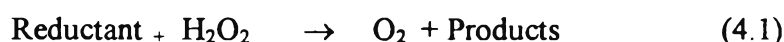


CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of hydrogen peroxide dosage on low concentrations of aniline and nitrobenzene

Hydrogen peroxide is an important parameter in Fenton process. It is the precursor in generating the hydroxyl radical ($\cdot\text{OH}$) in combination with Fe^{2+} (equation 2.4). Moreover, hydrogen peroxide can also react with Fe^{3+} to regenerate Fe^{2+} . Nevertheless, in the presence of excess amount of H_2O_2 , oxidation reaction can be limited by generation of O_2 instead of hydroxyl radicals and inhibition due to H_2O_2 consuming hydroxyl radicals as shown on the equation 4.1 and 4.2.



This part of the experiment was performed in order to study the effects of H_2O_2 concentration on the Fenton reaction for the treatment of aniline and nitrobenzene. In this part of experiment, 1 mM of aniline and nitrobenzene, 0.5 mM of Fe^{2+} , and an initial $\text{pH} = 3.0 \pm 0.1$ were fixed as the initial conditions, while H_2O_2 concentrations were varied as free H_2O_2 , 5 mM, 7.5 mM, 15 mM, 20 mM and 25 mM.

Figure 4.1 (a) shows the C/C_0 of aniline versus time. The results can be noted that in the absence of H_2O_2 , aniline degradation could not observe. After 80 minutes, the removal ratios of aniline were 66%, 77%, 91%, 100% and 100% with 5 mM, 7.5 mM, 15 mM, 20 mM and 25 mM of H_2O_2 respectively. Figure 4.1 (b) shows the C/C_0 of nitrobenzene versus time. Nitrobenzene was not decomposed significantly during the experiments in the absence of H_2O_2 . In addition, nitrobenzene was completely degraded with 15 mM, 20 mM and 25 mM of H_2O_2 at 20 minutes.

Both aniline and nitrobenzene were not completely degraded with the concentration of H_2O_2 as 5 mM and 7.5 mM. It can be described that the H_2O_2 dosage was not enough for generating hydroxyl radicals to degrade aniline and nitrobenzene as seen in Figure 4.1 (d). This Figure shows that at the concentration of H_2O_2 as 5 mM and 7.5 mM, the H_2O_2 totally degraded within 20 minutes. Thus the Fenton reaction was stopped. The pH values of solution decreased very fast in the first 5 minutes and after that it slightly decreased as shown on Figure 4.1 (c). Furthermore, while the higher concentrations of H_2O_2 were added, pH reduced to the lower value than when the lower concentrations were added. The pH values decreased in the range of 3.0 to 2.33. From the results, it can be indicated that the removal efficiencies of aniline and nitrobenzene were rapid at the first 5 minutes and then almost kept constant at after 20 minutes. Moreover, aniline and nitrobenzene degradation increased with increasing of H_2O_2 concentration. The results were the same with the previous studies. Brillas et al. (1998) reported that the presence of H_2O_2 in photocatalysis increased the rate of aniline destruction at the initial stages. Casero et al. (1997) found that the increasing of H_2O_2 concentration enhanced the efficiency of Fenton reaction. The decomposition rate of organic contaminants increased with the increasing of H_2O_2 (Lu, 1999).

The kinetic oxidation of aniline and nitrobenzene was also considered in order to understand the degradation behavior of both substances. In this studies aniline and nitrobenzene degraded swiftly at the initial state. The degradation of both substances drastically occurred during the first 10 minutes. Beyond this period, the reaction were slow down since it is expected that many inhibition reactions occurred. Therefore, the oxidation rates of aniline and nitrobenzene were discussed only the initial state at 10 minutes. As two factors (hydrogen peroxide and ferrous ion) played role here, the reaction tended to be the second order reaction rate. With the excess of one parameter (either hydrogen peroxide or ferrous ion), the pseudo-first order rate could be obtained. Kinetic equation for this research was shown below.

$$r = k[\cdot\text{OH}][\text{C}] \quad (4.3)$$

With the excess amount of $\cdot\text{OH}$ at initial state, the oxidation reactions of aniline and nitrobenzene were found to follow pseudo-first order reaction rate. The initial rate was calculated by follow question below.

$$r = k'C \quad (4.4)$$

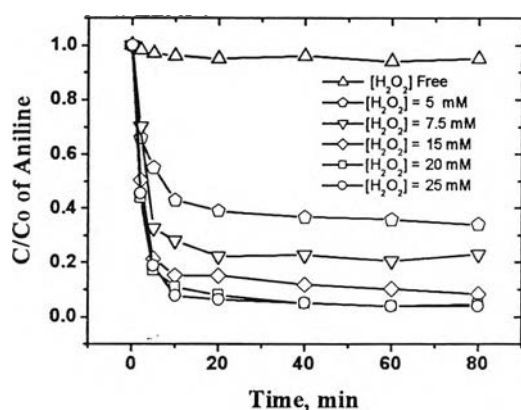
where; r = initial rate (M/min)

k' = rate constant (min^{-1})

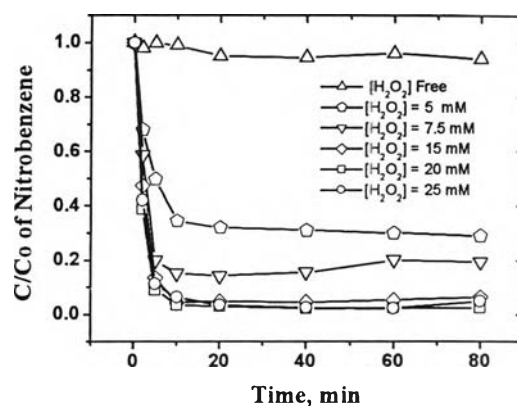
C = concentration of aniline or nitrobenzene (M)

The initial rate and k values are shown in Figure 4.1(e) and (f). The initial rates of aniline oxidation were $0.132 \text{ mM}\cdot\text{min}^{-1}$, $0.218 \text{ mM}\cdot\text{min}^{-1}$, $0.313 \text{ mM}\cdot\text{min}^{-1}$, $0.362 \text{ mM}\cdot\text{min}^{-1}$, and $0.343 \text{ mM}\cdot\text{min}^{-1}$. The k values for aniline degradation were 0.1317 , 0.2178 , 0.3131 , 0.3621 and 0.3426 min^{-1} with different concentrations of H_2O_2 ranging at 5 mM , 7.5 mM , 15 mM , 20 mM and 25 mM respectively. For nitrobenzene, the initial rates were $0.147 \text{ mM}\cdot\text{min}^{-1}$, $0.316 \text{ mM}\cdot\text{min}^{-1}$, $0.399 \text{ mM}\cdot\text{min}^{-1}$, $0.481 \text{ mM}\cdot\text{min}^{-1}$, and $0.441 \text{ mM}\cdot\text{min}^{-1}$ and k values were 0.1471 , 0.3161 , 0.3996 , 0.4805 and 0.4404 min^{-1} respectively for the initial concentration of H_2O_2 as 5 mM , 7.5 mM , 15 mM , 20 mM and 25 mM .

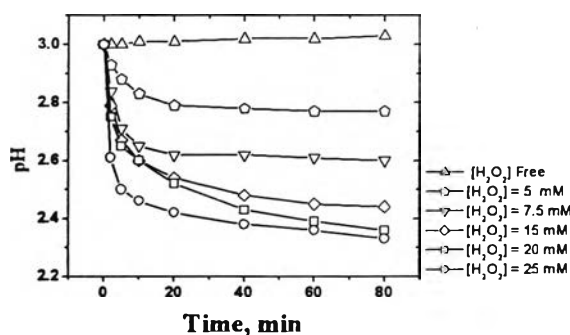
According to the results, it can be said that the initial rates and k values of aniline and nitrobenzene oxidation increased with increasing of H_2O_2 concentration. However at the H_2O_2 dose as 25 mM , the initial rate and k value decreased. This can be explained that in the high amount of H_2O_2 concentration, H_2O_2 could inhibit the reaction by consuming hydroxyl radical by itself as shown in equation 4.2. In comparing with aniline and nitrobenzene, Figure 4.1 (e) and (f) show that initial rate and rate constant of nitrobenzene were higher than aniline in every concentrations of H_2O_2 . The explanation of the different behaviors may arise from the different in functional groups of aniline and nitrobenzene. The electrophilic addition of hydroxyl radical with the double bond in nitrobenzene is more preferable than the hydrogen abstraction of the single bond of aniline (Lipczynska-Kochany, 1991). In this experiment set, we obtained the optimum H_2O_2 concentration as 20 mM .



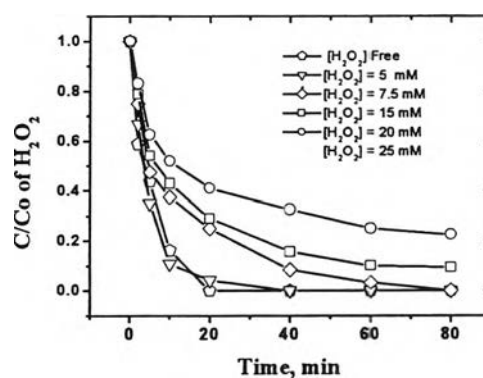
(a) Residual fraction of Aniline



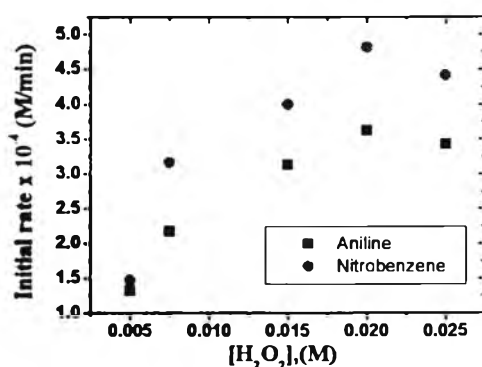
(b) Residual fraction of Nitrobenzene



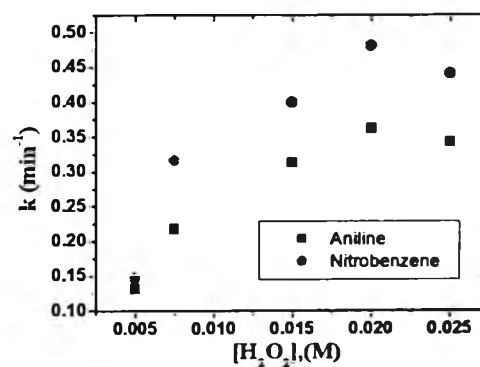
(c) pH values of the system



(d) Residual fraction of hydrogen peroxide



(e) Initial rates of aniline and nitrobenzene



(f) Rate constants of aniline and nitrobenzene

Figure 4.1 Effect of hydrogen peroxide dosage on low concentrations of aniline and nitrobenzene ($[\text{aniline and nitrobenzene}] = 1 \text{ mM}$, $\text{Fe}^{2+} = 0.5 \text{ mM}$, $\text{pH} = 3$)

4.2 Effect of ferrous ion dosage on low concentrations of aniline and nitrobenzene

Ferrous ion is main specie in Fenton process. It can catalyze hydrogen peroxide to produce hydroxyl radical with powerful oxidizing abilities to degrade certain toxic contaminants (Spacek et. al, 1995; Lipczynska-Kochany et. al, 1995; Watts et. al, 1996). However, ferrous ion also can be hydroxyl radicals scavenger (Pignatello, 1992) as shown in the equations 4.4.



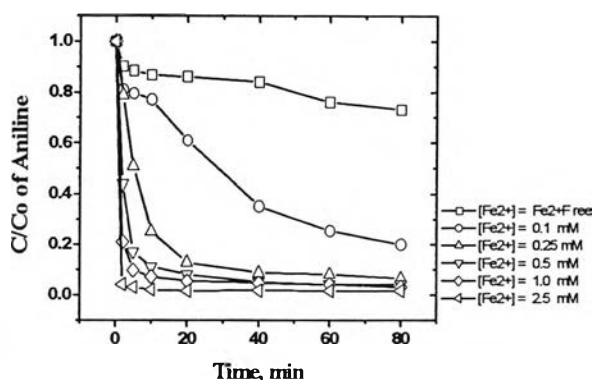
In the excess amount of ferrous ion, it can react with hydroxyl radical. Thus, the hydroxyl radical in the system will be decreased and the organic degradation will be reduced also. To evaluate the effect of ferrous ion, the experiments were conducted on various amounts of Fe^{2+} as free Fe^{2+} , 0.1 mM, 0.25 mM, 0.5 mM, 1 mM and 2.5 mM. Initial concentrations of the same amount of 1 mM of aniline and nitrobenzene, 20 mM of H_2O_2 and an initial pH of 3.0 ± 0.1 were used as the initial conditions.

The C/Co of aniline and nitrobenzene versus time shows in Figure 4.2 (a) and (b). From the results, it can be seen that the removal of aniline and nitrobenzene were very fast in the first 5 minutes and then the reaction was relatively slow until the end of reaction time. Moreover, Aniline and nitrobenzene degradation increased with increasing of Fe^{2+} concentration. This result is agree with the result reported by Lu et al. (1999). They found that the decomposition rate of organic contaminants increased with the increasing of Fe^{2+} . Casero et al. (1997) investigated that the degradation and mineralization of aromatic amine essentially depended on Fe^{2+} concentration. However, from this experiment at the 0.5 mM, 1 mM and 2.5 mM of Fe^{2+} , the Fenton efficiencies were almost the same within 80 minutes. Thus, the optimum Fe^{2+} concentration obtained from this experiment was 0.5 mM.

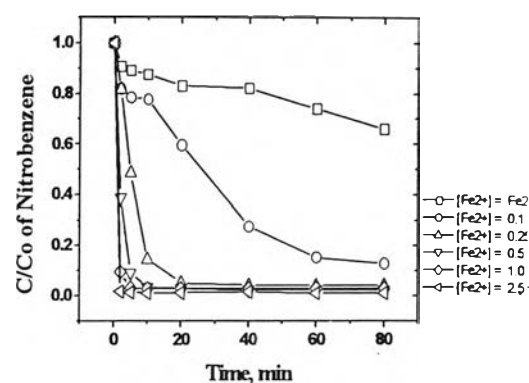
The pH versus time is shown in Figure 4.2 (c). It shows that the pH value decreased in the range of 3.0 to 2.30 during the reaction time. The C/Co of H₂O₂ versus time shows in Figure 4.2 (d). The results shows that at the low concentration of Fe²⁺ (0.1 and 0.25 mM), the H₂O₂ still remained in the solution. This data can be announced that the concentration of Fe²⁺ less than 0.25 mM was not enough for reacting with H₂O₂ to generate $\cdot\text{OH}$.

In the point of kinetic, the initial rate and k values are demonstrated in Figure 4.2 (e) and (f). The initial rates of aniline oxidation were 0.054 mM•min⁻¹, 0.133 mM•min⁻¹, 0.362 mM•min⁻¹ and 0.509 mM•min⁻¹. The k values for aniline degradation were 0.0541, 0.1332, 0.3621 and 0.5093 min⁻¹ with different concentrations of Fe²⁺ ranging at 0.1 mM, 0.25 mM, 0.5 mM and 1 mM respectively. For nitrobenzene, the initial rates were 0.055 mM•min⁻¹, 0.138 mM•min⁻¹, 0.481 mM•min⁻¹ and 0.774 mM•min⁻¹ and k values were 0.0554, 0.1384, 0.4805 and 0.7735 min⁻¹, respectively for the initial concentration of Fe²⁺ as 0.1 mM, 0.25 mM, 0.5 mM and 1 mM.

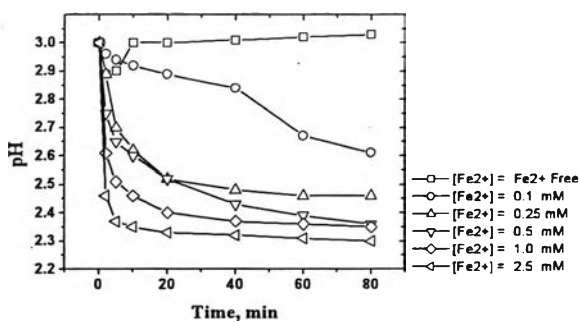
The results exhibit the initial rates and k values of aniline and nitrobenzene oxidation increased with increasing of Fe²⁺ concentration. It can be explained that the high amount of Fe²⁺ concentration can generate high amount of hydroxyl radical as showed on the equation 2.4. Moreover, Figure 4.2 (e) showed that initial rate of nitrobenzene higher than aniline. For the k value, the trends of k value also increased with increasing of Fe²⁺ concentration as shown in Figure 4.2 (f). In this study, the oxidation of aniline and nitrobenzene did not inhibit by increasing of Fe²⁺ concentration. The reason for this could be said that the amount of Fe²⁺ added in this experiment had not yet reached the degree of inhibition.



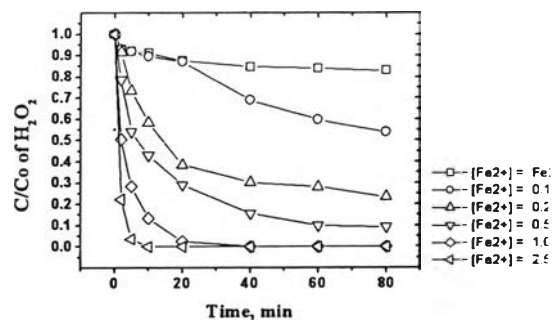
a) Residual fraction of Aniline



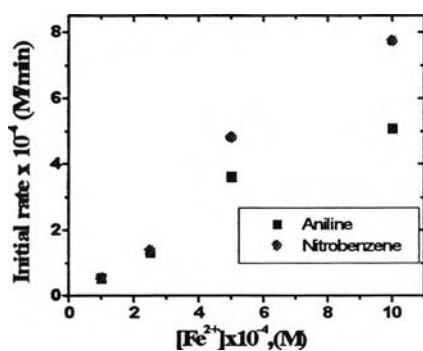
(b) Residual fraction of Nitrobenzene



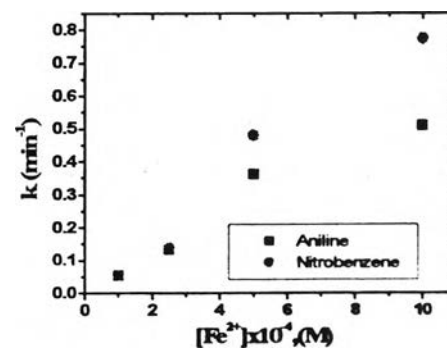
(c) pH values of the system



(d) Residual fraction of hydrogen peroxide



(e) Initial rates of aniline and nitrobenzene



(f) Rate constants of aniline and nitrobenzene

Figure 4.2 Effect of ferrous ion dosage on low concentrations of aniline and nitrobenzene ($[\text{aniline and nitrobenzene}] = 1 \text{ mM}$, $\text{H}_2\text{O}_2 = 20 \text{ mM}$, $\text{pH} = 3$)

4.3 Effect of pH on the degradations of aniline and nitrobenzene

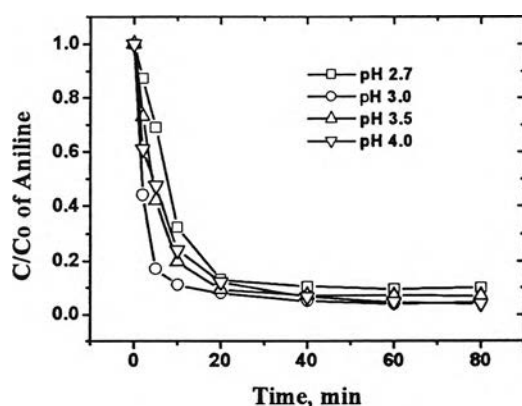
Fenton process is strongly affected by pH value. According to many previous studies, they said that Fenton process is effective only at acidic condition. At the pH value above 4, the degradation of organic compound may decrease due to the precipitation of Fe^{2+} (Faust and Hoigne, 1990). For this reason, the studied pH values in this experiment were in acidic condition. In order to investigate the effect of pH on the decomposition of aniline and nitrobenzene, the experiments were conducted on various pH values of 2.7, 3, 3.5 and 4. The equal initial concentrations of 1 mM of aniline and nitrobenzene, 20 mM of H_2O_2 and 0.5 mM of Fe^{2+} were used as the initial conditions.

The C/C_0 of aniline versus time was shown in Figure 4.3 (a). It could be observed that the differences of aniline decomposition at 80 min among the different pH values were not obvious. At the pH values of 2.7, 3.0, 3.5, and 4.0, percent removals of aniline at all initial pH values were 91%, 95%, 93% and 94% respectively. Figure 4.3 (b) showed the C/C_0 of nitrobenzene versus time. At the end of reaction time, the decompositions of nitrobenzene were 95%, 100%, 100% and 100% with initial pH as 2.7, 3.0, 3.5 and 4.0. The results in Figure 4.3 (a) and (b) exhibited that the initial pH does not have a significant influence on the decomposition of aniline and nitrobenzene. However, it is seen that initial pH plays a more apparent effect on the initial stage than the removal ratio of aniline at 80 min. The pH versus time was shown in Figure 4.3 (c). It indicates that although the initial pH values were different, the solution pH reduced to almost the same value. Figure 4.3 (d) showed the residual profiles of H_2O_2 versus time. It could be seen that the H_2O_2 was degraded very well at pH 3.0. However, all of the desired pH values were exerted positive effect on H_2O_2 at reaction time as 80 minutes.

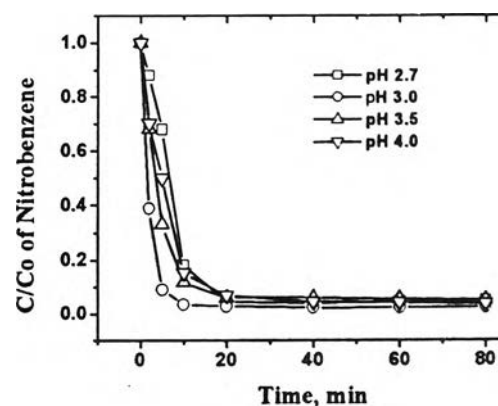
The initial rate and k value were shown in Figure 4.3 (e) and (f). The initial rates of aniline oxidation were $0.073 \text{ mM}\cdot\text{min}^{-1}$, $0.362 \text{ mM}\cdot\text{min}^{-1}$, $0.171 \text{ mM}\cdot\text{min}^{-1}$ and $0.162 \text{ mM}\cdot\text{min}^{-1}$. The k values for aniline degradation were 0.0734, 0.3621, 0.1705 and 0.1624 min^{-1} with the pH values 2.7, 3.0, 3.5 and 4.0 respectively. For nitrobenzene, the initial rates were $0.076 \text{ mM}\cdot\text{min}^{-1}$, $0.481 \text{ mM}\cdot\text{min}^{-1}$, 0.217

$\text{mM}\cdot\text{min}^{-1}$ and $0.145 \text{ mM}\cdot\text{min}^{-1}$ and k values were 0.0758, 0.4805, 0.2172 and 0.1445 min^{-1} respectively for the initial pH as 2.7, 3.0, 3.5 and 4.0.

According to the results, it could be said in acidic condition, initial pH exerted small effect on oxidation of both substances. However, the pH value as 3.0 gave the highest efficiency on degradation of aniline and nitrobenzene. This result is similar to the result reported by Brillas et al. (1998). In comparing with aniline and nitrobenzene, Figure 4.3 (e) showed that initial rate of nitrobenzene higher than aniline. The highest aniline removal efficiency was obtained at an initial pH 3.0. From the results in part 4.1, 4.2 and 4.3, we can conclude that the optimum initial conditions for treating 1 mM of aniline and nitrobenzene was at 20 mM of H_2O_2 , 0.5 mM of Fe^{2+} and at pH 3.0 or at the molar ratio of 1 : 10 : 0.25 (aniline and nitrobenzene : H_2O_2 : Fe^{2+}).

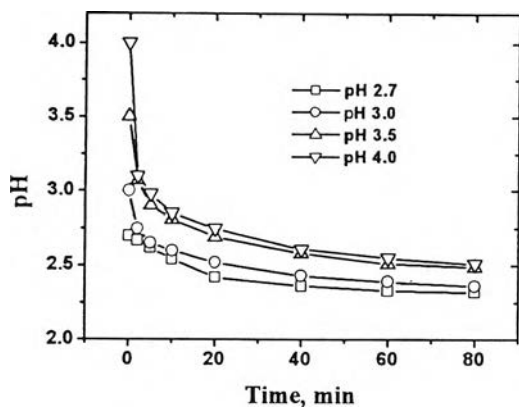


a) Residual fraction of Aniline

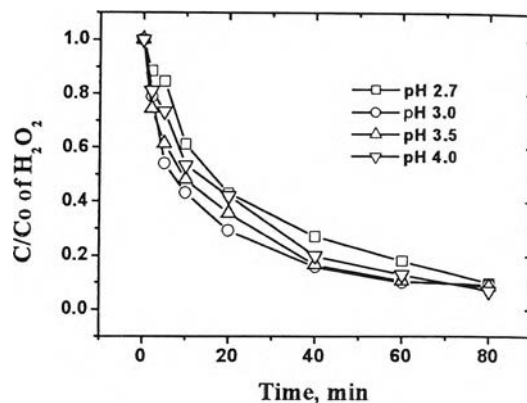


(b) Residual fraction of Nitrobenzene

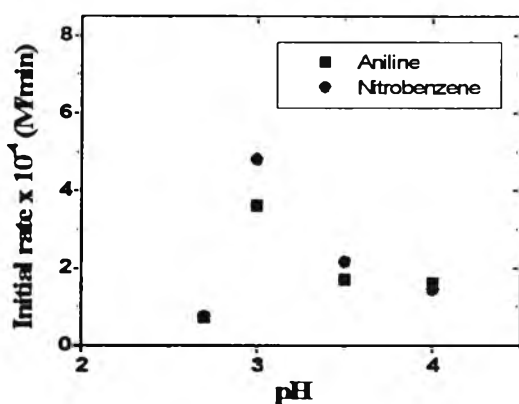
Figure 4.3 Effect of pH on the degradations of aniline and nitrobenzene ([aniline and nitrobenzene] = 1 mM, H_2O_2 = 20 mM, Fe^{2+} = 0.5 mM)



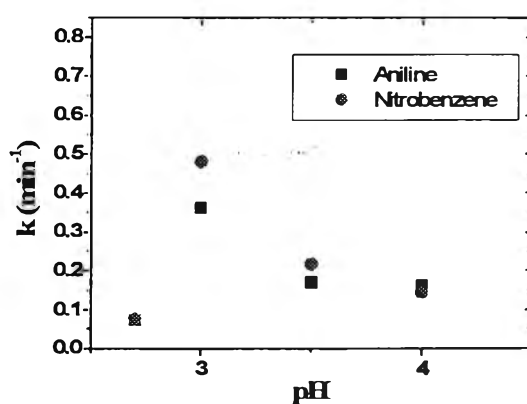
(c) pH values of the system



(d) Residual fraction of hydrogen peroxide



(e) Initial rates of aniline and nitrobenzene



(f) Rate constants of aniline and nitrobenzene

Figure 4.3 Effect of pH on the degradations of aniline and nitrobenzene ([aniline and nitrobenzene] = 1 mM, H_2O_2 = 20 mM, Fe^{2+} = 0.5 mM)

4.4 Effect of high concentrations of aniline and nitrobenzene on Fenton reaction

The concentration of substance is one of parameter which affects the Fenton efficiency. To study the effect of aniline and nitrobenzene concentration, this experiment part conducted with 10 mM of aniline and nitrobenzene. The optimum

condition obtained from 4.1, 4.2 and 4.3 was used as initial condition (20 mM of H_2O_2 , 0.5 mM of Fe^{2+} and pH 3.0). The results were showed in Figure 4.5 (a) to (d).

The results show that this condition did not effective for destruction 10 mM of aniline and nitrobenzene (Figure 4.5 (a) and (b)). However, it is important to point that H_2O_2 still remained in the solution at 80 minutes with 10 mM of aniline and nitrobenzene as shown in Figure 4.5 (d). This Figure shows that the H_2O_2 remaining were 9% and 72% with 1mM and 10 mM aniline and nitrobenzene respectively. This means that H_2O_2 did not degraded effectively within 10 mM of substances. In other word, it implies that the Fenton reaction was stopped with 10 mM of aniline and nitrobenzene. This may be due to the formation of ferrous ion complex with free ion in the solution.

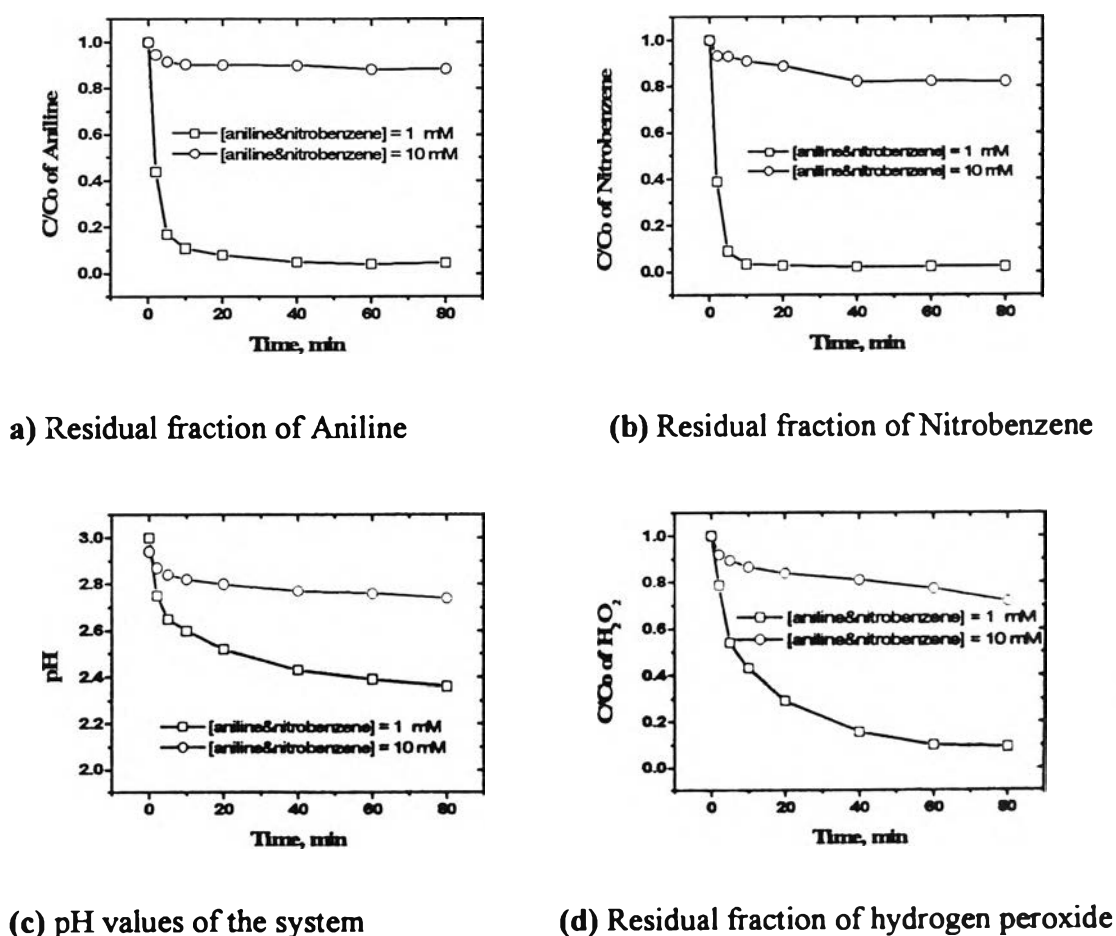


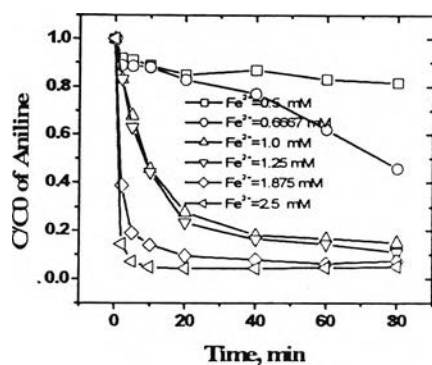
Figure 4.4 Effect of high concentrations of aniline and nitrobenzene on Fenton reaction ($\text{H}_2\text{O}_2 = 20$ mM, $\text{Fe}^{2+} = 0.5$ mM, pH = 3)



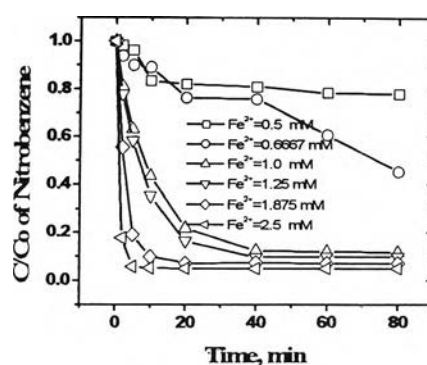
4.5 Effect of ferrous ion on high concentrations of aniline and nitrobenzene

This experiment was conducted on various amounts of Fe^{2+} as 0.5 mM, 0.6667 mM, 1 mM, 1.25 mM, 1.875 mM and 2.5 mM. Initial concentrations of equal 10 mM of aniline and nitrobenzene, 75 mM of H_2O_2 and an initial pH of 3.0 ± 0.1 were used as the initial conditions. Figure 4.5 (a) and (b) show the C/C_0 of aniline and nitrobenzene respectively. The result shows that the degradation of aniline and nitrobenzene increased with the increasing of Fe^{2+} concentration. The trend of this result is similar to the result in part 4.2. Moreover, the high efficiency for treating aniline and nitrobenzene were at 1.875 mM and 2.5 mM of Fe^{2+} while 0.5 mM and 0.6667 mM of Fe^{2+} gave poor efficiency. Therefore, we obtained the optimum Fe^{2+} dosage for treating high concentration of aniline and nitrobenzene at 1.875 mM. The pH values were reduced in the range of 3.0 to 1.7 as shown in Figure 4.5 (c). The residual H_2O_2 profile, in Figure 4.5 (d), shows that H_2O_2 rapidly degraded within the initial state at 10 minutes.

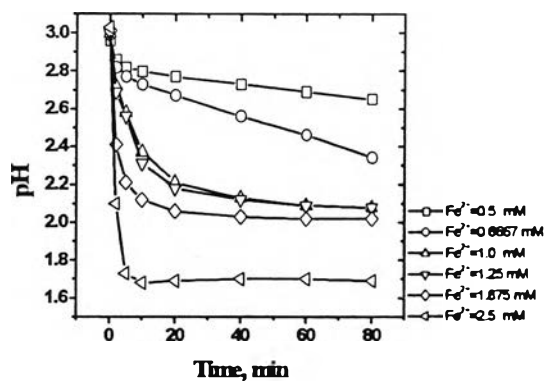
In kinetics point of view, the similar trend with part 4.2 was also observed as shown in Figure 4.5 (e) and (f). It shows that the high concentration of Fe^{2+} enhanced the rate constant and initial rate value. However, it is interesting that the rate constant and initial rate of aniline and nitrobenzene were almost the same. In this study, the oxidation of aniline and nitrobenzene did not inhibit by increasing of Fe^{2+} concentration. The reason for this could be explained that the amount of Fe^{2+} added in this experiment had not yet reached the degree of inhibition.



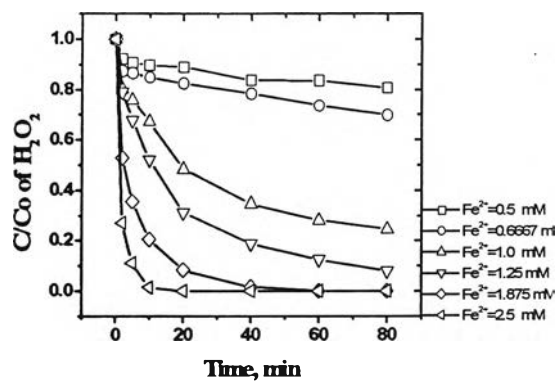
a) Residual fraction of Aniline



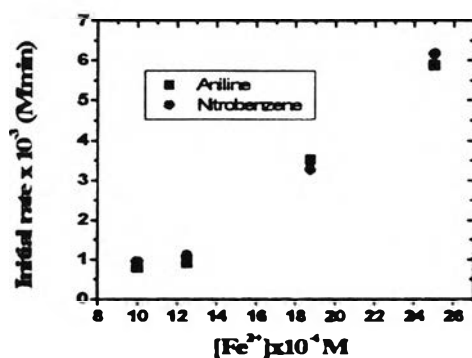
(b) Residual fraction of Nitrobenzene



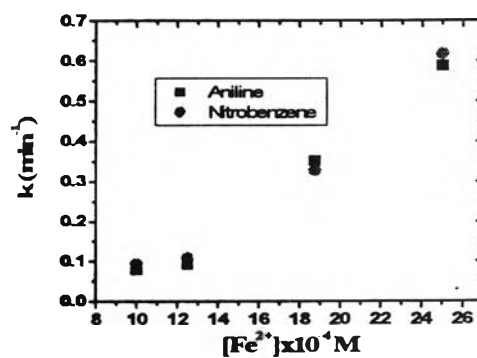
(c) pH values of the system



(d) Residual fraction of hydrogen peroxide



(e) Initial rates of aniline and nitrobenzene



(f) Rate constants of aniline and nitrobenzene

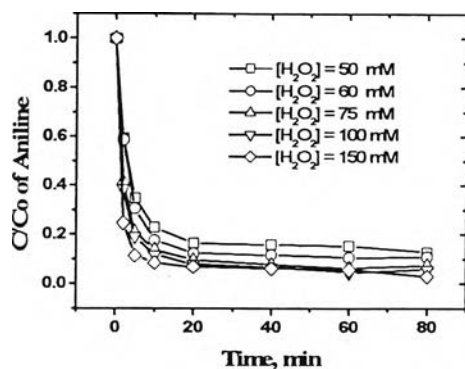
Figure 4.5 Effect of ferrous ion dosage on high concentrations of aniline and nitrobenzene ([aniline and nitrobenzene] = 10 mM, H_2O_2 = 75 mM, pH=3)

4.6 Effect of H₂O₂ concentration on high concentrations of aniline and nitrobenzene

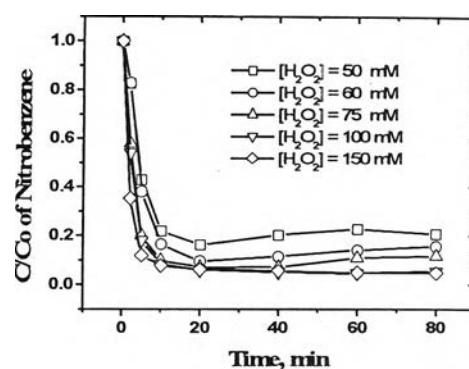
In order to investigate the effect of H₂O₂ on the decomposition of high concentration of aniline and nitrobenzene, the experiments were conducted on various amounts of H₂O₂ as 50 mM, 60 mM, 75 mM, 100 mM, and 150 mM. Initial concentrations of equal 10 mM of aniline and nitrobenzene, 1.875 mM of Fe²⁺ and an initial pH of 3.0±0.1 were used as the initial conditions.

The differences of aniline and nitrobenzene removal among the different H₂O₂ concentrations were not obvious as shown in Figure 4.6 (a) and (b). However, the highest removal efficiency of aniline and nitrobenzene were at the 0.1 M and 0.15 M of H₂O₂. Thus, we obtained the optimum H₂O₂ dosage for treating high concentration of aniline and nitrobenzene at 0.1 M. The decreasing of pH value was no significant difference (Figure 4.6 (c)). The trend of H₂O₂ degradation, Figure 4.6 (d), was the same with the earlier experiment.

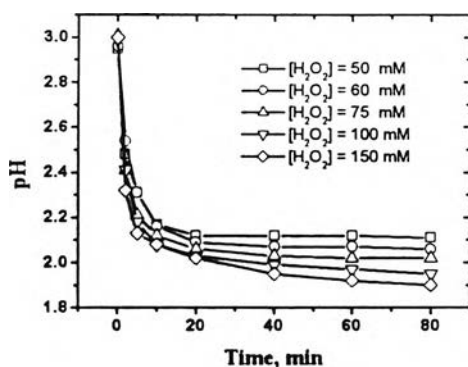
For kinetic result, Figure 4.6 (e) and (f) show that rate constant and initial rate increased with the increasing of H₂O₂ concentration. In this study, the amount of H₂O₂ added in this experiment had not yet reached the degree of inhibition. In comparing of aniline and nitrobenzene, it is obvious to point that the rate constant and initial rate of aniline higher than nitrobenzene. This may be explained by previous studied which reported the degradation of aniline. The studied found that nitrobenzene was one of intermediate oxidation of aniline (Sarasa et al., 2002; Sauleda, 2001; Brillas et al., 1998). In this study, when the mixture of aniline and nitrobenzene was degraded, aniline was oxidized to nitrobenzene. Thus, nitrobenzene in the solution was increased that leads to the decreasing of rate constant and initial rate of nitrobenzene. From the results in part 4.5 and 4.6, we can conclude that the optimum initial conditions for treating 10 mM of aniline and nitrobenzene was at 0.1 M of H₂O₂, 1.875 mM of Fe²⁺ and at pH 3.0 or at the mole ratio of 1 : 5 : 0.09 (aniline and nitrobenzene : H₂O₂ : Fe²⁺).



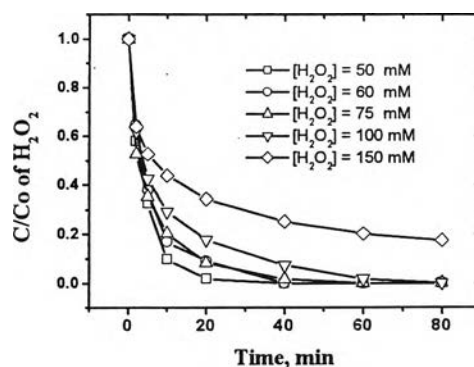
(a) Residual fraction of Aniline



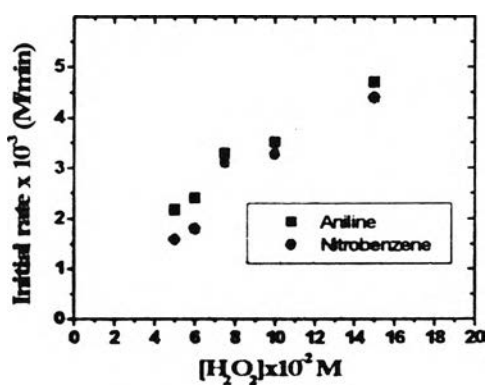
(b) Residual fraction of Nitrobenzene



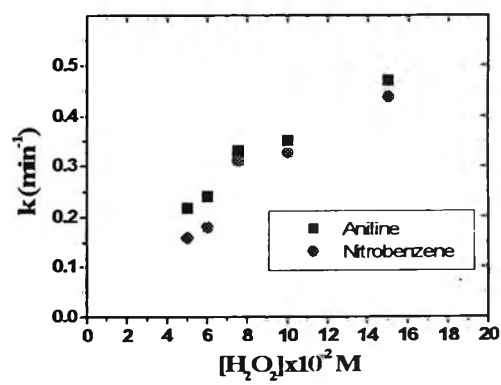
(c) pH values of the system



(d) Residual fraction of hydrogen peroxide



(e) Initial rates of aniline and nitrobenzene



(f) Rate constants of aniline and nitrobenzene

Figure 4.6 Effect of H_2O_2 dosage on high concentration of aniline and nitrobenzene ([aniline and nitrobenzene] = 10 mM, Fe^{2+} = 1.875 mM, pH=3)

4.7 Comparison between optimum conditions for treating low concentration and high concentration of aniline and nitrobenzene

According to the results, we found that the optimum condition for treating 1 mM of aniline and nitrobenzene was at 20 mM of H_2O_2 , 0.5 mM of Fe^{2+} and at pH 3.0 or as the ratio of 1: 10: 0.25 (aniline and nitrobenzene: H_2O_2 : Fe^{2+}). While, the optimum condition for 10 mM of aniline and nitrobenzene was at 100 M of H_2O_2 , 1.875 mM of Fe^{2+} and at pH 3.0 or as ratio of 1: 5: 0.09. It is important to point that at the increasing of concentration of aniline and nitrobenzene, the requirement of H_2O_2 and Fe^{2+} for treating both substances was decreased. The results show that when total concentration of aniline and nitrobenzene increased 10 times (2mM to 20 mM), ratio of H_2O_2 requirement decreased as 50% (1: 10 to 1:5). Moreover, ratio of Fe^{2+} requirement also decreased as 64% (1: 0.25 to 1: 0.09).

4.8 Competitive degradation behavior between aniline and nitrobenzene

This experiment set was established under the hypothesis that aniline and nitrobenzene may compete to react with hydroxyl radicals. In order to investigate the competitive behavior degradation between aniline and nitrobenzene, the experiments were conducted on various aniline and nitrobenzene ratios at 10/1, 5/1, 2/1, 1/1, 1/2, 1/5, 1/10, only aniline and only nitrobenzene. In this experiment, 67.5 mM of H_2O_2 , 1.25 mM of Fe^{2+} and pH value as 3.0 ± 0.1 were used as the initial conditions.

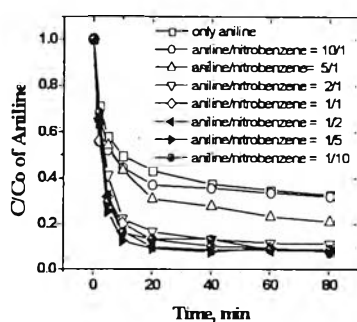
Figure 4.7 (a) shows the C/C_0 of aniline versus time. The results can be indicated that with only aniline, the degradation was moderate. The aniline degradation was improved in the presence of nitrobenzene even added small amount as ratio of aniline/nitrobenzene equal to 5/1. It is important to point that at the molar ratio of aniline/nitrobenzene up to 1/10, solution contained much more amounts of nitrobenzene comparing to aniline in previous case. The results also indicated that less degradation of aniline was observed during 60 minutes experimental period.

The degradation of nitrobenzene versus time was shown in Figure 4.7 (b). The results show that nitrobenzene was well degraded in the absence of aniline. Moreover, small amounts of aniline in the mixture exerted less effect on nitrobenzene degradation. This effect can be seen as the molar ratio of aniline to nitrobenzene from 1/10 to 1/1. At High amounts of aniline (more than 50% of nitrobenzene in the mixture), the result shows high amount of nitrobenzene remaining in the solution. This might be explained by the degradation of aniline to nitrobenzene. The pH profile as shown in Figure 4.7 (c) exhibits that the reduction of pH value during the reaction time was no significant different among of different aniline and nitrobenzene mole ratio. The pH value reduced in the range of 3.0 to 2.05. The lowest pH value was found when the molar ratio of aniline to nitrobenzene equal 1/1 and the highest pH value was found with high amounts aniline presented in the solution. The residual H_2O_2 , Figure 4.7 (d), points that the degradation of H_2O_2 increasing with increasing of nitrobenzene concentration. In comparing of treating efficiency by Fenton process, aniline was difficult to degrade comparing to nitrobenzene due to the hydrogen abstraction.

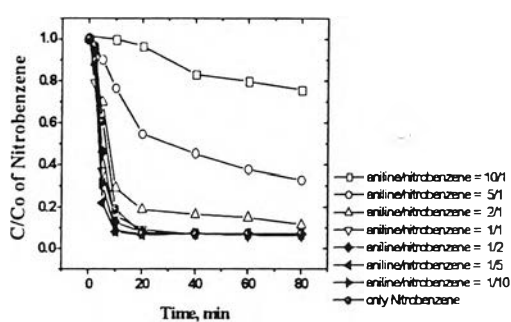
Figure 4.7 (e) and (f) show the initial rate and rate constant. The initial rates of aniline oxidation were $1.68 \text{ mM}\cdot\text{min}^{-1}$, $1.826 \text{ mM}\cdot\text{min}^{-1}$, $1.77 \text{ mM}\cdot\text{min}^{-1}$, $1.09 \text{ mM}\cdot\text{min}^{-1}$, $0.665 \text{ mM}\cdot\text{min}^{-1}$ and $0.32 \text{ mM}\cdot\text{min}^{-1}$. The k values for aniline degradation were 0.1346, 0.1826, 0.236, 0.2178, 0.2659 and 0.2381 min^{-1} with different aniline and nitrobenzene ratios as 5/1, 2/1, 1/1, 1/2, 1/5 and 1/10 respectively. For nitrobenzene, the initial rates were $0.073 \text{ mM}\cdot\text{min}^{-1}$, $0.561 \text{ mM}\cdot\text{min}^{-1}$, $1.396 \text{ mM}\cdot\text{min}^{-1}$, $1.942 \text{ mM}\cdot\text{min}^{-1}$, 3.26 mM and $3.29 \text{ mM}\cdot\text{min}^{-1}$ and k values were 0.029, 0.1122, 0.1861, 0.1942, 0.2608 and 0.242 min^{-1} , respectively with the aniline and nitrobenzene ratio as 5/1, 2/1, 1/1, 1/2, 1/5 and 1/10.

In comparing of initial rate, the initial rate of both substances was not much different. However at the molar ratio of aniline to nitrobenzene as 5/1, the degradation of aniline was predominant and at the molar ratio as 1/5, the degradation of nitrobenzene was predominant. It is obvious that nitrobenzene can be degraded at the faster rate than aniline. This degradation pattern is also seen in other molar ratios of aniline to nitrobenzene. In application of this work, the results show that if wastewater

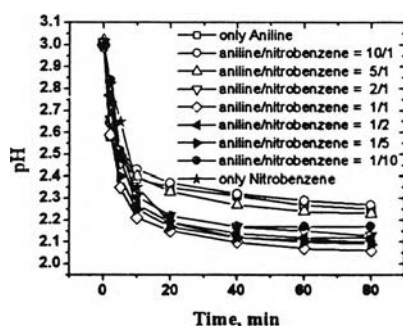
contains high amount of nitrobenzene and low amount of aniline, it was effective for treating both substances. But if wastewater contains high amount of aniline and low amount of nitrobenzene, the degradation of nitrobenzene was poor efficiency. Thus we need to separate them before go to wastewater treatment process.



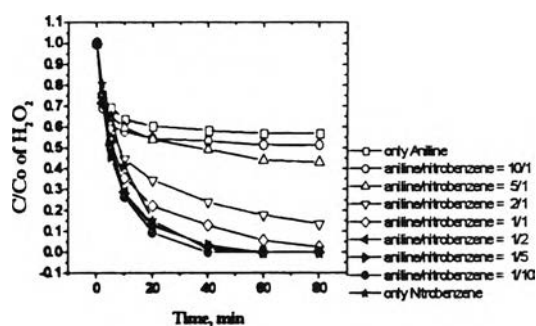
a) Residual fraction of Aniline



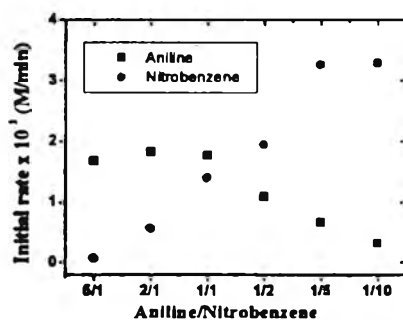
(b) Residual fraction of Nitrobenzene



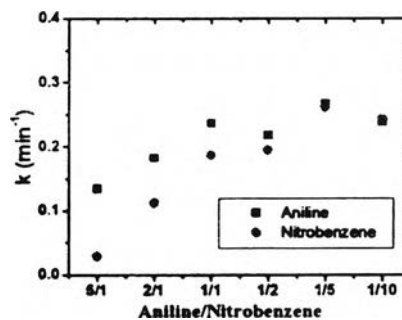
(c) pH values of the system



(d) Residual fraction of hydrogen peroxide



(e) Initial rates of aniline and nitrobenzene



(f) Rate constants of aniline and nitrobenzene

Figure 4.7 Competitive degradation behaviors between aniline and nitrobenzene ($\text{H}_2\text{O}_2 = 67.5 \text{ mM}$, $\text{Fe}^{2+} = 1.25 \text{ mM}$, $\text{pH} = 3$)

Figure 4.8 shows the C/C_0 of aniline at 20 minutes experimental period. Results show that at the molar ratio of aniline to nitrobenzene as 1/1, 1/5 and 1/10, the aniline degradation efficiencies were 87%, 91% and 87% respectively. While at the molar ratio of aniline to nitrobenzene equal to 5/1 and 10/1, the aniline degradation efficiencies were 69% and 57% respectively. The result strongly supported that the degradation of aniline was improved with the presence of nitrobenzene. However, at the molar ratio of aniline to nitrobenzene equal to 1/10, the aniline degradation efficiency was decreased. It means that if add amount of nitrobenzene more than this molar ratio, the aniline degradation efficiency will be decreased. This information suggests that the nitrobenzene can help in increasing aniline degradation efficiency at only certain amount.

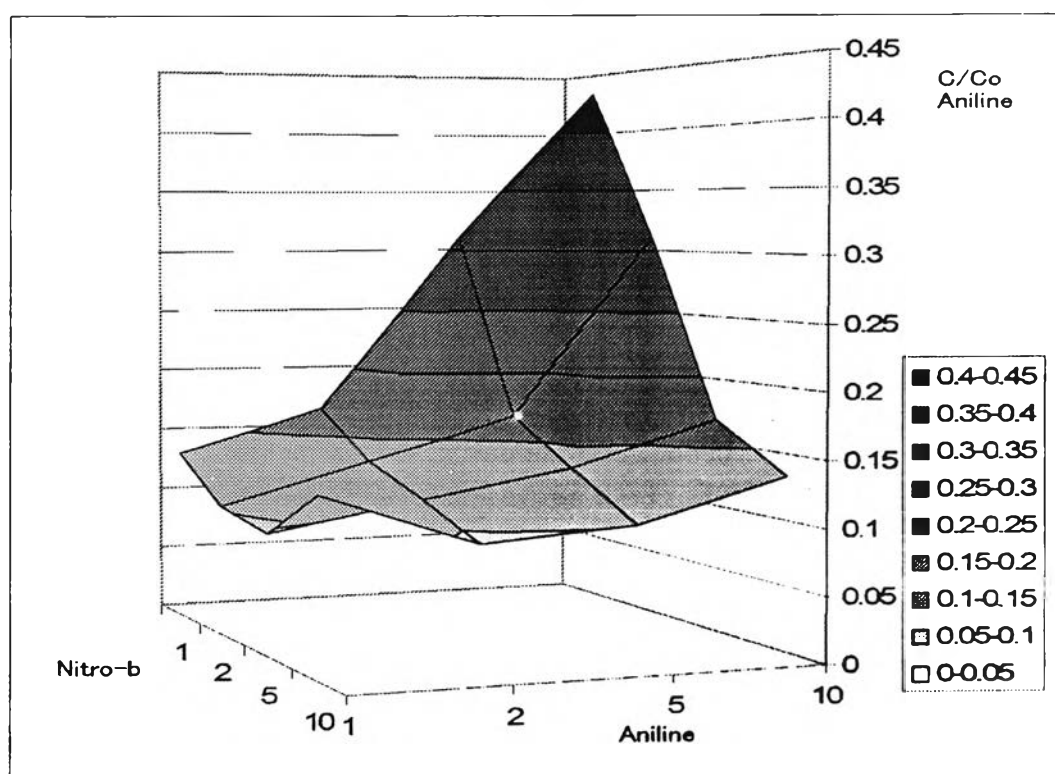


Figure 4.8 Residual fraction of aniline at 20 minutes

Figure 4.9 shows the C/C_0 of nitrobenzene at 20 minutes experimental period. Results show that at the molar ratio of aniline to nitrobenzene as 1/1, 1/5 and 1/10, the nitrobenzene degradation efficiency were 91%, 94% and 93% respectively. While at the molar ratio of aniline to nitrobenzene equal to 5/1 and 10/1 were 46% and 4% respectively. According to the results from Figure 4.7 (g) and (h), it could be concluded that even high amount of nitrobenzene was added into the solution (such as at ratio 1/10), the degradation efficiency of aniline and nitrobenzene was not much different from the degradation efficiency of ratio as 1/1. However, beyond the 1/1 ratio with the small increment of aniline added into the solution, the degradation efficiency of aniline and nitrobenzene was sharply dropped as seen from the ratio as 2/1 and 5/1. This finding is supported that the nitrobenzene degradation was predominant reaction when nitrobenzene was the domain species in the solution. In addition, if aniline becomes the major species in the solution, the nitrobenzene degradation efficiency is less pronounced.

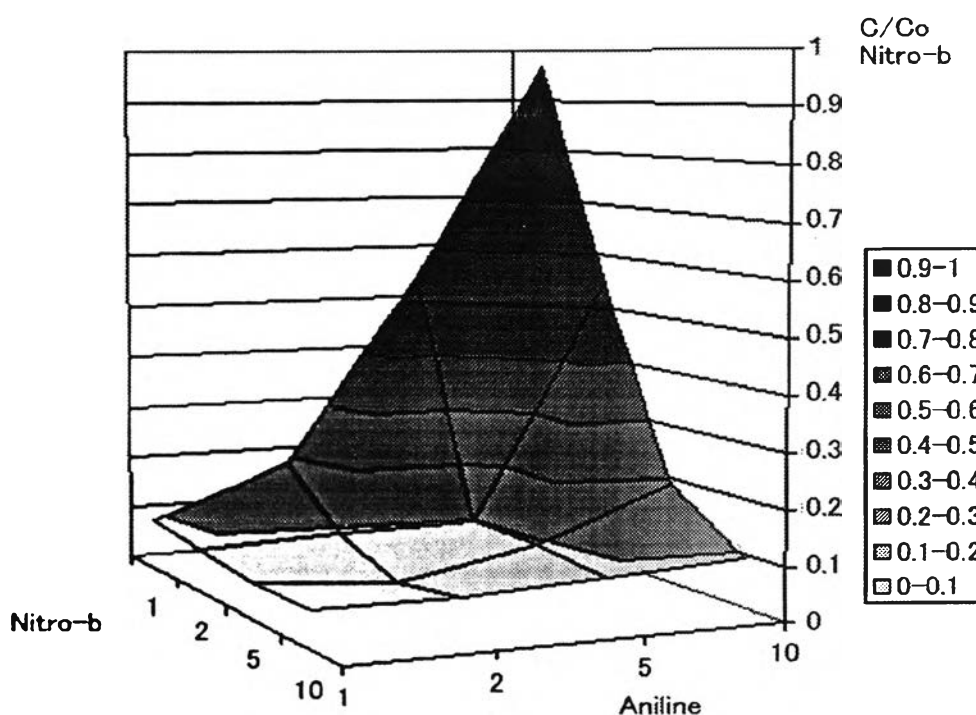


Figure 4.9 Residual fraction of nitrobenzene at 20 minutes

4.9 Mineralization of aniline and nitrobenzene

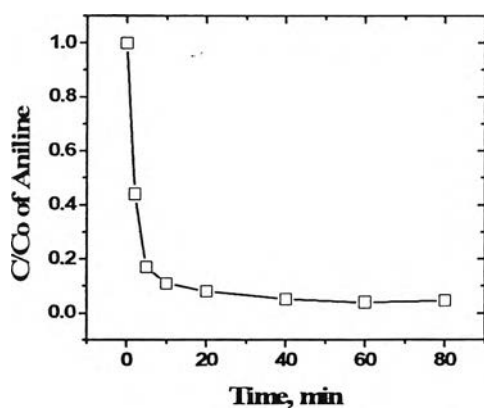
Since aniline and nitrobenzene were almost completely degraded within 80 minutes reaction time. However, aniline and nitrobenzene may be degraded into other intermediates. Therefore, these experiments were performed in order to investigate the mineralization of aniline and nitrobenzene. Total organic carbon (TOC) was measured to represent the mineralization of aniline and nitrobenzene.

In this experiment, 1 mM of aniline and nitrobenzene, 20 mM of H_2O_2 , 0.5 mM of Fe^{2+} , and pH value at 3.0 ± 0.1 were used as initial condition. The results in Figure 4.8 (a) and (b) show the degradation of aniline and nitrobenzene versus time. The result demonstrates that the degradation of both compounds was almost completed within 80 minutes. The pH values and H_2O_2 profiles were shown on Figure 4.8 (c) and (d) respectively.

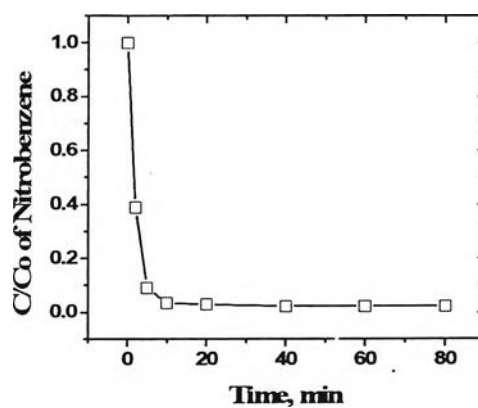
Although aniline and nitrobenzene was effectively degraded in Fenton process, the TOC result as shown in Figure 4.8 (e) exhibit that TOC removal was approximately 25% within the end of reaction time. This indicates that aniline and nitrobenzene can be oxidized or mineralized to carbon dioxide and water approximately 25% by Fenton reaction. It can be concluded that the mineralization of aniline and nitrobenzene could not be achieved in Fenton process.

However, in this study, aniline and nitrobenzene were mixed together in the solution. Therefore, it is important to evaluate the mineralization of aniline and nitrobenzene in different molar ratio of both substances. The experiment was set with various ratios of aniline and nitrobenzene as 0/2, 0.5/1.5, 1/1, 1.5/0.5 and 2/0 while 20 mM of H_2O_2 , 0.5 mM of Fe^{2+} and pH value as 3.0 ± 0.1 were used as initial condition. The result as shown in Figure 4.8 (f) can be observed that the TOC reductions were 8%, 17%, 25%, 35% and 40% with the aniline and nitrobenzene ratios as 0/2, 0.5/1.5, 1/1, 1.5/0.5 and 2/0 respectively. This reveals that nitrobenzene intermediates were much more stable than aniline intermediates. The previous researches reported the degradation of aniline (Sanchez et al., 1997; Brillas et al., 1998; Sauleda and Brillas, 2001; Pierpoint et al., 2003) that oxidation intermediates of aniline using ozonation and photocatalytic process were phenol, hydroquinone, benzoquinone, and

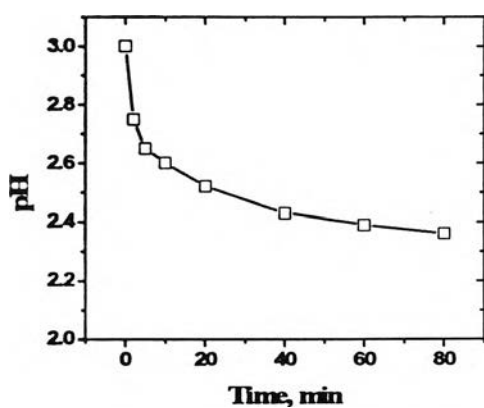
nitrobenzene, 1,2,4 benzenetriol, and maleic and fumaric acids. While, the degradation of nitrobenzene was investigated by Lipczynska-Kochany (1991), Nomiya et al. (2001). They reported that the oxidation intermediates of nitrobenzene using Fenton and hydrogen peroxide catalyzed by vanadium(V) process were *p*-nitrophenol, *m*-nitrophenol and *o*-nitrophenol.



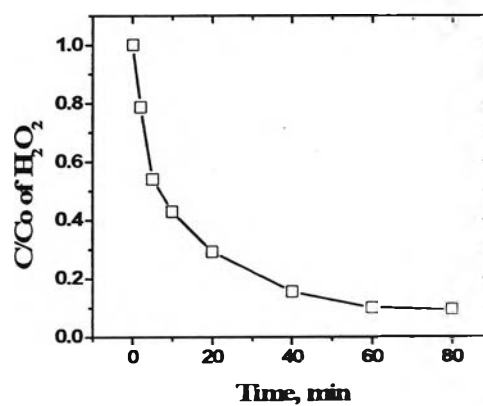
a) Residual fraction of Aniline



(b) Residual fraction of Nitrobenzene

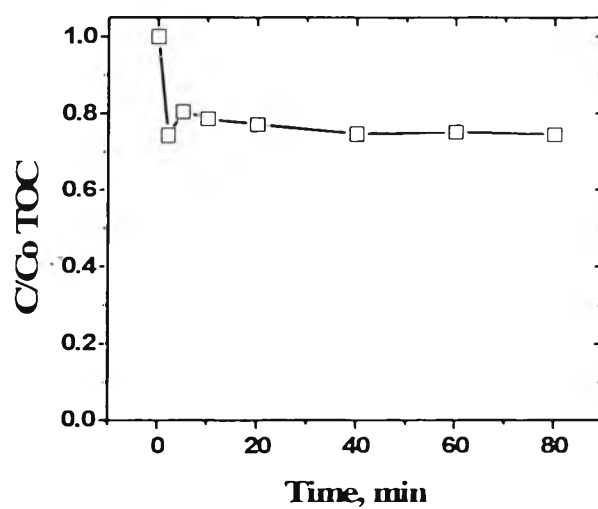


(c) pH values of the system

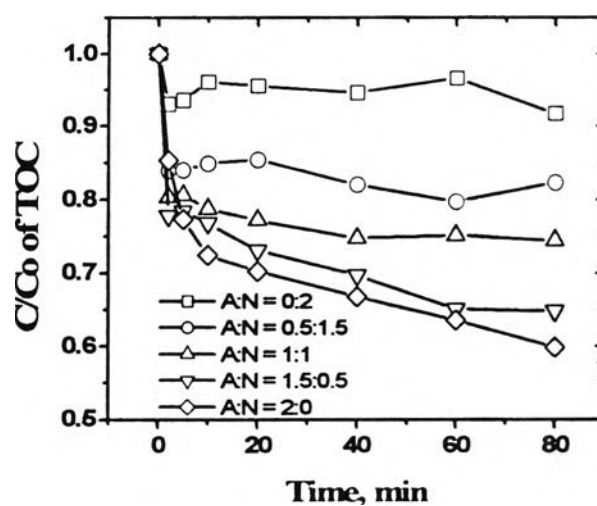


(d) Residual fraction of hydrogen peroxide

Figure 4.10 Mineralization of aniline and nitrobenzene ($\text{Fe}^{2+} = 0.5 \text{ mM}$ [aniline and nitrobenzene] = 1 mM, $\text{H}_2\text{O}_2 = 20 \text{ mM}$, $\text{pH} = 3$)



(e) Residual fraction of TOC



(f) Residual fraction of TOC with different molar ratio of aniline and nitrobenzene

Figure 4.10 Mineralization of aniline and nitrobenzene ($\text{Fe}^{2+} = 0.5 \text{ mM}$ [aniline and nitrobenzene] = 1 mM, $\text{H}_2\text{O}_2 = 20 \text{ mM}$, $\text{pH} = 3$)