CHAPTER II

THEORIES AND LITERATURE REVIEWS

2.1. Properties of 2,6-dimethylaniline

2.1.1. General Information

The trivial name of dimethylaniline is Xylidine, $(CH_3)_2C_6H_3NH_2$. There are six structural isomers, 2,2-Xylidine, 2,4-Xylidine, 2,5-Xylidine, 2,6-Xylidine, 3,4-Xylidine and 3,5-Xylidine. The names of six compounds indicate methyl group positions relative to the amino on the benzene ring. They can be obtained from coal tar as by-products in the fractional distillation or can be prepared by heating aniline hydrochloride with methanol at $220°C$. Xylidine is an aniline homologue and has similar properties of aromatic amine. Xylidines are brown liquids at room temperature except 3,4-Xylidine. They are sparingly soluble in water but miscible with ethanol and diethyl ether. They are sensitive to air and light and tend to darken on storage. They are toxic if inhaled, ingested, or absorbed through the skin. Xylidines and derivatives are widely used as raw materials to produce imaging chemicals like pigments and dyestuffs. All of these compounds are also used in the production of antioxidants, agricultural, pharmaceutical, rubber chemicals and other target organic molecules (Kornreich and Montgomery Jr., 1990). The chemical structure formula of this compound is indicated as in Figure 2.1.
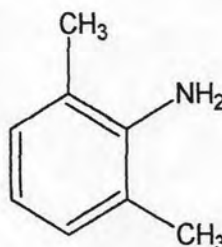

Figure 2.1 Structural formula of 2,6-dimethylaniline

(Source: http://www.sciencelab.com)

2.1.2. Physical and Chemical Properties

The Chemical and Physical Properties of 2,6-dimethylaniline are shown in Table 2.1

Table 2.1 Chemical and Physical Properties of 2,6-dimethylaniline

CAS NO.	$87 - 62 - 7$
Chemical formula	$(CH_3)_2C_6H_3NH_2$
Structural formula	As shown in Figure 3.1
Boiling range	216°C
Specific gravity	0.9842
Vapor pressure	0.02 kPa at 20°C
Vapor density	4.17
Solubility in water	0.7 g/100 ml water at 20°C
Soluble	Easily soluble in ethanol and diethyl ether. Very slightly soluble in cold water.
Water/Oil Distribution Coefficient	log(oil/water) = 1.8

Source: http://www.sciencelab.com

2.1.3. Toxicology Information

2,6-Dimethylaniline is a metabolite of the xylidine group of anaesthetics, including, for example, lidocaine, and is produced by the reduction of certain azo dyes by intestinal microflora. It may also enter the environment through degradation of certain pesticides.

2.1.3.1. Acute Toxicity

- **Human Toxicology**

2,6-Dimethylaniline can be absorbed into the body by inhalation of its aerosol, through the skin and by ingestion. A harmful contamination of the air can be reached rather quickly on

evaporation of this substance at 20°C. Because the vapor of 2,6-dimethylaniline is heavier than air. It decomposes on burning producing toxic and corrosive fumes, reacts violently with strong oxidants, reacts with hypochlorites forming explosive chloroamines and attacks plastic and rubber. Effects of short-term exposure are irritation to the eyes, the skin and the respiratory tract. Exposure at high levels may result in the formation of methaemoglobin. The effects may be delayed.

- **Animal Toxicology**

Oral Animal Toxicology LD50 is 707 mg/kg (mouse).

2.1.3.2. Chronic Toxicity

A Heinz-body hemolytic crisis may follow the development of methemoglobinemia. Heart, kidney, and liver damage may occur, possibly as secondary effects of hemolysis.

Carcinogenicity

- **Human carcinogenicity data**

Medical observation is indicated that effects of long-term or repeated exposure may possibly induce cancer to humans. The substance may have effects on the blood, resulting in anaemia. The carcinogenic effect to human of this kind of chemical was classified as 2B (possible for human) by IARC.

- **Animal carcinogenicity data**

2,6-Dimethylaniline was tested for carcinogenicity in one study in rats by pre- and postnatal administration in the diet. It induced adenomas and carcinomas as well as several sarcomas in the nasal cavity. It also produced subcutaneous fibromas and fibrosarcomas in both males and females and increased the incidence of neoplastic nodules in the livers of female rats.

Mutagenicity

2,6-Dimethylaniline gave conflicting results for gene mutation in bacteria. Sister chromatid exchange and chromosomal aberrations were induced in cultured mammalian cells.

The compound bound covalently to DNA in rat tissues but did not induce micronuclei in the bone marrow of mice treated in vivo.

2.2. Fenton Processes

Advanced Oxidation Processes (AOPs) have been viewed with great interest as a promising method for the removal of organic contaminants from water. In Table 2.2 is shown a potential for Water and Wastewater Treatment. Among various AOPs, Fenton's (H_2O_2/Fe^{2+}) has effectively treated various organic contaminants. The combination of hydrogen peroxide and a ferrous ion has been referred to as "Fenton's reagent". The reactivity of this system was first observed in 1894 by its inventor H.J.H. Fenton, but its utility was not recognized until the 1960s once the mechanisms were identified.

The main advantage is the complete destruction of contaminants to harmless compounds, e.g. CO_2, water and inorganic salts. The Fenton reaction causes the dissociation of the oxidant and the formation of highly reactive hydroxyl radicals that attack and destroy the organic pollutants (Neyens and Baeyens, 2003), under atmospheric pressure and room temperature. However, the limited range of pH (2-5) in which the reaction takes place and the recovery of iron species are the major drawbacks of this homogeneous process.

Table 2.2 Oxidation-Reduction Potentials of Chemical Reagents for Water and Wastewater Treatment

| Reaction	Potential in Volts (E^0) at 25 $^\circ$C
$F_2 + 2e^- \quad = \quad 2F^-$	2.87
$HO\bullet + H^+ + e^- \quad = \quad H_2O$	2.33
$FeO_4^{2-} + 8H^+ + 3e^- = Fe^{3+} + 4H_2O$	2.20
$O_3 + 2H^+ + 2e^- \quad = \quad O_2 + H_2O$	2.07
$H_2O_2 + 2H^+ + 2e^- = 2H_2O_2$ (acid)	1.76
$MnO_4^- + 4H^+ + 3e^- = MnO^2 + 2H_2O$	1.68
$HClO_2 + 3H^+ + 4e^- = Cl^- + 2H_2O$	1.57
$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$	1.49
$HOCl + H^+ + 2e^- \quad = \quad Cl^- + H_2O$	1.49
$Cl_2 + 2e^- \quad = \quad 2Cl^-$	1.36
$HOBr + H^+ + 2e^- \quad = \quad Cl^- + H_2O$	1.33
$O_3 + H_2O + 2e^- \quad = \quad O_2 + 2OH^-$	1.24
ClO_2 (gas) $+ e^- \quad = \quad ClO_2^-$	1.15
$Br_2 + 2e^- \quad = \quad 2Br^-$	1.07
$HOI + H^+ + 2e^- \quad = \quad I^- + H_2O$	0.99
ClO_2(aq) $+ e^- \quad = \quad ClO_2^-$	0.95
$ClO^- + 2H_2O + 2e^- = Cl^- + 2OH^-$	0.90
$H_2O_2 + 2H_3O + 2e^- = 4H_2O$ (basic)	0.87
$ClO_2 + 2H_2O + 4e^- = Cl^- + 4OH^-$	0.78

Source: Lide, 1992

2.2.1.3. Toxicology Information

According to the US regulation, no concentration of hydrogen peroxide is listed as the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) regulated substances (i.e., a persistent environmental hazard). Nor is the standard industrial strength hydrogen peroxide (that < 52% wt.) covered under the Federal Risk Management guidelines. However, a hazardous material permit-termed a Hazardous Materials Inventory Statement (HMIS) – may be required by local response agencies, depending on the concentration, volume, and location of hydrogen peroxide stored. If released to the environment, hydrogen peroxide will decompose to oxygen and water with concurrent generation of heat.

2.2.2. Fenton Reaction

In Fenton Process, hydrogen peroxide is decomposed by ferrous ion to produce highly reactive hydroxyl radical as expressed by Equation (2-1)

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH\bullet + OH^- \qquad (2\text{-}1)$$
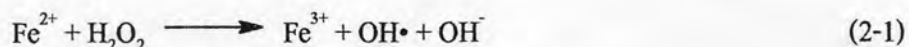
The hydroxyl radical can non-selectively attack the C-H bonds of organic molecules and is capable of degrading many solvents, haloalkanes, esters, aromatics, and pesticides (Haag and Yao, 1992). Huang et al. (1993) summarized the major advantages of using Fenton's process over other oxidation processes to treat hazardous wastes:

1) There are no chlorinated organic compounds formed during the oxidation process as in chlorination.
2) Both iron and hydrogen peroxide are inexpensive and non-toxic.
3) There are no mass transfer limitations because the reaction is homogeneous.
4) No light is required as a catalyst and, therefore, the design is much simpler than ultraviolet light systems.

2.2.1. Hydrogen Peroxide

2.2.1.1. General Information

Hydrogen peroxide was discovered by Therald, L.J. in 1818. Hydrogen peroxide is a ubiquitous compound present in natural water. Although pure hydrogen peroxide is fairly stable, it decomposes into water and oxygen when heated above about $60^{\circ}C$. One benefit of decomposition of hydrogen peroxide is that the released oxygen can stimulate aerobic biological activity. Hydrogen peroxide also decomposes in the presence of numerous catalysts, e.g., most metals, acids, bases, salt of metals, reducing agents, oxidizable organic materials, or flammable substances. Hydrogen peroxide is prepared commercially by oxidation of alkylhydro-anthraquinones or by electrolysis of ammonium bisulfate. It can also be prepared by reaction of barium peroxide with sulfuric acid or is prepared (with acetone) by oxidation of isopropanol.

Aqueous solution of hydrogen peroxide is mainly used for oxidation reactions, including blenching process, chemical syntheses, and for water and wastewater treatment. In drinking water purification, hydrogen peroxide is used to pre-oxidize organic constituents and to eliminate iron and manganese ions.
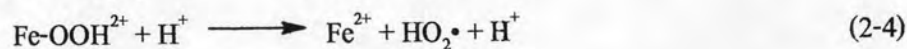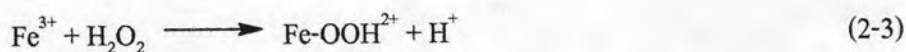
2.2.1.2. Physical and Chemical Properties

An aqueous solution of hydrogen peroxide is clear, colorless, water – like in appearance and nonflammable. It is miscible with cold water and is soluble in alcohol and ether. At high concentration, it has a slightly pungent or acidic odor. The chemical formula for hydrogen peroxide is H_2O_2 and its molecular weight is 34.015 g/mole.

5) Hydrogen peroxide can be electrochemically generated in situ, which may further increase the economic feasibility and effectiveness of this process for treating contaminated sites.

Under acidic condition and with an excess of ferrous ion, the hydroxyl radical generated can further react with ferrous ion to produce ferric ion:

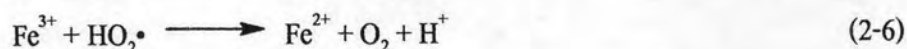$$Fe^{2+} + HO\bullet \longrightarrow Fe^{3+} + OH^- \qquad (2\text{-}2)$$

By properly controlling experimental conditions, ferric ion can be regenerated back to ferrous ion a subsequent reaction with another molecule of hydrogen peroxide:

$$Fe^{3+} + H_2O_2 \longrightarrow Fe\text{-}OOH^{2+} + H^+ \qquad (2\text{-}3)$$

$$Fe\text{-}OOH^{2+} + H^+ \longrightarrow Fe^{2+} + HO_2\bullet + H^+ \qquad (2\text{-}4)$$

The $HO_2\bullet$ radical produced have been shown to also participate in oxidation of some organic compounds, although they are much less reactive than hydroxyl radical.

The reaction of hydrogen peroxide with ferric ion is referred to as Fenton-like reaction (Equation (2-3) and (2-4)) (Walling and Goosen, 1973; DeLaat and Gallard, 1999)

$$Fe^{2+} + HO_2\bullet \longrightarrow Fe^{3+} + HO_2^- \qquad (2\text{-}5)$$

$$Fe^{3+} + HO_2\bullet \longrightarrow Fe^{2+} + O_2 + H^+ \qquad (2\text{-}6)$$

$$HO\bullet + H_2O_2 \longrightarrow H_2O + HO_2\bullet \qquad (2\text{-}7)$$

As seen in Equation (2-7), H_2O_2 can act as an $OH\bullet$ scavenger as well as an initiator (Equation (2-1))

Hydroxyl radicals can oxidize organics (RH) by abstraction of protons producing organic radicals ($R\bullet$), which are highly reactive and can be further oxidized (Walling and Kato, 1971; Venkatadri and Peters, 1993; Lin and Lo, 1997)

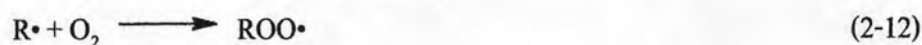$$RH + HO\bullet \longrightarrow H_2O + R\bullet \longrightarrow \text{further oxidation} \qquad (2\text{-}8)$$

If the concentrations of reactants are not limiting, the organics can be completely detoxified by full conversion to CO_2, water and in the case of substituted organics, inorganics salts if the treatment is continued.

Walling (1975) simplified the overall Fenton chemistry (reaction (2-1)) by accounting for the dissociation water.
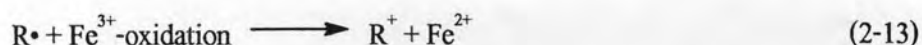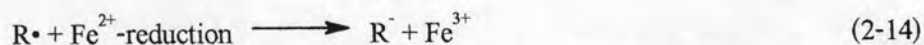
$$2Fe^{2+} + H_2O_2 + 2H^- \longrightarrow 2Fe^{3+} + 2H_2O \qquad (2\text{-}9)$$
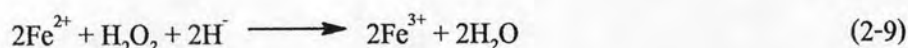
This Equation suggests that the presence of H^+ is required in the decomposition of hydrogen peroxide, indicating the need for an acid environment to produce the maximum amount of hydroxyl radicals. Previous Fenton studies have shown that acidic pH levels near 3 are usually optimum for Fenton oxidations (Hickey et al., 1995). In the presence of organic substrates (RH), excess ferrous ion, and at low pH, hydroxyl radicals can add to the aromatic or heterocyclic rings as well as to the unsaturated bonds of alkenes or alkynes.

They can also abstract a hydrogen atom, initiating a radical chain oxidation (Walling, 1975; Lipczynska-Kochany et al., 1995)

$$RH + OH\bullet \longrightarrow H_2O + R\bullet \qquad (2\text{-}10)$$

$$R\bullet + H_2O_2 \longrightarrow ROH + OH\bullet \qquad (2\text{-}11)$$

$$R\bullet + O_2 \longrightarrow ROO\bullet \qquad (2\text{-}12)$$

The organic free radicals produced in Equation (2-10) may then be oxidized by ferric ion, reduced by ferrous ion, or dimerised according to the following reactions (Tang and Tassos, 1997)

$$R\bullet + Fe^{3+}\text{-oxidation} \longrightarrow R^+ + Fe^{2+} \qquad (2\text{-}13)$$

$$R\bullet + Fe^{2+}\text{-reduction} \longrightarrow R^- + Fe^{3+} \tag{2-14}$$

$$2R\bullet\text{-dimerisation} \longrightarrow R-R \tag{2-15}$$

The sequence of Equation (2-1), (2-2), (2-10) and (2-13) constitute the present accepted scheme for the Fenton's reagent chain.

Fenton's reagent is known to have different treatment functions depending on the $H_2O_2/FeSO_4$ ratio. When the amount of Fe^{2+} employed exceeds that of hydrogen peroxide, the treatment tends to have the effect of chemical coagulation. When the two amounts are reversed, the treatment tends to have the effect of chemical oxidation.

2.2.3. Fluidized-bed Fenton Process

2.2.3.1. Reaction in fluidized-bed Fenton process

Fluidized-bed Fenton process lets ferric ion (Fe^{3+}), produced in the Fenton reaction, be transformed into iron oxide and accumulated onto the carrier surface via the crystallization or sedimentation. This process combines the functions of homogeneous chemical oxidation (H_2O_2/Fe^{2+}), heterogeneous chemical oxidation ($H_2O_2/$iron oxide), fluidized-bed crystallization, and reductive dissolution of iron oxide. This process not only attains high COD removal efficiency but also reduced the large amount of iron sludge being produced. Furthermore, iron oxide synthesis from the reaction of hydrogen peroxide and ferrous ion can also be used as the heterogeneous catalyst of hydrogen peroxide (Chou et al., 2003). The typical fluidized-bed reactor and its instrument set up are indicated as in Figure 2.2.

1. FBR
2. recycling pump
3. H_2O_2 feed pump
4. H_2O_2 container
5. Fe^{2+} feed pump
6. Fe^{2+} container
7. pH meter
8. 4 mm of glass bead
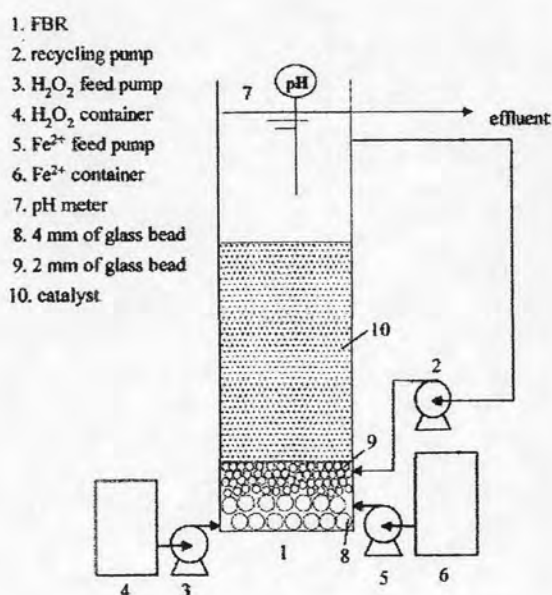9. 2 mm of glass bead
10. catalyst

Figure 2.2 Fluidized-bed Reactor (Chou et al., 2003)

The emphasis influencing of iron oxide growing on the surfaces of fluidized-bed carrier which are operated in fluidized-bed reactor are pH, specific iron loading, H_2O_2/Fe^{2+}, and superical velocity (Chou et al., 2004).

As Figure 2.3 illustrates the fluidized-bed Fenton reaction, the Fenton's reagent can produce the non-selective oxidant as OH radical via homogeneous reaction (a). Then, this strongly oxidant attacks the aromatic hydrocarbon to initiate ring opening in oxidation reaction (b). After that, the intermediate products from previous reaction appears, these lead into further oxidation (c). Also, ferric ion can be converted from the reducing one electron of ferrous ion in Fenton's reaction (d). Some ferric ion can be converted back to ferrous ion and initiate Fenton reaction further as in reaction (h). However, in the presence of solid carrier, the ferric hydrolysis product of Fenton's reaction can also crystallize and grow on the surface of the carriers (reaction (e)); hence, decreasing the precipitation in puffy ferric hydroxide forms (Chou et al., 1999b). At the same time, the synthesized ferric oxide can also serve as a catalyst for hydrogen peroxide decomposition in heterogeneous reaction (i) (Chou et al., 2003). When, considering iron oxide on the surface carriers, can re-dissolve via reductive dissolution (g) or heterogeneous reaction (f) also

to become ferrous ion form. In acidic environment, iron species can reform by the way ferric can alter to ferrous form also (d).
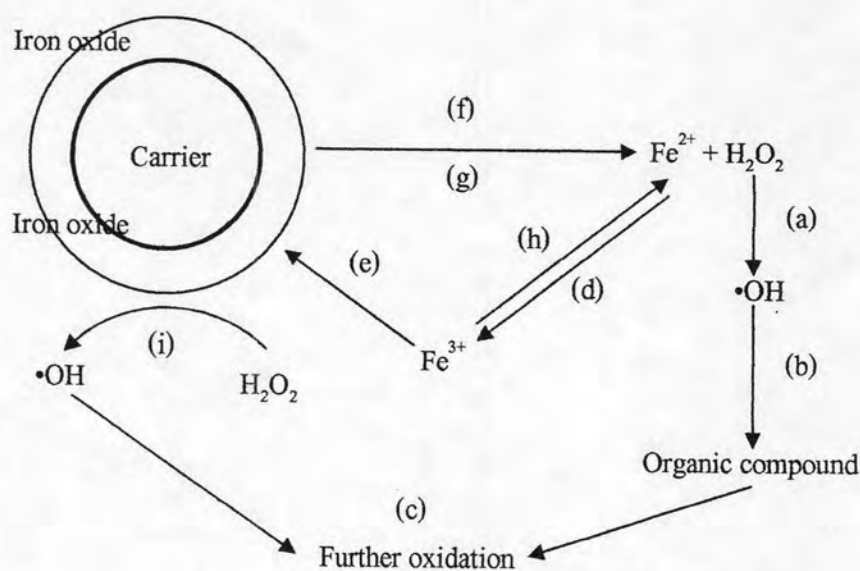

Figure 2.3 Fluidized-bed Fenton reactions

2.2.3.2. Carriers used by fluidized-bed Fenton process

Normally, carriers are used from previous study, such as SiO_2 and brick grain coated with γ-FeOOH (Chou and Huang, 1999a, 1999b; Chou et al., 1999 and Chou et al., 2004), Al_2O_3 and SiO_2 (Khunikakorn, 2005 and Ratanatamskul, 2006a, 2006b). The use of γ-FeOOH in Fenton process was found that they could effective oxidize organic compounds due to the catalysis of γ-FeOOH surface and ferrous ion generation. Ferrous ions are produced from the reductive dissolution of γ-FeOOH shown as below:

$$\gamma\text{-FeOOH}_{(s)} + 3H^+ + e^- \longrightarrow Fe^{2+} + 2H_2O \tag{2-16}$$
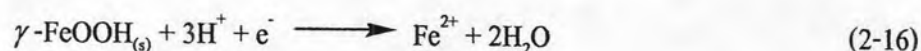
Chou et al. (1999a) used the supported γ-FeOOH acts as both the catalyst of hydrogen peroxide and the carriers of fluidized-bed reactor to oxidize benzoic acid. The ferric hydrolysis product of Fenton's reaction can crystallize and grow on this carrier to reduce the precipitation of

$Fe(OH)_3$. Almost the same as Al_2O_3 and SiO_2, the synthesis of γ-FeOOH on the carrier surface may occur via the oxidation of ferrous ion by hydrogen peroxide as below:

$$H_2O_2 + 2Fe^{2+} + 2H_2O \rightleftharpoons 2\gamma\text{-FeOOH} + 4H^+ \qquad (2\text{-}17)$$
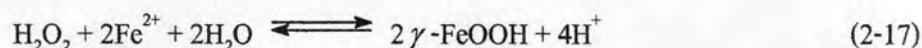
As seen in Equation (2-16) and (2-17), γ-FeOOH plays as the important role in fluidized-bed reactor because of the reductive dissolution of ferric to transfer electron to ferrous ion. The crystallization of ferric oxide also can reduce the large amount of sludge from this process.

2.2.4. Effect of system composition and process conditions

Many constituents of the water can affect the reaction rate and reaction stoichiometry due to absorption to surface active sites on the solid catalyst or through effects on the solution chemistry. Hence a process that has a high efficiency in degrading a contaminant in one type of water may be less efficient in another.

2.2.4.1. Effect of pH

The reaction rate of the homogeneous Fenton process tends to be highest at around pH 3 and decrease with increasing pH. The pH to change during the Fenton process, hence pH control is important in most processes.
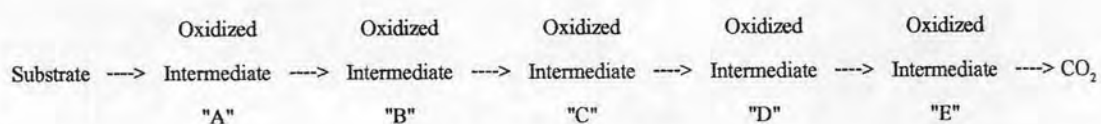
In a study by Chou et al. (2004) in which iron oxyhydroxide and Fenton's reagent were used in a fluidized-bed reactor (FBR), the pH was found to strongly affect the efficiencies of mineralization and ferric ion precipitation rates. When treating benzoic acid, they found that the degradation efficiency decrease with increasing pH, while the removal efficiency of total iron increased with pH in the pH range 2.8-4.5.

2.2.4.2. Fe : H_2O_2 ratio

The reaction rate tends to increase with increasing hydrogen peroxide concentration. However, the ferrous ion and hydrogen peroxide not only react to form hydroxyl radicals but are also scavengers of hydroxyl radicals. The ratio of ferrous ion to hydrogen peroxide should affect the rates of hydroxyl radical production and scavenging. Hence it is important to use the optimum Fe : H_2O_2 ratio. In a study on 2,4-D degradation by the anodic Fenton process, Wang and Lemley (2001) found that the optimum Fe(II) : H_2O_2 ratio was 1 : 10. This is close to the theoretical optimum ratio predicted by Tang and Huang (1996) in studies of the dark Fenton process.

Because of the indiscriminate nature by which hydroxyl radicals oxidize organic materials, it is important to profile the reaction in the laboratory for each waste to be treated. For example, in a typical application the following series of reactions will occur :

$$Substrate \xrightarrow{Oxidized} Intermediate \xrightarrow{Oxidized} Intermediate \xrightarrow{Oxidized} Intermediate \xrightarrow{Oxidized} Intermediate \xrightarrow{Oxidized} Intermediate \longrightarrow CO_2$$
$$"A" \quad\quad "B" \quad\quad "C" \quad\quad "D" \quad\quad "E"$$

Each transformation in this series has its own reaction rate and, as the case of phenolics illustrates, there may occur build-up of an undesirable intermediate (quinones), which requires sufficient H_2O_2 to be added to push the reaction beyond that point. This is frequently seen when pretreating a complex organic wastewater for toxicity reduction. As the H_2O_2 dose is increased, a steady reduction in COD may occur with little or no change in toxicity until a threshold is attained, whereupon further addition of H_2O_2 results in a rapid decrease in wastewater toxicity.

2.2.4.3. Oxygen

The presence of oxygen reduces the quantum yield of ferrous ion production from ferric ion oxalates. Balmer and Sulzberger (1999) carried out experiments under nitrogen to remove this effect and also saturated the water with synthetic air to maintain a constant oxygen concentration typical of a natural system. Utset et al. (2000) found that some substitution of

hydrogen peroxide by O_2 can occur; however, this limited the extent of degradation of the probe organic.

2.2.4.4. Inorganic anion concentration

Degradation rates by a Fenton process can be decreased due to the presence of certain anions that either scavenge hydroxyl radicals or form unreactive complexes with ferric ion. In a study of the degradation of 2,4-dichorophenoxyacetic acid (2,4-D) by Fe^{3+}/H_2O_2, Pignatello (1992) found that the inhibition of 2,4-D degradation followed the order $SO_4^{2-} \approx Cl^- >> NO_{2-} \approx ClO_4^-$, whereas the inhibition of ferric ion-catalyzed decomposition of H_2O_2 followed the order $SO_4^{2-} >> Cl^- > NO_{2-} \approx ClO_4^-$. It was concluded that sulphate ligands reduced the reactivity of Fe(III), while chloride was responsible for hydroxyl radical scavenging. Scavenging of hydroxyl radicals by chloride was also proposed by Kiwi et al. (2000) in a study of the degradation of dicholorvos by Fe^{2+}/H_2O_2 in the order $H_2PO_4^-$ was attributed to the formation of unreactive Fe^{3+} complexes.

2.2.4.5. Nature of the ligand

Organic ligands are used as complexing agent for ferric in the modified (photo-) Fenton process. The type of ligand used affects the efficiency of the process. Sun and Pignatello (1992) evaluated a wide range of chelating agents for their chelating ability and catalytic activity in the dark-modified Fenton process and the stability of the chelate. The most catalytically active ligands found in this study included picolinic acid, gallic acid, rhodizonic acid (NTA), hydroxyethyliminodiacetic acid (HEIDA), tetrahydroxy-1, 4-quinone and hexaketocyclohexane (HKCH).

When working on degradation of a range of pesticides using picolinic acid, gallic acid and rhodizonic acid as ligands, Sun and Pignatello (1993) found that the efficiency of the process depended on both the type of ligand and type of pesticide being used. These ligands have higher activities at pH 6 (especially for dark Fenton reactions) than oxalate and citrate; however, they tended to be less sTable under UV irradiation.

In a study of the degradation of Reactive Red 235 by a modified photo-Fenton process (using a mercury arc lamp, Fe(III), H_2O_2 and a ligand), Aplin (2001) found that the choice of the most effective ligand was dependent on the operating pH. At pH 3, dye degradation was the most rapid for oxalate (and was the same in the absence of ligands). At pH 4.5, degradation was also the most rapid for oxalate, however at pH 6, citrate gave the highest rate. Experiments were also carried out using glucarate, however dye degradation was relatively low due to the low photoactivity of Fe(III)-glucarate complexes. Hence the used must complex Fe(III) sufficiently strongly at the desired operating pH and be strongly photoactive.

In many applications, the oxidation of the chelating ligand may be considered an advantage provided it keeps the iron dissolved and catalytically active long enough for the desired extent of degradation of the contaminant to be achieved. This is because it removes the potential requirement for the ligand to be removed by other processes (Sun and Pignatello, 1992).

2.2.4.6. Effect of Temperature

The rate of reaction with Fenton's Reagent increases with increasing temperature, with the effect more pronounced at temperatures $< 20°C$. However, as temperatures increase above $40-50°C$, the efficiency of H_2O_2 utilization declines. This is due to the accelerated decomposition of H_2O_2 into oxygen and water. As a practical matter, most commercial applications of Fenton's Reagent occur at temperatures between $20-40°C$. Applications of Fenton's Reagent for pretreating high strength wastes may require controlled or sequential addition of H_2O_2 to moderate the rise in temperature which occurs as the reaction proceeds. This should be expected when H_2O_2 doses exceed 10-20 g/L. Moderating the temperature is important not only for economic reasons, but for safety reasons as well.

2.2.4.7. Effect of Reaction Time

The time needed to complete a Fenton reaction will depend on the many variables discussed above, most notably catalyst dose and wastewater strength. For simple phenol oxidation (less than 250 mg/L), typical reaction times are 30-60 minutes. For more complex or more

concentrated wastes, the reaction may take several hours. In such cases, performing the reaction in steps (adding both iron and hydrogen peroxide) may be more effective and safer than increasing the initial charges. Determining the completion of the reaction may prove troublesome. The presence of residual hydrogen peroxide will interfere with many wastewater analyses (see Interferences with Analytical Methods). Residual hydrogen peroxide may be removed by raising the pH to e.g., pH 7-10, or by neutralizing with bisulfite solution. Often, observing color changes can used to assess the reaction progression. Wastewaters will typically darken upon hydrogen peroxide addition and clear up as the reaction reaches completion.

2.2.4.8. Effect of Post Treatment

As a result of degrading complex organic materials into organic acid fragments, the pre-oxidized effluent is generally more amenable to conventional treatment, e.g., flocculation and biotreatment. The presence of iron in the reaction mixture makes it particularly suited to subsequent lime flocculation. In many cases, it may be possible to remove up to 80% of the wastewater COD through a combination of Fenton's Reagent and lime flocculation. Significantly, this may be achieved with hydrogen peroxide dose of 50-75% of the stoichiometry.

2.2.4.9. Effect of Iron Concentration

In the absence of iron, there is no evidence of hydroxyl radical formation when, for example, H_2O_2 is added to a phenolic wastewater (i.e., no reduction in the level of phenol occurs). As the concentration of iron is increased, phenol removal accelerates until a point is reached where further addition of iron becomes inefficient. This feature (an optimal dose range for iron catalyst) is characteristic of Fenton's Reagent, although the definition of the range varies between wastewaters. Three factors typically influence its definition:

A minimal threshold concentration of 2-15 mg/L iron which allows the reaction to proceed within a reasonable period of time regardless of the concentration of organic material;

A constant ratio of Fe : substrate above the minimal threshold, typically 1 part iron per 10-50 parts substrate, which produces the desired end products. Note that the ratio of iron : substrate may affect the distribution of reaction products; and

A supplemental aliquot of iron which saturates the chelating properties in the wastewater, thereby availing unsequestered iron to catalyze the formation of hydroxyl radicals.

Iron dose may also be expressed as a ratio to hydrogen peroxide dose. Typical ranges are 1 part Fe^{2+} per 5-25 parts H_2O_2 (wt/wt).

2.3. Literature Reviews

2.3.1. The Toxicology of 2,6-dimethylaniline

Yasuhara et al. (2000) investigated that whether the carcinogenic risk of 2,6-dimethylaniline, a metabolite of xylazine, may increase by ingestion of edible tissues from domestic animals treated with xylazine. From this study, suggested that the probability of nasal carcinogenic effects of dimethylaniline on consumers via ingestion of edible tissues from food-producing animals treated with xylazine is extremely low, since dimethylaniline levels in the blood of rats subjected to continuous administration of high doses of xylazine remained under the detection limit.

Kornreich and Montgomery, Jr. (1990) reported the toxicology and carcinogenesis studies of 2,6-Xylidine in Charles River CD rats. Under the conditions of these 2 years feed studies, 2,6-Xylidine was clearly carcinogenic for male and female Charles River CD rats, causing significant increases in the incidences of adenomas and carcinomas of the nasal cavity. A rhabdomyosarcoma, a rare tumor of the nasal cavity, was observed in dosed rats of each sex. In addition, the increased incidences of subcutaneous fibromas and fibrosarcomas in male and female rats and the increased incidence of neoplastic nodules of the liver in female rats may have been related to the administration of 2,6-Xylidine.

Short et al. (1989) studies the in vivo oxidative metabolism of 2,4- and 2,6-dimethylaniline in the dog and rat. The purpose of the present study was to examine pathways of in vivo metabolism of both isomers in the rat and dog. The major urinary metabolite of 2,4-dimethylaniline in the rat was N-acetyl-4-amino-3-methylbenzoic acid while in the dog it was 6-hydroxy-2,4-dimethylaniline. 2,6-dimethylaniline was metabolized principally to 4-hydroxy-2,6-dimethylaniline in both species, but the dog also produced significant quantities of 2-amino-3-methylbenzoic acid along with trace amounts of the glycine conjugate of the latter and 2,6-dimethylnitrosobenzene. In rats, repeated administration of either xylidine for 10 days failed to increase the appearance of metabolites, but 3-methylcholanthrene did increase the urinary concentration of N-acetyl-4-amino-3-methylbenzoic acid in 2,4-dimethylaniline dosed rats.

2.3.2. The removal oxidation of organic compound in heterogeneous catalysis in fluidized-bed reactor (FBR)

Muthuvel and Swaminathan (2007) examined that photoassisted Fenton mineralisation of an azo dye Acid Violet 7 was studied in detail using a Fe^{3+} loaded Al_2O_3 as a heterogeneous catalyst in the presence of H_2O_2 and UV-A light. The catalyst ferrioxalate–Al_2O_3 is more efficient than ferricnitrate–Al_2O_3. 35% Fe^{3+} loaded Al_2O_3 shows maximum efficiency in the degradation

Ratanatamskul et al. (2006a) studied color and COD removal of reactive dyes by fluidized-bed Fenton process from synthetic textile wastewater. This investigation reveals that fluidized-bed Fenton methods can remove the color and COD of these dyes. The effects of Fe^{2+} and H_2O_2 on dye decolorization and COD removal have been demonstrated in the study. The pH of all experiments was fixed at 3.0. Increasing the dose of ferrous enhanced the dye decolorization and COD removal. The optimal levels of H_2O_2 required for the process were also examined. High levels of H_2O_2 appeared to reduce COD removal. In addition, it is also found that decolorization of reactive dyes underwent a faster reaction rate than COD removal and condition for treating wastewater from industrial was $[COD]:[Fe^{2+}]:[H_2O_2] = 1:0.95:7.94$ and carrier 74.07 g/l at pH 3.

Khunikakorn (2005) investigated oxidation of aniline (AN) and nitrobenzene (NB) by fluidized-bed Fenton process using Al_2O_3 and SiO_2. Optimum pH for AN and NB oxidation were 3.2 and 2.8, respectively. Al_2O_3 was better than SiO_2 possible due to higher positive-charged surface at pH 2.8. In spite of comparable performance in organic oxidation, the fluidized-bed Fenton process was able to remove iron whereas the ordinary Fenton process could not. AN was found to be more vulnerable to hydroxyl radical oxidation than NB. When presenting at the same concentration, 72% of the generated hydroxyl radical reacted with AN whereas the rest of 28% were captured by NB. From the EDX analysis, iron oxide was crystallized onto the surface of the carriers and these iron-coated carriers could be reused successfully.

Hsueh et al. (2006b) studied that photoassisted Fenton degradation of Reactive Black 5 over a novel supported iron oxide catalyst at neutral pH using a fluidized-bed reactor (FBR), was utilized as a catalyst of the heterogeneous photoassisted Fenton degradation of azo-dye Reactive Black 5 (RB5). A simplified mechanism of Reactive Black 5 decomposition that is consistent with the experimental findings for a solution with a pH of up to 7.0 is proposed. About 70% decolorization was measured and 45% of the total organic carbon was eliminated on the surface of the iron oxide at pH 7.0 after 480 min in the presence of 0.055mM RB5, 5.0 g iron oxide/L, 29.4 mM H_2O_2, under 15W UVA.

Hsueh et al. (2006a) applied novel activated alumina-supported iron oxide-composite as a heterogeneous catalyst for photooxidative degradation of Reactive Black 5. A novel activated alumina-supported iron oxide-composite (denoted as FeAA-500) was prepared by so-called fluidized-bed reactor crystallization. The photo-catalytic activity of the FeAA-500 was evaluated in the photooxidative degradation of 0.1mM azo-dye Reactive Black 5 (RB5) in the presence of H_2O_2 and UVA light ($\lambda = 365$ nm) in a solution with a pH of 2.5. Complete decolorization of the model pollutant RB5 was achieved; the total organic carbon (TOC) removal ratio was 95%, and a trace amount of leached ferric ion was detected following 75 min of reaction when 2.0 g/L FeAA-500 was used as a catalyst. FeAA-500 has high photo-catalytic activity; it is therefore a promising heterogeneous photocatalysis of the degradation of organic compounds.

Chou et al. (2004) applied a novel supported iron oxyhydroxide (FeOOH) catalyst to treat benzoic acid by hydrogen peroxide using fluidized-bed crystallization reactor. The major components coated on the surface were identified as amorphous FeOOH and γ-FeOOH. In terms of the crystallization conditions of FeOOH, some parameters including the operational pH, superficial velocity, specific iron loading, and influent H_2O_2 concentration were investigated to quantify their effects on the crystallization efficiency. The crystallization reached the maximum between pH 3.0 and 4.0 and the crystallization increased with increasing H_2O_2/Fe^{2+} ratio, and then attained a plateau. The results indicated that, significant removal of benzoic acid (95%), TOC (49-59%) and ferric ion (70-90%) was attained within pH 3.4-3.7 and C_{Fei} of 28-130 mg/l.

Chou et al. (2001) investigated the kinetic approach of heterogeneous and homogeneous catalytic oxidation by supported γ-FeOOH in a fluidized-bed reactor. Experimental results indicate that the decomposition rate of H_2O_2 was proportional to its concentration and that the oxidation rate of BA depended on both H_2O_2 and BA concentrations. The change in the rate constant of heterogeneous catalysis by pH was described in terms of ionization fractions of surface hydroxyl group. Heterogeneous catalysis contributes primarily to the oxidation of BA at pH 4.4-7.0, the homogeneous catalysis is of increasing importance below pH 4.4 because of the reductive dissolution of γ-FeOOH.

Chou and Huang (1999b) examined decomposition of hydrogen peroxide in a catalytic fluidized-bed reactor. The decomposition of H_2O_2 by a novel supported γ-FeOOH catalyst was performed in a continuous fluidized-bed reactor. They attempted to determine the effects of pH, H_2O_2 concentration, and catalyst concentration on the decomposition of H_2O_2 including the kinetic behavior. At low H_2O_2 concentration, the decomposition rate of H_2O_2 was found to be proportional to both H_2O_2 and catalyst concentrations. At high H_2O_2 concentration, however, the rate decreased with the increasing H_2O_2 concentration.

Chou et al. (1999) investigated the effect of ferrous ion on the catalytic oxidation in the fluidized-bed reactor applying supported γ-FeOOH as the carrier. They found that both mineralization of organics and crystallization of ferric ion were simultaneously well performed under adequate condition. Moreover, the reductive dissolution and crystallization of γ-FeOOH as well as the oxidation of BA.

Brillas et al. (1998) compared the efficiency of Aniline mineralization by AOP's in many processes such as anodic oxidation, photocatalysis, electro-Fenton and photoelectro-Fenton processes. The aniline degradation in acidic medium of pH~3 under photocatalytic and electrochemical conditions has been investigated. The electrochemical experiments performed in the presence of both species (electro-Fenton conditions) leads to a fast aniline mineralization, which is notably increased by UVA irradiation (photoelectro-Fenton process). In photocatalysis with TiO_2 suspensions, the presence of H_2O_2 and ferrous ions in solution notably increases the aniline degradation rate at the initial stages of the process, whereas the opposite effect occurs at long irradiation times.

2.3.3. The removal oxidation of organic compound by other Fenton processes

Ting et al. (2008) studied that the kinetics of 2,6-dimethylaniline degradation by electro-Fenton process showed evidence of pseudo-first order degradation. When reaction pH was higher than 2, amorphous $Fe(OH)_3(s)$ was generated. Increasing ferrous ion concentration from 1.0 to 1.5mM increased the hydroxyl radicals and then promote the degradation efficiency of 2,6-dimethylaniline. The optimal hydrogen peroxide concentration for 2,6-dimethylaniline degradation in this study was 25 mM. The degradation of 2,6-dimethylaniline was increased with the increase of current density from 3.5 to 10.6 A/m^2.

Anotai et al. (2006) concluded the kinetics of aniline degradation by electro-Fenton processes was the aniline degradation rate was almost independent from Fenton's reagent concentrations as opposed to ordinary Fenton reaction which depend largely on Fe^{2+} and H_2O_2 dosages. The overall rate approaches half-order with respect to aniline concentration which

indicates that the decomposition of aniline was controlled by the reaction between aniline and •OH step rather than the Fe^{2+}-regeneration or •OH-production steps. This is the equation of electro-Fenton :

$$\left(\frac{d[\text{Aniline}]}{dt}\right)_{electro} = -k_{electro}[Fe^{2+}]^{-0.08}[H_2O_2]^{-0.14}[\text{Aniline}]^{0.46}$$

Lu et al. (2005) studied effect of chloride ions on the oxidation of aniline by Fenton's reagent. The objective of this study was to experimentally probe the mechanism of chloride ions specifically affecting aniline oxidation by Fenton's reagent. Results show that the inhibition caused by chloride ions can be overcome by extending the reaction time if the concentration of chloride ions is low. At a high concentration of chloride ions, however, the oxidation of aniline was inhibited, and actually ceased due to the complexation of Fe–Cl. If the ratio of $[Cl^-]/[Fe^{2+}]$ was ≤ 200, the inhibition effect was very significant. In other words, adding more ferrous ions rather than hydrogen peroxide can break the inhibition originating from the chloride ions at an initial stage of pH 3. The inhibition effect of chloride ions on the aniline reaction depended on the reaction pH; the extent of inhibition decreased with increasing the initial pH as long as the pH was less than 5. Consequently, the inhibition effect by chloride ions was primarily due to the complexation of iron species and chloride ions. The influence of chloride ions on aniline oxidation due to the competition of hydroxyl radicals was not significant.

Lu et al. (1999) showed that diclorvos decomposed in a two-stage reaction. The first stage is a Fe^{2+}/H_2O_2 reaction that diclorvos swiftly decomposed because of large amount of OH radical production to degrade organic. And, ferric ion produced in the first stage can react with hydrogen peroxide to produce hydroperoxyl radicals and ferrous ions. In second stage is a Fe^{3+}/H_2O_2 reaction that diclorvos decomposed less rapidly but ferric ion has a lower catalytic activity than ferrous ion and may complex with target organic substrates or their degradation intermediates that can produce weaker oxidants than hydroxyl radicals.

From the previous studies, the most important mechanism in fluidized-bed Fenton is heterogeneous chemical oxidation that can reduce the large amount of iron sludge by crystallization and sedimentation onto the carrier surface. Furthermore, FeOOH synthesized from the reaction of H_2O_2 and Fe^{2+} can be used as the heterogeneous catalyst. Fluidized-bed Fenton process may be more effective than Fenton Process so the assumption will be investigated in the following experiments.