



## CHAPTER IV

### RESULTS AND DISCUSSIONS

#### 4.1. Carriers

##### 4.1.1. Composition of carriers

Fluidized-bed Fenton process lets ferric ion ( $\text{Fe}^{3+}$ ), produced in the Fenton's reaction, be transformed into iron oxide ( $\text{FeOOH}$ ) attached onto the carrier surface via the crystallization or sedimentation. This process combines the functions of homogeneous chemical oxidation ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ), heterogeneous chemical oxidation ( $\text{H}_2\text{O}_2/\text{FeOOH}$ ), fluidized-bed crystallization, and reductive dissolution of  $\text{FeOOH}$ . Heterogeneous Fenton process has advantage that most of the iron remains in the solid phase. The solid phase is usually granular (metal oxides or sand), hence the treated water is easily separated from the iron.

In this study, alumina dioxide ( $\text{Al}_2\text{O}_3$ ), silica dioxide ( $\text{SiO}_2$ ), black, white, brown and colour gravels were used to compare the efficiency of 2,6-dimethylaniline, ferrous ion and total iron removals. The average particle size diameters of alumina dioxide and all gravels are between 2 and 4.86 mm and silica dioxide is between 0.84 and 2 mm.

As shown in Table 4-1, Gravel generally consists of O, Ca and C elements as main composition. This composition can result in water quality change in terms of alkalinity and hardness. The percentages by weight of Ca element in black, white and colour gravels were 38.75, 50.05 and 29.22, respectively and C element was component in black, white, brown and colour gravels by 9.43, 7.51, 12.59 and 11.66 percent by weight, respectively. O element included in all carriers, alumina dioxide ( $\text{Al}_2\text{O}_3$ ), silica dioxide ( $\text{SiO}_2$ ), black, white, brown and colour gravels, as the percentages by weight were 50.03, 36.61, 47.61, 38.08, 35.68 and 49.23, respectively. Al element was in  $\text{Al}_2\text{O}_3$  49.97 percent by weight and colour gravel 0.62 percent by weight.  $\text{SiO}_2$ , brown gravel and colour gravel composed of Si element 57.61, 48.34 and 6.37 percent by weight, respectively.

Table 4-1 Compositions of fresh carriers investigated from X-ray diffraction (XRD)

Element	Al <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>		Black Gravel		White Gravel		Brown Gravel		Colour Gravel	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
C*	-	-	-	-	9.43	16.46	7.51	14.55	12.59	20.84	11.66	19.21
O*	50.03	62.81	36.61	52.08	47.61	62.42	38.08	55.42	35.68	44.32	49.23	60.88
Al*	49.97	37.19	-	-	-	-	-	-	-	-	0.62	0.46
Si*	-	-	57.61	46.69	-	-	-	-	48.34	34.20	6.37	4.49
Ca*	-	-	-	-	38.75	20.28	50.05	29.08	-	-	29.22	14.43

\* : C is Carbon element

O is Oxygen element

Al is Aluminum element

Si is Silica element

Ca is Calcium element

#### 4.1.2. Carriers comparison

Effects of carriers on the oxidation of 2,6-dimethylaniline was investigated. Observed parameters were removal efficiency of target compound and ferrous ion in fluidized-bed Fenton Process. As Fenton's reagent producing hydroxyl radical can lead to oxidize the organic compound, fluidized-bed Fenton can reduce the amount of iron oxide which is the drawback of Fenton process. In previous study of Khunikakorn (2005), presented that aluminum oxide and silica dioxide were used to be the carriers in the fluidized-bed Fenton process to degrade nitrobenzene and aniline effectively, according to Ratanatamskul et al. (2006a) treating COD and color in reactive dyes wastewater by using aluminum oxide and silica dioxide as comparable carriers. Also in this study, aluminum oxide and silica dioxide were still considered to use; furthermore, 6 gravel types were investigated for determining different carriers.

The carriers which have different basic elements as Table 4-1 were operated. Each carrier was used 74.07 g/l (Hsueh et al., 2006a) in the optimum condition from Ting et al. (2008) who determined the optimum condition of 2,6-dimethylaniline degradation in electro-Fenton process, which was 1 mM of 2,6-dimethylaniline degraded by 20 mM of hydrogen peroxide and 1 mM of ferrous ion concentration at pH 2.

Figure 4.1 shows the comparison between Fenton without carrier and fluidized-bed Fenton in 2,6-dimethylaniline removal. It was found that the efficiency of 2,6-dimethylaniline removal was 80.27% in Fenton and when using carrier, most of carriers removed 2,6-dimethylaniline between 95.90% and 100%, except silica dioxide only 84.68% in 300 minutes. Muthuvel and Swaminathan (2007) also determined the heterophoto-Fenton process using a  $\text{Fe}^{3+}$  loaded  $\text{Al}_2\text{O}_3$  as carrier and catalyst in heterogeneous process was fast when compared with the homogeneous process initially.

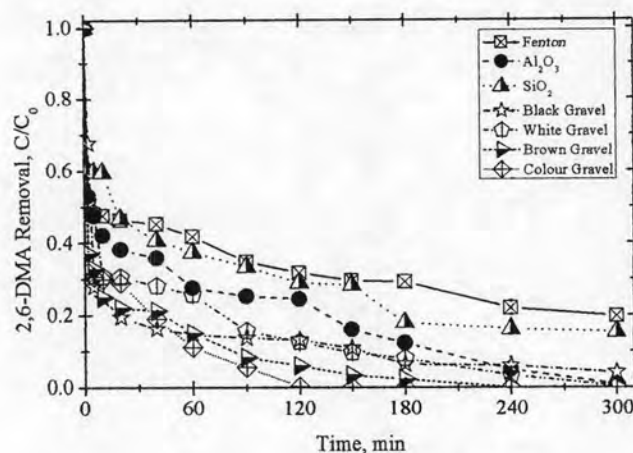
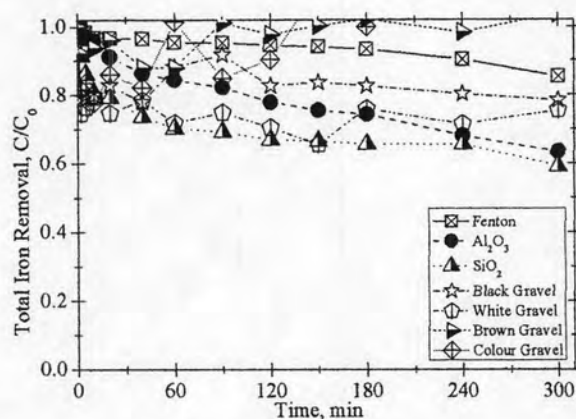


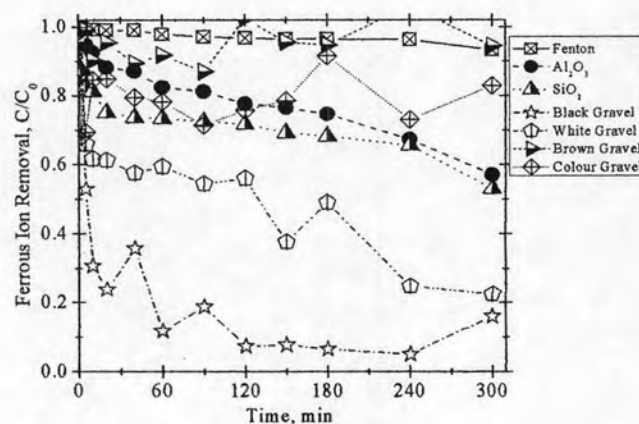
Figure 4.1 2,6-dimethylaniline removal in the comparison of different carriers;  
 $[2,6\text{-DMA}] = 1 \text{ mM}$ ,  $[\text{Fe}^{2+}] = 1 \text{ mM}$ ,  $[\text{H}_2\text{O}_2] = 20 \text{ mM}$ ,  $\text{pH} = 2$  and  $\text{Al}_2\text{O}_3 = 74.07 \text{ g/l}$

Ferrous ion in the solution transformed into iron oxide ( $\text{FeOOH}$ ) by Fenton's reaction and attached onto the carrier surface via the crystallization. This process not only attains high organic removal efficiency, but also reduces the large amount of iron sludge being produced. Figure 4.2(a) exhibits that total iron removal in the comparison of different carriers. Total iron

removal changed up and down until the end of reaction time (300 minutes) such as brown gravel, colour gravel, total iron removal was more than initial ferrous ion concentration. For alumina dioxide ( $\text{Al}_2\text{O}_3$ ), silica dioxide ( $\text{SiO}_2$ ), black gravel and white gravel, total iron removal decreased so this result implied that iron crystallized onto the surface of carriers as 36.62%, 40.85%, 21.70% and 24.54%, respectively. The iron onto the surface of carriers can be used as the heterogeneous catalyst and the amount of iron sludge was also reduced.



(a) Total iron removal



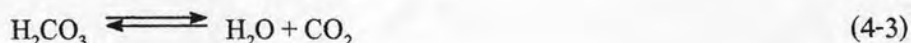
(b) Ferrous ion removal

Figure 4.2 Total iron removal (a) and ferrous ion removal (b)

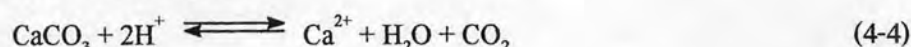
in the comparison of different carriers;

$[\text{2,6-DMA}] = 1 \text{ mM}$ ,  $[\text{Fe}^{2+}] = 1 \text{ mM}$ ,  $[\text{H}_2\text{O}_2] = 20 \text{ mM}$ ,  $\text{pH} = 2$  and  $\text{Al}_2\text{O}_3 = 74.07 \text{ g/l}$

Figure 4.2(b) shows that ferrous ion removal decreased because of the usage in Fenton's reaction and transformation to ferric in the solution and iron oxide on the carrier surface. Ferrous ion removal in alumina dioxide ( $\text{Al}_2\text{O}_3$ ) and silica dioxide ( $\text{SiO}_2$ ) decreased 42.90% and 47.00%, respectively. For black, white, brown, and colour gravels, ferrous ion removal changed up and down until the end of reaction time, which was similar to total iron removal, and the percentages of ferrous ion removal were 84.00%, 77.56%, 5.47% and 17.09%, respectively. This result caused of the reductive dissolution of FeOOH on the surface of carriers in acid condition, implied that the homogeneous catalysis by ferrous ion may play an important role as in Chou et al. (1999) who investigated that when pH below 4.4, ferrous ion concentration increased which can be attributed to the reductive dissolution of FeOOH following Equation (2-4)-(2-6). The total amount of iron released from crystallization on surface of carriers. Stone (1987) found that the rate of reductive dissolution was dependent on pH and organic reductant concentration. Therefore, the acidic condition favors reductive dissolution of  $\gamma$ -FeOOH which may increase the initial rate of Fenton's reaction. Chou and Huang (1999a) concluded that the reaction of OH radicals with benzoic acid occurred not only on the catalyst surface, but also in the aqueous solution (Fenton's reaction) through iron dissolution of the catalyst at initial pH 3.2. Moreover, surfaces, such as clay and aluminum oxides, not only accelerate the oxygenation of ferrous ion, but also induce the formation of FeOOH which are more reactive toward the dissolution reactions (Deng and Stumm, 1994). Anyway, Wehrli and Stumm (1988) exhibited the adsorption of ferrous ion onto a hydroxo functional group of an oxide surface can enhance the oxygenation of ferrous ion in a way similar to hydrolysis. This phenomenon can be explained by the fact that the coordination of ferrous ion by surface hydroxyl groups or by  $\text{OH}^-$  in solution increases the electron density at the ferrous ion center and facilitates the electron transfer from the ferrous ion center to  $\text{O}_2$  (Luther, 1990). Also, Deng and Stumm (1994) indicated that pH increased as  $\text{CO}_2$  diffused out of the solution and at the same time, ferrous ion was oxidized to  $\text{Fe}^{3+}$  as  $\text{O}_2$  is introduced slowly into solution. From the results, this experiment may occur  $\text{O}_2$ , as Equation (2-6) and (2-12), and  $\text{CO}_2$  as following Equation (4-1)-(4-4) because gravels consisted of  $\text{CaCO}_3$  (Table 4-1):



Over all of this Equation:



When  $\text{CaCO}_3$  dissolves in acid condition, as the reaction proceeds,  $\text{CaCO}_3$  disappears, acid ( $\text{H}^+$ ) is consumed, and carbon dioxide gas ( $\text{CO}_2$ ) is produced. From Table 4-2, when pH was more than 5, the primary forms of aqueous carbonate system were  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ , both well-known OH radical scavengers (Deng and Englehardt, 2006).

Table 4-2 pH change of 2,6-dimethylaniline degradation in fluidized-bed reactor measured by  $\text{pH}_{\text{initial}}$  and  $\text{pH}_{\text{final}}$

pH	Fenton	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	Black Gravel	White Gravel	Brown Gravel	Colour Gravel
$\text{pH}_{\text{initial}}$	2.00	2.01	1.99	2.01	1.98	2.04	2.00
$\text{pH}_{\text{final}}$	2.10	3.50	2.20	5.50	5.70	3.20	4.50

This study examined that for the Ca element carriers, pH changed more than others carriers and occur amount of sludge because  $\text{CaCO}_3$  can dissolve in acid solution and make size of carriers change. Furthermore, carbonate minerals and Ca element were the strong influence on the alkalinity and hardness. Alkalinity did not refer to pH, but instead referred to the ability of water to resist change in pH from neutral to acid.  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and brown gravel were the optimum alternative carriers for this experiment when it was considered in pH change, but in the part of total iron and ferrous ion removal, reductive dissolution of FeOOH from brown gravel was unstable. It might produce  $\text{CO}_2$  because brown gravel consisted of C element, which could form as carbonate when reaction was forward, and let reductive dissolution of FeOOH from carrier surfaces. When they were compared between  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , both were stable in reductive dissolution of FeOOH and could degrade 2,6-dimethylaniline, but  $\text{Al}_2\text{O}_3$  was more effective than  $\text{SiO}_2$  as 99.13% and 84.68%, respectively.

#### 4.2. Control experiments of 2,6-dimethylaniline degradation in fluidized-bed reactor

Control experiment is an important part for all experiment because this is the basement data to refer the pure efficiency of each parameter. Figure 4.3 shows 2,6-dimethylaniline removal by hydrogen peroxide and ferrous ion following these effective removals, 20.44%, and 21.85%, respectively. These implied that when Fenton process absence one of Fenton's reagents, the reaction will not be effective to oxidize target compound. If it has only hydrogen peroxide, the oxidation of 2,6-dimethylaniline will be ineffective and slow, but has only ferrous ion, the reaction aims to coagulation. Moreover,  $\text{Al}_2\text{O}_3$  adsorption of 2,6-dimethylaniline on carrier surface was only 5.16%. The mechanism of organic adsorption on the surface of  $\text{Al}_2\text{O}_3$  was examined by Benoit et al. (1993). Investigating that the adsorption of organic ligands on the surface of  $\text{Al}_2\text{O}_3$  (at pH 8) involved a surface ligand exchange reaction in which a surface hydroxyl group was displaced by the sorbing ligand. Both mono- and bidentate surface complexes might be formed (depending on the structure of the ligand). Adsorption of (partially or fully) protonated ligands resulted in a neutralization reaction between protons displaced from the ligand and hydroxide ions displaced from the surface (Schindler and Stumm, 1987; Westall, 1987).

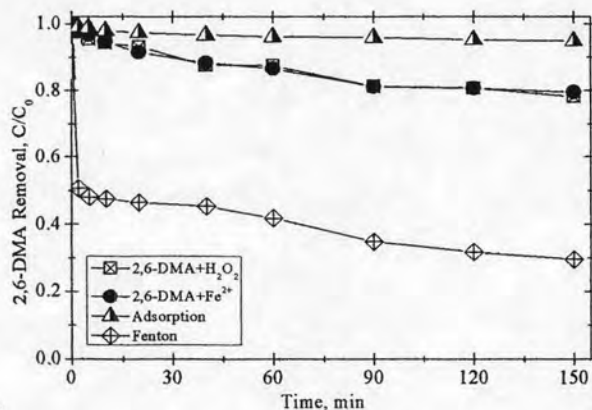


Figure 4.3 The control experiment in fluidized-bed reactor;

$[\text{2,6-DMA}] = 1 \text{ mM}$ ,  $[\text{Fe}^{2+}] = 5 \text{ mM}$ ,  $[\text{H}_2\text{O}_2] = 15 \text{ mM}$ ,  $\text{pH} = 3$  and  $\text{Al}_2\text{O}_3 = 74.07 \text{ g/l}$

### 4.3. Oxidation of 2,6-dimethylaniline in fluidized-bed Fenton process

#### 4.3.1. Effect of initial pH

In the reaction of 2,6-dimethylaniline degradation by ferrous ion catalyzing hydrogen peroxide, the pH dropped with time of reaction. In this experiment, solution pH was adjusted initially to 1, 2, 3 and 4 prior to reaction initiative. In a study by Chou et al. (2004) in which FeOOH and Fenton's reagents were used in a fluidized-bed reactor (FBR), the pH was found to strongly affect the efficiencies of mineralization and ferric ion precipitation rates. When treating benzoic acid, they found that the degradation efficiency decrease with increasing pH, while the removal efficiency of total iron increased with pH in the pH range 2.8-4.5. However, Ting et al. (2008) found that the optimum pH for 2,6-dimethylaniline degradation by electro-Fenton was 2 because at a high pH range (>2.0) was occurred by the formation of ferric and ferric hydroxide complexes with much lower catalytic capability than  $\text{Fe}^{2+}$ . Furthermore, a low pH also promoted hydrogen evolution reducing the number of active sites for generating ferrous ions.

The pH influences on the degradation of 2,6-dimethylaniline due to at higher pH 3, the degradation of organic chemicals decreased because ferric ion will form  $\text{Fe}(\text{OH})_3$ . It can be calculated that when the pH is greater than 3,  $\text{Fe}(\text{OH})_3$  will appear (Snoeyink and Jenkins, 1982). Moreover, Deng and Englehardt (2006) suggested that five mechanisms for inhibition. First, the absence of  $\text{H}^+$  can inhibit the decomposition of hydrogen peroxide to reduce production of  $\bullet\text{OH}$  (Walling, 1975). Second, hydrogen peroxide itself rapidly decomposes to water and oxygen with increasing pH above 5 (Meeker, 1965). Third, the ferrous catalyst is deactivated with the formation of FeOOH at pH above 5 (Bigda, 1995). Fourth, under neutral and alkaline conditions, the primary forms of aqueous carbonate system are  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ , both well-known OH radical scavengers. Finally, the oxidation potential of OH radical decreases with increasing pH from  $E_0 = 2.8\text{V}$  at pH 0 to  $E_{14} = 1.95\text{V}$  at pH 14 (Kim and Vogelpohl, 1998). And when the pH was below 3, crystallization of iron was dramatically lowered since iron solubility increased sharply with the decreasing pH (Chou et al., 2004).  $\text{Fe}^{3+}$  has a lower catalytic activity than  $\text{Fe}^{2+}$  and may complex with target organic substrates or their degradation intermediates that can



produce weaker oxidants than hydroxyl radicals (Equation (2-3)-(2-4)) (Lu et al., 1999). Then, Deng and Englehardt (2006) mentioned that pH below optimal can inhibit oxidation in three ways. First, at extremely low pH values, the  $[\text{Fe}(\text{H}_2\text{O})]^{2+}$  formed reacts relatively slowly with  $\text{H}_2\text{O}_2$ , producing less  $\bullet\text{OH}$  (Gallard et al., 1998). Second, the scavenging effect of  $\text{H}^+$  on OH radical becomes more important at a lower pH (Tang and Huang, 1996). Third, exceptionally low pH can inhibit reaction between ferric ion and hydrogen peroxide (Pignatello, 1992).

At pH 2 and 3 in Figure 4.4, 2,6-dimethylaniline was decreased more than 96.04% after 5 minutes, however; pH 3 was the most efficient condition of Fenton's reaction. This revealed that high efficiency of the oxidation processes utilizing the activation of hydrogen peroxide by iron salt is usually obtained when operating under the optimum acidic condition (Neyens and Baeyens, 2003).

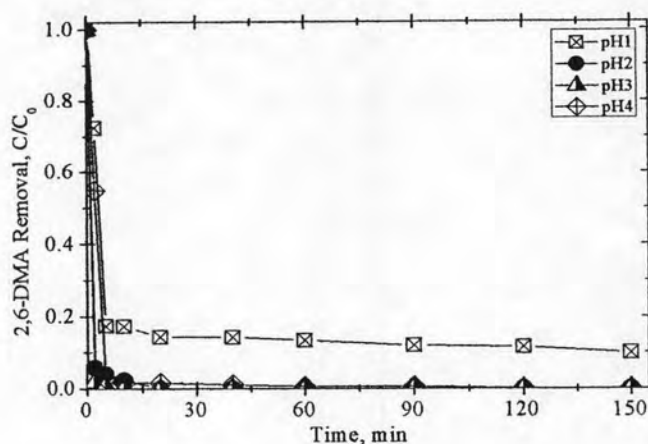
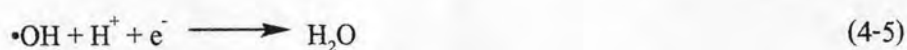


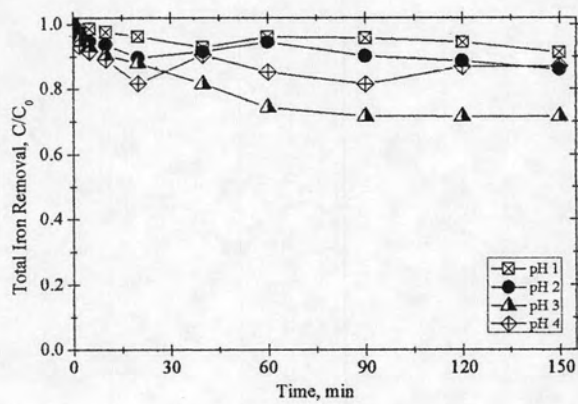
Figure 4.4 2,6-Dimethylaniline removal in the effect of initial pH on the removal efficiency of 2,6-dimethylaniline with FB-Fenton process;  
 $[\text{2,6-DMA}] = 1 \text{ mM}$ ,  $[\text{Fe}^{2+}] = 5 \text{ mM}$ ,  $[\text{H}_2\text{O}_2] = 15 \text{ mM}$ , and  $\text{Al}_2\text{O}_3 = 74.07 \text{ g/l}$ .

As shown in Figure 4.5(a) and 4.5(b), total iron and ferrous ion concentration removal at pH 1 and 2 were almost stable. Total iron removal in pH 1, 2, 3 and 4 was 8.71%, 13.90%, 28.40% and 12.98%, respectively and ferrous ion removal in pH 1, 2, and 3 was 7.27%, 12.66% and 87.20%, respectively. From this result, pH 1 and 2 was low pH so iron transformed rapidly from ferric to ferrous because crystallization on the surface of carriers was only 8.71% and 13.90%, respectively. In the present of solid phase, ferric ion can precipitate or crystallize onto solid surface to form iron pellet; hence, reducing the sludge production which required further disposal. Anyway, the reaction of hydrogen peroxide with ferrous ion is seriously affected causing the reduction in OH radical production. The low degradation at pH 1 is also due to the hydroxyl radical scavenging of  $H^+$  ion (Equation (4-5)) (Lucas and Peres, 2006).

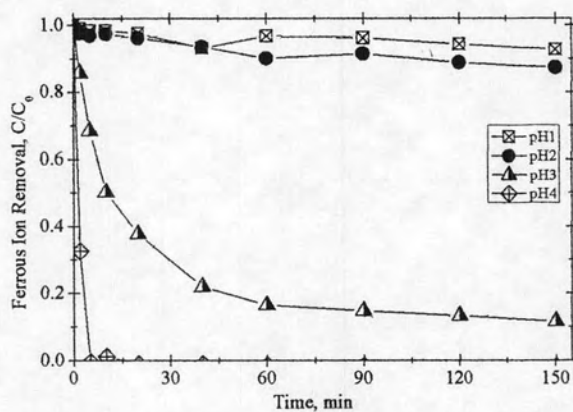


When hydroxyl radical transfer electron in acid condition will appear water which can not react in 2,6-dimethylaniline oxidation process.

At pH 3, decreasing ferrous ion removal because ferrous ion was reacted with hydrogen peroxide 87.20% and crystallized on the surface of carrier was 28.40%. This result implied that pH 3 could decrease the iron sludge and increase hydroxyl radical via Fenton's reaction from almost ferrous ion. And, the ferrous ion concentration at pH 4 could not detect by atomic absorption spectrophotometer (AAS) after 5 minutes, this result caused the detection limit of AAS was higher than this range. But total iron remaining in the solution was ferric ion, due to out of ferrous ion to react with hydrogen peroxide. 2,6-Dimethylaniline removal at pH 4 might be Fenton's-Like ( $Fe^{3+}/H_2O_2$ ) which produced  $HO_2\bullet$  radicals to oxidation of organic compounds but they are much less reactive than hydroxyl radicals as the Equation (2-3)-(2-4).



(a) Total iron removal



(b) Ferrous ion removal

Figure 4.5 Total iron removal (a) and ferrous ion removal (b) in the effect of initial pH on the removal efficiency of 2,6-dimethylaniline with FB-Fenton process;

$[2,6\text{-DMA}] = 1 \text{ mM}$ ,  $[\text{Fe}^{2+}] = 5 \text{ mM}$ ,  $[\text{H}_2\text{O}_2] = 15 \text{ mM}$ , and  $\text{Al}_2\text{O}_3 = 74.07 \text{ g/l}$ .

### 4.3.2. Kinetics determination

This reported the information of 2,6-dimethylaniline degradation by fluidized-bed Fenton process. Initial rate was used in order to eliminate any interference from intermediate competitions. For this method, a series of different concentration for one reactant at a time were performed. The effects of such reactant on the target compound oxidation could be determined by the initial slope between the “target compound concentration” and “time” plot. The reaction order with respect to each reactant could be determined as a slope on the normal linear scale plot between log of “obtained initial rate” and log of “reactant concentration”.

#### 4.3.2.1. Effects of initial ferrous ion concentration

Ferrous ion played an important role in catalyzing hydrogen peroxide to produce the OH radical via Fenton reaction. When ferrous ion was introduced in fluidized-bed reactor to treat 2,6-dimethylaniline, and the carrier was for crystallization and the heterogeneous catalyst of hydrogen peroxide when FeOOH coated on surface of carrier.

In this study, to obtain the optimum initial ferrous ion concentration, the investigation was carried out in the range of 1, 2.5 and 5 mM at pH 3 and hydrogen peroxide concentration as 15 mM. The removal efficiency of 2,6-dimethylaniline was more than 80% at the end of the reactions, 82.83%, 92.45% and 100%, respectively, as shown in Figure 4.6. 2,6-Dimethylaniline removal efficiency increased with increasing ferrous ion concentration because the oxidation rate of organics compounds by Fenton reaction was rapidly when a large amount of ferrous ion were present due to the high generation rate of hydroxyl radical (Lu et al., 2005) but if they were more than optimum point, the rate can be decreased.

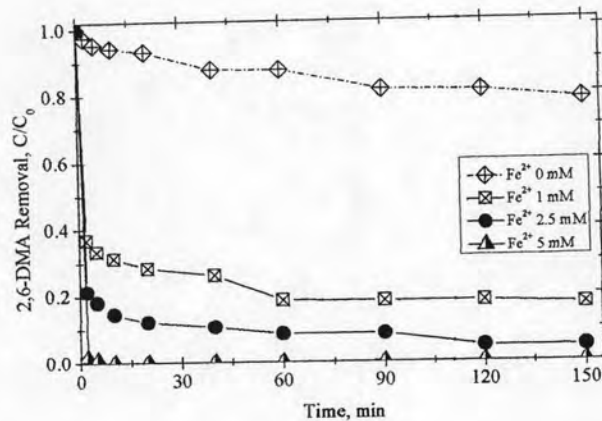


Figure 4.6 2,6-Dimethylaniline removal in the effect of initial ferrous ion concentration on the removal efficiency of 2,6-dimethylaniline with FB-Fenton process;  
 $[2,6\text{-DMA}] = 1 \text{ mM}$ ,  $[\text{H}_2\text{O}_2] = 15 \text{ mM}$ ,  $\text{pH} = 3$  and  $\text{Al}_2\text{O}_3 = 74.07 \text{ g/l}$

Complete oxidation requires high ferrous ion concentrations, in order to produce high concentrations of OH radical, and enough hydrogen peroxide concentration to produce oxidation, since when this oxidant was consumed the reaction was finished (Casero et al., 1997). Figure 4.7 reveals that hydrogen peroxide was used fast for producing OH radical until they were insufficiency to react with ferrous ion and 2,6-dimethylaniline concentrations. When this study varied 1 mM, 2.5 mM and 5 mM of ferrous ion concentration, hydrogen peroxide was spent 54.48%, 75.43% and 100%, respectively.

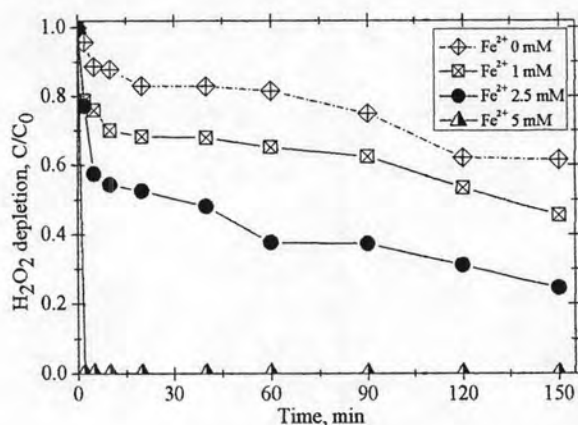
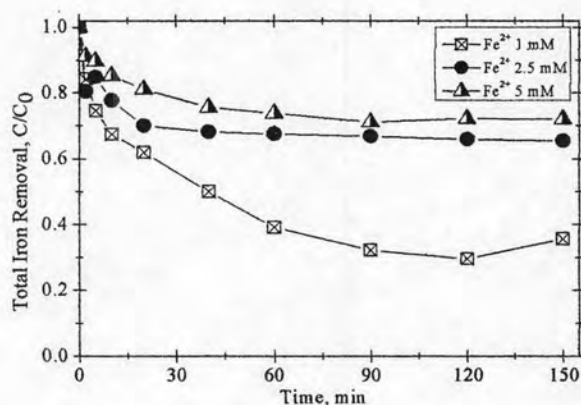
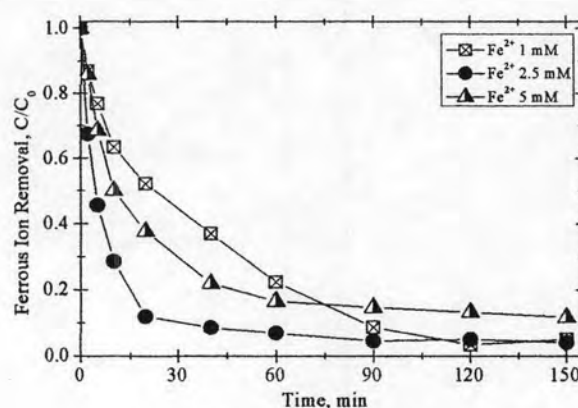


Figure 4.7 Hydrogen peroxide depletion in the effect of initial ferrous ion concentration on the removal efficiency of 2,6-dimethylaniline with FB-Fenton process;  
 $[2,6\text{-DMA}] = 1 \text{ mM}$ ,  $[\text{H}_2\text{O}_2] = 15 \text{ mM}$ ,  $\text{pH} = 3$  and  $\text{Al}_2\text{O}_3 = 74.07 \text{ g/l}$

Then, total iron and ferrous ion concentrations was still in process because of higher concentration of ferrous ion, hydrogen peroxide can not reduced all as in Figure 4.8(a) and 4.8(b). For 1 mM of ferrous ion concentration, total iron removal decreased 64.48% which was lower than 2.5 mM and 5 mM of ferrous ion concentration as 34.62% and 27.96%, respectively. Due to low concentration, crystallization formed rapidly on the surface of carrier. Ferrous ion removal with higher concentration at 5 mM decreased 88.32% which was lower than 1 mM and 2.5 mM of ferrous ion concentration as 94.94% and 95.93%, respectively. This result implied that higher concentration of ferrous ion, removal efficiency of total iron and ferrous ion were lower.



(a) Total iron removal



(b) Ferrous ion removal

Figure 4.8 Total iron removal (a) and ferrous ion removal (b) in the effect of initial ferrous ion concentration on the removal efficiency of 2,6-dimethylaniline with FB-Fenton process;

$$[2,6\text{-DMA}] = 1 \text{ mM}, [\text{H}_2\text{O}_2] = 15 \text{ mM}, \text{pH} = 3 \text{ and } \text{Al}_2\text{O}_3 = 74.07 \text{ g/l}$$

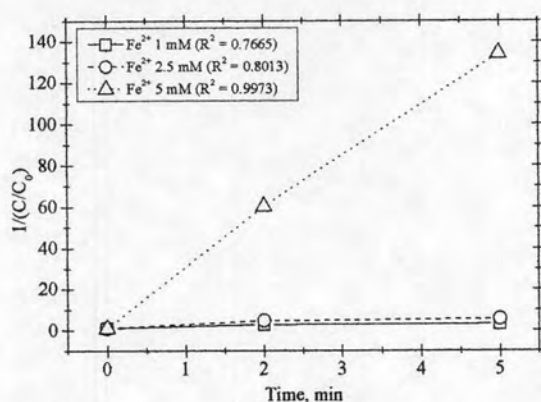
To analyze the kinetics of 2,6-dimethylaniline degradation, the plots of  $1/(C/C_0)$  versus time as pseudo-second order is presented in Figure 4.9(a) indicated that initial rates were linear-dependent with ferrous ion concentration.

Figure 4.9(b) shows reaction order with respect to ferrous ion was 2.55 which was the slope of the regression line with linear regression coefficient 0.83. The oxidation rate of 2,6-dimethylaniline can calculate as the following Equation:

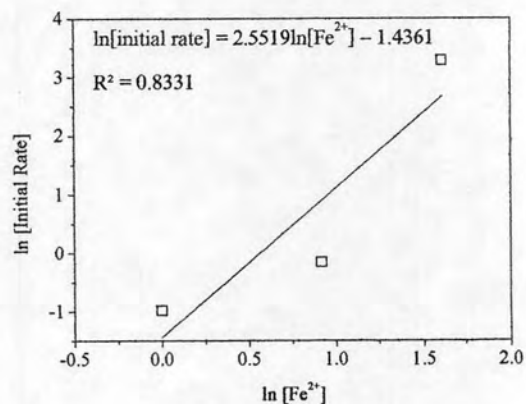
$$-\frac{d[2,6\text{-DMA}]}{dt} = k_{\text{Fe}^{2+}} [\text{Fe}^{2+}]^{2.55} \quad (4-6)$$

where  $d[2,6\text{-DMA}]/dt$  is in mM/min,  $k_{\text{Fe}^{2+}}$  is the apparent rate constants for fluidized-bed Fenton process with respect to ferrous ion as summarized in Table 4-3. This reported that initial rate constant in the effects of ferrous ion concentrations increase significantly from 0.38 to 26.45 mM/min. Otherwise, the ferrous ion had a catalytic decomposition effect on hydrogen peroxide. When ferrous ion concentration increased, the catalytic effect also accordingly increased. When the concentration of ferrous ion was higher, a great amount of ferric ion from the process of hydrogen peroxide decomposition by ferrous ion was easy to exit in the form of  $\text{Fe}(\text{OH})_3$  in acidic environment (Tamimi et al., 2008).

Then, ferrous ion precipitates as  $\text{Fe}(\text{OH})_3$  which requires additional separation and disposal. Since the rate of reductive dissolution is proportional to the surface area of oxide (Stone, 1987). The iron oxide can crystallize onto the surface of  $\text{Al}_2\text{O}_3$  by introducing hydrogen peroxide and  $\text{FeSO}_4$  in the fluidized-bed reactor. 2,6-dimethylaniline adsorbed on the  $\text{Al}_2\text{O}_3$  surface can readily exchange electrons with a ferric coated surface carrier, and can form inner-sphere surface complexes (Stumm and Sulzberger, 1992). Heterogeneous catalytic oxidation of 2,6-dimethylaniline donates electrons to enhance ferrous ion dissolution of  $\text{FeOOH}$  under acidic condition, which induces the homogeneous catalytic oxidation. Therefore, we can conclude that heterogeneous and homogeneous oxidation reactions are closely related (Chou et al., 1999).



(a) Relationship between  $1/(C/C_0)$  and time under different ferrous ion concentration



(b) Relationship between initial rate constant ( $\ln[\text{initial rate}]$ ) and initial ferrous ion concentration ( $\ln[\text{Fe}^{2+}]$ ) in normal scale

Figure 4.9 Effects of initial ferrous ion concentration on 2,6-dimethylaniline removal with FB-Fenton process as initial rate constant;

$$[2,6\text{-DMA}] = 1 \text{ mM}, [\text{H}_2\text{O}_2] = 15 \text{ mM}, \text{pH} = 3 \text{ and } \text{Al}_2\text{O}_3 = 74.07 \text{ g/l}$$

Table 4-3 Initial rate in 5 minutes of 2,6-dimethylaniline removal and percentage of 2,6-dimethylaniline removal in 150 minutes under different ferrous ion concentration;

$$[2,6\text{-DMA}] = 1 \text{ mM}, [\text{H}_2\text{O}_2] = 15 \text{ mM}, \text{pH} = 3 \text{ and } \text{Al}_2\text{O}_3 = 74.07 \text{ g/l}$$

$[\text{Fe}^{2+}]$ , mM	Initial rate, mM/min	% 2,6-DMA removal
1	0.38	82.83
2.5	0.85	95.44
5	26.45	92.90



#### 4.3.2.2. Effects of hydrogen peroxide concentration

Fenton's chemistry involved a complex collection of reaction pathways. Its utility as an oxidizing system relied on the formation of hydroxyl radical from hydrogen peroxide, through the reduction and oxidation cycles of iron and series of radical propagation and termination reactions. The influence of hydrogen peroxide concentrations on oxidation of 2,6-dimethylaniline were also investigated. From Figure 4.10, effects of hydrogen peroxide concentration were quite similar to those of ferrous ion. It showed that hydrogen peroxide concentration 1, 2.5, 5, 10, 15, and 20 mM can degrade 2,6-dimethylaniline, 39.42%, 73.33%, 92.90% and others 100%, respectively. Within first 2 minute the rapid consumptions of 5, 10, 15 and 20 mM of hydrogen peroxide concentration is exhibited.

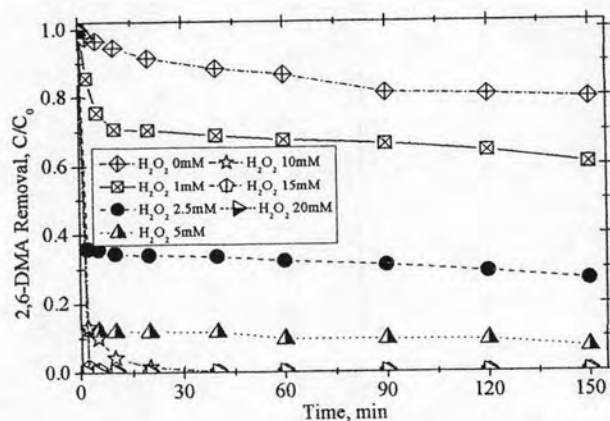
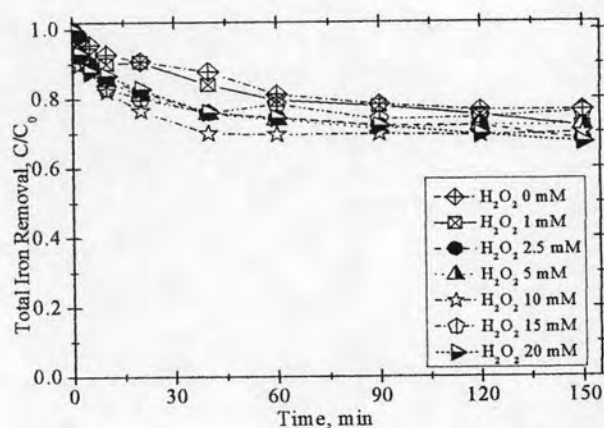


Figure 4.10 2,6-Dimethylaniline removal in the effect of hydrogen peroxide concentration on the removal efficiency of 2,6-dimethylaniline with FB-Fenton method;  
 $[2,6\text{-DMA}] = 1 \text{ mM}$ ,  $[\text{Fe}^{2+}] = 5 \text{ mM}$ ,  $\text{pH} = 3$  and  $\text{Al}_2\text{O}_3 = 74.07 \text{ g/l}$

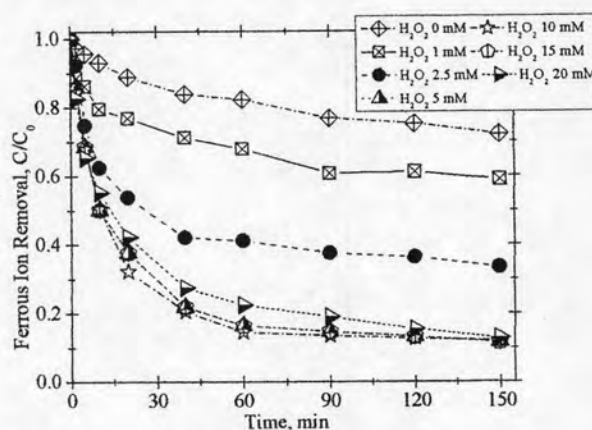
The change of total iron and ferrous ion concentration during the reaction is shown in Figure 4.11(a) and (b). The result indicates that there was non-different in total iron concentrations but a little difference in ferrous ion concentrations depending on the concentrations of hydrogen peroxide. The ferrous ion concentrations decreased with increasing hydrogen peroxide concentrations in the presence of 2,6-dimethylaniline and when the hydrogen peroxide concentration increased, the 2,6-dimethylaniline removal was higher because more ferrous ion and OH radical are formed at higher hydrogen peroxide concentration in solution. Moreover, if the hydrogen peroxide concentration was higher than a specific level, the degradation rate of 2,6-dimethylaniline slightly slow down. This can be explained by the scavenging effect. Generally, the critical hydrogen peroxide concentration is achieved. The reaction of hydrogen peroxide and OH radical in aqueous solution can be expressed by Equation (4-7)-(4-9) (Hsueh et al., 2006b).



Ferrous ion and hydrogen peroxide have an ability to compete with 2,6-dimethylaniline for OH radical under certain conditions. Since ratios of initial concentration of ferrous ion versus initial concentration of hydrogen peroxide used in variable value were less than one, Equation (4-7) became predominant (Neyens and Baeyens, 2003).



(a) Total iron removal



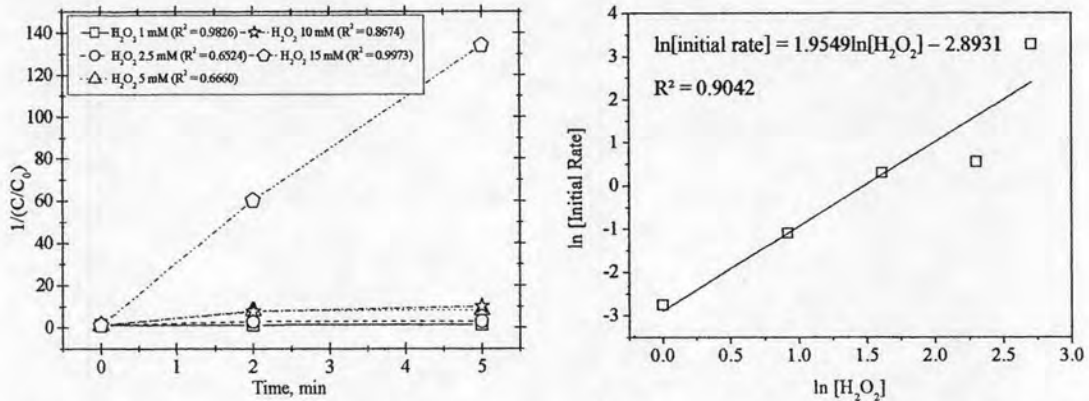
(b) Ferrous ion removal

Figure 4.11 Total iron removal (a) and ferrous ion removal (b) in the effect of hydrogen peroxide concentration on the removal efficiency of 2,6-dimethylaniline with FB-Fenton method;

$$[2,6\text{-DMA}] = 1 \text{ mM}, [\text{Fe}^{2+}] = 5 \text{ mM}, \text{pH} = 3 \text{ and } \text{Al}_2\text{O}_3 = 74.07 \text{ g/l}$$

If amount of hydrogen peroxide was much higher than the concentration of ferrous ion existing in solution, it implied that some part of hydrogen peroxide reacted with OH radical according to Equation (4-7) and  $\text{HO}_2\cdot$  is the perhydroxyl radical, which is a relatively weak oxidant compared to the OH radical. It has been proven that higher hydrogen peroxide concentration favors the above Equation (4-7)-(4-9). Furthermore, the initial organic concentration was much less than amount of initial hydrogen peroxide concentration due to the importance of hydrogen peroxide-scavenging reaction. Nonetheless, it was found that increasing in hydrogen peroxide slightly promoted the initial oxidation rate of 2,6-dimethylaniline.

To analyze the kinetics of 2,6-dimethylaniline degradation, the plots of  $1/(C/C_0)$  versus time as pseudo-second order is presented in Figure 4.12(a) indicated that initial rates were linear-dependent with added hydrogen peroxide.



(a) Relationship between  $1/(C/C_0)$  and time under different hydrogen peroxide concentration

(b) Relationship between initial rate constant ( $\ln[\text{initial rate}]$ ) and initial hydrogen peroxide concentration ( $\ln[H_2O_2]$ ) in normal scale

Figure 4.12 Effects of hydrogen peroxide concentration on 2,6-dimethylaniline removal with FB-Fenton process as initial rate constant;

$$[2,6\text{-DMA}] = 1 \text{ mM}, [Fe^{2+}] = 5 \text{ mM}, \text{pH} = 3 \text{ and } Al_2O_3 = 74.07 \text{ g/l}$$

Figure 4.12(b) shows reaction order with respect to ferrous ion was 1.95 which was the slope of the regression line with linear regression coefficient 0.90. The oxidation rate of 2,6-dimethylaniline can calculate as the following equation:

$$-\frac{d[2,6\text{-DMA}]}{dt} = k_{H_2O_2} [H_2O_2]^{1.95} \quad (4-10)$$

where  $d[2,6\text{-DMA}]/dt$  is in mM/min,  $k_{H_2O_2}$  is the apparent rate constants for fluidized-bed Fenton process with respect to hydrogen peroxide as summarized in Table 4-4 that should have been consumed rapidly by direct reaction with some descendant-generation intermediates so that very little has left for ferrous ion-catalysis reaction to form powerful radicals which can oxidized 2,6-dimethylaniline (Anotai et al., 2006). This reported that initial rate constant in the effects of

hydrogen peroxide concentrations increase significantly from 0.06 to 26.45 mM/min. It can be postulated that hydrogen peroxide should be added at an optimum concentration to achieve the best degradation. Relating that Kang et al. (2000) found Fenton process could remove color of the synthetic dye wastewater better when the hydrogen peroxide dosage increased. Also, Lu et al. (1999) reported that oxidation of DDVP by Fenton process proceeding to a greater extent when hydrogen peroxide increased.

Table 4-4 Initial rate in 5 minutes of 2,6-dimethylaniline removal and percentage of 2,6-dimethylaniline removal in 150 minutes under different hydrogen peroxide concentration; [2,6-DMA] = 1 mM,  $[\text{Fe}^{2+}] = 5 \text{ mM}$ , pH = 3 and  $\text{Al}_2\text{O}_3 = 74.07 \text{ g/l}$

$[\text{H}_2\text{O}_2]$ , mM	Initial rate, mM/min	% 2,6-DMA removal
1	0.06	39.42
2.5	0.33	73.33
5	1.34	92.90
10	1.73	100.00
15	26.45	100.00
20	ND*	100.00

\*ND = Non-detectable

#### 4.3.2.3. Effects of 2,6-dimethylaniline concentration

To investigate the effects of 2,6-dimethylaniline concentration on the oxidation rate by varying concentration from 0.5, 1 and 5 mM in 5 mM ferrous ion concentration, 5 mM hydrogen peroxide and  $\text{Al}_2\text{O}_3$  74.07 g/l at pH=3. As the result in Figure 4.13, 2,6-dimethylaniline concentration was rapidly degraded within 2 minute, but after that it was slow until nearly stable. The percent removals of 0.5, 1 and 5 mM 2,6-dimethylaniline were 59.17%, 92.19% and 100%, respectively. When increasing 2,6-dimethylaniline concentration from 0.5 mM to 5 mM, the initial degradation rate of 2,6-dimethylaniline was decreased. Also, Anotai et al. (2006) revealed that the aniline concentration increased from 0.005 to 0.05 M, the initial degradation rates were

also accelerated; however, was more evident in Fenton process. This was due to the fact that higher aniline concentration raised aniline ability to compete with ferrous ion for OH radical.

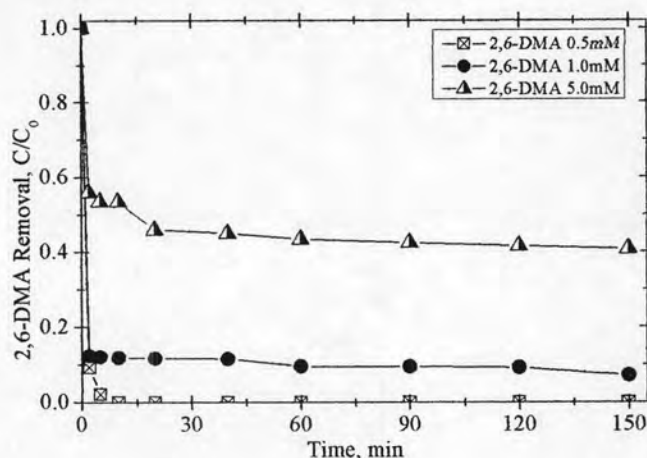


Figure 4.13 2,6-Dimethylaniline removal in the effect of 2,6-dimethylaniline on the removal efficiency of 2,6-dimethylaniline with FB-Fenton method;  
 $[\text{Fe}^{2+}] = 5 \text{ mM}$ ,  $[\text{H}_2\text{O}_2] = 5 \text{ mM}$ ,  $\text{pH}=3$  and  $\text{Al}_2\text{O}_3 = 74.07 \text{ g/l}$

To analyze the kinetics of 2,6-dimethylaniline degradation, the plots of  $1/(C/C_0)$  versus time as pseudo-second order is presented in Figure 4.14(a) indicated that initial rates were linear-dependent with initial 2,6-dimethylaniline.

Figure 4.14(b) shows reaction order with respect to ferrous ion was 0.28 which was the slope of the regression line with linear regression coefficient 0.82. The oxidation rate of 2,6-dimethylaniline can calculate as the following equation:

$$-\frac{d[2,6\text{-DMA}]}{dt} = k_{2,6\text{-DMA}}[2,6\text{-DMA}]^{0.28} \quad (4-11)$$

where  $d[2,6\text{-DMA}]/dt$  is in  $\text{mM}/\text{min}$ ,  $k_{2,6\text{-DMA}}$  was the apparent rate constants for fluidized-bed Fenton process with respect to 2,6-dimethylaniline as summarized in Table 4-5 This reported that initial rate constant in the effect of 2,6-dimethylaniline concentrations increased significantly from 2.0 to 4  $\text{mM}/\text{min}$ . It can be seen that when the initial 2,6-dimethylaniline concentration was

higher, the degradation ability of 2,6-dimethylaniline was increased. The concentration of 2,6-dimethylaniline as 0.5 mM and 1 mM showed the initial rate values were resemble because of low and approximate concentration, the Fenton's reaction worked with the similar efficiency.

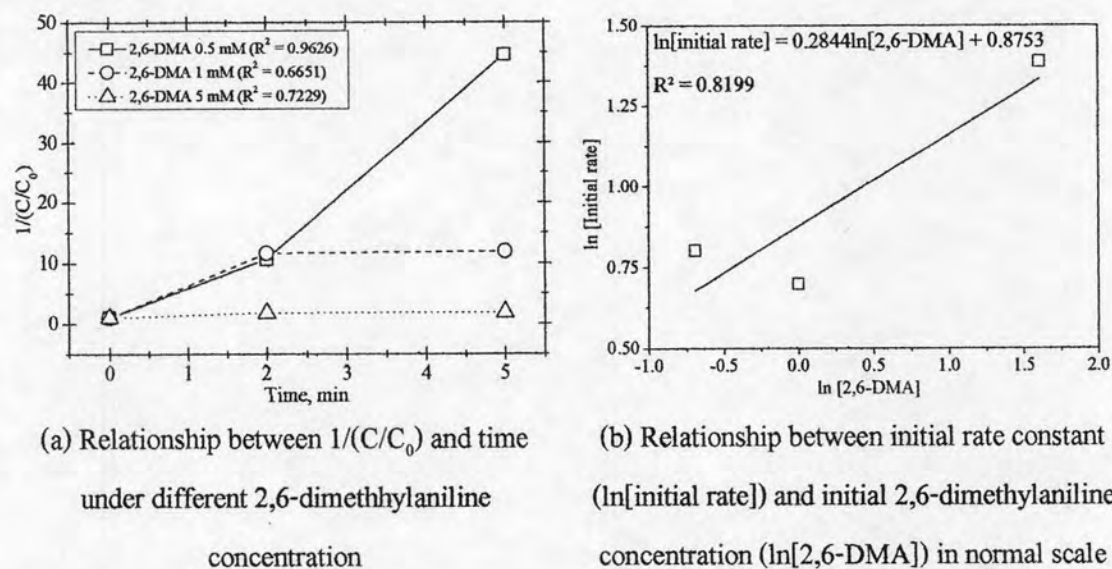


Figure 4.14 Effects of initial 2,6-dimethylaniline concentration

on 2,6-dimethylaniline removal with FB-Fenton process as initial rate constant;

$$[\text{Fe}^{2+}] = 5 \text{ mM}, [\text{H}_2\text{O}_2] = 5 \text{ mM}, \text{pH}=3 \text{ and } \text{Al}_2\text{O}_3 = 74.07 \text{ g/l}$$

Table 4-5 Initial rate in 5 minutes of 2,6-dimethylaniline removal and percentage of 2,6-dimethylaniline removal in 150 minutes under different 2,6-dimethylaniline concentration;  $[\text{Fe}^{2+}] = 5 \text{ mM}, [\text{H}_2\text{O}_2] = 5 \text{ mM}, \text{pH}=3$  and  $\text{Al}_2\text{O}_3 = 74.07 \text{ g/l}$

[2,6-DMA], mM	Initial rate, mM/min	% 2,6-DMA removal
0.5	2.23	100.00
1	2.01	95.07
5	4.00	59.17

#### 4.3.2.4. Overall kinetic rate

As the reaction orders of each part were known from Equation (4-6), (4-10) and (4-11), the initial rate equation for 2,6-dimethylaniline oxidation by fluidized-bed Fenton process can be written as:

$$-\frac{d[2,6\text{-DMA}]}{dt}, (mM/min) = k[\text{Fe}^{2+}]^{2.55}[\text{H}_2\text{O}_2]^{1.95}[2,6\text{-DMA}]^{0.28} \quad (4-12)$$

where “k” is the initial rate constant for 2,6-dimethylaniline oxidation by fluidized-bed Fenton process. The “k” value was determined by using a non-linear least square regression which minimizing the sum of error squares between the observed initial rates from the experiment of 2,6-dimethylaniline degradation and the calculated initial rate generated by Equation (4-12) and turned out to be  $4.10 \times 10^{-2}$ . Therefore, the final rate Equation became:

$$-\frac{d[2,6\text{-DMA}]}{dt}, (mM/min) = 4.10 \times 10^{-2}[\text{Fe}^{2+}]^{2.55}[\text{H}_2\text{O}_2]^{1.95}[2,6\text{-DMA}]^{0.28} \quad (4-13)$$

From above equation, it can conclude that the decomposition of 2,6-dimethylaniline was controlled by ferrous ion rather than hydrogen peroxide and 2,6-dimethylaniline.

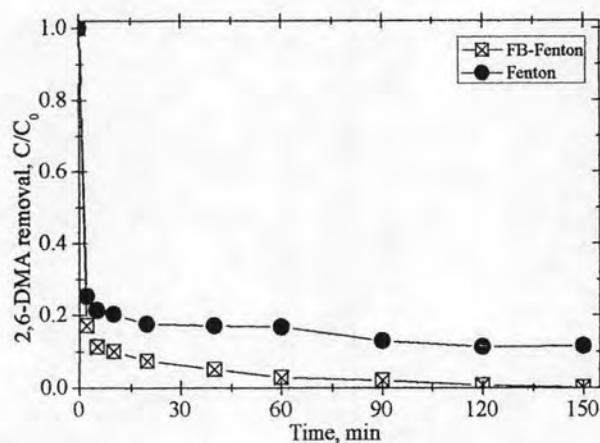
#### 4.3.3. Comparison between fluidized-bed Fenton and conventional Fenton in the optimum condition

From previous parts in this study, found that the optimum condition was 1 mM 2,6-dimethylaniline, 2.5 mM ferrous ion and 10 mM hydrogen peroxide at pH 3 because for ferrous ion, when use 5 mM, the reaction rate was too high and occurred the large amount of sludge after hydrogen peroxide was finished to be OH radical generation. Anyway, hydrogen peroxide at 10 mM was sufficient for this process.

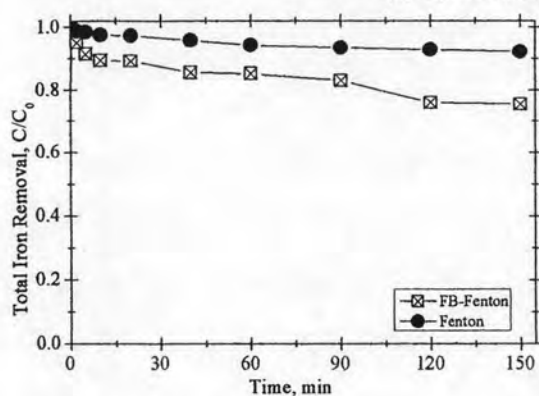
Figure 4.15(a) can be seen that initial 2,6-dimethylaniline removal efficiency for fluidized-bed Fenton 100% and 88.54% in Fenton. This is expected in the system with abundant ferrous ion since the major function of fluidized-bed Fenton is to crystallize ferric oxide onto the



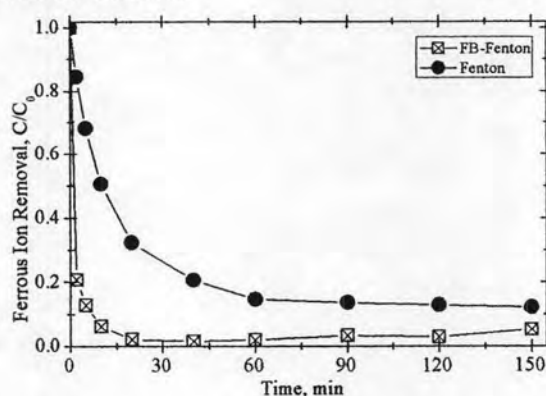
carried rather to improve the performance of organic oxidation. With the condition to use in this study, complete oxidation of 2,6-dimethylaniline can achieve within 150 minutes in fluidized-bed Fenton process, but in Fenton, disable to complete because of low rate of reaction. With the presence of carrier in fluidized-bed Fenton, the heterogeneous reactions became more complicated than Fenton with homogeneous solution. Hence, hydrogen peroxide reacted with ferrous reacted in more variety ways in the presence of  $\text{Al}_2\text{O}_3$  resulting the extra hydrogen peroxide and ferrous consumed. Certain amount of iron was removed from the solution by crystallization onto  $\text{Al}_2\text{O}_3$  surface as exhibited in Figure 4.15(b) and 4.15(c). The percentages of ferrous ion removal were 94.82% and 87.87% from fluidized-bed Fenton and Fenton processes, respectively.



(a) 2,6-Dimethylaniline removal



(b) Total iron removal



(c) Ferrous ion removal

Figure 4.15 Comparison between FB-Fenton and Fenton on

the removal efficiency of 2,6-dimethylaniline;

[2,6-DMA] = 1 mM,  $[\text{Fe}^{2+}] = 2.5 \text{ mM}$ ,  $[\text{H}_2\text{O}_2] = 10 \text{ mM}$ ,  $\text{pH}=3$  and  $\text{Al}_2\text{O}_3 = 74.07 \text{ g/l}$