

The Performance of Electro-Fenton Oxidation in the Removal of Pesticides from Wastewater Using Stainless Steel Electrodes

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Abstract. This study aims to investigate the effectiveness of the electro-Fenton process for the removal of a pesticide, namely chlorpyrifos, from wastewater. The electro-chemical reactor involved stainless steel electrodes and compressed air pump. Several operational parameters such as pH, current intensity (I), Fe²⁺ dose, and initial concentration of chlorpyrifos were investigated. Complete degradation was attained at initial chlorpyrifos concentration of 30 mg/L. While, at initial concentration of 240 mg/L the removal of chlorpyrifos was 72%. The optimum current intensity and Fe²⁺ dose were 300 mA and 20 mg/L respectively. The degradation of chlorpyrifos was favored at pH 3.0. The degradation of chlorpyrifos by electro-Fenton followed pseudo- first order pattern with good correlation.

Keywords: electro-Fenton, pesticides, wastewater.

1. Introduction

The rapid development of industrial activities has made the treatment of industrial wastewater treatment a major issue for environmental safety and public health [1], [2]. Industrial wastewaters may contain low-biodegradable contaminants such as pesticides and herbicides that cannot be readily remediated by conventional biological treatment processes [3]. In addition, pesticides and herbicides have carcinogenic and toxic nature [4]. Accordingly, pesticides should be removed or degraded to benign end products before they reach the sewer networks, surface water, or groundwater.

At the moment, treatment technologies for contaminated industrial wastewater are of extreme interest for both researchers and stakeholders of industrial companies. In this context, applications of innovative technologies provide more alternatives for industrial wastewater treatment [5]. Advanced oxidation processes (AOPs) have been recognized as particularly efficient technologies for degradation of bi-recalcitrant organics [6]. Among AOPs, Fenton reaction is an attractive and effective process for the degradation of bi-recalcitrant contaminants because of the low toxicity of Fenton reagents [7]. The electro-Fenton Process is one of the most efficient Fenton processes, which involves continuous production of hydroxyl radicals using electro-generated hydrogen peroxide [8], [9]. Electro-Fenton process was reported to achieve high degradation yields and may be considered as an environmentally clean process because electricity is a clean energy source that does not create secondary pollutants [7], [10], [11].

This study aims to investigate the potential of using Electro-Fenton process for treatment of pesticides industry wastewater. Chlorpyrifos has been chosen as a model substrate in this study. Influence of operational parameters such as Fe²⁺ dose, current intensity (I), pH, and initial concentration have been investigated. Kinetics were studied by pseudo first model.

2. Materials and Method

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2.1. Materials

Acetonitrile, chlorpyrifos (chemical formula is shown in Fig. 1), and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were obtained from Sigma-Aldrich. All of the chemicals were of analytical grade and used without further purification. HCl and NaOH solutions were used to adjust the pH of the solution.

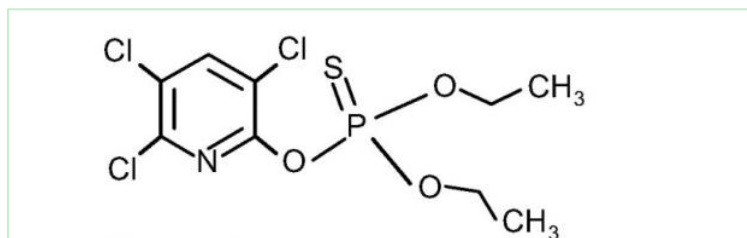


Fig. 1: Chemical structure of chlorpyrifos.

2.2. Experimental Procedure

Electro-Fenton experiments were conducted at room temperature (25° C) with an undivided 1000 mL cylindrical glass vessel containing 600 mL of chlorpyrifos solution. The cell was equipped with two stainless steel electrodes (50 mm x 50 mm x 5 mm) located in the center of the electro-Fenton reactor to have a uniform potential distribution. Compressed air was bubbled through the solution to increase the dissolved oxygen in the solution. The pH was adjusted and a certain amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added to the solution under vigorous magnetic stirring. The current was maintained at a certain level with a DC power supply operated in galvano-static mode to control the current intensity. An ammeter (PHYWE), and a voltmeter (DIGITAL VOLTMETER (G-1002-500)) were used to measure the current intensity (I) and the electric potential respectively.

2.3. Analytical Methods

An Agilent 1200 series HPLC system comprising of a photodiode array detector, and quaternary pump, was utilized for the quantification the concentration of chlorpyrifos. Samples with volume of 25 μL were injected by an auto-sampler into a 150 x 4.6 mm Apollo C18 column at a flow rate of 1.5 $\text{mL} \cdot \text{min}^{-1}$. The temperature of the column was adjusted to 40°C. The mobile phase was composed of 30% distilled water and 70% acetonitrile. The peaks of chlorpyrifos were detected after 5.9 min at wavelength of 230 nm. Total organic carbon (TOC) was measured by TOC analyzer (Analytik Jena AG Co., Germany) equipped with a non-dispersive infra-red detector (NDIR).

3. Results and Discussion

The electrochemical degradation behavior of chlorpyrifos was evaluated at different conditions of pH, current intensity, initial concentration, and Fe^{+2} dosage. In order to conclude the contribution of electro-Fenton degradation, current potential curves were plotted describing the percentage of remaining chlorpyrifos amount (C/C_0) versus the reaction time.

3.1. Effect of Initial Chlorpyrifos Concentration

The degradation of chlorpyrifos with different initial concentrations is shown in Fig. 2. The obtained results indicated that increasing the initial concentration of chlorpyrifos decreases the removal efficiency and prolonged reaction time is needed for degradation. After reaction time of 90 min, the removal efficiencies of chlorpyrifos with initial concentration of 240, 120, and 60 mg/L were 72%, 88%, and 96% respectively. While complete degradation of chlorpyrifos with initial concentration of 30 mg/L was attained after 60 min. This finding can be explained by an increase of chlorpyrifos molecules in the solution which needs a greater amount of hydroxyl radicals to attain complete degradation [12]. In addition it is suggested that the Fenton reagent were consumed before complete degradation of chlorpyrifos in high contaminated wastewater [13].

The removal of TOC followed a different trend to that of chlorpyrifos degradation as shown in Fig. 3. The mineralization rate was almost constant and slower than chlorpyrifos degradation rate. About 66% of TOC was removed after a reaction time of 120 min, while the degradation of chlorpyrifos was about 90%. This finding is mainly attributed to generation of refractory organic by-products during the oxidation of

chlorpyrifos [14]. In addition, the amount of the produced hydroxyl radicals may not be sufficient to mineralize the by-products molecules [12].

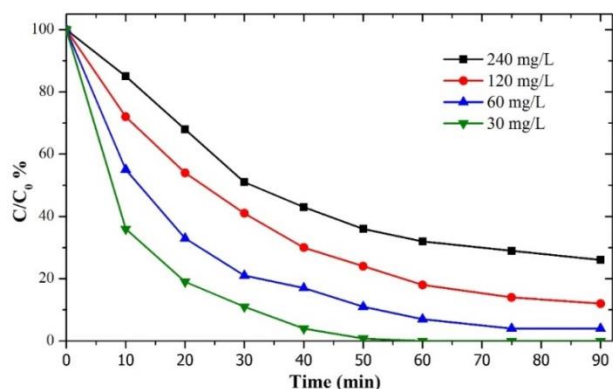


Fig. 2: Effect of initial chlorpyrifos concentration. pH= 3.0, I=300 mA, Fe²⁺ dose= 20 mg/L.

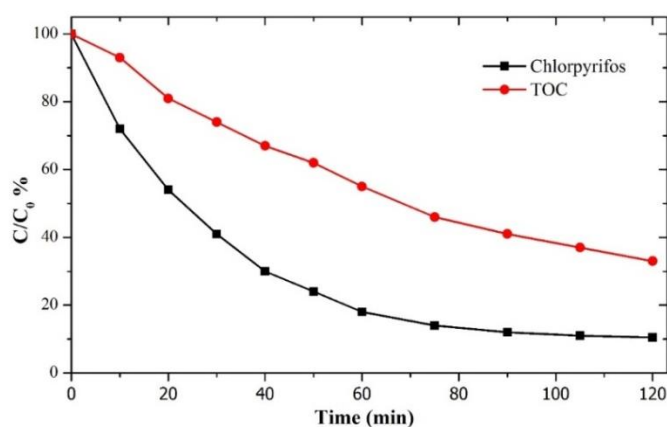


Fig. 3: Removal of TOC. Initial chlorpyrifos concentration = 120 mg/L, pH= 3.0, I=300 mA, Fe²⁺ dose= 20 mg/L.

3.2. Effect of Current Intensity

The degradation of chlorpyrifos under different current intensity is shown in Fig. 4. The raising of current intensity showed significant improvement of chlorpyrifos degradation yield. Increasing the current intensity from 100 to 200 mA raised the degradation efficiency of chlorpyrifos from 68% to 78% after a reaction time of 90 min. Raising the current intensity to 300 mA attained a degradation of 97% in 90 min. Further increasing of current intensity accelerated the chlorpyrifos degradation at early stages however the final removal of chlorpyrifos was almost the same. Accordingly, the optimum current intensity is considered 300 mA. This finding can be explained because the applied current is considered the driving force for the reduction of oxygen resulting to the generation of hydrogen peroxide near the cathode surface [7]. Higher current intensity enhances the production of hydrogen peroxide, and consequently improves the generation of hydroxyl radicals in the solution, which are responsible for the degradation [15].

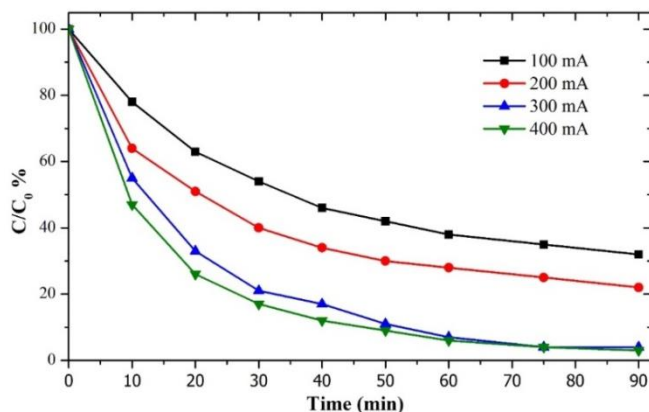


Fig. 4: Effect of current intensity. Initial chlorpyrifos concentration = 60 mg/L, pH= 3.0, Fe²⁺ dose= 20 mg/L.

3.3. Effect of pH

The degradation of chlorpyrifos at different pH is shown in Fig. 5. It is clear that the degradation of chlorpyrifos is favored at pH 3. Raising the pH from 3.0 to 5.0 decreased the degradation of chlorpyrifos from 97% to 86%. Further raising of pH to 7.0 considerably diminished the degradation rate of chlorpyrifos and the removal was only 51%. Similar trends were reported for degradation of different organic compounds by classic Fenton, photo-Fenton, and electro-Fenton processes [16]–[18]. In Fenton reaction, iron species precipitate as ferric hydroxides at pH higher than 5.0 [5]. In addition, H_2O_2 is not stable in basic mediums and rapidly decomposes to oxygen and water [7]. On the other hand, acidic condition is favored for the generation of H_2O_2 . However, at pH lower than 3.0 hydrogen generation is promoted reducing the number of active sites for generating hydrogen peroxide [7].

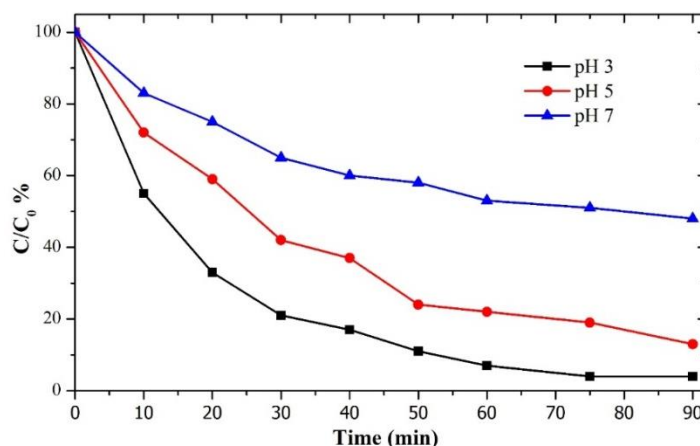


Fig. 5: Effect of pH. Initial chlorpyrifos concentration = 60 mg/L, $I = 30$ mA, Fe^{2+} dose = 20 mg/L.

3.4. Effect of Fe^{2+} Dose

The degradation of chlorpyrifos using different doses of Fe^{2+} is shown in Fig. 6. Fe^{2+} dose had strong influence on degradation of chlorpyrifos. Raising the dose from 5 to 10 mg/L improved the degradation of chlorpyrifos from 56% to 77% in 90 min. Using a Fe^{2+} dose of 20 mg/L attained chlorpyrifos removal of 97%. Further increasing of iron dose led to improve of degradation rate at early stages but the overall removal percentages of chlorpyrifos after 90 min were almost the same. Thus, the optimum dose was considered 20 mg/L. This finding is in accordance with previous reports discussed the degradation of organic contaminants by electro-Fenton process [12], [19]. The poor removal at low iron doses is attributed to the limited generation of hydroxyl radicals due to insufficient Fe^{2+} . In addition, at higher Fe^{2+} concentrations than needed doses, parasitic reactions take place and consume hydroxyl radicals [5].

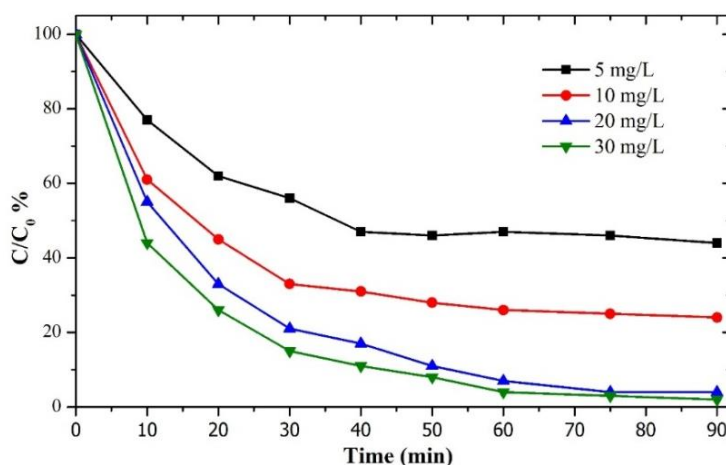


Fig. 6: Effect of Fe^{2+} dose. Initial chlorpyrifos concentration = 60 mg/L, pH = 3.0, $I = 300$ mA.

3.5. Degradation Kinetics

The pseudo first order model was used to study the kinetics of electro-Fenton process for degradation of chlorpyrifos with different initial concentrations. The pseudo first order model basically relates the rate of

degradation (r) and concentration of substrate (C) in water at reaction time (t) [20]. The model is expressed by equation (1) [6];

$$r = -\frac{dc}{dt} = K_{obs}C \quad (1)$$

Where k_{obs} : the degradation rate constant. Equation (1) can be simplified in equation (2) as follows [20]:

$$\ln\left(\frac{C_0}{C}\right) = K_{obs}t \quad (2)$$

Where C_0 is the initial concentration of chlorpyrifos. Fig. 7 shows the linear relationship between $\ln(C_0/C)$ and reaction time at pH 3.0 and optimum iron dose. K_{obs} and R^2 were calculated for different initial concentrations and illustrated in Table I. The results revealed that electro-Fenton processes for all initial concentrations of chlorpyrifos follow pseudo- first order pattern with good correlation.

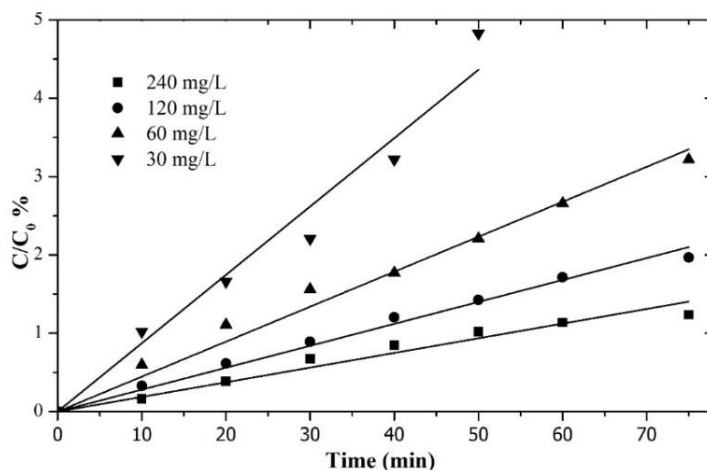


Fig. 7: Degradation kinetics of different initial chlorpyrifos concentration. pH= 3.0, I=300 mA, Fe^{2+} dose= 20 mg/L.

Table I: Reaction kinetics at different initial concentrations

Initial chlorpyrifos concentration (mg/L)	K_{app}	Standard error	R^2
30	0.0872	0.0042	0.986
60	0.0446	0.0011	0.994
120	0.0280	5.83×10^{-4}	0.996
240	0.0187	7.47×10^{-4}	0.987

4. Conclusions

The present paper studied the effectiveness of the electro-Fenton process for the remediation of pesticides present in wastewaters and in surface water. Chlorpyrifos was used as model substrate in this study. Electro-Fenton process was efficient for a wide range of initial chlorpyrifos concentration (30-240 mg/L). Complete degradation was attained at initial concentration of 30 mg/L in 60 min. At initial concentration of 240 mg/L the removal of chlorpyrifos was 72% in 90 min. The optimum current intensity was 300 mA. The process was favored at pH 3.0. The optimum dose of Fe^{2+} was 20 mg/L. The electro-Fenton processes for all initial concentrations of chlorpyrifos followed pseudo- first order pattern with good correlation. From the above results, electro-Fenton process is certainly suitable for the removal of pesticides fromL wastewaters.

5. References

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