

## Chapter II

### Theories and Literature Reviews

#### 2.1 Properties of Nitrobenzene

U.S. EPA, 1995; Agency for Toxic Substances and Disease Registry, 1990

##### 2.1.1 General Information

Nitrobenzene is a common industrial chemical. It is an oily yellow liquid at ambient conditions with an almond-like odor. It is only slightly soluble in water (0.19% at 20°C; 0.8% at 80°C) and will evaporate when exposed to air. This chemical has been found in at least 7 of the 1,177 National Priorities List sites identified by the U.S. Environmental Protection Agency (U.S.EPA). The formula of nitrobenzene is  $C_6H_5NO_2$  with the molecular structure as shown in figure 2.1

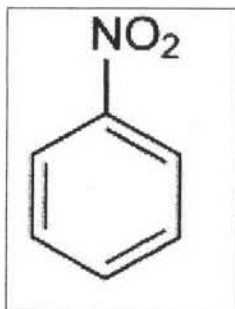


Figure 2.1 Structure of nitrobenzene

It is produced in large quantities for use in industries. Most of the nitrobenzene is produced in the United States and is primarily used to manufacture a chemical called "aniline". Nitrobenzene is also used to produce lubricating oils such as those used in motors and machinery. A small amount of nitrobenzene is used in the manufacture of dyes, drugs, pesticides, and synthetic rubber.

Nitrobenzene may be presented in water from industrial releases and will be broken down by sunlight, and lower levels may be found in air. Nitrobenzene in soil can move into the groundwater, taken up by plants, evaporated to the air, and broken down by bacteria. It is not expected to concentrate in fish or other aquatic lives.

### 2.1.2 Physical and Chemical Properties

Nitrobenzene is used mainly as an intermediate to produce another chemical. Repeated exposures to high levels result in a blood disorder in people. Its physical and chemical properties are shown in Table 2.1.

Table 2.1 Physical and chemical properties of nitrobenzene

Property	Value
Molecular formula	$C_6H_5NO_2$
Molecular weight	123.11 g/mol
Appearance	Pale yellow to brown, oily liquid
Odor	Almond odor
Vapor Density (air = 1)	4.3
Boiling point	211°C
Melting point	5.7°C
Water Solubility	2.9 g/L @ 25°C
Specific Gravity	1.20 @ 20°C/4°C
Vapor pressure	1.0 mm Hg @ 44.4°C
LogK <sub>oc</sub>	1.56
LogK <sub>ow</sub>	1.85
Reactivity	flammable
Flash point (closed cup)	88°C

### 2.1.3 Toxicology

Nitrobenzene can be toxic to organism because nitrobenzene reacts with red blood cells in the body to produce methemoglobin. In the person who has recently been exposed to nitrobenzene, the level of methemoglobin in his/her body may be elevated. However, since the toxic chemicals also produce methemoglobin, this system does not definitely verify the nitrobenzene exposure. In case of long-term exposure to nitrobenzene, the presence of its breakdown products, i.e, p-aminophenol and p-aminophenol, in the urine can be an evident indicator for nitrobenzene exposure. These tests require special equipment and cannot be routinely done in doctor's office. The results of these tests cannot be use determine the level of nitrobenzene exposure or whether to identify harmful health effects expected to occur.

A small amount of nitrobenzene may cause mild irritation if it contacts to skin or eyes directly. Repeated to a high concentration of nitrobenzene can result in methemoglobinemia, a condition in which the blood's ability to carry oxygen is reduced. Under this condition, the skin maybe turn a bluish color and the person may have nausea, vomiting, and shortness of breath. Other effects such as headache, irritability, dizziness, weakness, and drowsiness may also occur. There is also evidence that breathing high concentrations of nitrobenzene may damage the liver. Animal studies have reports 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. The general public potentially is exposed to nitrobenzene in the environment through inhalation of ambient air, ingestion of water, or dermal contact with products or water containing nitrobenzene. Two air surveys, one of almost 600 urban and suburban sites in the United States and one of more than 700 U.S. sites, reported mean concentration of nitrobenzene to be 0.17 ppb and 0.117 ppb, respectively. In a survey of hazardous waste site, nitrobenzene was detected in groundwater at three sites, at a geometric mean concentration of 1.4 ng/L, but was not detected in surface-water wimples from any sites. Occupational exposure to nitrobenzene generally is by inhalation of the vapor or dermal contact with the vapor or liquid. Direct release of nitrobenzene to air during its manufacture is minimized by passage of contaminated air through activated charcoal. Most (97% to 98%) of the

nitrobenzene produced is retained in closed systems for use in synthesis of aniline and other substituted nitrobenzene and anilines, thus limiting its release into air. Typical toxicological information of nitrobenzene exposure are :

- Toxicological Data* : Oral rat LD<sub>50</sub> : 780 mg/kg; skin rat LD<sub>50</sub> : 2,100 mg/kg; investigated as a mutagen, reproductive effector.
- Reproductive Toxicity* : In laboratory animals, this compound has caused both birth defects and damage to reproductive system.
- Carcinogenicity* : A two year study entitled "A Chronic Inhalation Toxicity Study of Nitrobenzene in B6CF1 Mice, Fischer 344 Rats and Sprague- Dawley Rats", was releases by the Chemical Industry Institute of Toxicology (CIIT). The report indicates that nitrobenzene has a weak carcinogenic activity in humans. Based upon the results of these animal testings, nitrobenzene should be handled as a potential carcinogen.

#### 2.1.4 First Aid Measures (Environmental Health and Safety)

[<http://www.jtbaker.com/msds/englishhtml/n4530.html>]

Nitrobenzene is the chemical substance that can be toxic to organisms in the body if ingested or contact as mentioned above. The first aid measures are :

- Inhalation* : If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Do not give mouth to mouth resuscitation. Call a physician immediately.
- Ingestion* : Induce vomiting immediately as directed by medical personal. Never give anything by mouth to an unconscious person. Call a physician immediately.
- Skin Contact* : In case of contact, immediately flush skin with plenty of soap and water for at least 15 minutes while removing contaminated clothing and shoes. Washing clothing before use. Call a physician immediately. Through cleansing of the

entire contaminated area of the body including scalp and nails is of the utmost importance.

*Eye Contact* : Immediately flush eye with gentle but large stream of water at least 15 minutes, lifting lower and upper eyelids occasionally. Call a physician immediately and consider methylene blue as an antidote.

## 2.2 Advanced Oxidation Processes (AOPs)

Advanced Oxidation Processes (AOPs) have been viewed with great interest as a promising method for the removal organic contaminants from water. AOPs rely on the formation of reactive and short-lived oxygen containing intermediates such as hydroxyl radical ( $\text{OH}^\cdot$ ). Hydroxyl radical is a powerful oxidant and short-lived, highly reactive, and non-selective reagent that is easy to produce. The hydroxyl radical can be produced in a homogeneous system by two ways (Munter, 2001).

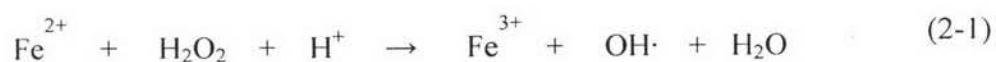
The first is “non-photochemical”; this method generating hydroxyl radicals without using light energy. This method includes ozonation at elevated values of pH (>8.5), combining ozone with hydrogen peroxide, combining ozone and catalyst, and Fenton system. Conventional ozone or hydrogen peroxide oxidation of organic compounds dose not completely oxidize organics to carbon dioxide and water. In some reactions, certain oxidation products still remain in the solutinn. Completing of oxidation reaction, as well as oxidative destruction, can be achieved by supplementing the reaction with UV radiation, which is the “photochemical” path that can also generate the hydroxyl radical. There are various kinds of AOPs such as alkaline ozonation, heterogeneous photocatalytic, Fenton processes, etc. In homogenous photolysis,  $\text{OH}^\cdot$  are generated at the surface of a semiconductor (Usally  $\text{TiO}_2$ ) in the presence of UVA. Homogenous oxidation produces an oxidant and includes methods such as Fenton’s reagent ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ), “peroxone” ( $\text{H}_2\text{O}_2/\text{O}_3$ ), and hydrothermal (high temperature water oxidation (Rodgers, 2001).

AOPs are being widely applied to treat contaminated groundwater, to purify and disinfect drinking waters and process waters, and to destroy refractory of organics in industrial wastewater.

### 2.3 Fenton Processes

Advanced oxidation processes (AOPs) have shown a potential for treating refractory compounds in a water. Among various AOPs, Fenton's ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ) 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 1867s by its inventor H.J.H. Fenton, but its application as an oxidizing process for destroying toxic organics was not applied until the late 1960s. Today, Fenton's reagent is used to treat a variety of industry wastes containing a range of toxic organic compound (wastes derived from dyestuffs, pesticide, wood preservatives and rubber chemicals).

Fenton's reagent is a mixture of  $\text{H}_2\text{O}_2$  and ferrous ions under acidic pH condition (3-5), which generates hydroxyl radical according to reaction.



Fenton oxidation can be carried at normal temperature and at atmospheric pressure. Fenton reaction exploit the reactivity of the hydroxyl radical ( $\text{OH}\cdot$ ), which has a very high oxidation potential and is able to oxidize almost all organic pollutants quickly and non-selectivity, produced in acidic solution by the catalytic decomposition of  $\text{H}_2\text{O}_2$ . Its position is second in the oxidation potential series next to fluorine. The mean lifetime of  $\text{OH}\cdot$  radicals depends on their chemical environment and was estimated to be in the order of 10  $\mu\text{s}$  in the presence of dissolved natural organic matters, bicarbonate and carbonate (Hoigen, 1998). The half-life of hydroxyl radicals in the presence of linoleate ( $\text{C}_{18}\text{H}_{31}\text{O}_2^-$ ), the conjugate base of linoleic acid, at 37 °C to be in the order of nano seconds.

The hydroxyl radical is one of the most reactive free radical and one of strongest oxidants. It has a very high oxidizing capacity equalling 2.8 V. (Prengle et al. 1978; Masten and Divies, 1994; Himebaugh, 1994) and attacks the organic compounds relatively non-selective with rate constants ranging from  $10^6 - 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$  (Buxton et al. 1988).

Table 2.2 Oxidation potential of common species (U.S. Peroxide, 2005)

Reactive Species	Oxidation Potential (V)
Fluorine	3.03
<b><i>Hydroxyl radical</i></b>	<b><i>2.80</i></b>
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical	1.70
Potassium permanganate	1.68
Hypobromous acid	1.59
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Chlorine	1.36

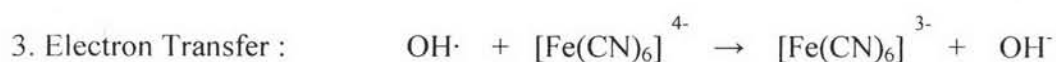
The chemical reactions of the hydroxyl radical in water are of four types (U.S. Peroxide, 2005) :



where the hydroxyl radical adds to an understand compound, aliphatic or aromatic, to form a free radical product (cyclohexadienyl radical shown above).



where an organic free radical are formed.



where ions of a higher valence state are formed, or an atom or free radical if a mononegative ion is oxidized.



where the hydroxyl radical reacts with another hydroxyl radical, or with an unlike radical, to combine or to disproportionate to form a stable product.

In applying Fenton's reagent for industrial waste treatment, the conditions of the reaction are adjusted so that first two mechanism (hydrogen abstraction and oxygen addition) predominate. Typical rates of reaction between the hydroxyl radical and organic materials are  $10^9 - 10^{10} \text{ k (M}^{-1} \text{ s}^{-1}\text{)}$ .

The key Fenton's reagents,  $\text{H}_2\text{O}_2$  and iron salt, are relatively inexpensive. Iron is highly abundant (and may be naturally occurring in the system being treated) and is non-toxic.  $\text{H}_2\text{O}_2$  is relatively easy to transport and handle, as well as being environmentally benign in dilute form.

Use of Fenton processes can lead to the complete mineralization of some organic compounds, converting them to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and inorganic ions. However, this would usually involve a large excess of chemicals which the production of substantial amounts of sludge is the major drawback of Fenton reaction.

### 2.3.1 Hydrogen Peroxide

#### 2.3.1.1 General Information

Hydrogen peroxide was discovered by Louis Jacques Thenard in 1818. Each hydrogen peroxide molecule ( $\text{H}_2\text{O}_2$ ) contains two bonded oxygen atoms, each with one hydrogen molecule) attached (H-O-O-H). Due to intermolecular repulsion,  $\text{H}_2\text{O}_2$  molecules have a skew-chain structure. Hydrogen Peroxide is an ubiquitous compound present in natural water. Although pure hydrogen peroxide is fairly stable, it decomposes into water and oxygen when heated above about  $60^\circ\text{C}$ . 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, salts 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 bleaching 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.

#### **2.3.1.2 Physical and Chemical Properties**

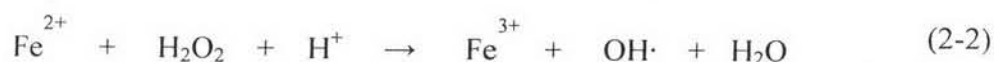
An aqueous solution of hydrogen peroxide is clear, colorless, water-like in appearance and nonflammable. It is miscible with cold water and is soluble in alcohol and ether. At high concentration, it has a slightly pungent or acidic odor. The chemical formula for hydrogen peroxide is  $H_2O_2$  and its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

#### **2.3.1.3 Toxicology**

According to the US regulation, no concentration of  $H_2O_2$  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 (those <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.

### 2.3.2 Fenton Reaction

In Fenton process, uses ferrous ions to react with hydrogen peroxide, producing hydroxyl radicals with powerful oxidizing abilities to degrade certain toxic contaminants (Pignatello, 1992, Casero et al., 1997 and Lu et al., 1999) is shown in Eq. (2-2).

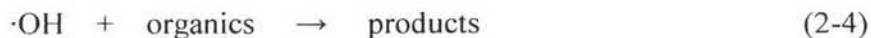


The hydroxyl radical can non-selectively attack the C-H bonds of organics molecules and is capable of degrading many solvents, haloalkanes, esters, aromatics, and pesticides (Haag and Yao, 1992). Huang, et al. (1993) summarized the major advantages of using Fenton's process over other oxidation processes 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 in expensive 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.
- (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 conditions and with an excess of ferrous ion, the hydroxyl radical generated can further react with ferrous ion to to form ferric ions or react with other organics:

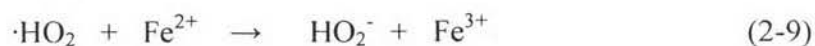
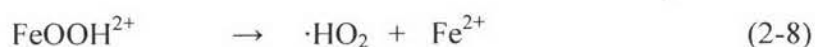




Hydroxyl radicals can react with hydrogen peroxide to produce other radicals, they may also combine with each other to produce hydrogen peroxide, as shown below:



Ferrous ions and radicals are produced during the reactions. The reactions are as shown in Eqs. (2-6), (2-7), (2-8) and (2-9):



The reaction rate in Eq. (2-7) is much slower than that of Eq. (2-2). This is due to the fact that ferrous ions are consumed quickly, but reproduced more slowly (Pignatello, 1992). Consequently, the oxidation rate of organic compounds is fast when a large amount of ferrous ions are present due to the high generation rate of hydroxyl radicals. However, the Fenton reaction may slow down because the rate of ferrous ions production is low.

The Fenton process consists of two phases: the  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  and  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$  stages (Lu et al., 1999). At the initial stage, ferrous ions react very quickly with hydrogen peroxide to produce large a amount of hydroxyl radicals (see Eq. (2-2)). The produced hydroxyl radicals can react rapidly with organic matter, thus at the first stage, organics are decomposed quickly; this is referred to as the  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  stage. The ferric ions produced in the first stage can react with hydrogen peroxide to produce hydroperoxyl radicals ( $\cdot\text{HO}_2$ ) and ferrous ions. The reactions are shown in Eqs. (2-7) and (2-8). Hydroxyl radicals are the main species causing the decomposition of

organics. They are much higher in oxidation strength than hydroperoxyl radicals. The reaction rate constant ( $M^{-1}s^{-1}$ ) of ferrous ions reacting with hydrogen peroxide to produce hydroxyl radicals is 53. The reaction rate constant of ferric ions reacting with hydrogen peroxide to form ferrous ions is 0.02 (Sun and Pignatello, 1993). Therefore, it can be concluded that the former reaction is far swifter than the latter, resulting in a higher rate of hydroxyl radical formation at the first stage of reaction than at the second stage of reaction. In the present, the two-stage reaction may have resulted from the lower generation of  $Fe^{2+}$  from  $Fe^{3+}$  (see Eqs. (2-7), (2-8), (2-9) and (2-10)), and the complexation of  $Fe^{3+}$  and degradation intermediates.

The factor affecting the efficiency of Fenton's reaction are wastewater characteristics such as phosphates, EDTA, formaldehyde, citric/oxalic acids and chloride, dosages of  $H_2O_2$  and  $Fe^{2+}$ , pH, reaction time and temperature. The most important factors are pH and dosages of  $H_2O_2$  and  $Fe^{2+}$ . The optimum pH range of Fenton's reaction is between 3 and 4. Because of the sensitivity of Fenton system to different wastewaters, it is recommended that the reaction should always be characterized through laboratory treatability tests before proceeding to the plant scale.

### **2.3.3 Types of fenton processes (Parsons, 2004)**

#### **2.3.3.1 Homogeneous processes**

When all the reactants are present in the dissolved phase, the process is said to be homogeneous. These processes may still, however, lead to the precipitation of some soluble species, such as metal hydroxides, but this is not part of the main process. The example of homogeneous Fenton processes are: Fenton processes ( $Fe(II)/H_2O_2$ /dark), Photo-Fenton processes ( $Fe(II)/H_2O_2$ /light), Fenton-like reagent ( $Cu(I)$ ,  $Co(II)$ ,  $Ti(III)$ ).

#### **2.3.3.2 Heterogeneous processes**

The source of iron used as a catalyst for the Fenton processes can be a solid surface, including iron-containing minerals or iron-coated silica particles (sand), as well as iron adsorbed onto zeolites.

A major disadvantage of wastewater treatment by homogeneous Fenton processes is that the iron must usually be removed from the water after treatment is complete. This can usually be achieved by adjusting the pH of the solution, however this can lead to the production of large volumes of iron-containing sludge. Heterogeneous Fenton processes are of particular interest, since most of the iron remains in the solid phase. The solid phase is usually granular (iron oxides, sand or zeolites), hence the treated water is easily separated from the iron. The examples of heterogeneous Fenton processes are: Iron oxide catalyst; goethite, lepidocrocite, hematite, limonite and magnetite).

#### 2.3.4 Fluidized-Bed Fenton Process

From equations (2-2) to (2-10), the major disadvantage of Fenton's reagent is the production of a substantial amount of ferric precipitation. To overcome and/or ease this problem, the fluidized-bed reactor (FBR) is one of the possible alternatives. In FBR, several important processes occur simultaneously including:

- (a) Homogeneous chemical oxidation ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ )
- (b) Heterogeneous chemical oxidation ( $\text{H}_2\text{O}_2/\text{iron oxide}$ )
- (c) Fluidized-bed crystallization
- (d) Reductive dissolution of iron oxides

The emphasis influencing of iron oxide growing on the surfaces of fluidized-bed carrier which are operated in FBR are pH, specific iron loading,  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ , and superficial velocity (Chou et al., 2004). As Figure 2.2 illustrates the fluidized-bed Fenton reaction, the Fenton's reagent can produce the non-selective oxidant as  $\text{OH}^\bullet$  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 appear, these lead into further oxidation (c). Also,  $\text{Fe}^{3+}$  can be converted from the reducing one electron of  $\text{Fe}^{2+}$  in Fenton's reaction (d). Some  $\text{Fe}^{3+}$  can be converted back to  $\text{Fe}^{2+}$  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., 1999). At the same time, the synthesized ferric oxide can also serve as a catalyst for hydrogen peroxide decomposition in a 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  $\text{Fe}^{2+}$  form. However, these reactions which are similar as equation (2-7) are slower than that equation (2-3) (Pignatello, 1992). In acidic environment, iron species can reform by the way ferric can alter to ferrous form also (d).

The full-scale application of the pellet reactor, a crystallizer of the fluidize-bed reactor, in the removal of hardness, heavy metals, fluoride, and phosphate has been demonstration by the DHV Company (Chou Huang, 1999a). This process combines the functions of homogeneous chemical oxidation ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ), heterogeneous chemical oxidation ( $\text{H}_2\text{O}_2/\text{iron oxide}$ ), fluidized-bed crystallization and reductive dissolution of iron oxide. This process not only attains high COD removal efficiency but also reduces the large amount of iron sludge being produced.

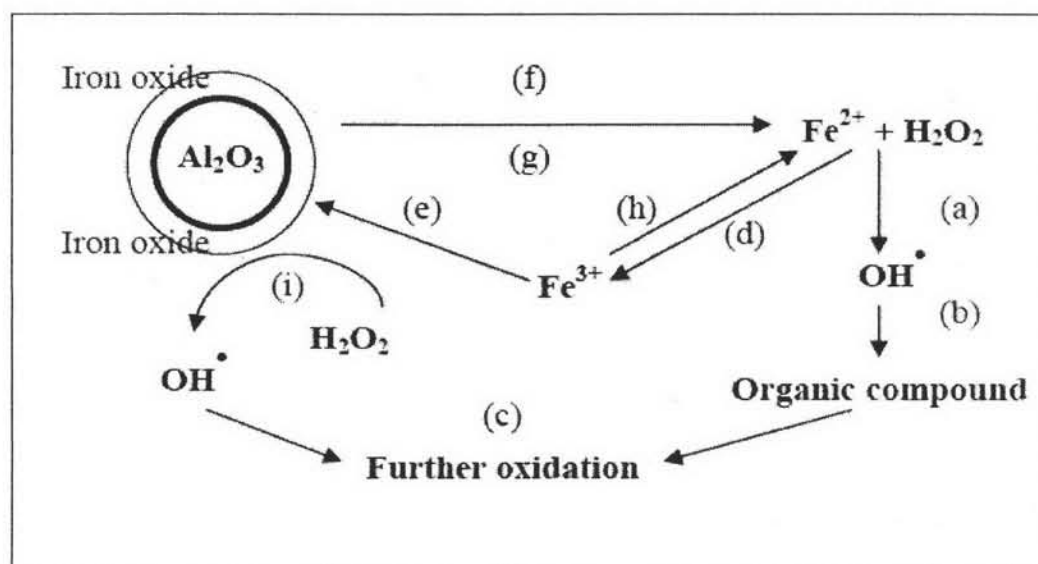


Figure 2.2 Fluidized-bed Fenton reactions

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; Pollution Abatement Technology Department Center for Environmental, Safety and Health Technology Development Industrial Technology Research Institute, 2003).

Key factors in the design of fluidized-bed Fenton process are:

- Selection of the carrier, including the material, gravity, and particle size.
- Design of distributors.
- Superficial velocity and recycle ratio.
- Feed mode and dosage of hydrogen peroxide and ferrous ion.
- Size, configuration and recycle ratio of reactor.

### **2.3.5 Effect of system position and process condition**

#### **2.3.5.1 pH**

The reaction rate of the Fenton process tends to be highest at around pH 3 and decrease with increasing pH. The pH tends to change during the Fenton process; hence pH control is important in most processes.

In a study by Chou et al., cited in Parson (2004), studied iron oxyhydroxide and Fenton's reagent in a fluidized-bed reactor (FBR), the pH was found to strongly affect the efficiencies of mineralization and  $\text{Fe}^{3+}$  precipitation rates. When treated benzoic acid, they found that the degradation efficiency decreased with increasing pH, while the removal efficiency of total iron increased with pH in the pH range 2.50-4.50.

#### **2.3.5.2 Temperature**

The rate of reaction with Fenton's reagent increases with increasing temperature, with the effect more pronounced at temperatures  $< 20\text{ }^{\circ}\text{C}$ . However, temperatures increase above 40-50  $^{\circ}\text{C}$ , the efficiency of  $\text{H}_2\text{O}_2$  utilization decline. This is

due to the accelerated decomposition of  $\text{H}_2\text{O}_2$  into oxygen and water. As a practical matter, most commercial applications of Fenton's reagent occur at temperatures 20-40 °C. Applications of Fenton's reagent for pretreating high strength wastes may require controlled or sequential addition of  $\text{H}_2\text{O}_2$  to moderate the rise in temperature with occurs as the reaction proceeds. This should be expected when  $\text{H}_2\text{O}_2$  dosages exceed 10-20 g/L. Moderating the temperature is important not only for economic reasons, but for safety reasons as well (Parson, 2004).

### 2.3.5.3 Reaction time

The time needed to complete a Fenton reaction, 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.

### 2.3.5.4 $\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}$ concentration

The reaction rate tends to increase with  $\text{H}_2\text{O}_2$  concentration. However, the ferrous ion and  $\text{H}_2\text{O}_2$  not only react to form hydroxyl radicals, but also scavengers of hydroxyl radicals. The ratio of  $\text{H}_2\text{O}_2$  to  $\text{Fe}^{2+}$  should effect the rate of hydroxyl radical production and scavenging. Hence it is important to use the optimum  $\text{H}_2\text{O}_2$  to  $\text{Fe}^{2+}$  concentration (Parson, 2004).

### 2.3.5.5 Inorganic ions concentration

Degradation rates by Fenton processes can be decreased due to the presence of certain anions that either scavenge hydroxyl radicals or form unreactive complex with  $\text{Fe}^{3+}$ .

Lu et al., cited in Parsons (2004) found that anions suppresses the degradation of dichlorvos by  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  in the order  $\text{H}_2\text{PO}_4^- \gg \text{Cl}^- > \text{NO}_3^- \approx \text{ClO}_4^-$ .

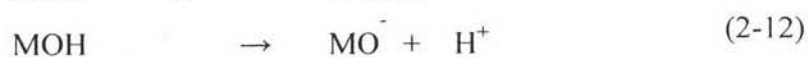
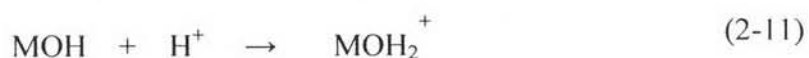


The inhibition by  $\text{H}_2\text{PO}_4^-$  was attributed to the formation of unreactive  $\text{Fe}^{3+}$  complexes.

#### 2.4 Point of Zero Charge (pzc)

The complication in contact with aqueous environment happens at the surface of an oxide. The development of a surface charge which can be positive or negative upon the pH surrounding is led by the amphoteric behavior of hydroxylated. The hydrated surface of an oxide presents ion exchange properties and there is a correlation between the exchange capacity and the net surface charge of the oxide. Simple oxides are cation exchangers in environments giving a negative surface charge and are anion exchangers in environments producing a positive surface charge. One of the most important characteristics of an oxide surface is the point of zero charge (pzc) which corresponds to the pH value of the liquid surrounding oxide particles when the sum of surface positive charges balance the sum of surface negative charges. The pzc value characterizes surface acidity when oxide particles are introduced in an aqueous environment their surface charge is positive if pH solution < pzc and is negative if pH solution > pzc (Reymond and Kolenda, 1999).

The protonation (p) and deprotonation (d) of amphoteric surface site are result of surface charge of an oxide in aqueous surrounding which will be denoted by MOH, where M stands for a metal. The corresponding surface reaction may be written as follows (Preocanin et al, 1998; Noh et al, 1988).



Moreover, equations (2-11) and (2-13) the association of conversions with surface charge group  $\text{MOH}_2^+$  and  $\text{MO}^-$  may take place. Surface reactions are usually consisting of neutralization in the bulk of the solution. Thus, the amphoteric behavior

of hydroxylated sites lead to the development of a surface charge which can be positive or negative charge upon the pH surrounding (Reymond, 1999).

## 2.5 Literature Reviews

### 2.5.1 Degradation of nitrobenzene by various chemical processes

Bhatkhandea et al. (2003) studied on the photocatalytic reaction to degrade nitrobenzene by using titanium dioxide catalyst. The results show that nitrobenzene can be readily degraded under the conditions being used. The nitrobenzene degraded and TOC removed were more than 90%. The optimum catalyst loading was 0.3%. The presence of anions, initial pH, and FeSO<sub>4</sub> concentration had no significant effect on the photocatalytic degradation of nitrobenzene. Used TiO<sub>2</sub> did not show any loss in activity. The intermediates detected were *o*-, *p*-, *m*-nitrophenols and dihydroxy derivatives indicating that the degradation proceeded via ·OH radicals.

Lu et al. (2005) explored the mechanism of chloride ions affecting on aniline oxidation by Fenton's reagent. The results indicated that the inhibition caused by chloride ions can be overcome by increasing the reaction time if the concentration of chloride ions is low.

Mu et al. (2004) proposed a reductive degradation of nitrobenzene (NB) in aqueous solution by zero-valent iron. It was found that, after 45 minute reaction, 1.23 mM of NB was removed at pH 3.0, while the corresponding value at pH 12.0 was 0.17 mM. Aniline formed also increase with increasing pH, i.e., from 0.71 mM at pH 3.0 to 0.08 mM at pH 12.0. Removal of NB increased from 0.13 to 1.60 mM when initial NB concentration increased from 0.41 to 1.60 mM; however, as the initial NB concentration rose to 2.03 mM, the removal dropped 0.93 mM. On the other hand, aniline formed from the reaction increased constantly with increasing NB concentration. Products from nitrobenzene reduction by zero-valent iron, apart from aniline, were azobenzene and azoxybenzene.

Piccinini et al. (1997) investigated on  $\text{TiO}_2$  photocatalytic mineralization of nitrobenzene, nitrosobenzene, phenylhydroxylamine, aniline and 4-nitrosophenol in aerated condition. Under slightly acidic condition, all these compounds underwent to carbon dioxide, whereas the nitrogen was converted to nitrate and ammonium ions. The temporal evolution of the  $\text{NO}_3^-/\text{NH}_4^+$  concentration ratio, besides other experimental conditions (pH, photon flux, reactant concentrations), depends largely on both the initial oxidation state of the nitrobenzene and the nature of the starting organic substrate.

Rodriguez et al., (2003) described the effect of temperature and initial concentration of  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{2+}$ ,  $\text{PhNO}_2$  and dissolved oxygen on the degradation rate of nitrobenzene by Fenton-like reagent ( $[\text{H}_2\text{O}_2] \gg [\text{Fe}^{2+}]_0$ ). This experimental reaction was addressed in a completely mixed-batch reactor under a wide range of experimental conditions; pH  $\sim$ 3.0; 278-318 K;  $1.5 < [\text{H}_2\text{O}_2]_0 < 26.5$  mM;  $0.04 < [\text{Fe}^{2+}]_0 < 1.1$  mM;  $0.3 < [\text{PhNO}_2]_0 < 2.5$  mM; and  $0 < [\text{O}_2]_0 < 1.4$  mM. As results, the degradation rate of  $\text{PhNO}_2$  behaved as pseudo-first order kinetics. The second-order rate constant for the overall rate of  $\text{H}_2\text{O}_2$  decomposition by  $\text{Fe}^{3+}$  was found to be  $0.83 \text{ M}^{-1} \text{ s}^{-1}$  at 298 K. Also, they found that there were the oxidation product *o*-, *m*-, and *p*-nitrophenols as intermediates in the ratio of 1:1.3 – 2.8:1.4 – 2.7 as compared with  $\text{PhNO}_2$  when conversion of the latter was less than 25%. The isomeric distributions of nitro-phenol appeared during the degradation of  $\text{PhNO}_2$  by ‘Fenton-like’ reagent, photolysis and radiolysis are presented in Table 2.3.

Table 2.3 The isomeric distribution of nitrophenols formed during the action of Fenton reagent, photolysis and radiolysis on the aqueous solutions of PhNO<sub>2</sub>.

Solutions of PhNO <sub>2</sub> Source of the attacking species	Ratio of the <i>o</i> -, <i>m</i> - and <i>p</i> -isomers	Reference
'Fenton-like' reagent <sup>a</sup>	1:1.3–2.8:1.4–2.7	Rodriguez et al., 2003
'Fenton-like' reagent <sup>b</sup>	1:0.6–1.0:0.8–1.2	Rodriguez et al., 2003
'Fenton-like' reagent	1:1.3:1.9	Norman and Radda, 1962
'Fenton-like' reagent	1:0.8:1.8	Loble et al., 1949
Photolysis <sup>c</sup>	1:0.6:0.7	Lipczynska-Kochany, 1992
Radiolysis		Radiolysis Loebel et al., 1950
pH 2	1:0.9:1.0	
pH 6	1:1.0:1.0	
Radiolysis (pH 5.5)		Matthews and Sangster, 1967
Air	1:0.6:0.7	
Nitrogen	1:0.7:1.8	

<sup>a</sup> Conversion of PhNO<sub>2</sub> was 15–25%.

<sup>b</sup> Conversion of PhNO<sub>2</sub> was 80–90%.

<sup>c</sup> In the presence of H<sub>2</sub>O<sub>2</sub>

Available from Rodriguez et al., (2003). Advances in environmental research, 7.

Rodriguez et al. (2000) reported that the combination of hydrogen peroxide or Fe (III) with UV radiation was found to be more effective in removing nitrobenzene than the application of only UV radiation. When  $H_2O_2$  was increased, more hydroxyl radicals were available to attack on the aromatic ring. The results indicated that most degradation happened during the first 60 minutes. The three-nitrophenol isomers were identified besides other by-products. The concentrations of the *ortho*- and *para*- nitrophenol isomers reached maximum concentrations at 60 minutes of reaction time, which led to a total degradation within three hours.

The role of pH optimization is emphasis effect to considering the high removal efficiency of organic matter in every process. High efficiency of the oxidation processes utilizing the activation of  $H_2O_2$  by iron salt is usually obtained when operating under acidic pH condition (Neyens, 2003). As in equation (2-3) and (2-7) in the Fenton's system, when pH is too high and low, the presence of proton can cause the formation of  $FeOOH^{2+}$  then the reaction is let to slow down. Addition, there are many researchers investigating on the degradation of organic compound in acidic range.

### **2.5.2 The removal oxidation of organic compound in heterogeneous catalysis by hydrogen peroxide**

Huang et al. (2001) examined the catalyzed decomposition of hydrogen peroxide and 2-chloropheno (2-CP) in the presence of iron oxides. The catalytic activity for hydrogen peroxide decomposition followed the following sequence: granular ferrihydrite > goethite > hematite. The strong diffusion resistance for granular ferrihydrite was ascribed either to its microporous structure or to the formation of oxygen in the pores of the iron oxide leading to the unexpected catalytic activity of granular ferrihydrite to hydrogen peroxide and 2-CP.

Kang et.al. (2000) studied on that the effect of reaction conditions on the oxidation efficiency on non-biodegradable landfill leachate in the Fenton process. The results indicated that the COD removal with hydrogen peroxide was most efficient in

the pH range of 2.5-4. The organic oxidation drastically decreased at pH value above 5. The increasing of ferrous dosage can increase the COD removal efficiency by coagulation, but up to a minimum dosage of 500 mg/l lead to change scarcely efficiency.

Kong et al. (1998) employs iron minerals, goethite, magnetite to catalyze hydrogen peroxide and initiated Fenton – like reaction to treat silica sand contaminated with diesel and/or kerosene in a batch system. Iron mineral system was less aggressive in contaminant degradation but was more efficient than  $\text{FeSO}_4$  system. Magnetite system provided more strong oxidation condition than goethite system due to coexistence of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and dissolution of iron; however, goethite system was more efficient than magnetite system in treatment efficiency by possible quenching effect of  $\text{H}_2\text{O}_2$  to iron precipitate in magnetite system.

Lin and Gurol (1996) searched for the effective AOPs for several synthetic organic pollutants in aqueous solution. Hydrogen peroxide in the presence of iron oxide seems to have significant advantages over  $\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{O}_3/\text{UV}$  and Fenton process because the oxidation efficiency remained unaffected by varying pH and alkalinity. BuCl was found to be directly dependent on the rate of hydrogen peroxide decomposition; i.e., about 2 moles of  $\text{H}_2\text{O}_2$  decomposed for the oxidation of one mole of BuCl under their conditions. An increase in iron oxide and hydrogen peroxide dosages significantly enhanced BuCl removal. The observed optimum molar ratio for  $\text{H}_2\text{O}_2 : \text{FeOOH}$  was 1:1.

Lu (2000) studied the chemical oxidation of chlorophenols with hydrogen peroxide/goethite. Results indicated that 2-chlorophenol can be decomposed with hydrogen peroxide catalyzed by goethite and the oxidation rate increased with decreasing goethite particle size. 2-chlorophenol degradation was almost retarded with 0.8 g/l of goethite because ferrous ion could not be produced at this condition.  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  can create a better oxidation efficiency in the presence of goethite and hydrogen peroxide than that in Fenton systems. The main mechanism of goethite catalyzing

hydrogen peroxide to oxidize chlorophenols may be considered to be the catalysis of ferrous ions on goethite surface.

Lu et al. (2002) revealed the role of goethite dissolution in the oxidation of 2-chlorophenol with hydrogen peroxide. Experiment results indicate that ligand and reductant can enhance the dissolution rate of the goethite, which is a surface – control reaction. Results in the study further indicate that 2-chlorophenol can be effectively degraded by Fenton-like reaction using goethite as a catalyst at a acidic pH. The extent of 2-chlorophenol degradation increase with increasing concentration of goethite which provide more surface sites for reductive dissolution.

Lunar et al. (2000) examined degradation of metol [N-methyl-p-aminophenol] by Fenton's reagent under optimal dark condition with 0.2 M,  $H_2O_2$   $9.0 \times 10^{-4}$  M  $Fe^{2+}$ , pH 3 -5, at room temperature and the initial COD of a  $5 \times 10^{-3}$  M. The experimental results demonstrated that the metol was reduced by approximately 50% within 2 h. After that, the COD reduction was very slow (about 20% in five days). The detection of aromatic compound can not found within the first 4 h of reaction indicating that residual organic matter was mainly made up of ring cleavage products. Metol conversion performed as a first-order reaction with respect to metol and  $Fe^{2+}$ . Complete destruction of residual organic matter could be achieved at high temperature (about 60°C) or by using the photo-Fenton reaction, which thus opens up prospects for an effective treatment of paminophenols in effluent from photographic processes.

Teel et al. (2001) conducted their experiments to remove trichloroethylene (TCE) in four Fenton's systems; i.e., a standard Fenton's systems, a modified soluble iron system with a pulse input of hydrogen peroxide, and two modified mineral catalyzed systems at pH 3 and 7. It was found that 78%, 99%, and 22% of the TEC was degraded, respectively. Experiments using hydroxyl radical scavengers showed that the standard Fenton's systems degraded TEC entirely by hydroxyl radical mechanisms, while approximately 10±15% of the degradation



achieved in the modified soluble iron and goethite – catalyzed systems at pH 3 was mediated by non - hydroxyl radical mechanisms. In the goethite system at pH 7, only non - hydroxyl radical mechanisms were evident.

Panizza et al. (2001) explored the removal of organic pollutants mainly containing naphthalene and anthraquinone-sulphonic acid from industrial wastewater by electrogenerated Fenton's reagents. They found that the reduction of oxygen to  $H_2O_2$  on graphite felt occurred at -1 V. Also, the greatest COD removal (87%) and color fading (89%) were obtained with a  $Fe^{2+}$  concentration of 3 mM for the electro-Fenton treatment process. The COD removal kinetic acted a pseudo-first order reaction. And, the chemical or electrochemical surface pre-treatment had no benefit influence in organics oxidation.

### 2.5.3 The application in fluidized-bed Fenton reactor (FBR)

Chou, et al. (2004) applied a novel supported iron oxyhydroxide (FeOOH) catalyst to treat benzoic acid by hydrogen peroxide, using a fluidized-bed crystallization reactor. Four operating variables, including pH, specific iron loading,  $H_2O_2/Fe^{2+}$  ratio, and superficial velocity, have been demonstrated to affect the crystallization efficiency. The crystallization reached the maximum between pH 3.0 and 4.0. When the specific iron loading increased from 0.12 to 1.2  $mg.m^{-2}.h^{-1}$  crystallization decreased gradually from 90% to 40%. The crystallization increased with increasing  $H_2O_2/Fe^{2+}$  ratio, and then attained a plateau. The superficial velocity must be maintained higher than 30  $m.h^{-1}$  to avoid the aggregation of suspension solids and formation of flocs that retained in the reactor.

Chou and Huang (1999a) investigated the effect of  $Fe^{2+}$  on the catalytic oxidation in the fluidized-bed reactor (FBR) applying supported  $\gamma$ -FeOOH as the carrier. When  $Fe^{2+}$  was not added in the FBR, the removal efficiency of benzoic acid remained around 96% at  $pH < 5.3$  and gradually decrease to 80% as pH increased to 7.0. In the FBR-Fenton process, both mineralization of organics and crystallization of  $Fe^{3+}$



were simultaneously well performed. Under adequate condition, benzoic acid was removed almost completely in the presence of 28 mg/l of ferrous ion or higher.

Chou and Huang (1999b), who decomposition of hydrogen peroxide in a continuous fluidized-bed reactor by a novel supported  $\gamma$ -FeOOH catalyst, found that the decomposition rate of  $H_2O_2$  was proportional to both  $H_2O_2$  and catalyst concentrations at low  $H_2O_2$  concentration. However, the rate decreased with the increasing  $H_2O_2$  concentrations at high  $H_2O_2$  concentrations. This can be explained by the substrate inhibition model.

Chou and Huang (1999c) found that the  $\gamma$ -FeOOH absorbed up to 11% of the input benzoic acid in the absence of hydrogen peroxide. The benzoic acid at an initial pH of 3.2 was completely removed in 6 hours, which was better than at initial pHs of 6.0 and 10.0. This can be partly explained by reductive dissolution of  $\gamma$ -FeOOH. The dissolved iron concentration increased with increasing  $H_2O_2$  dosage in the presence of benzoic acid. Without benzoic acid, the dissolved iron in the aqueous phase increasing only slightly to approximately 0.25 mg/l after 6.5 hours of reaction time at dosages from 200 to 1,600 mg/l of  $H_2O_2$ .

Miller and Valentine (1995) examined the relationship between contaminant (quinoline and nitrobenzene) degradation rate and the rate of hydrogen peroxide decomposition on filter media. The observed hydrogen peroxide decomposition followed the first order relationship in both batch and fixed bed experiments and the contaminant oxidation results are consistent with a reaction scheme whose central elements include : (1) a rate limiting filter medium surface catalyzed reaction initiating hydrogen peroxide decomposition with the formation of a reactive intermediate ; (2) a competing reaction of the intermediate with the filter medium surface ; and (3) reaction of the same intermediate with the aqueous organic contaminant.

Pak and Chang (1999) treated dye-manufacturing wastewater with Fe/MgO catalyst fluidized system and showed that the effluent was too clean to

distinguish any color during 30 days of operation and more than 60% of COD removal was obtained. After 30 days of operation, the effluent became slightly yellowish. The catalysts seemed to lose their activity. Biodegradability of the dye wastewater was enhanced significantly based on BOD/COD ratio during the initial phase of operation which was maintained at about 0.7.

Tai (1999) studied on the crystal growth kinetics of two-step growth process in liquid fluidized-bed crystallizers. A reliable method has been proposed to determine the parameters of the two-step growth. For sparingly soluble salts, the growth process was more complicated, but the two-step model could still be applied successfully under a similar environment of pH, ionic strength, and species ratio.