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# Optimization of electrocoagulation process for individual and simultaneous removal of cadmium and copper from simulated wastewater

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# ABSTRACT

This study delves into electrocoagulation for removing copper and cadmium from synthetic water, exploring both individual and binary removal. Employing the Box–Behnken design method, the research fine-tuned process operating factors including current density (10 to 50 mA/cm<sup>2</sup>), starting pH (3 to 7), and metal ion concentration (100 to 300 ppm). Optimal conditions for single-element systems yielded 99.02% copper removal (pH value of 5.63, current density value of 50 Am<sup>-2</sup>, copper concentration 100 ppm) and 98.45% cadmium removal (pH 6.15, current density 50 A/m2, cadmium concentration 124 ppm). Findings underscored the substantial current density impact on removal efficiency, surpassing the effect of pH and metal ion concentration. Notably, the current played a more pivotal role in cadmium removal than in copper removal. A robust R2 analysis of variance (98.85% for Cu and 99.50% for Cd) confirmed the satisfactory agreement between the second-order regression model and the experimental data, affirming the optimization validity of the electrocoagulation process. In binary systems, copper presence hindered cadmium removal, reducing efficiency from 63.63% to 50.91%. Conversely, the inhibitory effect on copper removal was comparatively lower due to copper's stronger selectivity towards Al(OH)<sub>3</sub>.

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# 1. Introduction

The electroplating industry generates various industrial effluents that contain large quantities of metal ions, including cadmium, lead, chromium, zinc, nickel, and copper. Wastewater containing heavy metals is considered a major concern owing to its nonbiodegradability characteristics as well as the higher toxicity of these heavy metals in addition to being carcinogenic [1, 2]. In plating processes, only 30-40% of all metals were used in plating the articles. The rest would be discharged as rinsing water during the plating process to the environment. According to international environmental standards, electroplating rinsing water can contain up to  $10^3 \text{ mgL}^{-1}$  of harmful heavy metals, which must be kept under control to an allowed level before being released into the environment [3].

There are several approaches, including ion exchange, adsorption, chemical coagulation, and chemical precipitation, for removing heavy metals from wastewater [4-9]. Nonetheless, these techniques each have their own drawbacks. Pretreatment of the adsorbents is necessary for the adsorption process and long-term processing. Byproducts of chemical processing, coagulation, and precipitation are produced in large amounts and have adverse effects on the ecosystem. Ion exchange is thought to be costly and necessitates significant maintenance costs[10]. Compared with the above methods, electrocoagulation (EC) was shown to be one of the best techniques for removing heavy metals [11-18]. Since coagulants are naturally formed during the EC process, heavy metals can be eliminated at considerable rates without the need for chemical additions [19].

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Nomenclature:			
BBD	Box–Behnken Design	RSM	Response surface methodology
Co	concentrations of metal ions before EC [ppm]	$x_1, x_2 \dots x_k$	coded format of operational variables
С	concentrations of metal ions after EC [ppm]	Y	Removal Efficiency percent term
ср	reiterated number of the central point	Greek symbols	
DOF	Degree of freedom		
EC	Electrocoagulation	$\beta_0$	intercept term
i,j	patterns index numbers	$\beta_i$	Linear 1 <sup>st</sup> order main effect
k	operational variables number	$\beta_{ii}$	2 <sup>nd</sup> oder main effect
Ν	Experiments number	$\beta_{ii}$	interaction effect
RE	removal efficiency		

When current is supplied within the aqueous medium, oxidation occurs at the anode while reduction occurs on the cathode side, [20]. Metal hydrooxides are created when the metal ions formed at the anode hydrolyser in the solution and function as coagulants to facilitate the removal of heavy metals. In the electrocoagulation process with an aluminum anode, the main reactions occurring at the electrode area are [21]: At the anode:

$$(Al)_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^{-}$$
 (1)  
 $2H_2O \rightarrow O_{2(q)} + 5H^+ + 5e^{-}$  (2)

At the cathode:  

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
(3)

In solution  

$$Al^{3+} + 30H^{-} \rightarrow Al(OH)_{3(s)}$$
(4)

Landfill leachate [22], textile [23], tannery [24], municipal [25], restaurant [26], pharmaceutical [27], and petroleum refinery wastewaters [28] are industrial effluents that have been effectively treated with EC in recent years. RSMs are mathematical and statistical techniques that are utilized to assess the impact of process parameters and establish the ideal circumstances for a certain response [29]. Regression statistical analysis is used in this method to identify the model that minimizes residual differences. Earlier optimization methods required several runs to enhance the process parameters, which increased the cost and duration of the trials. As a result, the process parameters are optimized using the RSM and the input and output models. There are several studies on the removal of Cu and Cd in combination with EC [30-36]. However, eliminating copper and cadmium in wastewater using EC and the RSM tool is not the subject of any published research papers. The goals of this work were to use the Box-Behnken design (BBD) of RSM to optimize the EC process parameters including current density, beginning pH, and metal ion concentration at the onset for eliminating copper and cadmium separately from simulated wastewater. Then based on the BBD outcomes, the effect of the weight percent of the binary system (Cd-Cu) on the concurrent elimination efficiency of heavy metals was investigated.

# 2. Materials and methods

A rectangular Perspex glass electrochemical reactor with a volume of 1250 mL (0.12 m wide  $\times$  0.12 m long  $\times$  0.12 m high) including a Perspex cover (0.15 m  $\times$  0.15 m  $\times$  0.028 m), was utilized in the EC runs. The lid has slits and holes for holding the electrodes and inserting the pH device probe or conductivity device probe respectively. Three stainless steel plates were used as cathodes in the electrochemical reactor's parallel plate design of the electrochemical reactor of (0.13  $\times$  0.08  $\times$  0.003 m) and double aluminum plates operating as anodes with the same demotions were used.

The gap between electrodes was maintained at 0.015 m. A power supply (digital type) (UNI-T- UTP3315PF) was utilized to provide a constant current during the operation of the run. One liter of distilled water was put in a 1 L beaker, and the required amount of heavy metals, such as CdCl2 or CuCl<sub>2</sub> was added. Then Na<sub>2</sub>SO<sub>4</sub> and KCl were added as supporting electrolytes at concentrations of 0.05 M and 0.013 M respectively to increase the conductivity and prevent the formation of deposits on the cathode surface hence lowering the cell voltage[33]. The solution was stirred with a magnetic mixer to ensure suitable stirring and then placed in the geometry body. The electrodes were connected to the power supply in a parallel configuration. This configuration was chosen because it can efficiently deliver the necessary levels of electrical conductivity and current dispersion in the electrolyte solution. All runs were performed for 60 min at a fixed temperature of 25 ±2°C utilizing a water bath type (Memmert, WNB22, Germany). Fig. 1 displays an illustrative representation of the EC test arrangement. A pH meter (digital type) (HNNA Instrument Inc., PH211, Romania) was utilized to test the pH of the electrolyte, and the pH was then adjusted to the appropriate acidity level for the experiment by adding 1 M HCl or 1 M NaOH. Conductivity and TDS were assessed utilizing (HM Digital Inc. Model COM-100, Korea). Every 10 minutes throughout the electrochemical treatment, samples were taken and evaluated for the presence of heavy metals utilizing atomic absorption spectroscopy (Varian SpectrAA 200 spectrometer).



**Figure 1.** The electrochemical apparatus: 1) Cell geometry, 2) Al anode,3) Stainless steel cathode, 4) Power supply, 5) Voltmeter, 6) Ameter, 7) pH-device, 8)Water bath

The removal efficiency was determined utilizing the following equation [33]:



(5)

$$RE\% = \frac{c_o - c}{c} \times 100 \%$$

## 2.1. Box-Behnken design

The BBD experimental design of response surface methodology has been utilized in several studies [37-40] as it requires fewer experimental runs than other techniques as well as it provides precise estimation of the model parameters; it is best suited for studies involving several independent variables (3 to 10). Three levels of factors are used by BBD to create quadratic models. For BBD to function, three elements of each level must be present [41]. Equation 6 could be applied to determine total experiments (N) required to develop BBD.

$$N = (2k^2 - 2k) + cp (6)$$

Here: k symbolizes the number of operational variables while cp reiterated the number of central points.

Table 1. Process parameters and their ranges.										
<b>Operational factors</b>	Box–Behnken design range									
Coded levels	Low (-1)	Middle (0)	High (+1)							
$x_1$ (Current density)	10	30	50							
[mA cm <sup>-2</sup> ]										
x <sub>2</sub> (pH)	3	5	7							
$x_3([M^{+2}])[g/l]$	100	200	300							

Table 2. Experimental design array in coded form											
	Run	Bulk	$x_{I}$	$x_2$	$x_3$						
	1	1	-1	1	0						
	2	1	-1	0	-1						
	3	1	-1	-1	0						
	4	1	-1	0	1						

5	1	0	0	0	
6	1	0	-1	-1	
7	1	1	1	0	
8	1	0	-1	1	
9	1	0	1	1	
10	1	0	0	0	
11	1	0	0	0	
12	1	1	0	-1	
13	1	0	1	-1	
14	1	1	-1	0	
15	1	1	0	1	

BBD offers correlation for evaluating the outcomes, where the data are placed in the following 2nd order polynomial equation: [42]:

$$Y = \sum (\beta_i x_i) + \sum (\beta_{ii} x_i^2) + \sum (\beta_{ij} x_i x_j) + (\beta_0)$$
(7)

In this case, Y is denoted by RE%, i and j stand for pattern index numbers,  $\beta o$  is the intercept term, and  $x_1, x_2,...$ , and  $x_k$  are variables in coded format. The linear 1<sup>st</sup>-order main effect is denoted by  $\beta i$ , the 2<sup>nd</sup>-order main effect by  $\beta i i$ , and the interaction effect by  $\beta i j$ . After performing ANOVA, the regression coefficient (R<sup>2</sup>) was calculated to evaluate how well the model matched the data. Table 1 shows the process parameters and their ranges based on BBD, while Table 2 shows the array of experimental designs. Three replications for the same run were conducted and the average value was adopted in the results with standard deviation less than 5%

# 3. Results and discussion

## 3.1. Individual removal

Fifteen tests were conducted for the optimization of copper removal and the same number for the removal of cadmium using a Box–Behnken design. The obtained data are shown in Table 3

Table 2 Desults of DDD

			Table 5.	Results 0	IBBD		
er	-		Î	RE <sub>Cu</sub> %		RE <sub>Cd</sub>	0
Run Ord	C. D. (mA/cm <sup>2</sup>	Hd	[M <sup>+2</sup> ] (g/	EXP.	Predic ted	EXP.	Predic ted.
1	10	7	200	90	89.737	70	70.575
2	10	5	100	94	94.562	76	75.875
3	10	3	200	86	86.112	66	64.825
4	10	5	300	87	86.887	63	63.725
5	30	5	200	95	95.666	81	81.667
6	30	3	100	95	94.325	75	76.300
7	50	7	200	98	97.887	97	98.175
8	30	3	300	89	89.300	70	70.450
9	30	7	300	92	92.675	76	74.700
10	30	5	200	97	96.666	82	82.137
11	30	5	200	96	96.120	83	82.667
12	50	5	100	99	100.31	99	98.675
13	30	7	100	98	97.700	85	84.550
14	50	3	200	95	94.762	92	91.425
15	50	5	300	99	97.937	95	95.125

The removal of copper ranged between 86 and 99.9%, while the removal of cadmium ranged between 63 and 99.4%. The results showed that the removal of copper was greater than that of cadmium under the same operating conditions. The outcomes of removal efficacy for each metal are further analysed utilizing Minitab-17 software. Eq. (8) and Eq. (9) show an empirical relationship between the independent variables and their response in terms of real units of independent variables utilizing the quadratic model of removal efficiency (RE). Table 4 outlines the ANOVA results. The model of copper removal is highly obvious, with a p value=0.0001 and F value=47.66, leading to a coefficient of determination (R<sup>2</sup>) as well as R2 (adjusted) and R<sup>2</sup> (predicted) values of 98.85%, 96.77%, and 85.21%, respectively. The variation between R<sup>2</sup>(adjusted) and R<sup>2</sup>(predicted) was lower than 20.0%. Incompatibility is nonsignificant, with a p value of 0.325, which is greater than 0.05, confirming the model significance [43]. The contribution of the current density is the highest at 56.19%, followed by that of the metal ion concentration and then that of the pH. These results are in agreement with the electrocoagulation mechanism, which depends on aluminium dissolving into the solution and is controlled by the current density [35].

$$RE_{Cu}\% = 77.04 + 0.2519 x_1 + 7.15 x_2 - 0.0577 x_3 - \frac{2.646}{10^3} (x_1)^2 - 0.6208 (x_2)^2 + \frac{3.2}{10^5} (x_3)^2 - \frac{3.13}{10^3} x_1 x_2 + \frac{6.63}{10^4} * x_1 x_3 + 0.000 x_2 x_3$$
(8)

$$RE_{cd}\% = 42.16 - 0.051 x_1 + 11.46 x_2 + 0.0148 x_3 + \frac{8.04}{10^3} (x_1)^2 - 0.908 (x_2)^2 - \frac{1.53}{10^4} (x_3)^2 + \frac{6.2}{10^3} x_1 x_2 + \frac{1.075}{10^3} x_1 x_3 - \frac{5}{10^3} x_2 x_3$$
(9)



Table 4. ANOVA for Cu removal											
DOF	Seq. SS	Contr. (%)	Adj. SS	Adj. MS	F value	P value					
9	248.263	98.85	248.263	27.585	47.660	0.0001					
3	214.403	85.37	214.403	71.468	123.47	0.0001					
1	141.120	56.19	141.120	141.12	243.80	0.0001					
1	22.7810	9.070	22.781	22.781	39.360	0.002					
1	50.5010	20.11	50.501	50.501	87.250	0.0001					
3	26.7760	10.66	26.776	8.9250	15.420	0.006					
1	3.04800	1.210	4.136	4.1360	7.1400	0.044					
1	23.3570	9.300	22.770	22.770	39.340	0.002					
1	0.37000	0.150	0.370	0.3700	0.6400	0.460					
3	7.08500	2.820	7.085	2.3620	4.0800	0.082					
1	0.06300	0.020	0.063	0.0630	0.1100	0.756					
1	7.02200	2.800	7.022	7.0220	12.130	0.018					
1	0.00000	0.00 0	0.000	0.0000	0.0000	1.000					
5	2.89400	1.150	2.894	0.5790							
3	2.22700	0.890	2.227	0.7420	2.230	0.325					
2	0.667	0.270	0.667	0.3330							
14	251.157	100.0									
	S.	$\mathbb{R}^2$	R <sup>2</sup> (adj.)	PRESS	R-sg(pred.)						
	0.7608	98.85%	96.77%	37.14	85.21%						
	<b>DOF</b> 9         3         1         1         3         1         3         1         5         3         2         14	DOF         Seq. SS           9         248.263           3         214.403           1         141.120           1         22.7810           1         22.7810           1         50.5010           3         26.7760           1         3.04800           1         23.3570           1         0.37000           3         7.08500           1         0.06300           1         7.02200           1         0.00000           5         2.89400           3         2.22700           2         0.667           14         251.157           S.         0.7608	Table 4. ANOV.           DOF         Seq. SS         Contr. (%)           9         248.263         98.85           3         214.403         85.37           1         141.120         56.19           1         22.7810         9.070           1         20.7760         10.66           1         3.04800         1.210           1         23.3570         9.300           1         0.37000         0.150           3         7.08500         2.820           1         0.06300         0.020           1         7.02200         2.800           1         0.00000         0.00           5         2.89400         1.150           3         2.22700         0.890           2         0.667         0.270           14         251.157         100.0           S. $\mathbb{R}^2$ 0.7608	$\begin{array}{ c c c c } { \mbox{Table 4. ANOVA for Cu removal}} \\ \hline { \mbox{POF} } & $\mbox{Seq. SS} & $\mbox{Contr.} \\ (\%) & $\mbox{Adj. SS} \\ (\%) & $\mbox{Adj. SS} \\ $\mbox{248.263} & $98.85 & $248.263 \\ $\mbox{3.1} & $214.403 & $85.37 & $214.403 \\ $\mbox{1.1} & $141.120 & $56.19 & $141.120 \\ $\mbox{1.1} & $22.7810 & $9.070 & $22.781 \\ $\mbox{1.1} & $20.5010 & $20.11 & $50.501 \\ $\mbox{3.0} & $26.7760 & $10.66 & $26.776 \\ $\mbox{1.1} & $3.04800 & $1.210 & $4.136 \\ $\mbox{1.2} & $0.3700 & $0.370 \\ $\mbox{3.0} & $2.820 & $7.085 \\ $\mbox{1.1} & $0.06300 & $0.020 & $0.063 \\ $\mbox{1.1} & $0.06300 & $0.020 & $0.063 \\ $\mbox{1.1} & $0.0000 & $0.000 \\ $\mbox{5.} & $2.89400 & $1.150 & $2.894 \\ $\mbox{3.} & $2.22700 & $0.890 & $2.227 \\ \hline \mbox{2.} & $0.667 & $0.270 & $0.667 \\ $\mbox{14} & $251.157 & $100.0 \\ \hline \mbox{14} & $251.157 & $100.0 \\ \hline \mbox{14} & $251.157 & $100.0 \\ \hline \mbox{14} & $251.157 & $100.0 \\ \hline \end{tabular}$	$\begin{array}{                                    $	Table 4. ANOVA for Cu removal           DOF         Seq. SS         Contr. (%)         Adj. SS         Adj. MS         F value           9         248.263         98.85         248.263         27.585         47.660           3         214.403         85.37         214.403         71.468         123.47           1         141.120         56.19         141.120         141.12         243.80           1         22.7810         9.070         22.781         22.781         39.360           1         50.5010         20.11         50.501         87.250           3         26.7760         10.66         26.776         8.9250         15.420           1         3.04800         1.210         4.136         4.1360         7.1400           1         23.3570         9.300         22.770         23.770         39.340           1         0.37000         0.150         0.3700         0.6400           3         7.08500         2.820         7.085         2.3620         4.0800           1         0.06300         0.020         0.063         0.0630         0.1100           1         7.02200         2.800         7.022         7.0220					

	Table 5.	ANOVA	for Cd	REMOVA
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Source	DOF	Seq. SS	Contr. (%)	Adj. SS	Adj. MS	F value	P value
Model. Cd	9	1795.51	99.50	1795.51	199.500	111.37	0.0001
Linear	3	1670.19	92.56	1670.19	556.730	310.79	0.0001
(x <sub>1</sub> )	1	1468.82	81.40	1468.82	1468.82	819.96	0.0001
(x <sub>2</sub> )	1	78.130	4.33	78.130	78.1300	43.610	0.001
(x <sub>3</sub> )	1	123.25	6.83	123.24	123.240	68.800	0.0001
Square	3	102.58	5.68	102.58	34.1900	19.090	0.004
$x_1^*x_1$	1	48.000	2.66	38.200	38.2000	21.330	0.006
$x_2^*x_2$	1	45.900	2.54	48.740	48.7400	27.210	0.003
x <sub>3</sub> *x <sub>3</sub>	1	8.6800	0.48	8.6800	8.6800	4.8500	0.079
2-Way Inter	3	22.740	1.26	22.740	7.5800	4.2300	0.077
$x_1^*x_2$	1	0.2500	0.01	0.2500	0.2500	0.1400	0.724
x <sub>1</sub> *x <sub>3</sub>	1	18.490	1.02	18.490	18.490	10.320	0.024
$x_2^*x_3$	1	4.0000	0.22	4.0000	4.0000	2.2300	0.195
Error	5	8.9600	0.50	8.9600	1.7900		
Lack of Fit	3	8.2900	0.46	8.2900	2.7600	8.29000	0.110
Pure-Error	2	0.6700	0.04	0.6700	0.3300		
Total	14	1804.47	100.00%				
Model-summary		S.	$\mathbb{R}^2$	R <sup>2</sup> (adj.)	PRESS	R-sg(pred.)	
		1.33841	99.50%	98.61%	134.14	92.57%	

With respect to cadmium removal, Table 5 shows the ANOVA results, in which  $R^2$ ,  $R^2$ (adjusted), and  $R^2$ (predicted) are 98.61%, 99.50%, and 92.57%, respectively, with p values less than 0.0001 and an F value of

111.37, confirming that the model is more significant than the copper removal model. The contribution of the current density is also the highest, at 81.40%, followed by the contribution of the metal ion concentration and then the pH. The contribution of the current to cadmium removal was greater than that to copper removal, confirming that electrocoagulation is controlled by the current density.

## 3.2. Influence of test factors on removal efficiency

RSM may be shown graphically to show the combined effects of the proposed parameters and their impact on the answer. Fig. (2-a & b) illustrates the influence of pH and metal ion concentration on the RE% of copper for various current densities (10-50 mA/cm<sup>2</sup>) and constant times of 60 min. The results show that increasing the current density results in an increase in the RE% at any pH or initial copper concentration, and this relation is almost linear. This phenomenon can be explained by the fact that a rise in current density could lead to an intensification in the generation of OH- and the dissolution of Al, leading to more generation of Al(OH)3 as a coagulant (increasing coagulant dosage rate), which then results in an increase in the adsorption of copper in addition to increasing the current density, enhancing the bubble production rate and size and leading to faster removal of pollutants. Similar observations were made in previous studies [33-35]. Based on the literature, pH has a vital role in EC efficiency; furthermore, a change in pH occurs during the test, and this change depends on the anode type and initial pH [44]. Fig. 2 shows that increasing the pH results in an increase in the RE% up to a pH of 6, after which it starts to decrease slightly over all current density ranges. This behavior can be explained by the fact that Al(OH)3 is amphoteric in nature, so at low acidity, it can solubilize to Al<sup>+3</sup>, and at high acidity, it can convert to Al(OH)<sub>4</sub><sup>-</sup> at acid concentrations greater than 8. In either case, the efficiency would decrease [45]. Similar observations were confirmed by previous studies [33-35, 46, 47]. Increasing the initial concentration of copper has an adverse effect on the RE% and can be clearly observed at a low current density, but at a higher current density, the effect is more sluggish. The interpretation of this phenomenon can be described as follows: since the current density is constant, the rate of Al(OH)<sub>3</sub> generation will be constant; hence, the adsorption rate will be constant. Therefore, any increase in the metal ion concentration will not participate in the adsorption process, leading to a lower removal efficiency. Similar trends were found in previous work [33, 471.

With respect to cadmium, the effect of metal ion concentration and pH on the RE of cadmium can be seen in Fig. 3-a & b for different current density ranges (10-50 mA cm<sup>-2</sup>) and at a fixed time of 60 min. A similar impact of the current density on the RE% in the case of copper removal was also observed in the case of cadmium removal; however, the relation deviated from linearity. In addition, a similar relationship between the RE% and pH as well as the initial concentration of cadmium was observed for copper removal, where the RE% increased with increasing pH and decreasing initial metal concentration.

#### 3.3. The optimum operating conditions for the confirmation test

System optimization for electrocoagulation is required to minimize energy waste. Throughout the optimization process in this discipline, a variety of criteria must be used to maximize the desired function ( $D_F$ ) and produce the optimal response [48]. Minimize, maximize, objective, within the extent, and none are all thought of as potential substitutes for the desired function. The removal of copper or cadmium was maximized by setting  $D_F=1.0$ . The method variables evaluated in this study were adopted based on Table 1. The highest and lowest limits were set for copper removal and cadmium removal, respectively. Two confirmatory tests were carried out utilizing the modified parameters, as indicated in Table 6. The optimization outcomes for these parameters and settings are shown in Table 7. A greater than 98% removal efficiency was reached for the removal of copper or cadmium, which falls within the range for optimum removal obtained by the software of the program. This is an indication of the successful application of BBD in the removal of heavy metals by EC. In addition, the EC could be more



efficient under acidic conditions when the initial concentration did not exceed 125 ppm.



**Figure 2.** Impact of metal ion concentration and pH at various current densities on Cu removal efficiency. a) Response surface and contour maps for the effect of pH and current density at 200 ppm Cu. b) Response surface plots and contour plots for the impact of metal ion concentration and current density at pH=5.



Figure 3. Impact of metal ion concentration and pH at current densities on cadmium removal efficiency. a) Response surface and contour maps for the effect of pH and current density at 200 ppm Cd. b) Response surface and contour maps for the impact of metal ion concentration and current density at pH=5.

Tabl	e 6.	Re	liab	ility	of	the	ideal	COD	elimina	ition	effici	ienc	y
------	------	----	------	-------	----	-----	-------	-----	---------	-------	--------	------	---

Run	Current density (mA/cm <sup>2</sup> )	pН	[M <sup>+2</sup> ] (ppm)	RE%
Cu	50	5.63	100.00	99.02
Cd	50	6.15	124.24	98.45

# 3.4 Binary removal

To study the binary effect of the two existing metals at the same time, the values of current density and pH should be determined. Since the maximum removal efficiency approached 100%, the study was performed under minimum conditions based on the Minitab-17 software optimizer to clearly determine the interaction effect between metals. The minimum operation conditions are shown in Table 8. To clarify how copper and cadmium interact in the EC process, the impact of the weight percentage of Cd on the removal efficiency of both copper and cadmium is shown in Fig. 4.

Table 7. Optimization of copper and cadmium removal.

	Response	Lower%		Upper%	Weight 1		Important			
Aim	$RE_{Cu}(\%)$	86		99.9			1			
	RE <sub>Cd</sub> (%)		63	99.4	_					
Movimum	Current density	pH [M <sup>+2</sup> ]		RE%	n	SE.	05% CI	05% PI		
Waxiniuni	(mA/cm <sup>2</sup> )	рп	(ppm)	Fit	$\mathbf{D}_{\mathrm{F}}$	Fit	9570 CI	<b>93</b> /0 <b>F</b> I		
Cu	50	5.63	100.00	100.56	1	0.676	(98.821; 102.296)	(97.942; 103.174)		
Cd	50	6.15	124.24	100.00	1		(97.31; 102.84)	(95.66; 104.49)		

Table 8. Minimum operating conditions for copper and cadmium removal

	Response		Lower%	Upper%		Weigh	nt	]	Important		
Aim	$RE_{Cu}(\%)$	86		99.9	1			1			
	RE <sub>Cd</sub> (%)		63	99.4							
Minimum	Current density	nH	[M <sup>+2</sup> ]	RE%	RE% Dr		SE.	95% CI	95% PI		
	(mA/cm <sup>2</sup> )	P	(ppm)	m) Fit	EXP.	21	Fit		207011		
Cu	10	3	300	82 592	81	1	0.899	(80.281;	(79 564: 85 619)		
Cu	10	5	500	02.372	01 1	1	0.077	84.902)	(7).504, 05.017)		
Cd	10 3 300 58.22 55		55	1	1.59	(54.15;	(52 80: 63 54)				
Cu	10	5	500	36.22	33	1	1.56	62.28)	(32.09, 03.34)		

This effect was studied at a current density of pH 3 (10 mA/cm<sup>2</sup>) with a total concentration of 300 ppm for the individual and mixed metals. The results revealed that the presence of copper led to a decrease in cadmium removal from 55% to lower than 25%. This is expected since the solubility of copper is greater than that of cadmium; in this case, the copper ions will cross cadmium ions and adsorb more quickly than cadmium on the surface of Al(OH)3. In addition, the presence of cadmium will reduce the copper removal efficiency from 80% to less than 55% for different weight percentages of copper. Xu et al. [34] reported that adding zinc ions to cadmium ions negatively affected cadmium removal efficiency during the EC process.

When copper was present, cadmium removal effectiveness was much lower than that in a system with only one element. As a result, copper had a severe inhibitory effect on Al(OH)3's ability to absorb cadmium, as shown by [49]:

$$IE(\%) = \frac{Cd_{(Cadmium)} - Cd_{(Cadmium)} - Cd_{(Cadmium)}}{Cd_{(Cadmium)}} \times 100$$
(10)

where  $Cd_{(Cd)}$  and  $Cd_{(Cd-Cu)}$  are the Cd removal percentages in the single and binary systems, respectively. The IE of cadmium was in the range of 63.63 to 50.91% for Cd% from 20 to 80% in the presence of copper. However, due to the stronger selectivity of copper for Al(OH)<sub>3</sub>, cadmium had a substantially less inhibitory effect on copper removal. The characteristics of the metal ions that exist, such as their ionic radius, electronegativity, potential, and redox potential, can be used to interpret the results in binary systems

ion	Coordination number	Ionic radius (Å)	Hydrated ionic radius (Å)	Pauling electronegativity
Cu(II)	6	0.73	8.38	1.9
Cd(II)	6	0.95	8.52	1.69

. Hence, the removal effectiveness of a target metal ion might be impacted



by the presence of additional metal ions in the solution [50]. Several ionic properties of copper and cadmium are presented in Table 9 [50]. Cadmium ions have a larger hydrated radius (8.52 Å) than copper (8.38 Å). Therefore, copper could be easily adsorbed on the Al(OH)3 flocks. The surface of the Al(OH)<sub>3</sub> flocks will be more strongly drawn to more electronegative ions. Copper has the highest electronegativity [51]. Previous research employing various adsorbents revealed similar findings [49, 52]. Ghernaout et al. studied the removal of Cu and Cd utilizing EC and reported that copper removal was greater than cadmium removal. However, the binary effect was not considered in their work.



Figure 4. Effect of cadmium weight present on the removal efficiencies each of cadmium and copper (current density 10mA/cm<sup>2</sup>,pH=3,total ions concentration=300ppm).

# 4. Conclusions

Electrocoagulation is considered safe as well as an easy route for the efficient removal of heavy metals such as copper and cadmium. Response surface methodology has been applied successfully for the optimization of the best operating conditions for the removal of copper and cadmium. The results showed that copper could be removed at the highest removal efficiency of 99.02% when using a current density of 50 mA/cm<sup>2</sup> from a solution containing Cu<sup>2+</sup> ions at 100 ppm with a pH of 5.63, while cadmium was removed at the highest removal efficiency of 98.45% when using a current density of 50 mA/cm<sup>2</sup> from a solution containing Cd<sup>2+</sup> ions at 124 ppm with a pH of 6.15. The results revealed that the contribution of the current density to the removal efficiency increased with increasing metal ion concentration and then increased with increasing pH in both cases (copper and cadmium removal). However, the contribution of the current to cadmium removal was greater than that to the removal of copper, confirming that electrocoagulation is sensitive to variations in the current density. The results for the binary system demonstrated that, in comparison to the single-element system, the removal efficiency of cadmium significantly decreased in the presence of copper. Therefore, copper strongly depressed cadmium uptake by Al(OH)<sup>3</sup>. The same conclusion was attained with respect to cadmium addition to copper but to a lesser extent.

## Authors' contributions

All authors contributed equally to the preparation of this article.

## **Declaration of competing interest**

The authors declare no conflicts of interest.

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This study did not receive any specific funds.

## Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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