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KINETICS OF DEGRADATION OF PERCHLOROETHYLENE UNDER ULTRASONIC IRRADIATION AND PHOTOOXIDATION IN AQUEOUS SOLUTION

Sonolysis and photodegradation of various compounds such as chlorinated aliphatic hydrocarbons are the recent advanced oxidation processes. Perchloroethylene (PCE) is one of these compounds mainly used as a solvent and degreaser. In this work, elimination of perchloroethylene in aqueous solution by ultrasonic irradiation and photooxidation by UVC were investigated. Head space gas chromatography with FID detector was used for analyses of PCE. Results showed that PCE could be effectively and rapidly degraded by ultrasonic irradiation, photooxidation by UVC and combination of these methods. The order of studied reactions for degradation PCE has been determined.

1. INTRODUCTION

Developments in various fields to satisfy human needs produced effluents containing new materials that are not degraded by conventional treatment methods [1]. Due to increase of resistance of molecules to biodegradation, conventional biological methods are not sufficient to perform the required treatment. Therefore, it is essential to use new technologies to break down these resistant molecules to biologically decay able ones which could be further oxidized by biological processes [2]. New technologies include photocatalytic oxidation processes, advanced oxidation processes such as Fen-

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ton, common use of ozone, UV and hydrogen peroxide and the use of ultrasonic process [3]. Chlorinated aliphatic hydrocarbons (CAHs) are considered as refractory organics which could not be destructed in biological degradation process. These compounds may enter water sources, cause contamination of water resources and affect the human health. Many studies were performed to remove various organic materials such as dyes, chlorophenol, and phenol from aqueous solutions by advanced oxidation processes [4, 5].

Perchloroethylene (PCE) is one of the chlorinated aliphatic hydrocarbons (CAHs) which is mainly used as a solvent and degreaser [6]. It is a volatile, nonflammable and colorless liquid with a stench that its threshold odor is 1 ppm [6]. Tetrachloroethylene is widely used in industry as a solvent in dry cleaning, as a degreasing agent for manufactured metal parts and as a precursor in the production of chlorofluorocarbons. Tetrachloroethylene is included in consumer products such as motor vehicle cleaners, stain removers, adhesive and wood cleaners [7, 8]. A summary of PCE's physical properties is shown in Table 1 [9].

Table 1

PCE properties

Molecular Weight [g/mol]	Chemical formula	Density at 20 °C [g/cm ³]	Solubility ^a at 25 °C [mg/dm ³]	Melting point [°C]	Boiling point [°C]	H^b [atm·m ³ /mol]
165.85	C ₂ Cl ₄	1.63	150	-22	121	1.8×10^{-2}

^aSolubility in water.

^bHenry's law constant.

Widespread use as well as improper handling and disposal are the reasons why PCE is frequently detected in various environments such as groundwater, surface water, wastewater, air and food [10–14]. PCE is considered as a probable carcinogenic chemical (group 2A) [7]. It has also many other adverse effects on humans [6–8, 15]. Due to its undesirable effects on health, U.S. Environmental Protection Agency (US EPA) has set the maximum contaminant level (MCL) and maximum contaminant level goal (MCLG) for PCE as 0.005 mg/dm³ and zero, respectively [16].

Conventional water and wastewater treatment processes including coagulation, sedimentation, filtration, chlorination and biological processes are inefficient in removal of chlorinated compounds such as PCE [17]. Air stripping, membrane processes and using of granular activated carbon are effective for removal of these compounds; but costly. Furthermore, they transfer the contamination to other parts of the environment [18]. Alternative technologies for degradation of chlorinated organic compounds include sonochemistry, photochemistry, electrochemistry, and combined treatment such as reductive dehalogenation and biodegradation [17]. Advanced oxida-

tion processes (AOPs) are capable of degrading chlorinated organic compounds such as PCE in to less harmful compounds by using ultraviolet light. Ultrasonic waves are among the advanced oxidation processes which produce hydroxyl radicals during cavitations [18].

Although several studies are available on and sonolysis of pollutants, especially at low concentrations, few studies have addressed the PCE degradation by sonolysis and photooxidation (UVC) at micro-molar concentrations [17–19]. In this work, the degradation rates of PCE at different concentration levels and different pH levels with using an ultrasound bath at 130 kHz frequency and photooxidation with UVC ray and were studied. Kinetic models of PCE degradation were also determined. This study also aimed to determine the rate of PCE degradation and kinetic reaction rates.

2. MATERIALS AND METHODS

Experiment. The experimental research was conducted at the Department of Environmental Health Engineering at Tehran University of Medical Sciences between April and September 2011.

Two reactors were used in the study. One reactor was an ultrasonic device (Elma LTD, Germany) used to generate 130 kHz frequency and acoustic intensity of 2.5 W/cm^2 . For sonication, a glass bottle of the capacity of 300 cm^3 was placed inside the ultrasonic device. Each sample was sonicated for 5, 10, 20, 30, 40, 50 and 60 min applying 130 kHz frequency separately. The characteristics of ultrasound reactor used in the study are listed in Table 2.

Table 2

Characteristics of ultrasound reactor used in the experiments

Parameter	Characteristics
Frequency	130 kHz
Power	500 W
Acoustic intensity	2.5 W/cm^2
Flow type	batch
Reactor volume	3.7 dm^3
Dimensions	$L = 30 \text{ cm}, W = 25 \text{ cm}, H = 3.2 \text{ cm}$

The other reactor was the ultraviolet radiation reactor used to apply UVC with 253.7 nm. A 55 W low pressure mercury lamp (TUV, Philips) was placed in a quartz tube. The whole module was put in a cylindrical Plexiglass in which the sample solu-

tions were exposed to the UVC light. The specifications of lamp and reactor are summarized in Table 3.

Solutions of various concentrations of PCE (0.3, 3, and 10 mg/dm³) were prepared by dissolving PCE (Merck Co., Germany) in distilled water. The temperature was monitored during sonication and was maintained constant at 25 °C by cooling water. Reaction time was considered as the independent variable to investigate the effect of different reaction times on processes such as ultrasonic (US), UVC, and US/UVC. Samples were taken from each reactor (US, UVC and US/UVC) at given reaction times (5, 10, 20, 30, 40, 50 and 60 min).

Table 3

Characteristics of UVC reactor used in the experiments

Parameter	Characteristics
Model	TUV
Company	Philips
Power	55 W (low pressure mercury)
Intensity	52 W/cm ²
Wavelength	253.7 nm
Flow type	batch
Reactor volume	8 dm ³
Reactor dimensions	$d = 15 \text{ cm}, L = 100 \text{ cm}$
UV Lampe dimensions	$d = 20 \text{ mm}, L = 90 \text{ cm}$

Analyses. Analyses were performed by the head-space gas chromatography technique. Concentrations of PCE samples were determined through GC-FID analysis (VARIAN CP-3800, Australia). The gas chromatography was fitted with a CP-Sil 8 CB capillary column (30 m, 0.32 mm ID, 0.25 µm film thickness). The injector temperature was 150 °C; initial oven temperature was 35 °C (held for 1 min) and increased to 100 °C at the rate of 16 °C·min⁻¹, held for 5 min. The inlet (0.2 cm³) was operated in 20% split mode. Helium (99.999%) was used as carrier gas at 1 cm³ min⁻¹. The lowest detection level (MDL) for PCE analysis by GC with the above mentioned method was considered 5 µg/dm³.

3. RESULTS AND DISCUSSION

The obtained data were fitted with first and second order models.

- First order kinetics model: The experimental data were fitted according to simple first order rate:

$$C = C_0 e^{-kt} \quad (1)$$

where k is the first order rate constant and it is estimated from the slope by plotting $\ln C$ versus time t . All the correlation factors (R^2) in this study were larger than 0.95, indicating that the degradation of PCE follows first order kinetics model.

• Second order kinetics model: The variation in the degradation concentration can be fitted by using the second order kinetic equation:

$$\frac{dc}{dt} = -kc^2 \quad (2)$$

For liner fitting, the equation can be rearranged as:

$$\frac{1}{c} - \frac{1}{c_0} = kt \quad (3)$$

where k is the second order degradation rate constant and it can be estimated from the slope after plotting $1/C$ versus t . The results showed that decomposition of PCE of the concentration of 10 mg/dm³ in the ultrasonic reactor, UVC and UVC/US reactor for all the concentrations follow up first order kinetics model. The kinetics constants in these reactors are given in Tables 4–6.

Table 4

First and second order degradation of PCE at various pH, subjected to US reactor

C_0 [mg/dm ³]	pH	Mean efficiency [%]	k [1/min]	R^2	Reaction order
10	9	57.31	0.0094	0.984	first
10	7	64.54	0.0148	0.995	
10	5	65.31	0.0162	0.991	
3	9	58.27	0.0155	0.997	second
3	7	68.56	0.0157	0.9	
3	5	70.31	0.0184	0.905	
0.3	9	29.38	0.043	0.991	
0.3	7	35.57	0.037	0.901	
0.3	5	39.42	0.0606	0.982	

Aqueous solutions with initial concentrations of PCE 0.3, 3, and 10 mg/dm³ at various pH were sonicated and photooxidized. Typical trend of $\ln C$ versus time for PCE at various initial concentrations and pH in the US/UVC reactor are shown in Figs. 1–3.

Table 5

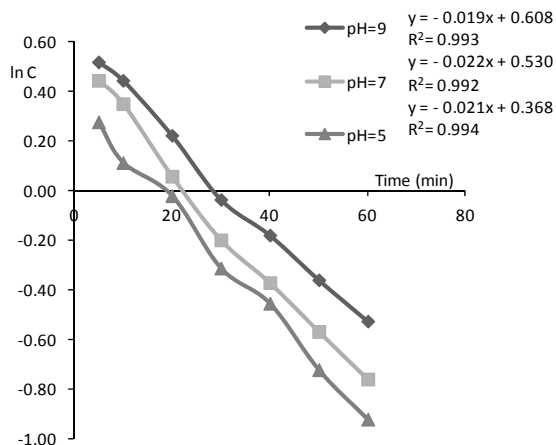
First order degradation of PCE at various pH, subjected to UVC reactor

C_0 [mg/dm ³]	pH	Mean efficiency [%]	k [1/min]	R^2	Reaction order
10	9	53.81	0.0082	0.994	first
10	7	49.65	0.0056	0.997	
10	5	62.58	0.0137	0.996	
3	9	76.15	0.0148	0.995	
3	7	77.16	0.0181	0.986	
3	5	82.61	0.023	0.987	
0.3	9	69.42	0.0287	0.987	
0.3	7	66.42	0.0247	0.984	
0.3	5	74.76	0.0391	0.992	

Table 6

First order degradation of PCE at various pH, subjected to US/UVC reactor

C_0 [mg/dm ³]	pH	Mean efficiency [%]	k [1/min]	R^2	Reaction order
10	9	88.85	0.0194	0.993	first
10	7	91.36	0.0221	0.992	
10	5	91.89	0.0215	0.994	
3	9	82.97	0.035	0.976	
3	7	88.057	0.0518	0.977	
3	5	86.67	0.0545	0.979	
0.3	9	71.24	0.0370	0.982	
0.3	7	81.38	0.0339	0.962	
0.3	5	82.05	0.0393	0.973	

Fig. 1. Degradation of aqueous solution of PCE of 10 mg/dm³ at various pH subjected to US/UVC; $T = 25$ °C

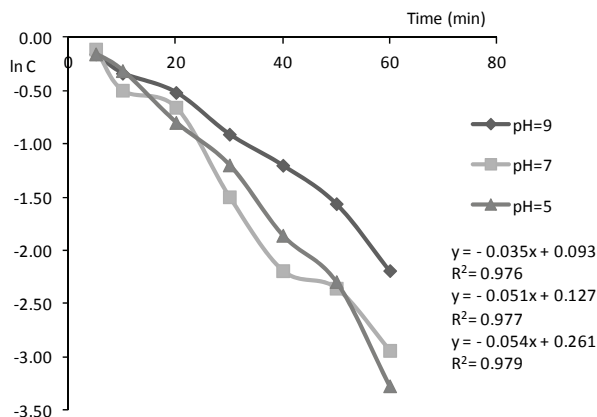


Fig. 2. Degradation of aqueous solution of PCE of 3 mg/dm³ at various pH subjected to US/UVC; $T = 25\text{ }^{\circ}\text{C}$

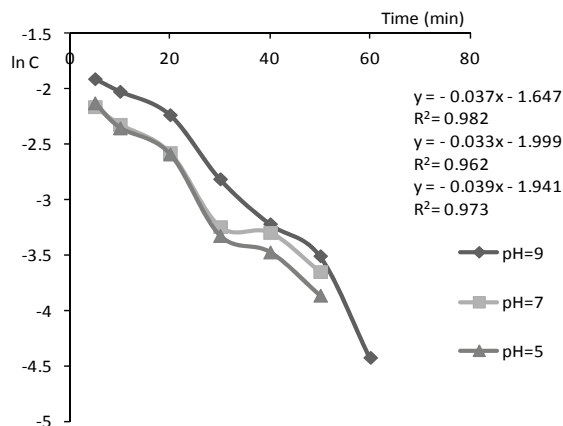


Fig. 3. Degradation of aqueous solution of PCE of 0.3 mg/dm³ at different pH subjected to US/UVC; $T = 25\text{ }^{\circ}\text{C}$

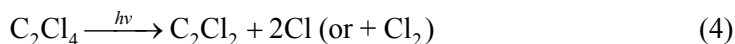
Decomposition of PCE of the concentration of 10 mg/dm³ in the ultrasonic reactor, in UVC and UVC/US reactor for all concentrations followed first order kinetics model and in the ultrasonic reactor of the concentration of 3 and 0.3 mg/dm³ followed second order kinetics model. Also with increase in the initial concentration of PCE, the apparent first and second order rate constants decreased, indicating non-elementary nature of the photolysis reactions. De Visscher et al. [20] studied the kinetic model for the sonochemical degradation of non-polar monocyclic aromatic compounds in aqueous solution. In this study, pyrolysis was mentioned as the degradation mechanism of monocyclic aromatic compounds in the cavitation bubbles [20]. Jiang et al. [21] studied kinetics and mechanisms of ultrasonic degradation of volatile chlorinated aromatics in aqueous solutions and showed that sonochemical decomposi-

tion of volatile compounds follows pseudo-first-order reaction kinetics [21]. The results of our study reconfirmed the conclusion of the experiment. Feiyan et al. [22] studied kinetics of volatile organic compounds (VOCs) with respect to various parameters pertinent to the operating conditions. The effects of various experimental parameters such as initial concentrations of the VOCs were determined [22]. Shirayama et al. [23] also studied photodegradation rates of chlorinated hydrocarbons such as PCE under the UV bandwidths of 185 and 254 nm in the presence and absence of dissolved oxygen in water. This study showed that photolysis of H₂O efficiently generated hydroxyl radicals which attack various dissolved organic compounds [23].

The dependence of degradation rate constants on initial concentration was similar to that in other studies [18, 20, 24]. In these studies, reaction mechanisms for the degradation of *p*-nitrophenol, carbon tetrachloride, parathion, *p*-nitrophenyl acetate, trinitrotoluene, perchloroethylene and monocyclic aromatic compounds in aqueous solution are investigated. Degradation rate of PCE at pH = 5 was higher than at other pH however the degradation rate did not change significantly for other pH.

Photolysis by UVC can destruct various organic compounds such as PCE by two methods [23, 24]. These methods are as follows:

- destruction of the double band of carbon; UVC excitation of C₂Cl₄ leads to destruction of the carbon–carbon band:



- direct photolysis of H₂O; generated efficiently hydroxyl radicals attack the various dissolved organic compounds as follows:



Ultrasonic waves are able to produce hydroxyl radicals during cavitations in the process of pyrolysis of water molecules [20]. De Visscher et al. [20] mentioned that kinetic model for the sonochemical degradation of monocyclic aromatic compounds in aqueous solution in high concentrations is due to pyrolysis in the cavitation bubbles, but in low concentrations degradation mechanism of chlorinated hydrocarbon is mostly related to the hydroxyl radicals [20].

4. CONCLUSIONS

Sonolysis and photolysis of PCE was performed under various variables such as initial concentration of PCE, pH, reaction time and type of reactor. The result of this study showed that the PCE degradation rate increased as its initial concentration decreased. The initial concentration proved to have a significant effect on the degradation of PCE. It also concluded that destruction of PCE was not strongly affected by the initial pH of solution; however at lower pH, the rate of PCE degradation is relatively higher.

The PCE degradation rate constants were changed as a function of initial concentration of PCE. It was shown that decrease in the degradation rate constant would be expected due to the increase of initial concentration of PCE.

Removal rate increases with increasing reaction time in all reactors. The decomposition of PCE of the concentration of 10 mg/dm³ in the ultrasonic reactor followed first order kinetics model. All concentrations in UVC and UVC/US reactors followed first order kinetics model. The removal percentage of PCE in the UVC/US reactor was higher than each one of the reactors alone, probably as a result of hydroxyl radicals induced by ultrasound and ultraviolet radiation.

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