CHAPTER 3

MANUSCRIPT IN TREATMENT OF TRICHLOROETHYLENE CONTAMINATED WASTEWATER USING FENTON'S REAGENT

3.1 Abstract

The treatment of trichloroethylene (TCE) was carried by using the Fenton's reagent. The study was conducted by optimization of Fenton's reagent, H_2O_2 and Fe^{2+}, and TCE ratio. Effect of TiO_2 addition and the recycling of iron and TiO_2 sludge were also studied. The economic was evaluated base on the treatment efficiency at the optimum conditions and ratio of initial substances.

The results showed that the optimum molar concentration ratio of H_2O_2:Fe^{2+}:TCE was 20:2:1. The TiO_2 added to the systems that conducted by this work insignificantly enhance treatment efficiency. The results of recycling of the reagents showed promising result.

Keywords: Fenton, TCE, TiO_2, Treatment Condition, Wastewater

3.2 Introduction

Industrial discharges of wastewater streams are the primary release of trichloroethylene (TCE) into the environment[1, 2]. TCE can be treated by many techniques. Unfortunately, each method has its shortcomings. Granular Activated Carbon (GAC) adsorption and air stripping are commonly used; however, neither technology results in the direct destruction of the organic contaminant. TCE can also be treated using biological degradation, but it takes time and has problem of microbial activity tapering off overtime[3]. In order to solve these problems, Fenton's reagent is a possible solution with reasonable short reaction time and cost. In general, the oxidant has been capable of achieving high treatment efficiencies (e.g.> 90%) with very fast reaction rates (90 % destruction in minutes) [5]. However, because of the sensitivity of Fenton's reagent to the conditions and pollutant in wastewater, it is recommended that the reaction always be characterized through laboratory treatability tests before proceeding to plant scale[4].

Titanium dioxide is one of the most powerful semi-conducting materials. It can usually be used as a photocatalytic substance [6-15]. Due to its properties of being able to transfer electrons through its surface, some evidences have shown that TiO_2 surfaces can effectively stabilize radicals and radical ions. The prolonged lifetime results in a greater chance for the occurrence of chemical reaction[8-11, 16].

The objective of this research is to optimize the conditions for using Fenton's reagent with and without the present of TiO_2 to treat TCE in wastewater with the intention to determine the optimal ratio of H_2O_2, Fe^{2+}, and TCE. The results of this work could possibly use for treatment of TCE in wastewater to prevent TCE from releasing to the environment.

3.2.1 Fenton's Reagent

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 (HO•), hydroperoxyl radicals (HO_2•), Fe^{3+}, and O_2 (Eqs.1–7).
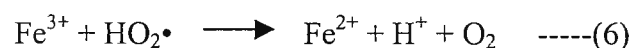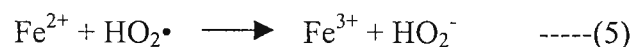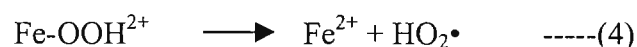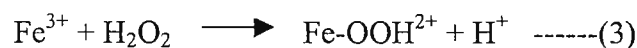
The chemical mechanisms have been proposed that hydroxyl radicals act as the oxidant species that are generated in the following chemical equation[5, 6].

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH• \quad \text{-----(1)}$$
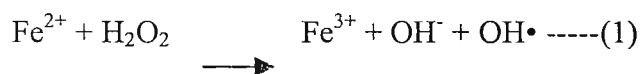
Hydroxyl radicals may be scavenged by reaction with another Fe^{2+}:

$$Fe^{2+} + OH• \longrightarrow Fe^{3+} + OH^- \quad \text{-----(2)}$$
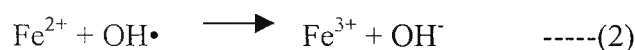
Fe^{3+} catalytically decomposes H_2O_2 following a radical mechanism that involves hydroxyl and hydroperoxyl radicals, including (1) and (2).

$$Fe^{3+} + H_2O_2 \longrightarrow Fe\text{-}OOH^{2+} + H^+ \quad \text{------(3)}$$

$$Fe\text{-}OOH^{2+} \longrightarrow Fe^{2+} + HO_2• \quad \text{-----(4)}$$

$$Fe^{2+} + HO_2• \longrightarrow Fe^{3+} + HO_2^- \quad \text{-----(5)}$$

$$Fe^{3+} + HO_2• \longrightarrow Fe^{2+} + H^+ + O_2 \quad \text{-----(6)}$$

$$H_2O_2 + OH• \longrightarrow HO_2• + H_2O \quad \text{-----(7)}$$

Among these oxidants, hydroxyl radicals has much higher oxidizing state than hydroperoxy radical, then the optimal conditions, which lead to Eq.(1), must be controlled. However, the degree of oxidation depends upon the ratio (R) of H_2O_2, Fe^{2+}, and contaminant.

There is no report on the exact products from the reaction between hydroxyl radical and TCE. However, Chen *et al.,* found no VOC intermediates or by-products in the oxidation process. He suggested that TCE be most likely mineralized to CO_2, Cl^-, and H^{+}[21].

In conclusion, because 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 scale.

3.2.2 Titanium dioxide

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 surface[16].

Band-gap model is very useful to explain the mechanism of the TiO_2-photocatalyzed oxidative degradation. Electronically excited TiO_2 from UV spectral exhibits strong oxidation potentials of the electron-depleted valence band (hole (h^+), eq.8).

$$TiO_2 \xrightarrow{h\nu} TiO_2 (e^- + h^+) \quad \text{-----(8)}$$

Electron then transfers from adsorbed substrate RX (eq.9) and adsorbed solvent molecules (H_2O and HO^-) (eq.10 and eq.11).

$$TiO_2 (h^+) + RX_{ad} \longrightarrow TiO_2 + RX_{ad}^{\bullet+} \quad \text{-----(9)}$$
$$TiO_2 (h^+) + H_2O_{ad} \longrightarrow TiO_2 + HO_{ad}^{\bullet} + H^+ \text{-(10)}$$
$$TiO_2 (h^+) + OH_{ad}^- \longrightarrow TiO_2 + OH_{ad}^{\bullet} \quad \text{-----(11)}$$

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.12).

$$TiO_2 (e^-) + O_2 \longrightarrow TiO_2 + O_2^{\bullet-} \quad \text{-----(12)}$$

The addition of H_2O_2 considerably enhances the rate of phtodegradation, most probably via reaction 13, or by surface-catalyzed dismutation of H_2O_2.

$$TiO_2 \, (e^-) + H_2O_2 \longrightarrow TiO_2 + OH^- + OH\bullet \quad \text{---(13)}$$

Organic pollutants adsorbed onto the surface of the titanium dioxide particles will then be oxidized by OH$\bullet$ radicals.

3.2.3 Synergic Effect between TiO$_2$ and Fenton's Reagent

From the procedures of photocatalization by TiO$_2$, the most important of these reactions is oxidation of adsorbed water or hydroxide ions by holes to produce OH$\bullet$.

$$h^+ + H_2O_{ad} \longrightarrow OH\bullet + H^+ \quad \text{-----(13)}$$
$$h^+ + 2OH^-_{ad} \longrightarrow OH\bullet + OH^- \quad \text{-----(14)}$$

Addition of dissolved transition metal has been observed to increase the rate of TiO$_2$ photocatalytic oxidation[9, 14, 16]. This observed increasing rate has been attributed to electron trapping at the semiconductor surface:

$$M^{n+} + e^- \longrightarrow M^{(n-1)+} \quad \text{-----(15)}$$

where M^{n+} represents Cu^{2+}, Fe^{3+}, or Mn^{3+}. If operative, reaction (15) prevents electron-hole recombination and results in an increased rate of formation of OH$\bullet$ radical through reactions (13) and (14). Moreover, in case of Fe^{3+}, converted Fe^{2+} may act as Fenton's reagent to produce additional OH$\bullet$. On the other hand, the detrimental effects of high metal concentrations have been attributed to oxidation of reduced metals by OH$\bullet$ radical, or to the reverse of reaction (16).

$$M^{(n-1)+} + h^+ \longrightarrow M^{n+} \quad \text{-----(16)}$$

In addition, a reaction pathway involving the formation of a ternary complex between the metal, the organic substrate, and H_2O_2 or O_2 may be significant when dissolved metals are present in TiO$_2$ photocatalytic systems.

Wei *et al.*, and Sclafani *et al.* also found that in the system, which contains suspended TiO_2, H_2O_2, and Fe^{2+}, phenol removal rate had been extremely enhanced[14, 16]. Since OH• was produced by Fenton's reaction, TiO_2 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 reaction[16].

From these above observations, TiO_2 will be used as a new role to enhance the Fenton's reagent furthermore than a photocatalyst. This will combine the advantage of these two treatment techniques, while reducing amount of costly TiO_2 needed to be used alone in the system with higher efficiency and practicability.

3.3 Materials and Methods

3.2.1 Experimental Devices

To ensure the validity of the results of this investigation, all glassware used for this study was of the highest quality. Hydrogen peroxide (35% by weight) from Sigma-Aldrich, Inc. USA, ferrous sulfate crystals ($FeSO_4$ $7H_2O$), trichloroethylene 99.9%, and TiO_2 powder, grain size 325 mesh, 99+% from Fisher Scientific International, USA were used in this work. All chemicals were reagent grade. The experiments were conducted in 165 ml glass vial reactors with sealed aluminum caps to prevent TCE leaking from the reactors. Pure water obtained from Milli-q UV plus ultra-pure water system was used to prepare all solutions.

Junior Orbit Shaker from Lab-Line Instruments, Inc., USA was used at 220 ppm to shake the reactors. To measure pH in the solution, pH meter ORION model 420 A was used. Centrifuger Sorvall RC 28S from E.I. du Pont de Memours and Company, USA was used to separate sludge from treated water.

3.3.2 Analytical Methods

Analytical methods for TCE measurement was adopted from Standard Methods method 6232 B- liquid-liquid extraction gas chromatographic method for trihalomethanes and chlorinated organic solvents[30]. Column was changed to GC column DB-1701 (length = 30 m., I.D. = 0.53 mm) from J&W Scientific. Dynamic Headspace Concentrator Tekmar model 4000 was used for extract TCE from water sample. In addition, temperature program was set as Table 3.1.

Table 3.1 GC column temperature program[30]

Level	Initial Temperature (°C)	Ramped Rate (°C/min.)	Final Temperature (°C)	Hold Time (min.)
1	30	4.0	70	0.00
2	70	70.0	150	1.00
3	150	30.0	240	1.00

Before each analysis, oven, injector, and detector temperatures were set as high as possible (less than the maximum temperature of stationary phase) to completely clean TCE from the system (injector temperature = 200°C, detector temperature = 325°C). Headspace concentrator was set at condition which gave the most consistent data.

3.3.3 Experimental Methodology

Three sets of samples were studied for each condition. Blank samples were tested for quality control and to ensure that there were no impurities or interferences that would alter the results in some unexpected way.

Wastewater from the cleaning process of the APS Company, furniture and fixtures manufacturer located in Songkhla, Thailand was analyzed for TCE. TCE was found at around 20 ppm. However, the presence of other organic contaminants in the wastewater was taken account, then the initial concentration of TCE in this study was set at the maximum concentration of 100 ppm.

3.3.3.1 Determination of the Optimal Conditions to Treat TCE in Wastewater

Synthetic wastewater contaminated with TCE at concentration of 100 ppm was prepared by ultra pure water and TCE reagent. The experiment was adopted from previous researches using Fenton's reagent[9, 30]. First, the TCE solution (synthetic wastewater) was adjusted and controlled the pH close to 3 before adding of Fe^{2+} stock solution and H_2O_2. Next, simultaneously determined the TCE and H_2O_2 concentration in the solution during the chemical reaction in a period of time to obtain the rates of TCE and H_2O_2 degradation (K_{TCE} and K_{H2O2}). H_2O_2 was analyzed by titration with $KMnO_4$ in acidic condition[32]. Then, Na_2SO_3 solution was added to stop the reaction. The solution then was adjusted pH above 10 with 5 N NaOH for to precipitate iron. The comparison of controlled reactors between the TCE/iron and TCE/H_2O_2 were carried out at the same time. The diagram of experimental procedures is shown in Figure 3.1. Ratio of initial chemical concentration (R_2) at 20:1:1, which close to the optimal R that reported by Weeks[15], was chosen for the first ratio in this study. The other 3 ratios, i.e. R_1 = 10:1:1, R_3 = 20:2:1, and R_4 = 40:2:1, were also studied.

3.3.3.2 Possibility of Using TiO_2 with Fenton's Reagent

This work used TiO_2 250-1,000 mg/L for the entile experiment. The TiO_2 was suspended in the systems, i.e. R_1, R_2, R_3, and R_4 as in Butler, Sclafani, and Wei's observation[8, 14, 18]. TiO_2 powder was added into the solution after H_2O_2. All parameters were analyzed as well as those with only Fenton's reagent. The whole procedure is shown in Figure 3.1.

3.3.3.3 Study of the Recycling of Iron and TiO_2

The iron and TiO_2 from the reactor after treated TCE at 4 conditions as shown in Table 3.2 were studied for reusable by separated the iron sludge from water with centrifugal force.

Conclusively, four different conditions; A, B, C, and D were studied in this section. Each condition contains different amount of oxidizing agent and catalyst. Ratio of initial substances molar concentration for each condition can be defined as in Table 3.2.

The centrifuger was set at 8,000 rpm for 20 minutes and RCF equals to 9643. Then, iron sludge was transformed into ferrous by digestion with strong sulfuric acid as shown in Figure 3.1

Table 3.2 Conditions setting in the study

Type	Conditions and Ratios by Molar
A	$R = H_2O_2$: TCE
B	$R = H_2O_2$: Fe^{2+}: TCE
C	$R = H_2O_2$: TCE and TiO_2 in mg/L
D	$R = H_2O_2$: Fe^{2+}: TCE and TiO_2 in mg/L
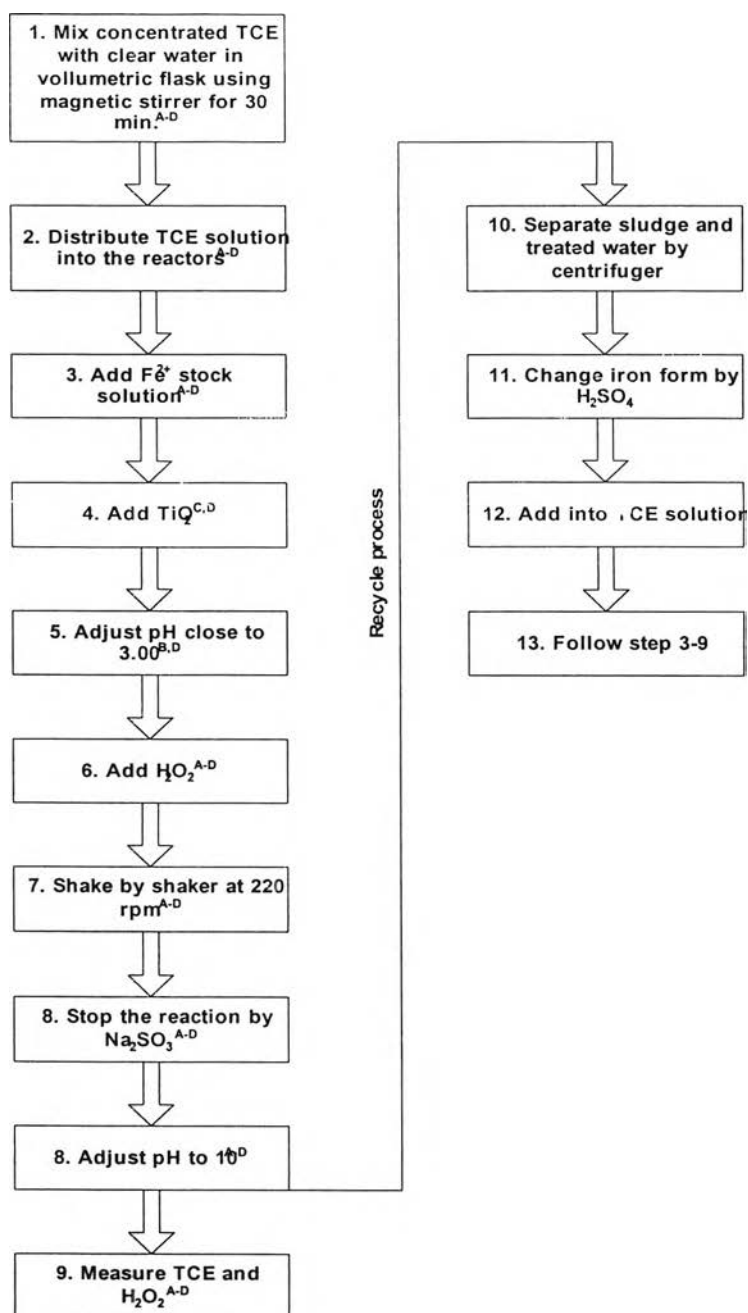
Figure 3.1 Diagram of experimental procedures

3.3.4   Economic Study

The economic evaluation was justified base on the most feasible treatment condition for TCE removal, cost of treatment, %TCE removal, ratio of TCE and H_2O_2 degradation (K_{TCE}/K_{H2O2}) and reaction time were considered.

3.4 Results and discussions

3.4.1 Optimal Conditions of Using Fenton's Reagent to Treat TCE in Wastewater with the Present of Suspended TiO_2

From 3.3.3.1, the results are shown in Figure 3.2, TCE from condition B and D were removed by 80.60 and 82.61 % respectively, while conditions A and C were removed only 6.12% and 8.96%, respectively. These results agreed with Goi's work that without iron and UV radiation, degradation of organic compounds is quite slow[31]. Base on these results, the studies focused on conditions B and D and data were collected to determine K_{TCE} and K_{H2O2}.

Figure 3.3 to 3.6 shows the comparison of TCE removal and H_2O_2 degradation between conditions B and D for the reactors of R_1-R_4. From the results, condition D always showed higher TCE removal than condition B, and, R_4 was the highest TCE removal. The comparison of all conditions is shown in Figure 3.6.
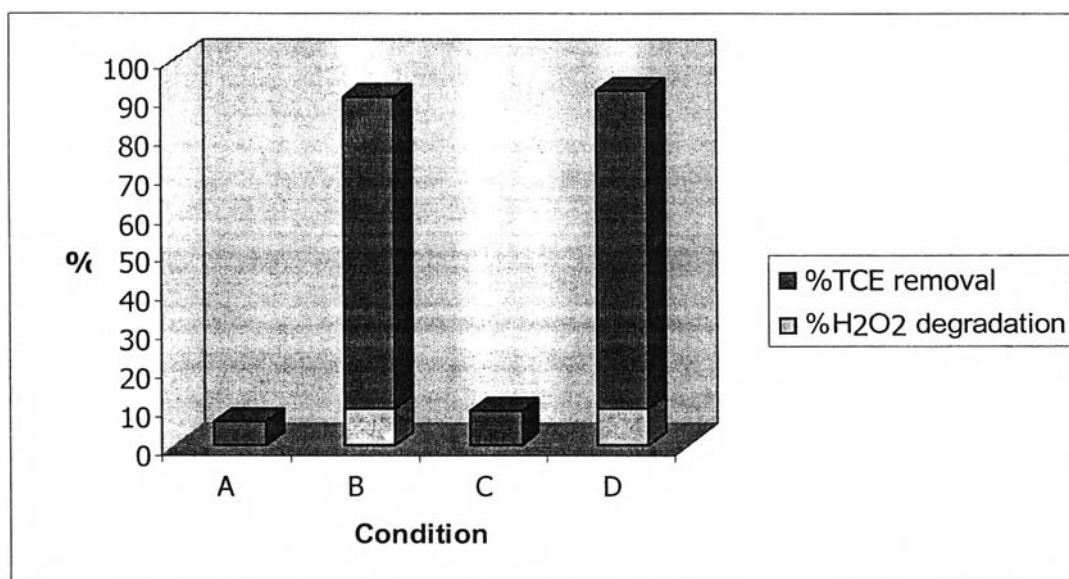
Figure 3.2 Comparison of TCE removal and H_2O_2 degradation from condition A, B,C and D; Initial TCE concentration = 100 ppm, reaction time = 30 min., condition A: R=20:1, B: R-20:1:1, C: R=20:1 TiO_2 = 500 mg/L, D: R = 20:1:1 TiO_2 = 500 mg/L
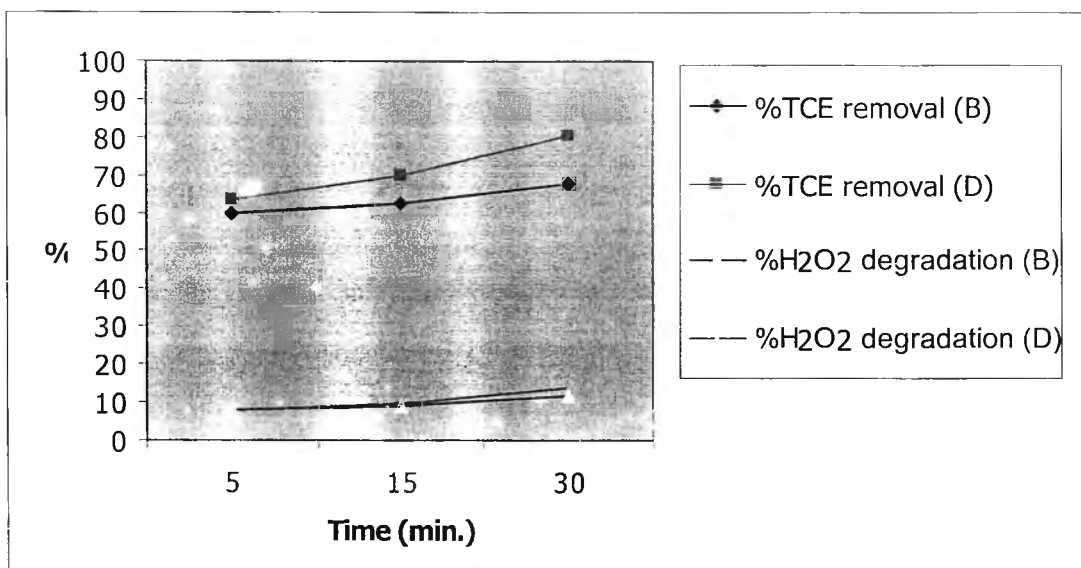
Figure 3.3 TCE removal and H₂O₂ degradation from condition B and D. Condition B; R_1 = 10:1:1, Condition D; R_1 = 10:1:1, TiO₂ = 500 mg/L
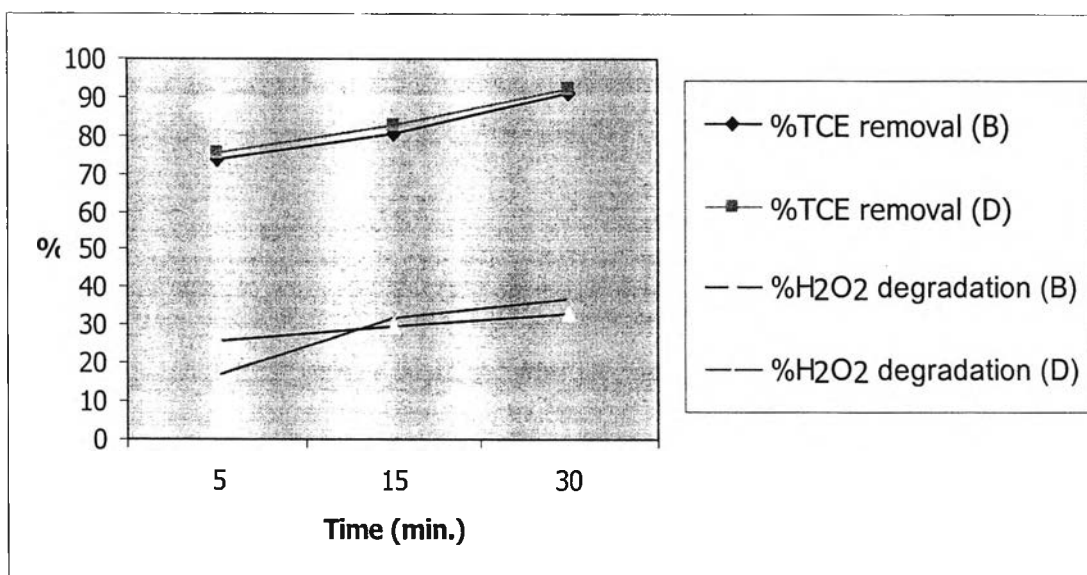

Figure 3.4 TCE removal and H₂O₂ degradation from condition B and D. Condition B; R_2 = 20:1:1, Condition D; R_2 = 20:1:1, TiO₂ = 500 mg/L
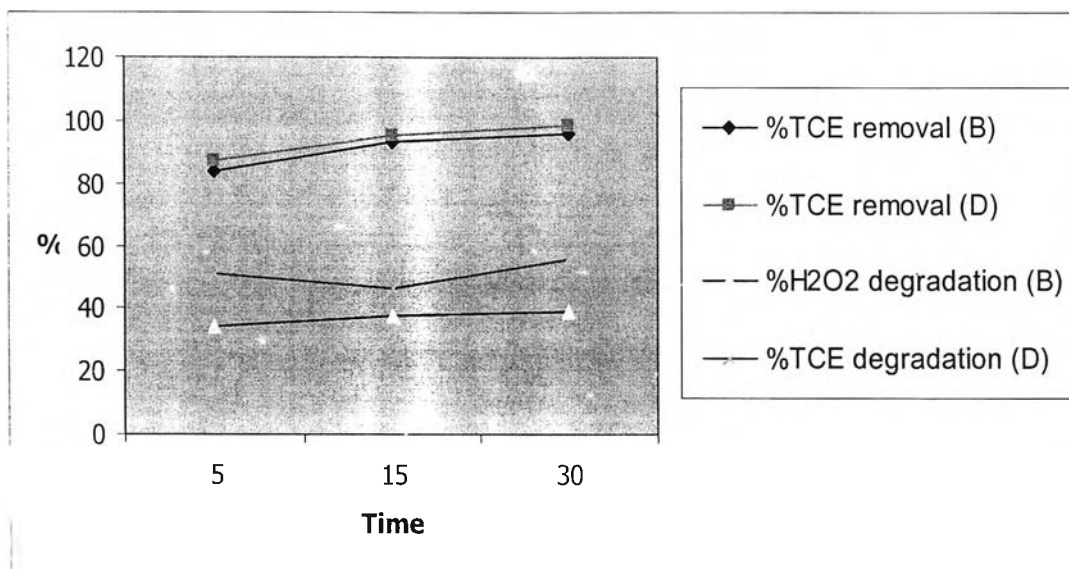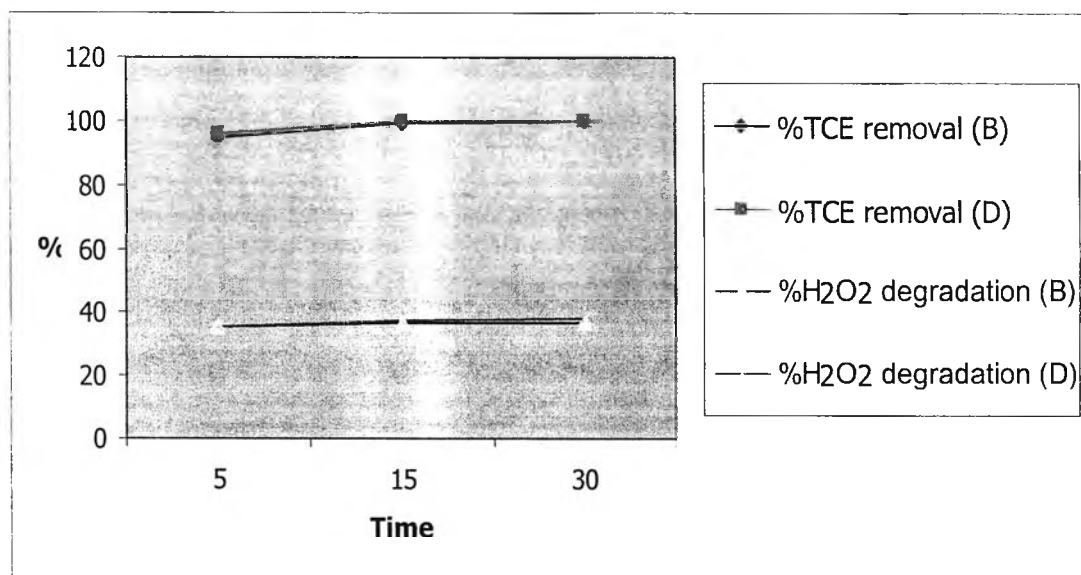
Figure 3.5 TCE removal and H_2O_2 degradation from condition B and D. Condition B; R_3 = 20:2:1, Condition D; R_3 = 20:2:1, TiO_2 = 1,000 mg/L

Figure 3.6 TCE removal and H_2O_2 degradation from condition B and D. Condition B; R_4 = 40:2:1, Condition D; R_4 = 40:2:1, TiO_2 = 250 mg/L
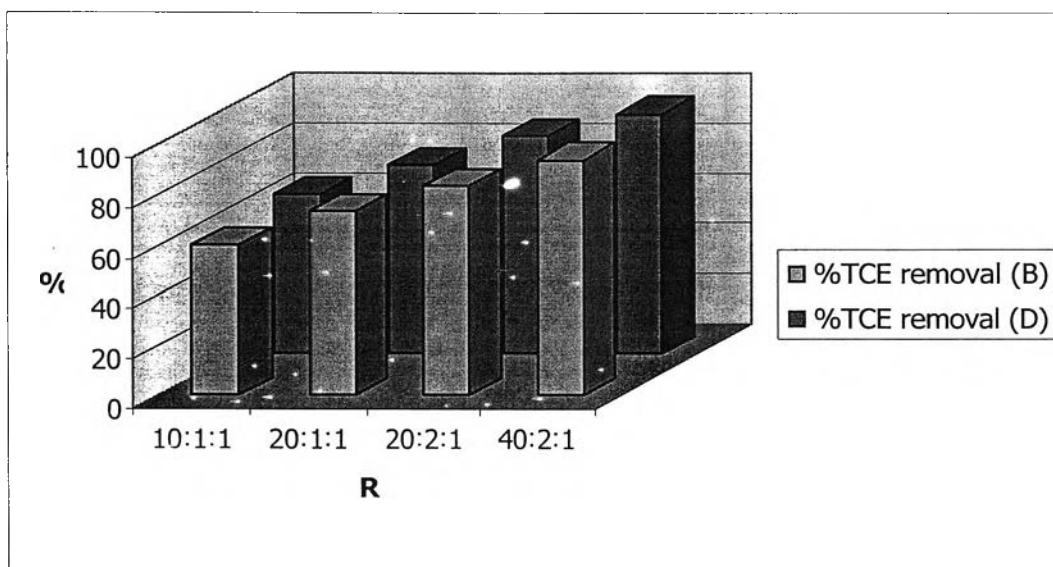
Figure 3.7 Comparison of TCE removal from different R, reaction time = 5 min.

Table 3.3 Comparison of K_{TCE} and K_{H2O2} among each condition

R	Condition	K_{TCE}/K_{H2O2}	Initial pH	Final pH
R_1	B	8.43	3.00	2.26
R_1	D	10.63	3.00	2.23
R_2	B	6.50	3.01	2.56
R_2	D	5.09	3.02	2.53
R_3	B	7.58	2.96	2.35
R_3	D	6.05	3.00	2.36
R_4	B	25.70	3.02	2.61
R_4	D	25.35	3.00	2.55

From the studies in 3.3.3.1 and 3.3.3.2, relationship between rate constant of TCE and H_2O_2 degradation (K_{TCE} and K_{H2O2}) in each condition is shown in Table 3.3. The results showed that TCE removal was more rapid than H_2O_2 degradation. The role of TiO_2 was shown in this table. R_4 gave the largest K_{TCE}/K_{H2O2} ratio. The results also showed the insignificant difference in condition B and D. However, the ratio of K_{TCE} and K_{H2O2} of all conditions were small. Then, to overcome this problem the sampling number should be increased and decreased the interval time between each sampling, i.e. sample collected at 5, 10, and 20 min. instead of 5, 15, and 30 min.

In this study, TiO_2 was varied without fixing the molar ratio of initial chemicals (R). The results showed that, the smallest amount of TiO_2 (250 mg/L) in R_4 comparing to 1,000 mg/L TiO_2 in R_3, very small difference between conditions B and D. The addition of TiO_2 to speed up the reaction as other reports did not work out for the amount that used in this work. However, to confirm this conclusion, a future studies should be conducted by fixing the ratios and varying amount of TiO_2.

According to the results of this work, R_3 with condition B was chosen to be the optimal ratio for using Fenton's reagent to treat TCE contaminated wastewater. Although TCE removal from R_3 was lower than R_4 and TCE removal from condition B was slightly lower than condition D, H_2O_2 addition was much less and no TiO_2 addition. Moreover, it may needs more Fe^{2+} iron than R_2, which gave lower TCE removal, but Fe^{2+} is rather inexpensive comparing to H_2O_2 and TiO_2.

3.4.2 Recycling of Reagent Sludge

The comparison of using fresh iron and recycled iron is shown in Figure 3.8, the results showed that TCE removal from recycled sludge was slightly different from fresh reagent and both R_3 and R_4 were almost similar. However, sludge separation, iron transformation and pH control to recycle iron must take account for the real wastewater treatment. The separation of iron sludge from treated wastewater could be reasonably performed through sludge thickening and dewatering.
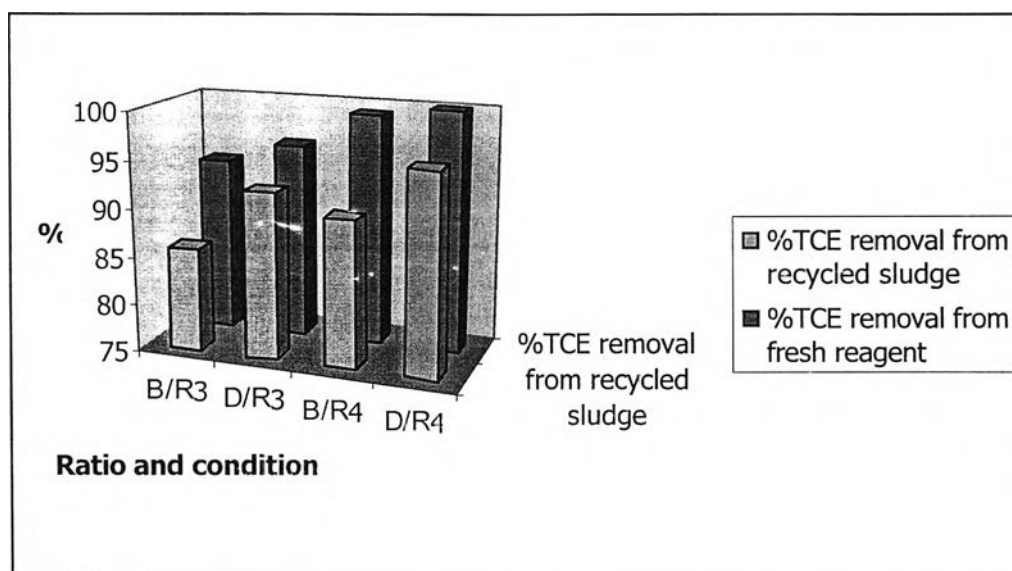
Figure 3.8 Comparison of %TCE removal between recycled sludge and fresh reagent from R_2 and R_4 respectively

3.4.3 Economic Study

Base on the result obtained from 3.4.1, treatment cost for 1L of 100 ppm TCE in wastewater using condition B and D and different R (R_1-R_4) was determined. Comparison of treatment cost is shown in Table 3.5

Refer to the Handbook of Fine Chemical and Laboratory Equipment from Sigma-Aldrich Corporation (2002); prices of chemicals used in this study are listed in Table 3.4[28].

Table 3.4 Prices of Chemicals

Chemical	Price
H_2O_2 35% wt/wt	$161.5 per 4L
$FeSO_4$ $7H_2O$ crystal	$337.40 per 12 kg
TiO_2	$228.7 per 10 kg

Table 3.5 Comparison of treatment cost for 1L of 100 ppm TCE in wastewater using condition B and D; reaction time 15 min.

R	Condition	TiO_2 (mg/L)	%TCE removal	Cost of Treatment ($)
R_1	B	-	62.25	0.033
R_1	D	500	71.34	0.046
R_2	B	-	80.60	0.059
R_2	D	500	83.43	0.071
R_3	B	-	93.32	0.065
R_3	D	1,000	93.68	0.088
R_4	B	-	99.15	0.118
R_4	D	250	98.65	0.124

From Table 3.5, R_3 and R_4 gave reasonably high %TCE removal. However, treatment cost of R_4 was almost double of R_3. Therefore, R_3 was considered to be the optimal ration for this treatment. Next, condition B and D of R_3 was compared in their treatment cost to determine for the optimal condition.

Treatment cost for 1L of 100 ppm TCE in wastewater for condition B and D using R_3 are $0.065 and $0.088, respectively. Considering 15 min. reaction time, % TCE removal was 93.32% and 95.44% for condition B and D, respectively, however, the treatment cost for condition D is 35.38% higher. Then, condition B should be preferred than condition D.

In conclusion, condition B using R_3 is considered to be the optimal ratio for this treatment. This condition and ratio could be applied for wastewater containing different amount of TCE than 100 ppm as in this study. However, to apply Fenton's reagent to wastewater containing much higher TCE concentration i.e., 500 ppm or wastewater containing various kinds of contaminants, further study is recommended.

Indeed, the experiments did not go smoothly in the early stage. The results of using Fenton's reagent to oxidize TCE did not match other researchers'

findings. The causes of problem were analyzed by the Root Cause Analysis as shown in Figure 3.9. Methanol and ethanol, which were used as co-solvent of TCE in the early experiment, were found to be the cause of problem. These alcohols inhibited the Fenton's reaction. After that, synthetic TCE in wastewater was prepared directly from concentrated TCE without using any co-solvent, ethanol.
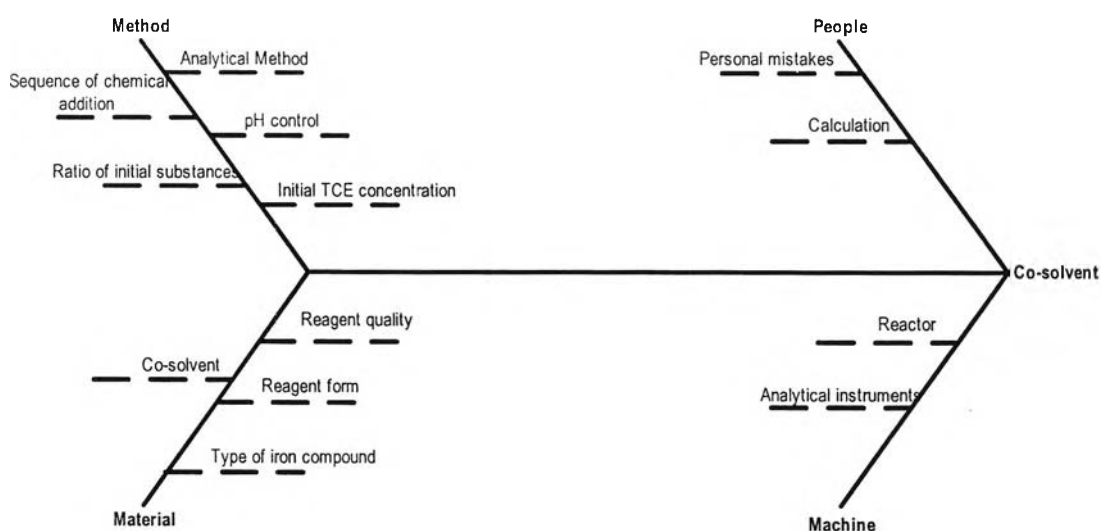

Figure 3.9 Root Cause Analysis

The Fenton's reaction inhibition from alcohol could be explained by eqs.17-21. Weeks (2000) reported that the rate constant of reaction 1 is very low $(37\text{-}76 \ M^{-1}s^{-1})$[15]. Then, the co-solvent; methanol or ethanol, could compete with Fe^{2+} to react with H_2O_2 as shown in eq.17 and 18[33]. Furthermore, reaction between hydroxyl radical and TCE was proposed by Getoff as shown in eq.19[34]. Rate constant of this reaction is $3.3*10^9$. In this case, hydroxyl radical could also react with the alcohols as shown in reactions 20-21[34-35]. Rate constant of reactions 20 and 21 are $8.3*10^8$ and $2.2*10^9 (M^{-1}S^{-1})$ respectively. The further study should be conducted to identify an exact explanation for this incident.

$$CH_3OH + 3\,H_2O_2 \longrightarrow CO_2 + 5\,H_2O \ \text{-----(17)}$$

$$C_2H_5OH + 2\,H_2O_2 \longrightarrow CH_3COOH + 3H_2O \text{-(18)}$$

$$OH\bullet + TCE \longrightarrow CCl_2CHClOH\bullet \text{-----(19)}$$

$$OH\bullet + CH_3OH \longrightarrow CH_2OH + H_2O \text{-----(20)}$$

$$OH\bullet + C_2H_5OH \longrightarrow C_2H_5O + H_2O \ \text{-----(21)}$$

3.5 Conclusions

The results obtained from this study show the optimal conditions for using Fenton's reagent for TCE removal in wastewater, the catalytic effect of TiO_2 powder, and the possibility of recycling of iron sludge. These results will be useful to apply to the real wastewater treatment. The interference from alcohol was also investigated.

The results showed that Fenton's reagent alone and Fenton's reagent with the present of TiO_2 (conditions B and D), gave much higher treatment efficiency than the other condition without ferrous iron. TCE removals were more than 90% within 15min. reaction time. The optimal ratio of initial substances (R) was H_2O_2:Fe^{+2}:TCE = 20:2:1. However, the role of TiO_2 was not clear in this studied since the results from conditions B and D were insignificantly different.

Percentage TCE removal from using recycled iron is closed to %TCE removal from using fresh reagent. However, cost of using recycled sludge, which include sludge separation, iron transformation, pH control, should be compared with using fresh reagent when it is used in the real wastewater treatment.

From cost estimation, using of Fenton's reagent without TiO_2 was preferred to other alternatives.

Methanol and Ethanol, which were used as co-solvent for TCE, were identified as the inhibitors of Fenton's reaction. This work indicates that wastewater characterization must take in account before using Fenton's reagent to treat the water.

Acknowledgement