Full Length Research Paper

Kinetic and degradation efficiency of trichloroethylene (TCE) via photochemical process from contaminated water

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Trichloroethylene (TCE) is a common pollutant in groundwater and one of the priority pollutants listed by the U.S. EPA. With regard to concentration ranges in previous studies exceeding environmental levels by far with millimolar concentrations of TCE, this study deals with the degradation of TCE at micromolar concentrations by UV/H_2O_2. The degradation rate of TCE at different dilute solution levels, 30, 300 and 3000 μg L^{-1} (0.22, 2.28 and 22.83 micromolar) at different initial pHs was examined. In addition, samples were taken from four contaminated wells to measure the degradation rate of TCE. It was shown that the degradation rate of TCE increased due to the reduction of initial concentration in both aqueous solution and groundwater samples. The TCE degradation constants in groundwater samples increased by a factor of 2.05, while the initial concentration reduced from 1345.7 to 97.7 μg1 L^{-1}. By increasing the molar ratios of H_2O_2 to TCE from 13 to 129, caused the degradation rates to increase in aqueous solutions. No harmful byproducts such as haloacetic acids (HAAs) were detected at these low levels of initial concentration of TCE during process. This study confirmed that application of UV/H_2O_2 process could be an effective method in treating contaminated groundwater by TCE at low concentrations.

Key words: Trichloroethylene, UV-radiation, UV/H_2O_2 process, groundwater remediation.

INTRODUCTION

The presence of organic pollutants in the subsurface indicates a serious threat to groundwater sources and has gained considerable attention over the last two decades (Sabatini et al., 1994; Ponza et al., 2010). Trichloroethylene (TCE) is possibly a carcinogenic compound to human and is one of the most common contaminant in groundwater. TCE is nonflammable, volatile, and has been used extensively as a solvent and degreasing agent in metal and glass industries, dry cleanings, household products such as rug cleaners or spot removers, and air fresheners (Ahmed and Ollis, 1984; Bahnemann et al., 1987). TCE is chemically converted to vinyl chloride (VC) in anaerobic condition which is a potential carcinogen by reductive dehalogenation. Due to its serious health effects, U.S. Environmental Protection Agency (EPA) has set the maximum contaminant level (MCL) and maximum contaminant level goal (MCLG) for TCE as 0.005 mg L^{-1} and zero, respectively.

Treatment technologies such as adsorption by activated carbon and air stripping are effective in removing TCE from contaminated waters, but these processes

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Table 1. The molar ratios of hydrogen peroxide to TCE at different concentrations of TCE in aqueous dilute solution and well water samples.

Initial concentration of TCE ($\mu g\ L^{-1}$)	H_2O_2 concentration ($mg\ L^{-1}$)	The molar ratio of hydrogen peroxide to TCE
	0.1	13
30	0.5	64.5
	1	129
	1	13
300	5	64.5
	10	129
	10	13
3000	50	64.5
	100	129
Well no. 1 (C_0=97.7 $\mu g\ L^{-1}$)	3.25	129
Well no. 2 (C_0=601.2 $\mu g\ L^{-1}$)	20.05	129
Well no. 3 (C_0=1012.3 $\mu g\ L^{-1}$)	33.76	129
Well no. 4 (C_0=1345.7 $\mu g\ L^{-1}$)	44.88	129

transfer the contaminant from one phase to another phase and the environmental hazards of TCE will still remain (Bajpai and Zappi, 1997). In most of the studies, TCE removal has been studied at the millimolar ranges, while it is repeatedly reported that groundwater are contaminated by TCE at micromolar ranges (Hamlin et al., 2002; Guertal et al., 2004; Dobaradaran et al., 2010; Barbaro and Neupane, 2001).

In this study, the application of photochemical process for TCE degradation was studied in details (different initial pHs, different TCE and H_2O_2 concentrations). Optimized values of pH and H_2O_2 concentrations for each initial TCE level were presented according to the examination of reaction kinetics at different conditions. In addition, application of this process was evaluated for treatment of four contaminated wells by TCE near a car industry in the vicinity of Tehran.

MATERIALS AND METHODS

Experiment set-up

Experiments were conducted in a stainless steel batch reactor (volume = 200 ml) with an immersed low-pressure lamp (power input = 6 W). The wavelength of low-pressure Hg lamp was 253.7 nm. Aqueous dilute solutions of different levels of TCE (30, 300 and 3000 $\mu g\ L^{-1}$ equal to 0.22, 2.28 and 22.83 micromolar respectively) were prepared by dissolving TCE (Merck, Germany) in de-ionized water. Samples were taken from the reactor at given reaction times (5, 10, 20, 25, 30, 35, 40, 45, 50 and 60 min).

Four contaminated wells by TCE near the car industry were selected. Sampling, preservation and handling of samples were done according to standard methods (APHA, AWWA and WEF, 2005). Different concentrations of hydrogen peroxide (0.1, 0.5, 1.5, 10, 50 and 100 mg L^{-1}) (Merk, Germany) were also prepared and H_2O_2 concentrations were measured by iodometric titration. As presented in Table 1, for different aqueous solutions of TCE and contaminated well water, different hydrogen peroxide concentrations were added at the molar ratios of H_2O_2 to TCE ranged from 13 to 129. General characteristics and TCE concentrations of well water (well no. 1 to 4) are shown in Table 2.

Laboratory analysis

Samples were analyzed with a Varian CP–3800 (Australia) gas chromatograph (GC), equipped with flame ionization detector (FID). The GC was fitted with a CP–Sil and CB capillary column (30 m, 0.32 mm id, 0.25 μm film thickness). Injector temperature was 150°C, initial oven temperature was 35°C (being held for 1 min) and increased to 100°C at a rate of 16°C min^{-1} (being held for 5 min). The inlet was operated in 20% split mode and helium (99.999%) was used as the carrier gas at 1 ml min^{-1}.

For detection of potential intermediates of TCE degradation during photolysis, GC/MS analysis with an Agilent (Agilent Technologies, Palo Alto, CA, USA) 6890 plus gas chromatograph equipped with a 5973 mass selective detector quadruple mass spectrometer was used. The gas chromatograph was fitted with a DB-1 capillary column (60 m, 0.25 mm id, 0.25 μm film thickness). The instrument temperatures were as following: injector temperature 150°C, initial oven temperature 40°C (held for 3 min), increased to 100°C at a rate of 10°C min^{-1}, held for 1 min then increased to 130°C at a rate of 30°C min^{-1}, held for 1 min. The inlet was operated in splitless mode.

Helium (99.999%) was used as carrier gas at 1.5 ml min^{-1}. The electronic beam energy of the mass spectrometer was set at 79 ev and the mass selective detector was operated in scan mode. Ion chromatography (Metrohm 883 basic IC equipped with ion separation and conductivity detector, 1.7 mM $NHCO_3$ and 1.8 mM Na_3CO_3 as eluents) and an Agilent 1100 HPLC/UV system (with C18 reversed phase column manufactured by Macherey- Nagel), were also used to detection of potential intermediates formed during process.

RESULTS AND DISCUSSION

Effect of initial concentration

Aqueous solutions of different pHs and various initial

Table 2. General characteristics and TCE concentrations of well waters (well no.1 to well no.4).

Parameter	Well 1*	Well 2*	Well 3*	Well 4*
Temperature, (°C)	27.9	27.5	27.3	27.1
Total dissolved solid (TDS), (mg L^{-1})	371	380	365	385
Electerical conductivity (EC), (μs cm^{-1})	558	568	549	580
pH	7.42	7.5	7.35	7.6
Ca^{2+} (mg L^{-1})	44.8	46.7	45	43.6
Mg^{2+} (mg L^{-1})	6.72	7.2	7.6	5.9
Na^+ (mg L^{-1})	69	75	65	73
Total hardness (TH), (mg L^{-1} $CaCO_3$)	140	146.7	144.1	133.6
NH_4^+ (mg L^{-1})	0.00	0.09	0.00	0.00
NO^{-3} (mg L^{-1})	5.89	6.01	4.95	7.15
SO_4^{2-} (mg L^{-1})	66.7	70.1	64	73.2
Cl^- (mg L^{-1})	70	76.5	67	74
TCE (μg L^{-1})	97.7	601.2	1012.3	1345.7

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*TCE, PCE, toluene, n-hexane, xylene, cyclohexane and n-pentane were detected in all wells. TCE, Trichloroethylene; PCE, perchloroethylene.

concentrations of TCE (30, 300 and 3000 μ L^{-1}) were illuminated. The results show that the reactions order is first order so typical C/C_o versus time for TCE degradation at different initial concentrations is shown in Figures 1a to f and Figures 2a to c. Also, typical C/C_o versus time for TCE degradation in well water samples is shown in Figure 2d.

Degradation rate constants of TCE, for all samples (the k values were measured three times for every concentration and the average present) at different initial pHs were obtained by linear regression on the logarithm of the concentration versus photolysis time. The apparent first order rate constants decreased as initial concen-tration of the TCE increased. It was reported that free radical is dominating destruction mechanism at micromolar and low TCE concentration levels during photolysis and also sonication of this compound (Hirvonen et al., 1996; Dobaradaran et al., 2010). The reactions are mainly dominated by the concentration of TCE in the solutions; the higher the TCE concentration and the lower the degradation rate, which is due to the limited UV photons (a constant) and free radicals ((Hirvonen et al., 1996). First order degradation constants of solutions at different pHs are presented in Figures 3a to c. It is obvious from these Figures that the degradation rate constants of TCE increase if the initial concentration of TCE is reduced from 3000 to 30 μg L^{-1}. The increase in degradation rate constants of TCE with decrease in concentrations were also observed in the well water samples during photolysis (Figure 3d). The TCE degradation rate constants in well water samples increased by a factor of 2.05, while the initial concentration of TCE reduced from 1345.7 to 97.7 μg L^{-1}.

At lower concentrations, the reaction between volatile organic carbons (VOCs) and hydroxyl radicals is more likely to take place which results in significance increase in destruction by OH° (Gogate and Pandit, 2004). The

degradation rates of TCE in well water samples were lower in comparison to aqueous dilute solution samples which revealed the presence of other organics and also radical scavengers such as chloride, sulfate and bicarbonate ions that naturally are present in groundwater (Table 2).

Effect of pH

The effects of initial pHs on TCE destruction with different initial concentrations in samples are shown in Figures 3a to d. No significant of initial pH on TCE degradation was observed. Varying the initial pH of solutions did not affect the TCE degradation rates in these low range levels of TCE.

Glaze et al. reported that initial pH had no significant effect on the organic compound destruction due to photolysis (Glaze et al., 1987). The presence of H^+ can slightly inhibit the TCE decay (Juncai and Chu, 2009) but at lower operating pH, the effect of the radical scavengers such as bicarbonate and carbonate ions, will be nullified (Gogate and Pandit, 2004).

During the photolysis processes of TCE at highest concentration (3000 μg L^{-1}), the pH of solutions gradually decreased from 11 to eight, seven to 4.8 and five to 4.2. This decline in pHs was accompanied by a reduction in TCE concentrations which suggests that proton (H^+) is one of the major end products of photoreduction of TCE. Although for the extreme acidic condition (pH=3), no significant pH variation was observed, because the H^+ generated in the reaction were less significant compared to those originally being present in the solution. During the degradation of TCE at 30 and 300 μg L^{-1} concentrations, low levels of the H^+ were produced such that pH of solutions did not decrease significantly.
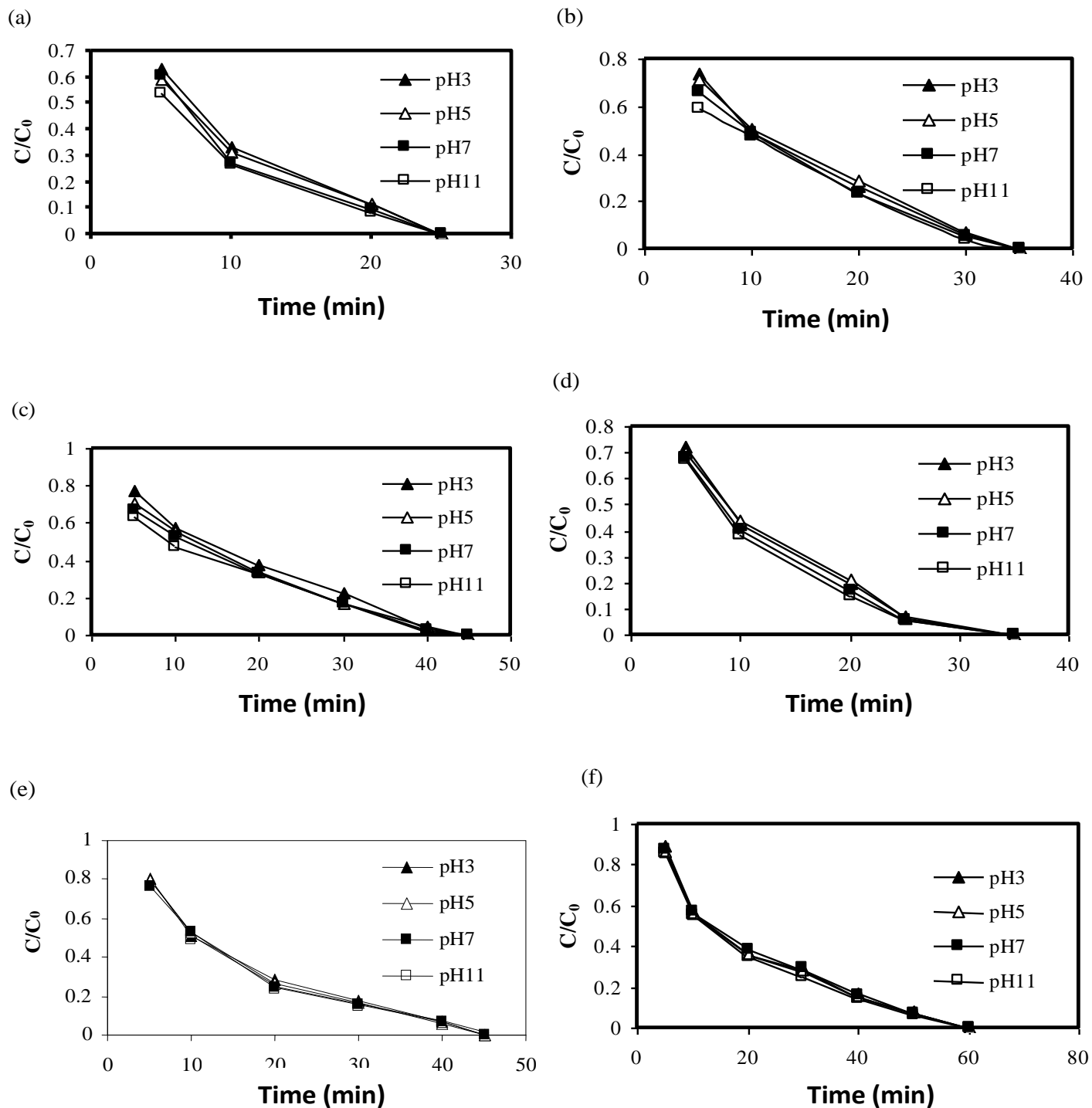
Figure 1. The photodegradation of TCE in aqueous solutions at different concentrations, pHs, and different concentrations of hydrogen peroxide: (a) 30 µg L^{-1} TCE, 1 mg L^{-1} H$_2$O$_2$, (b) 30 µg L^{-1} TCE, 0.5 mg L^{-1} H$_2$O$_2$, (c) 30 µg L^{-1} TCE, 0.1 mg L^{-1} H$_2$O$_2$, (d) 300 µg L^{-1} TCE, 10 mg L^{-1} H$_2$O$_2$, (e) 300 µg L^{-1} TCE, 5 mg L^{-1} H$_2$O$_2$, and (f) 300 µg L^{-1} TCE, 1 mg L^{-1} H$_2$O$_2$. TCE, Trichloroethylene

Effect of hydrogen peroxide and byproducts formation

As shown in Figures 3a to d, addition of hydrogen per-

oxide have significant effect on the degradation rates of samples.

Hydrogen peroxide decomposes under the influence of photolysis, as shown in reactions 1 to 3 (Elkanzi and
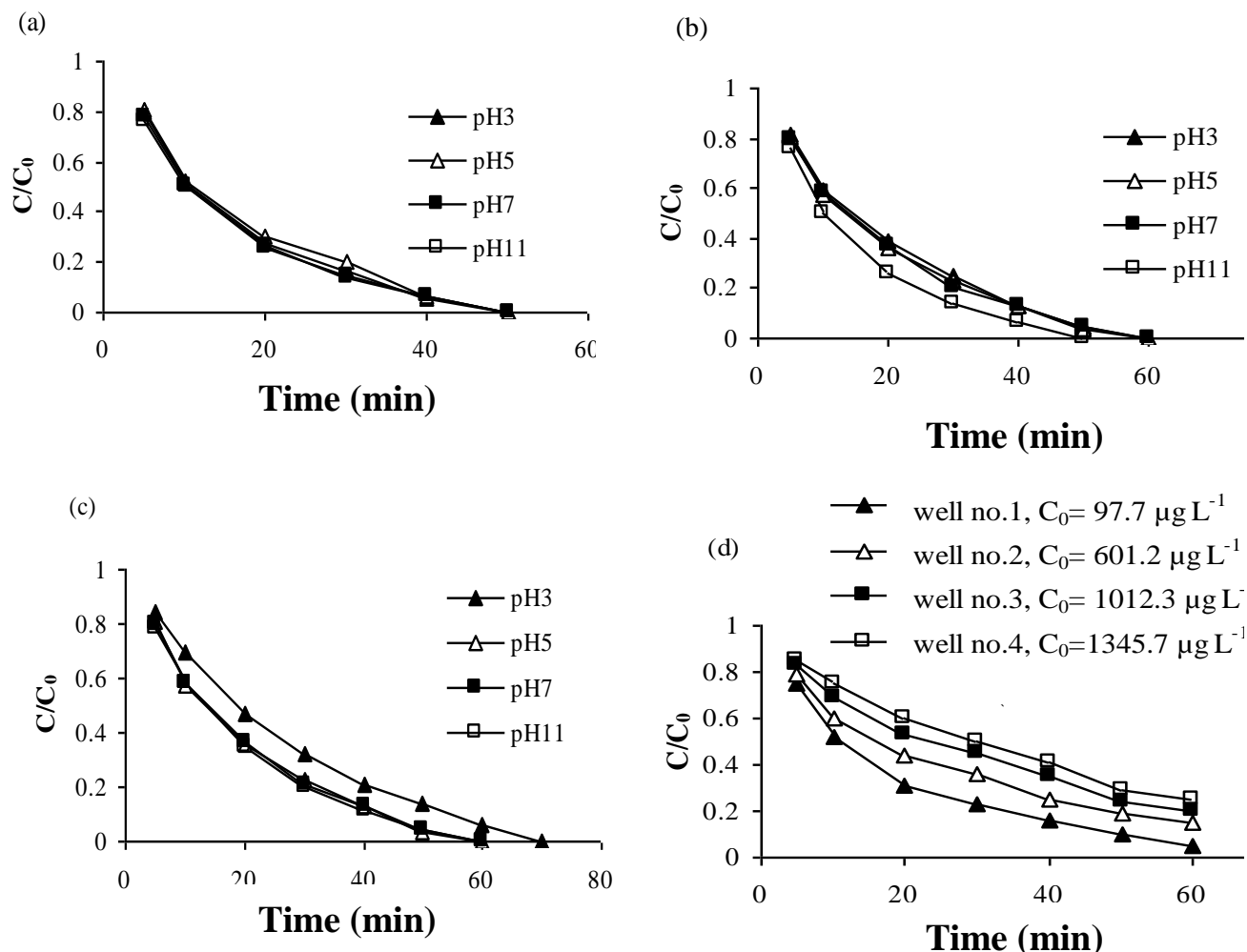
(a)

(b)

(c)

(d)

Figure 2. The photodegradation of TCE in aqueous solutions at different concentrations, pHs, and different concentrations of hydrogen peroxide: (a) 3000 µg L^{-1} TCE, 10 mg L^{-1} H_2O_2, (b) 3000 µg L^{-1} TCE, 50 mg L^{-1} H_2O_2, (c) 3000 µg L^{-1} TCE, 100 mg L^{-1} H_2O_2, and (d) well water samples. TCE, Trichloroethylene.

Kheng, 2000).

$$H_2O_2 + hv \rightarrow 2HO^{°} \qquad (1)$$

$$HO^{°} + H_2O_2 \rightarrow HO^{°}_2 + H_2O \qquad (2)$$

$$2\,HO^{°}_2 \leftrightarrow \quad H_2O_2 + O_2 \qquad (3)$$

Addition of H_2O_2 increases the degradation rates of TCE in all samples especially at low concentrations because more free radicals will be in processes, which is due to important role of hydroxyl radicals being produced by hydrogen peroxide photolysis (Dewulf et al., 2001). The molar ratios of hydrogen peroxide to TCE in different initial concentrations of TCE were 13, 64.5 and 129. At the molar ratio of 129 the best removal efficiency was observed. In this regard, for the degradation of TCE in well water samples, the molar ratio of 129 was selected. The efficiency of the UV/H_2O_2 process in TCE

degradation of well water samples was lower in comparison to aqueous samples because of other organics and radical scavengers being present in well water.

No harmful byproducts were detected at these low levels of initial concentration of TCE after final reaction time at our studied concentrations; so therefore we conducted the photolysis of TCE via UV/H_2O_2 process at a high concentration (C_0= 380 µM (50 mg L^{-1})), the following intermediates were formed: formic acid, dichloroacetic acid, dichloroacetylene, formaldehyde and glyoxylic acid and oxalic acid. Chloride was the major end product. After 70 min run time chloride 977 µM, formic acid 21 µM, dichloroacetic acid 7 µM, oxalic acid 7.8 µM and glyoxylic acid 1.86 µM were remained but dichloroacetylene and formaldehyde were completely removed. At lower initial concentrations of TCE UV photons and hydroxyl radicals that formed during process could destroy all content of TCE and its intermediates at the end of reaction time but at highest concentration (C_0=
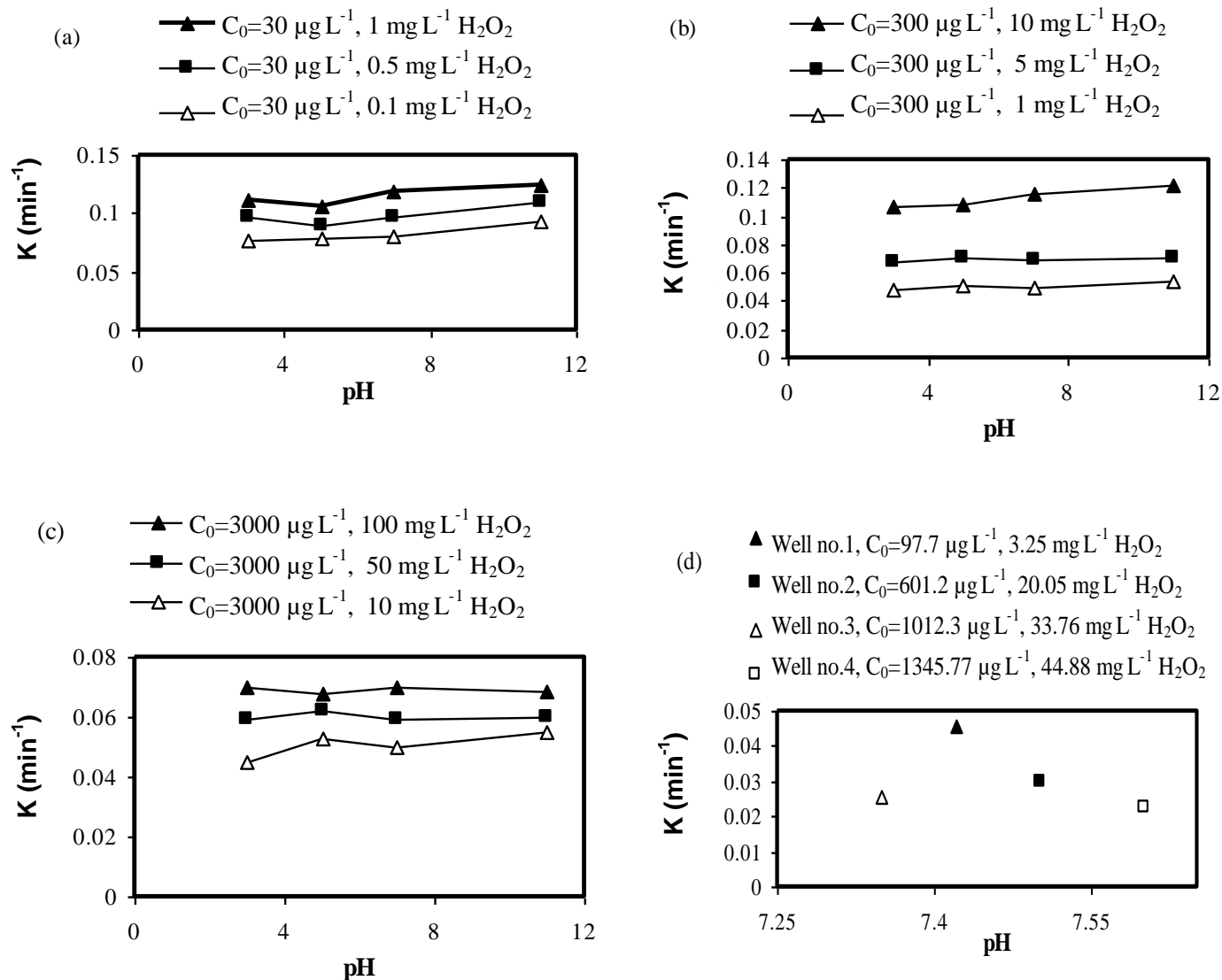
(a) $C_0=30 \ \mu g \ L^{-1}, 1 \ mg \ L^{-1} \ H_2O_2$
$C_0=30 \ \mu g \ L^{-1}, 0.5 \ mg \ L^{-1} \ H_2O_2$
$C_0=30 \ \mu g \ L^{-1}, 0.1 \ mg \ L^{-1} \ H_2O_2$

(b) $C_0=300 \ \mu g \ L^{-1}, 10 \ mg \ L^{-1} \ H_2O_2$
$C_0=300 \ \mu g \ L^{-1}, 5 \ mg \ L^{-1} \ H_2O_2$
$C_0=300 \ \mu g \ L^{-1}, 1 \ mg \ L^{-1} \ H_2O_2$

(c) $C_0=3000 \ \mu g \ L^{-1}, 100 \ mg \ L^{-1} \ H_2O_2$
$C_0=3000 \ \mu g \ L^{-1}, 50 \ mg \ L^{-1} \ H_2O_2$
$C_0=3000 \ \mu g \ L^{-1}, 10 \ mg \ L^{-1} \ H_2O_2$

(d) Well no.1, $C_0=97.7 \ \mu g \ L^{-1}, 3.25 \ mg \ L^{-1} \ H_2O_2$
Well no.2, $C_0=601.2 \ \mu g \ L^{-1}, 20.05 \ mg \ L^{-1} \ H_2O_2$
Well no.3, $C_0=1012.3 \ \mu g \ L^{-1}, 33.76 \ mg \ L^{-1} \ H_2O_2$
Well no.4, $C_0=1345.77 \ \mu g \ L^{-1}, 44.88 \ mg \ L^{-1} \ H_2O_2$

Figure 3. The degradation rate constants at different pHs and TCE concentrations: (a) 30 µg L^{-1} TCE, (b) 300 µg L^{-1} TCE, (c) 3000 µg L^{-1} TCE, (d) well water samples. TCE, Trichloroethylene.

380 µM) because of; a) the intermediates competition for the photon and free radicals and b) the intermediates may act as internal light filter that mainly reduce the light available for TCE and its intermediates destruction (Chu and Jia, 2009), all content of initial concentration of TCE (C_0= 380 µM) were not degraded completely. It must be noted that after 70 min reaction time, final degradation efficiency of TCE (C_0= 380 µM) was 95.5%. In a recent study Li et al. studied the formation of byproducts and kinetic modeling of TCE during direct photolysis. They reported chloride ion as major end product and some compounds such as formic acid, di and chloroacetic acids, glyoxilic acid, oxalic acid, formaldehyde, mono and dichloroacetylene and dichloroacetaldehyde as by-products (Li et al., 2004).

Conclusion

Photolysis of TCE was performed under various experimental conditions such as initial concentrations, pHs and H$_2$O$_2$ concentrations. The degradation rate constant of TCE increased, when the initial concentration of TCE decreased in both well water and aqueous solution samples. Initial pH of solution did not affect the TCE destruction. Hydrogen peroxide had significant effect on degradation rate of TCE in samples. Lower concentrations of TCE and addition of hydrogen peroxide led to lower EE/O values and consequently higher energy efficiency. No harmful byproducts such as haloacetic acids (HAAs) were detected at these low levels of initial concentration of TCE during UV/H$_2$O$_2$ process but we detected these

compounds at higher concentration. Finally, the results confirmed the potential use of UV/H_2O_2 for the treatment of groundwater at low concentrations (micromolar) of TCE; therefore it may be beneficial to dilute higher concentrations of TCE for better treatment.

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REFERENCES

Ahmed S, Ollis D (1984). Solar photoassisted catalytic decomposition of the chlorinated hydrocarbons trichloroethylene and trichloromethane. Solar Energy. 32: 597-601.

APHA, AWWA, WEF (2005). Standard methods for the examination of water and wastewater. 21st ed; Washington D.C., AWWA.

Bahnemann DW, Monig J, Chapman R (1987). Efficient photocatalysis of the irreversible one-electron and two electron reduction of halothane on platinized colloidal titanium dioxide in aqueous suspension. J. Phys. Chem. 91: 3782-4378.

Bajpai RK, Zappi ME (1997). Bioremediation of surface and subsurface contamination. Ann. N. Y. Acad. Sci. 829: 83-96.

Barbaro JR, Neupane PP (2001). Distribution and mass loss of volatile organic compared in the surficial aquifer at sites FT03, LF13, and WP14/CF15; Dover Air Force Base, Delaware, November 2000-February 2001, U.S. Ecological Survey Water Resources Investigations Report 02–4121.

Chu W, Jia J (2009). The photodegradation and modeling of a typical NAPL, trichloroethene, by monochromatic UV irradiations. Environ Sci. Technol. 43: 1455-1459.

Dewulf J, Van Langenhave H, De Visscher A, Sabbe S (2001). Ultrasonic degradation of trichloroethylene and chlorobenzene at micromolar concentrations: kinetics and modeling. Ultrason. Sono Chem. *8:* 143-150.

Dobaradaran S, Mahvi AH, Nabizadeh R, Mesdaghinia A, Naddafi K, Yunesian M, Rastkari N, Nazmara S (2010). Hazardous organic compounds in groundwater near Tehran automobile industry. Bull Environ Contam. Toxicol. 85: 530-533.

Dobaradaran S, Nabizadeh R, Mahvi AH, Mesdaghinia A, Naddafi K, Yunesian M, Rastkari N, Nazmara S (2010). Survey on degradation rates of trichloroethene aqueous solution by ultrasound. Iran J Environ. Health Sci. Eng. 7: 307-312.

Elkanzi EM, Kheng GB (2000). H_2O_2/UV degradation kinetics of isoprene in aqueous solution. J. Hazard. Mater. B73: 55-62.

Glaze WH, Kang JW, Chapin DH (1987). The Chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. Ozone: Science and Engineering. 9: 335-352.

Gogate RP, Pandit AB (2004). A review of imperative technologies for wastewater treatment II: hybrid methods. Adv. Environ. Res. 8: 553-597.

Guertal WR, Stewart M, Barbaro JR, Mchale TJ (2004). Analytical Results from groundwater sampling using a direct push technique at the Dover National test site, Dover Air Force Base, Delware, June-July 2001, File report 03-380; U.S. Geological Survey Water-Resources Investigation Report 02-4119, US. Geological Survey Open.

Hamlin SN, Beltiz K, Kraja S, Dawson B (2002). Groundwater quality in the Santa Ana watershed Report 02-4243; U.S Geological Survey Water Resources Investigations California-Overview and data summary.

Hirvonen A, Tuhkanen T, Kalliokoski P (1996). Formation of chlorinated acetic acids during UV/ H_2O_2-oxidation of groundwater contaminated with chlorinated ethylenes. Chemosphere. *32:* p. 1091.

Juncai J, Chu W (2009). The photodegradation of trichloroethylene with or without the NAPL by UV irradiation in surfactant solutions. J. Hazard. Mater. 161: 196-201.

Li K, Stefan MI, Crittenden JC (2004). UV photolysis of trichloroethylene:product study and kinetic modeling. Environ. Sci. Technol. 38: 6685-6693.

Ponza S, Parkpian P, Polprasert C, Shrestha RP, Jugsujinda A (2010). Removal of trichloroethylene (TCE) contaminated soil using a two-stage anaerobic-aerobic composting technique. J. Environ. Sci. Health Part A. 45: 549-559.

Sabatini DA, Knox RC, Harwell JH (1994). Surfactant-enhanced subsurface remediation. Emerging Technologies, American Chemical Society, Washington, DC.