 10^{-3}$ |
| k (min ⁻¹) | 8.25 $\times 10^{-3}$ | 4.85 $\times 10^{-3}$ | 6.3 $\times 10^{-3}$ | 3.57 $\times 10^{-3}$ | 5.65 $\times 10^{-3}$ | 2.59 $\times 10^{-3}$ | 8.38 $\times 10^{-3}$ | 5.09 $\times 10^{-3}$ |
| r ² | 0.9980 | 0.9935 | 0.9640 | 0.9123 | 0.9697 | 0.8595 | 0.9995 | 0.9977 |
| r _m /r _f | 0.0273 | | 0.28 | | 0.226 | | 0.205 | |

4.3 Effects of H₂O₂

Hydrogen peroxide plays an important role in photo-Fenton process. OH[•] is generated by the photolysis of hydrogen peroxide and the reaction between hydrogen peroxide and ferrous ion. Furthermore, regeneration of Fe³⁺ to Fe²⁺ is initiated when Fe³⁺ reacts with H₂O₂ to produce Fe(OH)²⁺ and then Fe(OH)²⁺ is transferred to Fe²⁺ and OH[•] in the presence of UV light. Nonetheless, H₂O₂ also can inhibit the oxidation reaction since H₂O₂ itself can be a hydroxyl radical scavenger. Equation (4.6) shows the reaction between H₂O₂ and OH[•] to produce OH₂[•] and water when a large amount of H₂O₂ was presented. OH₂[•] is a free radical with less oxidizing ability than OH[•]. Under the condition that OH₂[•] is produced instead of OH[•], this may result in the retardation of the oxidation reaction. Accordingly, this part of experiment was performed in order to study the effects of H₂O₂ concentration on photo-Fenton reaction for the treatment of formaldehyde and methanol. In these experiments, 0.333 M of CH₂O, 7.96x10⁻² M of CH₃OH, 6.67x10⁻² M of Fe²⁺, and initial pH 2.6±0.1 were applied as the initial conditions, and H₂O₂ concentrations were 0.333 M, 0.5 M, 0.667 M, 0.833 M, and 1 M.

All the results obtained from this part were exemplified in Figures 4.6(a) to (f). Figures 4.6 (a) and (b) show the residual fraction of formaldehyde and methanol versus time. Results indicate that, in the absence of H₂O₂, no formaldehyde degradation was observed, and methanol concentrations slightly decreased. The removal ratios of formaldehyde at the time of 5 minutes were 56%, 51%, 65.0%, 69% and 90% in the presence of 0.333, 0.500, 0.667, 0.833 and 1.0 M of H₂O₂, respectively. In addition, formaldehyde was almost completely degraded with 1.0 M and 0.833 M of H₂O₂ at 10 min and 40 min, respectively. After 80 min, the removal ratios of formaldehyde were 68%, 68%, and 94% with 0.333, 0.500, and 0.667 M of H₂O₂.

Figure 4.6 (b) shows the profile of methanol degradation using different dosages of H₂O₂. The degradation of methanol at the time of 5 minutes were 45%, 17%, 47%, 53% and 66%, and reached 61%, 33%, 79%, 91% and 96% after 80 minutes with 0.333, 0.50, 0.667, 0.833 and 1.0 M of H₂O₂, respectively. As observed

from the experiment, the removal ratios of formaldehyde and methanol seemed to increase with increasing H_2O_2 dosages. However, the lowest efficiency of formaldehyde and methanol oxidation was observed at the concentration of H_2O_2 of 0.5 M.



Figure 4.6 (c) shows the remaining ratios of H_2O_2 versus time. With the addition of 0.333 M, 0.50 M, 0.667 M, 0.833 M and 1 M of H_2O_2 , H_2O_2 reduced quickly at the beginning stage of the oxidation reaction. The remaining percentages of H_2O_2 at 15 min were 2%, 11%, 11%, 19%, and 1%, respectively. After 15 min, H_2O_2 gradually decomposed. Even though H_2O_2 almost completely decomposed within 15 min at the initial concentration of H_2O_2 of 0.333 M, the removal efficiency of formaldehyde and methanol were higher than that with 0.50 M of H_2O_2 . Moreover, at an initial concentration of H_2O_2 of 1 M, H_2O_2 decomposed swifter than other concentrations.

Figure 4.6 (d) shows the pH variations during the time of experiment. It indicates that, while the higher concentrations of H_2O_2 were added, pH reduced to the lower value than when the lower ones were conducted. At 5 min with the added amount of H_2O_2 ranging from 0.333 M, 0.50 M, 0.833 M, and 1.0 M, pH sharply reduced from their initial values of 2.6 ± 0.1 to pH 2.04, 1.86, 1.78, 1.73, and 1.66, respectively. After 5 min, with the added amount of H_2O_2 of 0.333 M, 0.667 M and 1.0 M, pH started to increase. With 0.500 and 0.833 M of H_2O_2 , the pH values started to increase after 10 min. As shown in Figure 4.6 (d), the pH reduction was proportional to the added amount of H_2O_2 ; the more H_2O_2 concentration was added, the more pH reduced.

The trend for initial rate and k of formaldehyde and methanol with different initial concentrations of H_2O_2 are depicted in Figures 4.6 (e) and (f) (see the initial rates and k values from table 4.4). It is evident that the initial rates of formaldehyde

and methanol increased with increasing H_2O_2 concentration. Moon et al. (1991) discovered that when $[\text{FeCl}_3] = 2.15 \times 10^{-4} \text{ M}$ and $[\text{H}_2\text{O}_2] < 5 \times 10^{-2} \text{ M}$, the reaction rate increased by increasing the hydrogen peroxide concentration. However, when H_2O_2 dosages were more than $5 \times 10^{-2} \text{ M}$, the reaction rate decreased with an increase in the hydrogen peroxide concentration. Li et al. (1997) also reported that 2, 4, 6-trinitrotoluene oxidation increased with increasing hydrogen peroxide concentration. In this study, increasing the concentration of hydrogen peroxide did not inhibit the oxidation of formaldehyde and methanol. Our result is the same as those reported by the literatures (Lu et al., 1999; Pignatello J. J., 1992; Li et al., 1997; Rahhal and Richter, 1988). The reason for this could be the amount of hydrogen peroxide added in this experiment had not yet reached the degree of inhibition.

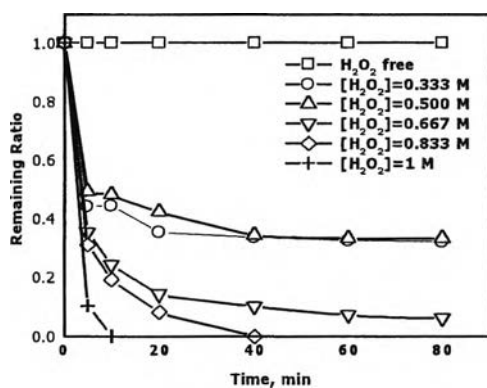


Figure 4.6 (a) Remaining ratio of formaldehyde with reaction time

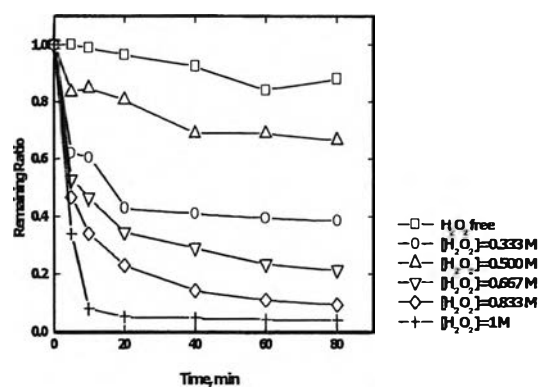


Figure 4.6(b) Remaining ratio of methanol with reaction time

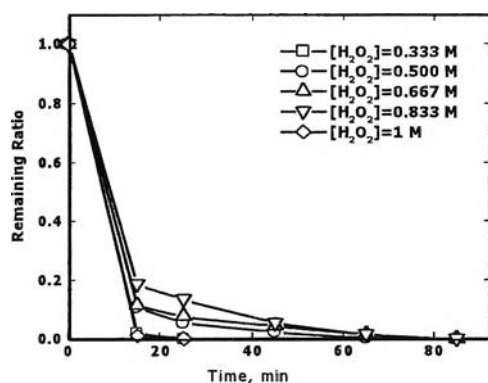


Figure 4.6 (c) Remaining ratio of H_2O_2 with reaction time

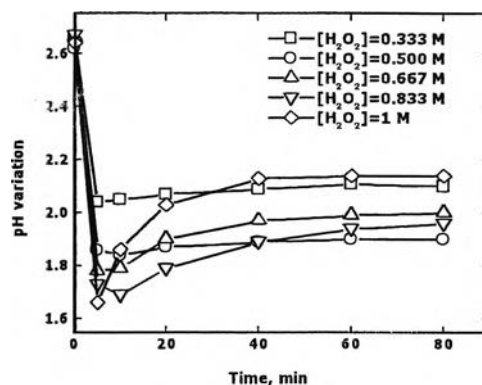


Figure 4.6(d) pH variation with reaction time

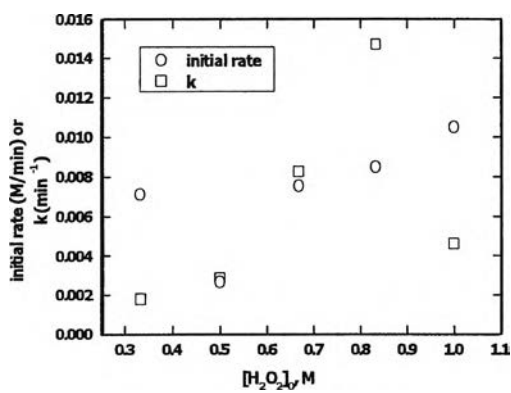


Figure 4.6 (e) Effect of H_2O_2 on initial rate and rate constant of formaldehyde

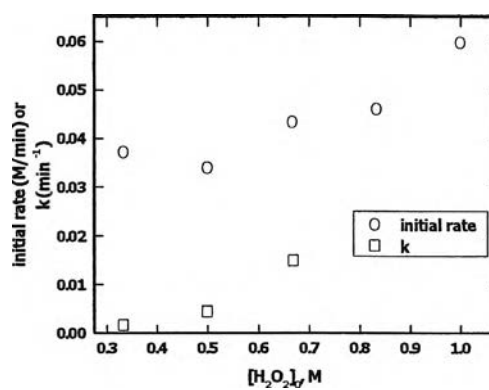


Figure 4.6 (f) Effect of H_2O_2 on initial rate and rate constant of methanol

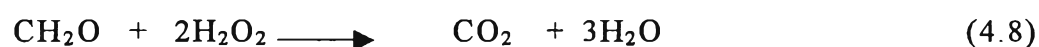
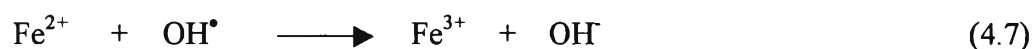
Table 4.4 Effect of H₂O₂ on formaldehyde and methanol oxidation

| [H ₂ O ₂] | 0.333 M | | 0.500M | | 0.667 M | | 0.833 M | | 1 M | |
|-------------------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|-----------------------|------------------------|------------------------|------------------------|
| | CH ₂ O | CH ₃ OH | CH ₂ O | CH ₃ OH | CH ₂ O | CH ₃ OH | CH ₂ O | CH ₃ OH | CH ₂ O | CH ₃ OH |
| % removal at 5 min | 56 | 38 | 51 | 1.67 | 65 | 47 | 69 | 53 | 89.7 | 66 |
| % removal at 80 min | 68 | 61.5 | 68 | 33.3 | 94 | 79 | 100 | 91 | 100 | 96 |
| initial rate (M min ⁻¹) | 3.72 x10 ⁻² | 6.03 x10 ⁻³ | 3.40 x10 ⁻² | 2.66 x10 ⁻³ | 4.33 x10 ⁻² | 7.55 x10 ⁻³ | 4.6 x10 ⁻² | 8.50 x10 ⁻³ | 5.97 x10 ⁻² | 1.05 x10 ⁻² |
| k (min ⁻¹) | 1.58 x10 ⁻³ | 1.78 x10 ⁻³ | 3.79 x10 ⁻³ | 2.85 x10 ⁻³ | 1.45 x10 ⁻² | 8.25 x10 ⁻³ | - | 1.47 x10 ⁻² | - | 4.60 x10 ⁻³ |
| r ² | 0.9688 | 0.9926 | 0.8386 | 0.7388 | 0.9874 | 0.9776 | - | 0.9454 | - | 0.9911 |
| r _m /r _f | 0.1621 | | 0.078 | | 0.174 | | 0.185 | | 0.207 | |

4.5 Effect of Ferrous Ions

Since hydrogen peroxide has an oxidation potential of 1.77 V, it has a less oxidizing power (Prengle and Mauk, 1978). Besides, formaldehyde and methanol can not be completely oxidized by only adding hydrogen peroxide to the solution. Ferrous ions are the main species that can catalyze hydrogen peroxide to produce hydroxyl radicals with a strong oxidizing ability (Collins et al., 1959). Additionally, ferrous ions also act as a photo catalyst in the photo-Fenton system; Fe³⁺ can be regenerated to Fe²⁺ in the presence of UV light. However, an excess amount of Fe²⁺ may inhibit the oxidation reaction because Fe²⁺ itself also can compete with target organic compounds to consume OH[•]. Equation (4.7) presents the reaction of Fe²⁺ with OH[•] resulting in less amount of OH[•] that can react with target organic compounds. In order to investigate the effects of Fe²⁺ concentration on photo-Fenton process for treating formaldehyde and methanol, these experiments were carried out with various amounts of Fe²⁺ with the initial concentrations of 0.333 M of CH₂O, 0.0796 M of CH₃OH, and an initial pH 2.6±0.1 were used as the initial conditions. The H₂O₂ concentration was fixed at the theoretical molar ratio to CH₂O, 2 per 1, calculated from Equation (4.8). Results obtained from this part are depicted in Figure 4.7 (a) to (f). Figures 4.7 (a) shows the effect of ferrous ion concentrations on the degradation of formaldehyde. As

the ferrous ion concentration increased from 0 M to 6.67×10^{-3} M, 2.27×10^{-2} M, 6.67×10^{-2} M, and 8.33×10^{-2} M, the removal percentages of formaldehyde degradation at 5 minutes were 5%, 32%, 55%, 65%, and 78%, and reached 48%, 62%, 79%, 94% and 95%, respectively at the end of 80 min of the reaction time period. Figure 4.7 (a) indicates that the removal efficiency of formaldehyde increased with an increase in the Fe^{2+} concentration. However, at Fe^{2+} concentrations of 6.67×10^{-2} M and 8.33×10^{-2} M, the removal efficiencies of formaldehyde were almost the same. This result may be caused by the Fe^{2+} inhibition that occurred when too high a concentration of Fe^{2+} was presented. Liou et al. (2003) also indicated that the OH^\bullet inhibition effect can occur in photo-Fenton reaction with high Fe^{2+} concentration.



The remaining ratios of methanol at the different concentrations of ferrous ions are shown in Figure 4.7 (b). Removal percentages at 5 and 80 min of methanol increased from 0.2% to 2%, 37%, 47%, and 49%, and from 32% to 44%, 63%, 79% and 82% when the ferrous ion concentrations increased from 0 M to 6.67×10^{-3} M, 2.27×10^{-2} M, 6.67×10^{-2} M, and 8.33×10^{-2} M, respectively. As shown in Figure 4.7 (b), the removal efficiency of methanol increased when the Fe^{2+} concentration increased. However, at the highest Fe^{2+} concentration, 8.33×10^{-2} M, used in this study the removal percentages of methanol were almost the same as that with 6.67×10^{-2} M of Fe^{2+} . This result was similar to the result depicted in Figure 4.7 (a): the effect of Fe^{2+} on formaldehyde oxidation. It may lead to the conclusion again that too high concentration of Fe^{2+} , Fe^{2+} itself may inhibit the oxidation reaction by reacting with OH^\bullet resulting in the retardation of the reaction.

Profiles of residual H_2O_2 versus time at different initial concentrations of Fe^{2+} are depicted in Figure 4.7 (c). As initial concentrations of Fe^{2+} increased from 0 M to

6.67x10⁻³ M, 2.27x10⁻² M, 6.67x10⁻² M, and 8.33x10⁻² M, the remaining ratios of H₂O₂ at 15 min decreased from 71% to 47%, 37%, 11%, and 9%, respectively afterwards H₂O₂ was gradually reduced. At 65 min, almost all of the H₂O₂ was decomposed at 6.67x10⁻² M and 8.33x10⁻² M of Fe²⁺. When the initial concentrations of 0 M, 6.67x10⁻³ M, and 2.27x10⁻² M were used, the remaining percentages of H₂O₂ at 85 min were 42%, 32%, and 19%, respectively. In both experiments with 6.67x10⁻² M and 8.33x10⁻² M of Fe²⁺, the remaining ratios of H₂O₂ were almost the same during the time of the oxidation reaction. This may be a result of the inhibition effect of Fe²⁺. When an over-high concentration of Fe²⁺ was presented, Fe²⁺ itself can react with OH[•] to produce Fe³⁺ and OH⁻ (Equation (4.7)) resulting in less Fe²⁺ that can react with H₂O₂ to produce OH[•].

Figure 4.7 (d) shows the profile of pH variation versus time at different concentrations of Fe²⁺. At 5 min of the oxidation reaction, the pH value decreased from the initial pH 2.6±0.1 to pH 2.55, 2.24, 2.06, 1.78, and 1.82 at the different initial dosages of Fe²⁺ of 0 M, 6.67x10⁻³ M, 2.27x10⁻² M, 6.67x10⁻² M, and 8.33x10⁻² M, respectively. At the initial concentrations of 0 M, 6.67x10⁻³ M, and 2.27x10⁻² M of Fe²⁺, pH decreased continuously during the time of reaction. While applying the initial concentrations of Fe²⁺ of 6.67x10⁻² M and 8.33x10⁻² M, pH started to increase after 5 min and 10 min, respectively. Figure 4.7 (d) indicates that the pH reduction is proportional to the added amount of Fe²⁺. With higher concentrations of Fe²⁺, at the beginning stage, pH reduced to lower value than those with the lower ones. The reduction of pH may be caused by a higher amount of formic acid presenting at the higher added amount of Fe²⁺ due to the higher oxidation efficiency. However, at an initial dosage of 8.33x10⁻² M of Fe²⁺, the pH reduced to a higher value than that produced with 6.67x10⁻² M of Fe²⁺. This may result from the excess Fe²⁺ reacting with OH[•] to produce Fe³⁺ and OH⁻ (Equation (4.7)).

As seen in Figures 4.7 (e) and (f), the initial rates of formaldehyde and methanol increased with increasing Fe²⁺ concentrations. And in the last stage, when Fe²⁺ increased, the k values of formaldehyde and methanol increased; the initial rates and k values are listed in Table 4.5. Figures 4.7 (e) and (f) also indicate that when Fe²⁺ was higher than 2.27x10⁻² M, the initial rate of formaldehyde and methanol

changed slightly; the benefit obtained from increasing amount of Fe^{2+} on initial rate was not obvious.

From these experiments, it may lead to the conclusion that the removal efficiency of formaldehyde and methanol increased with increasing Fe^{2+} concentration. However, OH^\bullet inhibition occurred at $8.33 \times 10^{-3} \text{ M}$ of Fe^{2+} . This result is similar to the result reported by Li et al. (1997). They indicated that the OH^\bullet inhibition effect can occur in photo-Fenton reaction with high Fe^{2+} concentration. It is because Fe^{2+} will react with OH^\bullet resulting in the less amount of OH^\bullet that can react with organic compounds as mentioned earlier.

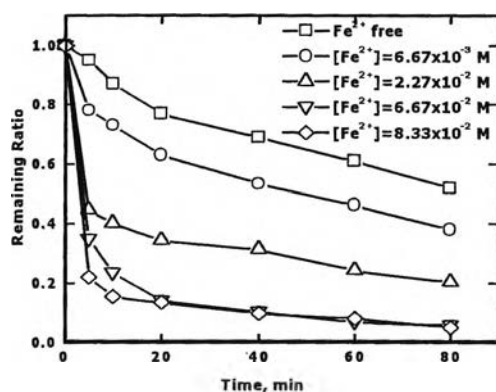


Figure 4.7 (a) Remaining Ratio of Formaldehyde with Reaction Time

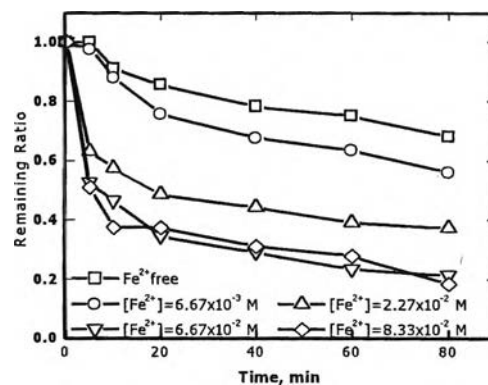


Figure 4.7 (b) Remaining Ratio of Methanol with Reaction Time

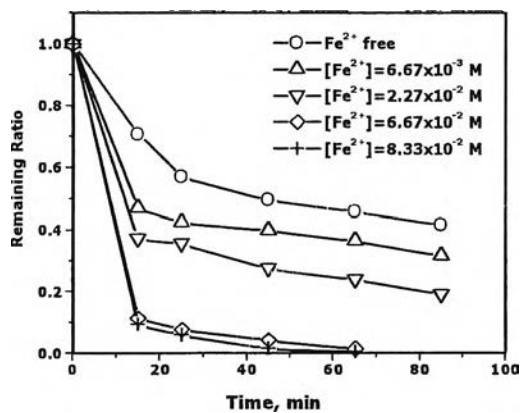


Figure 4.7 (c) Remaining ratio of H_2O_2 with reaction time

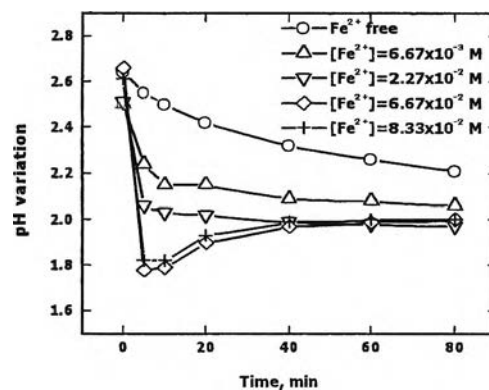


Figure 4.7 (d) pH variation with reaction time

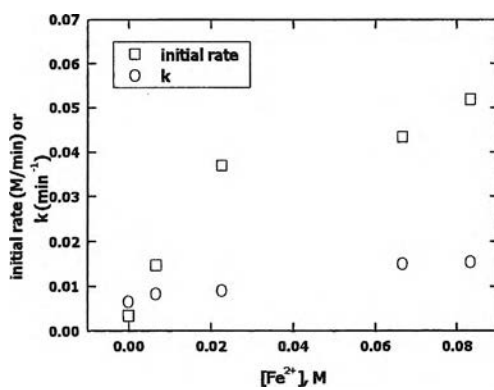


Figure 4.7 (e) Effect of Fe^{2+} on initial rate and rate constant of formaldehyde

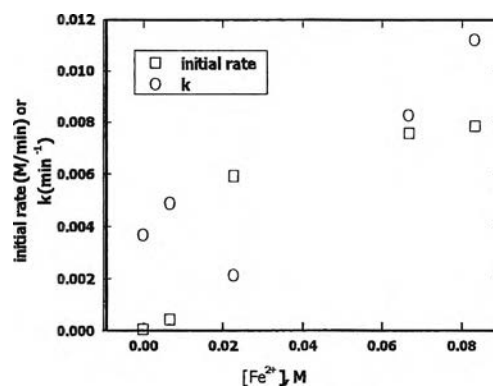


Figure 4.7 (f) Effect of Fe^{2+} on initial rate and rate constant of methanol

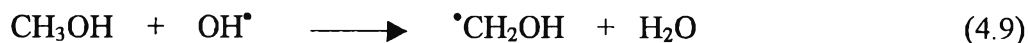
Table 4.5 Effect of Fe^{2+} on formaldehyde and methanol oxidation

| [Fe^{2+}] | 0 | | 6.67×10^{-3} M | | 2.27×10^{-2} M | | 6.67×10^{-2} M | | 8.33×10^{-2} M | |
|--------------------------------------|-----------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|
| | CH_2O | CH_3OH | CH_2O | CH_3OH | CH_2O | CH_3OH | CH_2O | CH_3OH | CH_2O | CH_3OH |
| % removal at 5 min | 5 | 0.2 | 22 | 2 | 55 | 37 | 65 | 47 | 78 | 49 |
| % removal at 5 min | 48 | 32 | 62 | 44 | 79 | 63 | 96 | 79 | 95 | 82 |
| initial rate (M min^{-1}) | 3.33×10^{-3} | 3.18×10^{-5} | 1.46×10^{-2} | 3.98×10^{-4} | 3.69×10^{-2} | 5.89×10^{-3} | 4.33×10^{-2} | 7.55×10^{-3} | 5.18×10^{-2} | 7.82×10^{-3} |
| k (min^{-1}) | 6.5×10^{-3} | 3.66×10^{-3} | 8.25×10^{-3} | 4.85×10^{-3} | 9.01×10^{-3} | 4.6×10^{-3} | 1.49×10^{-2} | 8.25×10^{-3} | 1.54×10^{-2} | 1.12×10^{-2} |
| r^2 | 0.996 | 0.9985 | 0.998 | 0.9935 | 0.985 | 0.9866 | 0.9899 | 0.9887 | 0.986 | 0.9615 |
| r_m/r_f | 0.0095 | | 0.0273 | | 0.16 | | 0.174 | | 0.151 | |

4.5 Effect of Methanol

As mentioned in the section "Introduction", approximately 10% of methanol was added to a commercial product of formaldehyde to keep its stability. OH^\bullet is a non-selective oxidant, which can react with almost all organic compounds. Therefore, methanol may compete with formaldehyde to consume OH^\bullet as expressed in Equation (4.9), resulting in the retardation of the oxidation reaction of formaldehyde. So as to investigate the effect of methanol on the degradation of formaldehyde treated by photo-Fenton process, three experiments with different concentrations of methanol were conducted in this part. Initial concentrations of 0.333 M of CH_2O , 0.667 M of H_2O_2 , and 6.67×10^{-2} M of Fe^{2+} were chosen as the initial conditions, and initial concentrations of CH_3OH were 0.0796 M, 0.333 M and 0.667 M. All the results obtained from this part are presented in Figures 4.8 (a) to (f). As shown in Figure 4.8 (a), the amount of formaldehyde decomposition within 5 minutes decreased from 65%, 41% and 21% when the initial concentration of methanol increased from 7.96×10^{-2} M, 0.333 M, and 0.667 M, respectively. At the end of 80 min, the removal percentages of formaldehyde decreased from 94%, 55%, and 40%, when the initial

concentration of methanol was increased as above. It indicated that the removal efficiency of formaldehyde decreased with an increase in the increasing methanol concentration. Due to the presence of high concentrations of methanol, 0.333 M and 0.667 M, the oxidation reaction of formaldehyde was almost stopped after 20 min.



The degradation profile of methanol at different initial concentrations is presented in Figure 4.8 (b). Methanol removed within 5 min were 47%, 24%, and 13%, and at the end of 80 min they were 79%, 39%, and 29%, with initial concentrations of 0.0796 M, 0.333 M, and 0.667 M, respectively. This result shows the same tendency as the results presented in Figure 4.8 (a); formaldehyde removal efficiency decreased as methanol concentrations increased. With increasing concentrations of methanol, the oxidation reaction was reduced, and it almost stopped after 20 min. It is recommended that the presence of methanol may retard the oxidation of formaldehyde and methanol itself, especially at such a high concentration of methanol.

Figure 4.8 (c) exemplify the remaining ratios of H_2O_2 with time in the presence of different initial concentrations of methanol. In most cases from this study, 0.0796 M of methanol was always presented with 0.333 M of formaldehyde, at 15 min only 11 % of H_2O_2 remained in the system. While applying higher dosages of methanol, 0.333 M and 0.667 M, 21% and 25% of H_2O_2 still existed in the reaction mixture at 15 min, and at 85 min 8% of H_2O_2 still existed in the system in both cases. At 85 min, all H_2O_2 had been decomposed when the initial concentration of CH_3OH of 0.0796 M was added.

Profiles of pH variation obtained from this set of experiments are shown in Figure 4.8 (d). At 5 min of the reaction, with initial concentrations of CH_3OH of 0.0796 M, 0.333 M, and 0.667 M, the pH value sharply reduced. After 5 min, with

0.0796 M of CH_3OH , the pH value started to increase gradually. When 0.333 M and 0.667 M of CH_3OH were applied, pH reduced gradually after 5 min.

As the concentrations of methanol increased, the initial rates and k values of formaldehyde and methanol decreased as presented in Figure 4.8 (e) and (f). (see the initial rates and k values of formaldehyde and methanol from Table 4.6). It is noticeable that the high concentrations of methanol presented in the solution can retard the oxidation reaction significantly.

From these results, it is concluded that methanol can compete with formaldehyde to react with hydroxyl radicals. Therefore, the presence of high concentration of methanol leads to retard the oxidation reaction of formaldehyde significantly; the high concentration of methanol was added, the less amount of formaldehyde was removed.

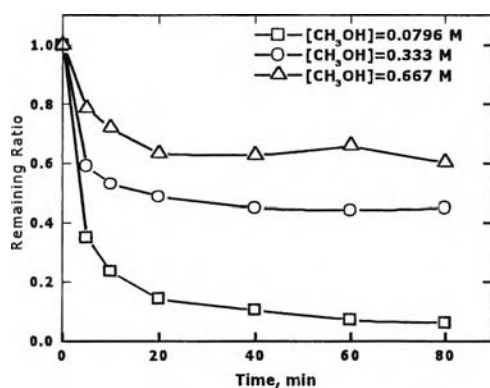


Figure 4.8 (a) Remaining ratio of formaldehyde with reaction time

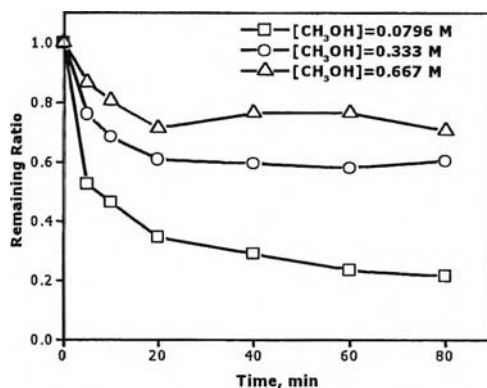


Figure 4.8 (b) Remaining ratio of methanol with reaction time

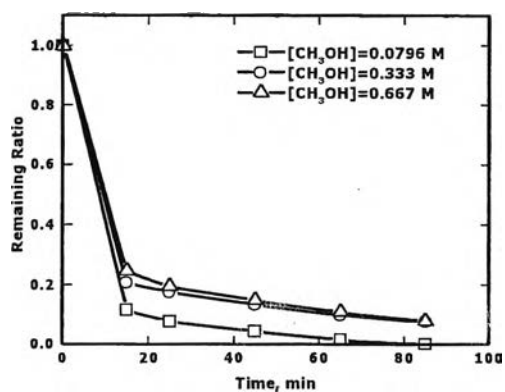


Figure 4.8 (c) Remaining ratio of H_2O_2 with reaction time

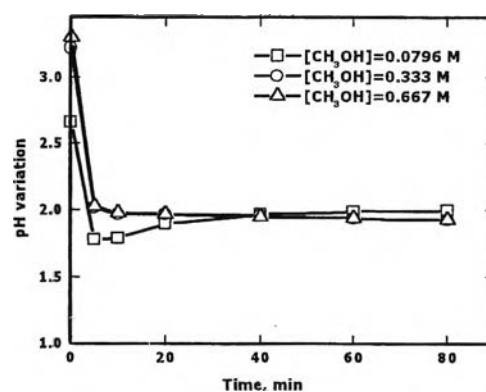


Figure 4.8 (d) pH variation with reaction time

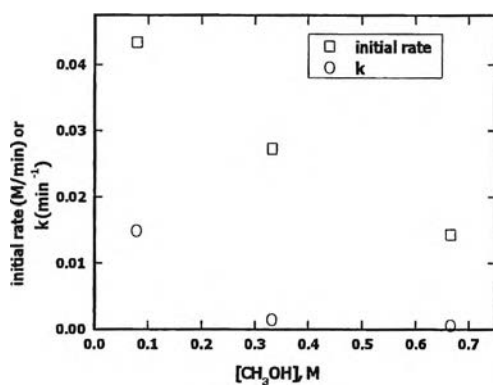


Figure 4.8 (e) Effect of methanol on initial rate and rate constant of formaldehyde

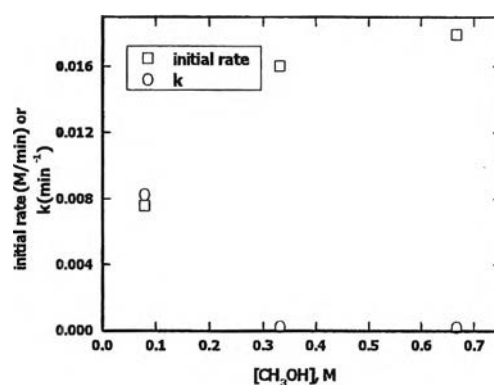


Figure 4.8 (f) Initial rate and rate constant of methanol at different concentrations.

Table 4.6 Influence of methanol on the oxidation reaction

| [CH ₃ OH] | 0.0796 M | | 0.333 M | | 0.667 M | |
|-------------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| | CH ₂ O | CH ₃ OH | CH ₂ O | CH ₃ OH | CH ₂ O | CH ₃ OH |
| % removal at 5 min | 65 | 47 | 41 | 24 | 21 | 13 |
| %removal at 5 min | 94 | 79 | 55 | 39 | 40 | 29 |
| initial rate (M min ⁻¹) | 4.33x10 ⁻² | 7.55x10 ⁻³ | 2.72x10 ⁻² | 1.6x10 ⁻² | 1.43x10 ⁻² | 1.79x10 ⁻² |
| k (min ⁻¹) | 1.49x10 ⁻² | 8.25x10 ⁻³ | 1.33x10 ⁻³ | 2.04x10 ⁻⁴ | 4.67x10 ⁻⁴ | 1.48x10 ⁻⁴ |
| r ² | 0.9800 | 0.9776 | - | - | - | - |
| r _m /r _f | 0.174 | | 0.588 | | 1.209 | |

4.6 Competition of Formaldehyde with Methanol

Due to the presence of methanol during the formaldehyde oxidation, methanol may compete with formaldehyde to react with hydroxyl radicals as expressed in Equation (4.9). The intrinsic rate constants for formaldehyde and methanol with OH[•] were almost the same value; 1x10⁹ M⁻¹ s⁻¹ and 9.7x10⁸ M⁻¹ s⁻¹, respectively. Therefore, the oxidation rate of formaldehyde could be almost the same as that of methanol.

According the following equation:

$$r_m/r_f = \frac{K_{OH} [CH_3OH] [\cdot OH]}{K_{OH} [CH_2O] [\cdot OH]} \quad (4.10)$$

Where r_m stand for the initial rate of methanol, r_f is the initial rate of formaldehyde. K_{OH} is intrinsic rate constants of pollutants to react with hydroxyl radicals: 1x10⁹ M⁻¹ s⁻¹ for formaldehyde and 9.7x10⁸ M⁻¹ s⁻¹ for methanol. [CH₃OH] is

the initial concentration of methanol; 0.0796 M. $[\text{CH}_2\text{O}]$ is the initial concentration of formaldehyde; 0.333 M, and $[\cdot\text{OH}]$ is the concentration of hydroxyl radical in the system.

By substituting these values in Equation (4.10), the theoretical value of r_m/r_f is equal to 0.232. Table 4.7 lists the r_m/r_f obtained from the experiments. It indicates that all values of r_m/r_f obtained from the experiments are lower than the theoretical value. Similar results are also presented in Table 4.8. By substituting 0.333 M and 0.667 M of methanol in Equation (4.10), the theoretical value of r_m/r_f is 0.97 and 1.94. However, r_m/r_f obtained from the experiments is 0.588 and 1.209, respectively, which were much lower than the theoretical value.

Table 4.7 Relationship between the initial rates of methanol to formaldehyde

| | r_m/r_f | $[\text{H}_2\text{O}_2]$, M | $[\text{Fe}^{2+}]$, M | initial pH |
|----------------------------------|-----------|------------------------------|------------------------|------------|
| UV/ H_2O_2 | 0.0095 | 0.667 | 0 | 2.6±0.1 |
| photo-Fenton | 0.174 | 0.667 | 6.67×10^{-2} | 2.6±0.1 |
| Effect of pH | 0.174 | 0.667 | 6.67×10^{-2} | 2.6±0.1 |
| | 0.056 | 0.667 | 6.67×10^{-2} | 3.0±0.1 |
| | 0.15 | 0.667 | 6.67×10^{-2} | 3.5±0.1 |
| | 0.137 | 0.667 | 6.67×10^{-2} | 4.0±0.1 |
| Effect of H_2O_2 | 0.162 | 0.333 | 6.67×10^{-2} | 2.6±0.1 |
| | 0.078 | 0.5 | 6.67×10^{-2} | 2.6±0.1 |
| | 0.174 | 0.667 | 6.67×10^{-2} | 2.6±0.1 |
| | 0.185 | 0.833 | 6.67×10^{-2} | 2.6±0.1 |
| | 0.207 | 1 | 6.67×10^{-2} | 2.6±0.1 |
| Effect of Fe^{2+} | 0.0095 | 0.667 | 0 | 2.6±0.1 |
| | 0.106 | 0.667 | 6.67×10^{-3} | 2.6±0.1 |
| | 0.16 | 0.667 | 2.27×10^{-2} | 2.6±0.1 |
| | 0.174 | 0.667 | 6.67×10^{-2} | 2.6±0.1 |
| | 0.151 | 0.667 | 8.33×10^{-2} | 2.6±0.1 |

Table 4.8 Effect of methanol on r_m/r_f

| | r_m/r_f | [CH ₃ OH], M | [H ₂ O ₂], M | [Fe ²⁺], M |
|--------------------|-----------|-------------------------|-------------------------------------|------------------------|
| Effect of methanol | 0.174 | 0.0796 | 0.667 | 6.67x10 ⁻² |
| | 0.588 | 0.333 | 0.667 | 6.67x10 ⁻² |
| | 1.209 | 0.667 | 0.667 | 6.67x10 ⁻² |

4.7 Methanol Oxidation by Photo-Fenton Process

Since methanol always presents with formaldehyde as mentioned earlier, the oxidation behavior of formaldehyde alone could not be studied. However, the oxidation of methanol could be investigated in this part in order to gain more understanding about the formaldehyde oxidation reaction. The experiments in this part can be divided into two sets. The first set is the degradation of methanol at different concentrations and the other is the effects of Fe²⁺ on methanol oxidation. Initial conditions used in the first set were as follows: 0.667 M of H₂O₂, 6.67x10⁻² M of Fe²⁺, initial pH 2.6±0.1, and initial CH₃OH concentrations were 0.0398 M, 0.0796 M, and 0.4126 M. For the last set, the initial conditions were conducted as follows: 0.0796 M of CH₃OH, 0.667 M of H₂O₂, initial pH 2.6±0.1, and the concentrations of Fe²⁺ were 0 M, 6.67x10⁻³ M, 2.27x10⁻² M, and 6.67x10⁻² M. All the results obtained from the first and the last sets were expressed in Figures 4.9 (a) to (c) and Figures 4.10 (a) to (c), respectively.

4.7.1 Degradation of Methanol at Different Concentration

Figure 4.9 (a) shows that most of CH₃OH was degraded within 5 min at an initial concentration of 0.0398 M. At an initial concentration of 0.0796 M, the removal ratio at 5 min was 69%, and then almost all of the CH₃OH disappeared within 20 min. With 0.4126 M of CH₃OH, only 15% and 45% of CH₃OH were

removed at 5 and 80 min, respectively (Table 4.9). It is remarkable that the removal efficiency of methanol decreased when increasing its concentration.

As seen in Figure 4.9 (b), at low concentration of CH_3OH , H_2O_2 disappeared swifter than that with the higher concentration. At 15 min, the remaining percentages of H_2O_2 were 1%, 42%, and 53% as the initial concentrations of CH_3OH ranging from 0.0398 M to 0.4126 M. With 0.0796 M of CH_3OH , almost no H_2O_2 residuals were observed at 25 min. When the initial concentration of 0.4126 M of CH_3OH was performed, 29% of H_2O_2 was detected at 85 min. It is indicated that the decomposition rate of H_2O_2 was slow when a high concentration of CH_3OH was added.

As depicted in Figure 4.9 (c), pH reduced rapidly in all cases after the oxidation reactions had begun. At initial CH_3OH concentration of 0.0398 M and 0.0796 M, pH started to increase after 10 min and 20 min, respectively. While at 0.4126 M of CH_3OH , pH reduced continuously during the time of the reaction as shown in Figure 4.9 (c). Figure 4.9 (c) also indicates that at an initial CH_3OH concentration of 0.0796 M, pH reduced to the lower value than at other concentrations.

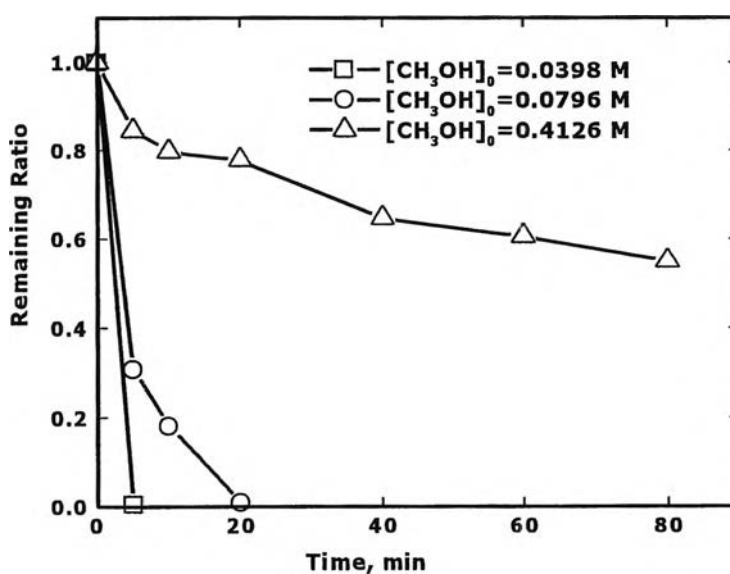


Figure 4.9 (a) Remaining ratio of methanol with reaction time

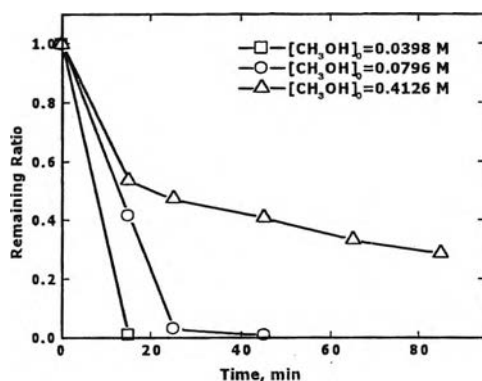


Figure 4.9 (b) Remaining ratio of H₂O₂ with reaction time

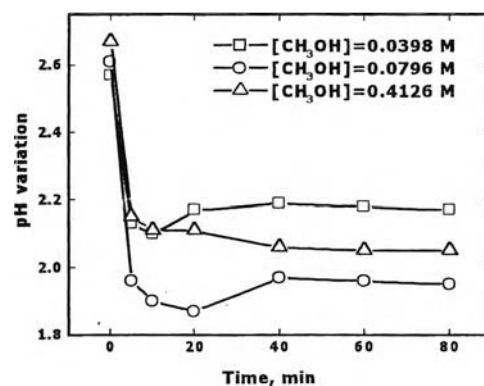


Figure 4.9 (c) pH variation with reaction time

Table 4.9 Degradation of methanol at different concentrations

| [CH ₃ OH] | 0.0398 M | 0.0796 M | 0.4128 M |
|------------------------|-----------------------|----------------------|-----------------------|
| % removal at 5 min | 99.5 | 69 | 15 |
| % removal at 80 min | 100 | 100 | 45 |
| initial rate (M/min) | 7.92×10^{-3} | 1.1×10^{-2} | 1.24×10^{-2} |
| k (min ⁻¹) | - | - | 5.56×10^{-3} |
| r ² | - | - | 0.9526 |

4.7.2 Effect of Fe²⁺ on Methanol Oxidation

As shown in Figure 4.10 (a), with the initial concentrations of Fe²⁺ of 0 M, 6.67×10^{-3} M, 2.27×10^{-2} M, and 6.67×10^{-2} M, the removal percentages of methanol at 5 min were 2%, 23%, 44%, and 69%, respectively; and at 80 min, they were 27% and 69% at 0 M and 6.67×10^{-3} M of Fe²⁺. When 2.27×10^{-2} M and 6.67×10^{-2} M of Fe²⁺ were added, most of methanol was oxidized at 20 and 60 min, respectively.

Figure 4.10 (b) shows the profile of H_2O_2 remaining as a function of time. At 15 min, the remaining percentages of H_2O_2 were 72%, 80%, 71%, and 42% as initial Fe^{2+} were 0 M, 6.67×10^{-3} M, 2.27×10^{-2} M, and 6.67×10^{-2} M, respectively. At 85 min, the remaining H_2O_2 were 65% and 67% at 0 M and 6.67×10^{-3} M of Fe^{2+} , respectively. When 2.27×10^{-2} M and 6.67×10^{-2} M of Fe^{2+} were applied, almost all H_2O_2 disappeared at 45 and 85 min, respectively.

As presented in Figure 4.10 (d), at 5 min, the higher the concentration of Fe^{2+} , the faster the pH reduced. At initial concentrations of 0 M, 6.67×10^{-3} M, 2.27×10^{-2} M, and 6.67×10^{-2} M of Fe^{2+} , pH reduced from an initial pH 2.6 to 2.50, 2.46, 2.30, and 1.96, respectively. At 0 M, 6.67×10^{-3} M of Fe^{2+} , pH continued to reduce after 5 min whereas for 2.27×10^{-2} M and 6.67×10^{-2} M of Fe^{2+} , pH reduced to 2.18 and 1.87 after 40 and 20 min, respectively, and then started to increase.

From this part of experiment, it can be concluded that the oxidation rate of methanol was quite slow at the high concentration (Figure 4.9 (b)). The oxidation rate of methanol significantly increased with increasing Fe^{2+} concentration (see the rates of methanol from table 4.10). Moreover, in the absence of formaldehyde, the rates of methanol oxidation in photo-Fenton process were apparently faster than those in the presence of formaldehyde. It is concluded that formaldehyde also can compete with methanol to consume hydroxyl radicals resulting in the low oxidation rate of methanol when formaldehyde presented. However, in the UV/ H_2O_2 process, without formaldehyde, the oxidation rates of methanol were almost the same as those with formaldehyde.



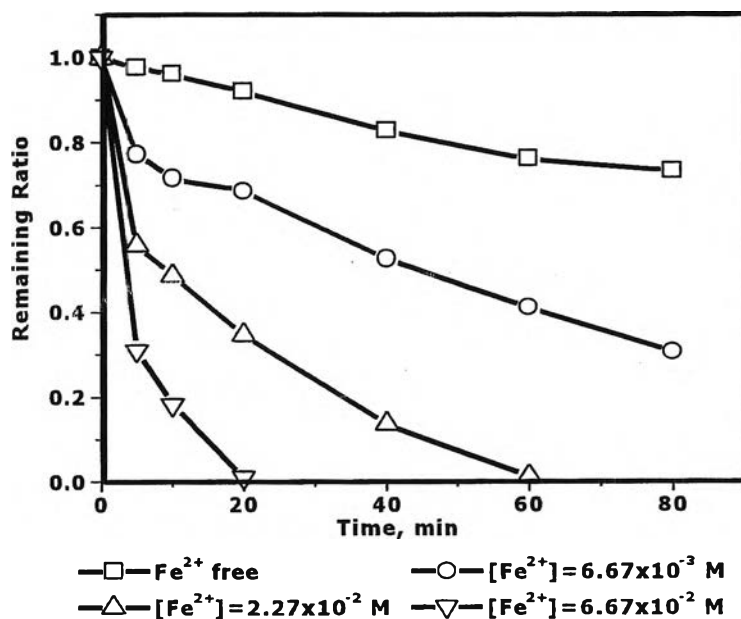


Figure 4.10 (a) Remaining ratio of methanol with reaction time

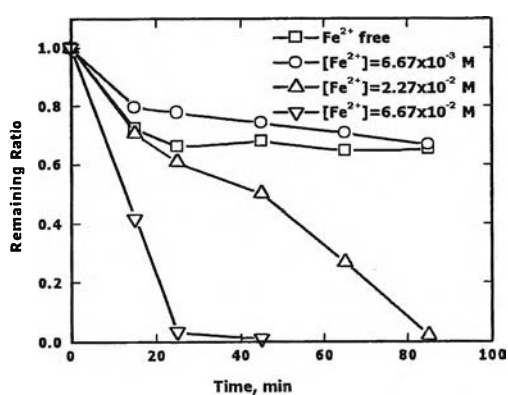


Figure 4.10 (b) Remaining ratio of H_2O_2 with reaction time

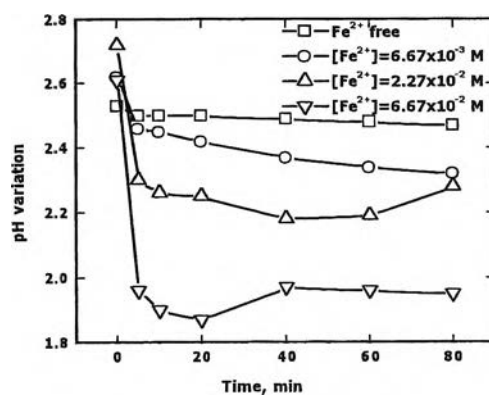


Figure 4.10 (c) pH variation with reaction time

Table 4.10 Effect of Fe^{2+} on methanol oxidation

| $[\text{Fe}^{2+}]$ | free | $6.67 \times 10^{-3} \text{ M}$ | $2.27 \times 10^{-2} \text{ M}$ | $6.67 \times 10^{-2} \text{ M}$ |
|---|-----------------------|---------------------------------|---------------------------------|---------------------------------|
| % removal at 5 min | 2 | 23 | 44 | 69 |
| % removal at 80 min | 27 | 69 | 100 | 100 |
| initial rate ($\text{M} \cdot \text{min}^{-1}$) | 3.58×10^{-4} | 3.62×10^{-3} | 7.01×10^{-3} | 1.1×10^{-2} |
| k (min^{-1}) | 3.82×10^{-3} | 1.33×10^{-2} | 8.35×10^{-2} | - |
| r^2 | 0.9629 | 0.9988 | 0.9387 | - |

4.8 Degradation of Formaldehyde and Methanol by Fenton Process.

Photo-Fenton was modified by applying UV light to Fenton reaction in order to increase the regenerate rate of Fe^{3+} to Fe^{2+} and activate H_2O_2 to produce hydroxyl radical. As a result, photo-Fenton process could provide a higher efficiency treatment of target organic compounds than Fenton process. However, there are some literatures reported that the difference between Fenton and photo-Fenton processes for treating organic pollutants was not obvious. Whereas, Li et al. (1997) reported that photo-Fenton process exhibited good decomposition ability on the explosive decomposition such as TNT, DNT, and MNT, because Fe^{2+} can be regenerated through the photoreduction of Fe^{3+} which produced a high reactive hydroxyl radical. However there is no report about how obvious the difference is between Fenton and photo-Fenton processes for treating formaldehyde and methanol. Therefore, the experiments in this part were performed in order to study the removal efficiency of formaldehyde and methanol treated by Fenton process and then compared with photo-Fenton processes. There are 5 sets of experiments presented in this part: formaldehyde and methanol oxidations by Fenton process and a comparison of Fenton and photo-Fenton processes at initial pH values of 2.6 ± 0.1 , 3 ± 0.1 , 3.5 ± 0.1 , and 4 ± 0.1 .

4.8.1 Formaldehyde and Methanol Oxidation by Fenton Process

In this experiment, 0.333 M of CH_2O , 0.076 M of CH_3OH , 0.667 M of H_2O_2 , and 6.67×10^{-2} M of Fe^{2+} were chosen as the initial conditions. All results are presented in Figures 4.11 (a) to (d). As shown in Figure 4.11 (a), at initial pH values of 2.6, 3, 3.5, and 4, the removal percentages of formaldehyde at 5 min were 66%, 60%, 57%, and 58%, respectively. After 80 min, they were 90%, 90%, 92%, and 89%, respectively. The removal percentage of formaldehyde at 5 min and 80 min fell from 57% to 66%, and 89% to 92%, respectively. Results indicate that initial pH value played an obvious effect on the beginning stage of the oxidation reaction. After 80 min, the removal ratios of formaldehyde at different pH values were almost the same.

Methanol oxidation by Fenton process with different initial pHs are exemplified in Figure 4.11 (b). The removal percentages of methanol at 5 min were 43%, 32%, 34%, and 43%, and at 80 min, they were 72%, 70%, 70%, and 70%, with initial pH values of 2.6, 3, 3.5, and 4, respectively. It is noticeable that both Figures 4.11 (b) and 4.11 (a) show similar results; the removal ratios of methanol at 5 min were more significantly affected by initial pH than at the end of the 80-min reaction period.

With different initial pH values of 2.6, 3, 3.5, and 4, the remaining percentages of H_2O_2 at 15 min were 14%, 20%, 19%, and 19%, respectively, and at 85 min, most of the H_2O_2 disappeared in all cases. As shown in Figure 4.11 (c), the remaining ratio of H_2O_2 at 15 min with different pHs was not obviously different. However, at an initial pH of 2.6 at 15 min, H_2O_2 disappeared faster than at other initial pH values. This may result in a highest removal ratio of formaldehyde and methanol at 5 min, obtained at an initial pH of 2.6 due to the fact that more H_2O_2 was used.

As shown in Figure 4.11 (d), at the different initial pH values, all pH variation displayed the same tendency. After the oxidation reaction was initiated, all initial pH values promptly reduced in the beginning stage of the oxidation reaction, then pH slightly reduced to its minimum value at 10 min after that pH started to increase

gradually. Results indicate that the pH variation in Fenton process shows the same tendency as in photo-Fenton process (Figure 4.4 (d)).

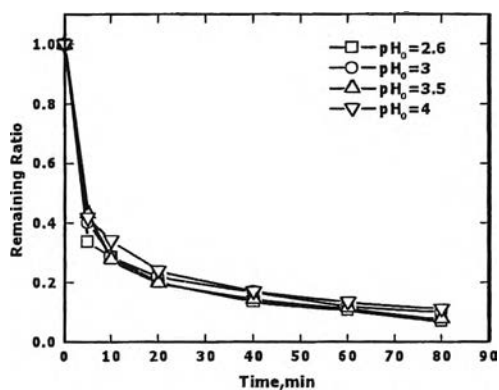


Figure 4.11 (a) Remaining ratio of formaldehyde with reaction time

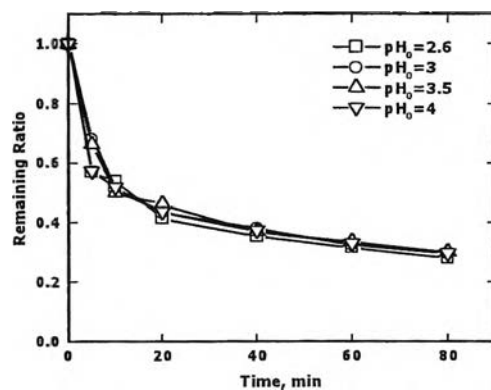


Figure 4.11 (b) Remaining ratio of methanol with reaction time

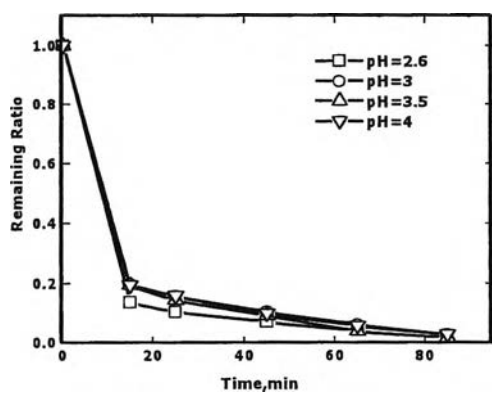


Figure 4.11 (c) Remaining ratio of H₂O₂ with reaction time

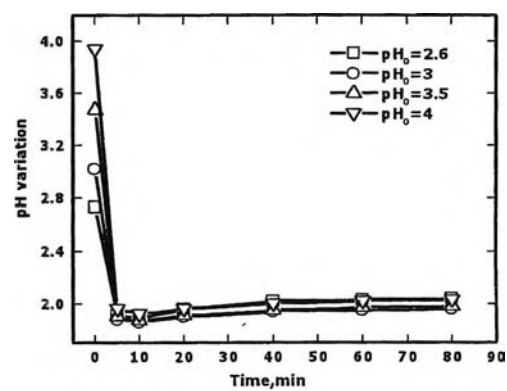


Figure 4.11 (d) pH variations with reaction time

Table 4.11 Oxidation of formaldehyde and methanol by Fenton process.

| initial pH | pH 2.6 | | pH 3 | | PH 3.5 | | pH 4 | |
|--------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| | CH ₂ O | CH ₃ OH | CH ₂ O | CH ₃ OH | CH ₂ O | CH ₃ OH | CH ₂ O | CH ₃ OH |
| % removal at 5 min | 66 | 43 | 60 | 32 | 57 | 34 | 58 | 43 |
| %removal at 5 min | 92 | 72 | 90 | 70 | 92 | 70 | 89 | 70 |
| initial rate (M/min) | 4.42 $\times 10^{-2}$ | 6.85 $\times 10^{-3}$ | 3.98 $\times 10^{-2}$ | 5.08 $\times 10^{-3}$ | 3.79 $\times 10^{-2}$ | 5.38 $\times 10^{-3}$ | 3.88 $\times 10^{-2}$ | 6.81 $\times 10^{-3}$ |
| k (min ⁻¹) | 1.14 $\times 10^{-2}$ | 6.48 $\times 10^{-3}$ | 1.33 $\times 10^{-2}$ | 6.51 $\times 10^{-3}$ | 1.53 $\times 10^{-2}$ | 6.96 $\times 10^{-3}$ | 1.27 $\times 10^{-2}$ | 6.48 $\times 10^{-3}$ |
| r ² | 0.9444 | 0.9972 | 0.9947 | 0.9955 | 0.9953 | 0.981 | 0.9905 | 0.9965 |
| r _m /r _f | 0.155 | | 0.128 | | 0.142 | | 0.176 | |

4.8.2 Comparison of Fenton and Photo-Fenton Processes at Initial pH 2.6

In the following experiments, Fenton and photo-Fenton processes were conducted with 0.333 M of CH₂OH, 0.0796 M of CH₃OH, 0.667 M of H₂O₂, 6.67×10^{-2} M of Fe²⁺, and an initial pH of 2.6. Results were illustrated in Figures 4.12 (a) to (d). As shown in Figure 4.12 (a), the removal ratios of formaldehyde treated by Fenton and photo-Fenton processes at 5 min and 80 min were 66% and 65%, and 93% and 94%, respectively. It is noticeable that at 5 min the removal efficiency of formaldehyde by Fenton process was slightly higher than that of photo-Fenton process. It is recommended that the inhibition of Fe²⁺ may occur due to the presence of high concentration of Fe²⁺. The difference between Fenton and photo-Fenton efficiencies seemed to be more obvious for methanol degradation than for formaldehyde, as revealed in Figure 4.12 (b). The decomposition percentages of methanol in Fenton and photo-Fenton processes at 5 min were 43% and 47%, and 72% and 79% at the end of 80 min.

As presented in Figure 4.12 (c), in photo-Fenton process, H_2O_2 decomposed slightly faster than in Fenton process. It is because in photo-Fenton process, H_2O_2 can be decomposed in several ways. Firstly, H_2O_2 can react with $\text{Fe}^{2+}/\text{Fe}^{3+}$ to generate hydroxyl radicals, and H_2O_2 can be initiated by UV light to produce two OH^\bullet . However, the difference between H_2O_2 decomposition in Fenton and photo-Fenton processes was not obvious, as presented in Figure 4.12 (c). In photo-Fenton process, pH values reduced to a lower value than that in Fenton process as expressed in Figure 4.12 (d). In Fenton process, pH value gradually increased after 10 min. of the reaction time period. Unlike in photo-Fenton process, pH started to increase gradually after 5 min.

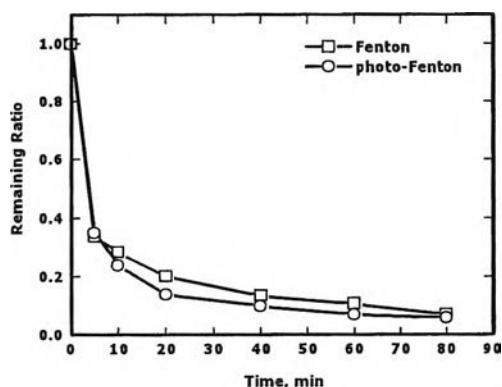


Figure 4.12 (a) Remaining ratio of formaldehyde with reaction time

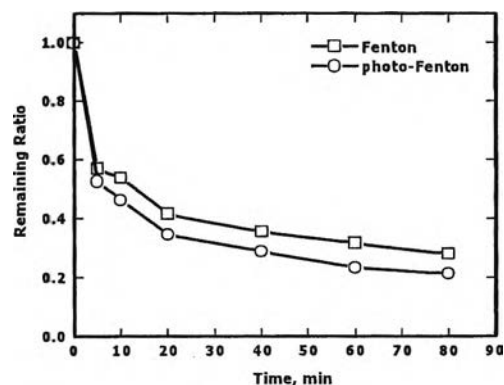


Figure 4.12 (b) Remaining ratio of methanol with reaction time

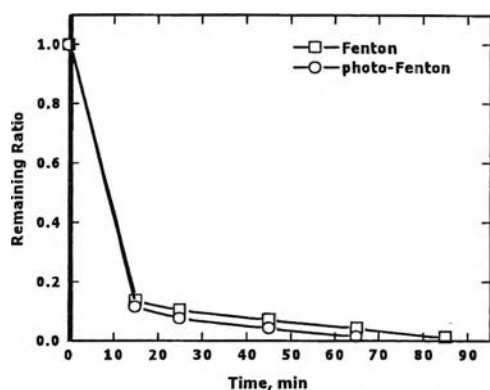


Figure 4.12 (c) Remaining ratio of H_2O_2 with reaction time

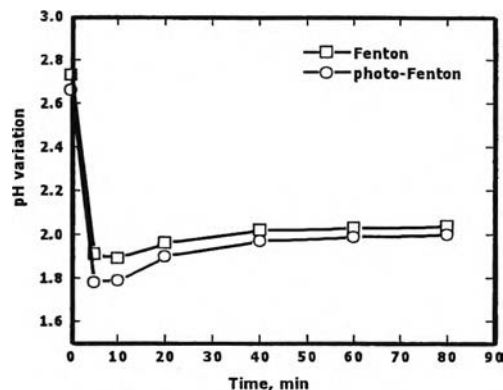


Figure 4.12 (d) pH variations with reaction time

4.8.3 Comparison of Fenton and Photo-Fenton Processes at Initial pH of 3

In this part, formaldehyde and methanol were treated by Fenton and photo-Fenton processes with the following experimental conditions: 0.333 M of CH_2O , 0.0796 M of CH_3OH , 0.667 M of H_2O_2 , and 6.67×10^{-2} M of Fe^{2+} . Both experiments were conducted at an initial pH of 3. At these experimental conditions, the removal efficiencies of formaldehyde by Fenton and photo-Fenton processes were almost the same, as shown in Figure 4.13 (a). The decomposition percentages of formaldehyde at 5 min and 80 min were 60% and 90% in Fenton process, and those were 59% and 92% in photo-Fenton process, respectively. It is noticeable that, at 5 min, the removal efficiency of formaldehyde by Fenton process was slightly higher than that of photo-Fenton process. This result is similar to the result depicted in Figure 4.12 (a). This finding may lead to the conclusion again that Fe^{2+} inhibition occurred when high concentrations of Fe^{2+} present.

Figure 4.13 (b) shows that in the early stage, methanol degraded faster in Fenton process than in photo-Fenton process. However at the end of 80 min, the removal efficiency of methanol by Fenton process was nearly the same as that of

photo-Fenton process. The decomposition ratio at 5 min of methanol treated by Fenton and photo-Fenton processes were 32% and 14%, and at 80 min, 70% and 69%.

As shown in Figure 4.13 (c), a significant drop of H_2O_2 was observed at the first point of measurement in both Fenton and photo-Fenton processes. Figure 4.13 (c) indicates that the amount of H_2O_2 degraded via Fenton process was nearly the same as that via photo-Fenton process. At 85 min, 3% and 0% of H_2O_2 were observed for Fenton and photo-Fenton processes, respectively. This result is similar to that observed in Figure 4.12 (c) where H_2O_2 decomposed at almost the same value by Fenton and photo-Fenton processes.

At 5 min of the oxidation reaction, pH reduced rapidly in both Fenton and photo-Fenton processes; and after 10 min, pH started to increase gradually as presented in Figure 4.13 (d). As depicted in Figure 4.13 (d), pH drops to the lower value in Fenton process than that in photo-Fenton process. This result is different from the other results obtained in this part. At initial pH of 2.6, 3.5, and 4, pH dropped to a lower value in photo-Fenton than that in Fenton process.

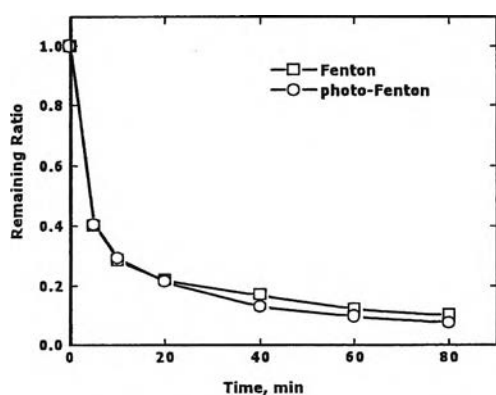


Figure 4.13 (a) Remaining ratio of formaldehyde with reaction time

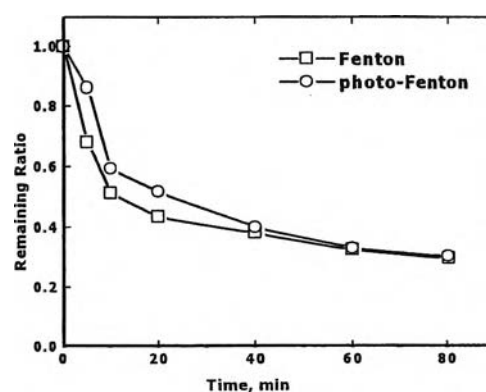


Figure 4.13 (b) Remaining ratio of methanol with reaction time

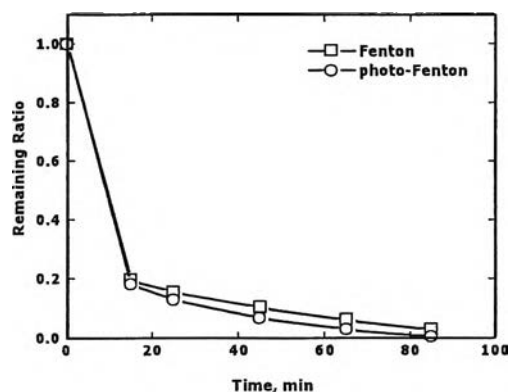


Figure 4.13 (c) Remaining ratio of H₂O₂ with reaction time

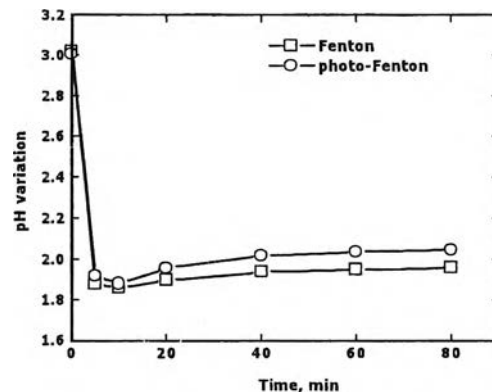


Figure 4.13 (d) pH variation with reaction time

4.8.4 Comparison of Fenton and Photo-Fenton Processes at Initial pH of 3.5

Figures 4.14 (a) to (d) show the results obtained from formaldehyde and methanol oxidation by Fenton and photo-Fenton processes at an initial pH of 3.5 ± 0.1 . The initial conditions used in this part were 0.333 M of CH₂O, 0.0796 M of CH₃OH, 0.667 M of H₂O₂, and 6.67×10^{-2} M of Fe²⁺. As exhibited in Figures 4.14 (a), (b), (c) and (d), a little difference in formaldehyde oxidation, methanol oxidation, H₂O₂ decomposition, and pH variation, between Fenton and photo-Fenton processes was observed. For formaldehyde oxidation, the removal percentages at 5 min obtained by Fenton and photo-Fenton processes were 57% and 60%, and at the end of 80 min were 92% and 92%, respectively. In the case of methanol oxidation, by applying Fenton process, the decomposition percentages at 5 min and 80 min were 34% and 70%, respectively. When photo-Fenton method was performed, they were 38% and 74%, respectively.

The remaining ratios of H₂O₂ and pH variation versus time are demonstrated in Figures 4.14 (c) and (d). For H₂O₂ decomposition, a similar trend was found at

different initial pH values; almost the same amount of H_2O_2 was decomposed in both Fenton and photo-Fenton processes during the time of reaction period. As depicted in Figure 4.14 (d), in both Fenton and photo-Fenton processes, pH dropped rapidly to almost the same value at 5 min and then increased gradually after 10 min.

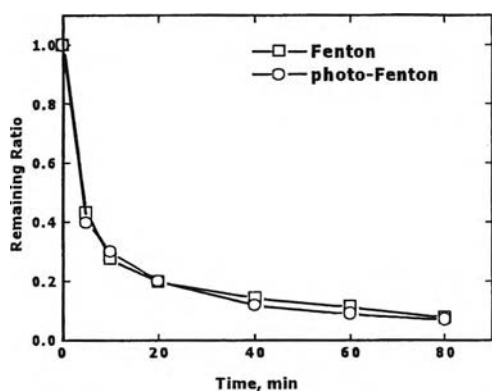


Figure 4.14 (a) Remaining ratio of formaldehyde with reaction time

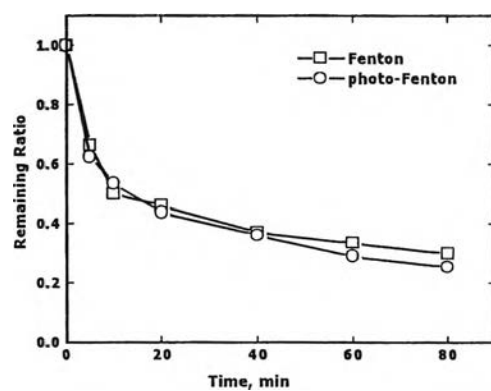


Figure 4.14 (b) Remaining ratio of methanol with reaction time.

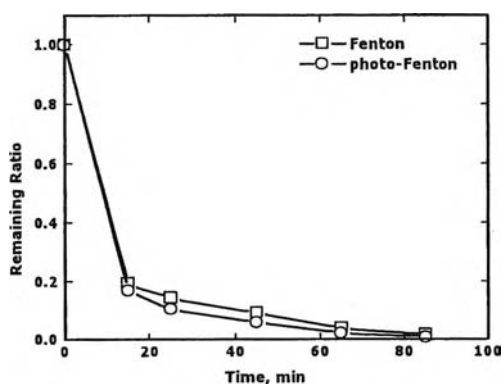


Figure 4.14 (c) Remaining ratio of H_2O_2 with reaction time

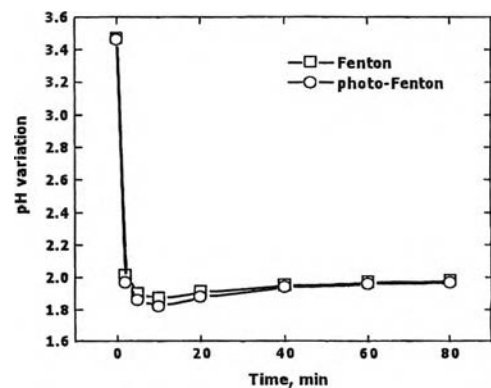


Figure 4.14 (d) pH variation with reaction time

4.8.5 Comparison of Fenton and Photo-Fenton Processes at Initial pH of 4

Figures 4.15 (a) to (d) demonstrate the results obtained from a comparison of formaldehyde and methanol treated by Fenton and photo-Fenton processes at an initial pH of 4.0 ± 0.1 . Initial 0.333 M of CH_2O , 0.0796 M of CH_3OH , 0.667 M of H_2O_2 , and 6.67×10^{-2} M of Fe^{2+} were chosen as the experimental conditions. Figures 4.15 (a) and (b) show a similar trend with at initial pH of 3.0 ± 0.1 . At 5 min, the removal percentages of formaldehyde treated by Fenton processes were greater than that of photo-Fenton process; they were 58% and 54%, respectively. This may be a result from the inhibition effect of Fe^{2+} due to excess amounts of Fe^{2+} in the system, as mentioned earlier. However, at 80 min, the removal efficiencies of formaldehyde treated by Fenton process were lower than that of photo-Fenton process; they were 89% and 92%, respectively.

The remaining ratio of methanol is depicted in Figure 4.15 (b). It is shown that methanol degradation demonstrated similar results to those obtained at initial pH of 3.0 ± 0.1 (Figure 4.14 (b)). At the early stage, Fenton employed a higher efficiency in methanol oxidation than photo-Fenton process. By applying Fenton and photo-Fenton processes, at 5 min, methanol can be oxidized by 43% and 31%, respectively. However, at the end of 80 min, those were 70% and 71%, respectively.

As shown in Figure 4.15 (c), rate of H_2O_2 decomposition by Fenton process was nearly the same as that by photo-Fenton process. This result is similar to the results obtained from other experiments; at initial pH value of 2.6, 3, and 3.5, the amount of H_2O_2 decomposed by Fenton reaction was slightly less than that of photo-Fenton process. Figure 4.15 (d) shows pH variation of this experiment, where pH was initially 4.0 ± 0.1 . Results indicate that pH decreased to lower value in photo-Fenton process. It is remarkable that this figure exemplifies a similar tendency as those obtained from experiments with the initial pH values of 2.6 ± 0.1 and 3.5 ± 0.1 (Figures 4.12 (d) and 4.14 (d)).

From this part of experiment, it can be concluded that initial pH plays an insignificant effect on formaldehyde and methanol oxidation by Fenton process. However, at initial pH 2.6, the oxidation rate seemed slightly faster than at other

initial pH values. Moreover, the differences between Fenton and photo-Fenton processes were not obvious at all the initial pH values.

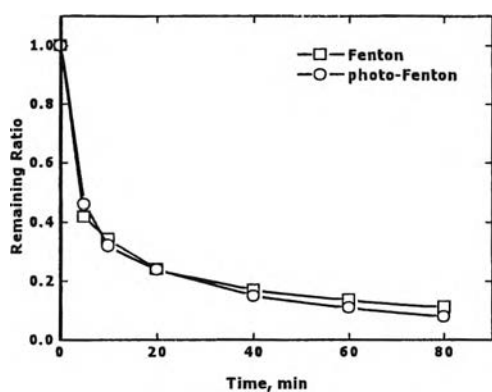


Figure 4.15 (a) Remaining ratio of formaldehyde with reaction time

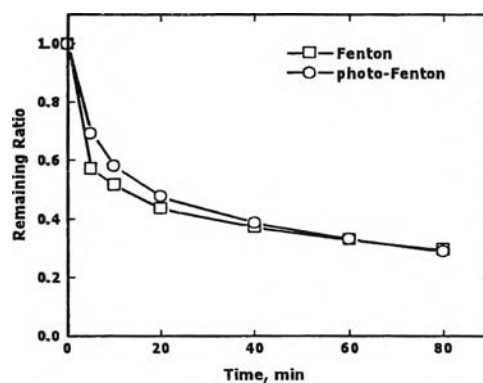


Figure 4.15 (b) Remaining ratio of methanol with reaction time

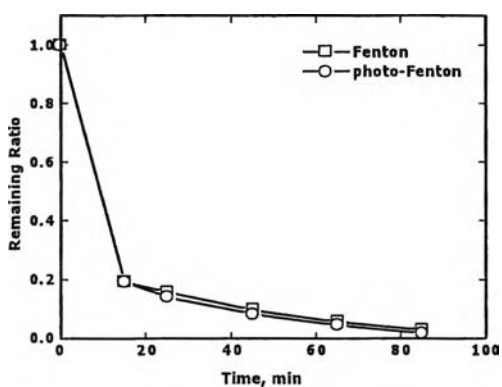


Figure 4.15 (c) Remaining ratio of H_2O_2 with reaction time

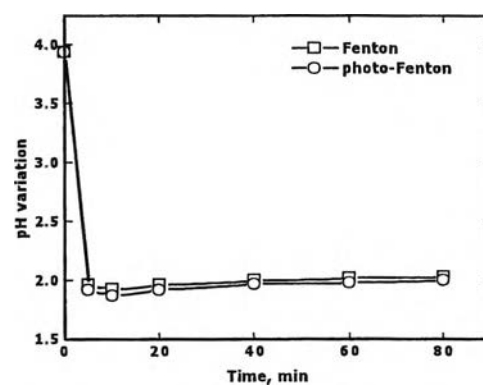


Figure 4.15 (d) pH variations with reaction time

4.9 UV Light Promoting the Oxidation Efficiency of Formaldehyde and Methanol

By applying UV light, Fe^{2+} can be regenerated via photo-Fenton reaction; Fe^{3+} reacts with H_2O_2 in the presence of UV light resulting in the regeneration of Fe^{2+} . Reduction of Fe^{3+} to Fe^{2+} is helpful to generate radicals in several elementary steps of the reaction mechanism (Utset et al., 2000). Additionally, a hydrogen peroxide can produce two hydroxyl radicals initiated by UV light. Both routes facilitate the formation of hydroxyl radicals and promote the degradation rates of organic compounds. However, the excess amount of OH^\bullet generated from the photolysis of H_2O_2 can inhibit the OH^\bullet generated from Fenton reaction due to the higher Fe^{2+} concentrations according to the principle of Le Chatelier. In order to evaluate the effect of UV light on the degradation of formaldehyde and methanol, Fenton and photo-Fenton processes were compared at different concentrations of Fe^{2+} (6.67×10^{-3} M, 2.27×10^{-2} M, and 6.67×10^{-2} M). Initial concentrations of 0.333 M of CH_2O , 0.0796 M of CH_3OH , 0.667 M of H_2O_2 and an initial pH of 2.6 ± 0.1 were chosen as the initial conditions. For all the experiments of photo-Fenton, 10 W of UV light with a wavelength of 254 nm was applied.

As seen in Figure 4.16 (a), the removal efficiency of formaldehyde treated by photo-Fenton process was higher than that by Fenton process. By applying Fenton process, the removal percentages of formaldehyde at 5 min were 26%, 31%, and 66% with initial concentration of Fe^{2+} at 6.67×10^{-3} M, 2.27×10^{-2} M, and 6.67×10^{-2} M, respectively, and they were 22%, 55%, and 65%, respectively, when photo-Fenton process was performed. At the end of 80 min, the removal percentages of formaldehyde by Fenton and photo-Fenton processes were 46%, 62%, and 93% and they were 62%, 79%, and 94% when the initial concentrations of Fe^{2+} were 6.67×10^{-3} M, 2.27×10^{-2} M, and 6.67×10^{-2} M, respectively (Table 4.12). Results indicated that the Fe^{2+} efficiency of photo-Fenton process with 10 W of UV light was larger than that of Fenton process at the same concentration of Fe^{2+} . Similar results have been reported by Li et al. (1997); photo-Fenton oxidation under the UV light condition would accelerate mineralization faster than that under the dark condition. Li et al. (1997) also reported that photo-Fenton process exhibited a good decomposition ability on the

explosive decomposition such as TNT, DNT and MNT because Fe^{2+} can be regenerated through the photoreduction of Fe^{3+} to produce highly reactive hydroxyl radicals. However, it also indicated that the OH^\bullet inhibition effect occurred at high Fe^{2+} concentrations in photo-Fenton process. Hence, UV light has a low promotion efficiency when there is a high concentration of Fe^{2+} in the system due to the fast reaction between Fe^{2+} and H_2O_2 .

Figure 4.16 (b) presents the degradation of methanol by Fenton and photo-Fenton processes at different concentration of Fe^{2+} . The result depicted in Figure 4.16 (b) shows that photo-Fenton process could accelerate the oxidation reaction of methanol significantly, especially when low concentrations of Fe^{2+} were present. When 6.67×10^{-3} M of Fe^{2+} was conducted, the removal percentages of methanol at 80 min by Fenton and photo-Fenton processes were 35% and 44%, respectively. Additionally, at 2.27×10^{-2} M of Fe^{2+} , 44% and 63% of methanol were removed at the end of 80 min by Fenton and photo-Fenton processes, and 72% and 79%, respectively, when 6.67×10^{-2} of Fe^{2+} was performed (Table 4.13).

Figure 4.16 (c) and (d) demonstrate the remaining ratio of H_2O_2 versus time and pH variation versus time, respectively. As seen in Figure 4.16 (b), H_2O_2 was decomposed by Fenton process less than that by photo-Fenton process, at the same Fe^{2+} concentration, since in photo-Fenton process, H_2O_2 can decomposed in several ways as mentioned earlier. For the pH variation, the same tendency was observed with 6.67×10^{-3} M and 2.27×10^{-2} M of Fe^{2+} in Fenton and photo-Fenton processes, where pH sharply reduced at the beginning stage then gradually decreased after 5 min. However, with 6.67×10^{-2} M of Fe^{2+} , pH decreased rapidly at the beginning stage, then increased gradually in both Fenton and photo-Fenton processes.

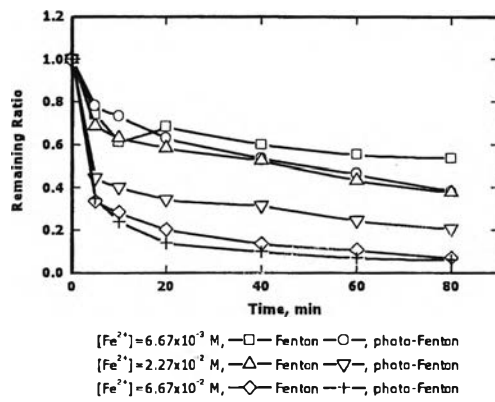


Figure 4.16 (a) UV light promoting the efficiency of formaldehyde degradation

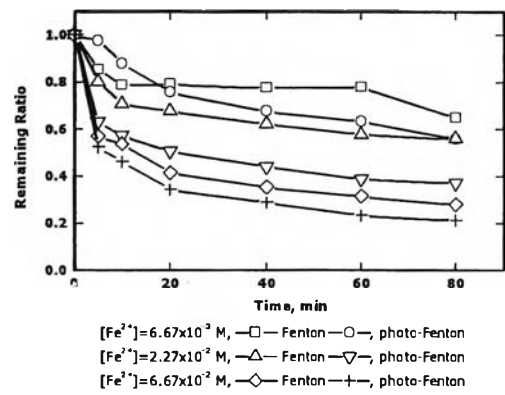


Figure 4.16 (b) UV light promoting the efficiency of methanol degradation

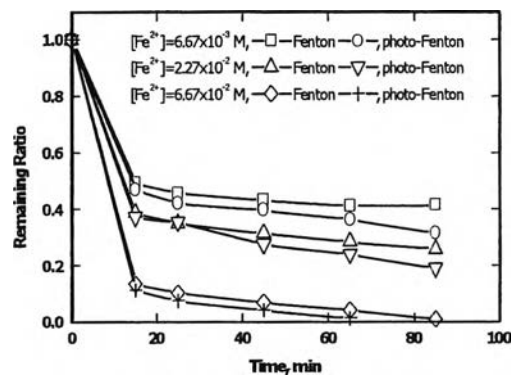


Figure 4.16 (c) Remaining ratio of H_2O_2 with reaction time

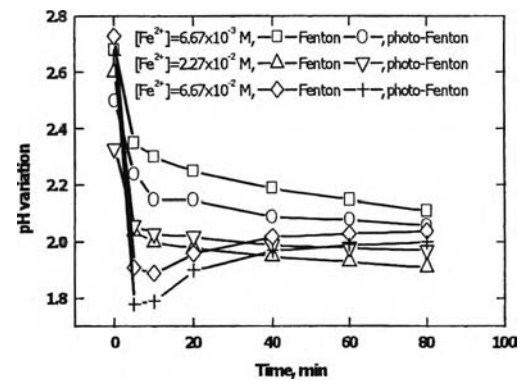


Figure 4.16 (d) pH variation with reaction time

Table 4.12 Degradation of formaldehyde by Fenton and photo-Fenton processes at different Fe^{2+} concentration

| $[\text{Fe}^{2+}]$ | $6.67 \times 10^{-3} \text{ M}$ | | $2.27 \times 10^{-2} \text{ M}$ | | $6.67 \times 10^{-2} \text{ M}$ | |
|---|---------------------------------|-----------------------|---------------------------------|-----------------------|---------------------------------|-----------------------|
| | Fenton | photo-Fenton | Fenton | photo-Fenton | Fenton | photo-Fenton |
| % removal at 5 min | 26 | 22 | 31 | 55 | 66 | 65 |
| % removal at 80 min | 46 | 62 | 62 | 79 | 90 | 94 |
| initial rate ($\text{M} \cdot \text{min}^{-1}$) | 1.74×10^{-2} | 1.46×10^{-2} | 2.06×10^{-2} | 3.69×10^{-2} | 4.4×10^{-2} | 4.33×10^{-2} |
| k (min^{-1}) | 4.04×10^{-3} | 8.25×10^{-3} | 7.49×10^{-3} | 9.01×10^{-3} | 1.14×10^{-2} | 1.45×10^{-2} |
| r^2 | 0.9297 | 0.9980 | 0.9883 | 0.9710 | 0.8919 | 0.9750 |

Table 4.13 Degradation of methanol by Fenton and photo-Fenton processes at different Fe^{2+} concentration

| $[\text{Fe}^{2+}]$ | $6.67 \times 10^{-3} \text{ M}$ | | $2.27 \times 10^{-2} \text{ M}$ | | $6.67 \times 10^{-2} \text{ M}$ | |
|---|---------------------------------|-----------------------|---------------------------------|-----------------------|---------------------------------|-----------------------|
| | Fenton | Photo-Fenton | Fenton | photo-Fenton | Fenton | Photo-Fenton |
| % removal at 5 min | 14 | 2 | 20 | 37 | 43 | 47 |
| % removal at 80 min | 35 | 44 | 44 | 63 | 72 | 79 |
| initial rate ($\text{M} \cdot \text{min}^{-1}$) | 2.31×10^{-3} | 3.98×10^{-4} | 3.15×10^{-3} | 5.89×10^{-3} | 6.85×10^{-3} | 7.55×10^{-3} |
| k (min^{-1}) | 2.91×10^{-3} | 4.85×10^{-3} | 3.2×10^{-3} | 5.24×10^{-3} | 6.48×10^{-3} | 8.25×10^{-3} |
| r^2 | 0.6610 | 0.9935 | 0.9649 | 0.9608 | 0.9945 | 0.9776 |

Tables 4.14 and 4.15 demonstrate how much UV light promoting the efficiency of formaldehyde and methanol oxidation. The ratios of UV light promoting the efficiency on the initial rates of formaldehyde were 0.84, 1.79, and 0.98 while the initial concentrations of Fe^{2+} increased from $6.67 \times 10^{-3} \text{ M}$ to $2.27 \times 10^{-2} \text{ M}$ and $6.67 \times 10^{-2} \text{ M}$, respectively. Similarly, when the Fe^{2+} concentration increased from $6.67 \times 10^{-3} \text{ M}$ to $2.27 \times 10^{-2} \text{ M}$ and 6.67×10^{-2} , the fraction of UV light promoting the

efficiency on initial rates of methanol changed from 0.17 to 1.87 and 1.10, respectively. It can be concluded that the highest benefit of UV light achieved at 2.27×10^{-2} M of Fe^{2+} ; with the higher concentration of Fe^{2+} , the benefit of UV light decreased. At 6.67×10^{-2} M of Fe^{2+} , the removal efficiencies of Fenton and photo-Fenton process were almost the same.

Table 4.14 UV light promoting the efficiency of formaldehyde oxidation

| [Fe^{2+}] | initial rate | | UV-promoting efficiency on initial rate | k | | UV-promoting efficiency on k |
|-----------------------|-----------------------|-----------------------|---|-----------------------|-----------------------|------------------------------|
| | Fenton | photo-Fenton | | Fenton | photo-Fenton | |
| 6.67×10^{-3} | 1.74×10^{-2} | 1.46×10^{-2} | 0.84 | 4.04×10^{-3} | 8.25×10^{-3} | 2.04 |
| 2.27×10^{-2} | 2.06×10^{-2} | 3.69×10^{-2} | 1.79 | 7.49×10^{-3} | 9.01×10^{-3} | 1.20 |
| 6.67×10^{-2} | 4.4×10^{-2} | 4.33×10^{-2} | 0.98 | 1.14×10^{-2} | 1.49×10^{-2} | 1.31 |

Table 4.15 UV light promoting the efficiency on methanol oxidation

| [Fe^{2+}] | initial rate | | UV-promoting efficiency on initial rate | k | | UV-promoting efficiency on k |
|-----------------------|-----------------------|-----------------------|---|-----------------------|-----------------------|------------------------------|
| | Fenton | photo-Fenton | | Fenton | photo-Fenton | |
| 6.67×10^{-3} | 2.31×10^{-3} | 3.98×10^{-4} | 0.17 | 2.91×10^{-3} | 4.85×10^{-3} | 1.67 |
| 2.27×10^{-2} | 3.15×10^{-3} | 5.89×10^{-3} | 1.87 | 3.2×10^{-3} | 5.24×10^{-3} | 1.64 |
| 6.67×10^{-2} | 6.85×10^{-3} | 7.55×10^{-3} | 1.10 | 6.48×10^{-3} | 8.25×10^{-3} | 1.27 |

4.10 Combination of Fenton and Photo-Fenton Processes

Due to the fast reaction of H_2O_2 with Fe^{2+} in the beginning stage of the oxidation reaction, applying UV light in the early stage may be not necessary. Therefore, Fenton and photo-Fenton processes were combined in this part of experiment in order to compare the efficiencies of photo-Fenton and combined Fenton/photo-Fenton processes. The initial conditions were set as follows: initial $[\text{CH}_2\text{O}] = 0.333 \text{ M}$, $[\text{CH}_3\text{OH}] = 0.0796 \text{ M}$, $[\text{H}_2\text{O}_2] = 0.667 \text{ M}$, $[\text{Fe}^{2+}] = 6.67 \times 10^{-2} \text{ M}$ for 4.10.1 and $[\text{Fe}^{2+}] = 6.67 \times 10^{-3} \text{ M}$ for 4.10.2, and an initial $\text{pH} = 2.6 \pm 0.1$. The reaction was started with Fenton reaction for 15 min before the UV lamp was turned on.

4.10.1 Comparison of the Combined Fenton/photo-Fenton and Photo-Fenton Processes with $6.67 \times 10^{-2} \text{ M}$ of Fe^{2+}

All the parameters obtained from this set are demonstrated in Figures 4.17 (a) to (d). As shown in Figure 4.17 (a), formaldehyde degradation by the combined Fenton/photo-Fenton process was lower than that by photo-Fenton process. The degradation of methanol is depicted in Figure 4.17 (b); the same tendency as that in formaldehyde degradation was observed. From Figures 4.17 (a) and (b), it is recommended that photo-Fenton method provided a higher efficiency of methanol oxidation than that the combined Fenton/photo-Fenton process.

Figures 4.17 (c) and (d) show the profile of remaining H_2O_2 and pH variations versus time. The combined Fenton/photo-Fenton method, in which H_2O_2 was lower than that in photo-Fenton process, was carried out and the results can be noticed in Figure 4.17 (c) resulting in the lower efficiency was observed in the combined Fenton/photo-Fenton process than in conventional photo-Fenton process. Figure 4.17 (d) presents a profile of the pH variation versus time. It was found that in the combined Fenton/photo-Fenton process, pH reduced to lower level than in photo-Fenton process.

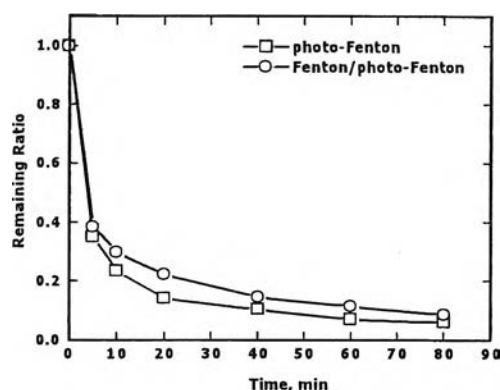


Figure 4.17 (a) Remaining ratio of formaldehyde with reaction time

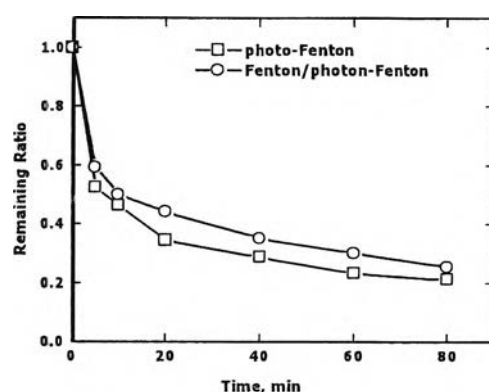


Figure 4.17 (b) Remaining ratio of methanol with reaction time

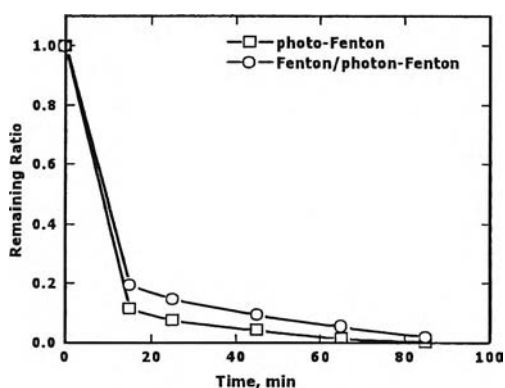


Figure 4.17 (c) Remaining ratio of H_2O_2 with reaction time

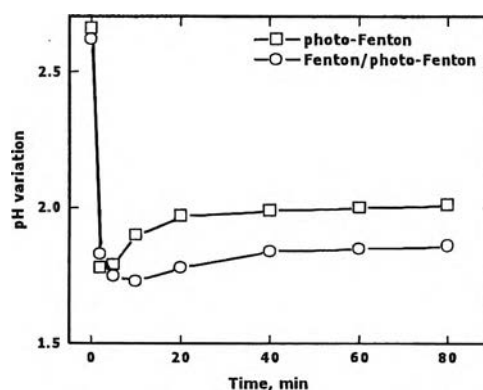


Figure 4.17 (d) pH variation with reaction time

4.10.2 Comparison of the Combined Fenton/photo-Fenton and Photo-Fenton Processes with 6.67×10^{-3} M of Fe^{2+}

Figures 4.18 (a) to (d) show a comparison of photo-Fenton and the combined Fenton/photo-Fenton processes with 6.67×10^{-3} M of Fe^{2+} . Other initial conditions used in this experiment were 0.333 M of CH_2O , 0.0796 M of CH_3OH , 0.667 M of H_2O_2 and an initial pH of 2.6 ± 0.1 . Figure 4.18 (a) indicates that the combined

Fenton/photo-Fenton process was less efficient in the formaldehyde degradation than photo-Fenton process. The removal ratios at 5 min and 80 min of formaldehyde treated by the combined Fenton/photo-Fenton process were 19% and 54%, respectively. When applying photo-Fenton process, they were 22% and 62% at 5 min and 80 min, respectively. For methanol oxidation, the removal efficiencies were almost the same in both the combined Fenton/photo-Fenton and conventional photo-Fenton processes as depicted in Figure 4.18 (b).

As illustrated in Figure 4.18 (c), in both the combined Fenton/photo-Fenton and conventional photo-Fenton processes, the H_2O_2 decomposition was almost the same. At the end of 85 min, approximately 30% of H_2O_2 still remained in both systems. In the combined Fenton/photo-Fenton process, pH reduced to a lower value than that of conventional photo-Fenton process as presented in Figure 4.18 (d). This result is similar to the result depicted in Figure 4.17 (d).

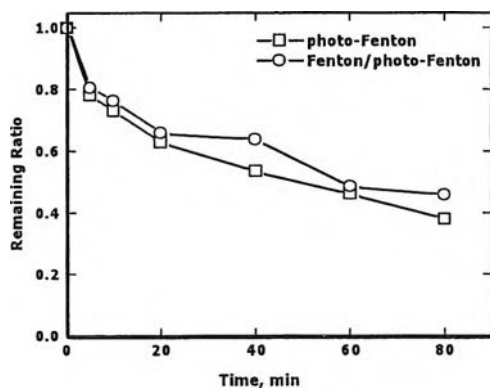


Figure 4.18 (a) Remaining ratio of formaldehyde with reaction time

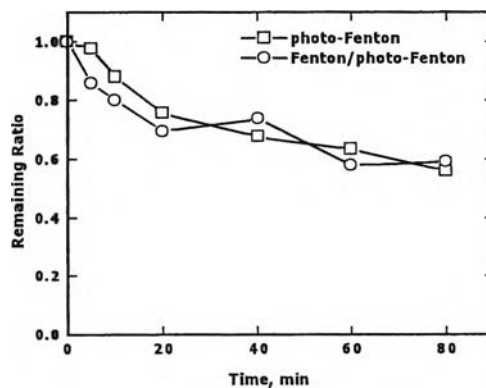


Figure 4.18 (b) Remaining ratio of methanol with reaction time

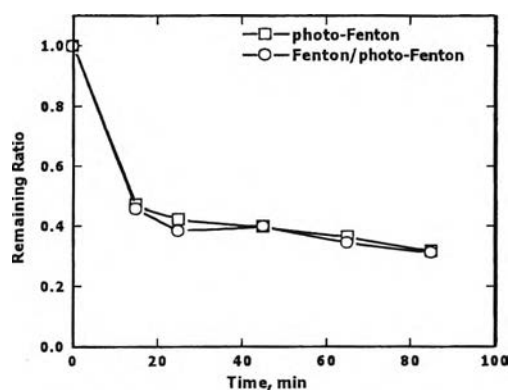


Figure 4.18 (c) Remaining ratio of H₂O₂ with reaction time

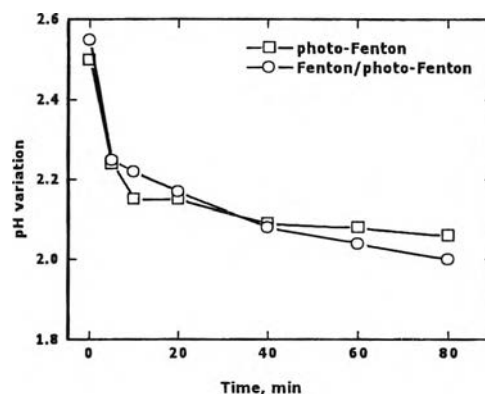


Figure 4.18 (d) pH variation with reaction time

4.11 Effect of Hydrogen Peroxide Addition Mode

H₂O₂ can decompose to oxygen or compete with target organic compounds to consume hydroxyl radical, resulting in the retardation of the oxidation reaction, if an excess amount of H₂O₂ was added initially. In order to investigate the best method for the addition of H₂O₂, the experiments utilized different methods for the addition of H₂O₂ were conducted. There were two sets of two experiments each in this part. Each set of experiments evaluates the removal efficiency of a one-step and two-step addition of H₂O₂. In the first set of experiments, 6.67×10^{-2} M of Fe²⁺ was added and in the second set of experiments, 6.67×10^{-3} M of Fe²⁺ was added. Initial conditions were as follows: initial [CH₂O]=0.333 M, [CH₃OH]=0.0796 M, pH=2.6±0.1, and [Fe²⁺]= 6.67×10^{-2} M and 6.67×10^{-3} M of Fe²⁺ for 4.11.1 and 4.11.2, respectively. For 1 step the addition of H₂O₂, 0.667 M of H₂O₂ was added initially. For 2-step addition of H₂O₂, 0.333 M of H₂O₂ was added at the initial and at 15 min of the oxidation reaction.

4.11.1 One-step and Two-step Addition of H_2O_2 with 6.67×10^{-2} M of Fe^{2+}

Results obtained from this set of the experiment are presented in Figures 4.19 (a) to (d). At 5 min, the removal ratio of formaldehyde that provided by 1-step of the addition of H_2O_2 was significantly higher than that of 2-step addition of H_2O_2 . However, at the end of 80 min, the removal ratios of formaldehyde by 1- and 2-step addition of H_2O_2 were almost the same (Figure 4.19 (a)). For methanol oxidation, by 1-step addition, the removal efficiency was higher than it was when H_2O_2 was added by 2 steps. At 5 min, the removal ratios of 1- and 2-steps addition of H_2O_2 were 47% and 32%, and at the end of 80 min they were 79% and 71%, respectively. These results indicated that the highest efficiency of methanol oxidation was obtained with 1-step addition of H_2O_2 (Figure 4.19 (b)).

Profiles of H_2O_2 residual versus time and pH variations versus time were presented in Figures 4.19 (c) and (d). As presented in Figure 4.19 (c), with 2-step addition of H_2O_2 , H_2O_2 was almost completely decomposed at 15 min. However, when 0.333 M of H_2O_2 was added at 15 min into the reaction mixture, H_2O_2 residual at 80 min was about 1800 mg/l; while, H_2O_2 was almost completely decomposed at 65 min with a 1-step addition of H_2O_2 . Results indicated that by adding H_2O_2 with 2 steps, H_2O_2 decomposed slower than that by adding H_2O_2 with 1 step. Figure 4.19 (d) illustrates the profile of pH variations versus time. It is obvious that after the oxidation reaction was initiated, pH sharply reduced and then kept almost constant after 5 min in a 2-step addition of H_2O_2 . When in a 1-step addition of H_2O_2 , pH reduced rapidly at the beginning stage, and then gradually increased after 5 min.

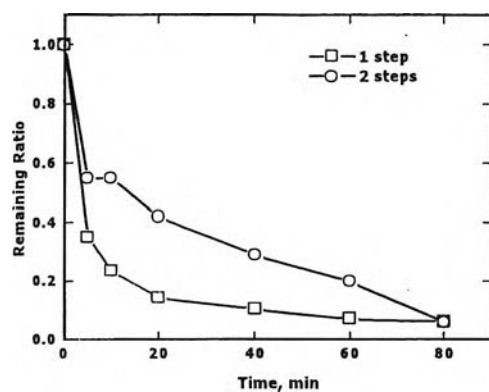


Figure 4.19 (a) Remaining ratio of formaldehyde with reaction time

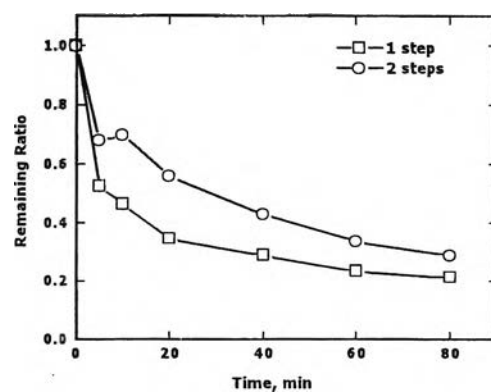


Figure 4.19 (b) Remaining ratio of methanol with reaction time

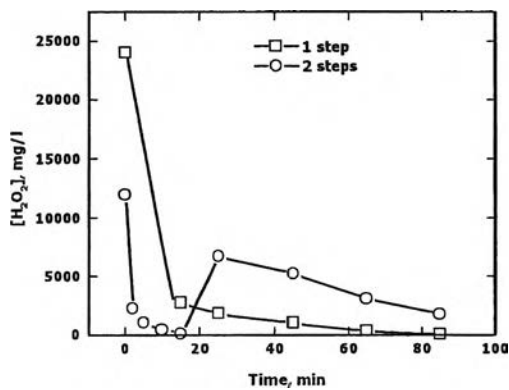


Figure 4.19 (c) Remaining ratio of H₂O₂ with reaction time

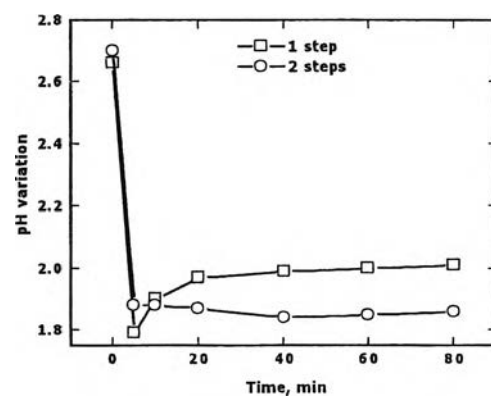


Figure 4.19 (d) pH variation with reaction time

4.11.2 One-step and Two-step Addition of H_2O_2 with $6.67 \times 10^{-3} \text{ M}$ of Fe^{2+}

As seen in Figure 4.20 (a), the removal efficiency of formaldehyde obtained by a 1-step addition of H_2O_2 was slightly higher than that by 2 steps. At the end of 80 min, the removal percentages of formaldehyde were 62% and 59% with 1- and 2-step addition of H_2O_2 , respectively. In contrast, the removal efficiency of methanol obtained by a 1-step addition of H_2O_2 was significantly lower than that by 2 steps, as shown in Figure 4.20 (b). The removal percentages of methanol at 80 min were 44% and 58% with the addition of H_2O_2 by 1 and 2 steps, respectively. This result is different from the result depicted in Figure 4.19 (c), which indicates that the highest oxidation efficiency of methanol was obtained with a 1-step addition of H_2O_2 .

Figures 4.20 (c) and (d) present the H_2O_2 residual versus time and pH variations versus time that obtained from this set of experiment. With adding H_2O_2 by 1- and 2-step, at the end of 85 min, the remaining H_2O_2 was almost the same, which is demonstrated in Figure 4.20 (c). For pH variation, in both cases, pH reduced rapidly in the beginning stage of the oxidation reaction and then pH decreased gradually after 5 min, as depicted in Figure 4.20 (d).

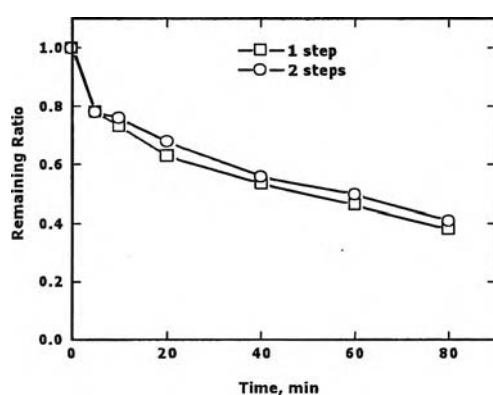


Figure 4.20 (a) Remaining ratio of formaldehyde with reaction time

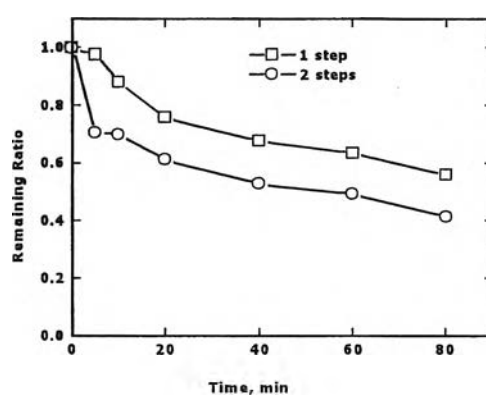


Figure 4.20 (b) Remaining ratio of methanol with reaction time

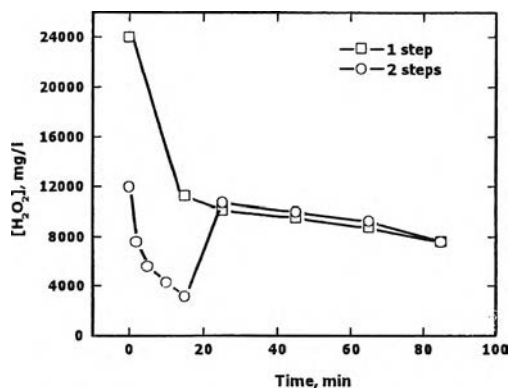


Figure 4.20 (c) Remaining ratio of H₂O₂ with reaction time

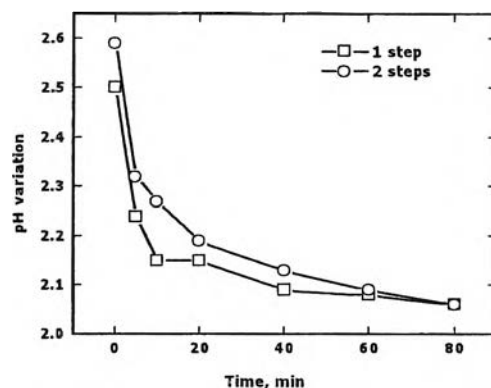


Figure 4.20 (d) pH variation with reaction time

4.12 Mineralization of Formaldehyde and Methanol

Although formaldehyde and methanol were almost completely degraded at the end of 80 min of the oxidation reaction, formaldehyde and methanol may be oxidized to other intermediates which have more toxic than the parental products. Therefore, the mineralization of formaldehyde and methanol may be not achieved. In this part, the degradation of formaldehyde and methanol by UV/H₂O₂, Fenton and photo-Fenton processes with a reaction time 4 hours, were performed in order to compare the mineralization behavior of formaldehyde and methanol by these three processes. The experiments were divided into 2 sets; they are the mineralization of formaldehyde and methanol with 6.67×10^{-2} M of Fe²⁺ (see 4.12.1) and the mineralization of formaldehyde and methanol with 6.67×10^{-3} M of Fe²⁺ (see 4.12.2). Initial concentrations of 0.333 M of CH₂O, and 0.0796 M of CH₃OH, and an initial pH of 2.6 ± 0.1 were selected as the experimental conditions. For all experiments in this part, 0.333 M of H₂O₂ was added during time interval.

4.12.1 Mineralization of Formaldehyde and Methanol with 6.67×10^{-2} M of Fe^{2+}

Figures 4.21 (a) and (b) show that complete formaldehyde and methanol degradation by Fenton and photo-Fenton processes were achieved at 140 min and 180 min, respectively. However, the degradation of formaldehyde by photo-Fenton process at 80 min seemed faster than that by Fenton process as shown in Figure 4.21 (a). Similarly, methanol degradation by photo-Fenton process was a little higher than that by Fenton process at 120 min; the methanol was almost completely decomposed in both Fenton and photo-Fenton processes at 180 min. However, in UV/ H_2O_2 process, 23% of formaldehyde and 35% of methanol still remained in the solution after 240 min.

Figure 4.21 (c) presents the profiles of H_2O_2 residual as a function of time. The H_2O_2 concentration gradually reduced in UV/ H_2O_2 process; however, it decomposed more swiftly in Fenton and photo-Fenton processes. Besides, in Fenton and photo-Fenton processes, after all formaldehyde was decomposed (140 min), H_2O_2 decomposed faster than that in the presence formaldehyde. For the pH variation, in the beginning stage, pH sharply reduced in Fenton and photo-Fenton processes and then it increased after 20 min and 40 min, respectively. Whereas in UV/ H_2O_2 process pH reduced continuously during 4 hours of the oxidation reaction (Figure 4.21 (d)).

For TOC removal in Fenton and photo-Fenton processes, complete TOC removal was achieved at 180 min and 240 min, respectively. Unlike in UV/ H_2O_2 process, only 4% of TOC removal was observed after 240 min, as shown in Figure 4.21 (e). It indicates that the mineralization of formaldehyde and methanol cannot be achieved by UV/ H_2O_2 process. It also shows that the mineralization of formaldehyde was achieved by Fenton and photo-Fenton process and the mineralization rate by photo-Fenton was higher than that by Fenton process.

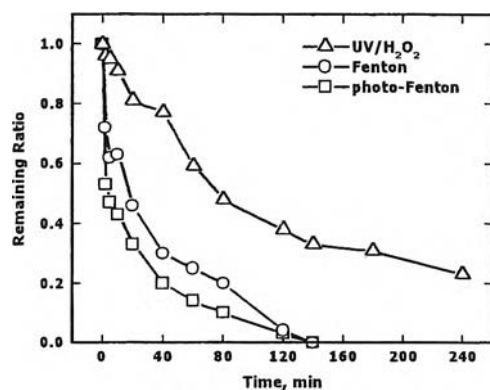


Figure 4.21 (a) Remaining ratio of formaldehyde with reaction time

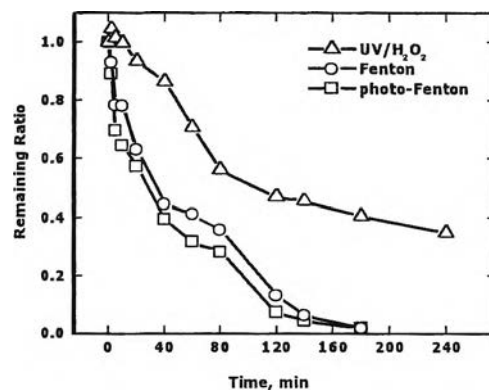


Figure 4.21 (b) Remaining ratio of methanol with reaction time

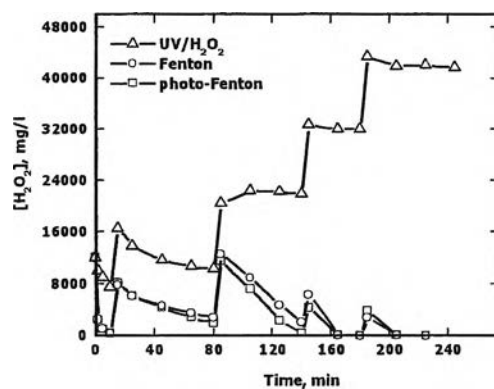


Figure 4.21 (c) Remaining ratio of H₂O₂ with reaction time

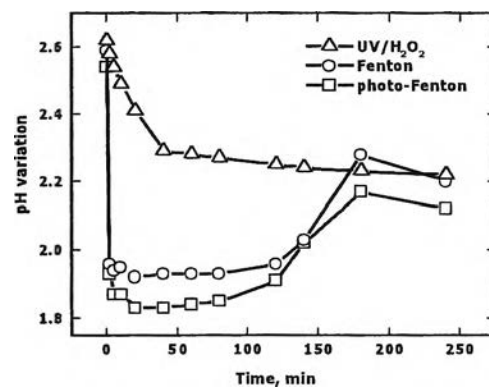


Figure 4.21 (d) pH variation with reaction time

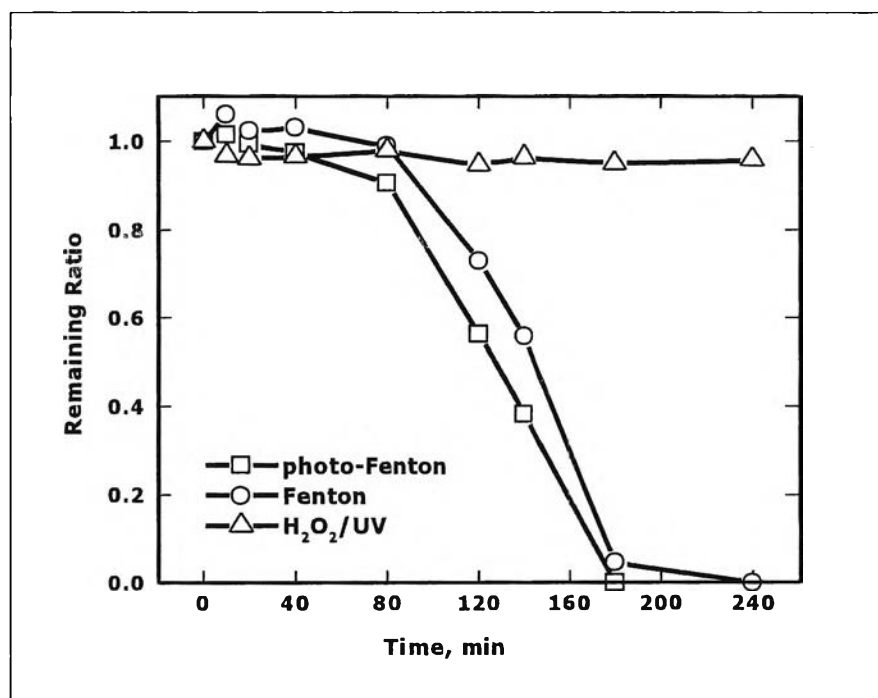


Figure 4.21 (e) Remaining ratio of TOC with reaction time

4.12.2 Mineralization of Formaldehyde and Methanol with 6.67×10^{-3} of Fe^{2+}

As illustrated in Figure 4.22 (a), in the presence of 6.67×10^{-3} M of Fe^{2+} , formaldehyde was almost completely decomposed by photo-Fenton process; at 240 min, only 5% of formaldehyde still remained in the system. Both in UV/ H_2O_2 and Fenton processes, formaldehyde residual after 240 min was 23%. Figure 4.22 (b) indicates that the remaining ratios of methanol at 240 min treated by UV/ H_2O_2 , Fenton and photo-Fenton processes were 25%, 35% and 7%, respectively. Results also indicated that by applying photo-Fenton process the removal efficiencies of formaldehyde and methanol were higher than that by UV/ H_2O_2 and Fenton processes.

Figure 4.22 (c) shows a profile of H_2O_2 residual with time. In photo-Fenton process, H_2O_2 was decomposed faster than in Fenton and UV/ H_2O_2 processes due to several ways of H_2O_2 decomposition. A profile of the pH variation with time in

UV/H₂O₂, Fenton and photo-Fenton processes shows that the pH values gradually reduced with time of the reaction, as presented in Figure 4.22 (d).

The remaining ratios of TOC with time are depicted in Figure 4.22 (e). At 240 min, TOC removal in UV/H₂O₂, Fenton and photo-Fenton processes were 0%, 4%, and 32%, respectively. From Figure 4.22 (e), it is noticeable that the tendency for TOC removal in photo-Fenton process was better than that in UV/H₂O₂ and Fenton processes. With the longer reaction time, TOC removal may achieve 100% with photo-Fenton process. While applying UV/H₂O₂ and Fenton processes, the complete mineralization of formaldehyde and methanol could not be achieved.

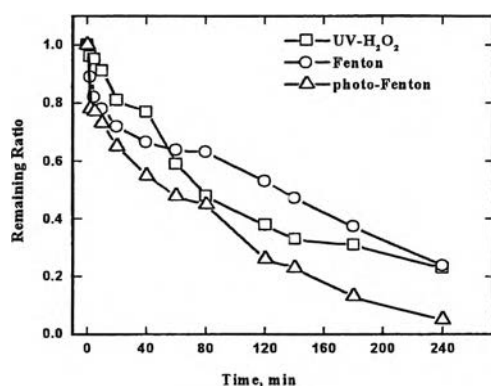


Figure 4.22 (a) Remaining ratio of formaldehyde with reaction time

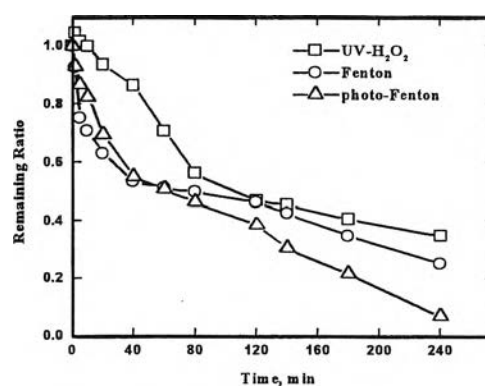


Figure 4.22 (b) Remaining ratio of methanol with reaction time

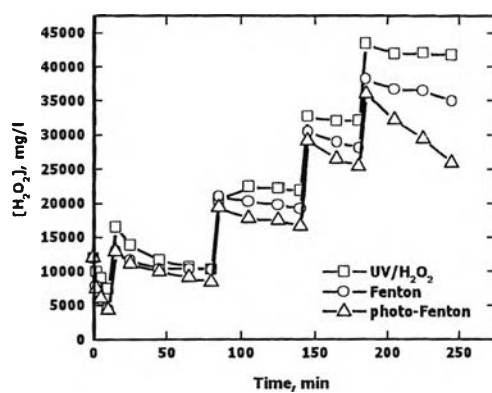


Figure 4.22 (c) Remaining ratio of H_2O_2 with reaction time

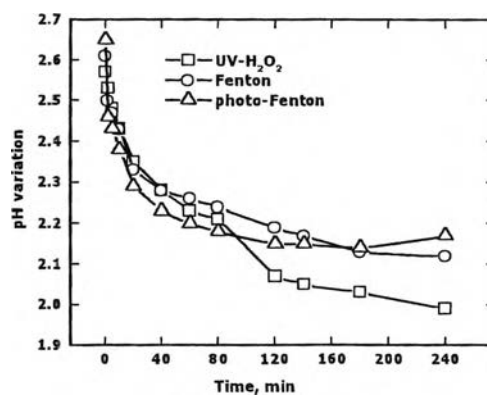


Figure 4.22 (d) pH variation with reaction time

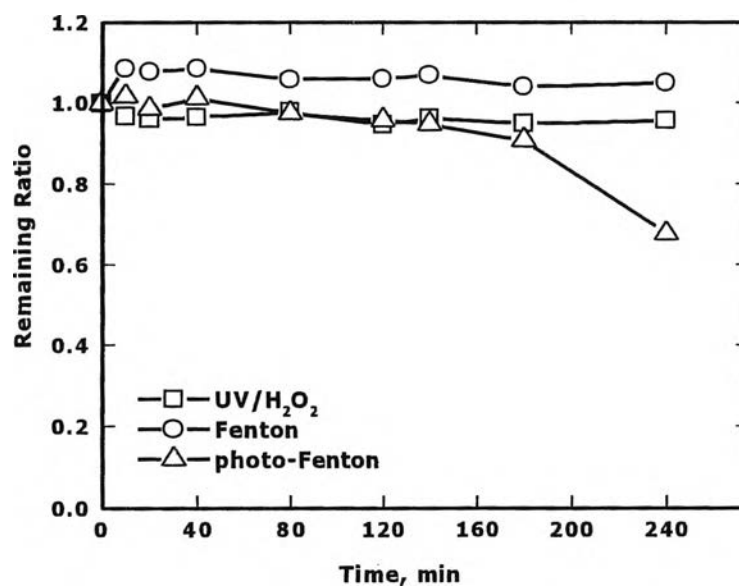


Figure 4.22 (e) Remaining ratio of TOC with reaction time

4.13 Toxicity Evaluation

In this part, three experiments using UV/H₂O₂, Fenton and photo-Fenton processes with initial conditions of 0.333 M of CH₂O, 0.0796 M of CH₃OH, and 6.67x10⁻² M of Fe²⁺ were chosen for the toxicity analysis. For all of the experiments, 0.333 M of H₂O₂ was added at 10 min, 40 min, 80 min, 140 min, and 180 min of the reaction time period. The effluent supernatants from those three processes were diluted 16 times before analysis. The method used for the toxicity test is known as the CellTiter 96[®] AQueous Non-Radioactive Cell Proliferation Assay. As depicted in Figure 4.24, by applying Fenton and photo-Fenton processes, the solutions toxicity were completely removed within 20 min of the oxidation reaction. Whereas, in UV/H₂O₂ process, the toxicity reduction was not observed within 240 min of the reaction; even though formaldehyde and methanol were almost completely degraded at the end of 240 min. Hence, the toxicity could not be removed by this process. This may be the result of CH₂O oxidized to other toxic intermediates by UV/H₂O₂ process. While Fenton and photo-Fenton processes can reduce all toxicity of the solution. It is recommended that the toxicity can be completely removed by applying Fenton and photo-Fenton processes.

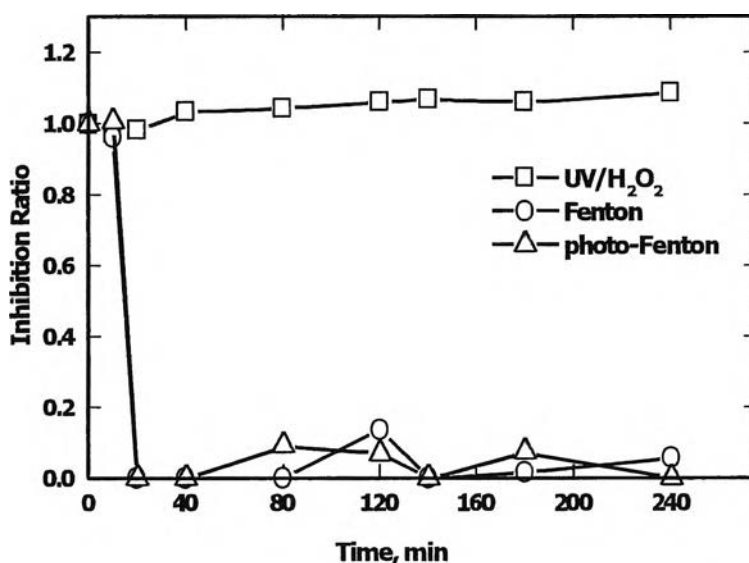


Figure 4.23 Toxicity variation during the oxidation reaction