DARK AND PHOTO-ASSISTED Fe²⁺ CATALYZED DEGRADATION OF CHLORINATED HYDROCARBONS BY HYDROGEN PEROXIDE

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ABSTRACT

A large variety of organic and inorganic compounds may be found in wastewater. Among these compounds, chlorinated hydrocarbons are characterized by their high toxicity and very low degradability by conventional treatments. This paper describes the experimental laboratory investigation conducted to evaluate and select an optimal oxidation method to treat trichloroethylene (TCE) and tetrachloroethylene (PCE) as model substances of the chlorinated hydrocarbons compounds. The Advanced Oxidation Processes (AOPs) studied utilizing hydrogen peroxide in dark process including Fenton process. The pH dependence, the influence of the initial concentration of hydrogen peroxide and Fe^{2+} and the type and valence of the photo-catalyst were studied to find the optimal conditions for complete and fast oxidation of both tested compounds. Experimental results indicated that the degradation rates of the selected model substances were strongly promoted by the photoassisted Fenton reaction. The volume-corrected energy efficiencies (mg/kWh) were estimated as an economical parameter to compare between the used photochemical processes. The reactions were accompanied by the generation of Cl⁻, which reached its maximum value at a short reaction time when using the photo-Fenton process, which indicate the completion of the decomposition reaction.

1. INTRODUCTION

Ground water and industrial wastewater contamination by chlorohydrocarbon e.g. TCE, PCE and other industrial and agricultural chemicals is now an issue of international concern. Also, TCE and PCE are important in the manufacture of pesticides which makes them a hazardous water pollutant with low biodegradability. During the review and development of technologies for treatment of synthetic organics, especially chlorinated organic compounds, it was determined that activated carbon, air stripping, and oxidation were all possible treatment techniques. Carbon adsorption and air stripping have been accepted and proven technologies for many of the organic constitutes present in the basin. Oxidation, on the other hand, has only recently been proposed as a cost-effective treatment technology for treating such these chloro-organic compounds [1].

A recent development in oxidation technology for aqueous organic compounds os the Advanced Oxidation Processes (AOPs). AOPs involve the generation of highly reactive free radical intermediates. The hydroxyl radical is most likely the key intermediate responsible for oxidation of aqueous solutes. The hydroxyl radical, the active species, which attacks and destroys the undesired compounds [2], can be produced by homogeneous and heterogeneous processes. Some, e.g. the UV/H_2O_2 and UV/O_3 systems, are widely known and in practical use [3,4]. Another homogeneous reaction, the Fenton reaction [5], produces hydroxyl radicals by interaction of H_2O_2 with ferrous salts according to Reaction (1):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\cdot \qquad \text{Reaction (1)}$$

In the dark, the reaction is retarded after complete conversion of Fe^{2+} to Fe^{3+}, Recently, it has been found that illumination of Fe^{2+} - Fe^{3+} - H_2O_2 system increases the degradation rate of many organic substances [6]. The reasons for the positive effect of irradiation on the degradation rate include the photo-reduction of Fe^{3+} to Fe^{2+} -ions, which produce new OH radicals with (Reaction (1)) or according to the following mechanism [7]

$$Fe^{3+} + H_2O_2 + hv \rightarrow Fe^{2+} + OH^\cdot + H^+ \qquad \text{Reaction (2)}$$
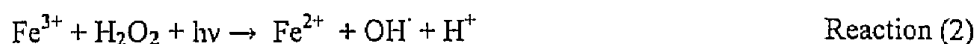
the additional effect of direct H_2O_2 photolysis

$$H_2O_2 + hv \rightarrow 2OH^\cdot \quad (\lambda < 400 \text{ nm}) \qquad \text{Reaction (3)}$$

The present work investigates a comparison between dark Fenton reaction and photo-assisted oxidation processes for the degradation of TCE & PCE as model substances of chlorinated hydrocarbons. For the development of effective wastewater treatment methods, complete degradation of the contaminants to harmless end products (CO_2) and inorganic salts (Cl^-) is important. In this work, the effect of pH, Fe^{2+}: H_2O_2 molar ratio, amount and valence of iron salt at a constant concentration of both TCE & PCE have been studied.

2. EXPERIMENTAL

2.1. Reagents

TCE (trichloroetylene, C_2Cl_3H) & PCE (tetrachloroethylene, C_2Cl_4) in the purest form, are available from Merck Chemical Company. Ferrous ($FeSO_4.7H_2O$) and ferric [$Fe_2(SO_4)_3.7 H_2O$] sulphate heptahydrate used as sources of Fe(II) and Fe(III), were all analytical grade and purchased from Merck. Hyderogen peroxide solution (30% w/w) in stable form was provided by Roth Company of Germany. Enzyme Catalase was obtained from Fluka Biochemika of Germany. All reagents employed were not subjected to any further treatment. Water used throughout was ultrapure deionized water.

2.2. Experimental Set-up

All experiments were performed in a batch reactor. The schematic diagram of the experimental set-up used in this study is shown in Figure (1). The reactor was cylindrical with 0.85L volume and was made from quartz glass, which was available for the transfer of the radiation. Irradiation was achieved by using UV lamp (high-pressure mercury lamp TQ 718 of 700 W, radiation flux used for only degradation of 221 W/h of 200-600nm, from Heraeus Nobleight Company in Germany) which was immersed in the glass tube. The UV lamp was equipped with a cooling water jacket system to maintain the reaction solution at a room temperature, which was placed in the reactor vessel. The reaction chamber was filled with the reaction mixture, which was placed between the reactor walls and UV lamp system. Mixing was accomplished by means of a closed circulating loop through the illuminated part of the photoreactor by the use of a peristaltic pump. The flow system was assembled with polytetrafluorethylene (PTFE) or glass tubing and connectors.

2.3. Experimental Procedures

For each experiment, synthetic aqueous solution of 50 mg/L of each model substance (TCE or PCE) (to simulate high-loaded chlorinated hydrocarbons containing industrial

wastewater) was prepared in ultrapure de-ionized water as solvent. The laboratory unit was filled separately with 0.85L of each TCE or PCE solution. For runs using UV/ H_2O_2 system, hydrogen peroxide was injected in the reactor before the beginning of each run. For runs, using Fenton reaction or Photo-Fenton processes (UV/H_2O_2/ Fe^{2+} & UV/ H_2O_2/Fe^{3+}), the pH value of the solution was set at the desired value by the addition of a H_2SO_4 solution before startup, then a given weight of iron salt was added. The iron salt was mixed very well with the tested model substance solution before the addition of a given volume of hydrogen peroxide. For the dark processes (Fenton reaction), the reaction time starts when the solution is injected by hydrogen peroxide. For light photo-processes, the time at which the ultraviolet lamp was turned on was considered time zero or the beginning of the experiment which was taking place simultaneously with the addition of hydrogen peroxide. The solution was circulated at a flow rate of 180 Lh^{-1} for one hour.

2.4. Analytical Methods

Samples are taken at appropriate time intervals from the reaction vessel and pipetted into (3ml) glass vials. The vials were filled so as to leave no headspace and sealed with Teflon-lined silicon septa and screw caps. The samples were immediately analyzed to avoid further reaction. One drop of enzyme catalase was also added to each sample to decompose any residual hydrogen peroxide and prevent hydrogen peroxide from reacting with organic substrates during the analysis. Hydrogen peroxide was measured by the iodometric titration method [8]. Concentration changes of TCE & PCE were determined by a gas chromatograph (Perkin-Elmer SIGMA 3) with glass column 3.6 m * 0.53 mm * 2.65 μm film thickness and FID detector. The conditions was as follows: the injector and detector temperatures were 200 and 240°C, respectively, the ramp temperature was 15°C/min, and a retention times of 4.4 & 5.6 min were used for TCE & PCE respectively.

After the Fenton and Photo-Fenton treatment of the solutions their pH values were adjusted to approximately 9.0 using 40% NaOH. In the basic medium iron ions precipitated and after that they were filtered through a paper (blue ribbon) filter. Total iron residual concentration was measured in the treated and filtered solutions according to [9]. In addition, samples were also analyzed to determine chloride by means of titration with silver nitrate [10].

3. RESULTS & DISCUSSION

3.1. Degradation Rate

Changes in the degradation rates obtained with TCE & PCE during UV, hydrogen peroxide photolysis, Fenton and Photo-Fenton reactions are shown in Figures ((2.a) & (2.b)) for TCE & PCE respectively. The degradation of both TCE & PCE followed mainly a pseudo-first order kinetics in our experiment. The regression analysis of the concentration cures versus reaction time indicated that the decomposition rate of the selected model substances TCE & PCE can be described by a pseudo-first order kinetics with respect to TCE & PCE concentrations:

$$dC_M/dt = -k_0 C_M, \tag{1}$$

where M is the selected model substance TCE or PCE and k_0 is the pseudo-first order rate constant. Pseudo-first order rate constants (k_0) and the 90 % conversion times for the degradation of both TCE & PCE by different Advanced Oxidation Processes calculated from the degradation curves are presented in Table (1).

Both TCE & PCE were degraded at a moderate rate by the dark oxidation with Fenton reaction (see Figure (2.a) & (2.b)). The results of this study demonstrated that UV radiation improves the performance of the Fenton reagent system quite significantly, and at the same concentrations of hydrogen peroxide, photo-Fenton reaction led to a more rapid decomposition of both TCE & PCE than that observed during the Fenton reaction. As listed in Table (1), the addition of UV radiation to the dark Fenton reaction led to 3 & 2_-fold decrease in the 90% conversion time for TCE & PCE respectively (from 60 to 20 min for TCE & from 90 to 45 min for PCE). Still, the application of the more complicated and therefore costly method is not reasonable, because more than 90% degradation in the Fenton treatment was reached in several minutes. The degradation of both TCE & PCE with hydrogen peroxide photolysis involved a very long reaction time if compared with the Fenton & photo-Fenton reactions, so that 90% destruction of both TCE & PCE required 120 & 180 min of treatment respectively. The experimental data in Figures 2.a & 2.b show that adding Fe^{3+} (the higher valance of iron metal) to the UV/H_2O_2 system enhanced the rate of both TCE & PCE oxidation by a maximum factor 2 and 1.5 Comparing with adding Fe^{+2}.

The residual iron can be removed by alkalization of the solution. Iron is precipitated at pH≥9.0 in the form of $Fe(OH)_3$. The residual concentrations of total iron after alkalization and subsequent filtration were much lower than the initial concentrations of Fe^{2+} and Fe^{3+} added (1mM) and did not exceed the values of 0.01 and 0.0085mM for Fe^{2+} and Fe^{3+} respectively.

3.2. Effect of pH Values

The pH value affects the oxidation of organic substances both directly and indirectly. The photo-Fenton reaction is strongly affected by the pH-dependence. The pH value influences the generation of OH radicals and thus the oxidation efficiency. Figure (3) shows the effect of the pH value during the use of Fenton and photo-Fenton treatment. A maximum degradation of 96.8% and 85.6% for TCE and PCE respectively were obtained with the photo-Fenton treatment at a pH=3, while 69.8% and 50.3% for TCE and PCE respectively were obtained with Fenton reaction at the same pH value and reaction time (30min). For pH values above 4 the degradation of TCE & PCE strongly decreases by using the both types of treatment because at higher pH values iron precipates as hydroxide that hindered the production of radicals and reduces the transmission of the radiation in case of using photo-Fenton treatment [11].

3.3. Effect of Fe^{3+}:H_2O_2 ratios

In dark Fenton reaction and photo-Fenton process (UV/H_2O_2/ Fe^{2+}) treatment various Fe^{2+}:H_2O_2 ratios were added to both TCE & PCE solutions. Figure (4) indicates that beyond a certain hydrogen peroxide concentration no further enhancement of the performance occurs. The introduction of Fe^{2+}:H_2O_2 ratio did not enhance the degradation rate. Thus, the addition of H_2O_2 exceeding the optimum dose may decrease the reaction rate of the target compounds with excess of H_2O_2 acting as a radical scavenger. This may be due to auto-decomposition of H_2O_2 to oxygen and water and the recombination of free radicals. Since free hydroxyl radicals react with H_2O_2, H_2O_2 itself contributes to the OH scavenging capacity [11]. Therefore, H_2O_2 should be added at an optimal concentration to achieve the best degradation.

The results of the present study demonstrated significantly higher degradation rates of both TCE & PCE in the Fenton treatment at a catalyst: hydrogen peroxide ratio 1: 40, and that agree with the recommended literately as optimal for the Fenton treatment [12, 13]. The present study showed that very low concentrations of both catalyst and hydrogen peroxide were used in the photo-Fenton process (catalyst: hydrogen peroxide ratio of 1:20). That solve

the waste disposal problem may present due to the production of the inorganic sludge by utilizing much amount of the metal salt (Fe^{2+}) by using Fenton treatment.

3.4. Effect of Amount of Fe^{+2}

Figure (5) shows the effects Fe^{+2} concentration on both TCE & PCE removal by using Fenton and photo-Fenton treatment. The presence of Fe^{2+} (0.75 & 1mM for TCE and 1 & 1.25 mM for PCE in case of photo-Fenton and Fenton respectively) was clearly a positive factor in both TCE & PCE removal, compared to the conditions without Fe^{2+}. However, the TCE & PCE removal rates were instead decreased with increasing Fe^{2+2} ($\geq$0.75 & 1mM for TCE and 1& 1.25mM for both types of treatment) concentration (Figure (5)). Inhibition of TCE & PCE removal were thought to be due to the OH scavenging by Fe^{2+} itself as its concentration increased. A higher addition of iron salt by using photo-Fenton treatment resulted in brown turbidity that hindered the absorption of the UV light required for photolysis and caused the recombination of OH radicals. In this case, Fe^{2+} reacted with OH radicals as a scavenger [14]. It is desirable that the ratio of H_2O_2 to Fe^{2+} should be as small as possible, so that the recombination can be avoided and the sludge production from iron complex is also reduced.

3.5. Dechlorination

In Advanced Oxidation Processes, the radical mechanism occurred by the effect of the produced hydroxyl radicals can also be distinguished by the direct dechlorination of the organic compounds. Figure (6) shows the concentrations of the free chloride produced during the oxidation of both TCE as model substance at different experiments. As shown in Figure, the Cl⁻ generated had their maximum values in the case of the oxidation with the Photo-Fenton Process. After 30 minutes of irradiation, the organically chlorine atoms were converted to inorganic chlorine ions (Cl⁻) by using photo-Fenton treatment. After 10 min of irradiation time, the concentration of the chloroorganic compounds is reduced by more than 70?%, a substantial increase of the (Cl⁻) concentration was recorded during further UV irradiation. The final increase of (Cl⁻) can be explained by the photomineralization of the chloroorganic compounds and not stripped out.

3.6. Volume Corrected Energy Efficiency

After the photo-catalytic oxidation has proven to be effective method for the destruction of chloro-organic hydrocarbons compounds in water, the efficiency and the crucial parameters for an up-scaling of this process have to be evaluated. In most cases the

goal of current technical application of advanced oxidation processes id the destruction of water pollutants and not the energy consuming complete degradation of the substrates content. Therefore the economical most important parameter is the efficiency of substrate consumption. The volume corrected energy efficiency of the substrate consumption Φ_s is defined as the ratio of destroyed substrate to the consumed electrical energy [15]. Its determination is based on Equation 2 (efficiency of the power supply is not included). Since the substrates concentration decays usually according to pseudo first order kinetics the irradiation times $t_{1/2}$ can be via the pseudo first order rate constant k_0 ($t_{1/2} = \ln 2/k$).

$$\phi_{-s} = \frac{C_0 * 1/2 * V}{P_{el} * t_{1/2}} \qquad (2)$$

where, Φ_s. is the volume corrected energy efficiency (mg/kWh), V is reaction volume (L), C_0 is the initial concentration of the substrate (mg/L), P_{el} is the actual electrical power (kW), $t_{1/2}$ is the half-life time (h).

As noticed from Figure (7), the photo-assisted chemical oxidation (UV/ H_2O_2/ Fe^{2+} & UV/ H_2O_2/ Fe^{3+}) of both TCE & PCE shows the higher efficiency with Φ_s = 16955 & 28499 mg/kWh for TCE and Φ_s = 4717 & 28499 mg/kWh for PCE for the above both types of pfoto-assisted oxidation respectively comparing with the other photochemical oxidation processes e.g. UV/H_2O_2 process and direct photolysis UV alone. In this study the photo-Fenton process consider the optimal and economical method for the degradation of such chlorinated organic compounds.

4. CONCLUSION

The results from this study showed that the degradation rate of TCE & PCE as model substances of chlorinated organic compounds was strongly accelerated by the photo-assisted chemical oxidation processes. The photo-assisted Fenton process, the combination of homogeneous system of UV/ H_2O_2/ Fe^{3+}, produced the highest photochemical elimination rate of both compounds in order of TCE > PCE. The oxidation rate was influenced by many factors, such as the pH value, Fe^{2+}: H_2O_2 molar ratio, the amount of iron salt and its valence.

The optimum operating conditions obtained for the best degradation were pH=3; Fe^{2+} or Fe^{3+}: H_2O_2 ratio=1:20; Fe^{2+} or Fe^{3+} =0.75 & 1 mM for TCE & PCE respectively.

The advantages of the photo-assisted Fenton process as an oxidataive pre-treatment step over the dark Fenton process are economic, less energy demand, efficient, low investment and harmless process products

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TABLES

TABLE 1. DEGRADATION OF TCE & PCE BY DIFFERENT AOPs. {0.4 & 0.2 mM Aqueous solution respectively by dark oxidation with Fenton reaction (H_2O_2/ Fe^{2+}) and photo-oxidation by UV (direct photolysis), hydrogen peroxide photolysis (UV/ H_2O_2) and photo-Fenton Processes (UV/H_2O_2/ Fe^{2+}, UV/H_2O_2/ Fe^{3+}).

Type of process	T_{90}		k_0	
	TCE	PCE	TCE	PCE
UV	360	420	0.0042	0.0029
UV/ H_2O_2	120	180	0.0169	0.0108
Fenton (0.6mM Fe^{2+}/12mM H_2O_2)	60	90	0.0433	0.0240
UV/ H_2O_2/Fe^{2+} (0.6mM Fe^{2+}/12mM H_2O_2/UV)	20	45	0.1227	0.0624
UV/ H_2O_2/ Fe^{3+}(0.6mM Fe^{3+}/12mM H_2O_2/UV)	10	30	0.2254	0.0825

FIGURES
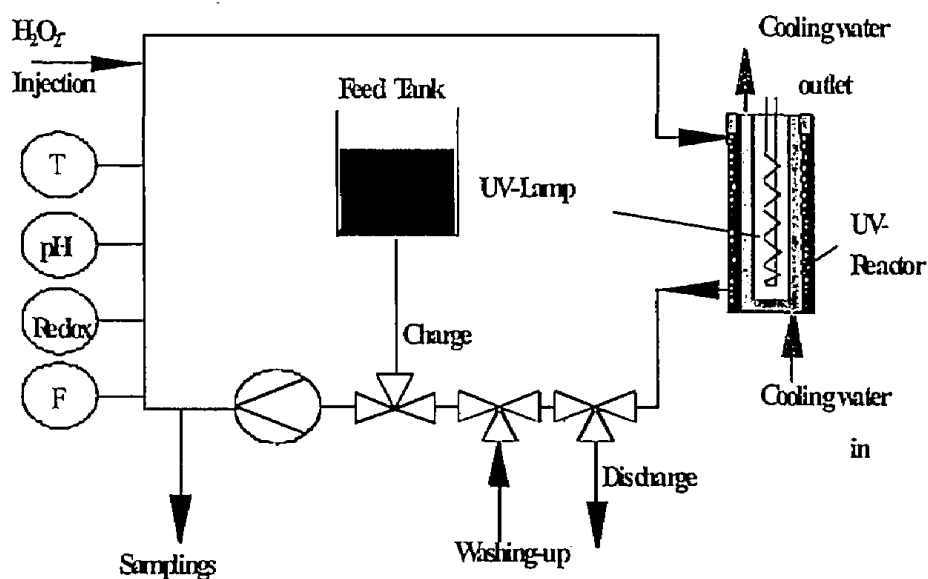
Fig, 1. Schematic diagram of dark and light photo-oxidation system experimental set-up.
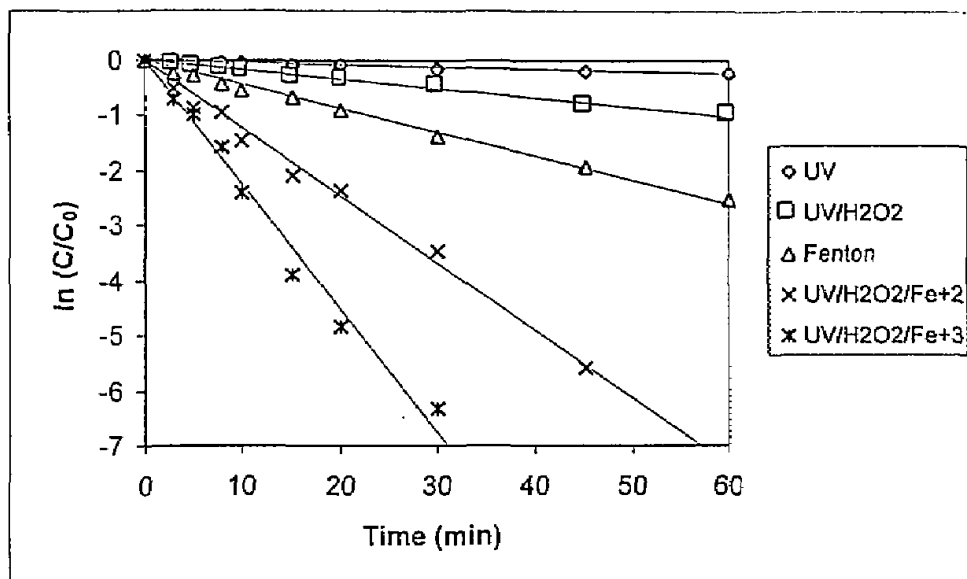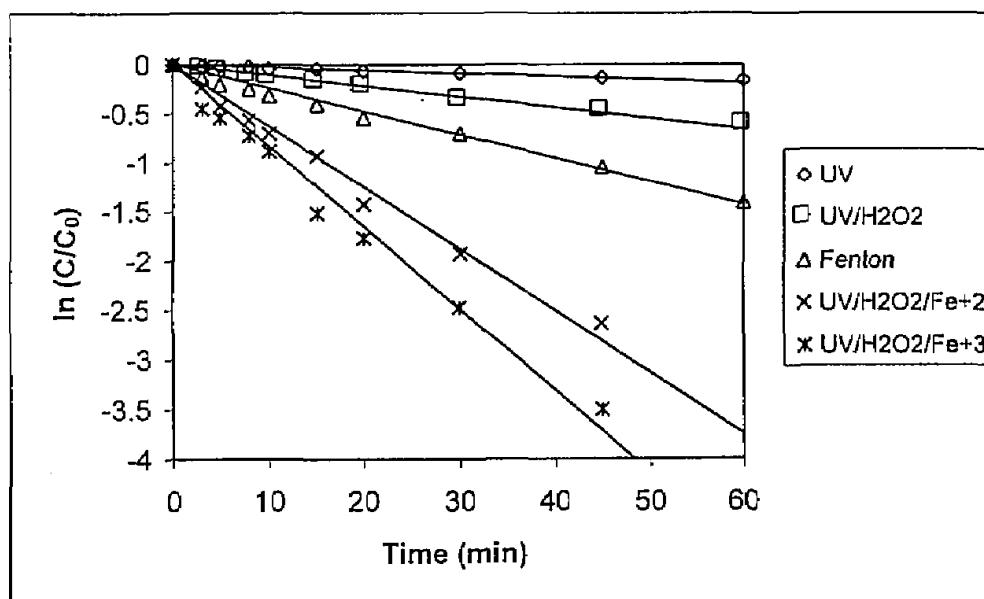
Fig. 2.a. First-Order Plot for Degradation of TCE by Dark and Photo-Assisted Oxidation Processes. [TCE (0.4mM), UV, UV/H_2O_2 (pH=5, H_2O_2=12mM), H_2O_2/ Fe^{2+},UV/ H_2O_2/ Fe^{2+}, UV/ H_2O_2/ Fe^{3+}, (pH=3, Fe^{2+}& Fe^{3+} =0.6mM, H_2O_2=12mM)]

Fig. 2.b. First-Order Plot for Degradation of PCE by Dark and Photo-Assisted Oxidation Processes. [PCE (0.2mM), UV, UV/H_2O_2 (pH=5, H_2O_2=12mM), H_2O_2/ Fe^{2+},UV/ H_2O_2/ Fe^{2+}, UV/ H_2O_2/ Fe^{3+}, (pH=3, Fe^{2+}& Fe^{3+} =0.6mM, H_2O_2=12mM)]
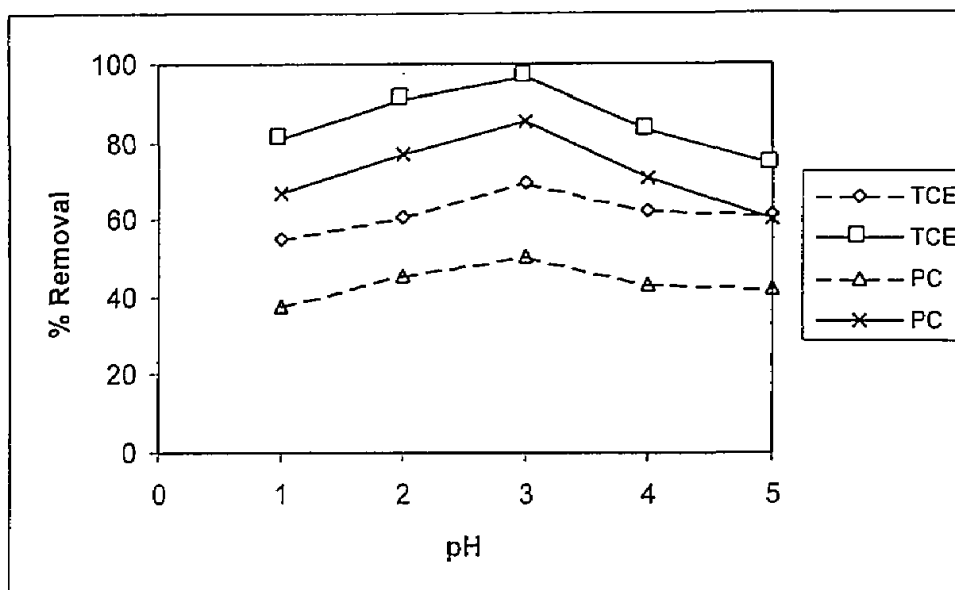
Fig. 3. Effect of pH Values on Dark and Photo-Assisted Oxidation Processes for TCE & PCE Degradation. [——— photo-Fenton, ------ Fenton-reaction, reaction time=30min].
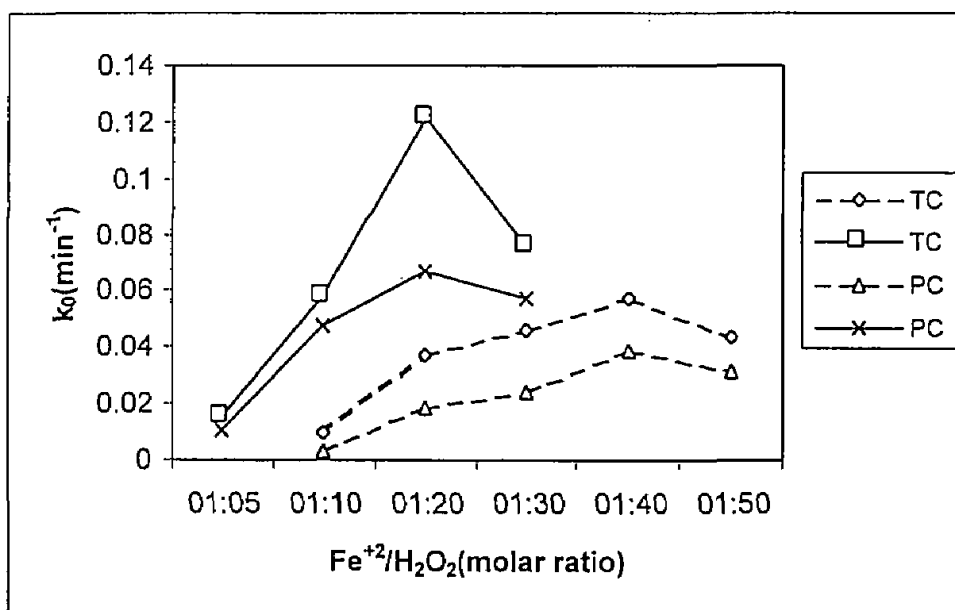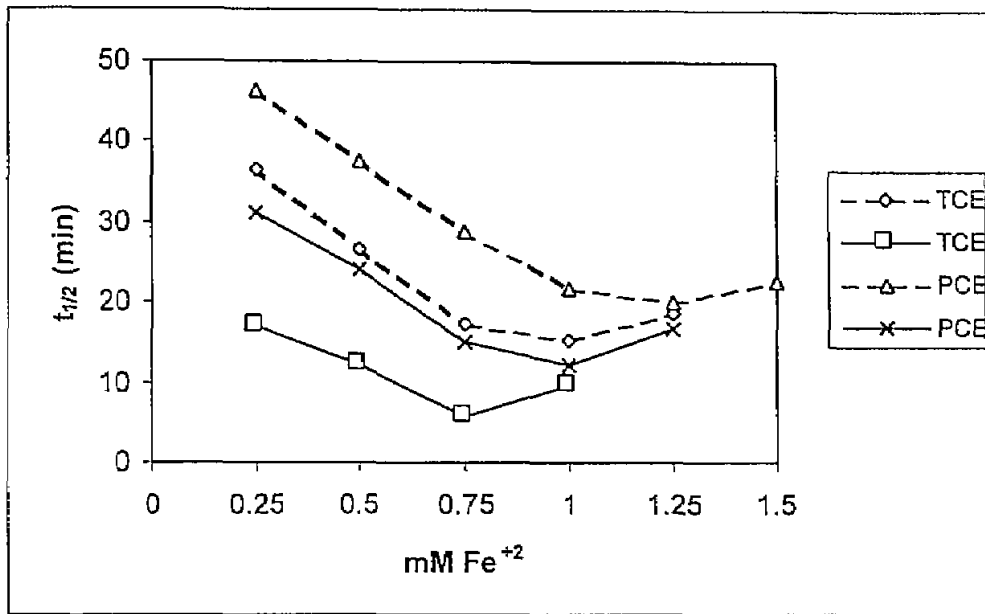

Fig. 4. Effect of Fe^{+2}:H_2O_2 on Dark and Photo-Assisted Oxidation Processes for TCE & PCE Degradation. [——— photo-Fenton, ------ Fenton-reaction, reaction time=30min].

Fig. 5. Effect of amount of Fe^{+2} on Dark and Photo-Assisted Oxidation Processes for TCE & PCE Degradation. [—— photo-Fenton, ------ Fenton-reaction, reaction time=30min].
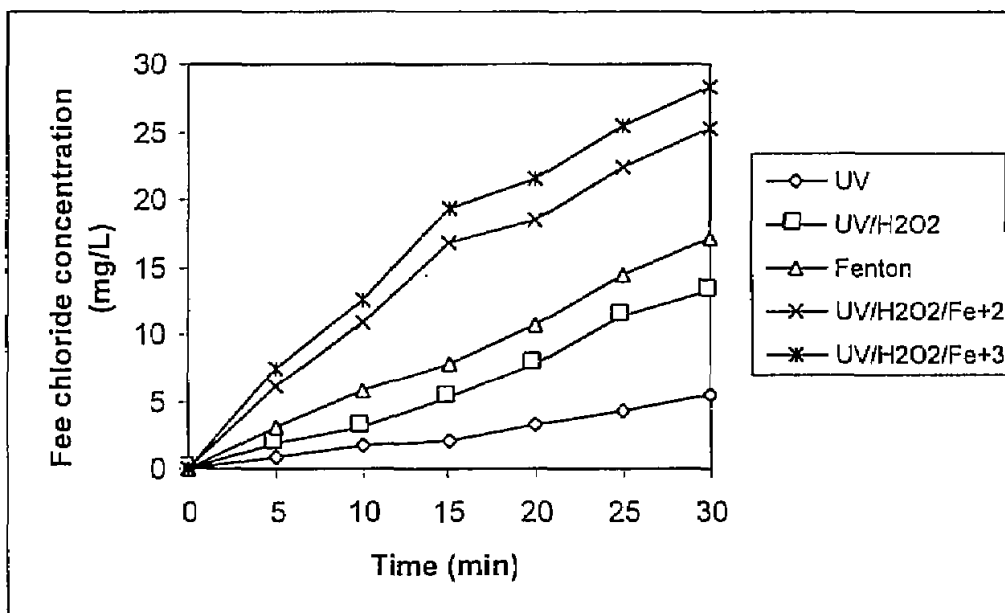

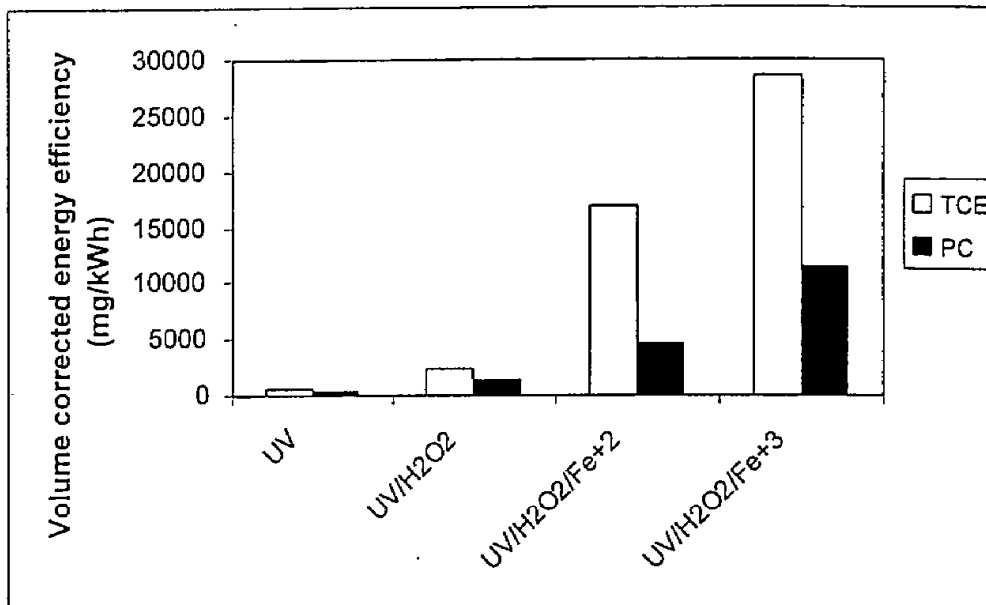Fig. 6. Resulting Free Chloride during Dark and Photo-Assisted Oxidation Processes for TCE Degradation.

Fig. 7. Estimation of Volume Corrected Energy Efficiency for Removal of TCE & PCE during Dark and

Photo-Assisted Oxidation Processes