

Removal of Lead from Water by Electrocoagulation Applying Response Surface Method (RSM) in A Uniquely Designed Rector

Ulker Bakir Ogutveren, Umran Tezcan Un, and Nihal Erginel

Abstract—Lead is highly harmful to living organisms even in very low concentration. Lead exposure in humans can have severe neurological and physiological repercussions. The objective of this study is treatment of lead from water by electrocoagulation using iron electrodes applying RSM in an uniquely designed reactor. The evaluation of the main and interaction effects of process variables such as current density, initial lead concentration, pH and Na₂SO₄ concentration as a supporting electrolyte on the removal efficiency of lead were analyzed applying RSM. The levels of the factors were determined with variance analysis and found to be 10-50 mAcm⁻² with the increments of 10 units for current density, 50-250 mgL⁻¹ with the increments of 50 units for initial lead concentration, 3-7 with the increments of 1 units for pH and 0.01-0.09 molL⁻¹ with the increments of 0.02 units for Na₂SO₄ concentration.

As a result of study, it was found that current density has a linear effect while current density and initial pH have quadratic effects on the removal efficiency. Lead removal efficiency reach a maximum value of 98.76% when the current density was 40 mA/cm² and initial pH was 4.7.

Index Terms—Electrocoagulation, iron electrode, lead removal, response surface method.

I. INTRODUCTION

The global industrial revolution has led to an unprecedented dissemination of toxic substances in the environment. Exposure to these pollutants especially through dietary intake of plant-derived food and beverages, drinking water, or air can have long-term effects on human health [1]. For example, long-term exposure to lead in humans can cause acute or chronic damage to the nervous system, while long-term exposure of cadmium in humans is associated with renal dysfunction and obstructive lung disease and has also been linked to lung cancer and damage to human's respiratory systems [2].

Different industrial wastes, particularly such as those from mining, electro-plating, lead smelting and metal-finishing industries, waste storage and treatment, chemical manufacturers, etc., discharge significant amounts of heavy

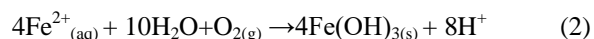
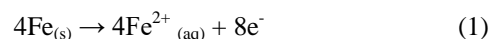
metals both in elemental and compound (organic and inorganic) forms. Since heavy metals cannot be degraded or destroyed, they persist in the environment. These metals are lead (Pb), copper (Cu), tin (Sn), silver (Ag), nickel (Ni), chrome (Cr), mercury (Hg), cadmium (Cd), iron (Fe), cobalt (Co), arsenic (As).

Lead is of particular interest because of its toxicity and its widespread presence in the environment. Lead is used in accumulator and battery production and is one of the most toxic metals besides Cd (cadmium) and Hg (mercury). Maximum allowable dosages are 0.00003 mg/L for mercury, 0.01 mg/L for cadmium and 0.006 mg/L for lead. Lead is highly harmful to living organisms even in very low concentration. Lead exposure in humans can have severe neurological and physiological repercussions. Because these symptoms may occur slowly, lead poisoning can be easily overlooked [3].

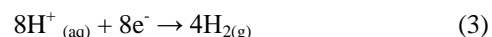
Removal of lead from industrial processes can be classified into several categories. Some of the most effective methods to remove lead from contaminated water are precipitation, stabilization, ion exchange, and adsorption. Electrocoagulation is an emergent technology and has proven its viability by removing a wide range of pollutants.

Electrocoagulation introduces metal cations in situ, electrochemically, using sacrificial anodes like aluminum or iron inside a reactor. Oxidation of iron in an electrolytic system produces iron hydroxide, Fe(OH)_n, where n=2 or 3, which are highly charged coagulants adsorbing pollutants and forming insoluble floc particles. According to Mollah et al., two mechanisms have been proposed for the production of Fe(OH)_n; one of them was shown in reactions 1-4 and more details have been given elsewhere [4].

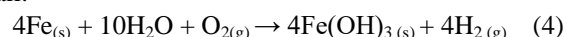
Anode:



Cathode:



Overall:



The advantages of electrocoagulation include high particulate removal efficiency, a compact treatment facility, relatively low cost, does not require supplementary addition of chemicals, reduces the volume of produced sludge and the possibility of complete automation [5].

In this study, the effect of different factors including current density, initial lead concentration, pH and Na₂SO₄

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concentration on removal of lead from wastewater by electrocoagulation. A uniquely designed four blade impeller iron anode was used in batch mode. This paper reports on significant outcomes of the configuration and evaluates the effect of operating factors on removal efficiency of the process. An empirical model, in terms of effective operational factors was developed through Response Surface Methodology, and an optimization of operational conditions was conducted.

II. MATERIAL AND METHODS

A. Experimental Set-Up

As a stock solution lead (II) nitrate $[\text{Pb}(\text{NO}_3)_2]$ (Merck) was prepared with 1000 ppm concentration. Before the experiments, stock solution was diluted to desired concentration with 500 mL volume. pH was adjusted to acidic level using 2N H_2SO_4 .

EC Apparatus included three parts; DC Power supply (Statron 2257), iron special designed anode as a stirrer and iron cylindrical cathode. An iron impeller blades with holes was used as anode. It had 4 blades of height 7cm, width 3.5 cm and the thickness of the blade was 0.5cm. Anode surface area with 14 holes of 1.2 cm diameter was 94 cm^2 . Cathode was an iron cylinder of 10.3 cm in diameter and 10 cm at the height. Experimental set up is shown in Fig. 1. Solution was poured into cathode and stirrer was dipped into solution with 2 cm height from the bottom.

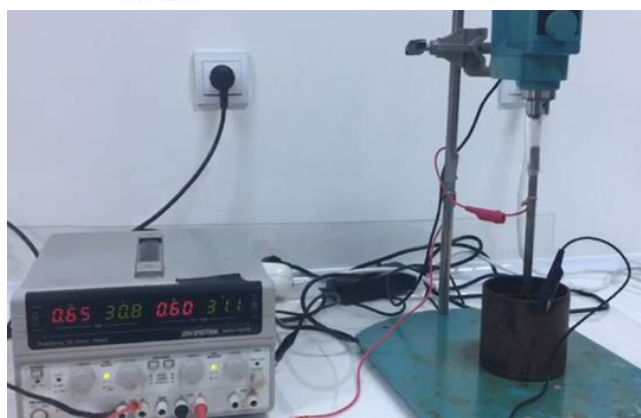
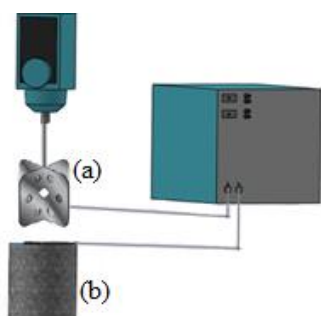


Fig. 1. EC Apparatus; (a) anode, (b) cathode.

Experiments were run 40 minutes with 50 rpm stirring speed. Temperature, pH and voltage were not controlled but just monitored. 5 mL of samples were taken with 10 minutes interval. All samples were filtered with blue band filter paper (Whatman), then final pH of the samples were adjusted to pH 3 before analytical analysis. Lead concentration of solution was determined using Atomic Absorption Spectrophotometer

(Varian SpectrAA 250 Plus).

The removal efficiency (RE%) after EC was calculated using equation (5)

$$RE\% = \left(\frac{C_0 - C}{C_0} \right) \times 100 \quad (5)$$

where C_0 and C are the concentrations of Pb before and after EC process, respectively in ppm.

All samples were analyzed in duplicate to ensure data reproducibility, and an additional measurement was carried out, if necessary

B. Response Surface Method

Response surface method (RSM) is a useful statistical technique for modeling and analyzing to research the influence of factors with many levels. When the effects of some parameters on the system performance were investigated the other parameters were kept constant in conventional experimental design methods. Thus effects of different parameters cannot be investigated at the same time in such systems. On the other hand, in RSM the effects of all parameters on the system performance can be investigated simultaneously. Therefore, this bring about some advantages such as decreasing the number of experiments, saving time and cost and using the natural sources effectively [6].

RSM, is capable of determining the interaction between the parameters, and which one is dominant in this interactivity and in the method [7]. Also RSM is an inevitable technique to show both linear and nonlinear relationships between independence variable named factors and response by setting a model that include linear and square terms, and interaction terms which represent the effects of two independent variables at the same time. RSM is used to determine the best combination and levels of factors that response near the optimum.

If there is curvature in the system, then a polynomial of higher degree must be used for two independent variables, such as the second-order model [8]. An example was given in equation (6).

$$\hat{y} = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i < j} \sum \beta_{ij} x_i x_j + \varepsilon \quad (6)$$

where \hat{y} is the estimated response, β_0 is the constant, β_i is the regression coefficient of i . independent variables, β_{ii} shows the regression coefficient of i . independent variables' quadratic effects, β_{ij} represents the coefficient of two-way interaction between i . and j . independent variable and ε is the error term.

In this study, Central Composite Design, the type of RSM, is implemented was used for the design of experiments and MINITAB 17.0 method was applied for evaluating experimental data. Variable factors as effective parameters were selected as current density, pH, initial Pb concentration and amount of Na_2SO_4 to be added and be assigned X_1, X_2, X_3 and X_4 respectively with coded value of levels as: -2, -1, 0, 1, 2. Five different levels of X_1 : 10, 20, 30, 40, 50 mAcm^{-2} ; X_2 : 3, 4, 5, 6, 7; X_3 : 50, 100, 150, 200, 250 mgL^{-1} X_4 : 0.01,

0.03, 0.05, 0.07 and 0.09 M Na₂SO₄. These values can be seen in Table I. The central composite design with four factors and two replications are used as experimental design.

TABLE I: VARIABLES AND THEIR CODED VALUES

Factor	Original Factor (X)	Factor Code				
		-2	-1	0	1	2
Current Density (mA/cm ²)	X ₁	10	20	30	40	50
Initial pH	X ₂	3	4	5	6	7
Initial Pb concentration (mg/L)	X ₃	50	100	150	200	250
Addition of Na ₂ SO ₄ (M)	X ₄	0.01	0.03	0.05	0.07	0.09

III. RESULTS AND DISCUSSION

In this study the effect of process variables such as current density, initial lead concentration, pH and Na₂SO₄ concentration as a supporting electrolyte on the removal efficiency of lead were analyzed applying RSM. Current density and initial pH are an important operating factor influencing the performance of the EC process. While current density determines the coagulant dosage rate in electrocoagulation performance, pH determines the intermediates and the pathway of the reaction. Additionally, the solution conductivity plays a significant role during the electrocoagulation process. In this study Na₂SO₄ was used as a supporting electrolyte to increase solution conductivity and to reduce the electrical energy consumption of the electrocoagulation.

TABLE II: ANOVA TABLE FOR REMOVAL OF LEAD

Analysis of Variance						
Source	DF	Adj SS	Adj MS	F-Value	P-Value	
Model	14	252,117	18,008	13,21	0,000	
Linear	4	186,955	46,739	34,29	0,000	
A	1	175,989	175,989	129,11	0,000	
B	1	4,148	4,148	3,04	0,089	
C	1	2,857	2,857	2,10	0,156	
D	1	3,962	3,962	2,91	0,096	
Square	4	58,082	14,521	10,65	0,000	
A*A	1	31,867	31,867	23,38	0,000	
B*B	1	7,678	7,678	5,63	0,023	
C*C	1	5,631	5,631	4,13	0,051	
D*D	1	0,040	0,040	0,03	0,866	
2-Way Interaction	6	7,080	1,180	0,87	0,529	
A*B	1	1,284	1,284	0,94	0,338	
A*C	1	2,426	2,426	1,78	0,190	
A*D	1	0,342	0,342	0,25	0,619	
B*C	1	0,112	0,112	0,08	0,776	
B*D	1	2,200	2,200	1,61	0,211	
C*D	1	0,717	0,717	0,53	0,473	
Error	39	53,159	1,363			
Lack-of-Fit	10	44,913	4,491	15,80	0,000	
Pure Error	29	8,246	0,284			
Total	53	305,276				

In Table II, A: Current Density, B: Initial pH; C: Initial Pb concentration; D: Addition of Na₂SO₄ (M)

Experiments were conducted in random order with two

replications having 27 experiments in each replication and percentage removal of lead was obtained. The ANOVA (Analysis of variance) was carried for three hypothesis having four variable factors. In the first hypothesis the mean level of factors was maintained equal followed by hypothesis with mean levels differing from each other (at least one of them will differ from rest) and the last hypothesis was focused on studying the variable interaction effects on the response. The simulations were carried using MINITAB 17.0 statistical software and results are tabulated in Table II. From Table II on removal of lead it can be observed that the both linear and square terms are affected because their p-value is smaller than significant level- α (p-value < 0.05).

Due to the interaction terms were found unaffected on response, also initial lead and Na₂SO₄ concentrations, these unaffected terms are removed from ANOVA table. The Final ANOVA table that include the linear and square terms of the current density and pH were effecting the response are handled like in Table III.

TABLE III: FINAL ANOVA TABLE FOR REMOVAL OF LEAD

Analysis of Variance					
Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	4	231,485	57,871	38,43	0,000
Linear	2	180,136	90,068	59,81	0,000
A	1	175,989	175,989	116,86	0,000
B	1	4,148	4,148	2,75	0,103
Square	2	51,349	25,674	17,05	0,000
A*A	1	45,958	45,958	30,52	0,000
B*B	1	13,183	13,183	8,75	0,005
Error	49	73,791	1,506		
Lack-of-Fit	20	65,545	3,277	11,53	0,000
Pure Error	29	8,246	0,284		
Total	53	305,276			

In Table III, A: Current Density, B: Initial pH

The coefficients of term placed in Final ANOVA Table are given in Table IV.

TABLE IV. THE CODED COEFFICIENTS OF EFFECTIVE TERMS

Coded Coefficients					
Term	Effect	Coef	SE Coef	T-Value	P-Value
VIF					
Constant		97,749	0,289	337,94	0,000
A	3,830	1,915	0,177	10,81	0,000
1,00					
B	-0,588	-0,294	0,177	-1,66	0,103
1,00					
A*A	-1,895	-0,947	0,172	-5,52	0,000
1,04					
B*B	-1,015	-0,507	0,172	-2,96	0,005
1,04					

Therefore, the regression model with coded values is given in terms of current density and pH as follows in equation (7):

$$\hat{y} = 97.75 + 1.9148x_1 - 0.294x_2 - 0.9474x_1^2 - 0.5074x_2^2 + \varepsilon \quad (7)$$

In general, the coefficient of determination (R-square-adj.) explains the total variability accounted by the independent variables in regression model. In this model, R-Sq(adj) was found to be 73.9% , which is adequate for explaining the variability. Also, the residuals of model have a Normal distribution (Fig. 2) with constant variance (Fig. 3). The surface plot of removal of lead as a function of current density and pH is shown in Fig. 4 and the contour plot is shown in Fig. 5. The nonlinearity of the model is clearly

represented by the surface plot.

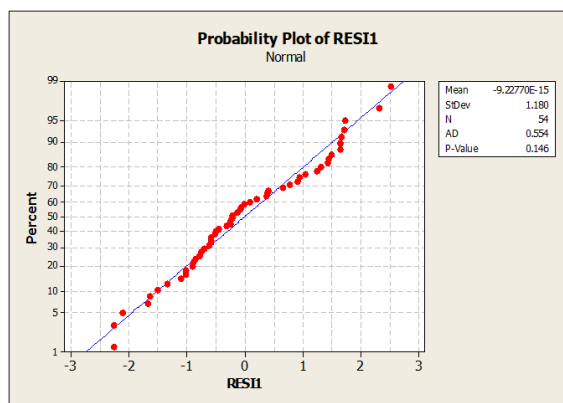


Fig. 2. The Normal probability plot.

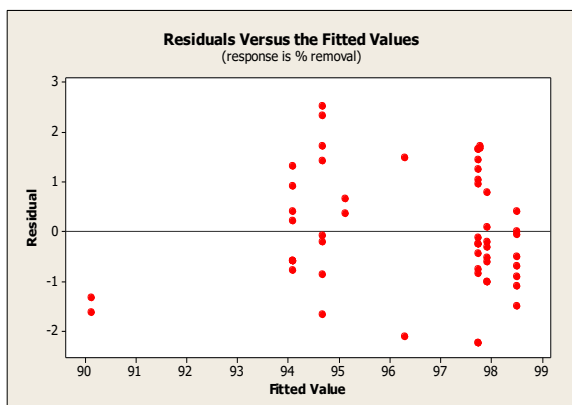


Fig. 3. The plot of residual versus predicted value.

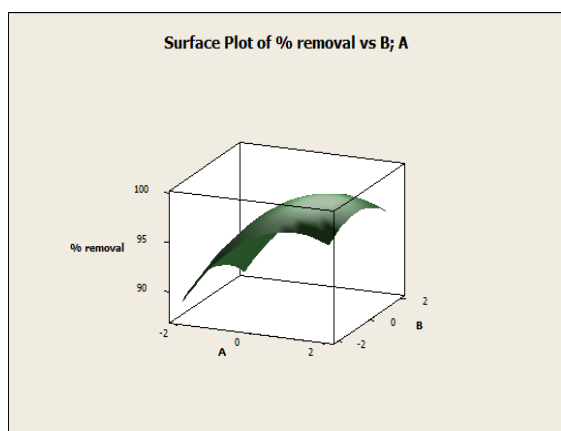


Fig. 4. The surface plot of removal of lead according to current density (A) and initial pH (B).

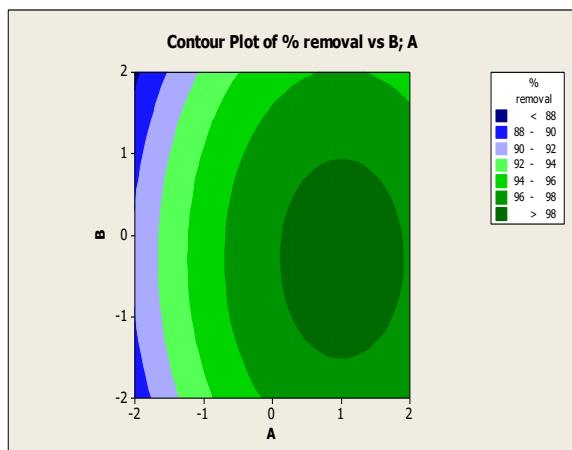


Fig. 5. The counter plot of removal of lead as a function of current density (A) and initial pH (B).

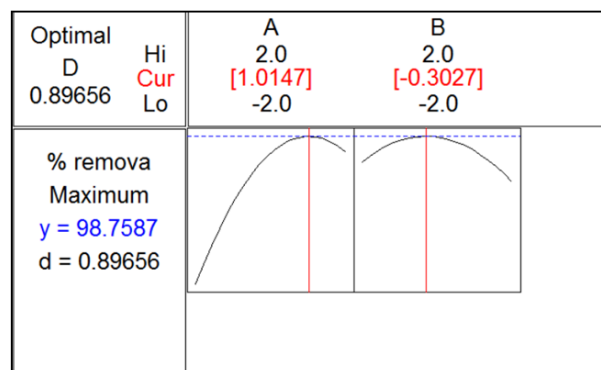


Fig. 6. The optimum values of responses with coded values of factors.

The optimum value for removal of lead were obtained from Fig. 5 and 6 with coded value. The maximum value of lead removal was found to be 98.76% at the current density of 40 mA/cm² at pH 4.7.

IV. CONCLUSION

In this study, removal of lead from water using electrocoagulation method was achieved using a uniquely-designed batch electrocoagulation reactor. The empirical model, in terms of effective operational factors, such as initial pH, current density, supporting electrolyte concentration and lead concentration was developed through Response Surface Methodology.

From the results a mathematical model correlating the effective factors like initial pH, current density was developed. Interaction terms were not considered in the correlation as they have no statistically significant effect on the lead removal efficiency. The R^2 (adjusted) value of 74% is appropriate and acceptable to explain the total variation of response.

Current density has a linear effect while current density and initial pH have quadratic effects on the removal efficiency of lead. Lead removal efficiency reach a maximum value of 98.76% when the current density was 40 mA/cm² and initial pH was 4.7.

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