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Degradation of High-Concentration of Perchloroethylene from Aqueous Solution Using Electro-Fenton Process

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ABSTRACT

Introduction: Perchloroethylene (PCE) is one of the most well-known chlorinated organic compounds recently detected in aqueous environments. The presence of PCE in aquatic ecosystems has caused many health problems and environmental challenges. Therefore, its removal and treatment from aqueous environments are essential.

Materials and Methods: The electro-Fenton (EF) process was carried out in a cylindrical reactor containing 250 mL contaminated water with PCE. The effects of parameters, including solution pH (3-12), current density (2-10 mA cm^{-2}), H_2O_2 concentration (20-70 µL H_2O_2 per 250 mL sample.), PCE concentration (5-50 mg L^{-1}), and electrolysis time (1-15 min) on PCE degradation were investigated. The kinetics and radical's scavenger of the EF process were examined to detect the exact mechanism of PCE degradation.

Results: The degradation of the PCE of 98.1% was obtained in the optimum condition, including solution pH of 5, the current density of 8 mA cm^{-2}, H_2O_2 concentration of 50 µL per 250 mL sample, PCE concentration of 15 mg L^{-1}, and electrolysis time of 10 min. The kinetics studies of the EF process indicated that the obtained results were in satisfactory agreement with the first-order model (R^2 = 0.9858, K_{app} = 0.2822). Also, the addition of ethanol and tertiary butanol caused an inhibiting effect.

Conclusion: The EF process was effectively applied to degrade PCE from polluted water as an efficient technique. The obtained results indicated that the generation of $^{\bullet}OH$ throughout the EF process was the key mechanism that controlled the EF process.

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Introduction

Chlorinated organic compounds (COCs) are the important group of organic compounds that are persistent and resistant to decomposition in the environment. They have caused many health problems and environmental challenges. Among COCs, perchloroethylene (PCE) is one of the most frequently found COCs in environment [1, 2]. More than 520,000 tons of PCE are used annually worldwide. Among the various industries, the laundry industry and dry-cleaning activity have the highest consumption of PCE. Of the total PCE, 50% was used for the dry-cleaning activity, 30% for chemical polymerization, 15% for metal cleaning and degreasing, and 5% for other activities [3]. Many toxicological and epidemiological studies have shown that PCE is toxic and carcinogenic. PCE exposure is related to various cancers, including cervical, kidney, esophageal cancer, and non-Hodgkin's lymphoma. NIOSH recognizes PCE as a carcinogen for humans, and also IARC grouped this compound in carcinogenic substances of the A-2 group (probable carcinogens) [4]. The United States Environmental Protection Agency has issued its maximum contaminant level at 5 µg L^{-1} by the Safe Drinking Water Act [5]. Many researchers in water and wastewater treatment have conducted considerable and extensive studies to remove and treat PCE from water sources. Conventional water and wastewater treatment processes have not been effective in removing PCE. Among different water and wastewater treatment processes, reverse osmosis, adsorption, and advanced oxidation processes (AOPs)have shown suitable performance for the degradation of PCE from contaminated water [3, 6].

AOP processes have a special place in water and wastewater treatment among the mentioned techniques. AOPs can effectively degrade and mineralize the resistant organic pollutants by generating strong oxidants, such as hydroxyl radicals (E0 = 2.80 V/SHE) [7]. Furthermore, recently AOPs as an environmentally friendly method received extraordinary attention because of their high efficiency for removing non-biodegradable organic pollutants from aquatic environments, such as wastewater, ground, and surface water by the in-situ generation of the •OH as the oxidizing agent. Among the AOPs, the Fenton reagent (mixture of H_2O_2 and Fe^{2+} ion) has attracted significant attention due to its strong oxidative capacity on organic contaminants [8, 9]. The main disadvantages of using the electro-Fenton (EF) process in water and wastewater treatment are, on the one hand, dependence on electrical energy and, on the other hand, the management of the produced sludge and also the neutralization of the treated effluent after the process. The EF process is the electrochemically assisted Fenton's reaction (reaction 1) [10, 11].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (1)$$

This study evaluated the effective parameters, such as pH, current density, H_2O_2 concentration, and reaction time for PCE degradation using the EF process. According to the author's search strategy, this is the first report based on the EF treatment process using iron electrodes to remove PCE from the aqueous solution. Most of the studies for degradation of PCE are based on platinum electrodes, diamond electrodes, and lead dioxide electrodes and are not cost-effective treatment processes.

Materials and Methods

Chemical

PCE (C_2Cl_4, assay ≥ 99.9%), sodium hydroxide (NaOH, assay ≥ 98%), tert-butanol ($C_4H_{10}O$, assay ≥ 99.5%), sodium sulfate (Na_2SO_4, assay ≥ 98.5%), sulfuric acid (H_2SO_4, assay ≥ 95%), hydrogen peroxide (H_2O_2, assay 30%), methanol (MeOH, assay ≥ 99.9%), and ethanol (C_2H_6O, assay ≥ 99%) were purchased from Merck Co. All stock solutions were prepared using distilled water.

Experimental procedure and apparatus

The experiments were done in the batch mode using a cylindrical Pyrex cell with a working volume of 0.25 L as the reactor. The stock solution of PCE was prepared in methanol, then, sample solutions were prepared in distilled water by diluting this stock solution in the range of 5–50 mg L^{-1}. The EF process unit was equipped with two iron electrodes with dimensions of 2.5 cm × 1 cm × 0.1 cm, which was placed parallel to each other, and the distance between electrodes of 3 cm and the constant concentration of 50 mM Na_2SO_4 was used in all the experiments. The solution pH was determined using a Metrohm 827 pH meter. A DC power supply was used to adjust the desired current density. At the end of each test, two ml of the sample were taken from the reactor, filtered using PTFE syringe filters, and finally used for analysis. The PCE concentration in the aqueous phase was determined using a high-performance liquid chromatography (HPLC) system. The HPLC column was an ODS-C_{18}, and the detection wavelength of the UV detector was set at 210 nm. The eluent was a methanol/water mixture (65/35, %v/v) [12].

Ethical issues

The current work was done in the autumn 2020, after receiving approval from the ethics committee of Kerman University of Medical Sciences [IR.KMU.REC. 1398.680].

Results

Effect of solution pH on the degradation of PCE

As a fundamental parameter, the solution pH affects the PCE degradation during the EF process. Therefore, the effect of solution pH in the range of 3 to 12 on the PCE degradation was investigated in the stable condition, including PCE concentration of 5 mg L^{-1}, the current density of 6 mA cm^{-2}, and H_2O_2 concentration of 30 µL (Figure 1). In the lowest pH value of 3, the degradation efficiency of 73.2% was achieved. Moreover, by increasing the solution pH to 5, 7, 9, and 12, a decrease in PCE degradation of 65.7%, 41.3%, 35.5%, and 9.8% was observed. According to the observed results, the PCE degradation at pH 3 is close to pH 5 (less than 8%) due to the issue that pH 3 is a harsh condition (equipment corrosion, high acid consumption, etc.). Therefore, solution pH of 5 was chosen as the optimum pH value.

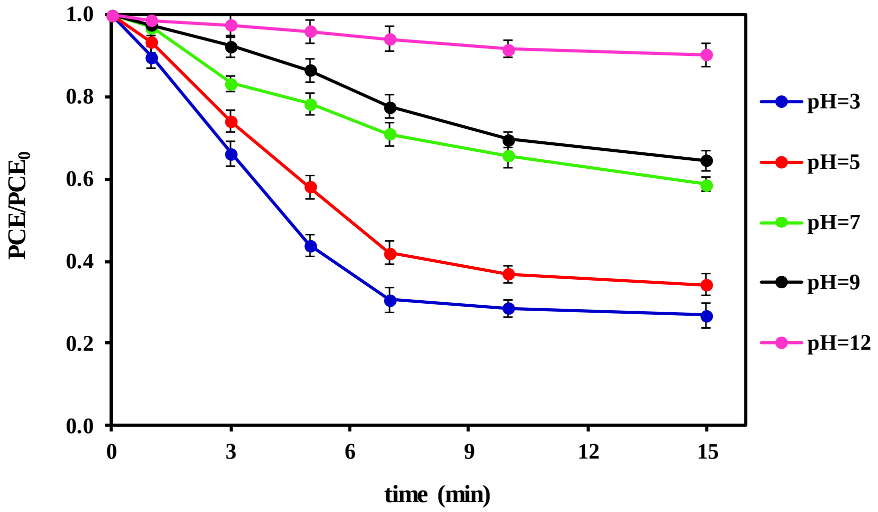

Figure 1: Effect of solution pH on PCE degradation (Conditions: PCE concentration of 5 mg L^{-1}, the current density of 6 mA cm^{-2}, and H_2O_2 concentration of 30 µL)

Effect of current density on the degradation of PCE

The effect of current density on the PCE degradation in the range of 2 to 10 mA cm^{-2} was investigated. The obtained result of PCE degradation during the EF process is presented in Figure 2. The PCE degradation increased by increasing the current density. Under the constant condition, including PCE concentration of 5 mg L^{-1}, pH solution of 5, and H_2O_2 concentration of 30 µL, after 15 min of electrolysis time, when the current density increased to 2, 4, 6, 8, and 10 mA PCE degradation reached 33.5%, 53.6%, 65.7%, 78.1%, and 82.6%, respectively. According to the observed result, the PCE degradation at the current density of 10 mA cm^{-2} is close to 8 mA cm^{-2} (less than 5%). Therefore, the current density of 8 mA cm^{-2} was chosen as the optimum current density.

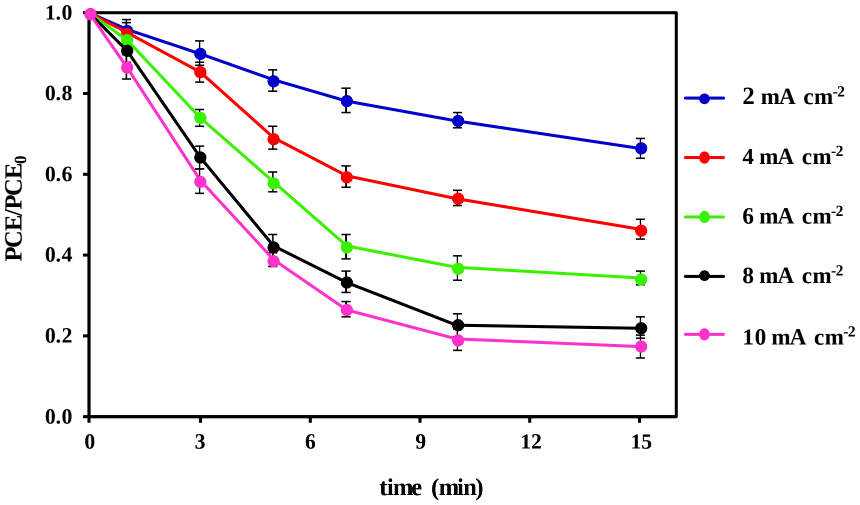

Figure 2: Effect of current density on PCE degradation (Conditions: PCE concentration of 5 mg L^{-1}, solution pH of 5, and H_2O_2 concentration of 30 μL)

Effect of H_2O_2 concentration on the degradation of PCE

The effect of H_2O_2 concentration (v/v%) on PCE degradation was investigated over a range of 20-70 μL per 250 mL sample, at pH 5, PCE concentration of 5 mg L^{-1}, and current density of 8 mA cm^{-2}. The effect of H_2O_2 concentration on PCE degradation is shown in Figure 3. According to the observed results, the concentration of H_2O_2 had a direct effect on the degradation efficiency, and by increasing the concentration of H_2O_2, the degradation efficiency was increased. The obtained result demonstrated that at low H_2O_2 concentrations of 20 μL and 30 μL, the PCE degradation rates were very slow and equal 62.5% and 78.1%, respectively. By increasing the H_2O_2 concentration to 40 μL and 50 μL, the PCE degradation enhanced to 88.6% and 98.4%, respectively. However, at higher concentration (70 μL), no significant improvement was observed for PCE degradation (99.1%). Hence, the maximum H_2O_2 concentration of 50 μL for the effective PCE degradation was considered.

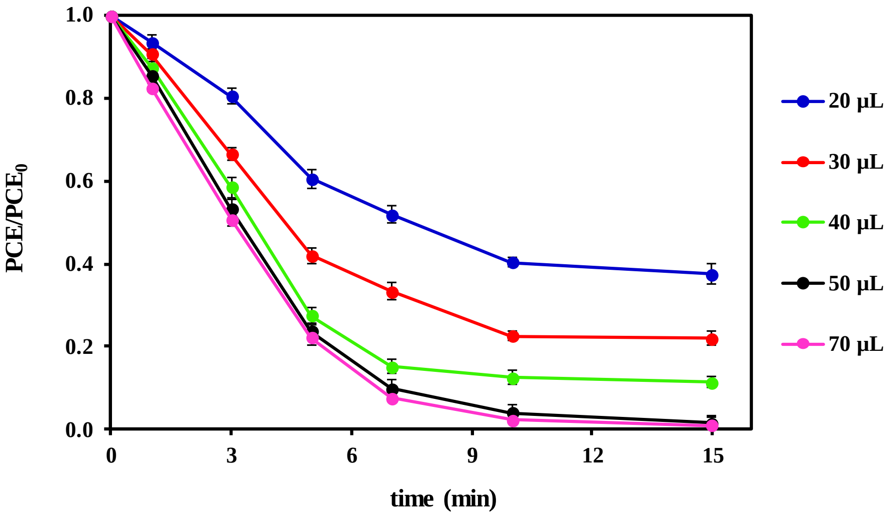

Figure 3: Effect of H_2O_2 concentration on PCE degradation (Conditions: PCE concentration of 5 mg L^{-1}, solution pH of 5, and current density of 8 mA cm^{-2})

Effect of PCE concentration on the degradation of PCE

The PCE concentration effect in the range of 5 to 50 mg L^{-1} was investigated in the constant condition, including solution pH of 5, the current density of 8 mA cm^{-2}, and the H_2O_2 concentration of 50 µL. The obtained result displayed that the degradation of the PCE is highly concentration-dependent. The observed results are presented in Figure 4. According the figure, the degradation of PCE decreased to 98.4%, 98.2%, 98.1%, 90.5%, and 79.4% when the concentration of the PCE was increased to 5, 10, 15, 30, and 50 mg L^{-1}, respectively. PCE degradation was insignificant after applying 10 min electrolysis time, and the obtained curve seems smooth. Therefore, a PCE concentration of 15 mg L^{-1} was chosen as the optimum concentration.

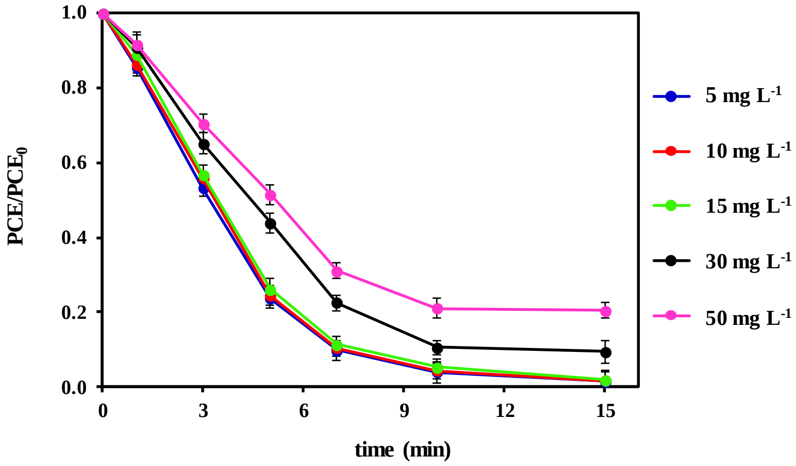

Figure 4: Effect of PCE concentration on PCE degradation (Conditions: solution pH of 5, current density of 8 mA cm^{-2}, and H_2O_2 concentration of 50 µL)

Kinetics

The first and second-order kinetic model studies of PCE degradation using EF process were performed in optimum conditions, including solution pH of 5, the current density of 8 mA cm^{-2}, H_2O_2 concentration of 50 µL, and PCE concentration of 15 mg L^{-1}. The obtained results are shown in Table 1 [13-15].

Table 1: Kinetics models parameter for the PCE degradation using EF process

Kinetics model	Equation	k_{app}	R^2
First-order	$\ln\left(\frac{C_0}{C_t}\right) = +kt$	0.2822	0.9858
Second-order	$\frac{1}{C_t} = kt + (\frac{1}{C_0})$	0.2199	0.8395

Radical scavenger

Radical scavenger experiments were carried out to better elucidate the mechanism of PCE degradation and identify the dominant radicals in the EF process. Radical scavengers studies with the constant concentration of 0.5 M were conducted under optimum treatment conditions (the optimum condition, including solution pH of 5, the current density of 8 mA cm^{-2}, H_2O_2 concentration of 50 µL, PCE concentration of 15 mg L^{-1}, and electrolysis time of 10 min); the results are provided in Figure 5. The figure reveals that there was a significant decrease in PCE degradation in the presence of ethanol (EtOH) and tertiary butanol (TBA). Without adding any scavenging agent (control), 98.1% of PCE was removed after 10 min; however, the degradation was inhibited when EtOH and TBA were separately added to the solution. The degradation yield was only 56.5% and 43.7% for EtOH and TBA, respectively.

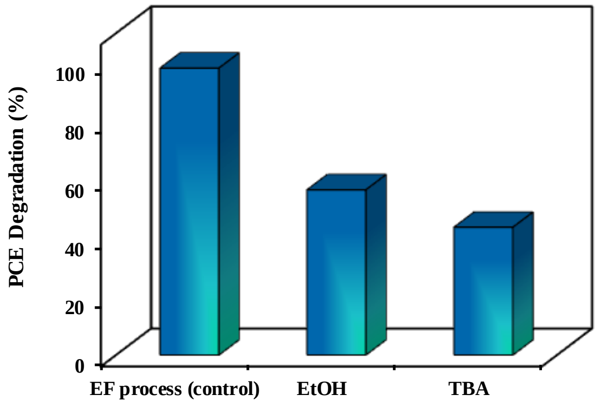

Figure 5: PCE degradation using EF process in the presence of different radical scavengers

Discussion

The optimum solution pH for the EF process should be < 5.0. Several studies have showed that the optimum pH for degradation is 3 and the extent of degradation decreases by increasing pH for pH > 3.0. In contrast, Fe^{2+} ions are unstable at pH > 5.0, and they quickly form Fe^{3+} ions, which tend to produce $Fe(OH)_n$ complexes. These complexes would form further $[Fe(OH)4]^-$ when the pH value was > 9.0. Besides, H_2O_2 is also unstable in basic solution and may decompose to give oxygen and water and lose its oxidation ability [16, 17]. The current density is the most critical parameter, affecting the reaction rate of electrochemical processes. As expected, PCE degradation increased with an increase in the current density.

These results accelerate the anodic scarification process, increasing the generated Fe^{2+} ions concentration [18-20]. Consequently, according to the Fenton reaction expressed by Eq. 1, generation of Fe^{2+} ions results in increased $^{\bullet}OH$ generation, and consequently, the PCE degradation increases. The effect of H_2O_2 concentration on PCE degradation was investigated over a range of 20-70 µL. At low H_2O_2 concentrations, the PCE degradation rates were very slow due to the insufficient $^{\bullet}OH$ in an aqueous solution. As the H_2O_2 concentration increased to 50 µL, the PCE degradation enhanced due to the generation of more radicals. However, for a higher concentration (70 µL), no significant additional improvement was observed due to the scavenging effect of $^{\bullet}OH$ and the inhibition of iron corrosion by hydrogen peroxide [21, 22]. As expressed by reaction (2), although other radicals ($HO_2^{\bullet}$ and $O_2^{\bullet-}$) are generated, they are much less reactive that may be neglected [23-25].

$$OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (2)$$

The results showed that increasing PCE concentration led to a decrease in PCE degradation, which is in accordance with the characteristics of the EF process. The observed phenomena can be interpreted, since a particular amount of active intermediates are produced. At the same time, the PCE concentration increased by increasing the PCE concentration. Consequently, the amount of $^{\bullet}OH$ was not enough for effective degradation of high concentration of a contaminant, which results in degradation reduction [26, 27].

Based on the obtained results of kinetic studies, the coefficient of correlation (R^2) of the applied model was over 0.98, confirming the increased ability of the model to fit the kinetic data of PCE degradation by EF process. The PCE degradation of 98.1% significantly decreased in the presence of EtOH and TBA as radical scavengers, indicating that the generated $^{\bullet}OH$ species controlled the primary mechanism of the degradation path throughout the EF process.

Conclusion

The present study was focused on the PCE degradation from an aqueous solution using the EF process.

The EF process is a promising approach for the degradation of PCE and other persistent pollutants, in the EF process, Fe^{2+} ions released from the anode electrode in the presence of H_2O_2 are produced to produce $^{\bullet}OH$.

The maximum PCE degradation was 98.1% under optimal conditions. The PCE degradation by EF process fitted well the first-order kinetic models. The key mechanism responsible for the PCE degradation was the $^{\bullet}OH$.

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Conflict of interest

The authors declare that they have no conflict of interest regarding the publication of the current paper.

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