



CHAPTER II

THEORIES AND LITERATURE REVIEWS

2.1 *O*-toluidine

2.1.1 General Information

O-toluidine (C₇H₉N) is a synthetic chemical that is a light yellow liquid at ambient temperature. It is used primarily in the manufacture of dye-stuffs (Boeningo, 1994). 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.

As shown in Figure 2.1, *o*-toluidine is an aromatic amine, which is among the best-known chemical carcinogens (Rubino et al., 1982). It is of moderate to low acute toxicity and has the potential to produce minimal skin irritation and mild eye irritation. The principal signs of toxicity following acute and short-term exposure to this chemical are methaemoglobinaemia and related effects in the spleen (World Health Organization [WHO], 1998).

2.1.2 Physical and Chemical Properties

O-toluidine is a synthetic aromatic chemical. It exists at ambient temperature as a light yellow liquid that rapidly darkens on exposure to air and light. *O*-toluidine has a boiling point of 200°C, a melting point of -16°C, and a vapor pressure of 0.2 kPa at 20°C. It is completely miscible with ethanol and diethyl ether, its solubility in water is moderate. *O*-toluidine can decompose on heating or on burning, with producing toxic fumes including nitrogen oxides. It can react with strong oxidants especially nitric acid (International Program on Chemical Safety [IPCS], 1995). Additional properties are presented in Table 2.1 (IPCS, 1995; Material Safety Data Sheet [MSDS], 1999).

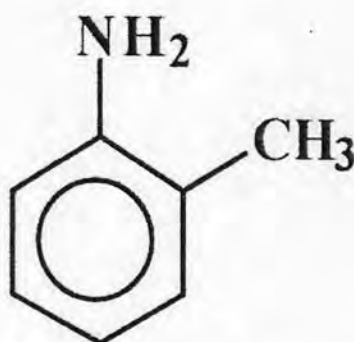


Figure 2.1 Structure of *o*-toluidine

Table 2.1 Physical and chemical properties of *o*-toluidine

Property	Value
Molecular formula	C ₇ H ₉ N / C ₆ H ₄ CH ₃ NH ₂
Molecular weight	107.2
Appearance	Colorless to yellow liquid, turns reddish-brown on exposure to air and light
Odor	Amine-like
Boiling point	200°C
Melting point	- 16°C
Relative density	1.01 (water = 1)
Solubility in water	1.5 g/100 mL at 25°C
Vapor pressure	0.2 kPa at 20°C
Relative vapor density	3.7 (air = 1)
Octanol/water partition coefficient (logK _{ow})	1.32
Flash point	85°C
Reactivity	Flammable

2.1.3 Toxicology

O-toluidine irritates the eyes and skin. Acute effects of exposure to *o*-toluidine include cyanosis, increase of metaemoglobin, blue lips or finger nails, blue skin, confusion, dizziness, headache, and shortness of breath. According to IPCS (1995), this substance is harmful to aquatic organisms in environment. The effects depend on the degree of exposure.

Instead of acute effects, *o*-toluidine also has chronic effects. This substance may cause effects on the blood, spleen, bladder and kidneys, resulting in tissue lesions, impaired functions and formation of methaemoglobin (Ward et al., 1996). Exposure to high concentration may result in damage to kidneys and bladder. Richter et al. (2006) studied the association of occupational exposure to *o*-toluidine (by using the local anesthetic prilocaine) with an increased risk of bladder cancer. By assessing the impact of prilocaine-treatment on DNA and hemoglobin (Hb) adducts from *o*-toluidine, the result was found that prilocaine anesthesia leads to a massive increase of Hb adducts in urothelia. This could be implied a carcinogenic risk which should be taken into account for prevention of exposure. Danford (1991) investigated the genetic effects of *o*-toluidine on bacteria, fungi, and mammalian cultures cells and found that it produced DNA damage and caused cell transformation. Therefore,

o-toluidine can be considered a general genotoxin demonstrable under special conditions, particularly with regard to metabolism.

2.1.4 Exposure

O-toluidine can be absorbed into the body by inhalation, through the skin, and by ingestion. It is harmful following acute oral exposure (LD₅₀s of 900 and 940 mg/kg body weight in rats) and is of low acute toxicity following dermal exposure (LD₅₀ of 3235 mg/kg body weight in rats) (Jacobson, 1972; Smyth et al., 1962). Due to the use of *o*-toluidine in manufacture, the most of human exposure is from occupational exposure. It can be seen by many researches studied the *o*-toluidine exposure on workers (Conso and Pontal, 1982; Vigliani and Barsotti, 1961; Ward et al., 1991).

O-toluidine can be transported, distributed and transformed into the environment, especially water resources. Yoshida et al. (1983) used an equilibrium model to asses partitioning of *o*-toluidine between environmental media. The distribution of *o*-toluidine was estimated to be 14.5% to air, 83.3% to water, 0.4% to soil, 1.9% to sediment, 2.3×10^{-5} % to biota (fish), and 0.21% to suspended sediment.

2.2 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) have been known since the 1970's. They are the processes that generating sufficient amount of hydroxyl radicals ($\bullet\text{OH}$) to affect water treatment by combinations of oxidants, ultraviolet irradiation and catalysts for the degradation of biorefractory or hazardous organic compounds in wastewater (Badawy et al., 2006). The $\bullet\text{OH}$, which has the electrochemical oxidation potential equals to 2.80 (Ozonia, 1977), is one of the most active oxidants known. It is nonselective for oxidizing compounds and able to operate at normal temperature and pressure (Tchobanoglous et al., 2003).

AOPs can be classified by considering the phase where the process takes place. Hence, homogenous or heterogeneous processes can be differentiated. AOPs classification can also consider the different possible ways of hydroxyl radical production. In this way, photochemical and non-photochemical processes can be distinguished. Table 2.2 shows the list of typical AOPs systems (Huang et al., 2003).

Table 2.2 List of typical AOPs systems

Homogeneous system		Heterogeneous system	
Photochemical	Non-photochemical	Photochemical	Non-photochemical
O ₃ /UV	O ₃ / H ₂ O ₂	TiO ₂ /O ₂ /UV	electro-Fenton
H ₂ O ₂ /UV			
electron beam	O ₃ /OH ⁻	TiO ₂ /H ₂ O ₂ /UV	fluidized-bed Fenton
ultrasound (US)			
H ₂ O ₂ /US	H ₂ O ₂ /Fe ²⁺ (Fenton's)		
UV/US			

From Table 2.2, the hydroxyl radicals can be produced in a homogeneous system by two ways: photochemical and non-photochemical methods (Munter, 2001). Non-photochemical method is a well known method for generating hydroxyl radicals without using light energy. This method includes ozone combining with hydrogen peroxide, ozone combining with hydroxide, and Fenton system. In some reactions, certain oxidation products still remain in the solution. Completing the 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. In heterogeneous system with photochemical reaction, hydroxyl radical is generated at the surface of a semiconductor (usually TiO_2) in the presence of UV light.

2.3 Chemistry of Fenton's Reagents

Fenton's reagent was discovered in 1894 by its inventor Henry J. Fenton, but its application as an oxidizing process for destroying toxic organics was applied in the late 1960s (Huang et al., 1993). Fenton reaction is one kind of AOPs used to produce $\cdot\text{OH}$ for degradation of pollutant. This reaction involves chemical reagents called Fenton's Regents, which are ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2).

Hydroxyl radical has a very high oxidation potential and is able to oxidize almost all organic pollutants rapidly, while Fe^{2+} is oxidized to ferric ion (Fe^{3+}) in a few seconds to minutes in the presence of excess amounts of hydrogen peroxide. However, reaction rates of Fenton's Reagent are generally limited by the slow rate of Fe^{2+} regeneration by Fe^{3+} .

The main advantage of Fenton processes is that it can lead to the complete mineralization of contaminants to harmless compounds, i.e. CO_2 , H_2O and inorganic ions. In addition, the Fenton reaction causes the separation of the oxidant and the formation of highly reactive hydroxyl radicals that attack and destroy the organic pollutants (Neyens and Baeyens, 2003). However, the limited range of pH in which the reaction takes place and the recovery of iron species are the major drawbacks of this homogeneous process. Pignatello (1992) stated that the Fenton process (in its unmodified form) is efficient only in the pH range 2-4. Therefore, the process is inefficient in most natural waters, which has pH range 5-9. The low efficiency in higher pH is due to the precipitation of ferric hydroxide (at pH higher than 3-4), which has a low catalytic activity. However, the mineralization of pollutants usually involves a large amount of chemicals which often prevents the process to be cost effective; hence, the Fenton process was usually used for a partial degradation (Huston and Pignatello, 1999).

Huang et al. (1993) summarized the major advantages of using Fenton's process over other oxidation processes to treat hazardous wastes, which are:

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

2.3.1 Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is an aqueous solution which has clear, colorless, water-like appearance. It is nonflammable and 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. Each hydrogen peroxide molecule contains two bonded oxygen atoms, each with one hydrogen molecule attached (H-O-O-H). Due to intermolecular repulsion, H_2O_2 molecules have a skew-chain structure.

Although pure hydrogen peroxide is fairly stable, it decomposes into water and oxygen when heated above about 60°C . One benefit of decomposition of hydrogen peroxide is that the released oxygen to stimulate aerobic biological activity. Hydrogen peroxide also decomposes in the presence of numerous catalysts, e.g., most metals, acids, bases, salt of metals, reducing agents, oxidizable organic materials, or flammable substances. 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.

H_2O_2 was first used to reduce odor in wastewater treatment plants, after that, it became a part of wastewater treatment process. H_2O_2 is a non-contaminating oxidant because its products are non-toxic substances, and can conform to strict environmental regulations (Elizardo, 1991). Besides, some contaminants may be oxidized into biologically degradable substances using H_2O_2 , and O_2 produced from H_2O_2 could be a supply for enhancing the biodegradation. However, H_2O_2 can be toxic to microorganisms if its concentration is too high (Pardieck et al., 1992).

H_2O_2 is one of the most powerful oxidizers known -- stronger than chlorine, chlorine dioxide, and potassium permanganate. And through catalysis, H_2O_2 can be converted into hydroxyl radicals ($\bullet\text{OH}$) with reactivity second only to fluorine. The Fenton system uses Fe^{2+} to react with H_2O_2 , producing $\bullet\text{OH}$ to degrade certain contaminant (Spacek et al., 1995; Lipczynska-Kochany et al., 1995; Watts and Dilly, 1996; Chen et al., 1998). The higher of the H_2O_2 concentration produces the faster of the decomposition (Rahhal and Richter, 1988). However, too high concentration of H_2O_2 will cause the decrease of reaction rate of the decomposition. This is due to the reaction of $\bullet\text{OH}$ and H_2O_2 , which can reduce the probability of organic pollutants attacked by $\bullet\text{OH}$ and cause oxidation rate to drop (Moon et al., 1991).

2.3.2 Hydroxyl Radical

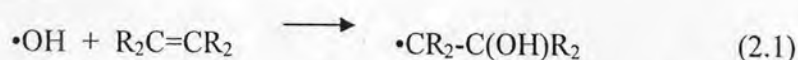
The hydroxyl radical ($\bullet\text{OH}$) is an extremely reactive, short lived and non-selective transient species. This radical is one of the most reactive free radical and one of strongest oxidants. It has a very high oxidizing capacity equal to 2.8 V. Table 2.3 shows the oxidation potential of $\bullet\text{OH}$ compared to other oxidants (Parsons, 2004). It can be seen that $\bullet\text{OH}$ is the second strongest oxidant, which is inferior only to fluorine. Hydroxyl radical can attack the organic compounds relatively non-selective with rate constants ranging from 10^6 - $10^{10} \text{ M}^{-1}\cdot\text{s}^{-1}$.

Table 2.3 Oxidation potential of common oxidant species

Oxidant	Oxidation Potential (V)
Fluorine	3.03
Hydroxyl radical	2.80
Ozone	2.07
Hydrogen peroxide	1.78
Potassium permanganate	1.68
Chlorine dioxide	1.59
Chlorine	1.36

There are four typical chemical reactions of the hydroxyl radical in water which are (Hoigné, 2008):

1. Addition:



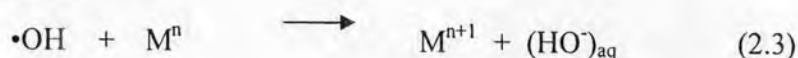
The hydroxyl radical adds to an unsaturated compound, aliphatic or aromatic, to form a free radical product such as cyclohexadienyl radical as shown above

2. Hydrogen Abstraction:



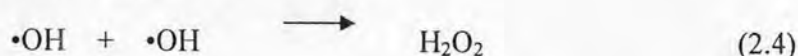
An organic free radical and water are formed as shown above.

3. Electron Transfer:



Ions of a higher valence state are formed, or an atom or free radical if a mononegative ion is oxidized as shown above.

4. Radical Interaction:



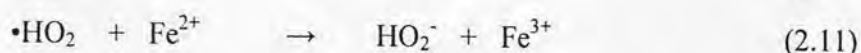
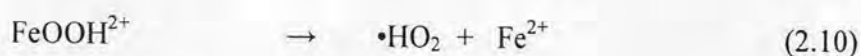
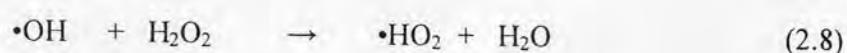
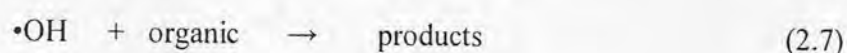
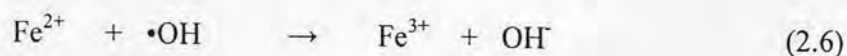
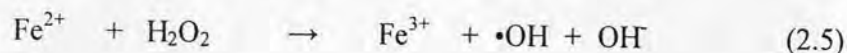
The hydroxyl radical reacts with another hydroxyl radical, or with an unlike radical, to combine or to disproportionate to form a stable product as shown above.

In applying Fenton's reagent for industrial waste treatment, the conditions of the reaction are adjusted so that first two mechanisms (hydrogen abstraction and oxygen addition) predominate. The key Fenton's reagents, H_2O_2 and iron salts are relatively inexpensive. Iron is highly abundant (and may be naturally occurring in the system being treated) and is non-toxic. H_2O_2 is relatively easy to transport and handle, as well as being environmentally benign in diluted form.

Use of Fenton processes can lead to the complete mineralization of some organic compounds, converting them to CO_2 , H_2O and inorganic ions. However, this would usually involve a large excess of chemicals which can produce substantial amounts of sludge which is the major drawback of Fenton reaction.

2.3.3 Fenton reaction

For the Fenton reaction, the process consists of two stages: the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ stages. At the initial stage, Fe^{2+} reacts with H_2O_2 , producing large amount of $\bullet\text{OH}$ (equation 2.5) with the rate constant of $76 \text{ M}^{-1}\text{s}^{-1}$. The rapidly produced $\bullet\text{OH}$ may react with Fe^{2+} to form Fe^{3+} (equation 2.6) or react with other organics (equation 2.7). Therefore, organics are decomposed quickly at the initial stage. The $\bullet\text{OH}$ can react with H_2O_2 to produce hydroperoxyl radicals ($\bullet\text{HO}_2$) (equation 2.8). In the second stage, the Fe^{3+} produced in the first stage can slowly react with H_2O_2 to produce $\bullet\text{HO}_2$ and Fe^{2+} . The reactions are shown in equation 2.9 and 2.10. The reaction rate between Fe^{3+} and H_2O_2 is very slow ($0.01 \text{ M}^{-1}\text{s}^{-1}$) compared to the rate of reaction between Fe^{2+} and H_2O_2 .



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



In the Fenton reaction, $\bullet\text{OH}$ is the main species causing the decomposition of organics. It is much higher in oxidation strength than hydroperoxyl radicals. Therefore, 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 (Pignatello, 1992; Lu et al., 1999; Lu et al., 2005).

The key features of the Fenton system are believed to be the reagent's conditions, i.e. Fe^{2+} , Fe^{3+} and H_2O_2 concentrations, and the reaction characteristics such as pH, temperature, and the quantity of organic and inorganic constituents. Because these parameters contribute to the overall reaction efficiency, it is important to understand the mutual relationships between these parameters in terms of hydroxyl radical production and consumption (Neyens and Baeyens, 2003). Yoon et al. (2001) studied the relationships between initial Fe^{2+} and H_2O_2 concentrations for degrading the organic substances and classified them into three categories according to the quantity of the $[\text{Fe}^{2+}]_0/[\text{H}_2\text{O}_2]_0$ ratio. Their results are:

1. High ratio of $[\text{Fe}^{2+}]_0/[\text{H}_2\text{O}_2]_0$ (≥ 2), the ratio reduce to less than 2 while the reaction is proceeding. This is because the $\bullet\text{OH}$ produced as a result of reaction

between Fe^{2+} and H_2O_2 . Because the decrease in this ratio, it can be implied that the Fe^{2+} was utilized as a major reactant.

2. Medium ratio of $[\text{Fe}^{2+}]_0/[\text{H}_2\text{O}_2]_0$ ($=1$), the presence of organic substance has an impact on the behavior of the H_2O_2 in two ways: (1) no further H_2O_2 decomposition occurs just after the initial decrease of H_2O_2 , since the reaction of organic substance with $\cdot\text{OH}$ (equation 2.7) overwhelms the reaction of H_2O_2 with $\cdot\text{OH}$ (equation 2.8); (2) the presence of excess organic substance can hinder the reaction between $\cdot\text{OH}$ and the Fe^{2+} (equation 2.6), which may have been the major route of $\cdot\text{OH}$ consumption in the absence of organic substance. Therefore, the remaining Fe^{2+} can react with the H_2O_2 and show a slightly higher consumption of H_2O_2 at the initial stage of the reaction compared to the reaction of Fe^{2+} and H_2O_2 without the presence of organic substance.

3. Low ratio of $[\text{Fe}^{2+}]_0/[\text{H}_2\text{O}_2]_0$ (≤ 1), the decomposition of H_2O_2 almost stop. The result can be explained in the same manner with using ratio of $[\text{Fe}^{2+}]_0/[\text{H}_2\text{O}_2]_0 = 1$. By using low ratio of $[\text{Fe}^{2+}]_0/[\text{H}_2\text{O}_2]_0$, the amount of H_2O_2 decomposed in the presence of organic substance is less than the absence of organic substance.

Wastewater characteristics also affect the efficiency of Fenton's reaction such as phosphates, EDTA, formaldehyde and citric/oxalic acids. 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 a plant scale.

2.4 Fluidized-bed Fenton

In recent years, Fenton reaction has been widely used in degradation of aromatic organic compounds in industrial wastewater. Although this reaction has the effectiveness from high reactivity and nonselectivity of the generated $\cdot\text{OH}$, the disposal of the large volume of the Fe(III)-iron sludge produced in Fenton reaction is a serious problem.

Fluidized-bed is used to transform Fe^{3+} generated in Fenton reaction into an iron oxide such as FeOOH . Iron oxide is generated on the carrier surface by crystallization or sedimentation (Hsueh et al., 2006). Moreover, the FeOOH synthesized in the reaction can act as a heterogeneous catalyst of the decomposition of H_2O_2 (Chou et al., 2001). The factors that effect on the adsorption of iron oxide at the surfaces of fluidized-bed carrier are pH, specific iron loading, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio, and superficial velocity (Chou et al., 2004). Many studies using iron oxide catalyst to treat organic contaminants were performed in batch reactors. Although the batch reactors are quite simple, there are some disadvantages about the operation time of each batch and the amount of wastewater.

The continuous reactors, on the other hand, can be operated continuously with a huge amount of wastewater (Schmidt, 1998). As a result, a continuous flow scheme has been applied to the fluidized-bed Fenton process (Chou et al., 1999; Chou et al., 2004).

The fluidized-bed Fenton process is one of alternatives to ease the production of a substantial amount of ferric precipitation, the major disadvantage of Fenton's reagent. In Fluidized-bed reactor, several 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

Figure 2.2 shows the fluidized-bed Fenton reaction, the Fenton's reagent can produce the non-selective oxidant as $\bullet\text{OH}$ via homogeneous reaction (a). Hydroxyl radical (OH^\bullet) is a strongly oxidant which attacks the organic compounds in oxidation reaction (b). The intermediate products from reaction (b) can lead into further oxidation (c). Fe^{2+} can also be converted to Fe^{3+} by oxidation with $\bullet\text{OH}$. Some Fe^{3+} reversible converted to Fe^{2+} by reacting with H_2O_2 or $\bullet\text{HO}_2$ (d). However, in the presence of solid carrier, the ferric hydrolysis product of Fenton's reaction can also crystallize and adsorb on the surface of the carriers (e); therefore, a substantial amount of ferric precipitation can be decrease (Chou et al., 1999). Furthermore, the synthesized ferric oxide can also serve as a catalyst for hydrogen peroxide decomposition in heterogeneous reaction (f) (Chou et al., 2003). By this step, the $\bullet\text{OH}$ generated can go further in organic compound degradation. Iron oxide on the surface of carriers can also re-dissolve via reductive dissolution or heterogeneous reaction (g) to become Fe^{2+} form.

Fluidized-bed Fenton process allows ferric ion (Fe^{3+}) produced in the Fenton reaction transform to iron oxide (FeOOH) and accumulate on the carrier surface via the crystallization or sedimentation. This process combines the functions of homogeneous chemical oxidation ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), heterogeneous chemical oxidation ($\text{H}_2\text{O}_2/\text{iron oxide}$), 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. Furthermore, iron oxide synthesized from the reaction of hydrogen peroxide and ferrous ion can also be used as the heterogeneous catalyst of hydrogen peroxide (Chou et al., 2003).

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

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

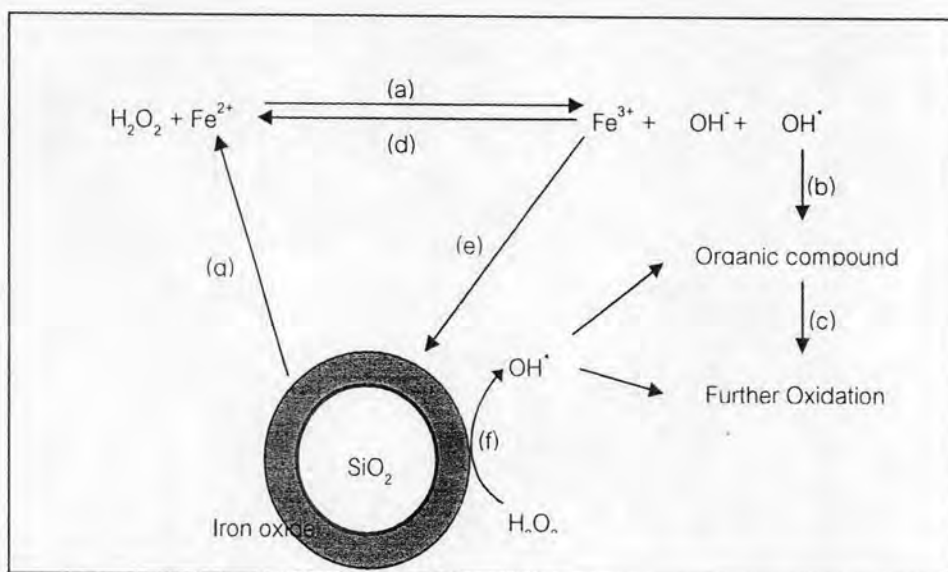


Figure 2.2 Fluidized-bed Fenton reactions

2.5 Silica Dioxide

Silica dioxide (SiO_2) is a white or colorless crystalline compound occurring abundantly as quartz, sand, flint, agate, and many other minerals. The properties of SiO_2 are shown in Table 2.4 (IPCS, 1997). Silica sand has been proved to be good media for mineral coating, especially iron oxides (Scheidegger et al., 1993); therefore, silica sand is suitable to be used for removing Fe^{3+} from Fenton process.

2.6 Statistical Experimental Design Methodology

The traditional approach used to design the experiments for process optimization is the one-factor-at-a-time approach. By this process, experimental factors are varied at a time, with the other factors being held at a constant. However, this approach does not take into account cross-effects from the factors considered and leads to a poor optimization result. When a multi factor system is present, it is more appropriate to employ statistically based optimization strategies to achieve such goal, with the minimum number of experiments. An alternative strategy is the experimental design approach, which implies the use of statistical tools that allow the simultaneous change of several variables (multi-variate analysis) (Montgomery, 2001). The experimental design methodology is a modern approach, which has been widely used in several applications including process modeling. Instead of the process optimization, the design of experiments (DOE) is used to identify or screen the important factors affecting a process or product and to develop statistically significant empirical models (Ramirez et al., 2005).

In order to optimize the process involving many factors, the screening test must be initially considered. The screening test is used to identify the significant factors, so the insignificant factors can be ignore for optimization study. The two-level factorial design is mostly used for identifying the significant factors. In this design, all possible combinations of the levels of the factors are investigated. This design only requires 2 levels of each factor of experiments, the high and low level. For any experiments which have "k" factors, the number of experiment runs required to complete is given by 2^k (Ahmad et al., 2008). By initially restricting the tests to only 2 levels, the number of runs can be minimized (Box et al., 1978; Anderson and Whitcomb, 1996).

Table 2.4 Physical and chemical properties of SiO_2

Property	Value
Molecular formula	SiO_2
Molecular weight	60.1
Appearance	Colorless or white crystals
Density	2.45 (± 0.15) (water = 1)
Water solubility	none
Boiling point	2230°C
Melting point	1656.5 °C (± 46.5 °C)

After determining the significant factors, the optimum operation conditions are obtained by using more complex experimental designs. One of the designs normally used is the Box-Behnken design. Box-Behnken design is a class of rotatable or nearly rotatable second-order designs based on three-level incomplete factorial designs (Box and Behnken, 1960). The number of experiments required for Box-Behnken design is defined as:

$$N = 2k(k - 1) + C_0 \quad (2.14)$$

where N is the number of experiments

k is the number of factors

C_0 is the number of central points (which usually is 5)

For three factors with three levels (high, center, and low), the graphical representation of Box-Behnken design can be seen in a cube form, as shown in Figure 2.3 (Ferreira et al., 2007). From this figure, the cube consists of the central point and the middle points of the edge. The X_1 , X_2 , and X_3 represent the value for each of three factors. The sum of all point in Figure 2.3 is the number of experimental runs, which is equal to the calculation from equation 2.14. An advantage of Box-Behnken design over other designs is that it does not contain combinations for which all factors are simultaneously at their highest or lowest levels. So this design is useful in avoiding experiments performed under extreme conditions, for which unsatisfactory results might occur.

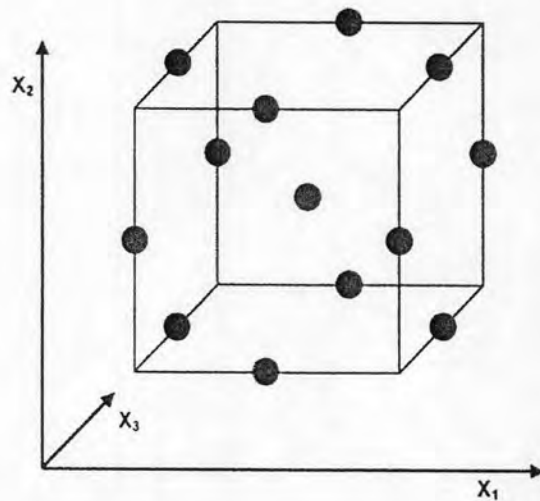


Figure 2.3 A cube for Box-Behnken design with three factors

2.7 Literature Reviews

2.7.1 Oxidative Degradation of Organic Compound in Heterogeneous Catalysis by Means of Hydrogen Peroxide

H_2O_2 is a strong oxidant and is applied to use in the removal of pollutants in wastewater (Venkatadri and Peters, 1993). Oxidation by H_2O_2 alone is not effective for high concentrations of certain refractory contaminants because of low rates of reaction at reasonable H_2O_2 concentrations. H_2O_2 can be activated by ozone, UV-light, or transition metal salts to form $\cdot OH$ which is a strong oxidant (Neyens and Baeyens, 2003). The use of iron oxide such as goethite ($\alpha\text{-FeOOH}$) with H_2O_2 was found to effectively oxidize organic compounds due to the catalysis on iron oxide surface and Fe^{2+} generation (Liou and Lu, 2008).

It is well known that the dissolution of goethite plays an important role in catalyzing the oxidation of organic chemicals. The dissolution of goethite is a surface-controlled reaction; therefore, the degradation of organic compounds increases with increasing concentrations of goethite because it provides more surface sites for reductive dissolution (Lu et al., 2002). There are some important factors affecting the oxidation efficiency of goethite/ H_2O_2 process. Lu (2000) investigated the effect of goethite particle size, goethite concentration, Fe^{2+} and Fe^{3+} on the 2-chlorophenol oxidation by the use of goethite and H_2O_2 . The results indicated that particle size and loading of goethite are important factors that affect the oxidation rate because they can influence the concentration of ferrous ions due to goethite dissolution.

2.7.2 Application of Fluidized-bed Fenton Process

Fluidized-bed reactors have been used in the chemical industry and wastewater treatment (Tai, 1999). For the Fenton process, a fluidized bed is used to transform $Fe(III)$ generated in the Fenton's reaction into an iron oxide on the carrier surface, to eliminate the problem from $Fe(III)$ -iron sludge (Hsueh et al., 2006).

Iron oxide generated in the reaction can also serve as a catalyst for oxidizing organic contaminants (Chou et al., 2001). Chou et al. (1999) studied the effect of Fe^{2+} on catalytic oxidation of benzoic acid in a fluidized bed reactor by applying supported $\gamma\text{-FeOOH}$ as the carrier. They found that when Fe^{2+} was not added in the reactor, the COD removal was caused by homogeneous catalysis of Fe^{2+} formed by reductive dissolution of $\gamma\text{-FeOOH}$. The efficiency of iron oxide catalyst is depended on its properties, which is affected by the crystallization conditions. Chou et al. (2004) investigated the factors influencing the preparation of supported iron oxide in fluidized-bed crystallization. The parameters that were found to significantly influence the crystallization efficiency were the operational pH, superficial velocity, specific iron loading, and influent H_2O_2 concentration.

Instead of a batch reactor that has been used extensively, a continuous flow pattern can be used in the fluidized-bed Fenton process as well because of its high efficiency in mass transfer (Chou and Huang, 1999; Levenspiel, 1999).

2.7.3 Optimization of Process by Statistical Experiment Design

There are many chemical and biological processes using the statistical experiment design for screening test or optimization. In biological processes, the operating conditions are vital to microorganisms, so it is reasonable to use the statistical experiment design to find the significant factors for operating conditions (Guo et al., 2009). Liu et al. (2006) studied the lipase production of *Burkholderia* sp. by considering the significant factors. The results showed the optimum condition and the most influential factor from 5 factors. They also found that the two-level factorial design was quick and effective to use. In chemical processes, the response surface methodology using statistical experiment design was found to be an effective technique for investigating the pollutant removal as a function of chemical parameters (Tiwari et al., 2008). For Fenton's reaction, the optimum condition can be identified by using the statistical experiment design (Ahamadi et al., 2005; Ramirez et al., 2005). Segura et al. (2008) determined the optimum condition for imidacloprid oxidation by photo-Fenton reaction. The results also showed that the iron concentration played the key role in the process kinetic whereas hydrogen peroxide concentration directly affected the extent of the oxidation process. The statistical experiment design was also proven to yield statistically results. The response surface plot can be employed to study the surface and locate the optimum point, while the prediction of pollutant treatment can be calculated. Ay et al. (2009) studied the advanced oxidation of an azo-dye, Direct Red 28 by photo-Fenton treatment in batch experiments using Box-Behnken statistical experiment design and response surface analysis. The results showed that the prediction of dyestuffs oxidation obtained from the response functions were in good agreement with the experimental results indicating the reliability of the method used. The response surface analysis also provided a better understanding for the roles of Fe(II) and H₂O₂ doses on degradation of the dyestuff for the large range of concentration.