

CHAPTER 2

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Trichloroethylene

2.1.1 Introduction

Trichloroethylene is also known as Trichlene and Vitran and by other trade names in industry. It is nonflammable, colorless liquid at room temperature with a somewhat sweet odor. TCE is now mainly used as a solvent to remove grease from metal parts. It can also be found in some household products, including typewriter correction fluid, paint removers, adhesives, and spot removers. Most people can smell TCE when the concentration of TCE in air is around 100 ppm¹.

2.1.2 Chemical and Physical Properties

The chemical and physical properties of TCE are shown in Table 2.1¹⁷.

Table 2.1 Chemical and physical properties of TCE

CAS No.	79-01-6
Chemical formula	C ₂ HCl ₃ (C = 18.28%, H = 0.77%, 80.95 %)
Structural formula	As shown Figure 2.1
Boiling range	87.14-87.55 °C; solidifies at -83°C
Specific gravity	1.465 at 20.4 °C; viscosity: 0.55 centipoise
Vapor pressure	60 mm.Hg at 20 °C
Vapor density	4.53 at 25 °C
Soluble	In ether, alcohol, and chloroform
Solubility in water	0.1 g/100g water at 25 °C
Henry's law constant (dimensionless)	0.49 at 25°C
Distribution coefficient: Water/air	3 at 20°C, 1.6 at 37°C

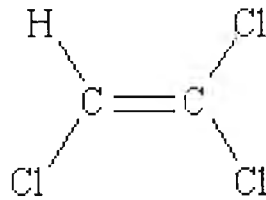


Figure 2.1 Structural formula of Trichloroethylene

2.1.1 Hazard Identification¹⁸

2.1.3.1 Potential Health Effects

Inhalation Inhalation is the major potential route of TCE exposure. Exposure to high concentrations of vapor or mist can cause central nervous system depression with symptoms of headache, dizziness, stupor, loss of consciousness or death depending of concentration and duration of exposure. Exposure to high concentrations can cause irregular heartbeat, cardiac arrest and death. Over exposure has shown to cause adverse effects on the liver, kidney, nervous system, and other internal organs.

Skin Prolonged or repeated contact of liquid can cause irritation, defatting of skin, and dermatitis. Absorption of liquid through intact skin is possible, causing systemic poisoning, but this is an unlikely route of significant toxic exposure.

Eye Liquid in eyes produces pain and irritation with mild temporary damage possible. Vapor can irritate eyes.

Ingestion Single dose toxicity is low to moderate. If vomiting occurs, TCE can be aspirated into the lungs, which can cause chemical

pneumonia and systemic effects. Ingestion can cause adverse health effects as described in the inhalation section above.

2.1.2 Toxicology Information

2.1.4.1 Acute Toxicity

Inhalation The human health effects from inhalation of TCE are summarized in Table 2.2.

Table 2.2 Acute toxicity for TCE from inhalation

Exposure rate (ppm)	Health Effects
200	Mild eye irritation
400	Slight eye irritation and minimal light-headedness after 3 hours
1,000-1,200	Eye and nasal irritation, light-headedness and dizziness after 6 minutes
2,000	Eye and respiratory tract irritation and, drowsiness, dizziness, and nausea within 5 minutes.
15,000	Ventricular arrhythmias and very rapid respiration
Higher concentrations or prolonged overexposure	Unconsciousness and death

Source: (Siegrist, 2000)

Inhalation LC₅₀: 12,000 ppm – 4 hours (rat)

Dermal LD₅₀: >20g/kg (rabbit)

Oral LD₅₀: 5,650 mg/kg (rats)

2.1.4.2 Chronic Toxicity

Chronic TCE overexposure could cause toxic effects in the liver, lymphatic system (one species), kidney, and cardiovascular system of experimental animals. Humans exposed to TCE could become intolerant to ethyl alcohol, with small quantities causing inebriation and skin blotches. The overexposure will result in illness, injury or even death depends on the level and duration of exposure.

Carcinogenicity TCE has been evaluated for possible cancer causing effects in laboratory animals. Ingestion studies in rats at dosages of up to 1,000 mg/kg found an increase in kidney tumors in male rats. The International Agency for Research on Cancer (IARC) has concluded that with respect to TCE, there is sufficient evidence of carcinogenicity to experimental animals and limited evidence of carcinogenicity to humans resulting in a classification in Group 2A as a substance probably carcinogenic to humans. TCE is not listed on the Occupational Safety & Health Administration (OSHA) or National Toxicology Program (NTP) carcinogen lists^{2, 19}.

Mutagenicity Most studies measuring DNA damage (strand breaks, unscheduled DNA synthesis, *in vitro* and *in vivo* micronucleus and chromosomal aberrations) have been negative, but some positive findings have been reported¹⁸.

Reproductive Toxicity Laboratory animal studies on mice, rats and rabbits have been conducted to evaluate the potential reproductive and developmental effects of TCE exposures.

2.1.3 Regulations²

USEPA (U.S. Environmental Protection Agency) regulates TCE as a Hazardous Air Pollutant under the Clean Air Act (CAA) 1990 Amendments and as a Volatile Organic Compound (VOC) subject to emission standards under the CAA Section 111. Under the Safe Drinking Water Act, the Maximum Contaminant Level (MCL) for community and nontransient, noncommunity water systems is set at 0.005 mg/L. The World Health Organization (WHO) recommended a provisional guideline value for TCE in drinking water of 0.070 mg/L. TCE is regulated under Resource Conservation and Recovery Act (RCRA) as a Halogenated Organic Compound (HOC) and under the Land Disposal Restrictions. Under the latter, hazardous wastes that contain total concentrations of HOCs of at least 1,000 mg/L (liquids) or 1,000 mg/kg (nonliquids) are prohibited from land disposal. Under 40 CFR 268.40 and 268.48, treatment standards are given for wastewater and nonwastewater extract concentrations at 0.054 and 6.0 mg/L respectively. TCE is also regulated under Sections 110 and 313 of the Superfund Amendment Reauthorization Act (SARA) and under the Clean Water Act (CWA) Sections 301, 307, and 311. Priority data needs established under Section 110 includes exposure levels in humans living near hazardous waste sites and other populations and epidemiological studies on health effects, including carcinogenicity. Under The Emergency Planning and Community Right-to-Know Act (EPCRA) Section 313 (Community Right-to-Know and the Toxic Chemical Release Inventory [TRI], 40 CFR Part 372 Subpart D, 1992), TCE is one of the 19 substances for which the de minimus for reporting changes from 1.0 percent to 0.1 percent. Under TRI, since 1989, manufacturers of at least 25,000 lb/yr (11,350 kg/yr) and other handlers of at least 10,000 lb/yr (4,540 kg/lb) must report releases of TCE to any environmental medium. The OSHA Permissible Exposure Limit (PEL) for time-weighted average (TWA)

exposure in a 40-hour workweek to TCE in workroom air is 100 ppm (537 mg/m³) with a ceiling value of 200 ppm (1,070 mg/m³).

2.1.4 TCE in Environment

Relatively high vapor pressure and low adsorption coefficient to a number of soil types indicates ready transport through soil and low potential for adsorption to sediments. The mobility in soil is confirmed in soil column studies and riverbank infiltration studies³. Four to six percent of environmental concentrations of TCE adsorbed to two silty clay loams ($K_{OC} = 87$ and 150). No adsorption to Ca-saturated montmorillonite and 17% adsorption to Al-saturated montmorillonite were observed²⁰.

Trichloroethylene is relatively reactive under smog conditions with 50% degradation in 1 to 3.5 hours. An atmospheric residence time based upon reaction with hydroxyl radical is 5 days with production of phosgene, dichloroacetyl chloride, and formylchloride. In the animal body, TCE may break down to dichloroacetic acid (DCA), trichloroacetic acid (TCA), chloral hydrate, and 2-chloroacetaldehyde. These products have been shown to be toxic to animals and could probably be toxic to humans. Once TCE is in water, much will evaporate into the air according to the high Henry's Law Constant. Half-life of evaporation has been reported to be on the order of several minutes to hours, depending upon the turbulence. Nevertheless, TCE is not hydrolyzed by water under normal conditions. It does not absorb light of less than 290 nm and therefore should not directly photodegrade. In groundwater, the diminishing rate is much slower because of the much slower evaporation rate. Very little TCE breaks down in the soil and it can pass through the soil into underground water.

Marine monitoring data only suggest moderate bioconcentration (2-25 times). Bioconcentration factors of 17 to 39 have been reported in bluegill sunfish and rainbow trout.

2.2 Fenton's Reagent

2.2.1 Introduction

Many metals have special oxygen transfer properties, which improve the efficiency of hydrogen peroxide. By far, the most common of these is iron which, when used in the prescribed manner, results in the generation of highly reactive hydroxyl radical ($\text{OH}\cdot$). Its inventor H.J.H. Fenton first observed the reactivity of this system in 1894, but its utility was not recognized until 1930s once the mechanisms were identified. Today, Fenton's reagent is used to treat a variety of industrial wastes containing a range of toxic organic compounds (phenols, formaldehyde, BTEX, and complex wastes derived from dyestuffs, pesticides, wood preservatives, plastics additives, and rubber chemicals). Fenton's reagent was able to oxidize 93-100% (by weight) of dissolved TCE in groundwater and 98-102% (by weight) of TCE in soil slurries¹¹. The process may be applied to wastewater, sludge, or contaminated soils, with the effects being⁴:

- Organic pollutant destruction
- Toxicity reduction
- Biodegradability improvement
- BOD / COD removal
- Odor and color removal

Esplugas *et al.* (2002) compared different advanced oxidation processes (O_3 , $\text{O}_3/\text{H}_2\text{O}_2$, UV, UV/ O_3 , UV/ H_2O_2 , $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, and photocatalysis) for phenol degradation in aqueous solution. Kinetic constants, pH influence, stoichiometric coefficient and optimum oxidant/pollutant ratio were studied. Fenton reagent was found to be the fastest one for phenol degradation, while ozonation provided the lowest cost²².

2.2.2 Chemical Reactions

Fenton's reagent is a mixture of hydrogen peroxide (H_2O_2) and ferrous salt. It produces hydroxyl radicals that are strong oxidizers. Fenton's reagent is not stable. Once H_2O_2 and Fe^{2+} are mixed, several reactions take place simultaneously. These reactions produce hydroxyl radicals ($\text{OH}\cdot$), hydroperoxyl radicals ($\text{HO}_2\cdot$), Fe^{3+} , and O_2 (Eqs. (1)–(7)).

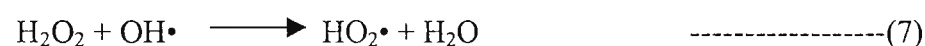
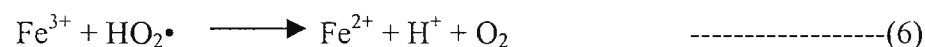
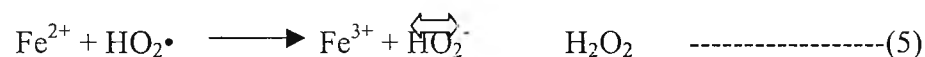
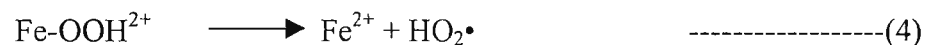
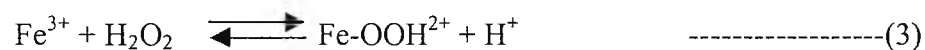
The chemical mechanisms that have been proposed that hydroxyl radicals act as the oxidant species that are generated in the following chemical equation^{21, 23}.



Hydroxyl radicals may be scavenged by reaction with another Fe^{2+} :



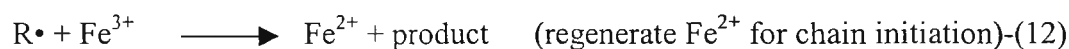
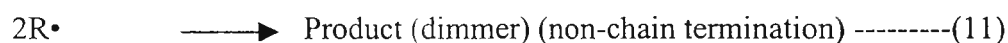
Fe^{3+} catalytically decomposes H_2O_2 following a radical mechanism that involves hydroxyl and hydroperoxyl radicals, including (1) and (2).



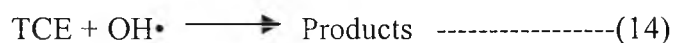
In the initial equation (Eq.1), hydrogen peroxide (H_2O_2) reacts with ferrous iron (Fe^{2+}) to produce a hydroxyl radical ($\text{OH}\cdot$). It is generally agreed that the $\text{OH}\cdot$ then reacts with other substances (Eqs.2, 7) only in the aqueous phase. After Fe^{2+} has been converted to Fe^{3+} , most Fe^{3+} will precipitate from solution as $\text{Fe}(\text{OH})_3$, depending on the pH level. Remaining soluble Fe^{3+} may be cycled back to Fe^{2+} via Eqs.4 or 6. The hydroperoxyl radical ($\text{HO}_2\cdot$) (Eqs.5, 6) in turn depends on the reaction between $\text{OH}\cdot$ and H_2O_2 (Eq.7), which in turn is dependent on the competition of another faster reaction involving $\text{OH}\cdot$ (Eq.2). The system becomes

a chain reaction as iron is reduced from Fe^{3+} to Fe^{2+} , and Fe^{2+} is once more available for reaction with H_2O_2 . However, due to Fe^{3+} precipitation and competing reactions, Fenton's reaction proceeds at a much slower rate after the initial burst of $\text{OH}\cdot$ in the initial reaction (Eq.1)¹⁵. Conclusively, hydroxyl radicals react strongly with the dissolved organic compounds, H_2O_2 , and Fe^{2+} ions in solution. They also react with other hydroxyl radicals themselves. Although, hydroxyl radicals, hydroperoxyl radicals, hydrogen peroxide, and oxygen are all oxidants, hydroxyl radicals have the strongest oxidation capability, and are considered responsible for oxidizing various organic compounds. Then, the conditions that will lead to (Eq.1) must be controlled.

Anyway, the reaction rates of hydroxyl radicals are much faster than the generation of these radicals, which gives them a very short life span. Oxidation of the organic initially depends on the selectivity of the hydroxyl radicals for the target organic compounds and then on the selectivity and availability of these radicals to propagate the reaction¹⁵.



In addition to free radical scavengers, the process is inhibited by (iron) chelants such as phosphates, EDTA, formaldehyde, and citric/oxalic acids. However, a simple overall reaction between TCE and Fenton's reagent can be shown as below¹⁵:



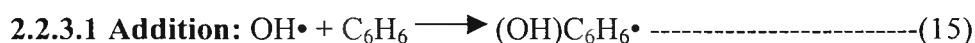
There is no report about the exact products from this reaction. However, Chen *et al.*, found no VOC intermediates or by-products in the oxidation process. He suggested that TCE be most likely mineralized to CO₂, Cl⁻, and H⁺²¹. They also found that due to competition between H₂O₂ and TCE for OH• in aqueous solutions and soil slurries, the presence of TCE significantly decreased the degradation rate of H₂O₂ and was preferentially degraded by OH•.

Weeks *et al.* (2000) studied the degradation of TCE in aqueous systems and soil slurries by Fenton's reagent. In aqueous systems, optimal ratio of initial substances of Fenton's reaction; H₂O₂:Fe²⁺:TCE, 19:1:1 by molar ratio was obtained. They also used pseudo-first-order reaction to explain degradation rate of TCE in the system. In soil slurries, TCE degradation rates were observed to decrease in soil slurries because of the sinking of OH• by organic carbon in soil¹⁵.

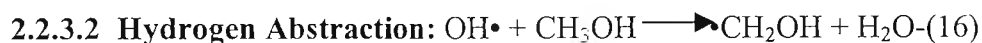
In conclusion, because the degree of oxidation depends upon the dosage of H₂O₂ and Fe²⁺ and the sensitivity of Fenton's Reagent to some under certain conditions in wastewater, it is recommended that the reaction must be characterized through laboratory treatability tests before proceeding to plant scale²⁴.

2.2.3 Reactions of Hydroxyl Radical⁴

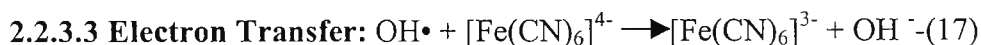
The chemical reactions of the hydroxyl radical in water are of four types:



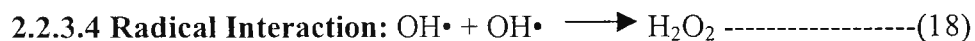
Where the hydroxyl radical adds to an unsaturated compound, aliphatic or aromatic, to form a free radical product (cyclohexadienyl radical shown above).



Where an organic free radical and water 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 unlikely radical, to form a stable product.

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

2.2.4 Factors Affecting Fenton's Reagent

Reaction rates with Fenton's Reagent are generally limited by the rate of $\text{OH}\cdot$ generation (i.e., concentration of iron catalyst) and less so by the specific wastewater being treated. There are some conditions that affect the efficiency of Fenton's Reagent⁴.

2.2.4.1 Effect of Iron Concentration

In the absence of iron, there was no evidence of hydroxyl radical formation when, for example, H_2O_2 is added to a phenolic wastewater (i.e.,

no reduction of phenol occurred). As the concentration of iron is increased, phenol removal accelerates until a point is reached where further addition of iron becomes insignificant. This feature (an optimal dose range for iron catalyst) is characteristic of Fenton's Reagent, although the definition of the range varies between wastewaters. Three factors typically influence its definition:

A minimal threshold concentration of 3-15 mg/L Fe allows the reaction to proceed within a reasonable period of time regardless of the concentration of organic material;

- A constant ratio of Fe: substrate above the minimal threshold, typically 1 part Fe per 10-50 parts substrate, which produces the desired end products. Note that the ratio of Fe: substrate may affect the distribution of reaction products; and
- A supplemental aliquot of Fe which saturates the chelating properties in the wastewater, thereby availing unsequestered iron to catalyze the formation of hydroxyl radicals.
- Iron dose may also be expressed as a ratio to H₂O₂ dose. Typical ranges are 1 part Fe per 5-25 parts H₂O₂ (wt/wt).

2.2.4.2 Effect of Iron Type (Ferrous or Ferric)

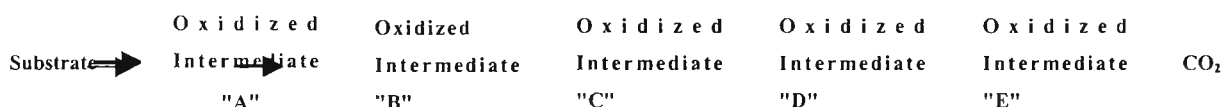
For most applications, the iron used could be either Fe²⁺ or Fe³⁺ salts to catalyze the reaction -- the catalytic cycle begins quickly if H₂O₂ and organic material are in abundance. However, if low doses of Fenton's Reagent are being used (e.g., < 10-25 mg/L H₂O₂), some research suggests ferrous iron may be preferred. The iron salt could be a chloride or sulfate salt, although, chloride generated at high rates of reaction.

It is also possible to recycle the iron following the reaction. This could be done by raising the pH, separating the iron floc, and re-acidifying

the iron sludge. There have been some recent developments in supported catalysts that facilitate iron recovery and reuse.

2.2.4.3 Effect of H₂O₂ Concentration

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



Each transformation in the series has its own reaction rate and, as the case of phenolics illustrates, there may occur build-up of an undesirable intermediate (quinones), which requires sufficient H₂O₂ to be added to push the reaction beyond that point. This is frequently occurred when pretreating a complex organic wastewater for toxicity reduction. As the H₂O₂ dose is increased, a steady reduction in COD may occur with little or no change in toxicity until a threshold is attained, whereupon further addition of H₂O₂ results in a rapid decrease in wastewater toxicity.

2.2.4.4 Effect of Temperature

The rate of reaction with Fenton's Reagent increases with increasing temperature, with the effect more pronounced at temperatures < 20 °C. However, as temperatures increase above 40-50 °C, the efficiency of H₂O₂ utilization declines. This is due to the accelerated decomposition of H₂O₂ into oxygen and water. As a practical matter, most commercial applications of Fenton's Reagent occur at temperatures between 20-40 °C.

Applications of Fenton's Reagent for pretreating high strength wastes may require controlled or sequential addition of H_2O_2 to moderate the rise in temperature which occurs as the reaction proceeds. This should be expected when H_2O_2 doses exceed 10-20 g/L. Moderating the temperature is important not only for economic reasons, but for safety reasons as well.

2.2.4.5 Effect of pH

The effect of pH on reaction efficiency is illustrated below:

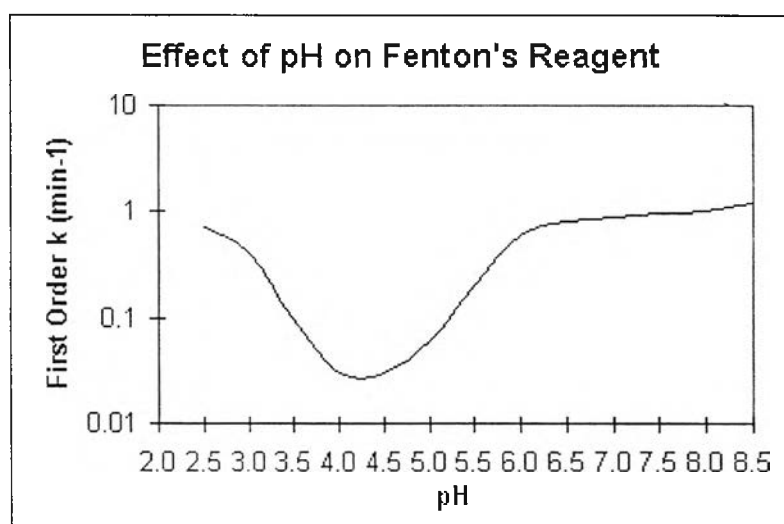


Figure 2.2 Effect of pH on Fenton's reagent

Source: US Peroxide, 2001

The optimal pH occurs between pH 3 and pH 6. The drop in efficiency on the basic side is attributed to the transition of iron from a hydrated ferrous ion to a colloidal ferric species. In the latter form, iron catalytically decomposes the H_2O_2 into oxygen and water, without forming hydroxyl radicals. There have been some recent developments using nonradical scavenging sequestering agents (e.g., NTA and gallic acid) to extend the useful pH range to pH 8-9, but no commercial applications are known. The drop in efficiency on the acid side is less dramatic given the

logarithmic function of pH, and is generally a concern only with high application rates.

A second aspect of pH deals with its shift as the reaction progresses. Provided an initial wastewater pH of 6.0, the following profile is typical of Fenton's reactions.

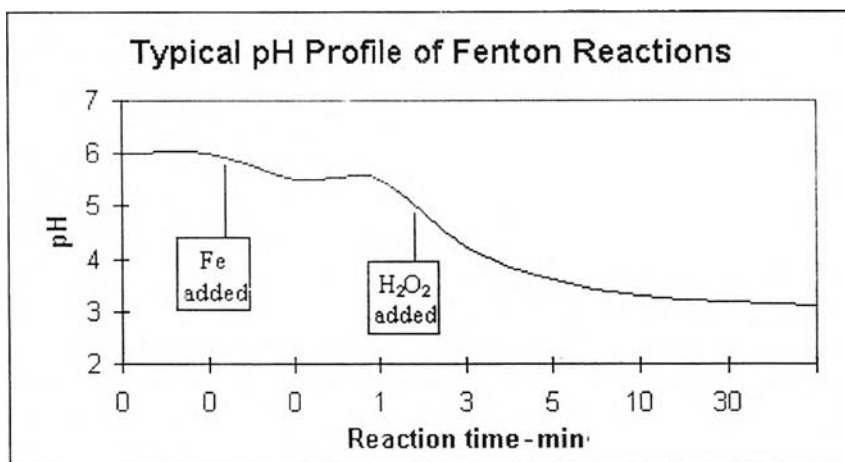


Figure 2.3 Typical pH profile of Fenton's reactions

Source: US Peroxide, 2001

The first inflection is caused by the addition of FeSO_4 catalyst which typically contains residual H_2SO_4 . A second, more pronounced drop in pH occurs as the H_2O_2 is added, and continues gradually at a rate, which is largely dependent on catalyst concentration. This drop in pH is attributed to the fragmenting of organic material into organic acids. This pH change is often monitored to ensure that the reaction is progressing as planned -- the absence of such a pH decrease may mean that the reaction is inhibited and that a potentially hazardous build-up of H_2O_2 is occurring within the reaction mixture.

In highly concentrated waste streams (>10 g/L COD), it may be necessary to perform the oxidation in steps and re-adjust the pH upwards to pH 4-5 after each step to prevent low pH from inhibiting the reaction.

2.2.4.6 Effect of Reaction Time

The time needed to complete a Fenton reaction will depend on the many variables discussed above, most notably catalyst dose and wastewater strength. For simple phenol oxidation (less than 250 mg/L), typical reaction times are 30 - 60 minutes. For more complex or more concentrated wastes, the reaction may take several hours. In such cases, performing the reaction in steps (adding both iron and H₂O₂) may be more effective (and safer) than increasing the initial substances.

Determining the completion of the reaction may prove troublesome. The presence of residual H₂O₂ will interfere with many wastewater analyses. Residual H₂O₂ may be removed by raising the pH to 7-10, or by neutralizing with bisulfite solution. Often, observing color changes can be used to assess the reaction progression. Wastewaters will typically darken upon H₂O₂ addition and clear up as the reaction reaches completion.

2.2.4.7 Effect of Post Treatment

As a result of degrading complex organic materials into organic acid fragments, the pre-oxidized effluent is generally more amenable to conventional treatment, e.g., flocculation and biotreatment. The presence of iron in the reaction mixture makes it particularly suited to subsequent lime flocculation. In many cases, it may be possible to remove up to 80% of the wastewater COD through a combination of Fenton's Reagent and lime flocculation. Significantly, this may be achieved with an H₂O₂ dose of 50-75% of the stoichiometry.

2.2.5 Procedures required in achieving Fenton's reaction

The procedure requires adjusting the wastewater pH to 3-5, followed by adding the iron catalyst (as a solution of FeSO_4), and adding slowly the H_2O_2 . If the pH is too high, the iron precipitates as $\text{Fe}(\text{OH})_3$ and catalytically decomposes the H_2O_2 to oxygen -- potentially creating a critical situation.

Reaction rates with Fenton's Reagent are generally limited by the rate of $\text{OH}\cdot$ generation (i.e., concentration of iron catalyst) and less so by the specific wastewater being treated. Typical Fe: H_2O_2 ratios are 1:5-10 wt/wt, though iron levels < 25-50 mg/L can require excessive reaction times (10-24 hours). This is particularly true where the oxidation products (organic acids) sequester the iron and remove it from the catalytic cycle.

2.3 Titanium dioxide

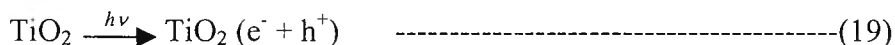
2.3.1 Introduction

Over the last several years, numerous studies have demonstrated the efficiency of photocatalytic oxidation of organic compounds in aqueous TiO_2 suspensions^{6, 13, 17-18, 25-27}. In principle, a photocatalytic reaction may proceed on the surface of TiO_2 powders via several steps, namely (a) production of electron-hole pairs, photogenerated by exciting the semiconductor with light energy; (b) separation of electrons and holes by traps available on the TiO_2 surface; (c) a redox process induced by the separated electrons and holes with the adsorbates present on the surface; (d) desorption of the products and reconstruction of the surface¹⁶.

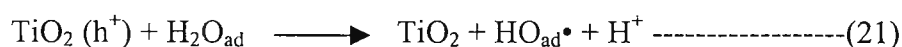
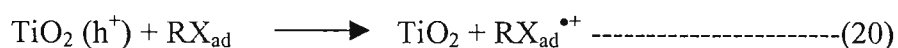
2.3.2 Mechanism of the TiO_2 -Photocatalyzed Oxidative Degradation¹¹

For a mechanistic explanation of the semiconductor catalyzed oxidative degradation of organic material in aqueous systems, the band-gap model has proven to be very useful.

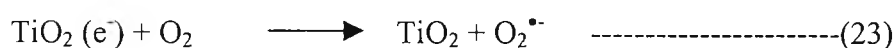
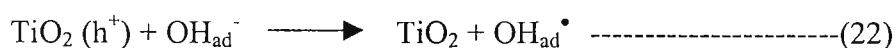
Spectral absorption characteristics of TiO₂ allow its excitation in the UV-C (100-280 nm), UV-B (280-320 nm), and UV-A (320-400 nm) regions. Electronically excited TiO₂ exhibits strong oxidation potentials of the electron-depleted valence band (hole (h⁺), eq. 19).



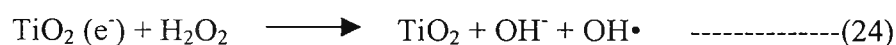
Two oxidation reactions have been experimentally observed: electron transfer from adsorbed substrate RX (eq. 20) and electron transfer from adsorbed solvent molecules (H₂O and HO⁻) (eq. 21 and eq. 22).



The second reaction mechanism appears to be of greater importance in oxidative degradation processes, most probably due to the high concentration of H₂O and OH⁻ molecules adsorbed at the particle surface. Molecular oxygen which must be present in all oxidative degradation processes is the accepting species in the electron-transfer reaction from the conduction band of the photocatalyst to oxygen (eq. 23).



It has also been shown that the addition of H₂O₂ considerably enhances the rate of photodegradation, most probably via reaction 24, or by surface-catalyzed dismutation of H₂O₂.



Organic pollutants adsorbed onto the surface of the titanium dioxide particles will then be oxidized by OH[•] radicals. This heterogeneous photoprocess has been found to be pH dependent, the properties of the solid-liquid interface

(e.g. the electrical double layer) being modified as the pH of the solution is varied. Consequently, the efficiency of the adsorption-desorption processes and, hence, the separation of the electron-hole pairs is also significantly affected.

TiO₂ photocatalytic characteristic modified by doping with metals, such as iron and chromium to make it more active was reported by some researchers. The reports also demonstrated that Fe-doped titanium showed higher activity than pure TiO₂. The degradation rate of the organic contaminants is faster than in the experiment with only Fe²⁺, Fe³⁺ or TiO₂. This was because of the addition of metal atoms to the TiO₂ lattice could reduce the charge carriers recombination rate. Anyway, to modify the surface of TiO₂ by doping metal atom requires high temperature and also some more steps to calcine the metal to the TiO₂ surface⁷.

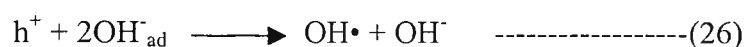
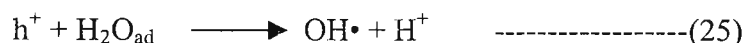
2.3.3 Comparison between TiO₂ and Fenton's reagent

Theoretical advantages of TiO₂/UV processes on Fenton's systems derive from the characteristics of TiO₂ (it is stable, insoluble, nontoxic and resistant to corrosion), the possibility of recycling the photocatalyst (the separation of iron after treatment has to be considered in a Fenton's process) and the wide pH interval at which the TiO₂ with UV radiation process causes decontamination (Fe/H₂O₂ systems require acidification for the wastewater to be treated^{6, 12}).

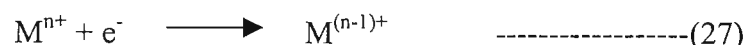
On the other hand, to treat wastewater by TiO₂ photocatalyst is more expensive than the Fenton's system. Generally, TiO₂ is used in powder form and suspended in the reactor in concentrations range from 200-2,500 mg/L depends on each pollutant and the reactor operation conditions^{8-10, 13-14, 16, 28}. Refer to 'Aldrich' handbook of fine chemical and laboratory equipment, TiO₂ powder, 99.9% purity costs \$22.80 per 100g²⁷. However, commercial grade TiO₂ is much cheaper (\$0.05 per pound)²⁹.

2.3.4 Synergic Effect between TiO₂ and Fenton's Reagent

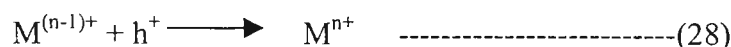
From the procedures of photocatalization by TiO₂, the most important of these reactions is oxidation of adsorbed water or hydroxide ions by holes to produce OH•.



Addition of dissolved transition metal has been observed to increase the rate of TiO₂ photocatalytic oxidation^{9, 14, 16}. This observed increasing rate has been attributed to electron trapping at the semiconductor surface:



where Mⁿ⁺ represents Cu²⁺, Fe³⁺, or Mn³⁺. If operative, reaction (27) prevents electron-hole recombination and results in an increased rate of formation of OH• radical through reactions (25) and (26). Moreover, in case of Fe³⁺, converted Fe²⁺ may act as Fenton's reagent to produce additional OH•. On the other hand, the detrimental effects of high metal concentrations have been attributed to oxidation of reduced metals by OH• radical, or to the reverse of reaction (27).



In addition, a reaction pathway involving the formation of a ternary complex between the metal, the organic substrate, and H₂O₂ or O₂ may be significant when dissolved metals are present in TiO₂ photocatalytic systems.

Wei *et al.*, and Sclafani *et al.* also found that in the system, which contains suspended TiO₂, H₂O₂, and Fe²⁺, phenol removal rate had been extremely enhanced^{14, 16}. Since OH• was produced by Fenton's reaction, TiO₂ can effectively stabilize radicals and radical ions. Thus photogenerated surface-associated redox

intermediates may have a longer lifetime than the same intermediates chemically generated in the solution. The prolonged lifetime results in a greater chance for the occurrence of chemical reaction¹⁶.

In conclusion, there are many clear evidences of achieving Fenton's reaction effectively in various kinds of pollutants especially for chlorinated organic solvents. TiO_2 was generally used as a powerful photocatalyst. Other than being a major initial substance of Fenton's reagent, H_2O_2 can also enhance TiO_2 suspended photocatalytic system. The transition metals were shown to affect photocatalytic degradation of pollutants both in detrimental and incremental ways. However, there is possible trend to combine these two systems to improve the treatment efficiency of TCE, which was the target pollutant for this study. Therefore, the optimal conditions of the system need to be studied to achieve the goal of this research.