

CHAPTER IV



RESULTS AND DISCUSSIONS

4.1 Degradation of TCE

The obtained data of TCE degradation by heat and UV activated persulfate oxidation (Table 4.1) were straight-line fit ($R^2 \sim 0.92$) with a pseudo-first-order decay model.

4.1.1 Heat activated persulfate oxidation method

4.1.1.1 Effects of concentration of persulfate on heat persulfate oxidation

The TCE removal efficiencies after 5 hours of the heat persulfate oxidation system at persulfate/TCE molar ratios of 5:1, 10:1, 15:1 were 90.6%, 93.3%, and 99.9%, respectively. From Figure 4.1, TCE removal percentages using persulfate/TCE molar ratios of 5:1 and 10:1 were moderately similar and less than using a persulfate/TCE molar ratio of 15:1. Normalized TCE concentration (C/C_0) on a log scale versus reaction time at different concentrations of persulfate are presented in Figure 4.2. Specific reaction rate (rate constant, k) at persulfate/TCE molar ratio of 15:1 was approximately 3 times higher than those of 5:1 and 10:1 (1.40 hr^{-1} , 0.49 hr^{-1} , and 0.46 hr^{-1} , respectively).

The system at higher persulfate/TCE molar ratio should generate more sulfate free radicals and hydroxyl radicals and would result in higher rate of TCE degradation. Nevertheless, stoichiometry of all reactions was unknown and too complicate because of many oxidants reacting with TCE such as $\text{SO}_4^{\bullet-}$, HO^{\bullet} , $\text{S}_2\text{O}_8^{2-}$ and HSO_4^- . Limitation of heat persulfate oxidation system by persulfate concentration was distinguished from the performances of heat persulfate oxidaiton at oxidant/TCE molar ratios of 5:1 and 10:1 which were relatively similar and less than that of 15:1. Hence, appropriate persulfate/TCE molar ratio of heat persulfate oxidation at 40°C should be at least 15:1 otherwise persulfate oxidation will be limited by the oxidant dose.

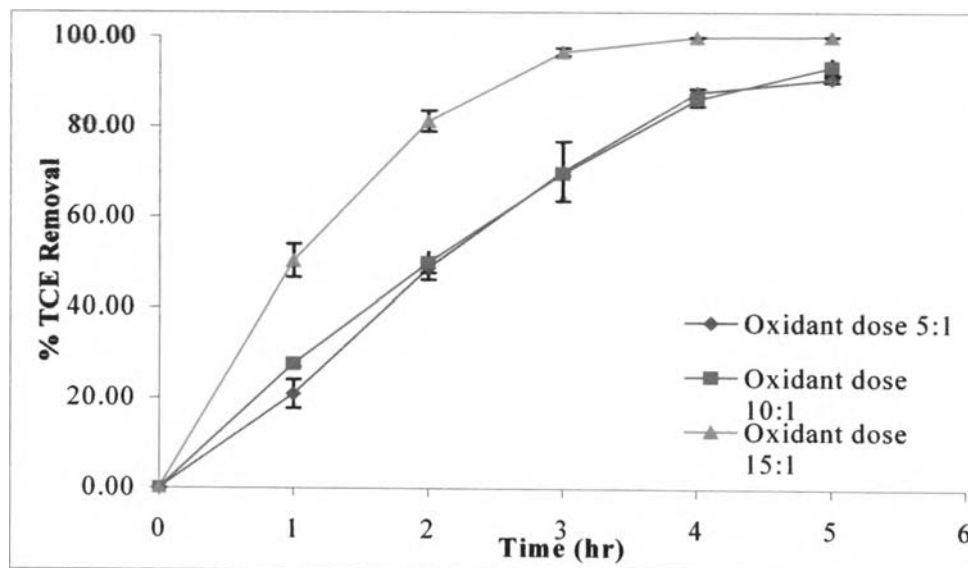


Figure 4.1 TCE removal percentage using heat activated persulfate oxidation at various persulfate/TCE molar ratios (oxidant doses)

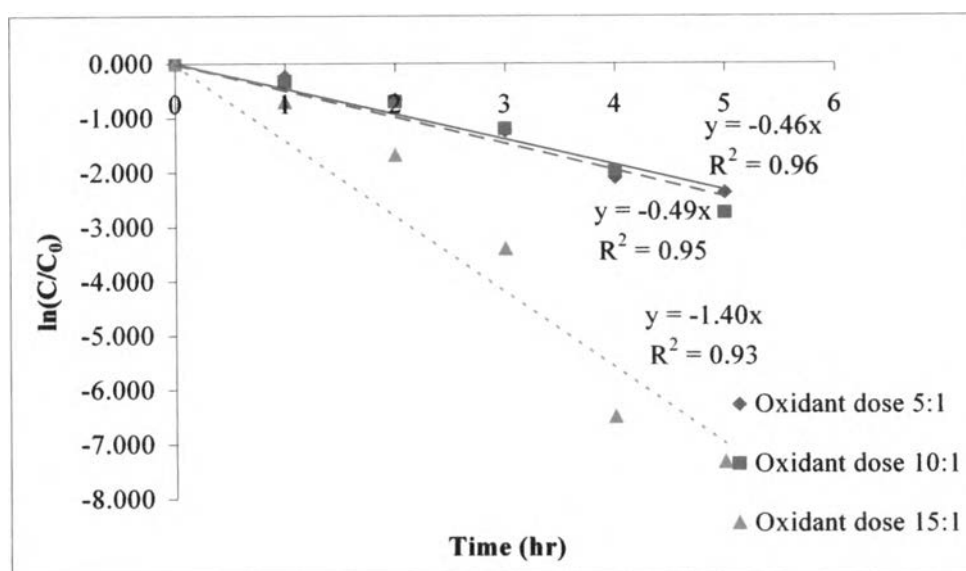


Figure 4.2 Pseudo-first-order plot of TCE degradation using heat activated persulfate oxidation at various persulfate/TCE molar ratios (oxidant doses)

4.1.1.2 Effects of concentration of TCE on heat persulfate oxidation

The optimal condition from the study of effects of concentration of persulfate on heat persulfate oxidation, an oxidant/contaminant ratio of 15:1, was used in this section. The TCE removal efficiencies after 5 hours of heat persulfate oxidation system at TCE concentrations of 10, 50, and 100 ppm were almost similar (99.9%, 99.8%, and 99.9%, respectively) (Figure 4.3). Specific reaction rate at TCE concentration of 10 ppm was slightly higher than those of 50 ppm and 100 ppm (1.40 hr^{-1} , 1.22 hr^{-1} , 1.15 hr^{-1} , respectively) (Figure 4.4).

The results supported that heat persulfate oxidation at 40°C with an oxidant/contaminant ratio of 15:1 was adequate for the reaction in accordance with

quantity required for stoichiometry because, in the range of 10 ppm to 100 ppm TCE, persulfate oxidation system was still effective. Although the rate constants slightly decreased at higher concentrations, TCE removal percentages did not change.

Although determination of stoichiometry of the reaction was out of the scope of this study, practical purpose of the study could be fulfilled. Heat persulfate oxidation at 40°C with an oxidant/contaminant ratio of 15:1 might be appropriate for every TCE concentration because the molar ratio of persulfate and TCE might be adequate for the degradation according to the stoichiometry.

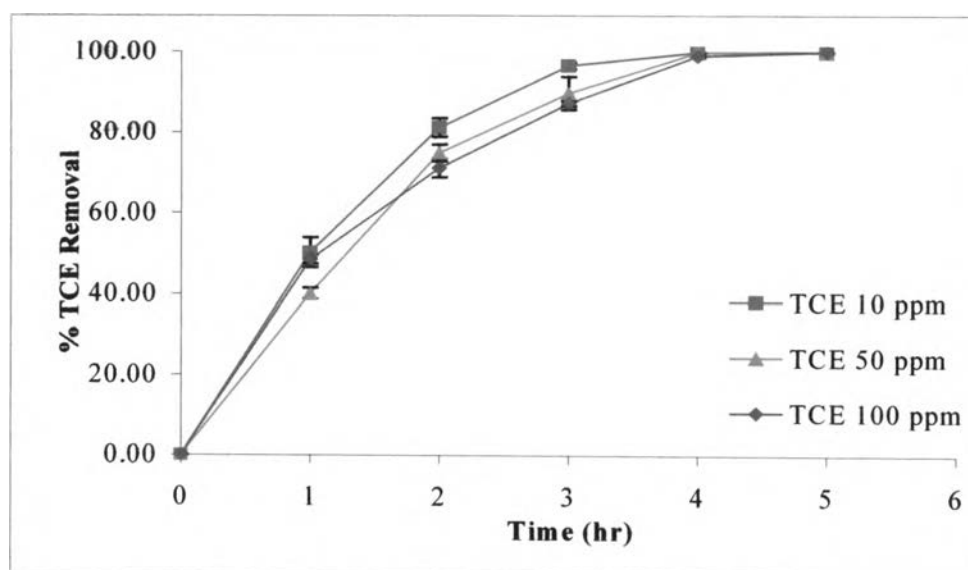


Figure 4.3 TCE removal percentage using heat activated persulfate oxidation at different concentration of TCE

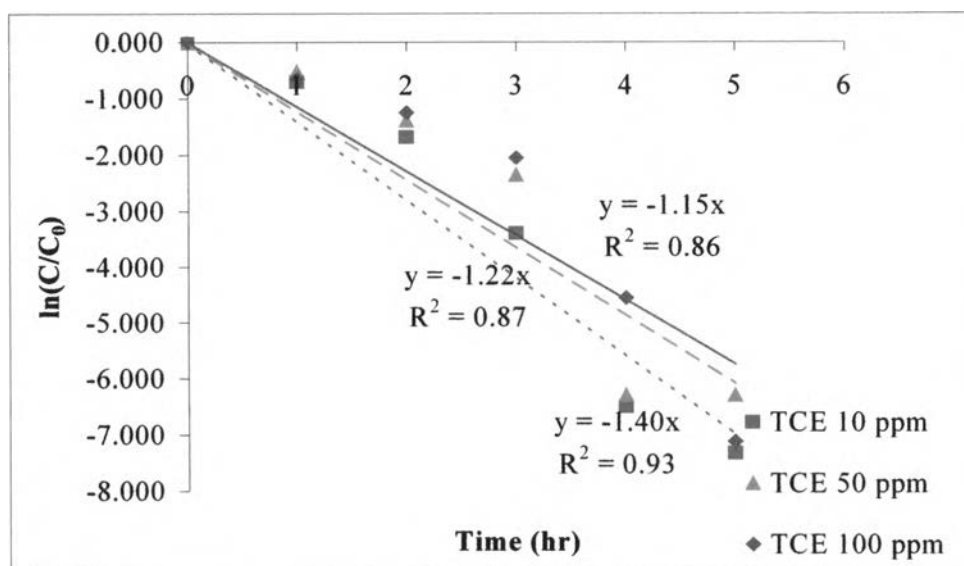


Figure 4.4 Pseudo-first-order plot of TCE degradation using heat activated persulfate oxidation at different concentration of TCE

4.1.2 UV activated persulfate oxidation method

4.1.2.1 Effects of concentration of persulfate on UV persulfate oxidation

In the UV persulfate oxidation system, the TCE removal efficiencies after 5 hours at persulfate/TCE molar ratios of 5:1, 10:1, 15:1 were 91.5%, 99.8%, and 99.8%, respectively. TCE removal percentages (Figure 4.5) at persulfate/TCE molar ratios of 15:1 and 10:1 were moderately similar and higher than using an oxidant/TCE molar ratio of 5:1. Specific reaction rate (Figure 4.6) at persulfate/TCE molar ratio of 10:1 (1.37 hr^{-1}) was slightly higher than that of 15:1 (1.21 hr^{-1}) and was much higher than that of 5:1 (0.43 hr^{-1}).

When using the molar ratios of 5:1 and 10:1, higher concentration of persulfate resulted in higher TCE removal efficiency and specific reaction rate or reaction rate constant (k) due to higher generated sulfate free radicals and hydroxyl radicals (Figures 4.5 and 4.6). Between the molar ratios of 10:1 and 15:1 used, TCE removal percentages and rate constants were not obviously different. The relatively constant values of TCE removal percentages and rate constants might be obtained from adequate persulfate/TCE molar ratio. Therefore, the molar ratio of 10:1 in the UV persulfate oxidation system might be sufficient.

Nevertheless, there was a factor that might limit the performance of the UV activated persulfate oxidation system. The factor was lamp power (in accordance with UV intensities or the number of UV lamps). From Parson (2004) and Oppenländer (2003), the amount of persulfate used in term of mass will required electric energy per order, proportionally. E_{EO} (electric energy per order, kWh order⁻¹ m⁻³) was the electric energy needed for the degradation of a contaminant by one order of magnitude in a unit volume of contaminated water or air. Therefore, the requirement for electric energy must be changed accordingly. Limitation of this system might be a result from limited electric energy. Anyhow, limitation by inadequate electric energy was only observation from the literature reviews because the actual effect of electric energy or lamp power was not determined in this study.

The optimal condition of the UV activated persulfate oxidation system in this study obtaining the highest value of TCE removal percentage and specific reaction rate was UV persulfate oxidation at oxidant/TCE molar ratio of 10:1.

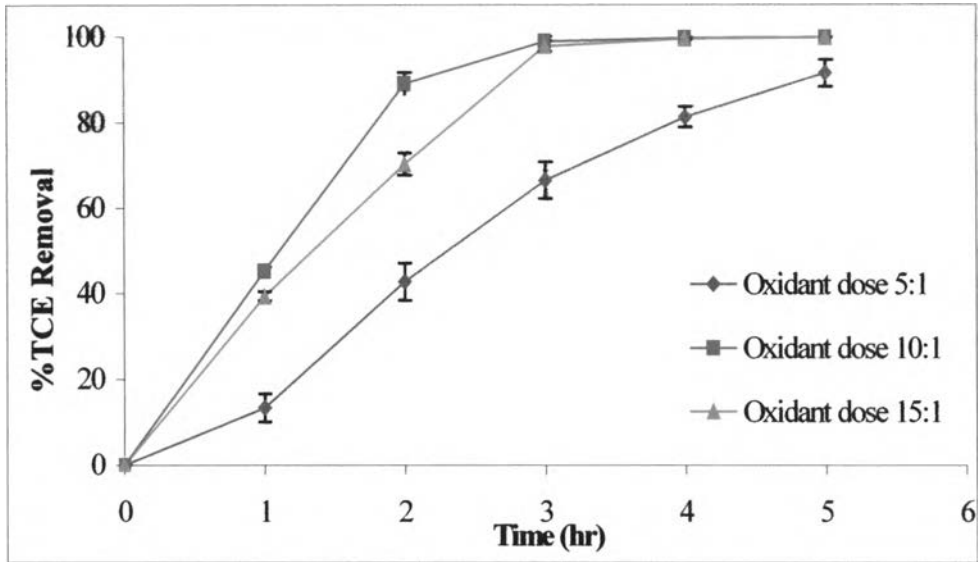


Figure 4.5 TCE removal percentage using UV activated persulfate oxidation at various persulfate/TCE molar ratios (oxidant doses)

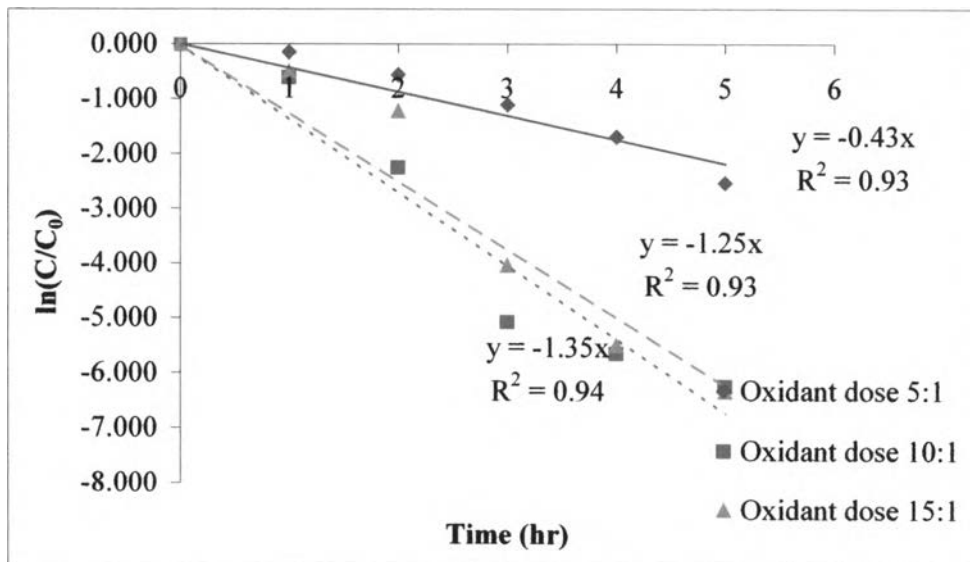


Figure 4.6 Pseudo-first-order plot of TCE degradation using UV activated persulfate oxidation at various persulfate/TCE molar ratios (oxidant doses)

4.1.2.2 Effects of concentration of TCE on UV persulfate oxidation

The optimal condition from the study of effects of concentration of persulfate on UV persulfate oxidation, a persulfate/contaminant ratio of 10:1, was used in this section. The TCE removal efficiencies (Figure 4.7) after 5 hours of UV persulfate oxidation system at TCE concentrations of 10, 50, and 100 ppm were 99.8%, 90.8%, and 95.7%, respectively. Specific reaction rate (Figure 4.8) at TCE concentration of 10 ppm (1.35 hr^{-1}) was much higher than that of 50 ppm (0.43 hr^{-1}) and 100 ppm (0.49 hr^{-1}).

The increase of TCE concentration from 10 ppm to 50 ppm and 100 ppm led to the decrease in performance of UV persulfate oxidation system. Hence, it cannot conclude that persulfate/TCE molar ratio of 10:1 was sufficient for the TCE degradation in the UV activated persulfate oxidation system. If the persulfate/TCE molar ratio of 10:1 is sufficient for stoichiometry of the reaction, performance of the system might stay the same at higher concentration of TCE. Consequently, there should be other fixed factors that affected the reaction when increasing concentration of TCE or persulfate. Since electric energy per order (E_{EO}) value may depend on concentration of a contaminant, at higher concentration of the contaminant, required E_{EO} in accordance with electric power will increase (Oppenländer, 2003). In this case, either the oxidant dose was adequate or not, it might not have sufficient energy for activating the oxidant at high TCE concentration (50 ppm and 100 ppm). Therefore, lack of adequate electric power might be the factor that effects on limited performance of UV activated persulfate oxidation system.

Hence, an increase of the number of lamps or lamp power might be able to increase the performance of UV persulfate oxidation at high concentration of TCE.

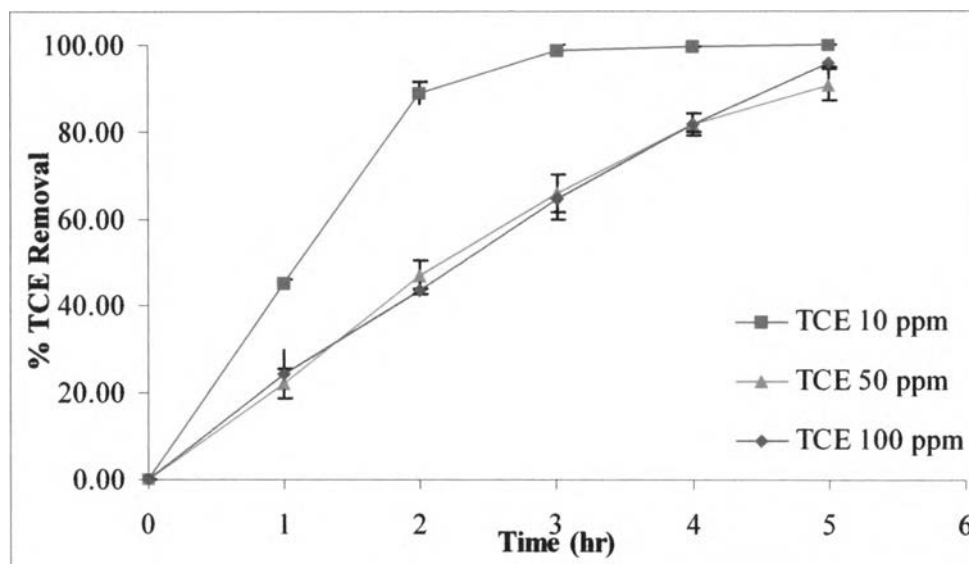


Figure 4.7 TCE removal percentage using UV activated persulfate oxidation at different TCE concentration

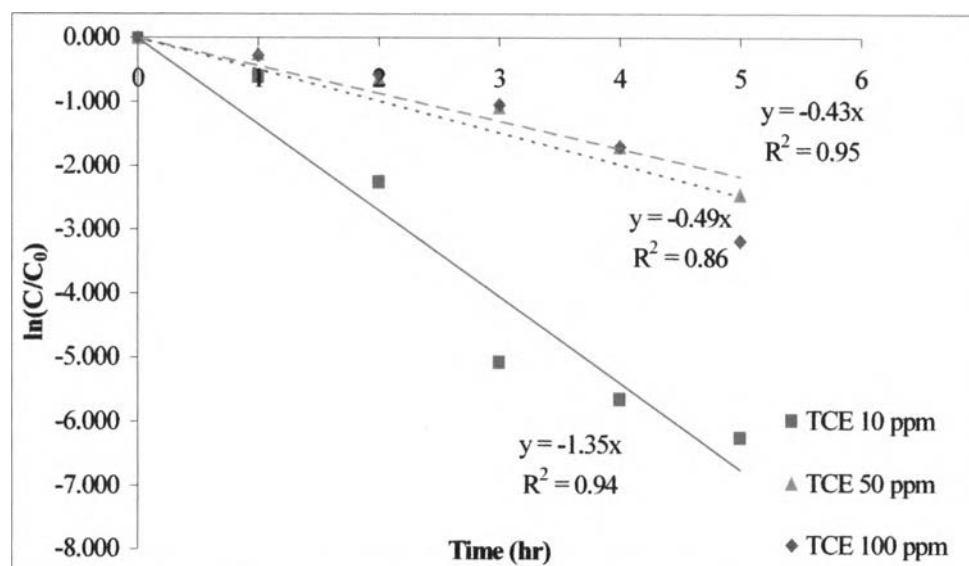


Figure 4.8 Pseudo-first-order plot of TCE degradation using UV activated persulfate oxidation at different concentration of TCE

4.1.3 Comparison of the performance of heat and UV activated persulfate oxidation

At the optimal condition for degrading 10 ppm TCE, both methods degraded TCE with the relatively similar efficiency (for heat activated persulfate oxidation, 99.9% of TCE removal and 1.40 hr^{-1} of rate constant, and, for UV activated persulfate oxidation, 99.8% of TCE removal and 1.35 hr^{-1} of rate constant). Nevertheless, according TCE removal percentages and rate constant values from Table 4.4, in the degradation of 50 ppm and 100 ppm TCE, heat activated persulfate oxidation method (99.8%, $k = 1.22 \text{ hr}^{-1}$ and 99.9%, $k = 1.15 \text{ hr}^{-1}$, respectively) was able to degrade TCE more effective than UV activated persulfate oxidation method (90.8%, $k = 0.43 \text{ hr}^{-1}$ and 95.7%, $k = 0.49 \text{ hr}^{-1}$, respectively). Each persulfate oxidation system was limited by a different factor which was persulfate concentration for heat activating, and was lamp power for UV activating.

Table 4.1 Comparison of TCE removal percentage at final reaction time and specific reaction rate of all experiments

Sample Name	% TCE Removal	Specific reaction rate	
		k (hr^{-1})	R ²
X _{1,1,1}	90.6	0.46	0.96
X _{1,2,1}	93.3	0.49	0.95
X _{1,3,1}	99.9	1.40	0.93
X _{1,3,2}	99.8	1.22	0.87

(Cont.)

Sample Name	% TCE Removal	Specific reaction rate	
		k (hr ⁻¹)	R ²
X _{1,3,3}	99.9	1.15	0.86
X _{2,1,1}	91.5	0.43	0.93
X _{2,2,1}	99.8	1.35	0.94
X _{2,3,1}	99.8	1.25	0.93
X _{2,2,2}	90.8	0.43	0.95
X _{2,2,3}	95.7	0.49	0.86

(X_{a,b,c} ; a = persulfate oxidation method ; 1= activated by heat ; 2 = activated by UV
, b = molar ratio of persulfate and contaminant ; 1 = 5:1 ; 2 = 10:1 ; 3 = 15:1
, c = concentration of TCE ; 1= 10 ppm, 2 = 50 ppm ; 3 = 100 ppm)

To compare the performance of the methods, not only TCE removal percentage and specific reaction rate were determined, but also energy consumption of each system should be considered. In heat activated persulfate oxidation system, the amount of heat energy was 62,760 kJ for 1000 L of water. In UV activated persulfate oxidation system, the amount of required energy (E_{EO} or electric energy per order, kWh order⁻¹ m⁻³) was 180 kJ order⁻¹ m⁻³. If lamp power is increased to 1 kW, E_{EO} will be 9,000 kJ order⁻¹ m⁻³ (see calculations in Appendix D).

An elementary comparison of the methods reviewed that heat persulfate oxidation method should be more effective than UV persulfate oxidation method. In

contrast with the comparison of energy consumption, a lot of energy was required for heat persulfate oxidation which was almost 350 times of energy required for UV persulfate oxidation method (20W) and 7 times for 1 kW system. Furthermore, the required heat energy was not included heat loss from surroundings that might increase a large amount of energy used. Although required energy for UV persulfate oxidation method was depend on treatment time that can increased E_{EO} for UV persulfate oxidation method, heat energy of heat persulfate oxidation method will be higher due to heat loss at the same time. Furthermore, required energy for heat persulfate oxidation method was depend on quantity or volume of wastewater much more than UV persulfate oxidation method.

Finally, for removal efficiency aspect, the heat persulfate oxidation system was more effective because of higher percent TCE removal and rate constant. For energy consumption aspect, the UV persulfate oxidation system was more effective due to less energy used.

4.1.4 Persulfate oxidation method without heat and UV activated condition

The TCE removal percentages after 5 hours of persulfate oxidation system without heat and UV activated condition at persulfate/TCE molar ratios of 5:1, 10:1, 15:1 were 32.7%, 32.7%, and 36.7%, respectively (initial concentration of 10 ppm TCE). TCE removal percentage using persulfate/TCE molar ratios of 5:1 was the same as that of 10:1 and slightly less than using an persulfate/TCE molar ratio of 15:1.

The average TCE removal percentage of the persulfate oxidation system without heat and UV activated condition was 34.0% (SD = 1.09, CV = 3.2%). The average TCE removal percentage was approximately 3 times less than those of heat and UV activated persulfate oxidation system (90.6% – 99.9%). The efficiency of this system was much lower because, at ambient temperature, persulfate oxidizes compounds through a persulfate anion (Liang et al, 2003; Huang et al., 2002b) and persulfate ions were not activated to various oxidants such as sulfate radicals and hydroxyl radicals.

4.2 Residual formation

4.2.1 By-products measurement

Samples from heat and UV activated persulfate oxidation with the highest and lowest performance of TCE degradation ($X_{1,1,1}$, $X_{1,3,1}$, $X_{1,3,2}$, $X_{1,3,3}$, $X_{2,1,1}$, $X_{2,2,1}$, $X_{2,2,2}$ and $X_{2,2,3}$ according to Table 4.1) were sacrificed for the analysis of by-products by a gas chromatography with mass spectrophotometer. Although 2-chloroacetamide and residual TCE were detected in sample $X_{2,1,1}$ and $X_{2,2,3}$, respectively, concentrations were very low (near detection limit of the machine) and other samples were not detected other by-products. Finally, it might conclude that other by-products, which were not CO_2 , were undetected in significant quantity.

4.2.3 pH change

pHs were measured to determine the performance of buffer system which were controlled by buffer solution (1.8 g/L monobasic sodium phosphate and 0.4 g/L dibasic sodium phosphate). The final pHs (Table 4.2) presented that the buffer was effective for 10 ppm TCE solution but it was ineffective in cases of high concentrations of TCE (50 ppm and 100 ppm). Decreased pH might be a result of TCE mineralization by persulfate oxidation which generated hydrogen ion. The following stoichiometry is one of the reactions that might mainly affect the system.



Table 4.2 Final pH of all experiments (Initial pH of 6.36)

Method	TCE Conc. (ppm)	Persulfate/TCE Molar Ratio	pH
Heat activated	10	5:1	6.34
persulfate		10:1	6.36
oxidation		15:1	6.29
	50	15:1	5.85
	100	15:1	5.63

(Cont.)

Method	TCE Conc. (ppm)	Persulfate/TCE Molar Ratio	pH
UV activated	10	5:1	6.33
persulfate		10:1	6.33
oxidation		15:1	6.30
	50	10:1	5.97
	100	10:1	5.63

4.4 Volatilization

Volatilization of TCE was calculated to determine how the side reaction effect on the efficiency of heat and UV activated persulfate oxidation system. TCE has high potential to volatilize from aqueous phase to air phase because of high Henry's law constant, low water solubility and high vapor pressure (USEPA,1992). The TCE removal efficiencies should be determined whether they were derived from chemical oxidation process or volatilization. The values of TCE in gas phase and water phase in sample vials at different temperature were calculated from Henry's law constant, illustrated in the Table 4.3 (see calculations in Appendix D).

Table 4.3 Concentration of TCE in water phase and gas phase at 25°C (temperature of UV oxidation method) and 40°C (temperature of heat persulfate oxidation method)

Temperature (°C)	TCE concentration (ppm)					
	For 10 ppm TCE		For 50 ppm TCE		For 100 ppm TCE	
	Water phase	Gas phase	Water phase	Gas phase	Water phase	Gas phase
25	9.50	3.54	47.52	17.71	95.04	35.42
40	9.11	6.33	45.57	31.66	91.13	63.32

(Water volume=50 mL, Gas volume=7 mL)

Although volatilization might cause overestimation of the actual TCE degradation according to the Table 4.3, blanks of each method decreased less than 8 % (see TCE remaining percentage of blanks in Appendix A). Therefore the removal efficiencies might be mainly obtained from degradation by persulfate oxidation.