

Fenton Process for Treatment of Contaminated Groundwater

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(Manuscript received on August 23, 2001)

We investigated the optimal experimental conditions and reaction kinetics for the decompositions of PCE, TCE, naphthalene, and chloroform using conventional Fenton oxidation process. Additionally, the influence of pH on the decompositions of PCE was also evaluated. The results indicated that the optimal pH value was around 3. The dosage of Fenton's reagent and the molar ratio of hydrogen peroxide to ferrous ion for an approximately complete decomposition was found to depend on the properties of the organic compound. Due to their unsaturated structures, the results show that PCE, TCE, and naphthalene could be all effectively decomposed by Fenton's reagent oxidation. Their unsaturated structures could be mostly destroyed within first 1-2 minutes at a low dosage with an certain molar ratio of hydrogen peroxide to ferrous ion. However the saturated compound such as chloroform was more difficult to decompose even with a relatively high dosage of Fenton's reagent.

Key words : Fenton oxidation, TCE, PCE, Naphthalene, Reaction kinetics

1. Introduction

In the presence of ferrous ion, hydrogen peroxide is decomposed into hydroxyl radicals, and hydroxyl radicals oxidize the ferrous ions into ferric ions. In the presence of organic compounds, the hydroxyl radicals oxidizes the degradable compounds into the free radicals and water. The further chain oxidation of the organic radicals then leads to the total decomposition of organic compounds, leaving only carbon dioxide and water.

As a hazardous waste treatment technology, oxidation process using Fenton's reagent as a hazardous waste treatment technology has the following major advantages ; no chlorinated organic compounds are formed during the oxidation process, as in chlorination and ozonation ; there is no mass transfer limitation due to the homogeneous catalytic nature of the process ; it produces nontoxic ferrous sulfate and hydrogen peroxide; it is inexpensive¹⁾. Due to the unselective oxidation property of the hydroxyl radicals, Fenton's reagent has been widely applied in the treatment of hazardous organic compounds. The hydroxyl radicals combine with carbon in the

organic carbon in the organic compounds attacking treatment of hazardous organic compounds. The hydroxyl radicals combine with carbon in the compounds attacking and substituting certain functional groups, thereby convert most organic compounds into harmless carbon dioxide and water.

Sudoh et al.²⁾ previously investigated the feasibility of the Fenton oxidation of phenolic compounds and found that phenol was oxidatively degraded to oxalic acid and carbon dioxide. Sedlack³⁾ also reported that chlorophenols, chlorobenzene, and dichlorobiphenyls could be effectively degraded by Fenton's reagent. It is supposed that the most direct mechanism for the decomposition of chlorinated aromatic hydrocarbons(CAHs) proceeds through hydroxylation followed by ring cleavage and mineralization.

Kuo et al.⁴⁾ applied Fenton's reagent to decolorize dye wastewater, and obtained an average percent removal of chemical oxygen demand of approximately 88 % was obtained. Furthermore, Fenton's reagent has been suggested as a means to oxidize octachlorodibenzo-p-dioxin, hexachlorobenzene in silica sands or natural soils⁵⁻⁶⁾.

The overall goal of the current study is to treat

some toxic organic compounds contaminated in groundwater, and is also to investigate the reaction kinetics of PCE, TCE, naphthalene, and chloroform in an aqueous solution using conventional Fenton oxidation with either batch or the continuous addition of hydrogen peroxide. Accordingly, Pseudo-continuous conventional Fenton's oxidation was used to simulate Fenton's oxidation since in both processes involve the continuous addition of the hydrogen peroxide.

2. Experimental

2.1. Reagents

Reagent grade PCE, naphthalene, spectrophotometric grade TCE, and HPLC grade chloroform were all obtained from the Aldrich Chemical Company. The purities of these organic compounds were 99 %, 98 %, 99.5 %, and > 99 %, respectively. Hydrogen peroxide and ferrous sulfate, both reagent grade, were obtained from the Fisher Scientific Company with purities of 31.5 % and 98 %, respectively.

2.2. Stock solutions

Stock solutions of the selected organic compounds were prepared by dissolving them in double distilled water in a stirred glass flasks, which was sealed with parafilm around the stopper in order to prevent any organic vapor from leaking, by dissolving them in the double distilled water.

It took several days that were required to totally dissolve the crystal naphthalene, meanwhile the liquid PCE, TCE, and chloroform were much easier to dissolve and took only 3~4 hours. No co-solvents were used here. The concentration of the naphthalene, chloroform, PCE, and TCE stock solutions was about 25, 50, and 100 ml, respectively. When the samples were analyzed, the initial exact concentrations were also determined.

2.3. Chemical analysis

The PCE and TCE were analyzed using a GC (Hewlett Packard 5890, Series II) with a capillary column of crosslinked methyl silicon gum of 30 m \times 0.53 mm \times 0.69 μ m film thickness. The naphthalene was analyzed using a GC/MS (MS : Hewlett Packard, 5972 Series, mass selective

detector) with a GC capillary column of crosslinked 5 % PhMe silicon of 30 m \times 0.25 mm \times 0.25 μ m film thickness. In order to minimize any chemical analysis error, the GC and GC/MS were constantly well maintained constantly and regularly calibrated.

2.4. Reactor design

A closed and zero head-space glass reactor with a total volume of 600 ml was used in the current study in order to prevent any leakage of organic vapors from leaking. Moreover, the reactor was double-jacketed and to maintained at a constant temperature using a thermostat. A schematic diagram of the reaction system is illustrated in Figure 1. In order to prevent the rubber stoppers from absorbing organic vapors, the stopper were carefully wrapped with Teflon tape. A pH controller was used to maintain keep a constant solution pH value based on the intermittent addition of NaOH or HClO₄. In the current experiment, HClO₄ was purposely used instead of HCl because the chloride ions are a a hydroxyl radical scavenger⁷⁾.

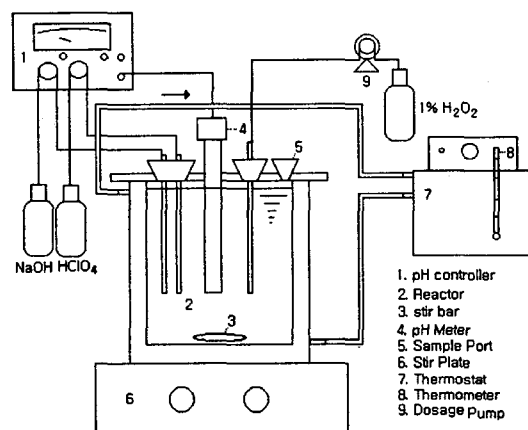


Fig. 1. Schematic diagram of conventional Fenton's oxidation.

Moreover, hydrogen peroxide will reacts with chloride ions to produce elemental chlorine. In this pseudo-continuous Fenton oxidation, a dosage pump was used to deliver the H₂O₂(1 %) at a rate of 0.575 ml/min(or 0.336 mM/min).

2.5. Fenton oxidation process

The batch Fenton oxidation experiments were

conducted in a completely mixed reactor under a constant temperature (25 °C), ionic strength (0.5 M NaClO₄), and pH value. In addition, the influence of different pH values was evaluated at pH 2, 3, and 4. Both hydrogen peroxide (original solution at a concentration of 31.5 %) and ferrous sulfate were added at the beginning of the reaction. At a pre-selected reaction times, samples (1 mL) were taken to the analysis of the residual concentration of the organic compounds being studied. After sampling, the pH value of the sample was immediately adjusted to above pH 10 using 1.0 M NaOH to terminate any further oxidation and the organic compound content was analyzed using a GC or GC/MS.

The procedures for the pseudo-continuous Fenton oxidation experiments were all the same as those mentioned for the batch Fenton oxidation experiments, except that hydrogen peroxide (freshly diluted solution at a concentration of 1 %) was continuously pumped into the reactor using a dosage pump at a rate of 0.575 mL/min.

3. Results and Discussion

The characteristics of these selected organic compounds are essential not only to the reactor design but also to the reaction process control. Naphthalene is semi-volatile, while PCE, TCE, and chloroform are all highly volatile. Though the evaporation rate of naphthalene is slow, the reaction conditions, such as vigorously stirring, may accelerate it. Accordingly, a closed zero head-space and double-jacket glass reactor with a total volume of 600 mL was used for all of these selected compounds. In order to eliminate any side effects due to the adsorption of some organic vapors onto the rubber stoppers, all of the rubber stoppers were carefully wrapped in Teflon tape. In addition, blank samples were analyzed to evaluate the accuracy of the experiments.

In practice, batch reactors are usually employed for wastewater treatment using Fenton's reagent oxidation, because wastewater compositions vary greatly, and the reaction time can be easily extended to meet the requirements of discharge regulations. Batch systems have the advantages of being very tolerant, easy to manage, and simple

to model. In the current study, both hydrogen peroxide and ferrous ions were added into the reactor at the beginning of reaction, the samples were taken at certain time intervals.

Figures 2~8 show the destruction of PCE, TCE, and naphthalene by batch Fenton oxidation at different H₂O₂ dosages, Fe²⁺ dosages, and pH values, respectively. The results indicated that PCE, TCE, and naphthalene could be decomposed rapidly and completely decomposed with a low dosage of Fenton's reagent. As such, an approximately total removal was achieved for all compounds within 2~4 minutes at a specific dosage. The molar ratio of hydrogen peroxide to PCE, TCE, and naphthalene was about 13:1, 5:1, and 10:1, respectively. Since the concentrations of organic contaminants in ground water are usually very low, and about 90 % of the chemical cost is hydrogen peroxide, such dosages are considerably cost-effective.

It is well known that organic compounds with unsaturated structures, such as double bonds, aromatic rings, and amino or nitro functional groups, are easily destroyed by hydroxyl radicals. Therefore, aromatic compounds, such as benzene, toluene, and xylene, and compounds with double bonds, such as organic acids, ketones, and aldehydes, are readily destroyed, leaving only carbon dioxide and water in most cases. Meanwhile, the hydroxyl radicals have only a small affinity for highly chlorinated aromatic compounds, and it does not react at all with saturated hydrocarbons⁸⁾. Both PCE and TCE have one double bond, while naphthalene has two aromatic ring structures.

Consequently, they were easily attacked by the hydroxyl radicals. It is clear from all these figures (Figure 2-9) that the reactions were so fast that more than 80 % of the oxidative decomposition took place in the first 0.5~1.0 minute.

The reactions also reached equilibrium very quickly, and an extended processing time had a minimal effect on the further decomposition.

It should be mentioned that hydrogen peroxide and ferrous ions played a more important role, or at least an equally important role in destroying these organic compounds. For example, at a constant dosage of 10⁻³ M Fe²⁺ (Figure 2), the removal efficiencies of PCE were almost the same after all reactions reached equilibrium in spite

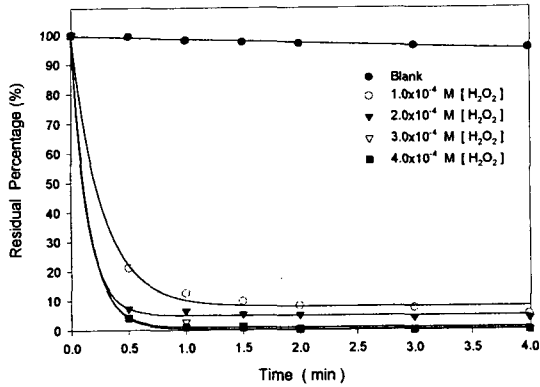


Fig. 2. Decomposition of PCE by Fenton Oxidation with different H₂O₂ dosages under [Fe²⁺] = 1.0 × 10⁻³ M. Temp. = 25 °C, pH = 3.0, ionic strength = 0.05 M NaClO₄, C_o(initial concentration) = 50 mg/L.

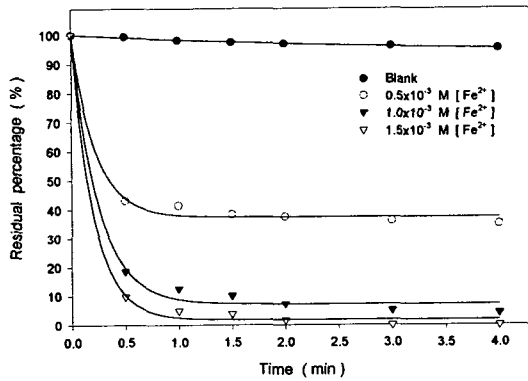


Fig. 3. Decomposition of PCE by Fenton Oxidation with different Fe²⁺ dosages under [H₂O₂] = 1 × 10⁻³ M. Temp. = 25 °C, pH = 3.0, ionic strength = 0.05 M NaClO₄, C_o = 50 mg/L.

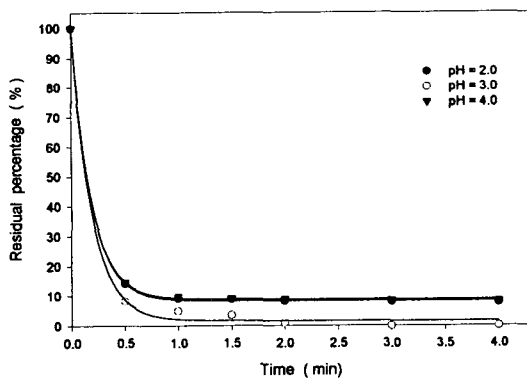


Fig. 4. Decomposition of PCE by Fenton Oxidation with different pH values ([H₂O₂] = 1 × 10⁻³ M ; [Fe²⁺] = 1.5 × 10⁻³). Temp. = 25 °C, ionic strength = 0.05 M NaClO₄, C_o = 50 mg/L.

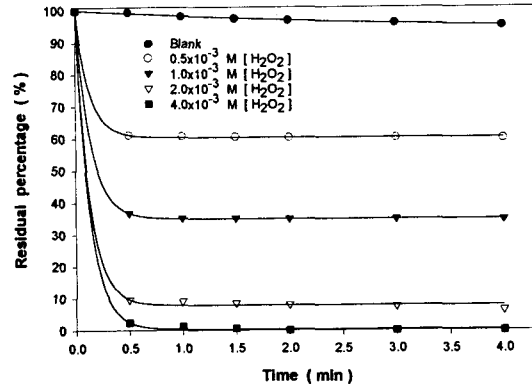


Fig. 5. Decomposition of TCE by Fenton Oxidation with different H₂O₂ dosages under [Fe²⁺] = 3.0 × 10⁻³ M. Temp. = 25 °C, pH = 3.0, ionic strength = 0.05 M NaClO₄, C_o = 50 mg/L.

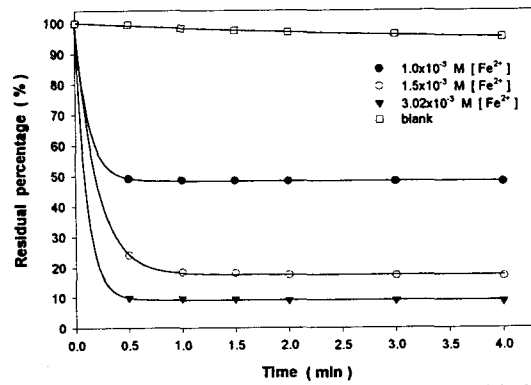


Fig. 6. Decomposition of TCE by Fenton Oxidation with different Fe²⁺ dosages under [H₂O₂] = 2.0 × 10⁻³ M. Temp. = 25 °C, pH = 3.0, ionic strength = 0.05 M NaClO₄, C_o = 100 mg/L.

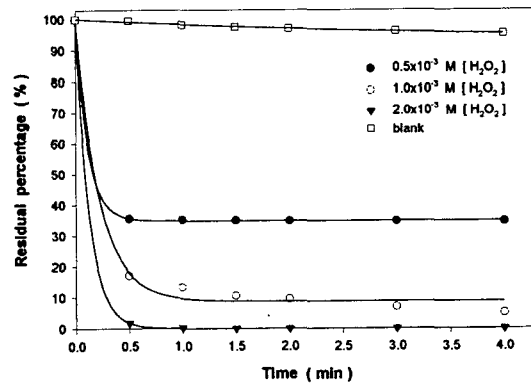


Fig. 7. Decomposition of naphthalene by Fenton Oxidation with different H₂O₂ dosages under [Fe²⁺] = 3.0 × 10⁻³ M. Temp. = 25 °C, pH = 3.0, ionic strength = 0.05 M NaClO₄, C_o = 25 mg/L.

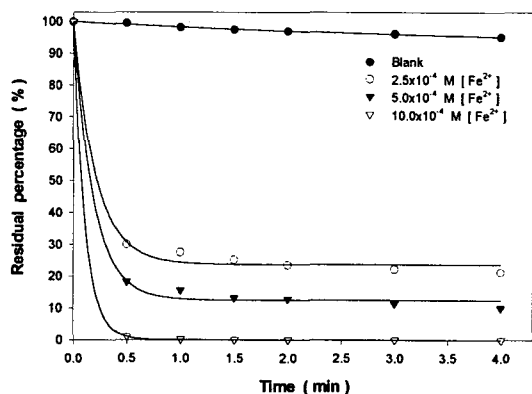
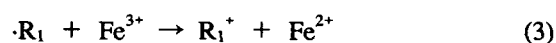
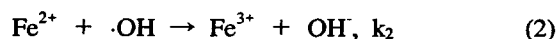
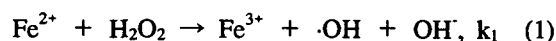


Fig. 8. Decomposition of naphthalene by Fenton Oxidation with different Fe^{2+} dosages under $[\text{H}_2\text{O}_2] = 2.0 \times 10^{-3}$ M. Temp. = 25 °C, pH = 3.0, ionic strength = 0.05 M NaClO_4 , $C_0 = 25$ mg/L.

of the H_2O_2 dosages, e.g., 1×10^{-3} or 4×10^{-3} M. Meanwhile, in the decompositions of TCE and naphthalene, both hydrogen peroxide and ferrous ion dosages effect significant influence on the removal efficiency, except that the decomposition of naphthalene required slightly more time to reach equilibrium. Accordingly, this would appear to a strong evidence to suggest that the rates of the oxidative reactions(1-2), in which Fe^{2+} was oxidized to Fe^{3+} , were faster than the rate of reductive reaction(3), in which Fe^{3+} was is reduced to Fe^{2+} .



In the batch experiment, the rapid depletion of Fe^{2+} at the beginning of the reaction forces the free radical chains to stop immediately. In addition, all these selected organic compounds exhibited a greater affinity for the hydroxyl radicals than Fe^{2+} since increasing the dosage of Fe^{2+} can be dramatically improved the removal efficiency because Fe^{2+} itself is a hydroxyl radical scavenger.

The pH influence was also evaluated at pH 2, 3, and 4. For both PCE and TCE, the highest removal efficiency was obtained at pH 3(Figure 4). According to Qiang et al.⁹⁾, in Fenton's oxidation the decomposition rate of hydrogen peroxide

reaches a maximum at pH 3.5. With the progressive hydrolysis of the ferric ions, this hydrolysis product provided a relatively large catalytically active surface for conducting with H_2O_2 . As a result, the decomposition of H_2O_2 was accelerated, and more free hydroxyl radicals were are produced.

In contrast, the saturated structure of chloroform, which provides no readily attackable site by hydroxyl radicals is considerably more difficult to be destroyed. Figure 9 indicates that at a constant dosage of 1.5×10^{-3} M ferrous ion, there exists an optimal hydrogen peroxide dosage was, i.e., 2.0×10^{-3} M. Any increase above this optimal dosage, increasing the dosage of hydrogen peroxide will decreased the removal efficiency. When the dosage was increased to 8.0×10^{-3} M, the removal efficiency dropped to 10 %. Accordingly, this indicates that with higher than optimal dosage of hydrogen peroxide dosage, the chloroform was probably first decomposed and then recovered to its original form.

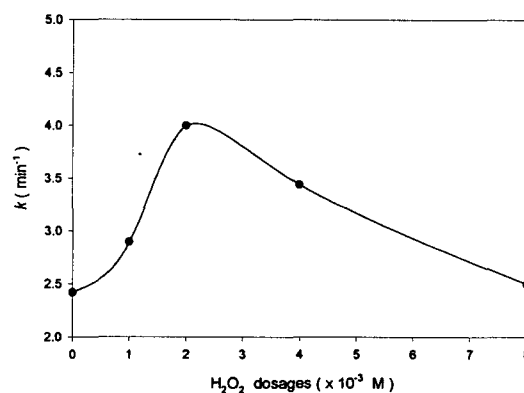


Fig. 9. Decomposition rate of chloroform by Fenton Oxidation with different H_2O_2 dosages under $[\text{Fe}^{2+}] = 1.5 \times 10^{-3}$ M. Temp. = 25 °C, pH = 3.0, ionic strength = 0.05 M NaClO_4 , $C_0 = 50$ mg/L.

The oxidation theory of hydroxyl radicals is unable to explain this phenomenon. Otherwise, increasing the dosage should definitely increase the removal efficiency of chloroform. Similar results were also obtained with different dosages of ferrous ions(Figure 10). Unlike the decomposition of PCE, TCE, and naphthalene, there exists an optimal molar ratio of hydrogen peroxide to ferrous ion, which was calculated as 4:3.

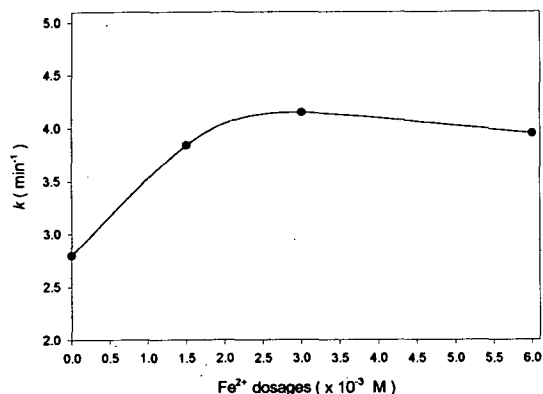


Fig. 10. Decomposition rate of chloroform by Fenton Oxidation with different Fe^{2+} dosages under $[\text{H}_2\text{O}_2] = 2.0 \times 10^{-3}$ M. Temp. = 25 °C, pH = 3.0, ionic strength = 0.05 M NaClO_4 , $C_0 = 50$ mg/L.

Chen et al.¹⁰⁾ studied the ultrasonic dechlorination of chloroform in water in the presence of hydrogen peroxide. Their experimental results indicated that the optimal hydrogen peroxide concentration had a molar ratio of $\text{H}_2\text{O}_2 : \text{CHCl}_3 = 50 : 1$. The addition of ferrous ions (20 mg/l) into the solution will increase the efficiency. Under optimal conditions, the removal efficiency of chloroform could reach 94 %.

As mentioned above, the batch oxidation is capable of decomposing PCE, TCE, and naphthalene very effectively even at a low dosage of Fenton's reagent. This information is very useful for the application of Fenton's oxidation¹¹⁾ in the treatment of wastewater containing organic contaminants with unsaturated structures. However, it was difficult to derive any reaction kinetics information from the batch Fenton's oxidation since the reaction proceeded so fast. In order to slow down the oxidation reaction, pseudo-continuous mode was then adopted. In this mode, the hydrogen peroxide solution was first diluted to a w/w concentration of 1 %, and then pumped into the reactor at a rate of 2.80×10^{-4} M/min.

The results indicated that all oxidation reactions of PCE, TCE, and naphthalene were greatly slowed down which made kinetic study possible. According to Figure 11, it is clear that all reactions follow a pseudo-first order kinetic expression. The kinetic constants and half-lives of the decompositions of PCE, TCE, and naphthalene using the

pseudo-continuous Fenton oxidation are listed in Table 1. Among the three organic compounds studied, PCE was the most readily decomposed. However, there was little difference between these reaction rates since their kinetic constants had the same order of magnitude.

In general, the removal efficiency of the pseudo-continuous oxidation was higher than that of the batch oxidation with identical dosages because in the previous reaction the hydroxyl radicals were produced gradually. For both PCE and TCE, 4.0×10^{-3} M H_2O_2 was required in the batch oxidation to obtain an approximately total removal. While, 2.7×10^{-3} M H_2O_2 was required in the pseudo-continuous oxidation.

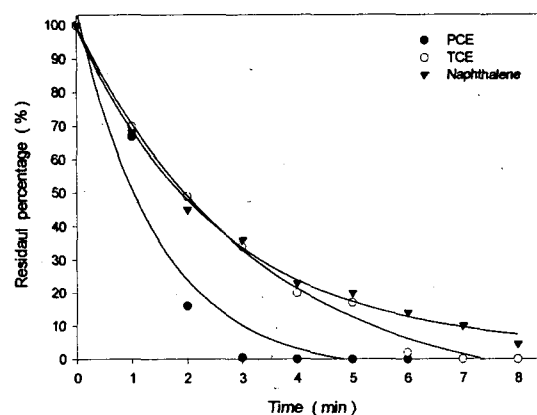


Fig. 11. Decomposition of PCE, TCE, and naphthalene by pseudo-continuous Fenton Oxidation. Reactor volume = 600 mL, Temp. = 25 °C, pH = 3.0, ionic strength = 0.05 M NaClO_4 , $[\text{H}_2\text{O}_2] = 3.36 \times 10^{-4}$ M/min, $C_0 = 50$ mg-PCE/L, 100 mg-TCE/L, 25 mg-naphthalene/L, dosages of Fe^{2+} for PCE, TCE, and naphthalene = 1.5×10^{-3} , 3.0×10^{-3} , 1.0×10^{-3} M, respectively.

Table 1. Kinetic constants and half-lives of PCE, TCE, and naphthalene

Compound	$k(\text{sec}^{-1})$	$t_{1/2}(\text{sec})$	R^2
PCE	1.37×10^{-2}	50.6	0.995
TCE	6.67×10^{-2}	103.9	0.991
Naphthalene	6.50×10^{-2}	106.6	0.967

$t_{1/2}$ = half-life

R = correlation coefficient

However, the result is just opposite for the naphthalene decomposition, in which 1.0×10^{-3}

M H_2O_2 in the batch oxidation yielded the same effect as 2.7×10^{-3} M H_2O_2 in the pseudo-continuous oxidation. The structures of PCE and TCE are very simple, containing only one double bond and two carbon atoms. Due to the double bond is easily broken, only a small amount of little oxidant needs to be consumed for the further decomposition of the intermediate compounds. Meanwhile, for a more complicated structure like that of naphthalene, which contains 2 rings and ten carbon atoms, a lot of much oxidant will still needs to be consumed for the further decomposition of the multi-carbon intermediates after the ring is broken apart. Accordingly, It is proposed that for naphthalene, in the pseudo-continuous oxidation more organic intermediates were decomposed than in the batch mode. This result was obtained by measuring the yield of CO_2 in both modes.

4. Conclusions

We investigated the optimal experimental conditions and reaction kinetics for the decompositions of PCE, TCE, naphthalene, and chloroform using conventional Fenton oxidation process. The experiments were conducted in a completely mixed batch or continuous reactor with the addition of hydrogen peroxide under a constant temperature, pH, and ionic strength.

Fenton oxidation process yielded good results in decomposing specific organic compounds, as exemplified by PCE, TCE, and naphthalene.

These organic compounds were mostly decomposed within the first 1-2 minutes. For an approximately total removal in the batch oxidation, the molar ratios of hydrogen peroxide to PCE, TCE, and naphthalene were 13:1, 5:1, and 10:1, respectively. In the pseudo-continuous oxidation, the rate constants for the PCE, TCE, and naphthalene oxidations were 1.37×10^{-2} , 6.67×10^{-2} and $6.50 \times 10^{-1} \text{ sec}^{-1}$, respectively.

The results indicated that chloroform was considerably more difficult to decompose due to highest valence of carbon(IV). The highest removal efficiency of chloroform was only 20 % even with

a relatively high dosage of Fenton's reagent. and the optimal molar ratio of hydrogen peroxide to ferrous ion was about 4:3.

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