

OPTIMIZATION OF LEVOFLOXACIN REMOVAL FROM AQUEOUS SOLUTION USING ELECTROCOAGULATION PROCESS BY RESPONSE SURFACE METHODOLOGY

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ABSTRACT

This study was aimed to investigate the response surface methodology (RSM) to evaluate the effects of various experimental conditions on the removal of levofloxacin (LVX) from the aqueous solution by means of electrocoagulation (EC) technique with stainless steel electrodes. The EC process was achieved successfully with the efficiency of LVX removal of 90%. The results obtained from the regression analysis, showed that the data of experiential are better fitted to the polynomial model of second-order with the predicted correlation coefficient (pred. R^2) of 0.723, adjusted correlation coefficient (Adj. R^2) of 0.907 and correlation coefficient values (R^2) of 0.952. This shows that the predicted models and experimental values are in good agreement. The results of the kinetic study showed that the second-order kinetic model was in good agreement with the experimental results and suggested that the mechanism of chemisorption controlled the LVX adsorption. The experimental results indicated that the adsorption of LVX on iron hydroxide flocs follows Sips isotherm with the value of the correlation coefficient (R^2) of 0.937. Sips isotherm shows that both homogenous and heterogeneous adsorption can be occurred.

Keywords: pharmaceuticals, wastewater treatment, stainless steel electrodes, kinetic, isotherm

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الإزالة المثلى لليفوفلوكساسين من المحاليل المائية بطريقة التكتل الكهربائي باستخدام منهجية سطح الاستجابة

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باحث

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المستخلص

الهدف من هذه الدراسة هو استخدام منهجية سطح الاستجابة (RSM) لتقييم تأثير الظروف التجريبية المختلفة على أزاله ليفوفلوكساسين (LVX) من المحاليل المائية عن طريق تقنية التكتل الكهربائي (EC) مع اقطاب الفولاذ المقاوم للصدأ. تم تحقيق عمليه التكتل الكهربائي بنجاح مع كفاءه أزاله 90 %. وفقا للنتائج التي تم الحصول عليها من تحليل الانحدار ، ويبين ان البيانات التجريبية هي أفضل تركيبها للنموذج متعدد الحدود من المرتبة الثانية مع معامل الارتباط المتوقع (R^2 pred.) هو 0.723 ، معامل الارتباط المعدل (R^2 Adj.) هو 0.907 وقيم معامل الارتباط (R^2) هو 0.952. وهذا يدل على ان النماذج المتوقعة والقيم التجريبية هي في اتفاق جيد. وأظهرت نتائج الدراسة الحركية ان النموذج الحركي من المرتبة الثانية كان في اتفاق جيد مع النتائج التجريبية واقترح ان اليه الكيمائية تسيطر على الامتزاز LVX. وأشارت النتائج التجريبية إلى ان الامتزاز من LVX على كتل متلبد من هيدروكسيد الحديد يتبع Sips isotherm مع قيمه معامل الارتباط (R^2) هو 0.937. Sips isotherm يظهر ان كلا الامتزاز متجانسة وغير متجانسة يحدث.

الكلمات المفتاحية: المستحضرات الصيدلانية، معالجة مياه الصرف الصحي، اقطاب الفولاذ المقاوم للصدأ، الحركية، الايسوثرم

INTRODUCTION

The application of fertilizers, pesticides and herbicides for increasing agricultural production lead to major problems: pollution of water resources allotted to agriculture in addition to increasing groundwater pollution, which seemingly stems from activities of agricultural (5). One must take into account the availability of good management to the water (16). Rivers are the most significant natural sources for human life, but it is being contaminated with industrial wastewater, sewage, and other activities of human (3). In addition, the quality of water is affected by nature, such as climate, hydrological and geological, as well as different anthropogenic such as industrial sewage water, municipal discharge and agriculture drainage (1). Although many benefits of pharmaceuticals and higher consumption of human and veterinary medicine may cause the release of wastewater containing compounds of pharmaceuticals from different sources, the release of the accumulated materials and residues, especially antibiotics and their metabolites in water sources. This is a major challenge to the environment and public health (29). Even at low concentrations, pharmaceutical compounds can cause serious environmental damage. These compounds, particularly the antibiotics, affect the quality of soil, surface water, and groundwater. It is necessary to improve certain efficient and cost-effective treatment techniques to remove these contaminants (38). Antibiotics are the greatest pharmaceutical contaminants notice in the aquatic environment (24). Various categories of antibiotics were detected in water sources such as surface water and groundwater, as well as in some conditions in drinking water (24). Fluoroquinolones (FQ_s) is a group of antibiotics pharmaceuticals, which are used generally in the handling of both diseases affecting humans and animals. FQ_s constitute one of the greatest main groups of antibiotics worldwide depending on annual global sales(17). The annual consumption of FQ_s was indicated to be more than 44,000,000 tons worldwide due to use against bacterial diseases (18). Because metabolized FQ_s are incomplete through therapy human or animal, it is discharged from 20-80% of these

compounds in wastewater(34). Studies indicate that the continuous introduction of these contaminants with their metabolites in wastewater and the inefficiency of several traditional sewage treatment plants in their removal may pose possible health risks to humans through drinking water and the food chain (21). Levofloxacin (LVX) is an antibiotic belong to the third generation quinolones. The LVX is consumed widespread and the absence of treatment processes that target these contaminants causing in their diffusion in the aquatic environment(14). LEV is resistant to degradation and typically escapes from traditional wastewater treatment plants. Consequently, a permanent appearance of LEV in wastewater may lead to toxicity and bioaccumulation in the aquatic environment (15). As a result, it was necessary to improve an effective method to remove LEV from wastewater. There are many techniques applied to the removal of antibiotics from wastewater such as ion exchange (33), liquid membrane (2), photo electrocatalytic degradation (22), ozonation (19), photo-Fenton process (8) and adsorption(30). Among these techniques presented, Adsorption is an effective technique used widely to treat low antibiotic concentration. In recent times, antibiotic absorption on absorbent materials depending on metal oxides such as hydroxides of iron and aluminum(9, 31), montmorillonite (6) were reported. This study suggests the electrocoagulation (EC) process to remove LEV from water, which was chosen due to its widespread use, high water solubility, high remaining toxicity and lack of biodegradability. Recently a study has shown that the EC provides an alternative method attractive for water treatment. Aluminum or iron is usually used as an electrode in the electrocoagulation process. The electrocoagulation process is described by easy and simple operated equipment, short process time, low sludge production and no addition of chemicals (32). The main objective of this study is to study the features of the electrocoagulation technique and its effectiveness in the removal of levofloxacin (LVX) from aqueous solutions. The experiment design and response surface methodology (RSM) have been used to

improve the operational conditions of the electrocoagulation to remove LVX.

MATERIALS AND METHODS

Chemicals

Levofloxacin ($C_{18}H_{20}FN_3O_4 \cdot \frac{1}{2}H_2O$, molecular weight 370.38 g/mol) was bought from Julphar Gulf Pharmaceutical Industries. Sodium chloride (NaCl) was used to increase conductivity in the solution. In addition, such as HCl and NaOH was used to adjust the pH. Distilled water was used in all experiments solutions. Electrodes used in the experiments made of stainless steel material.

Experimental setup and procedure

The EC tests were done with 1000 ml of samples in a cylindrical glass cell. The EC processes generally carried out in an electrochemical reactor consisted of an electrolytic cell containing a pair of electrodes: the anode and cathode. The EC experiments were done using stainless steel electrodes with dimensions of 2 mm thickness and 8.5 cm in diameter. It was placed in the electrolytic cell immersed horizontally in the wastewater to be treated and connected to an external power source (digital direct current power supply DC) with voltage in the range of 0–30 V and current in the range of 0–5 A. The solution was agitated mechanically by a magnetic stirrer (Isolab, Germany) at a speed of 120 rpm through runtime. The electrocoagulation reactor used in experiments is shown in **Fig. 1**.

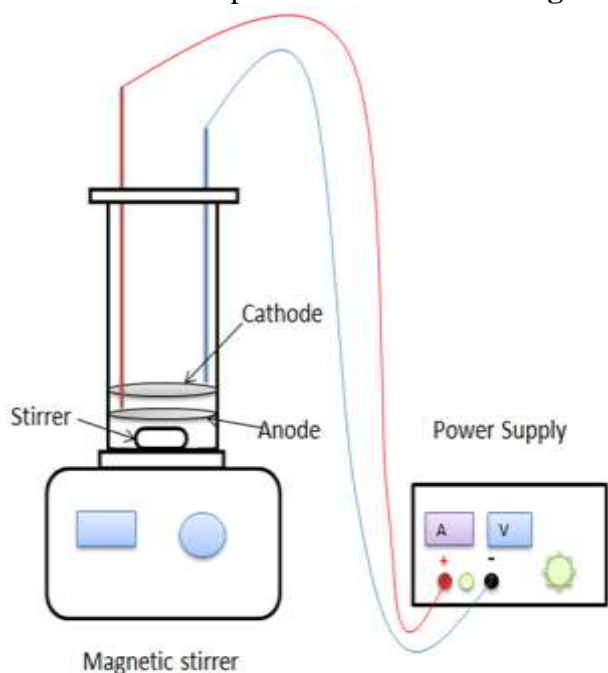


Fig. 1. schematic diagram for the experimental electrocoagulation apparatus

To prepare the electrodes for each experiment they should be washed first with a 0.2 M solution of hydrochloric acid for 2 min and rinse with distilled water and then dried. After each experiment, the same process was applied. The pH of the solution was adjusted by adding 0.01 N of NaOH or 0.01 N of HCl before each experiment and measured by pH meter (WTW, inoLab 720, Germany) laboratory. All experiments were carried out in the batch system. The sample was taken from the EC cell at the end of the runtime and the suspended materials were then allowed to be stable for 30 minutes. The wastewater samples treated were passed through a 0.45 μ m pore size membrane (Whatman, Germany) and then analyzed with a UV-Vis spectrophotometer (Shimadzu UV –1800, Japan) at a wavelength of 293 nm was utilized to determine the amount of LVX remaining. The concentration of LVX was measured from the calibration curve that plotted against absorbance and concentration. The removal efficiency of the levofloxacin was estimated by measuring the concentration before and after the process, according to the following equation:

$$\text{Removal LVX} = \frac{C_0 - C_t}{C_0} 100\% \quad (1)$$

Where C_0 is the initial concentration of LVX (mg/l); C_t is the concentration at any time of LVX (mg/l)

Statistical design

In the present study, central composite design (CCD) was employed to improve the efficiency of LVX removal by means of improving the operational conditions using response surface methodology. Response surface methodology (RSM) was generally applied to optimize experimental conditions. However, the RSM consists of a group of mathematical and statistical techniques for optimizing the process factors and building quadratic models providing the statistical relationship between the variables. The purpose of RSM is to select the optimal experimental conditions of the system or to select which area meets the operating specifications. The CCD was applied to evaluate 4 selected parameters (A: initial LVX concentration, B: pH, C: current density, D: time of electrolysis) on the efficiency of LVX removal and optimizing the operating conditions of the treatment process in

electrocoagulation process. The removal efficiency of the levofloxacin was fitted to an overall function indicating the reaction between independent and dependent variables by means of the second-order polynomial equation. Experimental data from the CCD was examined and fitted to a model of the second-order polynomial which can be represented as below:

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \beta_{ij} X_i X_j \quad (2)$$

Table 1. Operating ranges for each parameter in the electrocoagulation process

Co (mg/L)		CD (mA/cm ²)		pH		t (min)	
(-1)	(+1)	(-1)	(+1)	(-1)	(+1)	(-1)	(+1)
5	100	5	20	3	9	5	60

Co: the initial concentration of LVX, CD: The current density, t: time of electrolysis. Design-Expert version 10.0.2.0 was used for the experimental parameters design and statistical analysis of data in the EC process. The verification of the accuracy value of the adequacy of the model was developed using an analysis of variance (ANOVA).

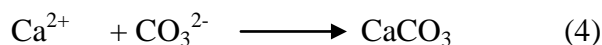
RESULTS AND DISCUSSION

Preliminary assessment of the EC process

Effect of the conductivity: Solution conductivity is an important factor for electrochemical processes. Salt (NaCl) is typically used to increase the conductivity of the wastewater to be treated. It should be noted that the conductivity of wastewater affects the efficiency of removal, cell voltage and energy consumption in the process of electrocoagulation. Furthermore, increasing wastewater conductivity to be treated in the process of EC using NaCl has other advantages, for example, chloride ions could largely reduce the adverse impacts of other

Where Y is the denote of the expected response to remove LVX, β_0 is the intercept parameter, β_i is the linear coefficients, β_{ii} is the quadratic coefficients, β_{ij} is the interaction coefficients, X_i and X_j are the coded values of independent factors (4, 7, 36). Various ranges for each parameter were examined to control the effect of determined parameters on the efficiency of the process to remove LVX. The selection of operating ranges for each parameter can be shown in Table 1.

anions, such as SO_4^{2-} and HCO_3^- . The existence of CO_3^{2-} anions leads to precipitation of Ca^{2+} cations which forms an insulating layer on the cathode surface (Eqs. (3) and (4)) and leads to growing the ohmic resistance of the electrochemical cell (12).



In this study, preliminary studies have been conducted to evaluate the effect of the concentration of salt (NaCl) to remove LVX using electrodes stainless steel. As shown in **Fig. 2**, LVX removal was increased from 64 to 80% by increasing NaCl concentration from 200 to 600 mg/L. This was due to the increase in the concentration of NaCl which led to increase the conductivity of the solutions and as a result, the improve efficiency of LVX removal.

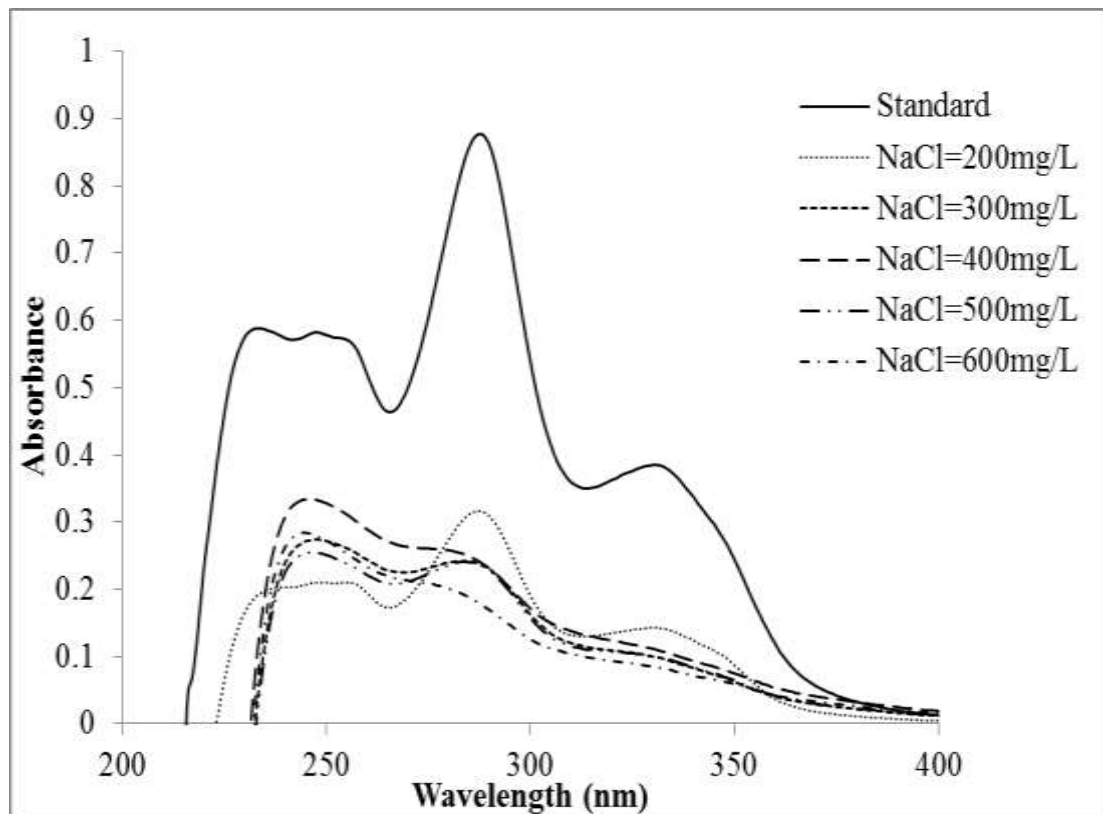


Fig. 2. Effect of the conductivity on the efficiency of LVX removal (Experimental conditions: initial concentration = 10 mg/L, pH = 4, inter-electrode distance = 1.5 cm, time of electrolysis = 30 min, current density = 20 mA.cm⁻²)

Effect of distance between the electrodes

The distance between the electrodes plays an important role in the electrochemical processes as the electrostatic field depends on the spacing between the cathode and the anode. The decline in the ohmic possibility of the electrocoagulation cell is proportional to the inter-electrode distance and furthermore, the spacing between electrodes influences the electrolysis power consumption particularly when wastewater conductivity is low (20). To study the effect of distance between the electrodes on the removal efficiency of the LVX, the distance between electrodes was changed in the range of 0.5 to 3.0 cm and other experimental conditions remained constant. As shown in **Fig. 3**, at the minimum spacing between electrodes, the LVX removal efficiency decreased from 80 to 77% when the spacing between electrodes decreased from 1.5 to 0.5 cm. This is a result of the reality that the iron hydroxides produced in order to work as the flocs and remove the contaminant by

means of precipitation degraded through collision with each other because of high electrostatic attraction(13). The contaminant removal efficiency increased by increasing the spacing between electrodes from the minimum until the optimal spacing. Because by increasing the spacing between electrodes, a reduction in electrostatic effects can be occurred that slow the movement of the ions generated. This provides additional time for the metal hydroxide generated to form flocs which leads to an increase in the removal efficiency of contaminants from the solution (20). The removal efficiency was decreased from 80 to 69% by increasing the distance between the electrodes from 1.5 to 3.0 cm, because when the distance between the electrodes increases, the ion transmission path increases. This leads to a reduction in the electrostatic attraction which led to the formation of less than the quantity required flocs to remove contaminants (20).

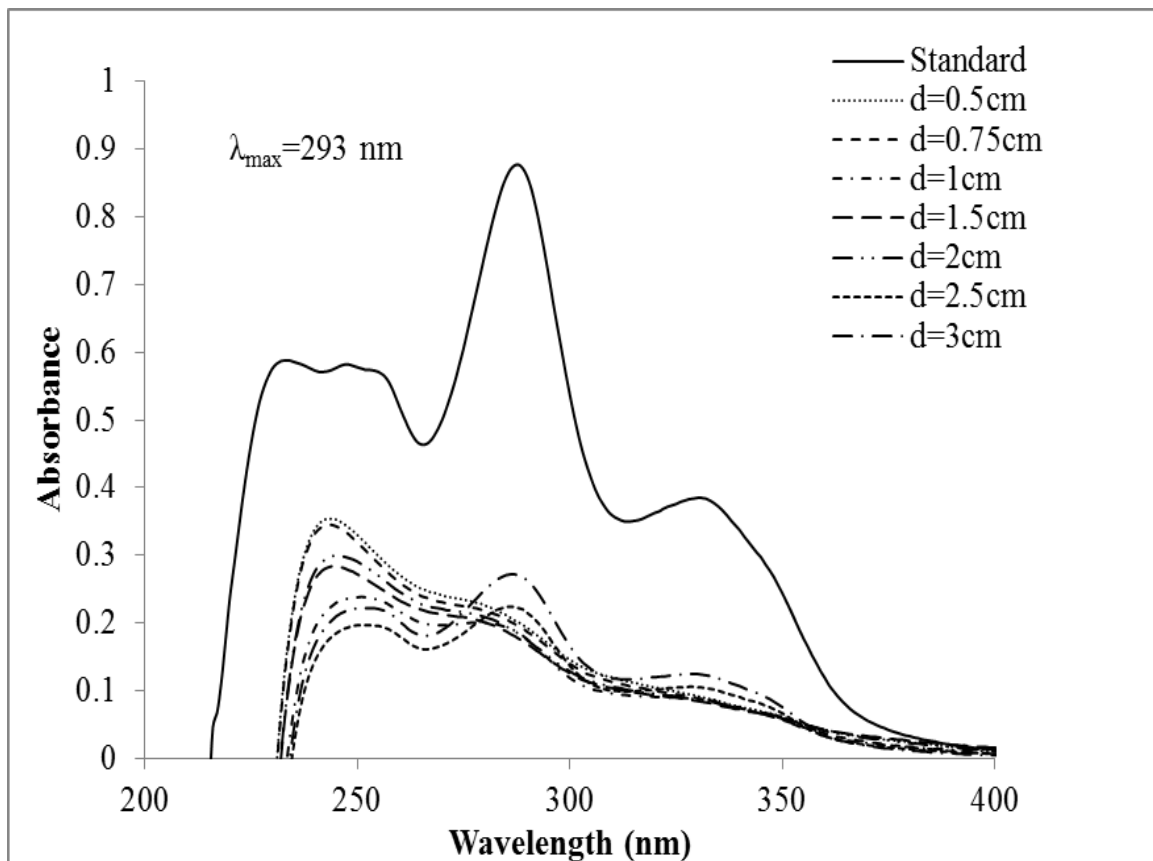


Fig. 3. Effect of inter-electrode distance on the efficiency of LVX removal (Experimental conditions: initial concentration = 10 mg/L, pH = 4, time of electrolysis = 30min, current density = 20 mA.cm⁻², NaCl = 500m g/L)

The experimental conditions are summarized along with the results obtained from 30 experiments according to the design of the response surface methodology (RSM) in Table 2. As shown in Table 2, the removal efficiency of LVX was changed from 50 % to 90 %.

Fitting of the model and statistical analysis

Thirty experiments designed by RSM were conducted to evaluate the simple and combined effects of the four main parameters including, initial pH of the solution, initial LVX concentration, time of electrolysis and current density on the efficiency of LVX removal and optimizing the operating conditions of the EC process. The obtained results were fitted to the model of quadratic in

order to determine a mathematical relationship between the applied factors and the observed response. The developed RSM model equation is expressed as below:=

$$\begin{aligned} \text{Removal (\%)} = & 106.077 + 0.912A - \\ & 21.113B - 0.473C + 0.523D - \\ & 0.054AB - 0.02AC - 2.4 \times 10^{-4}AD + \\ & 0.184BC - 0.043BD + 0.016CD - \\ & 0.004A^2 + 1.483B^2 + 0.016C^2 - 3.78 \times \\ & 10^{-3}D^2 \end{aligned} \quad (5)$$

Where A: initial LVX concentration, B: initial pH of the solution, C: current density, D: time of electrolysis. The suitability of the model was verified and summarized the experimental results obtained in Table 3

Table 2. Experimental conditions of four parameters in the CCD matrix and results of LVX removal obtained in the experiments

Run	Actual values				Removal (%) (experimental)	Removal (%) (predict)	Error
	C ₀ (mg.L ⁻¹)	pH	CD (mA.cm ⁻²)	Time (min)			
1	52.5	5	12.5	5	53	57.55	4.55
2	80.13	6.16	16.9	16.5	51	49.15	-1.9
3	24.87	6.16	8.14	16.5	50	51.59	1.59
4	24.87	3.84	8.14	48.5	71.85	75.11	3.26
5	52.5	5	12.5	32.5	66	67.2	1.2
6	24.87	6.16	8.14	48.5	53.75	55.86	2.11
7	52.5	5	20	32.5	69.6	70.35	0.75
8	80.13	3.84	8.14	48.5	80	81.81	1.81
9	80.13	6.16	8.14	48.5	57.37	55.61	-1.8
10	80.13	3.84	8.14	16.5	73.82	74.76	0.94
11	52.5	5	12.5	60	75.8	71.12	-4.7
12	80.13	6.16	8.14	16.5	52.85	51.76	-1.1
13	24.87	3.84	16.9	48.5	82	82.96	0.96
14	52.5	5	12.5	32.5	67	67.2	0.2
15	52.5	5	12.5	32.5	67.49	67.2	-0.3
16	24.87	6.16	16.9	48.5	67	67.36	0.36
17	24.87	3.84	16.9	16.5	68	71.02	3.02
18	80.13	3.84	16.9	48.5	80	80.01	0.01
19	52.5	5	5	32.5	66.77	65.85	-0.9
20	52.5	5	12.5	32.5	67.5	67.2	-0.3
21	5	5	12.5	32.5	62	59.64	-2.4
22	52.5	5	12.5	32.5	66.5	67.2	0.7
23	80.13	6.16	16.9	48.5	53	57.46	4.46
24	52.5	3	12.5	32.5	90	89.7	-0.3
25	24.87	3.84	8.14	16.5	72	67.64	-4.4
26	52.5	5	12.5	32.5	67	67.2	0.2
27	52.5	7	12.5	32.5	56.38	56.53	0.15
28	80.13	3.84	16.9	16.5	70.64	68.49	-2.2
29	24.87	6.16	16.9	16.5	60.75	58.62	-2.1
30	100	5	12.5	32.5	55	57.25	2.25

Table 3. ANOVA results for response surface of quadratic model

Response	Source	Analysis of variance				
		Sum of square	degree freedom	Mean square	F-value	P-value Prob>F
LVX removal (%)	Model	2830.35	14	202.17	21.31	< 0.0001
	Residual	142.29	15	9.49	-	-
	Lack of Fit	140.56	10	14.06	40.55	0.0004
	Pure Error	1.73	5	0.35	-	-

According to obtained results in Table 3, the ANOVA analysis indicates that the model of quadratic was significant with a confidence level of 95% and F-value of 21.31. The observed P-value probability was less than 0.05 indicate model terms are significant. According to the results obtained from the regression analysis, the data of experiential are better fitted to the polynomial model of

second-order with the predicted correlation coefficient (pred. R²) of 0.7235, adjusted correlation coefficient (Adj. R²) of 0.9075 and correlation coefficient values (R²) of 0.9521. The difference between the value of Adjusted R² and Predicted R² is less than 0.2, this shows that the predicted models and experimental values are in good agreement. Additionally, the amount of 18.68 for adequate precision is

greater than 4 which shows an adequate indicator to noise ratio.

Effect of parameters

Effect of initial concentration

Mass transfer of solutes between solid and aqueous phase is depends on the initial concentration, which gives a great driving force to overcome all resistance of solutes (38). The results of the study revealed that the increase in the initial concentration of the LVX pollutants led to a decline in the removal efficiency of LVX. As shown in **Fig. 4**, at the center point of important working parameters mentioned, including 42 min reaction time, 3.84 pH and 16.27 mA.cm⁻² current density, the removal efficiency of LVX increasing

from 60% to 80% by decreasing its concentration from 80.13 to 24.86 mg.L⁻¹. This is because of the fact that the amount of iron hydroxide flocs produced may not be enough to adsorption for the greater amount of contaminant particles at higher initial LVX concentrations. According to the law of Faraday, the metal hydroxide flocs formed during a certain period of time stay constant for different concentrations of LVX at a constant current density. However, the metal hydroxide flocs requirements are more important to concentration high LVX, and as a result, the amount of flocs becomes not enough to capture the quantities additional of LVX (4).

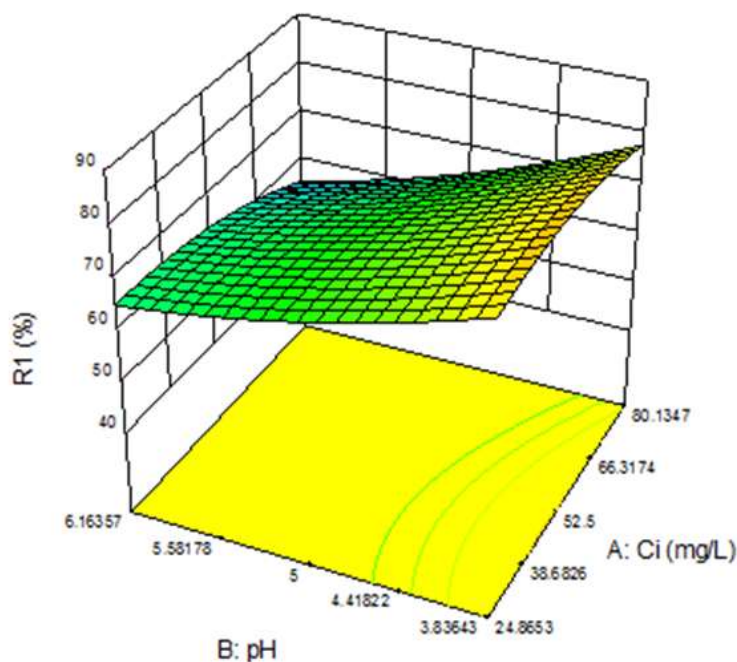


Fig. 4. Effect of initial LVX concentration on the efficiency of LVX removal

Effect of pH: The value of pH has been proven to be one of the important parameters affecting the effectiveness of the electrochemical processes, especially on the efficiency of the EC process (28). To study this effect, the initial pH value of the solution was taken within a range of 3 to 9. The solution of LVX was adjusted to the required pH for each run by adding certain concentrations of sodium hydroxide. The effect of the pH value on the efficiency of LVX removal during the electrocoagulation process was illustrated in **Fig. 5**. The results

obtained showed that decreasing the pH of the solution led to improve the efficiency of removing of pollutants and the optimum efficiency of removal was noticed at a pH value of 3.84. The efficiency of LVX removal decreases by either reducing or increasing the pH in the solution from the optimal pH. The results obtained revealed that at high value of pH conditions, metal hydroxide which is the hydrolysis products of Fe³⁺ are soluble, and thus they are not able to absorb contaminants. [Fe(OH)₂]⁺ and Fe(OH)₃ are the leading type of hydrolysis reactions(25).

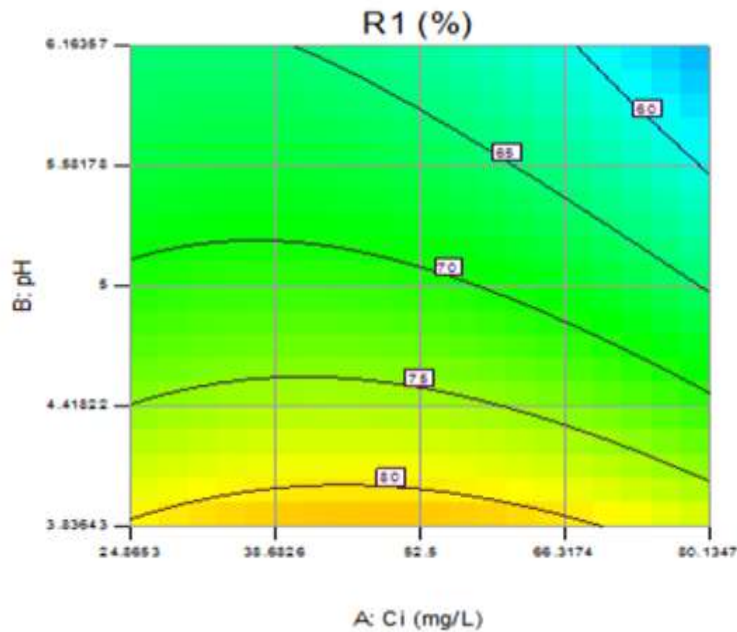


Fig. 5. Effect of pH on the efficiency of LVX removal

Effect of the current density

The current density (CD) is a significant factor to control the rate of reaction within the reactor, in all electrochemical processes. It is known that the CD controls the rate of bubble generation and the production rate of coagulant which influences the growth of flocs (23). To study the influence of current density on the removal efficiency of LVX, the EC process was conducted using different current densities from 5 to 20 mA.cm⁻². According to the results presented in **Fig.6**, the efficiency of LVX removal was increased from 76% to 82% by increasing the current density from 8.136 to

16.86 mA.cm⁻² at the center point of important working parameters mentioned, including 3.84 pH, 42 min reaction time and 42.79 mg.L⁻¹ LVX concentrations. The current density showed a strong impact on the electrocoagulation process, particularly on shortened treatment time and the kinetics of removal. Increase the current density impacts the anodic dissolution amount and this gives a more amount of precipitate to remove contaminants. Furthermore, the rate of bubble produced increases with an increase in the current density that is useful to remove contaminants through H₂ flotation (7).

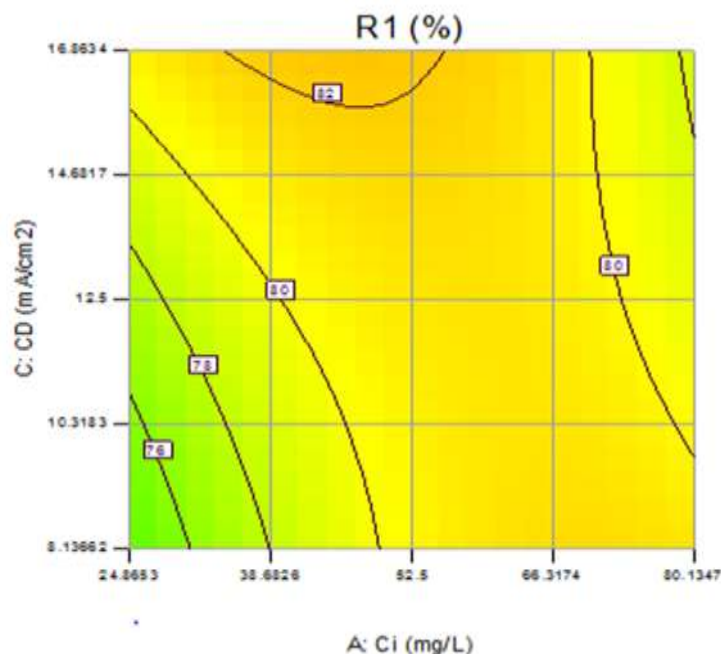


Fig. 6. Effect of current density on the efficiency of LVX removal

Effect of reaction time

The time of electrolysis (t) affects the efficiency of the treatment in the electrochemical processes (11). The time of electrolysis determines the production rate of Fe^{3+} or Fe^{2+} ions from iron electrodes (11). To study the effect of reaction time on the removal efficiency of LVX, the EC process was conducted using different periods from 5 to 60 min. As shown in **Fig.7**, the efficiency of LVX removal was increased from 70% to 80% by increasing the time of electrolysis from 16.5 to 48.5 min at the center point of important working parameters mentioned, including 42.79 mg.L^{-1} LVX concentration,

3.836 pH and 16.27 mA.cm^{-2} current density. Based on Faraday's law (Eq. 6), by an increase in the electrolysis time and current density, the rate of anode dissolution is rise that will raise Fe^{2+} dose produced from anode causing a more amount of precipitate to remove contaminants:

$$\text{ELC} = \frac{ItM}{zF} \quad (6)$$

Where ELC, z, F, I, t, and M are the amount of electrode consumption (g), the electron number, Faraday's constant ($96,485 \text{ C/mol}$), the current in (amp), the reaction time in (sec), and the molecular weight of the electrode used (g/mol), respectively(35).

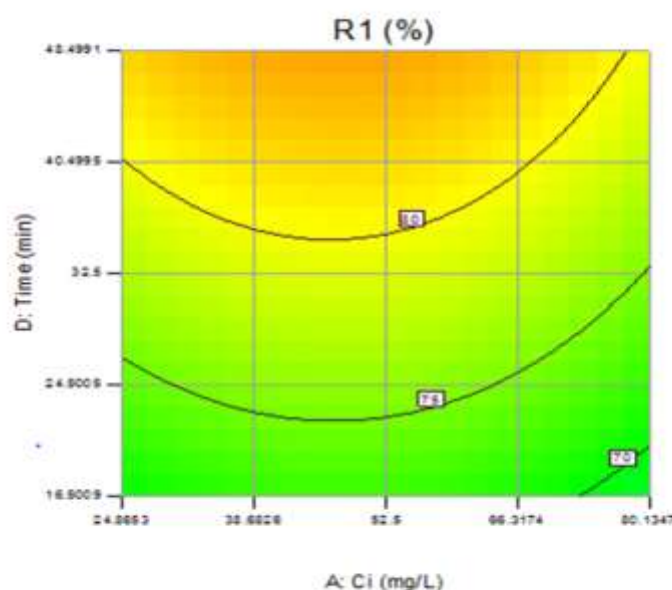


Fig. 7. Effect of electrolysis time on the efficiency of LVX removal

Kinetics and isotherms

The contaminant is usually adsorbed at the flocs surface that electrochemically produced, after two sequential separate processes: (i) the metal flocs are generated through the electrochemical process; (ii) followed by a process of physic-chemical, namely adsorption on the flocs surface. The pollutant removal is comparable to traditional adsorption except for the coagulants generation. It can be possible to estimate the electrode consumption according to the law of Faraday and the flocs amount produced which can be stoichiometrically evaluated. The iron flocs are present in the solution to remove the contaminants formed by way of adsorption mechanism. From this, the removal of pollutants can be modeled such that the adsorption phenomena and adsorbed

pollutant amount estimates according to (Eq. 7).

$$q_t = \frac{(C_o - C_t)V}{M} \quad (7)$$

Where:

q_t is the amount of levofloxacin (LVX) adsorbed per gram of medium (mg/g), C_o is the initial concentration of LVX (mg/l), C_t is the concentration at any time of LVX (mg/l), M is the weight of electrode dissolution (g), V is the volume of solution (L). To study the mechanisms of the LVX adsorption process, the obtained experimental results were fitted to Freundlich, Langmuir, Sips, Temkin and Toth isotherm(10).

Kinetic modeling: The study of adsorption kinetics is significant in order to give valuable importance to the reaction pathway and the suitable absorption mechanism. The

adsorption mechanism is depends on the physical and chemical characteristics of adsorption in addition to the process of the mass transfer. The LVX absorption dynamics on iron hydroxide flocs at the optimum conditions were investigated with respect to various initial LVX concentrations, by means

of kinetic models: first order models, second order models, and pseudo first order models. The parameters of kinetic models were illustrated and calculated in **Table 4**. Regression correlation coefficient values (R^2) concluded that LVX adsorption followed the second order kinetic model.

Table 4. Kinetic parameters to remove the LVX in optimum conditions for the EC process

Model	Equation	Parameter	Reference	
First-order kinetics	$C_{(t)} = C_0 e^{-K_1 t}$ (8)	Co(mg/L)	$K_1(\text{min}^{-1})$	R^2 (27)
		5	0.032	0.045
		10	0.05	0.245
		20	0.053	0.23
		30	0.045	0.292
Second-order kinetics	$\frac{1}{C_{(t)}} = \frac{1}{C_0} + k_2 t$ (9)	Co(mg/L)	$K^2((\text{mg/L})^{-1} \cdot \text{min}^{-1})$	R^2 (27)
		5	0.0095	0.873
		10	0.015	0.985
		20	0.008	0.985
		30	0.0037	0.977
Pseudo-first-order kinetics	$C_{(t)} = C_e + (C_0 - C_e)e^{-k_{app} t}$ (10)	Co(mg/L)	$K_{app}(\text{min}^{-1})$	R^2 (27)
		5	0.098	0.868
		10	0.1	0.707
		20	0.107	0.754
		30	0.095	0.774
50	0.092	0.874		

K_1 is the constant of first order kinetics (min^{-1}), K_2 is the constant of second order kinetics ($(\text{mg/L})^{-1}, \text{min}^{-1}$), k_{app} is the apparent pseudo first-order rate constant (min^{-1}), R^2 is the correlation coefficient.

Isotherm modeling

During the EC process, the iron hydroxide flocs as the adsorbent were formed. The investigated of the absorption of pollutants on a surface of the iron hydroxides produced using five adsorption isotherm namely Langmuir, Freundlich, Sips, Temkin, and Toth models. Isotherm of adsorption can be employed to assess the adsorption capacity of adsorbent and obtain an insight into the

response of adsorbent and adsorbate. The model with the best suitable correlation to the equilibrium curve can provide valuable information about the mechanism of adsorption. The adsorption experiments were conducted at five various initial LVX concentrations of 5, 10, 20, 30 and 50 mg/L in optimal conditions and the equilibrium were obtained. The obtained experimental results can be seen in **Fig. 8**.

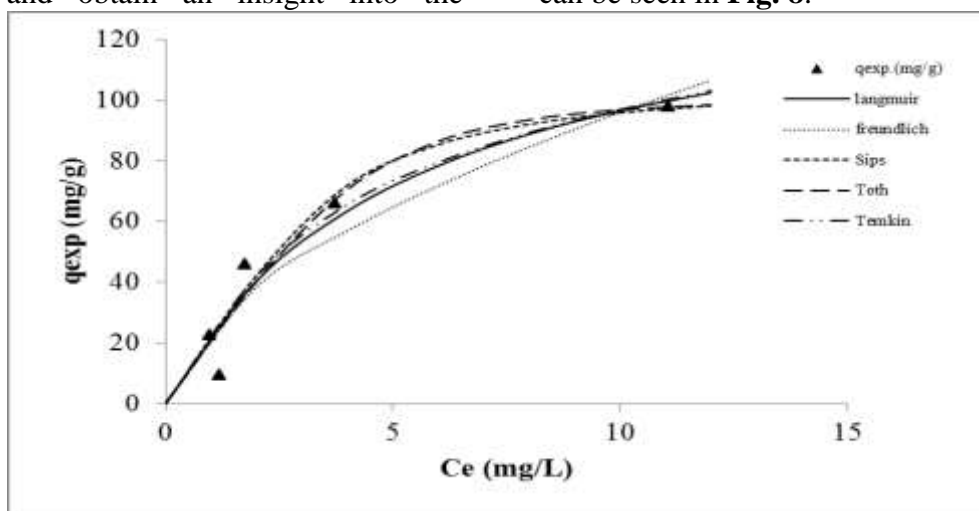


Fig. 8. Isothermal fits for EC removal of Levofloxacin: Freundlich, Langmuir, Toth, Temkin and Sips isotherm (C_e (mg/L) and q_{exp} (mg/g) is the equilibrium concentration of LVX and equilibrium adsorption capacity, respectively.)

The correlation coefficient (R^2) and the constants related to the isotherms were calculated and illustrated in Table 5.

Table 5. The calculations of Adsorption isotherms for the removal of Levofloxacin in an optimized electrocoagulation process conditions

Model	Equation	Parameters	Reference
Freundlich	$q_e = K_f C_e^{1/n}$ (11)	K_f (mg/g)(mg/l) ^{1/nf}	25.84
		n	1.754
		R^2	0.873
Langmuir	$q_e = \frac{q_m b C_e}{1 + b C_e}$ (12)	q_{max} (mg/g)	147.91
		b (l/mg)	0.188
		R^2	0.913
Sips	$q_e = \frac{k_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}}$ (13)	K_s	21.79
		β_s	1.691
		a_s	0.207
Toth	$q_e = \frac{q_m C_e}{(b + C_e^m)^{1/m}}$ (14)	R^2	0.937
		q_{max} (mg/g)	101.1
		b	90.7
		m	2.838
Temkin	$q_e = B \ln A_T + B \ln C_e$ (15)	R^2	0.93
		B (J/mol)	34.107
		A_T (L/g)	1.71
		$B = \frac{RT}{b}$ (16)	0.931

It seems from the table 5, that all these adsorption isotherm models can describe effectively experimental results due to their correlation coefficient (R^2) more than 0.873. However, depending on the greatest correlation coefficient values which revealed that the adsorption levofloxacin by the metal hydroxide flocs agrees well Sips isotherm model with a correlation coefficient of 0.937. Sips isotherm shows that both homogenous and heterogeneous adsorption occurs.

CONCLUSION

The present work was an effective step to enhance our knowledge about the removal of LVX using the EC technique with stainless steel electrodes. The purpose of this study was to investigate the influence of independent parameters on the removal efficiency of LVX from the aqueous solution using electrocoagulation technique. The experiential design was executed depending on CCD with response surface methodology. Response surface methodology was employed to evaluate the effect of independent variables on the efficiency of LVX removal and achieve their optimum condition. The obtained experimental results indicated that response surface methodology was an appropriate means to improve the operating conditions of the electrocoagulation process to remove the LVX. ANOVA revealed a high correlation

coefficient (R^2) of 0.9521, which indicates an acceptable modification of the model of second-order regression with the obtained results. The electrocoagulation process was achieved successfully with the efficiency of LVX removal of 82.5% under the optimum experimental conditions of the current density of 16.27 mA.cm⁻², inter-electrode distance 1.5 cm, pH value 3.836, reaction time 42 min, and initial LVX concentration of 42.79 mg.L⁻¹ and NaCl concentration of 500 mg.L⁻¹. The results of the kinetic study showed that the second-order kinetic model was in good agreement with the experimental results and suggested that the mechanism of chemisorption controlled the LVX adsorption. The experimental results indicated that the adsorption of LVX on iron hydroxide flocs follows Sips isotherm with the value of the correlation coefficient (R^2) of 0.937. Sips isotherm shows that both homogenous and heterogeneous adsorption occurs. Finally, the electrocoagulation process used in this work provided a sensitive, fast and dependable technique for LVX removal.

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