

Malathion Removal through Peroxi-Electrocoagulation and Photocatalytic Treatments. Optimization by Statistical Analysis

Jesús Gabriel Rangel-Peraza¹, Manuel Antonio Reyes Prado¹, Leonel Ernesto Amabilis-Sosa², Yaneth A. Bustos-Terrones², Blenda Ramírez-Pereda^{2,*}

¹ Tecnológico Nacional de México-División de Estudios de Posgrado e Investigación. Instituto Tecnológico de Culiacán. Juan de Dios Batiz 310. Col. Guadalupe, Postal Code 80220. Culiacán, Sinaloa, México.

² CONACYT-División de Estudios de Posgrado e Investigación. Instituto Tecnológico de Culiacán. Juan de Dios Bátiz 310. Col. Guadalupe, Postal Code 80220. Culiacán, Sinaloa, México.

*E-mail: blenda.ramirez@itculiacan.edu.mx

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The use of Malathion as an insecticide is widespread in Mexico for pests control in agriculture. Malathion biodegradation is not possible due to its high toxicity. In the present work the Malathion degradation by an Electrocoagulation process was investigated. Studies were conducted to evaluate the efficiency of pesticide removal in the presence of H₂O₂ and ZnO. A Latin-square design was used to investigate the contribution of independent variables as applied voltage, electrode material and type of treatment applied on Malathion concentration, removal time and kinetic rate constant. Results demonstrated that the pollutant degradation follows a pseudo-first order kinetic with a maximum value of 0.0171 min⁻¹. ANOVA tests showed that the presence of H₂O₂ and ZnO improve the removal of Malathion. On the other hand, all the independent variables had a significant influence on the rate of the oxidation process. During optimization process was found that the electrocoagulation with aluminum electrodes in a range of 20-30 V with the addition of H₂O₂ the kinetic removal rate increases to 0.0447 min⁻¹.

Keywords: Electrochemical process, Degradation kinetics, Malathion, Latin-square design, Statistical analysis

1. INTRODUCTION

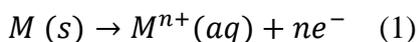
The growing demand for food in the world leads to the overuse of agrochemicals for pest and disease control [1]. In recent years, there has been an accelerated increase in the use of insecticides, specifically organophosphorous (Parathion, Chloropyrifos, Malathion) [2]. Pesticides are transported to aquatic and terrestrial ecosystems by runoff, infiltration and erosion of soils. Due to their toxic,

bioaccumulative and carcinogenic characteristics, they could contaminate the different environmental matrices and become a risk to the human health and aquatic life [3].

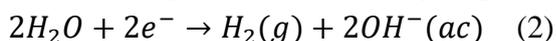
Mexico is characterized by its agricultural production aimed at both domestic and international consumption. According to the National Institute of Statistics and Geography (INEGI) more than 10% of the national territory is dedicated to cultivation in the open air. Due to the characteristics of this type of cultivation, the use of pesticides is indispensable. Among the most commonly used pesticides is Malathion. The use of this chemical poses a high ecological risk, since wastewater usually with high contents of this pesticide is transported to the waterbodies through agricultural drains. Recent studies have shown that concentrations between 3.3 mg L^{-1} and 5 mg L^{-1} can cause cytotoxicity to cells of the human central nervous system [4]. Hepatotoxic effects have also been reported in marine species [5] and rats [6,7]. Therefore, an alternative should be found to minimize the environmental impact of these pollutants before being discharged into agricultural drains.

Pesticides are known for their complex chemical structures, high toxicity and slow biodegradation rates. According to this, they cannot be degraded by conventional methods [8]. In recent decades electrochemical processes have excelled in the treatment of recalcitrant contaminants. The use of electric current as a fundamental method for wastewater treatment has great advantages because it reduces the use of chemicals, and the sludge generated in this process is also reduced. Besides, they are environmentally compatible methods and easy to implement. Numerous researches demonstrate that electrochemical treatments are effective in reducing the concentration of pesticides in contaminated water and soils [9,10].

Among the reported chemical treatments, the Electrocoagulation (EC) process stands out. In EC, two materials are used as electrodes. A metal can be used as a sacrificial anode, which provides ions that are capable of acting as coagulants under certain conditions (Eq. 1) (Murthy and Parmar 2011). The solution of the metal leads to the formation of several chemical species such as hydroxydes, polyhydroxys, among others, depending on the pH of the system. These species are responsible for forming coagulating agents capable of eliminating organic matter [11].



At the same time, there are complementary reactions in the cathode that give rise to the reaction of interest. Generally the evolution of hydrogen (H_2) is one of the reactions of interest (Eq. 2) [12].



The most commonly used metals in EC processes are Aluminum and Iron. However, the use of other materials such as Stainless Steel [13] and Magnesium [11] has been also reported. On the other hand, it has been reported that EC can be combined with other oxidation processes to improve the removal efficiency of polluting organics. Generally the use of hydrogen peroxide (H_2O_2) increases the percentage of the Chemical Oxygen Demand (COD) eliminated. Barrera-Diaz et al. [14] demonstrated that the use of H_2O_2 during an EC process increased the COD removal. The same situation is reported by Nasrullah et al. [15], who suggest that the removal efficiency increased 10% when adding 2% of H_2O_2 to a palm oil mill effluent treated by EC.

As in any electrochemical process, the operational variables directly impact the results achieved. In this sense, the size of the electrodes, their geometry and the distance between them play a fundamental role in the efficiency of the treatment. In addition, the solution pH, the residence time and the volumetric

flow are important parameters for the design and operation of electrochemical reactors. The above variables must be taken into account when pilot or full scale electrochemical system is developed. However, these operational parameters must first be optimized at laboratory scale.

The optimization of the electrochemical process is possible through mathematical tools. The Response Surface Methodology (RSM) is a common technique for wastewater treatment optimization. Even, EC processes have been optimized through RSM [16, 17]. The above methodology is a good strategy for a process optimization because a mathematical model is obtained and a maximum, minimum or a target process response can be achieved by minimizing the residual variation of the mathematical model obtained [18]. However, this model cannot be obtained when operational parameters are not numerical (quantitative variable). Another good option for process optimization, when qualitative variables are studied, is the Latin-square designs. Latin-square are used in statistical analysis in many fields, for example, agriculture [19].

In this sense, the main objective of this research was to theoretically and experimentally maximize the Malathion removal efficiency and rate in an electrochemical reactor. The optimization of the electrochemical reactor was carried out by taking into account some operational parameters. The synergic effect of other Advanced Oxidation Process (AOPs) with EC was also assessed. Finally, the pseudo-first order kinetic parameter of pesticide removal was evaluated through the EC process.

2. EXPERIMENTAL

2.1. Materials

All reagents used at work were reactive grade quality and supplied by J. Baker. A synthetic effluent was prepared from commercial Malathion at 88.7% obtained from Velsimex. The initial concentration of pesticide used for the experiments was $45 \text{ mg L}^{-1} \pm 1.3 \text{ mg L}^{-1}$.

2.2. Electrodes

The materials used as electrodes were Aluminum (Al), Stainless Steel (SS) and Galvanized Steel (GS). Rectangular plates of dimensions 2x15 cm were used with an effective area of 60 cm^2 . For each experiment, the same material was used in anode and cathode in a monopolar-parallel arrangement.

2.3. Electrochemical Reactor

A batch borosilicate cylindrical reactor with diameter dimensions 8.5 cm and height of 12.5 cm was used. Inside the reactor, the electrodes were connected to an energy source brand Matrix model MDP-3005L-3. Voltages of 10, 20 and 30V were evaluated. Figure 1 shows the diagram of the electrochemical reactor used. The working volume was 500 ml.

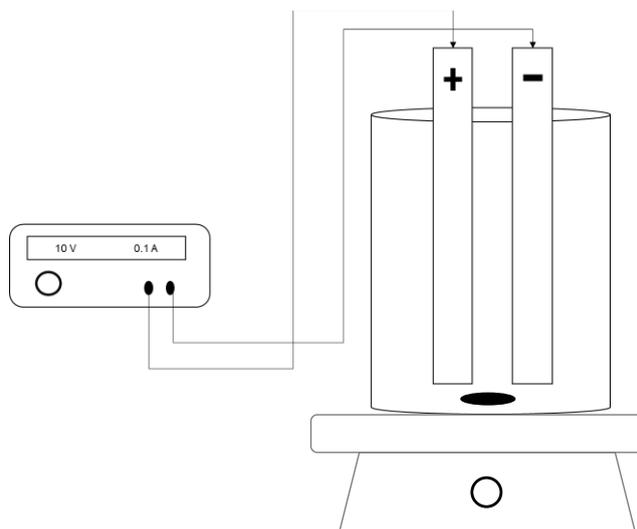


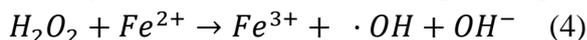
Figure 1. Schematic diagram of the experimental system

2.4. Electrocoagulation and AOPs (EC/AOPs)

Electrocoagulation in combination with other AOPs has been studied. It has proven that the synergistic effect improves the pollutants removal [20]. In order to assess the effect of combining the EC process with other AOPs, it was decided to conduct experiments in the presence of H₂O₂ and Zinc Oxide (ZnO). The experiments were carried out under the same EC conditions.

2.5. Peroxi-electrocoagulation (H₂O₂-EC)

H₂O₂ is a molecule with strong oxidizing power that, in the presence of iron it is able to produce hydroxyl radicals (•OH). The reaction between the two previous reagents is known as Fenton Reaction (Ec. 4). •OH radicals can oxidize organic pollutant matter and completely degrade it to carbon dioxide (CO₂) and water (H₂O). Some authors agree to call the peroxi-electrocoagulation process when EC process is carried out by adding H₂O₂ [21]. The synergy between the action of hydroxyl radicals and formed iron hydroxides would lead to improved process efficiency.



In this study, dosing the process with H₂O₂ was carried out to check its effect on pesticide removal. It was worked with a concentration of 0.1% commercial H₂O₂ (30% v/v).

2.6. Photo-electrocoagulation (Ph-EC)

ZnO is considered one of the most representative semiconductor materials. For its characteristics, it is used in photocatalysis processes for wastewater treatment [22]. Photocatalysis consists of generating a hollow electron pair (e⁻/h⁺) in the atoms of a semiconductor material. When a beam of light affects an electron of this type of material, the particle is able to jump from its valence band to its conduction band leaving a gap. The generated pair can produce oxidation-reduction reactions [23]. Organic matter is

susceptible to oxidation, therefore these compounds can be removed during the photochemical process. From this perspective, the pesticide EC process can improve its efficiency when this process is combined with photocatalysis (Ph-EC). In order to evaluate the efficiency of the Ph-EC process, a concentration of 1.6 mg L^{-1} of ZnO was added prior to initiation of the electrochemical treatment. The experiments were kept under the presence of light based on the operational conditions of the photoreactor suggested by Rodriguez-Mata et al. [24].

2.7. Analytical Procedures

The Malathion concentration was determined using the USEPA method 8141B (2007) using an Agilent 7890B gas chromatograph coupled to a mass spectrometer (5977A MSD) equipped with a Split injector at a temperature of 300°C during the chromatographic cycle, with a purge time of 0.75 min. An Agilent DB-5ms column (30 m x 0.25 mm, 0.25 mm, 122-5532) was used. The temperature program was as follows: furnace ($80\text{-}300^\circ\text{C}$ to $10^\circ\text{C}/\text{min}$, maintained 5 min) and detector at 300°C , with a total execution time of 20 min. Injection volumes of $4 \mu\text{l}$ were used in each analysis. For the mass detector, a Flame Photometric Detector (FPD), transfer line temperature and ion source were used at 300°C , as well as electron impact ionization at 70 eV.

2.8. Experimental Design

Experimental designs are very useful for evaluating the influence of different operating parameters on response variables. They are also used for finding the best operating conditions (optimization) of processes. In this study, an experimental design was used to optimize the removal of Malathion in an EC reactor. An orthogonal array called Latin-square design was used based on the conditions in which this pesticide is found in agricultural field adsorbent filters. The control variables of the experimental design were: the electrode material, process type and voltage applied, with three treatment levels per factor. The response variables analyzed were Malathion concentration with time and pseudo-first order kinetic rate. The experimental array was randomized in order to avoid a statistical bias by performing experimental design treatments in an orderly manner.

2.9. Kinetic Study

The kinetic study of a reaction represents the transformation velocity of the reagents into products. Generally the kinetics of a reaction is obtained experimentally in order to know the mathematical equation that describes the phenomenon and the kinetics rate constant (k). Several researches demonstrate that the removal of pesticides by electrochemical methods follows a pseudo-first order kinetic (Eq. 5) [25, 26].

$$C = C_0 e^{-kt} \quad (5)$$

The determination of the removal kinetics estimates the best conditions to carry out the elimination of any contaminant and propose more efficient treatments.

3. RESULTS AND DISCUSSION

3.1. Optimization of Malathion removal

Electrocoagulation experiments for Malathion removal were carried out according to the results of the Latin Square Design (Table 1). As it is shown, a great variation of the removed concentration of Malathion is observed in the treatments performed in this study. The Malathion concentration removal varied from 15.87 mg L⁻¹ to 41.78 mg L⁻¹. These values represent a removal percentage range from 40% to 96%, in 80 to 240 minutes. The results can be compared with [27] who reported malathion degradation by a photo-Fenton process and reached removal values between 40 - 73% in 75 min, however their concentrations were much lower than concentrations of the present investigation. The best removal efficiency was found in treatment 4.

Figure 2 shows the influence of operational variables of EC process on Malathion removal. Mean Malathion removal values of 30.20 mg L⁻¹, 27.85 mg L⁻¹ and 30.54 mg L⁻¹ were obtained for Aluminium, Galvanized Steel and Stain Steel electrodes, respectively. According to Tukey's range test ($\alpha = 0.05$), no significant removal differences were obtained for the different electrode materials used in EC. Figure 2a shows the effect of these electrodes on Malathion removal in EC.

Table 1. Experimental combinations and results for Malathion removal

Orthogonal Design			Response Variables				Kinetic	
No.	Electrode	Treatment	Voltage (V)	Time (min)	Malathion removed (mg L ⁻¹)	Removal (%)	<i>k</i> (min ⁻¹)	<i>R</i> ²
1	Al	EC	10	120	15.87	40.69	0.0041	0.9313
2	SS	H ₂ O ₂ -EC	30	160	30.64	65.84	0.0069	0.9745
3	GS	Ph-EC	20	200	23.12	54.23	0.0071	0.9914
4	Al	H ₂ O ₂ -EC	20	200	41.78	96.58	0.0171	0.9392
5	SS	Ph-EC	10	280	29.85	73.23	0.0080	0.9816
6	GS	EC	30	140	24.33	57.14	0.0079	0.9446
7	Al	Ph-EC	30	80	32.96	68.33	0.0168	0.9566
8	SS	EC	20	220	31.14	71.15	0.0053	0.8860
9	GS	H ₂ O ₂ -EC	10	240	36.10	78.92	0.0043	0.9635

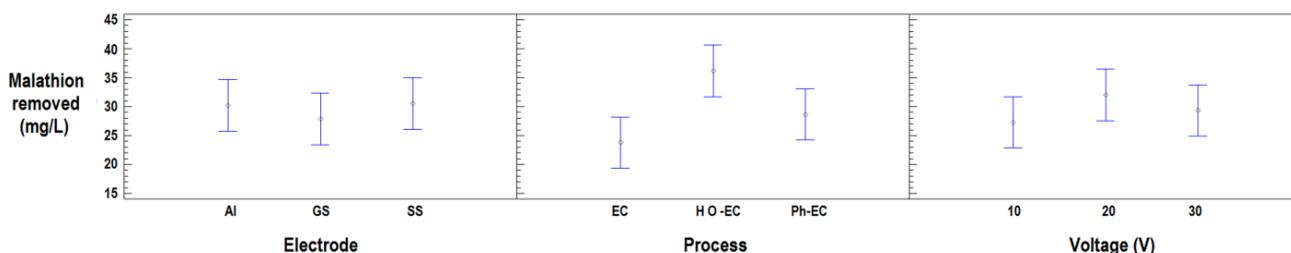


Figure 2 Means and 95 percent Tukey HSD Intervals for Malathion removal. (a) Electrode, (b) Process, (c) Voltage

According to [28], voltage plays a key role in the treatment of EC. This study suggests that when higher voltage applied in an EC process, higher electric current involved and therefore higher removal values are expected. However, in this study, no significant differences were observed for Malathion removal when different voltage was applied (Figure 2c). The fact that neither electrodes nor voltage were significant operational variables in EC is demonstrated in ANOVA ($p=0.05$) shown in Table 2. According to these results, only the type of EC process showed a statistical effect on Malathion removal.

ANOVA demonstrated that combining EC with other AOPs improves treatment efficiency. More than 96% of the initial Malathion concentration was eliminated when EC reactor was dosed with H_2O_2 . As it was expected, H_2O_2 externally added enhanced removal efficiency, in accordance with other authors who reported that the hydrogen peroxide addition to the electrocoagulation experiments, significantly improve COD and color removal efficiency [29, 30, 31]. The use of ZnO in a Ph-EC process slightly increased Malathion removal. No reports were found about the use of ZnO to improve the EC process. Only, the use of Aluminum anode activated with Zn as alloy has been proposed and it improved the removal efficiencies on the simultaneous removal of phosphates, Zn^{2+} and Orange II [32].

It is noteworthy that the best results were obtained during the peroxi-electrocoagulation treatment working with a voltage of 20 V and using Aluminum as electrode. Under these conditions, peroxi-electrocoagulation process removed 41.78 mg L^{-1} of Malathion. This result could demonstrate the feasibility of use of peroxi-electrocoagulation process as an option for the removal of this pesticide in adsorbent filters used in agricultural drains in the study area. This high Malathion concentration can be found in these adsorbent systems. The removal of this pesticide from adsorbent filters can also be an opportunity for the reuse of the adsorbent materials.

Table 2 ANOVA test results for Malathion removal concentration

Source	Sum of Squares	Degree of Freedom	Mean Square	F-Ratio	p-Value
MAIN EFFECTS					
Electrode	25.7552	2	12.8776	0.26	0.7723
Treatment	467.848	2	233.924	4.81	0.0316
Voltage (V)	68.0125	2	34.0063	0.7	0.518
RESIDUAL	535.34	11	48.6672		
TOTAL	1096.96	17			

3.2. Malathion removal kinetics

Based on the results obtained in this study, the removal of Malathion under the EC treatments could meet the pseudo-first order kinetics. These results coincide with the reports made by [33], who

indicate that the photodegradation of Malathion through UV, UV/H₂O₂ treatments, among others, meets pseudo-first order kinetics. These results contrast to the investigation carried out by [34], who indicated that pesticides elimination by electrocoagulation followed a pseudo-second-order process. The concentration of Malathion with time was adjusted to a linear kinetic model for all treatments.

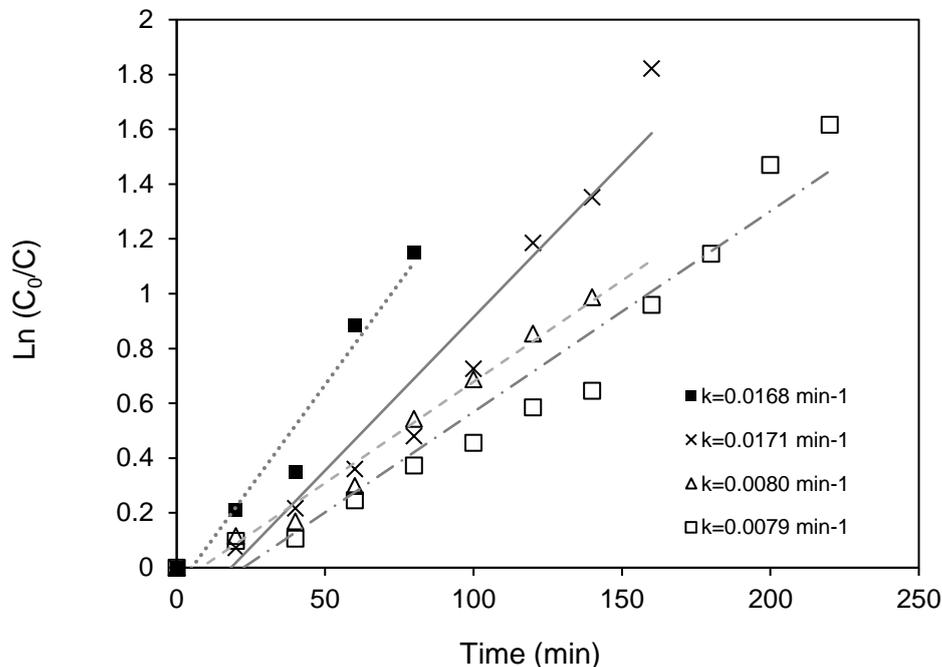


Figure 3 Malathion degradation kinetics

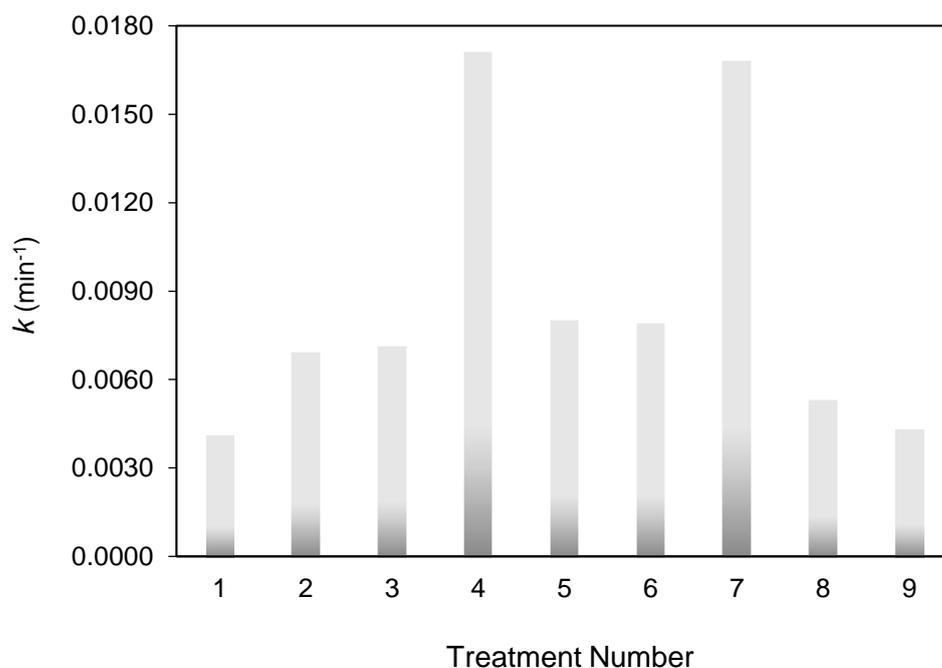


Figure 4 Pseudo-first order rate constants (*k*) for Malathion removal

Figure 3 shows the linear behavior of some representative removal treatments selected from experimental design. The pseudo-first order kinetic rate (*k*) was obtained by using the least squares

regression. The slope of linear model is the kinetic rate (k) and it represents the velocity of Malathion removal in the EC process. Kinetic rate and the coefficient of determination (R^2) for each treatment are reflected in the last two columns of Table 1. According to the kinetic study carried out, the higher rates correspond to treatments 4 and 7. Both constants have values three times higher than the rest of the treatments (Figure 4).

Table 3 shows the influence of the operational variables studied on the kinetic rate of Malathion in EC process. Based on ANOVA results, all operational variables showed a significant influence on the rate of the oxidation process.

Table 3 ANOVA test results for Kinetic removal rate (k)

Source	p -Value
Electrode	0.0083
Treatment	0.0485
Voltage (V)	0.0307

The means and 95 percent confidence intervals of the kinetic rates were depicted in Figure 5. As it is observed in Figure 5a, higher removal rates are obtained when the EC process is carried out using aluminum as electrode ($p=0.05$). This result is consistent with other reports, where the electrocoagulation with Aluminum has proved to be efficient on the Acetamiprid degradation [35]. Investigations conducted by [36] demonstrated high removal efficiencies in the elimination of Ciprofloxacin using Aluminum as electrodes. Likewise, Phosphate was 100% removed from wastewater through electrocoagulation with the same electrode material [37]. Although, it is noteworthy that numerous investigations have exposed that iron electrodes exhibit similar performance in electrocoagulation process [38, 39, 40].

The influence of H_2O_2 and its catalytic action on the removal of the pesticide is also highlighted. This result coincides with [41], who found that the addition of H_2O_2 to advanced oxidation systems is a good alternative to accelerate the formation of radicals $\bullet OH$. This effect is also observed in the Ph-EC system, where higher removal rates are observed in comparison to EC process (Figure 5b). Finally, no statistical difference between kinetic rates was observed when EC system is operated at 20 V and 30 V, but the mean values obtained under these conditions were higher respect to the mean values obtained when the process was operated at 10 V (Figure 5c). Although there were no significant differences between 20 and 30 V, the system showed an increase in the kinetic removal rate when it increased voltage from 10 to 20V. The results are in correspondence with several publications where it is demonstrated that the current density is closely related to the voltage and also has a significant influence on the process [42, 43, 44]. In this sense, both, the use of aluminum and a voltage from 20 V to 30 V guaranteed less treatment time, while the peroxi-electrocoagulation obtained higher removal efficiencies.

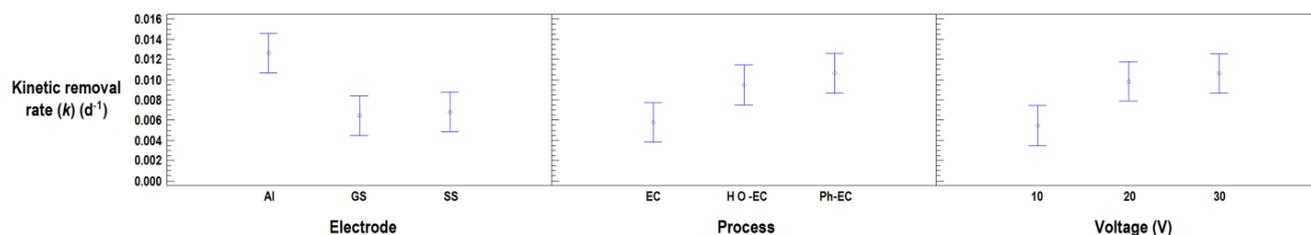


Figure 5 Effect of operational variables on Pseudo-first order rate constants. (a) Electrode, (b) Process, (c) Voltage

Based on statistical analysis, this study suggests the use of the peroxi-electrocoagulation process, with aluminum electrodes and maintaining at minimum voltage of 20 V. The results obtained in this study also suggest that kinetic rate is a better response variable for this kind of wastewater treatment. It was observed that when similar removal efficiencies are achieved, Malathion removal showed less sensitive response to statistical analysis. Therefore, kinetic removal gives a better understanding of the EC process. This response variable provided useful information for the analysis of critical scale-up factors. The kinetic analysis prior to the scaling efforts is of vital importance to reduce operation times and costs.

3.3. Validation of statistical analysis results

Statistical analysis demonstrated that the best conditions for removing Malathion through an EC process is to perform this process in the presence of H_2O_2 and using Al as electrode. However, statistical analysis showed no significant difference between 20 V and 30 V. The velocity rate and the efficiency of EC process were similar at both voltages used. However, the peroxi-electrocoagulation treatment at 30 V and using Al as electrode was not carried out in any of the orthogonal array runs. In order to validate the statistical analysis, additional experiments were conducted in order to demonstrate the optimization of EC process.

Table 4 Malathion removal for Orthogonal Design and Statistical Optimization

Electrode	Treatment	Voltage (V)	Malathion removed (mg L ⁻¹)	Removal (%)	k (min ⁻¹)	R^2
Al	H ₂ O ₂ -EC	20	41.78	97.50	0.0171	0.9392
Al	H ₂ O ₂ -EC	30	44.30	99.87	0.0447	0.9223

Both treatments were carried out with five repetitions of each treatment. The results obtained were compared by using the Student's t-test and F-test. No significant difference was observed when the Malathion removal was compared. However, significant difference was found between the treatments

when statistical analysis was carried out for the kinetic rate. Besides, it was demonstrated once again that the removal of Malathion in both treatments follows a pseudo-first order kinetic with a maximum velocity constant of (0.0447 min^{-1}). The velocity rate obtained under these conditions was 2.5 times higher compared to the best treatment obtained through orthogonal design (Table 4).

4. CONCLUSIONS

An orthogonal design was carried out to evaluate the removal of Malathion using three advanced oxidation processes. EC was demonstrated to be an effective process for Malathion elimination. The combination of EC with the addition of H_2O_2 and the use of ZnO in presence of light improved the efficiency of the reaction.

Based on the results obtained of the orthogonal design, the peroxi-electrocoagulation process obtained the best results by eliminating more than 99.9% of the initial concentration of the pesticide using aluminum electrodes at a constant voltage of 30 V. On the other hand, it was demonstrated for all cases that the degradation follows a pseudo-first order kinetic.

In this study, higher removal rates were found when using the $\text{H}_2\text{O}_2/\text{EC}$ and Ph/EC processes. In general, aluminum could be considered as the best electrode material because higher rates were found. Besides, higher removal rates were found when higher voltages were used in EC systems. The statistical optimization of the EC process was experimentally validated and the optimal removal and kinetics values were finally obtained.

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