Application of full factorial experimental design and central composite design for the modeling and optimization of electrocoagulation process for the removal of Tylosin

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Abstract

In this study the removal of Tylosin (Tylo) from wastewater was experimentally investigated by using electrocoagulation (EC) process. Iron grid was used in the reactor as material for the electrode (cathode) which is a waste. Full Factorial Design (FFD) and Central Composite Design experiments (CCD) were used for the optimization of the electrocoagulation process in order to evaluate the effect of process variables and their interaction on Tylosin removal. The first and the second–order models obtained showed the classification of these parameters based on their level of significance. Pareto analysis results and the values of Student's distribution showed that the most influencing factor was the initial Tylosin concentration with a negative effect, followed by the electrolysis time, the current density and the temperature. The analysis of variance (ANOVA) of the two models showed high values for the determination coefficients ($R^2_{First\text{-}order}$ = 0.9408, $R^2_{Second\text{-}order}$ =0.9257) for the predicted values using the Response Surface Methodology (RSM). According to the first order model the interactions: temperature-initial concentration of Tylo (x_1-x_2) temperature-electrolysis time (x_1-x_4), initial concentration of Tylo-current density (x_2 -x_3), initial concentration of Tylo- electrolysis time (x_2-x_4), and current density-electrolysis time (x_3-x_4) were significant excepted the interaction between temperature- current density. The strongest interaction was only between the initial concentration of Tylo and current density (x_2 -x_3). Graphical response surface and contour plots were used to locate the optimum point. The electrocoagulation process was able to achieve 98% of Tylosin removal yield.

Keywords: *Electrocoagulation, Tylosin, Factorial design, Central composite design.*

I. Introduction

Many of contaminants from wastewater are not completely eliminated in the treatment plant. Degradation of recalcitrant pollutants such as hormones, pesticides and antibiotics is limited and as a result, they commonly turn up into the aquatic environment [1]. Recently, much attention has been devoted to the fate of pharmaceutically active compounds such as antibiotics in soil and water [2]. Among macrolides, Tylosin (Tylo) is the most commonly administered drug for the prevention and the treatment of respiratory, enteric and other diseases in cattle, swine and poultry production; it is also used in dairy farms [2-5] and is the most detected in the USA [5]. Kolpin *et al.* [6] analyzed 139 streams in the

USA where they found up that Electrocoagulation (EC) technique was among the most interesting electrochemical technologies for the treatment of different wastewaters. In comparison with conventional coagulation, EC has several advantages, such: simple operation, small quantity of produced sludge and more effective and rapid removal of organic pollutants from wastewaters [7-11].

Yehya et al. [12] tested treatments involving electrocoagulation process to the removal of carbamazepine and reported the removal of 62% of carbamazepine under slightly acidic initial conditions (*pH* 4) with a current density as high as 44 mA cm^{-2} (I= 4.5 A) using aluminum electrodes and verified the efficiency. Srirangsan et al. [13] studied the removal of biodiesel wastewater by electrocoagulation process and confirmed the efficiency of an aluminum anode and graphite cathode (Al-C) combination at *pH* 6. The authors reported the removal of 55.7% of the chemical oxygen demand (COD), 97.5% of suspended solids and 97.8% of the oil. Chou *et al* [14-22] reported total decontamination of synthetic salicylic acid solutions using aluminum electrodes at 1.2 mA cm^{-2} with a reasonable efficiency. Deshpande *et al* [15, 23] described the excellent decontamination of a pharmaceutical effluent using a cast iron anode with the removal of 72% of chemical oxygen demand *(COD)* and the improvement of the biochemical oxygen demand *(BOD)/COD* ratio from 0.18 to 0.3, pointing out the enhancement of the wastewater biodegradability. Another study was reported by Daniel *et al.* [16] and was concerned with the removal of the anti-inflammatory dexamethasone from aqueous solution and hospital wastewater by electrocoagulation by using commercial aluminum electrodes (61 cm^2 effective area); the main effect of the electrocoagulation was that it removed colloids and reduced the organic load of the hospital wastewater. The results obtained showed an increase in the removal of dexamethasone (up to 38.1%) with a rise of the current applied and a decrease of the inter-electrode distance, in aqueous solutions.
However, no studies did investigate the use of electrocoagulation process to treat Tylosin. Therefore, the objective of the present work was the modeling and optimization of an electrocoagulation process for the removal of Tylosin. In this process, many factors can influence its efficiency, such as pH, temperature, applied electric current, the electrolyte concentration and the application time. The optimization of these factors may significantly increase the process efficiency. Conventional and classical methods of studying a process by maintaining other factors involved at an unspecified constant level does not depict the combined effect of all the factors involved. This method is also time consuming and requires a number of experiments to determine optimum levels, which are unreliable [17].
These limitations of a classical method can be eliminated by optimizing all the affecting parameters collectively by statistical experimental design such as response surface methodology (RSM) [18-23]. RSM is an experimental design technique that uses mathematical and statistical techniques to analyze the influence of independent variables on a specific dependent variable (response) and searching optimum conditions for desirable responses [18-22].
The main objectives of this work were to investigate the individual and the interaction effects of four operating parameters, mainly: temperature (x_1), initial Tylosin concentration (x_2), current density (x_3) and electrolysis time (x_4) on the yield of the degradation of Tylosin by using a full factorial design (FFD); and to optimize those process variables by the application of the Response Surface Methodology (RSM) according to a Central Composite Design (CCD).

II. Materials and methods

A. Target compound

Tylosin (Formula: $C_{46}H_{77}NO_{17}$ and a molecular weight 916.1 $g.mol^{-1}$) was obtained from Sigma Aldrich (100% purity). It is a white powdered solid; its chemical structure is given in Figure 1.

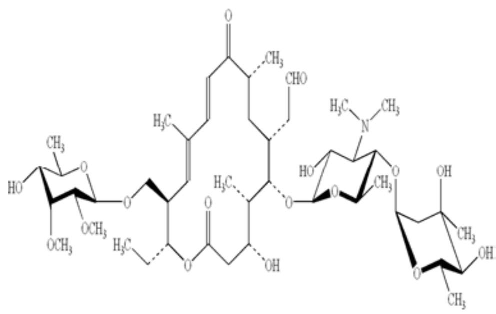

Figure 1. Chemical structure of Tylosin.

B. Experimental set-up and procedure

The experimental set-up is schematically shown in Figure 2. The electrocoagulation unit consisted of a 1 L electrochemical reactor with three iron electrodes, two electrodes as the anode and a grid electrode as the cathode. The electrode dimensions were 55mm×50mm×1 mm. The electrodes were connected to a precision DC power supply (GPS-3030D, Gw INSTEK, China). Mixing was provided by a magnetic stirring bar. Before each run, electrodes were treated with an HCl (0.2 $mol.L^{-1}$) aqueous solution and rinsed again with distilled water for cleaning prior use to avoid passivation. The experimental parameter ranges were selected as follows: temperature (30- 50°C), initial Tylosin concentration (47.5- 122.5 $mg.L^{-1}$), current density (7.5- 12.5 $mA.cm^{-2}$) and electrolysis time (45- 95 min). Antibiotic solution was prepared by dissolving Tylosin in distilled water (500 mg L^{-1}). The conductivity of the experimental solution was adjusted by adding NaCl.

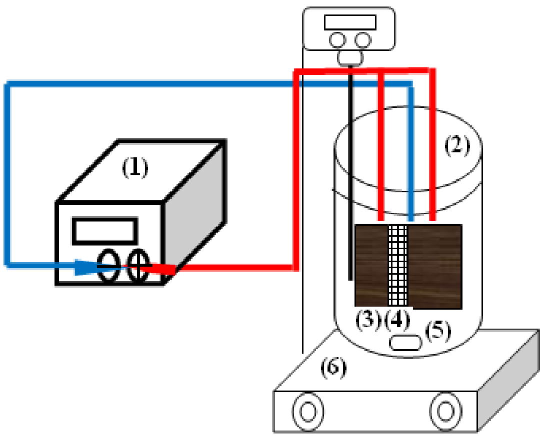

Figure 2. Electrocoagulation set-up: (1) DC power supply; (2) Batch reactor; (3) Anodes; (4) Cathode; (5) Magnetic stir bar; (6) Magnetic stirrer.

C. Analytical methods

The Tylosin residual concentrations in the aqueous solution were spectrophotometrically determined at the maximum absorption wavelength (290 nm)determined by (UV−vis) system (Nanocolor UV/VIS, Macherey-Nagel, Hoerd, France)and calibration curve, samples were taken and filtered through 0.45µm membrane syringe filter (Water corporation 25 mm GHP, USA) before the determination of Tylosin residual concentrations.

D. Experimental design

Experimental design based on full factorial and central composite designs were applied to investigate the effects of the four independent variables (temperature (x_1), initial Tylosin concentration (x_2), current density (x_3) and electrolysis time (x_4), on the response functions. The response is expressed as the percentage removal(*y %)* of Tylosin, it is determined from the relation given below :

$$y(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

with C_0 and C_t the initial and at time t concentrations of Tylosin antibiotic, respectively, in ($mg.L^{-1}$).

More details about the construction of full factorial design and a central composite design as previously reported [17-21]. The real values of each factor and their corresponding levels are collected in Table 1.

Table 1. Values and levels of the operating parameters

Operating Factors	levels				
	-*α*=-2	-1	0	+1	+*α*=+2
Z_1 : *T* (°C)	20.0	30.0	40.0	50.0	60.0
Z_2 : C_0($mg .L^{-1}$)	10.0	47.5	85.0	122.5	160.0
Z_3 :*i* ($mA.cm^{-2}$)	5.0	7.5	10.0	12.5	15.0
Z_4 : *t* (min)	20.0	45.0	70.0	95.0	120.0

The central composite design was composed of experiments of factorial design, experiments realized at the center work domain and eight-star points (Table 2).

The correlation of the independent variables and the response were estimated by first order polynomial (Eq.(2)) and a second-order polynomial (Eq. (3)) as follows:

$$\hat{y} = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{12}\,x_1x_2 + b_{13}\,x_1x_3 + b_{14}\,x_1x_4 + b_{23}\,x_2x_3 + b_{24}\,x_2x_4 + b_{34}\,x_3x_4 + b_{123}\,x_1x_2x_3 + b_{124}\,x_1x_2x_4 + b_{134}\,x_1x_3x_4 + b_{234}\,x_2x_3x_4 + b_{1234}\,x_1x_2x_3x_4 \quad (2)$$

$$\hat{y} = b_0 + \sum_{i=1}^{4} b_i\,x_i + \sum_{i=1}^{4} b_{ii}\,x_i^2 + \sum_{i=1}^{4}\sum_{j=i+1}^{4} b_{ij}\,x_i\,x_j \quad (3)$$

III. Results and discussion

Based on the experimental design results (Table 2), the coefficients of the polynomial models were calculated by means of the application of student's t distribution and related *P*-values (Table 3 and 4), the *P*-value greater than 0.05 at 95 % is unmeaning, because it shows that the related coefficient is insignificant in the model [10].

Table 2: $2^{k=4}$ full factorial design and results of Tylosin removal

Run	Natural values of parameters				Coded values of parameters					Observed value
N°	Z_1	Z_2	Z_3	Z_4	X_0	X_1	X_2	X_3	X_4	$y(\%)$
1	30	47.5	7.5	45	+1	-1	-1	-1	-1	41.59
2	30	47.5	7.5	95	+1	-1	-1	-1	+1	73.95
3	30	47.5	12.5	45	+1	-1	-1	+1	-1	49.37
4	30	47.5	12.5	95	+1	-1	-1	+1	+1	77.42
5	30	122.5	7.5	45	+1	-1	+1	-1	-1	24.59
6	30	122.5	7.5	95	+1	-1	+1	-1	+1	53.22
7	30	122.5	12.5	45	+1	-1	+1	+1	-1	31.05
8	30	122.5	12.5	95	+1	-1	+1	+1	+1	58.46
9	50	47.5	7.5	45	+1	+1	-1	-1	-1	45.33
10	50	47.5	7.5	95	+1	+1	-1	-1	+1	76.35
11	50	47.5	12.5	45	+1	+1	-1	+1	-1	67.88
12	50	47.5	12.5	95	+1	+1	-1	+1	+1	92.82
13	50	122.5	7.5	45	+1	+1	+1	-1	-1	28.00
14	50	122.5	7.5	95	+1	+1	+1	-1	+1	54.40
15	50	122.5	12.5	45	+1	+1	+1	+1	-1	39.92
16	50	122.5	12.5	95	+1	+1	+1	+1	+1	34.27
17	40	85	10	70	+1	0	0	0	0	63.53
18	40	85	10	70	+1	0	0	0	0	61.90
19	40	85	10	70	+1	0	0	0	0	62.42
20	40	85	10	70	+1	0	0	0	0	61.38
21	40	85	10	70	+1	0	0	0	0	61.97
22	20	85	10	70	+1	-2	0	0	0	40.57
23	60	85	10	70	+1	+2	0	0	0	63.69
24	40	10	10	70	+1	0	-2	0	0	91.58
25	40	160	10	70	+1	0	+2	0	0	36.25
26	40	85	5	70	+1	0	0	-2	0	30.11
27	40	85	15	70	+1	0	0	+2	0	71.65
28	40	85	10	20	+1	0	0	0	-2	25.88
29	40	85	10	120	+1	0	0	0	+2	89.16

Table 3. Analysis of variance (ANOVA) for the developed models (first order model and the second order model)

First order model						
Source of variation	Sum of squares	Degree of freedom	Adjusted mean square	*F*- vlue	*P*-value	$R^2_{First\text{-}order}(\%)$
Regression	6004.55	14.00	428.90	6.81	0.01	94.08
Risidual error	377.93	6.00	62.99			
Total	6382.48					
Second order model						
Source of variation	Sum of squares	Degree of freedom	Adjusted mean square	*F*- vlue	*P*-value	$R^2_{Second\text{-}order}(\%)$
Regression	10425.71	14.00	744.69	12.46	0.00	92.57
Residual error	836.41	14.00	59.74			
Total	11262.12					

Table 4. Estimated model coefficients and corresponding *T* and *P*-values.

First order model				Second order model			
Coefficient	Coefficient estimate	*T*-Value	*P*-Value	Coefficient	Coefficient estimate	*T*-Value	*P*-Value
b_0	53.04	261.91	0.00	b_0	208.61	62.12	0.00
b_1	1.83	9.05	0.00	b_1	3.15	19.04	0.00
b_2	-12.55	-61.97	0.00	b_2	-12.98	-78.49	0.00
b_3	3.36	16.59	0.00	b_3	5.70	34.48	0.00
b_4	12.07	59.62	0.00	b_4	13.32	80.57	0.00
b_{12}	-3.17	-15.67	0.00	b_1^2	-3.02	-19.35	0.00
b_{13}	0.49	2.43	0.00	b_3^2	-3.33	-21.35	0.00
b_{14}	-2.48	-12.26	0.00	b_4^2	-1.67	-10.72	0.00
b_{23}	-2.92	-14.44	0.00	b_{12}	-3.17	-15.67	0.00
b_{24}	-2.47	-12.22	0.00	b_{14}	-2.48	-12.26	0.00
b_{34}	-2.73	-13.47	0.00	b_{23}	-2.92	-14.44	0.00
b_{123}	-2.98	-14.72	0.00	b_{24}	-2.47	-12.22	0.00
b_{124}	-1.93	-9.52	0.00	b_{34}	-2.73	-13.47	0.00
b_{134}	-2.04	-10.06	0.00				
b_{234}	-1.43	-7.06	0.00				

The regression equations with coded variables obtained for describing the Tylo removal using EC-Fe process can be presented as follows:

$$\hat{y} = 53.04 + 1.83x_1 - 12.55x_2 + 3.36x_3 + 12.07x_4 + 3.17\ x_1x_2 - 2.48x_1x_4 - 2.92\,x_2x_3 - 2.47\,x_2x_4 - 2.73\,x_3x_4 - 2.98x_1x_2x_3 - 1.93x_1x_2x_4 - 2.04\,x_1x_3x_4 - 1.43\,x_2x_3x_4 \quad \text{Eq. (4)}$$

$$\hat{y} = 63.12 + 3.15\,x_1 - 12.98\,x_2 + 5.70\,x_3 + 13.32\,x_4 - 3.02\ x_1^2 - 3.33x_3^2 - 1.67\,x_4^2 - 3.17\,x_1x_2 - 2.48x_1x_4 - 2.92x_2x_3 - 2.47\,x_2x_4 - 2.73x_3x_4 \quad \text{Eq.(5)}$$

A good adjustment of the Eq.(4) and Eq.(5) to the experimental data was checked through the obtained high correlation coefficients values R^2 = 0.94 and $R^2 \cong 0.93$ respectively.

IV. An Analysis of the first order model

The estimation and the comparison of the parameter's effects (temperature, initial Tylo concentration, current density and electrolysis time) were carried out using Pareto analysis. The percentages factor effects (Pi) were determined by using the following equation:

$$P_i = \left(\frac{b_i^2}{\sum_{i=1}^{n} b_i^2} \right) \times 100 \qquad i \neq 0 \tag{6}$$

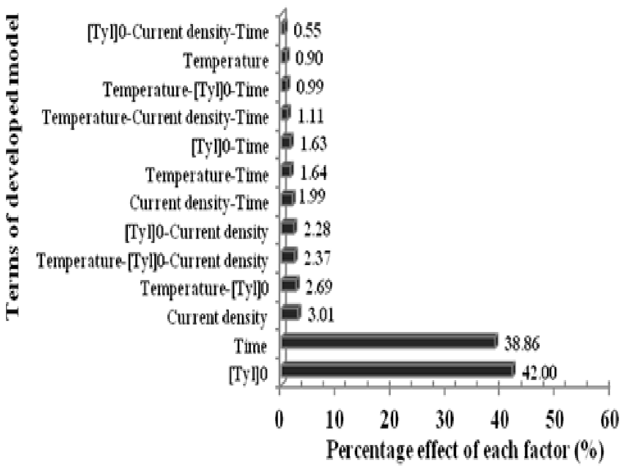

Figure 3. Pareto graphic analysis

According to Pareto analysis (Figure 3) it can be seen that initial Tylo concentration had the most important effect on the response b_2 (42.00%) which had a negative effect on the response (b_2=-12.55). The negative sign (b_2=-12.55) suggests that the increase of initial Tylo concentration from 10 to 160 mg L^{-1} decreased the removal yield of Tylo from 92 % to 39 % (Figure 4).

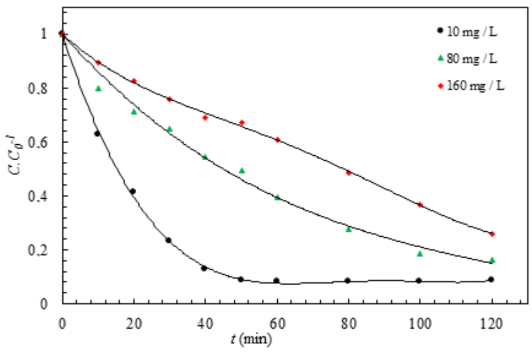

Figure 4. Effect of initial concentration on the efficiency of Tylosin removal

Conditions: i=15 mA.cm^{-2}, T=35°C, $[NaCl]$= 1.25 g.L^{-1} and ω=120 rpm

The apparent kinetic rate constants (k_{app}) obtained for the initial concentrations of 10 and 160 mg $L^{-1}$of Tylo (Table 5) were found to be 0.451 and 0.008 min^{-1}, respectively, after 60 min of reaction time.

Table 5: Apparent Rate Constant (k_{app}) and R^2 Values

Initial concentration of Tylo (mg /L)	k_{app}	R^2
10	0.0451	0.98
80	0.0143	0.99
160	0.0080	0.99

The most likely reason can be deduced from Faraday's law [15], which provides the same amount of iron dissolved at the same current density and time for all Tylosin concentrations. Consequently, the same amount of coagulant species would be produced in the liquid phase, which justifies the lower removal efficiency obtained at higher Tylosin concentrations. Indeed, the flocs produced at high Tylosin concentration were insufficient to complete antibiotic removal. Similar results are reported by Daneshvar *et al*. [2] Ait Ouaissa *et a*l. [18] also reported that the lower removal efficiency of tetracycline by electrocoagulation process was caused by a lower amount of coagulant $Al(OH)_3$ species, which became therefore limiting.

The second significant factor effect was electrolysis time (x_4) with a positive effect (b_4 =12.07) followed by the current density (x_3) has also a significant effect on the response with a positive effect (b_3 = 3.17), these results were expected because the dosage of ions released from anode was increased by increasing the current density and electrolysis time, according to the Faraday's law [10]. Tylosin removal efficiency increased by increasing the electrolysis time and the current density from 5 to 9 mA cm^{-2} as shown in Figure 5.

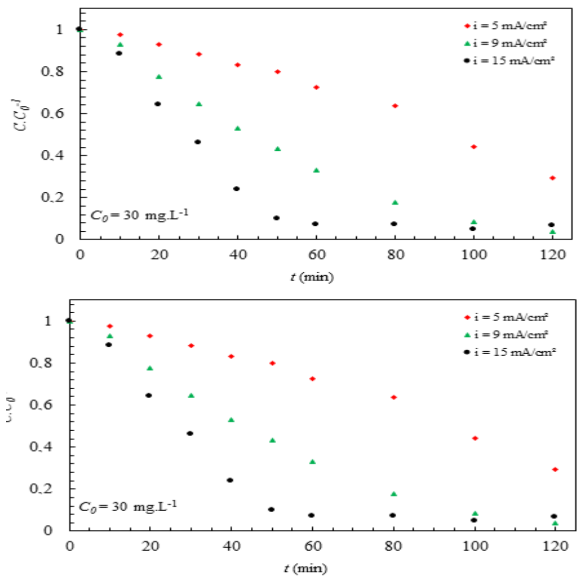

Figure 5. Effect of current density (i) on the efficiency of Tylosin removal. Conditions: C_0= 30 mg.L^{-1}, ω=120 rpm $[NaCl]$= 1.25 g.L^{-1} and T=35°C

Faradic yield (Eq.(7)) and energy consumption were studied at various current density using Faraday's law (Eq.(8)) [15] and Eq. (9) to estimate energy consumption.

$$\varphi = \frac{\Delta M}{\Delta M'} \quad (7)$$

$$\Delta M = \frac{MIt_{EC}}{nF} \quad (8)$$

$$E = UIt_{EC} \quad (9)$$

where ΔM is the mass of dissolved iron estimated by Faraday's law (in g), $\Delta M'$ is the real mass of dissolved iron (g), φ is the Faradic yield, M the molecular weight of iron (g.mol^{-1}), n the number of electrons, U is the cell potential measured between the electrodes, I is the current, t_{EC} is the electrolysis time and F is Faraday's constant (F=96487 C.mol^{-1}). After 70 min electrolysis, experimental results showed that current density did not have a significant effect on the Faradic yield in the studied range, 5–15 mA cm^{-2} and the value was close to 101% in Table 5, which highlights that oxygen release at the anode was minimized. However, energy consumption increased with increasing current density from 4.49 to 25.03 kWh. kg^{-1} when the current density increased from 5 to 15 mA.cm^{-2}. On the other hand, the same Tylo removal efficiency (90%) was obtained for an initial Tylo content of 85 mg.L^{-1}with 5, 9 and 15 mA cm^{-2} at 180, 95 and 70 min electrolysis time, respectively.

It was noted also that, the temperature of the solution had positive effect (b_1=1.83). In order to confirm this result, the influence of temperature was studied at different temperatures (i.e., 35, 50, and 65 °C) with an initial solution concentration of 30 (Figure 6) and 160 mg.L^{-1} (Figure 6). It can be seen from Figure 6 that the removal efficiency of Tylo is negligible whatever its initial concentrations.

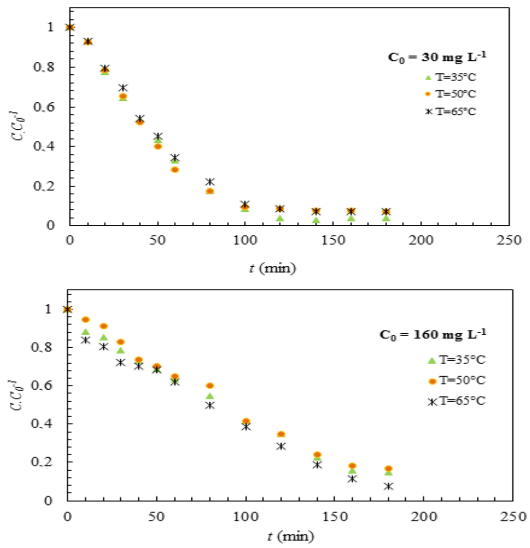

Figure 6. Effect of temperature on the efficiency of Tylosin removal. Conditions: [Tyl]= 30 mg.L^{-1}, i=9 mA.cm^{-2}, [NaCl]= 1.25 g.L^{-1}, and ω=120 rpm

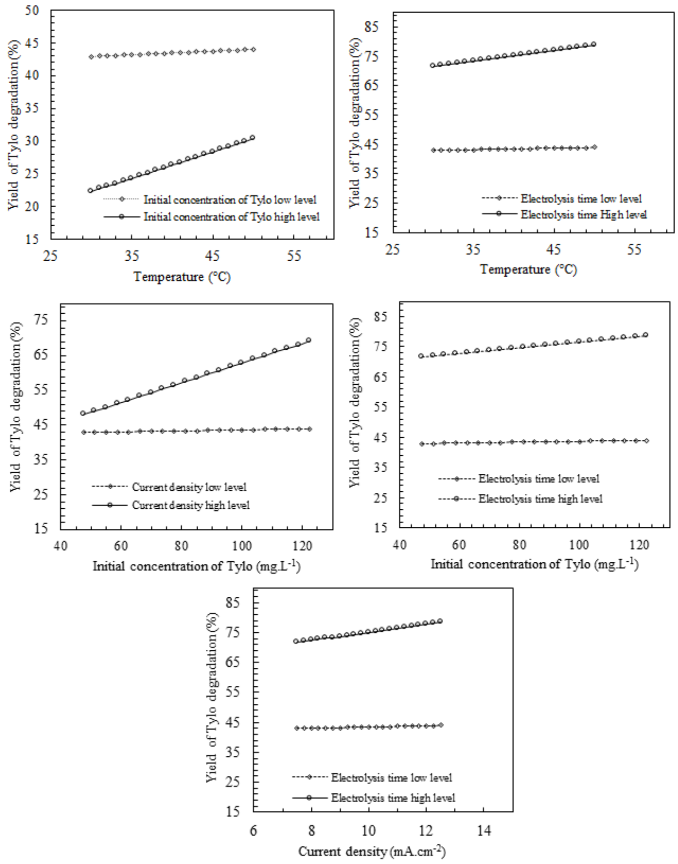

Figure 7. Signifiant interactions graphs.

According to the first order model the following interactions: temperature-initial concentration of Tylo (x_1x_2) temperature-electrolysis time (x_1x_4), initial concentration of Tylo-current density (x_2x_3), initial concentration of Tylo-electrolysis time (x_2x_4), and current density-electrolysis time (x_3x_4) were significant only the interaction between temperature-current density was not significant. All significant interactions found by the model are displayed in Figure 7. According to the interaction graphs, the strongest interaction was between the initial concentration of Tylo and current density (x_2x_3).

B. Optimization conditions for Tylo degradation using CCD methodology

The quadratic model (Eq. (5)) obtained by central composite design (CCD) was used to find the optimal values of the operating parameters giving the highest removal efficiency of Tylo. The response surfaces and contour plots (Fig. 8) were drawn using STATISTICA software. Analysis of these figures clearly indicated that the optimal conditions found for the yield of Tylo degradation were respectively: T= 40°C, C_0 = 10 mg L^{-1}, i= 15 mA.cm^{-2} and t= 70 min. Under these conditions, the obtained Tylosin degradation yield was 97.84 %.

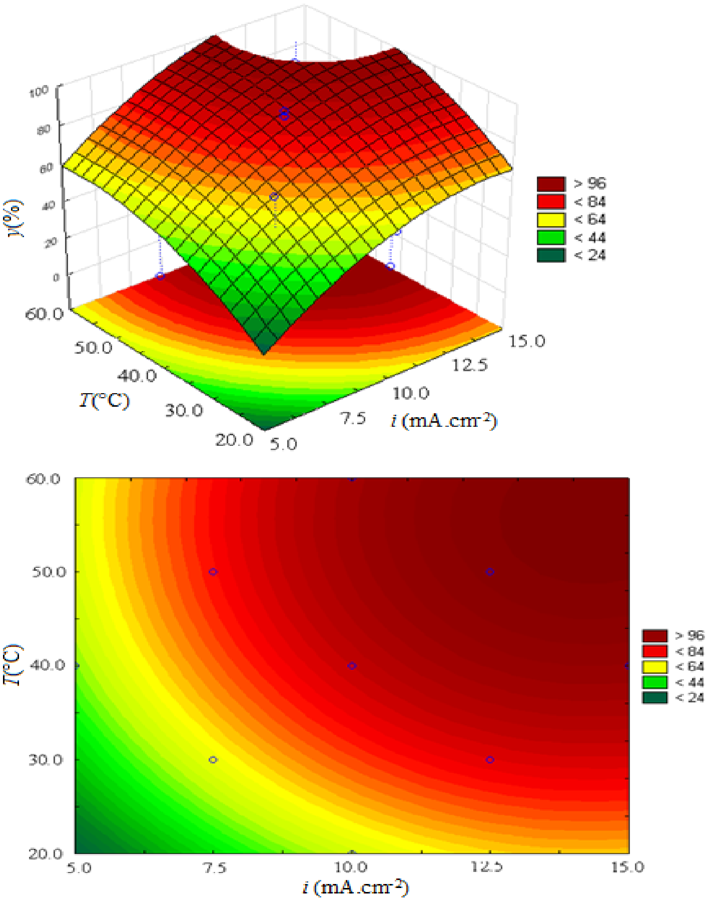

Figure 8. Response surfaces (a) and contour plots (b) showing the effect of temperature (x_1) and current density (x_3) on yield of Tylosin removal (initial Tylosin concentration (C_0=10 mg.L^{-1}) and the electrolysis time (t=70 min)).

To validate the second-order model, an experiment was carried out by choosing a value of each factor (C_0= 10 mg L^{-1}, i= 10 mA cm^{-2}, t= 70 min and T= 40°C)in the contour plots proposed by CCD to reach the predict response (88%). Figure 10 presents the absorption spectra of Tylosin solution before and after EC process. The obtained results revealed that the removal efficiency (89%) was in a good conformity with the predicted values, the difference between the two results was 1 %, which confirms the once again that the model was valid (Figure 9).

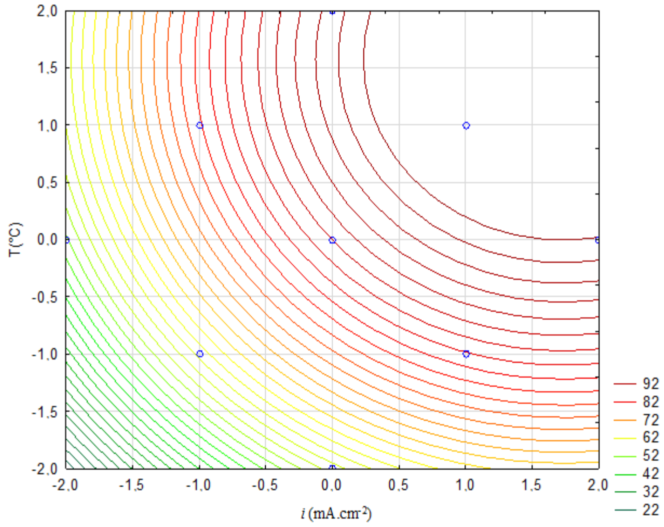

Figure 9. Model validation

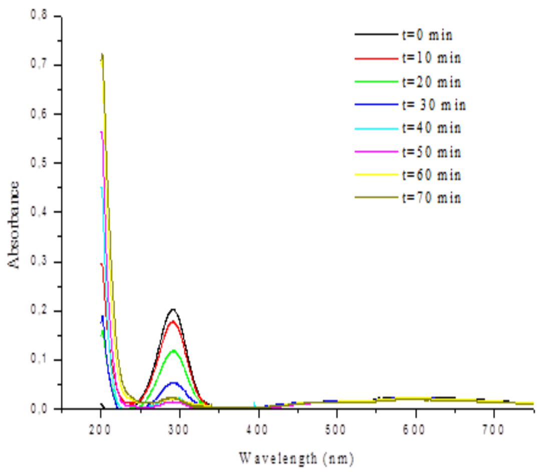

Figure 10. Absorbance spectra of Tylosin before and after electrocoagulation at different electrolysis times: C_0= 10 mg L^{-1}, i= 10 mA cm-², t= 70 min and T= 40°C

V. Conclusion

The degradation of Tylosin by electrocoagulation process was modeled and optimized by full factorial design and central composite design respectively. The results of this work can be summarized as follows:

- In this work, the relationship between four operating factors and degradation yield of tylosin removal was studied. The first order model was developed according to the two levels factorial design to determine the main effects and the interactions of temperature, initial concentration of tylosin, current density and electrolysis time on the reaction yield of tylosin removal. The analysis of these effects permits to state that the most influential factor is the initial Tylo concentration with a negative effect (-12.55), the second in the order is the electrolysis time with an effect of (+12.07), the third is the current density (+3.36) and the fourth is temperature with an effect (+1.83). Interactions: temperature-initial concentration of Tylo (x_1x_2) temperature-electrolysis time (x_1x_4), initial concentration of Tylo-current density (x_2x_3), initial concentration of Tylo-electrolysis time (x_2x_4), and current density-electrolysis time (x_3x_4) were significant, according to the interaction graphs the strongest interaction was only between the initial concentration of Tylo and current density (x_2 x_3).

- A Central Composite Design was found to be suitable for the process optimization of several variables. The CCD regression analysis, response surface and contour plot method were effective in identifying the optimum conditions of tylosin removal yield. The optimal conditions determined by response surfaces and contour plots were: T= 40°C, C_0 = 10 mg.L^{-1}, i= 15 mA.cm^{-2} and t= 70 min.
  To validate the model, an experiment was performed by setting the operational parameters at these optimal values.

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