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Treatment of trichloroethylene contaminated wastewater using Fenton's reagent

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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.

(Fenton, TCE, TiO_2, treatment condition, wastewater)

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 could also treated using biological degradation, but takes time and has problem of the 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[4]. However, because of the sensitivity of Fenton's reagent to the conditions and pollutant in wastewater, it is recommended that the reaction must be characterized through laboratory tests before proceeding to plant scale [3].

Titanium dioxide is usually used as a photocatalytic substance [6-14]. 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 [7-10, 15].

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.

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 [7, 16].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\bullet \quad (1)$$

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

$$Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH^- \quad (2)$$

Fe^{3+} catalytically decomposes H_2O_2 following a radical mechanism that involves hydroxyl and hydroperoxyl radicals.

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{-}OOH_2^{+} + H^+ \quad (3)$$

$$Fe\text{-}OOH_2^{+} \rightarrow Fe^{2+} + HO_2\bullet \quad (4)$$

$$Fe^{2+} + HO_2\bullet \rightarrow Fe^{3+} + HO_2^- \quad (5)$$

$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + H^+ + O_2 \quad (6)$$

$$H_2O_2 + OH\bullet \rightarrow HO_2\bullet + H_2O \quad (7)$$

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^+ [17].

Synergic Effect between TiO_2 and Fenton's Reagent

Over the last several years, numerous studies have demonstrated the efficiency of photo catalytic oxidation of organic compounds in aqueous TiO_2 suspensions1 [6, 12]. From the procedures of photocatalization by TiO_2, addition of dissolved transition metal has been observed to increase the rate of TiO_2 photo catalytic oxidation [8, 13, 15]. This observed increasing rate has been attributed to electron trapping at the semiconductor surface:

$$M^{n+} + e^- \rightarrow M^{(n-1)+} \quad (8)$$

where M^{n+} represents Cu^{2+}, Fe^{3+}, or Mn^{3+}. If operative, reaction (8) prevents electron-hole recombination and results in an increased rate of formation of OH• radical. Moreover, in case of Fe^{3+}, converted Fe^{2+} 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 (9).

$$M^{(n-1)+} + h^+ \rightarrow M^{n+} \quad (9)$$

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 photo catalytic 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 [13, 15]. 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 [15].

From these above observations, TiO_2 will be used as a new role to enhance the Fenton's reagent furthermore than a photo catalyst. 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.

MATERIALS AND METHODS

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 ($FeSO_4 \cdot 7H_2O$), trichloroethylene 99.9%, and TiO_2 powder, grain size 325 mesh, >99% from Fisher Scientific International, USA were used in these works. 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 in the study 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. Centrifuge Sorvall RC 28S from E.I. du Pont de Memours and Company, USA was used to separate sludge from treated water.

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 [18]. 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 1.

Table 1. GC column temperature program [18].

Step	Ramp rate, °C/min	Final temp, °C	Hold time, min
1	4.0	70	0
2	70.0	150	1
3	30.0	240	1

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 and detector temperature, 325°C). Headspace concentrator was set at optimum conditions which gave the most consistent data.

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.

Determination of the Optimal Conditions for Using Fenton's Reagent 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 [14, 17]. 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 determination of the TCE and H_2O_2 concentration in the solution during the chemical reaction in a period of time was obtained 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 [19]. Then, Na_2SO_3 solution was added to stop the reaction. The solution then was adjusted pH above 10 with 5 N NaOH to precipitate iron. The comparison of controlled reactors between the TCE/iron and TCE/H_2O_2 were carried out at the same time. Ratio of initial chemical concentration (R_2) at 20:1:1, which close to the optimal R that reported by Weeks [14], 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.

Possibility of Using TiO_2 to Enhance Fenton's Reagent

This work used TiO_2 250-1,000 mg/L for the entire 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, 13, 15]. 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.

Study of the Recycling Iron and TiO_2

The objective of this study is to recycle iron in treated water back to the next treatment cycle. By doing this, ferrous iron, which is one of the major components of the Fenton's reagent, or TiO_2 could be saved. Thus, only H_2O_2 is needed for the next cycle.

To recycle ferrous iron, pH was increased to above 10 to precipitate iron in the solution. Iron sludge was separated from water by centrifuging. The centrifuge was set at 8,000 rpm for 20 minutes and RCF equals to 9643. And then, iron sludge was transformed into ferrous iron form by digestion with sulfuric acid. The procedure is also shown in Figure 1. 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 2.

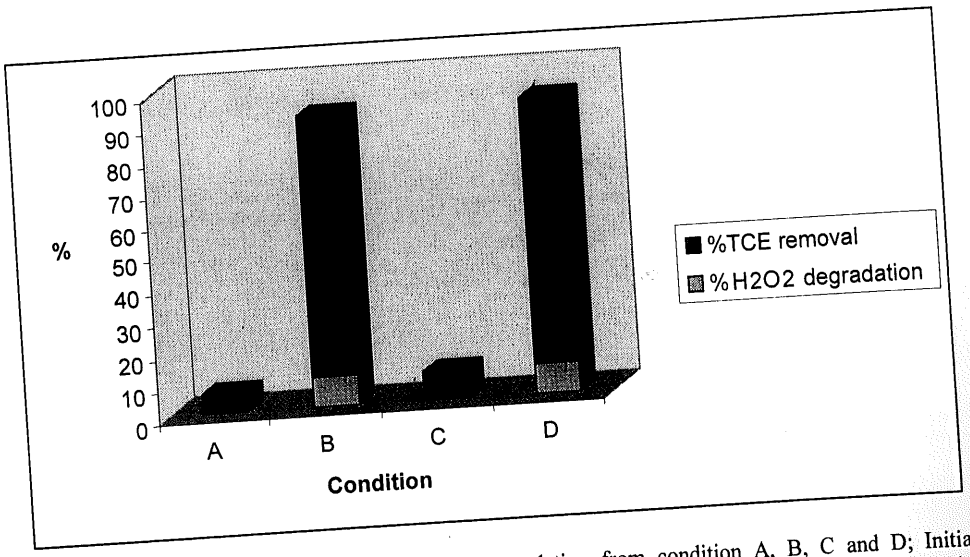

Figure 1. Comparison of TCE removal and H_2O_2 degradation from condition A, B, C and D; Initial TCE concentration = 100 ppm, reaction time = 30 min., condition A: R=20:1, B: R-20:1:1, C: R=20:1 TiO_2 = 500 mg/L, D: R = 20:1:1 TiO_2 = 500 mg/L.

Table 2. Conditions setting in the study.

Type	Conditions and Molar ratio
A	$R_1 = H_2O_2$: TCE
B	$R_2 = H_2O_2$: Fe^{2+}: TCE
C	$R_3 = H_2O_2$: TCE and TiO_2 in mg/L
D	$R_4 = H_2O_2$: Fe^{2+}: TCE and TiO_2 in mg/L

Economic Study

The economic evaluation was justified base on the most feasible treatment condition for TCE removal, cost of treatment; %TCE removal and reaction time were considered.

RESULTS AND DISCUSSIONS

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

From the determination of the optimal conditions for TCE treatment using Fenton's Reagent, the results shown in Figure 1, TCE from condition B and D 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 [20]. Figure 2 to 5 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 6.

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

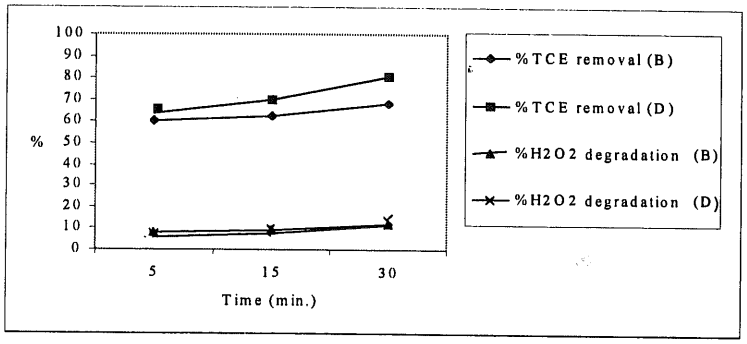

Figure 2. TCE removal and H_2O_2 degradation from condition B and D. Condition B; R_1 = 10:1:1, Condition D; R_1 = 10:1:1, TiO_2 = 500 mg/L.

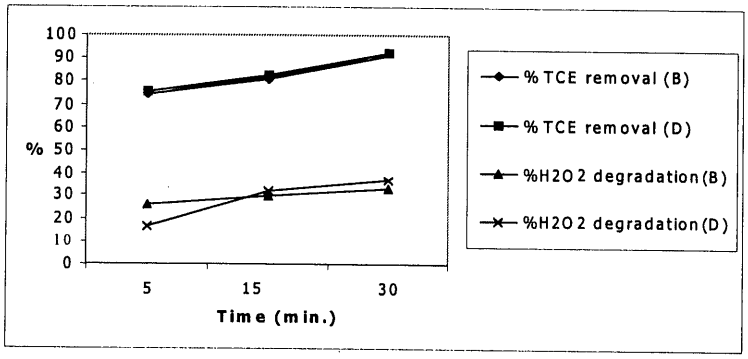

Figure 3. TCE removal and H_2O_2 degradation from condition B and D. Condition B; R_2 = 20:1:1, Condition D; R_2 = 20:1:1, TiO_2 = 500 mg/L.

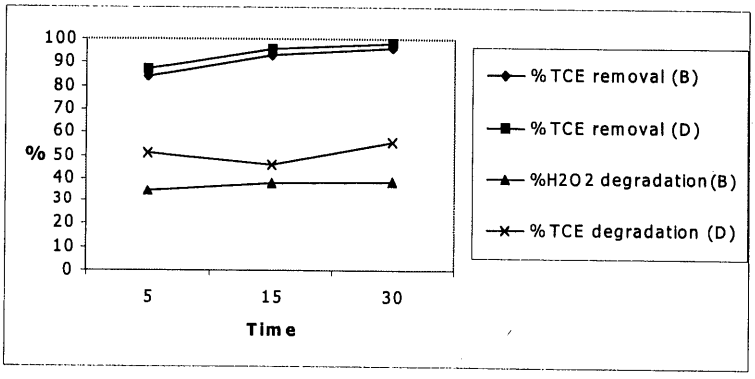

Figure 4. TCE removal and H_2O_2 degradation from condition B and D. Condition B; R_3 = 20:2:1, condition D; R_3 = 20:2:1, TiO_2 = 1,000 mg/L.

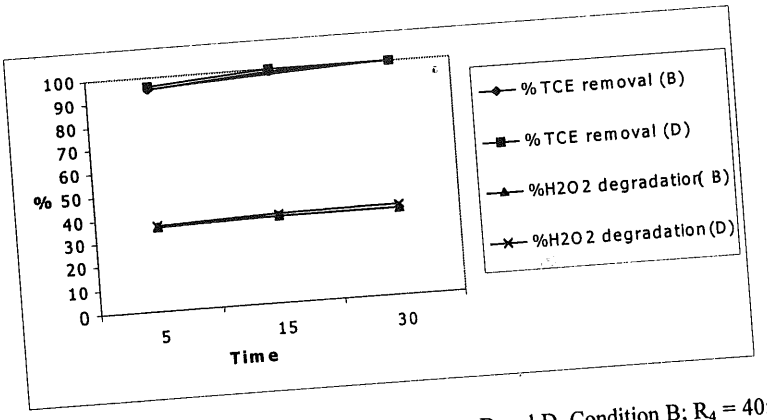

Figure 5. TCE removal and H_2O_2 degradation from condition B and D. Condition B; R_4 = 40:2:1, condition D; R_4 = 40:2:1, TiO_2 = 250 mg/L.

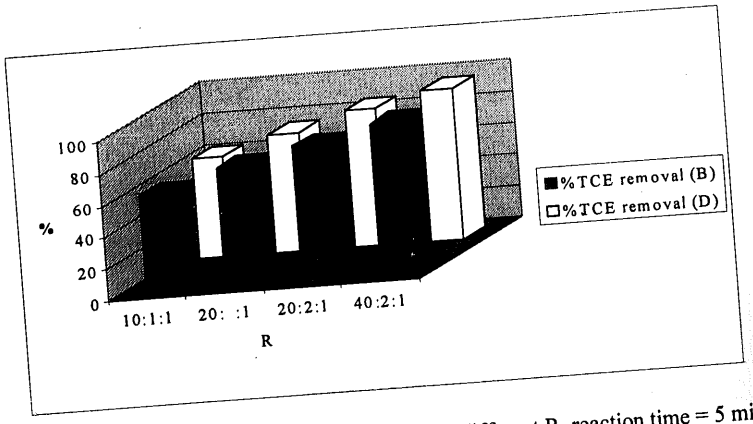

Figure 6. Comparison of TCE removal from different R, reaction time = 5 min.

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.

Recycling of Reagent Sludge

The comparison of using fresh iron and recycled iron is shown in Figure 7, 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.

Economic Study

Base on the result obtained from 2.3.1, treatment cost for 1 L 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 is Table 3. The prices of chemicals used in this study referred to the Handbook of Fine Chemical and Laboratory Equipment from Sigma-Aldrich Corporation (2002) [21].

From Table 3, 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.

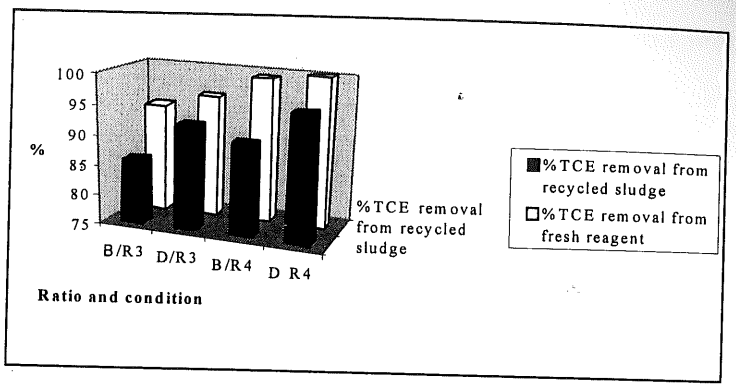

Figure 7. Comparison of %TCE removal between recycled sludge and fresh reagent from R_2 and R_4 respectively.

Table 3. Comparison of treatment cost for 1L of 100 ppm TCE in wastewater using condition B and D; reaction time 15 min.

R	Condition	TiO2 (mg/L)	%TCE Removal	Treatment cost ($)
R1	B	-	62.25	0.033
R1	D	500	71.34	0.046
R2	B	-	80.60	0.059
R2	D	500	83.43	0.071
R3	B	-	93.32	0.065
R3	D	1,000	93.68	0.088
R4	B	-	99.15	0.118
R4	D	259	98.65	0.124

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 minutes, 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 preferred than condition D.

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. Methanol and ethanol, which were used as co-solvent of TCE in the early experiments, were found to be the cause of problem. This methanol inhibited the Fenton's reaction. After that, synthetic TCE in wastewater was prepared directly from concentrated TCE without using any co-solvent.

The Fenton's reaction inhibition from methanol could be explained by equations. (10)-(14). Weeks (2000) reported that the rate constant of reaction 1 is very low (37-76 $M^{-1}s^{-1}$) [14]. Then, the co-solvent; methanol or ethanol, could competed with Fe^{2+} to react with H_2O_2 as shown in eq.10 and 18 [22, 23]. Furthermore, reaction between hydroxyl radical and TCE was proposed by get off as shown in eq.(12) [24]. Rate constant of this reaction is $3.3*10^9$. In this case, hydroxyl radical could also react with the methanol as shown in reactions 20-21 [24, 25]. Rate constant of reactions (13) and (14) 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

$$CH_3OH + 3\ H_2O_2 \rightarrow CO_2 + 5\ H_2O \quad (10)$$

$$C_2H_5OH + 2\ H_2O_2 \rightarrow CH_3COOH + 3H_2O \quad (11)$$

$$OH\bullet + TCE \rightarrow CCl_2CHClOH\bullet \quad (12)$$

$$OH\bullet + CH_3OH \rightarrow CH_2OH + H_2O \quad (13)$$

$$OH\bullet + C_2H_5OH \rightarrow C_2H_5O + H_2O \quad (14)$$

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 15 minutes. The optimal ratio of initial substances (R) was H_2O_2: Fe^{+2}: TCE = 20:2:1. This condition and ratio could be applied for wastewater containing different amount of TCE more than 100 ppm. 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. 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 compared with using fresh reagent when applied to use 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.

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