Contamination of Trichloroethylene in Drinking Water System and Its Degradation

Devi Lal Adhikari*, Chikashi Sato and Shobha Kanta Lamichhane***
** Department of Physics, Prithvi Narayan Campus, Pokhara, Tribhuvan University, Nepal*
***School of Engineering, Idaho State University, USA*
Correspondence : sklamichhane@hotmail.com

Abstract

Photolysis and sonolysis of trichloroethylene (TCE) in water was investigated using a cup-horn, flow-through reactor system. Water containing titanium dioxide was deliberately contaminated with TCE. These solutions were irradiated with ultraviolet light (UV) and ultrasonic waves (US). The decrease in the TCE concentration was observed in water under both US and UV treatments. Present findings declare that the use of UV and US decreased the TCE concentration. With the reactor specifications used, the photolysis and sonolysis processes can produce water meeting the drinking water standard (MCLs of $5\mu g/L$) for TCE.

Keywords: *photolysis, sonolysis, TCE concentration.*

Introduction

TCE (Trichloroethylene) is one of the volatile organic compounds (VOCs) present in drinking water. It is one of the industrial chemical products having a serious carcinogenic effect on human health. The structural and model formula of TCE is shown in Fig. 1. Once TCE was widely used as an anesthetic for surgery, but nowadays it is being used mainly as a solvent to remove grease from metal parts. It is also found in some household products such as typewriter correction fluid, paint removers, adhesives, and spot removers. The automotive and metals industries are the main users of TCE in the present world (www.google.com, 24 May 2012).

(a) Model structure (b) Structural formula

Fig.1: TCE structure model and formula (From Wikipedia, the free encyclopedia)

TCE leaked on the ground can move down through the soil and into ground water where it can pollute private and public drinking water supplies. TCE can also move through ground water to rivers and lakes and then quickly volatilizes into the air. Being volatile organic compound, it is rarely found in open surface water (Minnesota Department of Health 20-Sep-2011). The scientific information on human health effects of TCE comes from the studies of animals and people who were exposed to high TCE levels in the course of work.

The residence time of TCE in groundwater is much greater than that in surface water. In addition, TCE does not break down readily in the soil. While a small amount of TCE may dissolve in groundwater, it may also form pools of dense non-aqueous phase liquid (DNAPL) as a plume or it may volatilize, possibly resulting in emission as a soil vapour gas. Through the process of vapour intrusion, TCE can accumulate in buildings at dangerous levels (Emily Monosson, Feb 6, 2008).

The contamination of even a small amount of TCE in drinking water makes the water impotable. The maximum contaminant limit of TCE in drinking water is $5\mu g/L$ (U.S. EPA, 2003). If water contains the amount of TCE more than the above mentioned level, then the water is not suitable for safe drinking. The first known incidence of TCE contamination in groundwater was reported by two English public chemists in 1949 (Lyne et al., 1949). Removal of TCE from drinking water is of great concern due to their toxicity and their persistence in the environment (Neil et al., 2002). There are so many ways of degrading the TCE present in drinking water to make it feet able for drinking purpose. Out of many ways, the use of US and UV could also be an effective way to degrade TCE present in ground water.

Results and Discussion

Since TCE is a harmful chemical for human health, the water contaminated with TCE should be treated well before its supply in public taps. TCE needs to be removed well from the water resources to meet the drinking water standards of 5μg/L. During the course of time different methods have been practiced to remove the TCE present in drinking water. Among all, nowadays the use of US (ultrasound) and UV (ultraviolet light) is pulling the attention of human beings to degrade TCE present in drinking water. Degradation of TCE refers to a reaction to reduce the concentration of TCE. The degradation rate of TCE increases due to the reduction of initial concentration in both aqueous solution and groundwater via photochemical process (Sina et al., 2012). Jun Yao (2003) used a continuously stirred tank reactor (1-CSTR) and three continuously stirred tank reactor (3-CSTR) in series to determine the degradation rate constants for TCE as

$$k = \left(\frac{C_{in}}{C_{ss}} - 1 \right) \Big/ t_d \quad \ldots\ldots\ldots\ldots\ldots\ldots \ (1)$$

$$k_1 = \left(\frac{C_{in}}{C_{ss1}} - 1 \right) \Big/ t_{d1} \quad \ldots\ldots\ldots\ldots\ldots\ldots \ (2)$$

$$k_2 = \left[\frac{C_{in}}{C_{ss2}(1 + k_1 t_{d1})} - 1 \right] \Big/ t_{d2} \quad \ldots\ldots\ldots\ldots \ (3)$$

$$k_3 = \left[\frac{C_{in}}{C_{ss3}(1 + k_1 t_{d1})(1 + k_2 t_{d2})} - 1 \right] \Big/ t_{d3} \ \ldots\ldots\ldots (4)$$

where, k is the degradation rate constant (per min) in the single CSTR reactor, k_1 is the degradation rate constant (per min) in the US compartment, k_2 is the degradation rate constant (per min) in the partition compartment, k_3 is the degradation rate constant (per min) in the UV compartment, C_{in} is the concentration (mM) in the influent of US compartment, C_{ss} = steady-state effluent concentration (mM) for the single CSTR reactor; C_{ss1}, C_{ss2}, and C_{ss3} = steady-state effluent concentrations (mM) for the first, second, and third CSTR of 3-CSTR, respectively. The degradation rate constants in different reactors or compartments may be determined using Eqs. (1) through (4). In the combination of the reactors, first one consists of US horn, third consists of UV lump and the second is the partition used to separate the US and UV compartments.

US Degradation

Over the past few years, Sonication has been explored intensively as a means of efficient water treatment. Ultrasound induced cavitation is a sequence of the formation, rapid growth, and violent collapse of microscopic gas bubbles in liquid (Antoniadis *et al.*, 2007). US induce high pressure waves (compression) and low pressure waves (rarefaction), which rapidly move through the liquid media. Compression and rarefaction waves break the attractive forces between the liquid molecules and create gas bubbles. The gas bubbles grow until they reach a critical size as additional ultrasound energy enters the liquid. Once reaching a critical size, the gas bubbles implode or collapse. The collapse of bubbles produce intense local heating and high pressures, with a very short lifetime (Dehghani, 2005).

Under these conditions, water vapor undergoes thermal dissociation to yield $H^\bullet$, $HO^\bullet$, and $H^\bullet O_2$ radicals in the presence of O_2 (Weissler, 1959; Kang and Hoffmann, 1998). It has been found that sonolysis of TCE became greater at higher temperatures in the range of 5-30°C in the presence or absence of surfactant (Hugo et al., 2001). The proposed mechanisms for the sonochemical action are based on gas-phase high-temperature pyrolytic initiation steps that involve cleavage of the relatively weak C-Cl bond. The influent and effluent concentration and the degradation rate constants are shown in Table 1.

For the treatment of a variety of chemical contaminants in an aqueous solution, the sonochemical methods have been reported to be one of the effective methods (Colussi et al., 1999, Hung et al., 1999, Hung et al., 2000). The presence of high levels of surfactant may reduce the effectiveness of ultrasonic degradation of chlorinated hydrocarbons. Surface-active molecules interact strongly with cavitation bubbles, both chemically (Destaillats et al., 2000) and by influencing the physics of cavitation (Kumar et al., 1997). The potential of ultrasonic irradiation is an alternative to surfactant recycling technologies in non-aqueous-phase liquids (NAPL) remediation.

The degradation of chlorinated organic compounds, such as TCE was studied by (Lei et al., 2003) using nanosized FePd bimetallic particles. In their study, the decomposition rate constant of p-chlorophenol in an aqueous solution increased with increasing ultrasonic intensity (Lei et al., 2003). To enhance the reactivity of zero-valent iron (ZVI) nanoparticles in sonolysis of TCE, surface modification of ZVI nanoparticles was performed by Yunchul et al. (2010) using Pd and carboxymethyl cellulose (CMC). Their study found that the surface modification formed CMC-stabilized FePd bimetallic nano particles (CMC-FePd).

UV Light Degradation

A mercury lamp produces UV light very efficiently at 254 nm. More recent studies employed medium pressure (MP) UV lamps, which emit UV light in a broader range of wavelengths, from 200 to 300 nm (Bolton et al., 2003). According to the EPA UV Disinfection Guidance Manual (2006), the light output from mercury-based UV lamps is directly related to the mercury vapor pressure. Ultraviolet radiation is an emerging technology on the frontiers of water treatment. The scientific community continues to improve the UV technology and develop a better understanding of the fundamentals of how UV works. The continuing effort will eventually lead to a more effective UV process design.

UV is capable of degrading organic contaminants in an aqueous system in several processes: i) direct photolysis, ii) indirect photolysis, iii) photolysis in conjunction with an oxidizer, iv) heterogeneous photocatalysis, and v) photolysis with ultrasonic energy (Photosonolysis) (Toy, 1990; Bahnenann et al., 1994).

If a contaminant is photochemically active, it absorbs light. In such a case, direct photolysis can be an effective method for water treatment (Bahnemann et al., 1994). In direct photolysis, the contaminants must absorb the incident light (UV/ visible) and suffer degradation in their photochemically excited state (Bahnemann et al., 1994). Under typical conditions, most molecules absorb light weakly and degrade with low efficiencies (Bahnemann et al., 1994).

When UV light is directly irradiated in a dilute aqueous TCE solution, it generates chloride ions as a major end product and several reaction intermediates, such as formic acid, di- and mono-chloroacetic acids, glyoxylic acid, and, to a lesser extent, mono- and dichloroacetylene, formaldehyde, dichloroacetaldehyde, and oxalic acid (Ke Li et al., 2004). The TCE decay reactions proposed by Ke Li et al. are as follows:

(1) $\mathrm{TCE} + h\nu \rightarrow \mathrm{ClCH{=}C^{\bullet}Cl} + \mathrm{Cl^{\bullet}}$
(2) $\mathrm{TCE\ (H_2O)} + h\nu \rightarrow \mathrm{ClCH(OH) - CHCl_2}$
(3) $\mathrm{TCE} + h\nu \rightarrow \mathrm{HC{\equiv}CCl} + \mathrm{Cl_2}$
(4) $\mathrm{TCE} + h\nu \rightarrow \mathrm{ClC{\equiv}CCl} + \mathrm{HCl}$
(5) $\mathrm{TCE} + \mathrm{Cl^{\bullet}} \rightarrow \mathrm{Cl_2HC - C^{\bullet}Cl_2}$.

Indirect photolysis occurs when a species other then the chemical of interest absorbs sunlight and initiates a series of reaction that result in the transformation of the chemical (Angela et al., 2004). The kinetic equation for indirect or sensitized photolysis can be expressed as (Schnoor, 1996):

$$\frac{dC}{dt} = -k_2 CN = -k_p C \tag{5}$$

where k_2 is the indirect photolysis rate constant ($M^{-1}L^{3}\ T^{-1}$), N is the concentration of the non-target intermediary (mML^{-3}), C is the concentration of organic chemical (mML^{-3}), and k_p is the overall pseudo-first-order rate constant for sensitized photolysis (T^{-1}).The degradation rate for heterogeneous photo-catalysis of organic compounds was described by Langmuir-Hinshelwood kinetics equation (2.4-6), (Ollis et al., 1984):

$$r = -\frac{dC}{dt} = \frac{k'KC}{1+KC} \tag{6}$$

where r= rate of degradation of the organic substance (mM/min); k' = rate constant (mM/min); K = adsorption constant (mM^{-1}); and C = initial concentration of organic compound (mM).

The use of UV with an oxidizer (such as ozone and hydrogen peroxide) to produce more hydroxyl radical (•OH) is termed as photolysis in conjunction with an oxidizer. Hydroxyl radical is the most powerful oxidant after fluorine in the sense of oxidizing potential and will attack most organic compounds (Jun Yao, 2003).

Photosonolysis refers to a reaction of photolysis and sonolysis in combination. Photosonolysis of TCE in water was investigated by Sato et al. (2001) using a cup-horn flow-through reactor system. In their experiments, water containing titanium dioxide was deliberately contaminated with a mixture of volatile organic compound (TCE and other individual VOC). These solutions were exposed to ultraviolet light (UV) and ultrasonic waves (US) separately and simultaneously (UVUS). The evaluated values of the first-order degradation rate constants and the removal efficiencies showed that concurrent use of UV and US increased the VOC degradation rate and removal efficiency beyond the additive effect of UV and US. The results suggested that the UVUS effect on the decomposition of the VOC is synergistic over the additive effect of UV and US. With the reactor specifications used, the photosonolysis process can remove 90% of VOCs and produce water meeting the drinking water standard (MCLs of 5 μg/L) for TCE (Sato et al., 2001).

Heterogeneous photocatalysis is a rapidly expanding technology for water and air treatment. It can be defined as the acceleration of photoreaction in the presence of a catalyst. The initial interest in the heterogeneous photocatalysis was started when Fujishima and Honda discovered in 1972 the photochemical splitting of water into hydrogen and oxygen with TiO_2 (Fujishima, A., Honda, K., 1972). Then the extensive work has been carried out to produce hydrogen from water by this novel oxidation reduction reaction using a variety of semiconductors. In recent years interest has been focused on the use of semiconductor materials as photocatalysts for the removal of organic and inorganic species from aqueous or gas phase. This method has been suggested in environmental protection due to its ability to oxidise the organic and inorganic substrates (Fox, M.A., Dulay, M.T., 1993).

Table 1: Concentration and degradation rate constants of TCE during US and UV runs.

Configuration	Influent concentration, C_{in} (mM)	Effluent concentration, C_e (mM)	Degradation rate constants, k (min^{-1})
US	0.102	0.077	0.030
UV	0.099	0.016	0.180

Yao et al., 2003

Molecules absorb light in certain regions of the electromagnetic spectrum. Inherently, the electronic transitions corresponding to UV/visible light absorption are energetically sufficient to lead to the photochemical reactions. Therefore, the electromagnetic spectrum that is necessary for photochemical reaction is confined to UV/visible light with wavelengths of 110-750 nm (Lyman et al., 1982). The chemicals present in water undergo a sequence of chemical reactions and hence purify water. The influent and effluent concentration and the degradation rate constants for TCE are shown in Table 1.

Conclusion

The usefulness of the use of US and UV for water treatment process can be understood through the determination of degradation rate constant as follows:

1) $k = 0.030\ min^{-1}$ during US runs, where C_{in} = 0.102mM and C_e = 0.077mM.
2) $k = 0.180 min^{-1}$ during UV runs, where C_{in} = 0.099mM and C_e = 0.016mM.

This shows that the use of both ultrasound and ultraviolet light can reduce the presence of TCE concentration in the water. This indicates, the degradation rate constant of TCE is higher during UV runs than during US runs, showing that the concentration of TCE decreases more while using ultraviolet light than using ultrasound.

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