

## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Aniline

##### 2.1.1 Physical and chemical properties

Aniline is an oily colourless liquid. It does not readily evaporate at room temperature. Aniline is prepared commercially by the reduction of nitrobenzene. It is used to make a wide variety of products such as polyurethane foam, agricultural chemicals, synthetic dyes, stabilizers for the rubber industry, herbicides, varnishes and explosives. Sulfonation of aniline yields sulfanilic acid, the parent compound of the sulfa drugs. Aniline is also important in the manufacture of rubber-processing chemicals. The physical and chemical properties are shown in Table 2.1.

##### 2.1.2 Toxicology of aniline

Aniline is toxic to organism because it damages hemoglobin, a protein that normally transports oxygen in the blood. This damaged hemoglobin can not carry oxygen known as methemoglobinemia and its severity depends on exposure level and time. Methemoglobinemia is the most prominent symptom of acute aniline poisoning in humans, resulting in cyanosis (a purplish blue skin color). Dizziness, headaches, irregular heart beat, convulsions, coma, and death may also occur. Direct contact with aniline can also produce skin and eye irritation. Long-term exposure to lower levels of aniline may cause symptoms similar to those experienced in acute high-level exposure. There is no reliable information on whether aniline has adverse reproductive effects in humans. Studies in animals have not demonstrated reproductive toxicity for aniline. First aid measures of aniline were shown in Table 2.2.

**Table 2.1** Physical and chemical properties of aniline (Schuchardt, 2000)

<b>Properties</b>	<b>value</b>
Molecular formula	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>
Molecular Weight; g/mole	93.13
pH value @ 36 g/l H <sub>2</sub> O; 20 °C	8.8
Melting Point; °C	-6.2
Boiling Point; °C	184.4
Density @ 20 °C; g/cm <sup>3</sup>	1.022
Flash Point; °C	70
Ignition Temperature; °C	615
Solubility in Water @ 20°C; g/L Ethanol @ 20°C Organic Solvents	36 free soluble miscible
Thermal Decomposition 20°C	190

**Table 2.2** First aid measures of aniline (Schuchardt, 2000)

<b>Contact by</b>	<b>How to first aid</b>
Inhalation	Taking to fresh air. Apply mouth-to-mouth resuscitation or mechanical ventilation if necessary. Summon doctor
Skin	Wash off with plenty of water. Dab with polyethylene glycol 400. Immediately remove contaminated clothing.
Eye	Rinse out with plenty of water for at least 10 minutes with the eyelid held wide open. Immediately summon eye specialist.
Swallowing	Make victim drink plenty of water, induce vomiting. Immediately summon doctor.

## 2.2 Nitrobenzene

### 2.2.1 Physical and chemical properties

Nitrobenzene is a colorless to pale yellow oily liquid that presents a fire hazard. Nitrobenzene does not occur naturally. It is a synthetic compound, more than 95% of which is used in the production of aniline, a major chemical intermediate that is used in the manufacture of polyurethanes. Nitrobenzene is also used as a solvent in petroleum refining, as a solvent in the manufacture of cellulose ethers and cellulose acetate, and in the manufacture of dinitrobenzenes and dichloroanilines (Weant & McCormick, 1984; Rogozen et al., 1987). It is also used in the synthesis of other organic compounds, including acetaminophen (ACGIH, 1991). Some chemical and physical properties of nitrobenzene are given in Table 2.3.

**Table 2.3. Some physical and chemical properties of nitrobenzene (ATSDR, 1990)**

Property	Value
Specific gravity	1.2037 at 20 °C
Molecular formula	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>
Melting point	5.7 °C
Boiling point	211 °C
Flash point (closed cup)	88 °C
Solubility in water	1900 mg/litre at 20 °C
	2090c mg/litre at 25 °C
Solubility in organic solvents	Freely soluble in ethanol, benzene, acetone

### 2.2.2 Toxicology of nitrobenzene

A small amount of nitrobenzene may cause mild irritation if it contacts the skin or eyes directly. Repeated exposures to a high concentration of nitrobenzene can result in methemoglobinemia, a condition in which the blood's ability to carry oxygen is reduced. In this condition, the skin may turn a bluish color and may have nausea, vomiting, and shortness of breath. Effects such as headache, irritability, dizziness, weakness, and drowsiness may also occur. There is also some evidence that breathing high concentrations of nitrobenzene may damage the liver. Animal studies have reported effects on the blood and liver from exposure to nitrobenzene. A single dose of nitrobenzene fed to male rats resulted in damage to the testicles and decreased levels of sperm.

### 2.3 Advanced oxidation processes (AOPs)

Destruction and mineralization of organic pollutants in wastewater have led to the development of advanced oxidation processes (AOPs), which almost completely rely on the generation of reactive free radicals, such as hydroxyl radicals ( $\cdot\text{OH}$ ). The hydroxyl radical is a powerful oxidant used in toxic contaminant degradation (Spacek, 1995; Lipczynska-Kochany, 1995). Hydroxyl radical has electrophilic property and its reaction is very high second order rate (Sonntag, 1996). Several methods,  $\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ , ozone, ozone/UV, ozone/ $\text{H}_2\text{O}_2$  processes and photocatalysis, are available for generating  $\cdot\text{OH}$ . Particularly, the conventional Fenton process has recently emerged as a promising technology due to its high efficiency and non toxic element (Elizardo, 1991; Pignatello, 1992). Moreover, this process is easy to operate and inexpensive.

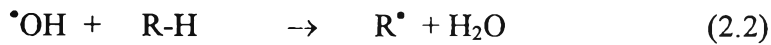
## 2.4 Hydroxyl radical

Hydroxyl radical is one of the most important oxidants generally found in air, water, and biological systems. It is characterized by one-electron deficiency compared to the thermodynamically stable specie, OH<sup>-</sup>. This radical is ubiquitous in the environment and is found in low concentrations in surface water and the atmosphere (Sedlak and Andren, 1991; Mill et al., 1980). Hydroxyl radical is a powerful oxidant, short-lived, highly reactive, and non-selective reagent that is easy to produce. It has a stronger oxidation potential than ozone, 2.80 V for <sup>•</sup>OH and 2.07 for ozone (Prengle and Mauk, 1978) as shown in Table 2.4. This table shows standard reduction potentials of some oxidants. The mean lifetime of hydroxyl radicals depends on their chemical environment and was estimated to be in the order of 10 μs in the presence of dissolved natural organic matter, bicarbonate and carbonate (Hoigne, 1998).

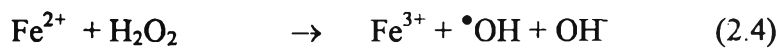
**Table 2.4** Standard reduction potentials of some oxidants (Hunsberger, 1977)

Oxidants	Standard reduction potential [Volt vs. NHE]
Fluorine (F <sub>2</sub> )	3.03
Hydroxyl radical (OH <sup>•</sup> )	2.80
Ozone (O <sub>3</sub> )	2.07
Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	1.78
Chlorine (Cl <sub>2</sub> )	1.36

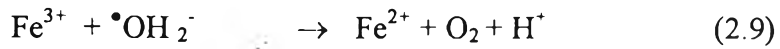
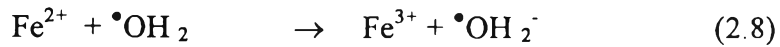
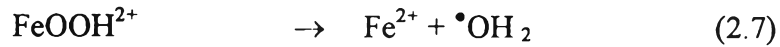
Hydroxyl radicals can oxidize organic and inorganic substrates by different types of reactions (Legrini, 1993; Hoigne, 1998) such as electron transfer, hydrogen abstraction and electrophilic addition (equations 2.1-2.3).

**Electron transfer****Hydrogen abstraction****Electrophilic addition****2.5 Conventional Fenton process**

Fenton process is referred to the combination of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and ferrous ion ( $\text{Fe}^{2+}$ ). By the reaction between ferrous ion and hydrogen peroxide, the reactive hydroxyl radical is generated which is the key mechanism of this process as shown in equation 2.4 and 2.5. Its detailed mechanism (Walling, 1975; Barb, 1951) is as follows:

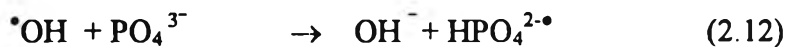


The ferric ion ( $\text{Fe}^{3+}$ ) produced from equation 2.4 can react with  $\text{H}_2\text{O}_2$  to generate  $\bullet\text{OH}_2$  (equation 2.6 and 2.7), which is a free radical with less oxidizing ability than  $\text{OH}\bullet$  (Barb, 1951; Walling, 1977).



In the presence of excess hydrogen peroxide,  $[\text{Fe}^{2+}]$  is small relative to  $[\text{Fe}^{3+}]$ , since Equation (2.6) is generally much slower than Equation (2.4). It is evident that ferrous ions are consumed quickly, but reproduced slowly (Lu, 1999; Pignatello, 1992).

Moreover, it was indicated that the hydroxyl radicals are scavenged by inorganic ions, such as  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{Cl}^-$ , as can be seen in Equations (2.10) to (2.13). Hydroxyl radical scavengers presented in many effluents can drastically reduce the efficiency of pollutant oxidation in direct proportion to their concentrations via the reactions as follows (Duguet et al., 1989):

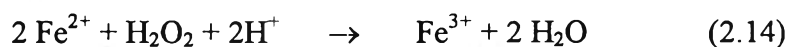


## 2.6 Factors affecting Fenton efficiency

There are many parameters affecting Fenton efficiency. The principal factors which can affect the Fenton reaction are the initial pH, concentration of  $\text{H}_2\text{O}_2$ , and concentration of  $\text{Fe}^{2+}$ .

### 2.6.1 Effect of pH

Fenton's reaction is strongly dependent on solution pH (equation 2.14). Solozhenko et. al (1995) and Hsueh et. al (2005) reported that the decolorization of azo dye in Fenton system could proceed only in acidic condition (pH 3). At solution pH values above 4, the degradation affecting the organic compound may decrease due to the precipitation of  $\text{Fe}^{2+}$  (Faust and Hoigne, 1990). Moreover, Kavitha and Palanivelu (2005) investigated the degradation of nitrophenols in Fenton process. The results of the study showed that Fenton process was an effective treatment method for nitrophenols under acidic conditions.



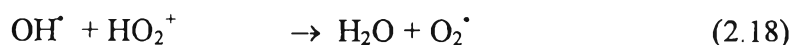
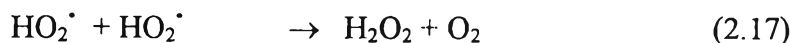
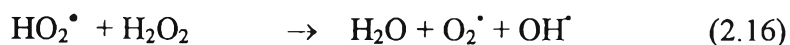
### 2.6.2 Effect of hydrogen peroxide and ferrous ion

Hydrogen peroxide and ferrous concentration are the key parameters in Fenton oxidation as shown on equation 2.4. The decomposition rate of organic contaminants increased with the increasing of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  (Lu, 1999; Brillas, 1998). Moreover, Casero et al. (1997) reported that high concentrations of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  were required to achieve mineralization. However, excess amount of  $\text{H}_2\text{O}_2$  acts as a hydroxyl radical scavenger as shown in the following Equation:

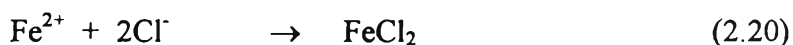
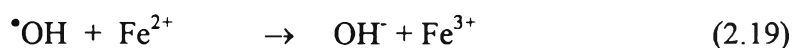


From equation 2.15,  $\text{OH}_2\cdot$ , low potential radicals, were produced. The reactions of this radicals led to the decreasing of the organic compound oxidation (see Equation (2.16) to (2.18)) (Schultei, 1991; Kochang and Bolton, 1992; Gmelin, 1996).





In the excess amount of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{2+}$  may become  $\text{OH}^\bullet$  scavenger because  $\text{OH}^\bullet$  will react with  $\text{Fe}^{2+}$  resulting in the inhibition of the oxidation reaction as shown in equation 2.19. Furthermore, the  $\text{Fe}^{2+}$  can limit the Fenton process by formation of ferrous ion complexes with free ion in the solution such as  $\text{Cl}^-$  as follow equation 2.20.



## 2.7 Application of Fenton process

As mentioned earlier, Fenton process is widely used in pollutant treatment processes. Many researches reported the application of Fenton process as shown below.

Solozhenko et al. (1995) reported the decolorization of azodye by Fenton process. It was found that this system could proceed only in acidic conditions. The decolorization might be accelerated by sunlight and increasing temperature.

Walter and Stephanie (1997) evaluated the degradation of trihalomethanes (THMs) in the Fenton process. The bromoform removal efficiency was at 85% within 3 minutes reaction time for a bromoform concentration of 295  $\mu\text{g/l}$ . Furthermore, increasing the initial organic concentration enhanced the oxidation of THMs.

Casero et al. (1997) studied the decomposition of aromatic amines in the Fenton process. They found that Fenton oxidation could be employed for effectively degrading aromatic amines in aqueous effluent. High concentrations of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  were required to achieve mineralization.

Sheng et al. (1999) studied the treatment of surfactant wastewater by the Fenton process. Anionic alkylbenzene sulfonate (ABS) and linear alkylbenzene sulfonate (LAS) were used as target compounds. Over 95% ABS and LAS surfactant removal was achieved at conditions of 90 mg/l  $\text{FeSO}_4$  and 60 mg/l  $\text{H}_2\text{O}_2$ . It showed that Fenton oxidation was more strongly dependent on  $[\text{FeSO}_4]$  than  $[\text{H}_2\text{O}_2]$ .

Lu et al. (1999) investigated the Fenton's reagent to oxidize dichlorvos insecticide. Results show that the dichlorvos decomposition in this system was divided into a two-stage reaction. The first stage was the reaction before 30 s in which the decomposition rate of dichlorvos was high; this stage was referred as  $\text{Fe}^{2+} / \text{H}_2\text{O}_2$  reaction. The second stage was the reaction that took place after 30 s. The decomposition rate of dichlorvos in this stage was slower; this was a  $\text{Fe}^{3+} / \text{H}_2\text{O}_2$  reaction. The optimum pH for the Fenton reaction to decompose dichlorvos in solution was around 3 to 4. As the added amount of hydrogen peroxide or ferrous ions increased, the decomposition rate of dichlorvos also increased.

The degradation of aromatic compounds has been studied (Sonntag, 1996; Sonntag and Schuchmann, 1991). For example, benzene and its derivatives react rapidly with  $\cdot\text{OH}$  radicals to yield cyclohexadienyl-type radicals (Figure), which immediately add dissolved molecular oxygen to the ortho or para position of the OH functional group (Sonntag and Schuchmann, 1991). The endoperoxide that is produced via intramolecular  $\text{O}_2$  radical addition to a double bond of the molecule is mainly responsible for the formation of open chain products with six or fewer carbon atoms. The main reaction product of  $\cdot\text{OH}$  radical initiated oxidation of benzene is phenol, in addition to cyclohexa-2, 5-diene-1, 4-diol, hydroquinone, and catechol (1,2-dihydroxybenzene).

The degradation of nitrophenols by Fenton process was studied by Kavitha and Palanivelu (2005). The results showed that nitrate ion was identified as major nitrogen by-product during nitrophenols oxidation. The processes can be modeled as a pseudo-first order when  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  are in excess with that of target nitrophenol compounds. The treatment efficiency for the nitrophenols follows the sequence: nitrophenol > dinitrophenol > trinitrophenol. The reactivity follows Hammett's law with regard to the effect of nitro groups on phenolic functionality for Fenton process.

Burbano et.al (2005) reported the degradation of MTBE in Fenton process. They found that the majority of MTBE degradation and generation of intermediates occurred during the initial phase. This first phase was controlled by Fenton reaction. The oxidation reaction was followed pseudo-first order kinetics. The subsequent phase was controlled by Fenton-like processes and had a negligible contribution to the overall degradation. Experiments at acidic pH yielded the best results of MTBE degradation, and there is no significant difference in result between the results at pH 3.0 and 5.0.

## 2.8 Degradation of aniline by AOPs

Sauleda and Brillas (2001) evaluated the mineralization of aniline in acidic solutions by ozonation. The study was conducted on  $1.07 \text{ mmol dm}^{-3}$  aniline or with  $1.38 \text{ mmol dm}^{-3}$  4-chlorophenol at acidic conditions.  $\text{Fe}^{2+}$  and UVA were used as ozonation catalysts. The results showed that the initial mineralization rate could be accelerated with the presence of  $\text{Fe}^{2+}$  and UVA due to increased production of oxidizing hydroxyl radicals. However, in adding  $\text{Fe}^{2+}$ , the degradation process was inhibited by the formation of stable complexes of  $\text{Fe}^{3+}$  with oxalate and other short organic diacides. *p*-Benzoquinone and nitrobenzene were identified as aniline oxidation intermediates.

Sanchez et al. (1997) studied the photocatalyzed destruction of aniline in UV-illuminated aqueous titanium dioxide. A Langmuir isotherm was fixed as the kinetic model of the process. The main parameter for the yield of photodegradation was the pH value. The effective yields were at very acid and basic media and also at pH values near the point of zero charge of titanium dioxide. The presence of small amounts of  $\text{Fe}^{2+}$  could increase the yield of photodegradation. Hydroxylated aromatic compounds such as phenol and hydrohydroquinone, paraquinone were detected as aniline intermediates in this system.

Brillas et al. (1998) investigated the aniline degradation by photocatalysis, electro-Fenton and photoelectron-Fenton processes. In electrochemical experiments, the addition of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  could help the aniline mineralization, which was enhanced by UVA irradiation. Moreover, benzoquinone, hydroquinone, phenol and 1,2,4-benzenetriol were found as aniline intermediates. In photocatalysis, the initial aniline degradation rate increased notably with the presence of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ . In contrast, little effect of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  addition was observed at long reaction times.

Qi et al. (2002) studied the decomposition of aniline in supercritical water. The experiments indicated that the supercritical water oxidation (SCWO) process was effective for destruction of aniline. This method is also appropriate for treating high concentration aniline wastewater. High temperature, long reaction time and increasing initial aniline dosage caused a pronounced effect on aniline decomposition.

Wenhua et al. (2000) investigated the degradation of aniline wastewater in a photocatalytic process with titanium dioxide immobilized on porous nickel as a catalyst. According to the results, this process has been shown to be efficient for the decomposition of aniline. A long irradiation time was required for complete mineralization. The main parameters, which affected the aniline degradation rate were aniline concentration, oxygen concentration and  $\text{H}_2\text{O}_2$  dosage.

## **2.9 Degradation of nitrobenzene by AOPs**

Lee and Park (1996) investigated the decomposition of nitrobenzene in supercritical water. The experiments were performed with and without oxygen. From the results, the presence of oxygen increased the nitrobenzene degradation rate. Moreover, the nitrobenzene concentration had a minimal effect on the decomposition kinetic.

In the ozonation of nitrobenzene in aqueous solutions, the combination of ozone with UV radiation does not significant for increasing the degradation and mineralization rates. pH value showed little effect on the combination O<sub>3</sub>/UV. The mineralization rate was increased by addition of Fe<sup>+3</sup> (Contreras et al., 2001).

Rodriguez et al. (2002) compared the effects of different irradiation sources on the treatment of nitrobenzene. The use of sunlight as a source of energy provided the effective mineralization of nitrobenzene in the photo-Fenton process. In addition, TOC reduction increased with increasing initial hydrogen peroxide concentration. For long irradiation times, the degradation of nitrobenzene was similar to that in the presence of Fe<sup>2+</sup> and Fe<sup>3+</sup>.

Piccinini et al. (1997) studied the mineralization of nitrogen-containing benzene derivatives in photocatalytic process. The results showed that nitrogen, nitrosobenzene, ammonia, nitrate, and nitrite ion were the main intermediates of nitrobenzene.

In this research, some of initial conditions were set by obtaining from many previous studied. For example, the initial H<sub>2</sub>O<sub>2</sub> concentration was obtained for the work of Solozhenko et al. (1995) as it is reported that the degree of azodye elimination was maximum at the ratio of H<sub>2</sub>O<sub>2</sub>/azodye as 15/1. Walter and Stephanie (1997) evaluated the degradation of bromoform was effective at the ratio of H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> as 5/1. Thus, this condition was used to design the initial Fe<sup>2+</sup> concentration. Solozhenko et. al (1995) and Hsueh et. al (2005) reported that in Fenton system could proceed only in acidic condition (pH 3). In this study, the pH 3 was selected as the initial pH value.