CHAPTER II

THEORIES AND LITERATURE REVIEWS

2.1 Advance Oxidation Processes

Advance Oxidation Processes (AOPs) are typically characterized by the generation and use of highly reactive chemical oxidant (Table 2.1) such as hydroxyl radical (·OH). These procedures consist of the chemical, photochemical and catalytic systems such as H_2O_2/Fe^{2+}, H_2O_2/O_3, UV/H_2O_2, $H_2O_2/Fe^{3+}/UV$, TiO_2/UV, $TiO_2/UV/O_3$ and $Fe^{2+}/UV/O_3$. ·OH is a non-selective and very strong oxidant able to react with most organics giving dehydrogenated or hydroxylated derivatives until their complete mineralization (Oturan, 2000; Boye et al., 2003; Flox et al., 2007). The reaction rate constants of ·OH are shown in Table 2.2. These radicals react with organic pollutants and thus lead to their degradation or conversion by hydrogen abstraction reaction, by redox reaction or by electrophilic addition, into CO_2, water and inorganic ions (Oturan, 2000). The most commonly used AOPs for removal of persistent organic pollutants from water is based on the Fenton reaction. Fenton reaction involves several sequential reaction steps which can be described as follows: (Walling and Goosen, 1973)

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + \cdot OH, \qquad (2.1)$$

$$\cdot OH + \text{Organics} \longrightarrow \text{Products}, \qquad (2.2)$$

$$Fe^{3+} + H_2O_2 \longrightarrow FeOOH^{2+} + H^+, \qquad (2.3)$$

$$FeOOH^{2+} \longrightarrow Fe^{2+} + \cdot HO_2, \qquad (2.4)$$

$$Fe^{2+} + \cdot HO_2 \longrightarrow Fe^{3+} + HO_2^-, \qquad (2.5)$$

$$Fe^{3+} + \cdot HO_2 \longrightarrow Fe^{2+} + O_2 + H^+. \qquad (2.6)$$

In the equations above, the radicals ·OH, $\cdot OH_2$ and $\cdot OH_2^-$ are consumed and regenerated in the reaction system, which is influenced by H_2O_2, Fe^{2+} and Fe^{3+} as shown in Figure 2.1 and equations (2.1) and (2.4) to (2.6). When electricity is employed in the process, Fe^{3+} can be reduced to Fe^{2+} more efficiently and rapidly which increases the reaction rate. The electro-Fenton process can be generally divided into three groups. The first group (EF-H_2O_2 method) uses Fe^{2+} and electrogenerated H_2O_2. The second type utilizes H_2O_2 and electrogenerated Fe^{2+} and the last group called Fenton sludge recycling (FSR) system which regenerates Fe^{2+} from Fe^{3+}. The Electro-Fenton process is carried out with a conventional anode and the oxidation power of electrogenerated H_2O_2 is enhanced by addition of Fe^{2+} to the solution because ·OH is formed from the classical Fenton's reaction between Fe^{2+} and H_2O_2 (Pignatello, 1992; Zuo and Hoigné, 1992). This catalytic reaction is propagated from Fe^{2+} regeneration, which takes place by the reduction of Fe^{3+} with H_2O_2 (reaction 2.1), with hydroperoxyl radical $\cdot OH_2$ (reaction 2.6) and/or with organic radical intermediates R· (reaction 2.7)

Table 2.1: Advance oxidation processes (Wojnárovits and Erzsébet, 2008)

Methods	**Reactive intermediate**
Ozone treatment: O_3 or O_3/H_2O_2	$\cdot OH$, $HO_2^{\cdot}/O_2^{\cdot -}$, $O_3^{\cdot -}$
Fenton processes: H_2O_2/Fe^{2+} or $H_2O_2/O_3/Fe^{2+}$ (acid media)	
Photo-Fenton processes using UV light in addition	$\cdot OH$
Photo-induced oxidation by UV (λ = 185 nm and 254 nm) or UV/O_3, UV/H_2O_2, respectively, using e.g. as catalyst	$\cdot OH$, $HO_2^{\cdot}/O_2^{\cdot -}$, $O_3^{\cdot -}$
Photocatalytic treatment: UV-Vis light	$\cdot OH$
Radiation-induced oxidation of pollutants using accelerated electrons, γ-rays, X-rays; synergistic effect in the presence of O_3/O_2, eventually H_2O_2 as additive	$\cdot OH$, $HO_2^{\cdot}/O_2^{\cdot -}$, $O_3^{\cdot -}$, e_{aq}^{-}, $H\cdot$
Electrochemicaloxidation	$\cdot OH$, $H\cdot$
Ultrasonic treatment (sonolysis of water)	
Thermal oxidation used for liquid industrial wastes	

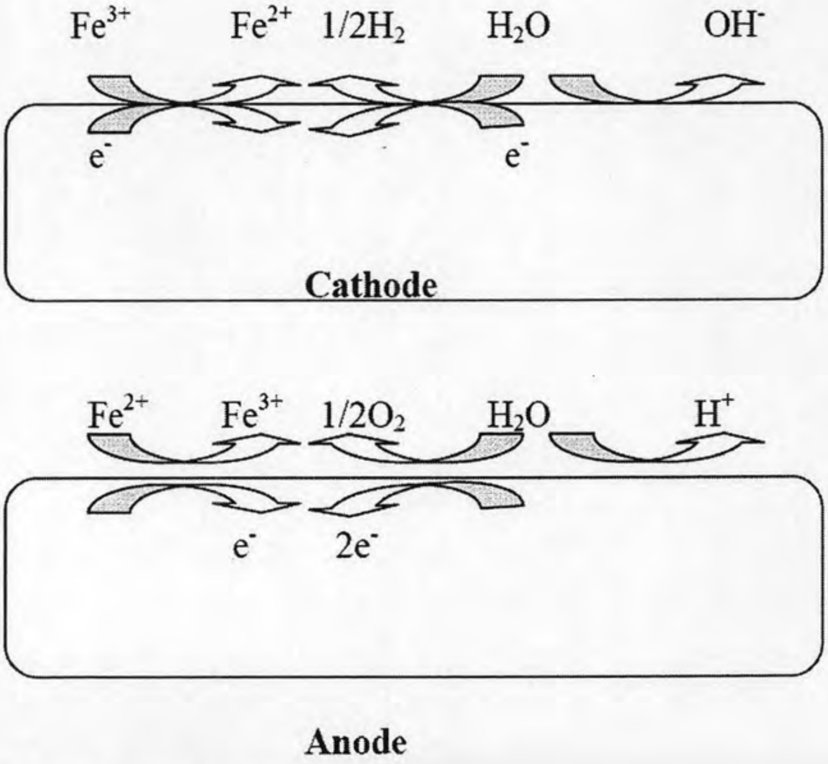

Figure 2.1: electro-Fenton reaction

Table 2.2: Reaction rate constants (k, $M^{-1}s^{-1}$) of hydroxyl radical (Richard, 1998)

Compound	**Reaction rate constant of ·OH**
Monocyclic Aromatic Hydrocarbon	
- Benzene	7.8×10^{9}
- Ethylbenzene	7.5×10^{9}
- Toluene	3.0×10^{9}
Chloronated Solvents	
- Trichloroethylene (TCE)	4.0×10^{8}
- Vinyl Chloride	1.2×10^{10}
Insecticides	
- Aldicarb	8.1×10^{9}
- Carbofuran	6.0×10^{8}
- Endrin	7.8×10^{8}
Herbicides	
- Atrazine	2.6×10^{9}
- Dalapon	7.3×10^{9}
Industrial Intermediates	
- Nitrobenzene	3.9×10^{9}
- Aniline	1.4×10^{10}
- Phenol	6.6×10^{9}
- Bromoform	1.3×10^{8}

$$Fe^{3+} + R\cdot \rightarrow Fe^{2+} + R^{+} \qquad (2.7)$$

2.1.1 Hydrogen peroxide

H_2O_2 is a powerful and versatile oxidant used in several applications. It is used to bleach textiles and paper products, to manufacture or process foods, minerals, petrochemicals, and consumer products such as detergents. H_2O_2 is considered an environmentally friendly chemical since it has none of the problems of gaseous release or chemical residues associated with other chemical oxidants. Its environmental applications include municipal odor control, BOD and COD removal from industrial wastewater, control of bulking, toxicity reduction and biodegradability improvement of recalcitrant compounds. H_2O_2 is commercially prepared by the oxidation of alkylhydroanthra-quinones and by the electrolysis of ammonium bisulphate. According to Chamarro et al. (2001), the peroxide dose is important in order to obtain a better degradation efficiency. The oxidizing efficiency of hydrogen peroxide can be significantly increased by a combination with UV radiation or metal salts. And from the study of Ku et al. (1998) which focused on the decomposition of EDTA in aqueous solution using H_2O_2 in the presence of Cu^{2+} ions, it was found that H_2O_2 was very stable at pH 3, when the system was in the absence of irradiation. However, the disappearance rates of H_2O_2 were markedly increased by UV irradiation in the absence or in the presence of Cu^{2+}, at the same pH. These results were supported by Ghiselli et al. (2004) who indicated that the formation of ·OH from H_2O_2 was enhanced in the presence of a catalyst, such as uncomplexed iron in both the (+II) and (+III) valence states. Under acidic conditions, the reaction between H_2O_2 and Fe^{2+} generates the hydroxyl radical (reaction 2.1), which, with a standard potential of 2.8 V (reaction 2.8) (Kavitha and Palanivelu, 2004), is second only to fluorine, one of the most powerful oxidizers known. Its high reactivity allows it to oxidize most organics as well as many inorganic compounds. The formation potential of typical oxidants are listed in Table 2.3.

$$\cdot OH + H^+ + e^- \longrightarrow H_2O \quad E^o = 2.8\ V \qquad (2.8)$$

2.1.2 Fenton Processes

Fenton (1894) reported that hydrogen peroxide could be activated by ferrous salts to oxidize tartaric acid. H_2O_2 is typically used together with Fe^{2+} to form Fenton's reaction. This technology uses the Fenton reaction as the source of ·OH. Fenton's reagent is a mixture of H_2O_2 and Fe^{2+}. The rate constant for the reaction of Fe^{2+} with H_2O_2 is high and Fe^{2+} is oxidized to ferric ion (Fe^{3+}) in a few seconds to minutes in the presence of excess amounts of H_2O_2. Reaction rates with Fenton's reagent are generally limited by the rate of OH• generation and less so by the specific wastewater being treated. The major advantage of Fenton process is that the reagent components are safe to handle and environmentally benign (Kavitha and Palanivelu, 2004) and seems to be promising for the purification of water polluted by persistent and/or toxic organic pollutions. However, its application has been limited due to the excess amount of ferric hydroxide sludge generated that requires additional separation process and disposal (Chou et al., 1999) such as precipitation tank, sedimentation tank, sand drying bed, etc., which further raises the overall treatment cost.

2.1.2.1 Electro-Fenton process

In recent years, indirect electro-oxidation method known as electro-Fenton is being developed for wastewater remediation. Besides direct electrochemical treatment, which allow the anodic or cathodic transformation of pollutants, indirect treatments promoting the electrochemical generation of strong oxidants have also undergone rapid development (Pozzo et al., 2004) and can be divided into three types as mentioned before.

Table 2.3: Formation potential of typical chemical reactants (Panizza et al., 2000; Troster et al., 2002)

Oxidants	**Formation potential**
$H_2O/\cdot OH$ (hydroxyl radical)	2.80
O_2/O_3 (ozone)	2.07
$SO_4^{2-}/S_2O_8^{2-}$ (peroxodisulfate)	2.01
MnO_2/MnO_4^{2-} (permanganate ion)	1.77
H_2O/ H_2O_2 (hydrogen peroxide)	1.77
Cl^-/ClO_2^- (chlorine dioxide)	1.57
Ag^+/Ag^{2+} (silver(II) ion)	1.5
Cl^-/Cl_2 (chlorine)	1.36
$Cr^{3+}/Cr_2O_7^{2-}$ (dichromate)	1.23
H_2O/O_2 (oxygen)	1.23

The first type uses Fe^{2+} and electrogenerated H_2O_2 which can be produced from the two-electron reduction of sparged oxygen on cathode such as graphite, reticulated vitreous carbon, or carbon-PTFE cathodes (Sudoh et al., 1986; Hsiao and Nobe, 1993; Brillas, 1996). Its disadvantage is the low current efficiency in acidic condition. The second type utilizes H_2O_2 and electrogenerated Fe^{2+} which is produced via the oxidation of iron, the sacrificial anode (Pratap and Lemley, 1994; Huang et al., 1999). The final type (FSR) applies H_2O_2 and electrogenerated Fe^{2+} produced via the reduction of ferric sulfate or ferric hydroxide sludge to ferrous ion (Chou et al., 1999). It is widely accepted that electrochemical oxidation is a promising technique for wastewater treatment and several model aromatic compounds have been used in order to assess the performance of different electrode material including the configuration of the reactor.

Many research works have been focused on the efficiency in oxidizing various pollutants of different electrodes, improvement of the electrocatalytic activity and electrochemical stability of electrode material, investigation of factors affecting the process performance, and exploration of the mechanisms and kinetics of pollutant degradation. Sires et al. (2007a) found the degradation of triclosan from saturated aqueous solution of pH 3.0 was completely removed by four electro-Fenton system which were Pt/carbon felt, BDD/carbon felt, Pt/O_2 diffusion and BDD/O_2 diffusion. Its decay in these cells followed the decreasing sequence: Pt/carbon felt > BDD/carbon felt > Pt/O_2 diffusion > BDD/O_2 diffusion, in agreement with the generation rate of $\cdot OH$ from Fenton's reaction which is the main oxidant of triclosan. In addition to the electrode materials, an increase in the electrode surface is important in the mass production of hydrogen peroxide, a three-dimensional electrode is attractive in industrial applications over a two-dimensional electrode, for its large electrode surface and higher mass transfer were used for removal of color from real dyeing wastewater as described by Wang et al. (2007). Efficiency of the electrochemical techniques in water treatment was also demonstrated in heterogeneous electro-oxidation and indirect electro-reduction studies (Oturan et al., 2000). The advantage of electrochemical process is mineralization of pollutants without sludge in the effluent that is a need of improvement of such techniques in AOPs. Iron sludge was eliminated by electro-regeneration of Fe^{2+} in term of current efficiency in the optimum conditions (Qiang et al., 2002).

$$Fe^{3+} + e^{-} \longrightarrow Fe^{2+}. \qquad (2.10)$$

According to the study of Flox et al. (2006), they found that the great oxidation ability of electro-Fenton and photoelectron-Fenton systems (used an undivided cell with a Pt or boron-doped diamond (BDD) anode and an O_2-diffusion cathode at 35.0 °C) was due to the large production of $\cdot OH$ at the anode surface from water oxidation and in the medium mainly from Fenton's reaction between catalytic Fe^{2+} and cathodically generated H_2O_2. Moreover, the capability of the electro-Fenton process has been confirmed by Harrington and Pletcher (1999), i.e., more than 90% COD removal of solutions containing phenol, aniline, acetic acid, formaldehyde, and three azo dyes, with current efficiencies higher than 50% and acceptable energy consumptions.

The current density is another important parameter that can affect on the mineralization of the pollutant. Ting et al. (2007) performed the effect of current density on the color removal indicated that the production rate of H_2O_2 increased when increase the current density therefore the removal efficiency increased with increasing current density. But, the removal efficiency was insignificant when the apparent current density exceeded 68 A/m^2. The same result was obtained from the study of Özcan et al. (2007), i.e., the degradation rate of picloram increased by increasing applied current from 30-300 mA.

2.1.2.2 Photoelectro-Fenton process

The latest development of Fenton process is the combination of sunlight/UV-irradiation and electro-oxidation known as photoelectron-Fenton (PEF). This process is also based on Fenton's reaction by using photo-induced Fenton processes (Brillas et al., 2000; Brillas and Casado, 2002; Boye, et al., 2003; Ventura, et al., 2002; Chou, et al., 1999; Wang, et al., 2005; Yuan and Lu, 2005). This method can improve the electro-Fenton method by illumination with UV or visible light during or after electrolysis (Brillas et al., 1996; 1998; Casado and Brillas, 1996; Boye et al., 2002). Photolysis or ultrasound alone was not effective, while photocatalysis or assisted photochemistry need additional reagent like H_2O_2 or TiO_2 and it is the same for assisted sonolysis (Yaun and Lu, 2005). As compared and described by Hernández et al. (2008) that the rate constant for the PEF process with 0.2 mM Fe^{2+} was the greatest and was more than twice as large as that for simple photolysis. The differences in the values of the rate constants presumably reflect the relative levels of available $\cdot OH$ provided by each of the treatment processes. PEF method can be feasible for the mineralization of refractory organic contaminants. Kavitha and Palanivelu (2004) described that the UV and sunlight in photo-Fenton processes provided photons to stimulate the regeneration of ferrous ion, for the cyclic production of $\cdot OH$ together with de-carboxylation of ferric carboxylates thereby enhancing the mineralisation process. Thus, the PEF process genernates a greater quantify of free radicals because of the contribution of both mechanisms (Brillas et al., 2004; Boye et al., 2002) supported by Irmak et al. (2005) who found that, in the presence of UV light, degradation of 4-chloro-2-methylphenol (PCOC) was observed to be faster due to photolysis of Fe^{3+} complex of PCOC and complexes of degradation products, e.g. oxalic acid (Zuo and Hoigne, 1992) and the additional photo-reduction of $Fe(OH)^{2+}$ species (reaction 2.11). Flox et al. (2007) showed the comparable efficiencies of PEF removed by both UVA and solar light, more than 96% of mecoprop mineralization but solar light allows a much faster and less expensive decontamination. Kavitha and Paleanivelu (2004) found the maximum mineralizing efficiency for phenol with solar and UV-Fenton processes were 96% and 97%, respectively, also determined.

The reaction of PEF process can described by (1) the production of greater amount of ·OH from photo-reduction of $Fe(OH)^{2+}$, the predominant Fe^{3+} species in acid medium (Pignatello et al., 2006; Sun and Pignatello, 1993) (reaction 2.10); and (2) the photodecomposition of complexes of Fe^{3+} with generated carboxylic acids such as oxalic acid and ferric acid or regeneration of Fe^{2+} from additional photo-reduction of Fe^{3+} species (Pignatello, 1992; Sun and Pignatello, 1993; Faust and Hoigné, 1990; Benkelberg and Warneck, 1995) (reaction 2.11) confirmed by Boye et al. (2003), all of products generated from the treatment process (such as glycolic, glyoxylic, formic, malic, maleic, fumaric and oxalic) are destroyed by electro-Fenton treatment, except oxalic acid which forms stable complexes with Fe^{3+}. These complexes were rapidly photodecarboxylated by UV light in the photoelectron-Fenton treatment. The photo-reduction of Fe^{3+} is advantage to Fenton process because the reduced iron can react with H_2O_2 to produce ·OH (Sahunil et al., 2003). Supported by Ting et al. (2007), the amount of ·OH occurred from photo-Fenton oxidation process is an important parameter for COD and color removal in wastewater in which the decreasing of COD and color related to the amount of ·OH occurred.

$$Fe(OH)^{2+} + h\nu \longrightarrow Fe^{2+} + \cdot OH \qquad (2.10)$$

$$R(CO_2)\text{-}Fe^{3+} + h\nu \longrightarrow R(\cdot CO_2) + Fe(II) \longrightarrow \cdot R + CO_2 \qquad (2.11)$$

Safarzadeh et al. (1996) revealed that carboxylates were formed during the photocatalyzed oxidation as shown in reaction 2.11 and were expected to play an important role in the treatment and mineralization of organic molecules. Safarzadeh (1993) showed that the irradiation of a ferrioxalate/H_2O_2 mixture with UV-visible light was a very effective system for the destruction of various organic pollutants in water media. Moreover, since these aromatic metabolites were practically as more as OT toward the ·OH, their oxidation continued with various oxidation reactions including hydrogen atom abstraction (demethylation), ·OH addition to aromatic rings (hydroxylation), electron transfer. At the very advance oxidation steps, the formed poly-hydroxylated or quinoid aromatic intermediates underwent an oxidative ring opening reaction into short-chain carboxylic acids which were finally mineralized (Oturan, 2000; Boye et al., 2003; Edelahi et al., 2003; Sirés et al., 2007a,b,c; Oturan et al., 2008). Boye et al. (2002) who studied 4-Chlorophenoxyacetic acid (4-CPA) degradation efficiency by anodic oxidation, anodic oxidation in the presence of electro-generated H_2O_2, electro-Fenton and photoelectro-Fenton methods and found that the highest TOC decay found for photoelectro-Fenton, with complete mineralization after 3 hours, can be related to the higher production rate of ·OH due to reaction (2.10) and/or additional photodecomposition of stable intermediates.

2.1.2.3 Effect of pH

Many researchers indicated that the optimum condition pH for Fenton processes is in acid range and the extent of degradation decreased with increasing pH greater 3 (Kuo, 1992; Dutta et al., 2002; Malik and Saha, 2003). The pH solution controls the production of ·OH and the concentration of Fe^{2+} (Pignatello and Oliveros, 2006; Abad et al., 2007; Muruganandham and Swaminathan, 2004; Sun, 2007). It is considered that more $Fe(OH)^+$ is formed at low pH (2-4) and the activity of $Fe(OH)^+$ is higher than Fe^{2+} in Fenton reaction (Malik and Saha, 2003). Boye et al. (2003) also indicated that both electro-Fenton and photoelectro-Fenton treatments are very efficient in the pH range 2.0-4.0. In contrast, Fe^{2+} is unstable at a pH > 4.0 and they easily form Fe^{3+}, which have a tendency to produce ferric hydroxo complexes. These complexes would form further $[Fe(OH)_4]^-$ when the pH value was greater than 9.0. Beside, H_2O_2 is also unstable in basic solution and may decompose to give oxygen and water and lose its oxidation ability (Wang, 2008). Hence, pH plays an important role in the electro-Fenton process. The production of ·OH and efficiency of catalyst depend largely on pH. The majority of previous works has been found that most effective pH was around 3 in order to promote the decomposition of H_2O_2 (reaction 2.1) as described by Wang et al. (2007). Low pH is favorable for the cathodic production of hydrogen peroxide because the conversion of dissolved oxygen to hydrogen peroxide consumes protons in acidic solution. According to Flox et al. (2006) who studied on the effect of pH between 2.0 and 6.0 for the degradation of indigo carmine, it was found that TOC removal in the pH range 2.0-4.0 was faster than that of pH 6.0 and quickest TOC decay occurred at pH 3.0 related to the highest generation rate of the main oxidant ·OH (reaction 2.1) and the degradation rate at pH 6.0 corroborates the small oxidizing power to produce ·OH in the medium. This was supported by Kim et al. (1999) and Kang et al. (2000) who studied the photo-Fenton process and found that this method was very effective for detoxification of organic compound in wastewater at pH 3.0. At neutral pH of 7, the efficiency for decomposition of H_2O_2 was low because at high pH, H_2O_2 converted to H_2O, O_2 and small amount of ·OH as described by Sahunil et al. (2003). At higher pH, oxides or hydroxides precipitates are formed; hence, slowing down the reaction. Moreover, these precipitates must be removed at the end of the process with additional cost (Pignatello, 1992 and Mcginnis et al., 2000).

2.1.2.4 Effect of catalysts Fe^{2+}/Fe^{3+}

Fenton reactions are based on a hydrogen peroxide solution and Fe^{2+} or Fe^{3+} salts in an acid medium. Fenton-like reactions can also use other metal salts in an acid medium. The use of the Fe^{2+}/H_2O_2 couple as an oxidant for wastewater treatment is attractive in many ways; iron is non-toxic, the second most abundant metal and the fourth most abundant element found in the Earth's crust where it is found as Fe^{2+} or Fe^{3+} ions, and H_2O_2 is easy to handle and is environmentally benign (Arslan and Gurses, 2004). Decomposition of H_2O_2 catalyzed by the metal ion generates a hydroxyl radical (·OH). Fe^{3+} (added or generated from Fe^{2+}) gives rise to a radical chain mechanism (reaction 2.1, reactions 2.3, 2.4-2.5). The species $\cdot HO_2$ is a weak oxidant. The identity of this species is still under discussion; however, it is accepted that, besides $\cdot OH$ radicals, active intermediates species such as FeO^{2+} or FeO^{3+} (iron as Fe(+IV) and Fe(+V), respectively) can take part of the oxidation process, as suggested by Kremer (1999) and Bossmann et al. (1998). The H_2O_2/Fe^{3+} system is more sensitive to pH than the H_2O_2/Fe^{2+} one because, at pH values lower than about 2, inhibition of prior complexation of Fe^{3+} by H_2O_2 occurs (reaction 2.3) and, when the pH increases above 3, precipitation of Fe^{3+} to amorphous oxyhydroxides ($Fe_2O_3 \cdot nH_2O$) decreases the iron concentration in solution as described by Pignatello (1992) and Lunar et al. (2000). Chamarro et al. (2001) pointed out that the iron concentration was important for the reaction kinetics. Increasing catalyst concentration can increase the degradation of organic pollutants as reported by many studies such as Rodríguez et al. (2001) who found the disappearance rate of phenol and nitrobenzene increased when increased the molar ratio of Fe(III)/organic. Özcan et al. (2007) found the degradation rate increased with increasing Fe^{3+} concentration up to 0.1 mM. Wang et al. (2007) found that the decolorization efficiency increased from 9% to 46% when ferrous ions increased. Finally, Boye et al. (2003) also found slight influence of higher Fe^{2+} concentration upon the degradative behavior of 2,4,5-T.

2.2 *o*-Toluidine

2.2.1 Properties of *o*-toluidine

o-toluidine or 2-methylaniline or 2-methylbenzenamine or 2-aminotoluene or 1-amino-2-methylbenzene or 2-amino-1-methylbenzene is an organic compound with the formula of C_7H_9N. The chemical structure of *o*-toluidine is showed in Figure 2.2. It is the simplest and one of the nitroaromatic amines. *o*-toluidine is a colorless to pale yellow liquid with a weak, pleasant odor. It can evaporate less than 1 mm Hg at 68°F. It has flash point at 185°F and slightly soluble. It is a combustible liquid and can produce the poison gas in fire. It can cause violent reactions when contacts with strong oxidant such as chlorine, bromine, and fluorine. It is used to make various dyes, printing textiles, blue-black, making colors fast, medical testing. It is also used in the production of rubber, chemicals, and pesticides and as a curing agent for epoxy resin systems. *o*-toluidine is also used as a corrosion inhibitor in paint formulations and possibly has limited uses in analytical laboratory procedures. There are no known domestic or household uses for *o*-toluidine. It is normally employed in its hydrochloride salt (*o*-toluidine hydrochloride),

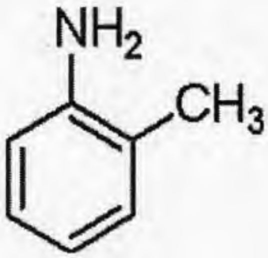

Figure 2.2: Chemical structure of *o*-toluidine

this is unlikely to significantly alter the observed health effects of the parent chemical. Global production data for o-toluidine were not identified. In the USA in 1975, more than 900 one of the chemical were produced, and another 1000 one were imported. Total production of o-toluidine in Great Britain is approximately 6000 tons per year, 90% of which is exported. Approximately 610 and 545 tons of *o*-toluidine were imported into Japan in 1992 and 1993, respectively (Gregg et al., 1998). From this reasons, it may enter the environment via industrial and municipal waste treatment plant discharges. Some substances increase in concentration, or bioaccumulation, in living organisms as they breathe contaminated air, drink contaminated water, or eat contaminated food. These chemicals can become concentrated in the tissues and internal organs of animals and humans. The concentration of o-toluidine found in fish tissues is expected to be about the same as the average concentration of *o*-toluidine in the water from which the fish was taken.

Acute toxic effects may include the death of animals, birds, or fish, and death or low growth rate in plants. Acute effects are seen two to four days after animals or plants come in contact with a toxic chemical substance. *o*-toluidine has moderate acute toxicity to aquatic life and moderate-to-high acute toxicity to birds. Insufficient data are available to evaluate or predict the short-term effects of *o*-toluidine to plants or land animals. For chronic toxic effects, it may include shortened lifespan, reproductive problems, lower fertility, and changes in appearance or behavior. It has moderate chronic toxicity to aquatic life.

2.2.2 Human health effect

o-toluidine is on the Hazardous Substance List because it is regulated by OSHA and cited by ACGIH, NTP, CAG and NFPA. The International Agency for Research on Cancer (IARC, 1987) has classified *o*-toluidine in Group 2B (possibly carcinogenic to humans), based upon sufficient evidence for carcinogenicity in animals and inadequate evidence for carcinogenicity in humans. This chemical is on the special health hazard substance list because it is a cancer causing agent and a mutagen. There may be no safe level of exposure to a carcinogen, so all contact should be reduced to the lowest possible level. The exposure limits are for air levels only. When skin contact also occurs, it may be overexposed, even though air levels are less than the limits listed. On the basis that the carcinogenicity of *o*-toluidine may involve a genotoxic mechanism, it is not possible to reliably identify a threshold at which exposure to *o*-toluidine would not result in some risk to human health (Gregg et al., 1998).

The acute (short term) health effects may occur immediately or shortly after exposure to *o*-toluidine. High exposure can lower the ability of the blood to carry oxygen (a condition called methemoglobinemia), causing bluish skin or lips (cyanosis), dizziness, headaches, collapse and even death. It can affect on health when breathed in and/or contact the skin and eyes, which could lead to permanent damage. Breathing the vapor or skin contact with the liquid can be induced methemoglobinemia disease. It can damage the kidneys and bladder, causing bloody urine after repeated exposure or long-term (chronic) exposure (Gregg et al., 1998). It has been shown to cause bladder, liver, blood vessel and other types of cancer in animals. Many scientists believe there is no safe level of exposure to a cancer causing agent. Such substances may also have the potential for causing reproductive damage in humans. According to the information presently available to the New Jersey Department of Health, it has not been tested for its ability to adversely affect reproduction.

2.2.3 Treatment application of nitroaromatic amines

Naturally occurring nitroaromatics are seldom but the contamination of soil and water with such compounds is a widespread environmental problem. Because of their extreme xenobiotic character they were persistent. Relevant information on the effects of *o*-toluidine on aquatic or terrestrial organisms was not identified. However, toxicity thresholds for the inhibition of algal growth (Microcystis aeruginosa, 0.31 mg/liter; Scenedesmus quadricauda, 6.3 mg/liter) have been reported (Gregg et al, 1998). Blotevogel et al. who studied the transformation and degradation of nitrodiphenylamines, toluidines and aniline by sulfate-reducing bacteria under anoxic condition found that nitrodiphenylamines were transformed and cleaved to their monomeric products. Cleavage of the dimeric compound resulted in the formation of aniline. Further studies with *Db. anilini* showed slow degradation of aniline and toluidines under sulfate-reducing conditions as previously reported by Schnell and Schink (1991). In addition, toluidines could be desintegrated by *D. toluolica*. After carboxylation of *p*-toluidine to 4-aminophenylacetic acid, complete usage of this compound as a source for carbon and energy was observed.