CHAPTER II

LITERATURE REVIEW

2.1 Trichloroethylene (TCE)

2.1.1 Usage

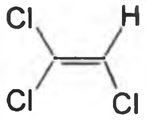
TCE has been extensively used as a component of industrial cleaning solution and as a universal degreasing agent. It is an outstanding extraction solvent for greases, oils, fats, waxes, and tars, and used in textile industry. Furthermore, TCE is used as a raw material to make other chemicals including in production of pharmaceuticals, polychlorinated aliphatics, flame retardance chemicals, and insecticides and it also be found in some household products such as typewriter correction fluid, paint removers, adhesives, and spot removers (ATSDR, 1997).

In Thailand, the use of TCE has increased in the last two decades due to a development of industrial sector (ERTC, 2001). The quantity of imported TCE in 2001 was increased from 3522.6 tons in 2001 to 7363.6 tons in 2002 (Thai Customs Department as cited in Sutinun, 2003). TCE was mainly used for cleaning and degreasing from metals and textiles, for substitution of chlorofluorocarbon (CFC), and as a raw material for production of other chemicals (ERTC, 2001).

2.1.2 Physical and chemical properties

Physical and chemical properties of the contaminant investigated in this study are presented in Table 2.1.

Table 2.1 Physical and chemical properties of TCE

Property	Characteristic	Reference
Structure		ATSDR (1997)
Formula	C_2HCl_3	SANSS (1990) [a]
M.W. (g/mol)	131.4	HSDB (1944) [a]
Density (g/mL)[2]	1.465	McNeil (1979) [a]
Solubility (mg/L)[1]	1366	Tewari et al.(1982) [a]
Henry's law constant (atm.m^3/mol) at 25°C	9.09×10^{-3}	Hodd et al. (1993)[b]
at 40°C	17.82×10^{-3}	Vane and Giroux (2000)[b]
Vapor Pressure (mmHg)[1]	74	Mackay and Shiu (1981) [b]
Log K_{ow}	3.03	Tewari et al.(1982) [b]
Boiling Point	86.7°C	McNeil (1979) [a]

[1] At 25°C , [2] At 20°C, [a] As cited in ATSDR (1997), [b] As cited in Mongomery J.H. (2000)

2.1.3 TCE in aquatic environment

TCE is one of the most frequently detected volatile organic chemicals in groundwater in the United States (Fisher et al., 1987 as cited in US EPA, 1992). TCE has been found in at least 861 the National Priorities List (NPL) sites from 1,428 NPL sites which were hazardous waste sites identified as the most serious in the nation by the Environmental Protection Agency (ATSDR, 1997). TCE concentrations at contaminated sites ranged from a trace concentration to maximum concentration in water. In the United States, maximum concentration of TCE in groundwater at different contaminated sites varied from 0.04 to 1,000 ppm (Environmental protection department, 1999). The concentrations of TCE in contaminated groundwater at two contaminated sites in Thailand were 7.22 ppm and 968.15 ppm (ERTC, 2001). The concentrations were much higher than Maximum contaminant level (MCL) of TCE for drinking water in the U.S. which is only 0.005 mg/L (US EPA, 2004).

2.1.4 Health Effects

Exposure to large quantities of TCE can make people become dizzy or sleepy and become unconscious at very high amounts. Death may happen in a case of inhalation at high levels. High amounts of TCE may cause liver or lung cancer in some studies with mice and rats (ATSDR, 1997). Furthermore, TCE was classified as a potential human carcinogen by US EPA (1998) as cited in Liang et al. (2003).

2.1.5 Regulations

In 2004 Edition of the drinking water standard and health advisories, the US Environmental Protection Agency has set the maximum contaminated level (MCL) of

TCE to 0.005 mg/L. (US EPA, 2004). In Thailand, from the notification of the National Environmental Board No. 20, B.E. 2543 (2000), issued under the Enhancement and Conservation of National Environment Quality Act B.E. 2535 (1992), published in the Royal Government Gazette, Vol. 117 Special part 95 D (September 15, B.E. 2543 (2000)). TCE concentration should not exceed 0.005 mg/L in groundwater (PCD, 2000).

2.2 Persulfate Chemistry

The reaction of persulfate ions with several organic and inorganic substances has been thoroughly studied (Kolthoff and Muller, 1951; House, 1962). Persulfate is one of the high potential oxidizing agents, which can oxidize many organics to carbon dioxide by a persulfate anion or highly reactive sulfate free radicals. At ambient temperature, persulfate can oxidize compounds through a persulfate anion with a standard oxidation potential of 2.01 V. When the persulfate anion is activated by heat, ultraviolet light or some metal catalysts, a sulfate free radical ($SO_4^{-\bullet}$), an oxidant with a standard oxidation potential of 2.6V, will be generated as illustrated in the following equation (Liang et al, 2003; Huang et al., 2002b).

$$S_2O_8^{2-} + \text{heat / UV} \longrightarrow 2SO_4^{-\bullet}$$

$$SO_4^{-\bullet} + e^- \longrightarrow SO_4^{2-};\ E^0 = 2.6V$$

Additionally, high reactive radicals such as hydroxyl radicals ($HO^{\bullet}$) may be generated from the photolysis or heat decomposition of persulfate ions in aqueous mediums (Wilmarth and Haim, 1962; Nosov, 1966; Dogliotti and Hayon, 1967; Hayon and Mcgrarvey, 1967; Berlin, 1986; Tanner and Osman, 1987 as cited in Huang et al., 2002b). The high values of the standard oxidation-reduction potential of sulfate and hydroxyl radicals result in the high performance of persulfate oxidation for degrading contaminants when compared with other oxidants, illustrated in Table 2.2.

Table 2.2 Standard redox potentials of various oxidants

Oxidants	Redox potential (E^0) (Volts)
Fluorine	3.03
Hydroxyl radical	2.70*
Sulfate radical	~2.60**
Atomic oxygen	2.42
Ozone	2.07
Persulfate anion	2.01
Hydrogen peroxide	1.78
Permanganate	1.68

(Tabular data from Latimer, 1952 unless noted. *Buxton et al., 1988, **Eberson, 1987 as cited in Liang et al., 2003)

Nevertheless, persulfate is usually used with UV light or under high temperature because of its low efficiency at atmospheric temperature and in order to generate its radical oxidation mechanisms. The series of radical chain reactions may be generated from photolytic or heat decomposition of persulfate leading to degradation of organic compounds as illustrated in the following equations (Berlin, 1986).

$S_2O_8^{2-} \xrightarrow{\text{heat/h}\nu} 2SO_4^{-\bullet}$ ....(1)

$S_2O_8^{2-} + M \longrightarrow 2SO_4^{-\bullet} + M^{\bullet}$ ....(2)

(M represents organic compounds)

$SO_4^{-\bullet} + H_2O \longrightarrow HO^{\bullet} + HSO_4^{-}$ ....(3)

$SO_4^{-\bullet} + M \longrightarrow M^{\bullet} + \text{products}$ ....(4)

$HO^{\bullet} + M \longrightarrow M^{\bullet} + \text{products}$ ....(5)

$M + S_2O_8^{2-} \longrightarrow SO_4^{-\bullet} + \text{products}$ ....(6)

$SO_4^{-\bullet} + HO^{\bullet} \longrightarrow \text{Chain termination}$ ....(7)

$SO_4^{-\bullet} + M^{\bullet} \longrightarrow \text{Chain termination}$ ....(8)

$2SO_4^{-\bullet} \longrightarrow \text{Chain termination}$ ....(9)

$HO^{\bullet} + M^{\bullet} \longrightarrow \text{Chain termination}$ ....(10)

$2\,HO^{\bullet} \longrightarrow \text{Chain termination}$ ....(11)

$2\,M^{\bullet} \longrightarrow \text{Chain termination}$ ....(12)

2.3 Application of persulfate oxidation

2.3.1 Heat activated persulfate oxidation

Heat activated persulfate oxidation was studied for the degradation of TCE, 1,1,1-trichloroethane (TCA), polychlorinated biphenyls (PCBs) and methyl *tert*-butyl ether (MTBE). The significant parameters, which affected the performances of the oxidation, were temperature, persulfate concentration and treatment time.

Liang et al. (2003) examined persulfate oxidation of TCE and TCA at 20°C, 40°C, 50°C, and 60°C and at pH 6 with an ionic strength of 0.1 M. The effects of oxidant/contaminant molar ratios, which were 2:1, 5:1 and 10:1, were studied at the optimum temperatures, 40°C for TCE, and at 50°C for TCA. The degradation followed pseudo-first-order reaction and higher temperature, higher duration time, and higher dose of oxidant provided more effective degradation. At 20°C, TCE was slightly degraded while TCA was not degraded. At 60°C with an oxidant/contaminant ratio of 10:1, TCE was completely mineralized within less than 1 hour and 100% TCA removal was observed after 6 hours. The confirmation of TCE and TCA mineralization was performed by measuring chloride ion concentration but the values were not the same as calculated chloride ion concentration from the removal efficiency because of chloride lost.

The kinetics of thermally activated persulfate oxidation of MTBE was studied at different values of pH, temperature, dose of oxidant and ionic strength (Huang et al., 2002b). The effects of temperature and persulfate concentration on degradation performance were the same as those of Liang et al. (2003)'s study. The reaction rates decreased when increasing pH and ionic strength in a range of 2.5-11 and 0.11-0.53 M, respectively. Furthermore, the reaction rate of MTBE in groundwater was much less than in phosphate-buffer solution because of the presence of bicarbonate ions as radical scavengers in the groundwater.

The persulfate oxidation of PCBs in aqueous phase was studied at 40°C, at initial pH 4.5, and with persulfate concentration of 10 mg/L. PCB removal of 94% occurred within 56 hours (Govindan et al., n.d.).

2.3.2 UV activated persulfate oxidation

UV persulfate system (10^{-2} M $S_2O_8^{2-}$) was able to degrade 2-chlorobiphenyl (2-CB) at higher rate, when compared with UV/TiO_2 system (25 mg/L of TiO_2). The degradation was similar in UV persulfate in aqueous TiO_2 suspensions. For persulfate oxidation in the dark, 2-CB was degraded at lower rate than that of UV/$S_2O_8^{2-}$ and UV/TiO_2/ $S_2O_8^{2-}$ systems (approximately 23% within 80 min.) (Wang and Hong, 1999).

Hawk and Fuller (1997) studied electrolytic oxidation of 2',2'-dichlorobiphenyl using ruthenium oxide electrode, persulfate and UV irradiation. Persulfate oxidizer affected the oxidation but the detail of the effect of the oxidant could not be determined because of inadequate information.

UV persulfate method could not oxidize chain oils completely (Kola et al., 2002). A range of the oxidation efficiency between different oils was around 25%-46%. When Triton-x-1000 surfactant of 2% (w/w) was supplemented, the oxidation efficiency increased to 75% for tail oil.