

# Optimization of copper removal from aqueous solutions in a continuous electrochemical cell divided by cellulosic separator

Ali Asghar Najafpoor, Mojtaba Davoudi and Elham Rahmanpour Salmani

## ABSTRACT

Copper, as an inseparable part of many industrial discharges, threatens both public and environmental health. In this work, an electrochemical cell utilizing a cellulosic separator was used to evaluate Cu removal using graphite anodes and stainless steel cathodes in a continuous-flow mode reactor. In the experimental matrix, Cu concentration ( $1\text{--}5\text{ mg L}^{-1}$ ), electrolysis time (20–90 min), and current intensity (0.1–0.4 A) were employed. Results showed that the maximum removal efficiency of copper was obtained as 99%. The removal efficiency was independent of initial copper concentration and directly related to electrolysis time and current intensity. Energy consumption was more dependent on current intensity than electrolysis time. Under optimal conditions (75.8 min electrolysis time, 0.18 A current intensity, and  $3\text{ mg L}^{-1}$  copper concentration), the removal efficiency was obtained as 91% while  $7.05\text{ kWh m}^{-3}$  electrical energy was consumed. The differences between the actual and predicted data under optimal conditions were 0.42% for copper removal and 0.23% for energy consumption, which signify the performance and reliability of the developed models. The results exhibited the suitability of the electrochemical reduction for copper removal from aqueous solutions, which was facilitated under alkaline conditions prevailing in the cathodic compartment due to applying a cell divided by a cellulosic separator.

**Key words** | cellulosic separator, central composite design, copper removal, electrochemical cell, optimization

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## INTRODUCTION

Heavy metals such as cadmium, chromium, arsenic, copper, nickel, lead, mercury, and manganese are elements that appear in trace levels in various segments of the environment, especially aquatic bodies, mainly through discharges from various industries including electroplating, mining, textile, batteries, ceramic, glass, metal processing, hydrometallurgy, and microelectronics (Ma *et al.* 2014). Furthermore, agricultural activities by using fertilizers and pesticides are involved in their emission (Bilal *et al.* 2013). Human health is threatened as a result of exposure to heavy metals which are able to accumulate in the body of organisms through inhalation, ingestion, or dermal contact (Ma *et al.* 2014). Toxicity, carcinogenicity, teratogenicity, and persistence properties are known as drastic risks of heavy metals (Lee *et al.* 2012).

Copper, which has the most appearances in aquatic ecosystems among different metals (Hossain *et al.* 2012), is the

second metal in terms of toxicity for drinking water after mercury (Awual *et al.* 2013). Copper (Cu(II)) in trace amounts is an essential micronutrient for many plants and animals (Awual *et al.* 2013) and also is required by the human body because of its role in biochemical processes and enzyme synthesis (Ma *et al.* 2014). However, high doses of Cu(II) can deposit in the liver, cause liver and kidney failure, damage the central nervous system, lead to Wilson's disease, and finally contribute to gastrointestinal disturbance (Bilal *et al.* 2013). Detrimental toxic effects of excess amounts of copper have been known for soil organisms, aquatic biota, and many plant species, especially aquatic plants, due to its intervention in the transmission process across the cell wall (Awual *et al.* 2013). All these have prompted the US Environmental Protection Agency (EPA) to classify copper as a priority pollutant (Wen *et al.* 2015). The US EPA has defined

1.3 mg L<sup>-1</sup> as the maximum permissible limit of Cu(II) in industrial effluents (Shawabkeh *et al.* 2004).

On a global scale, much effort has been made in adopting and practicing different techniques to respond to heavy metal pollution of industrial effluents. Numerous methods have been applied to remove copper from aqueous solutions including chemical and electrochemical coagulation, membrane filtration, ion exchange, and adsorption. Each of these techniques, along with its benefits, has some drawbacks which limit its application for metal elimination (Gong *et al.* 2012; Jiang *et al.* 2014).

Technologies that use electrochemical mechanisms are among the most widely applied methods of industrial wastewater treatment. Electrochemical techniques are divided into major categories of electro-coagulation, photo-assisted electrolysis, electro-oxidation and reduction. No need for external reagent addition, absence of solid residues, and no necessity for tertiary treatments of final effluent distinguish electrochemical oxidation and reduction approach from many other methods (Sala & Gutierrez-Bouzan 2012). Electrochemical removal of pollutants can occur through oxidation or reduction pathways. Anodic oxidation is performed directly through electron transfer reactions on the anode surface, or indirectly by means of *in situ* generated strong oxidants such as OH radicals (Maljaei *et al.* 2009). Reduction reactions are carried out on the cathode surface simultaneously with the oxidation reactions in the anodic compartment. The most common cathodic reaction is the conversion of water molecules to hydrogen gas. Cathodic reduction is also considered for the removal of inorganic pollutants such as heavy metals from industrial effluents. An example would be the reduction of the bivalent cation of copper to elemental copper and its adsorption on the cathode surface (Danilov *et al.* 2001):



Direct reduction of copper is not the only way to remove it from the solution. If a divided electrochemical cell, rather than an undivided one, is used, parallel reactions will produce hydroxide ions under alkaline conditions of the catholyte chamber (Davoudi *et al.* 2014). As a result, the formation of metal hydroxides and increased removal rate of metal ions would be inevitable:



Copper hydroxide easily transforms into copper oxide and precipitates at room temperature in alkaline solutions (Cudennec & Lecerf 2003). Alternatively, it can be floated on the surface of solution through the bubbles of hydrogen gas produced at the cathode surface.

Therefore, one can conclude that divided electrochemical cells have advantages over undivided cells for faster removal of heavy metals. The higher rates of oxidation/reduction reactions (Hastie *et al.* 2006), lower generation of toxic residues such as disinfection by-products especially in the presence of chloride ions (Sadiq & Rodriguez 2004), delayed anode scaling and increased duration of service life due to acidic pH of anolyte (Davoudi *et al.* 2014) are among the other advantages resulting from divided electrolysis cells, especially in practical applications of the electrochemical oxidation/reduction process. In the current state, an electrolysis cell is usually divided by using ion exchange membranes. They have been utilized, for example, for the removal of dye Orange II (Hastie *et al.* 2006), azo dye Reactive Black 5 (Méndez-Martínez *et al.* 2012), Reactive Orange 4 (Del Río *et al.* 2009), perfluorooctanoic acid and perfluorooctane sulfonic acid (Schaefer *et al.* 2015), antimicrobial sulfamethazine (El-Ghenymy *et al.* 2013), and nitrate nitrogen (Zhang *et al.* 2016). However, the use of divided cells has been preferred only in a restricted number of electrochemical studies mainly due to the high expense, lack of environmental compatibility of the common membranes (Hastie *et al.* 2006), and higher cell energy consumption (Bagastyo *et al.* 2014). Thus, exploring a cheap membrane with an eco-friendly nature and good permeability for electrons can change the current state in favor of separated cells.

Cellulose is a naturally occurring organic compound found in the cell wall of plants. The hydrophilic cellulose fibers, due to porosity and permeability characteristics and their capability to keep a layer of water, can be a good physical barrier in an electrolysis cell to separate anolyte from catholyte contents. The trapped water layer within the cellulosic separator will also allow electrons to transfer through the solution from anolyte to catholyte. Hence, the electric flux between two electrodes of anode and cathode will not be disrupted. The successful application of a cellulose separator has been previously proven for electrochemical treatment of simulated tannery wastewater (Davoudi *et al.* 2014).

This paper deals with the removal of copper from aqueous solutions using a set of continuous-flow experiments

in an electrochemical cell divided by a cellulosic separator. The experiments were performed to evaluate the influence of operational variables including initial concentration of pollutant, time of reaction, and electrical current intensity on the copper removal rate. The parameters were optimized to achieve the maximum removal of copper in parallel with the lowest possible energy consumption.

## METHODS

### Solution preparation, setting up, and procedure

Stock solution of Cu(II) (concentration of  $1,000 \text{ mg L}^{-1}$ ) was obtained by dissolving  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in double distilled water. Experiments were carried out on solutions containing determined concentrations of copper in presence of sodium chloride ( $7.5 \text{ g L}^{-1}$ ) as supporting electrolyte. Concentrated nitric acid was used for storing samples prior to final analysis for  $\text{Cu}^{2+}$ . Sulfuric acid solution (10%) was prepared for washing steel electrodes before reuse. All the chemicals were of analytical grade, purchased from Merck.

The electrochemical reactor was made of plexiglass sheets in a total volume of 270 mL ( $150 \text{ mm} \times 60 \text{ mm} \times 30 \text{ mm}$ ). The reaction chamber was divided in the middle by inserting a cellulosic separator, making two anodic and cathodic compartments. The cellulosic separator with total thickness of 5 mm, which was composed of a thin layer of

hydrophilic cotton, was placed between two reticular PVC screen plates. The performance of the separator in preventing mixing of anolyte and catholyte became apparent by checking the pH of solutions on both sides of the separator using a pH meter (Hach). Graphite rods were used as anode and stainless steel sheets as cathode. Both electrodes were placed quite close to the separator. Electrodes were connected to a DC power supply (Iran pars, Iran). A schematic view of the electrolysis cell is shown in Figure 1.

Electrolysis was carried out in a continuous set-up. Thus, in each run, solution was flowed from the pump reservoir to the anolyte section and continued its pass through the catholyte compartment to the outlet port. It is worth noting that in each experiment, the effluent passed only once through the cell and it was not recirculated. Before turning on the power source, 300 mL of prepared mixture was loaded into the pump reservoir while 200 mL was transferred into the electrolysis reactor. The pump valve was adjusted in such a way that the volume of 200 mL passed through the chamber at a designated time. Finally, samples were withdrawn from the catholyte section when the reactor reached the steady state (at 1.5 hydraulic retention times). The samples were centrifuged at 3,000 rpm for 10 min before instrumental analysis. In the interval between trials, graphite electrodes were washed by distilled water and steel electrodes were cleaned using sandpaper following washing and drying. The separator also was regenerated by

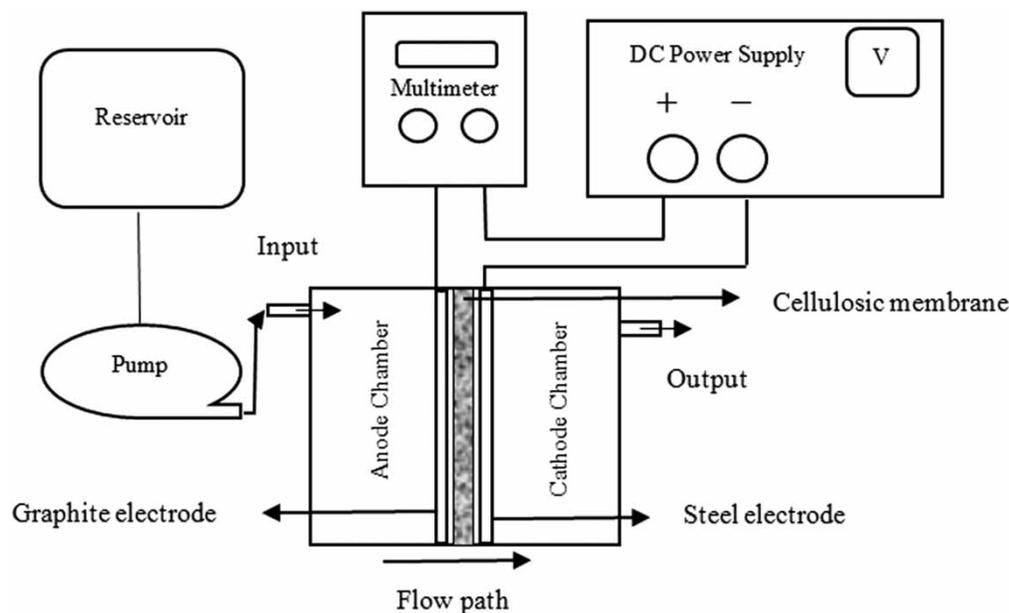


Figure 1 | A schematic view of continuous experimental set-up.

submerging in 10% sodium chloride solution for 1 hour prior to new experiments. Copper content was determined by flame atomic absorption spectrophotometry (Varian AA240FS). The removal percentage of copper was achieved by putting the initial ( $C_0$ ) and final ( $C_t$ ) values of Cu(II) in the equation:

$$\text{Copper removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (5)$$

## Experimental design

In this research, response surface methodology (RSM) under Design-Expert 7 software (trial version) was applied for determining the experimental conditions and modeling the experimental results. RSM, as a multivariate technique which applies mathematical and statistical methods, can be used to fit a polynomial equation to a set of data for the final goal of finding the optimized levels of different variables when a response is influenced by several factors (Bezerra et al. 2008). Central composite design (CCD) under RSM was used to design the experiments. CCD is an ideal choice for sequential experimentation which can test lack of fit even at low number of design points. Based on specified independent variables, which were chosen based on literature review and preliminary tests and according to the selected second order experimental design, an experimental matrix was developed by RSM for carrying out the experiments. The number of experiments with three factors (initial copper concentration, 1–5 mg L<sup>-1</sup>; reaction time, 20–90 min; and current intensity, 0.1–0.4 A) at five coded levels ( $-\alpha$ ,  $-1$ ,  $0$ ,  $+1$ ,  $+\alpha$ ) was 20 based on  $N = k^2 + 2k + cp$ , where  $k$  is the number of factors and  $cp$  is the number of replicates at the central point (Bezerra et al. 2008). Therefore, 15 experiments consisting of eight factorial points and six axial points were augmented with five replications at the design center in order to evaluate the pure error. They were carried out in a randomized order as required in design procedures. Table 1 shows independent variables at coded and actual levels. Table 2 presents the experimental conditions suggested by CCD.

To evaluate the performance of the process, responses were analyzed using the quadratic model as presented below:

$$y = B_0 + \sum_{i=1}^k B_i X_i + \sum_{i=1}^k B_{ii} X_i^2 + \sum_{1 \leq i < j}^k B_{ij} X_i X_j + \varepsilon \quad (6)$$

**Table 1** | Operational factors ranged at actual and coded levels

Variables	Symbols	Range of actual and coded variables				
		$-\alpha$	$-1$	$0$	$+1$	$+\alpha$
Initial copper concentration (mg L <sup>-1</sup> )	$A(x_1)$	1	1.81	3	4.19	5
Retention time (min)	$B(x_2)$	20	34.19	55	75.81	90
Current intensity (A)	$C(x_3)$	0.1	0.16	0.25	0.34	0.4

where  $y$  is the response;  $B_0$  is the constant term;  $B_i$ ,  $B_{ij}$ , and  $B_{ii}$  represent the coefficient of linear, interaction and quadratic parameters, respectively;  $X_i$  and  $X_j$  are variables and  $\varepsilon$  represents the error (Bezerra et al. 2008). The experimental data on copper removal percentage and electrical energy consumption were fitted to Equation (6) and the model was assessed by means of analysis of variance (ANOVA) under Design-Expert 7 software to find interactions between variables and responses. The quality of fit in developed regression models was explained by the coefficient of determination ( $R^2$ ), adjusted  $R^2$ , and predicted  $R^2$ . The statistical significance of models was checked using  $F$ -value,  $p$ -value (at confidence level of 95%) and adequate precision ratio.

## RESULTS AND DISCUSSION

In the first stage of this study, a set of electrochemical experiments provided by CCD were conducted to investigate the effect of various operating factors, initial Cu concentration, reaction time, and current intensity, on the removal rate of copper from aqueous solutions in a continuous mode system. In the second stage, to achieve the maximum removal of copper at minimum energy consumption, the optimal zone of operating conditions was determined.

### Fitting models and ANOVA

According to Table 2, different values for copper removal and energy consumption were achieved at various combinations of levels of independent variables. The remarkable difference between the least and the most observed values of responses expresses the proper selection of operational parameters range. The experimental results were used to approximate a polynomial model for each response. The response functions with the determined coefficients in

**Table 2** | Suggested experimental matrix by CCD based on observed and predicted results

Run order	Independent variables			Copper removal %		Energy consumption kWh m <sup>-3</sup>	
	Initial copper concentration (mg L <sup>-1</sup> )	Retention time (min)	Current intensity (A)	Actual	Predicted	Actual	Predicted
1	5	55	0.25	95	96.97	8.99	8.84
2	1.81	34.19	0.16	80	79.67	2.6	2.77
3	1.81	75.81	0.34	93	93.61	18.04	18.11
4	1	55	0.25	99	97.77	8.93	8.81
5	3	90	0.25	95	96.08	14.81	14.59
6	3	55	0.4	81	79.55	15.76	15.82
7	3	55	0.25	96.94	96.47	9.05	8.97
8	4.19	75.81	0.16	91	88.7	5.91	6.16
9	3	55	0.25	96	96.47	8.93	8.97
10	3	55	0.25	96.98	96.47	8.93	8.97
11	1.81	75.81	0.16	90	89.65	6.06	6.25
12	3	55	0.25	94.98	96.47	8.93	8.97
13	4.19	34.19	0.16	80	78.95	2.64	2.77
14	4.19	75.81	0.34	93.55	93.38	18.10	18.14
15	3	55	0.25	98	96.47	8.93	8.97
16	3	20	0.25	80	79.66	3.20	3.15
17	1.81	34.19	0.34	82	83.83	7.94	7.89
18	3	55	0.25	96	96.47	8.99	8.97
19	3	55	0.1	69.93	72.12	1.78	1.45
20	4.19	34.19	0.34	83.99	83.83	7.99	8.01

terms of coded factors for copper removal and energy consumption obtained by Design-Expert software are presented in Equations (7) and (8), respectively:

$$Y_1 = +96.47 - 0.24x_1 + 4.88x_2 + 2.21x_3 - 0.058x_1x_2 + 0.18x_1x_3 - 0.050x_2x_3 + 0.32x_1^2 - 3.04x_2^2 - 7.29x_3^2 \quad (7)$$

$$Y_2 = +8.97 + 0.007x_1 + 3.4x_2 + 4.27x_3 - 0.023x_1x_2 + 0.027x_1x_3 + 1.68x_2x_3 - 0.053x_1^2 - 0.038x_2^2 - 0.12x_3^2 \quad (8)$$

The  $x$  terms are defined in Table 1. Model validity for each response was checked by ANOVA and the outputs are presented in Table 3. ANOVA results indicate that models are predictable at confidence level of 95%. The significance of developed models and terms included in the models was determined by applying the Fisher distribution ( $F$ -test). Since the  $p$ -value is  $<0.05$  and  $F$ -value is high

enough for both responses, the models are deemed to be significant.

The experimental data along with the model predictions are shown in Table 2. High values of the determination coefficient ( $R^2 = 0.977$  for copper removal percentage and  $R^2 = 0.999$  for energy consumption) show good correlation between predicted and experimental data (Davoudi et al. 2014). With regard to  $R^2$  values, only 2.3% and 0.1% of all variations could not be justified by the models, respectively. Very high significance of models is also evident from adjusted and predicted  $R^2$  values. For both responses, there was not much difference between  $R^2$  and  $R^2_{adj}$  and the difference between adjusted and predicted correlation coefficients was also less than 0.2. Adequate precision greater than 4 is favorable for a proper signal to noise ratio. For both responses, this index was desirable. Thus, accuracy and reliability of experiments can be inferred from the high  $F$ -values and determination coefficients, and  $p$ -values less than 0.0001, in the developed models. Furthermore, for both models, data were normally distributed

**Table 3** | ANOVA results of the quadratic model developed for removal efficiency of copper (a) and energy consumption (b)

Source	Sum of squares		df	Mean square		F-value		p-value	
	a	b		a	b	a	b	a	b
Model	1261	430.5	9	140	47.83	47.06	1266	<0.0001	<0.0001
A – Cu concentration	0.77	0.000	1	0.77	0.000	0.258	0.020	0.6220	0.8901
B – Reaction time	325	158	1	325	158	109.3	4186	<0.0001	<0.0001
C – Current intensity	66.6	249.5	1	66.6	249.5	22.39	6606	0.0008	<0.0001
AB	0.027	0.004	1	0.027	0.004	0.009	0.110	0.9257	0.7466
AC	0.264	0.006	1	0.264	0.006	0.088	0.156	0.7717	0.7006
BC	0.019	22.7	1	0.019	22.7	0.006	601.2	0.9368	<0.0001
A <sup>2</sup>	1.48	0.040	1	1.48	0.040	0.497	1.078	0.4969	0.3235
B <sup>2</sup>	133	0.020	1	133	0.020	44.72	0.536	<0.0001	0.4806
C <sup>2</sup>	766.8	0.207	1	766.8	0.207	257.5	5.49	<0.0001	0.0410
Residual	29.77	0.377	10	2.977	0.037				
Lack of fit	24.23	0.366	5	4.846	0.073	4.374	31.87	0.0656	0.0008
Pure error	5.54	0.011	5	1.108	0.002				

$R_a^2 = 0.977$ , Adj.  $R_a^2 = 0.9562$ , Pred.  $R_a^2 = 0.8504$ , and adequate precision (a) = 21.027.

$R_b^2 = 0.999$ , Adj.  $R_b^2 = 0.9983$ , Pred.  $R_b^2 = 0.9935$ , and adequate precision (b) = 121.46.

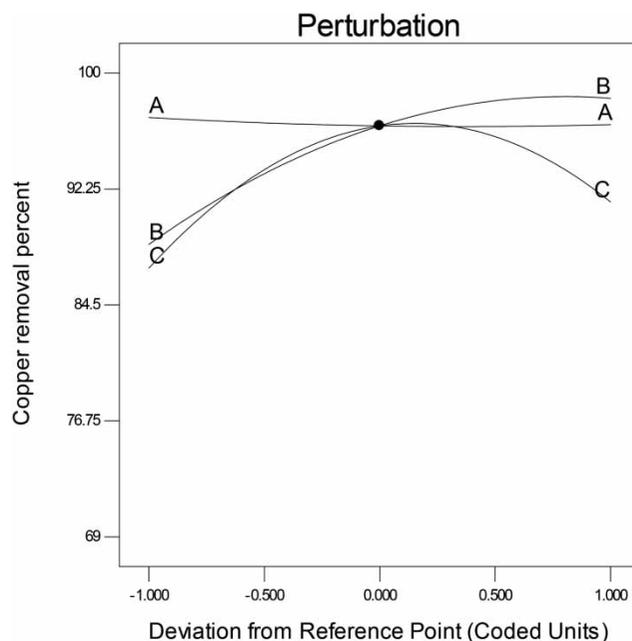
df: degrees of freedom.

regarding the fairly straight line of the normal plot of residuals (graphs are not shown).

### Assessing the effect of operational parameters

The regression model developed for the copper removal is presented in Equation (7). A constant value of 96.47% was obtained for the copper removal, which was independent of any of the main or interaction effects of factors. No significant interaction effect on the copper removal percentage was inferred from Equation (7). The main and quadratic effects of variables are presented collectively in the perturbation plot of Figure 2.

The coefficient of term  $x_1$  ( $-0.24$ ) in the fitted model for the copper removal efficiency was very small in comparison with the two other main terms, which implies that the effect of initial copper concentration on the removal efficiency was very weak ( $p$ -value = 0.622) and hence can be overlooked in this study. This phenomenon may be due to the uninterrupted electroreduction of  $H_2O$  and  $O_2$  molecules at the cathode surface (according to Equations (2) and (3)) that provided excess amounts of  $OH^-$  ions in the reaction with  $Cu^{2+}$  to form insoluble  $Cu(OH)_2$  (according to Equation (4)). However, it should be noted that a different trend for the removal rate would be expected if a wider range of Cu concentration were explored. The effect of initial concentration of copper on its removal



**Figure 2** | Perturbation plot for the exhibition of main and quadratic effects of factors on the removal of copper (A: initial copper concentration from 1.8 to 4.19  $mg L^{-1}$ , B: electrolysis time from 34.19 to 75.8 min, and C: current intensity from 0.16 to 0.34 A).

trend in the current work was studied at five levels in the range of 1 to 5  $mg L^{-1}$ . This range is in accordance with a real concentration of  $4.5 \pm 1.6 mg L^{-1}$  found in raw wastewater originating from the washing process of the textile

industry (Sharma *et al.* 2007). Rabbani *et al.* (2012) also reported  $2.28 \pm 0.24 \text{ mg L}^{-1}$  copper concentration in the leachate samples taken from a solid waste landfill. Chang *et al.* (2016) investigated copper removal from natural and man-made water bodies at concentrations of 0.2 to  $3 \text{ mg L}^{-1}$ . Awual *et al.* (2013) studied the copper removal at  $2 \text{ mg L}^{-1}$  concentration, while in another study 0.5, 1, 2, and  $5 \text{ mg L}^{-1}$  copper concentrations were selected in the adsorption experiments conducted by Kutty *et al.* (2016).

In spite of the independence of the copper removal rate from its initial concentration, the maximum removal rate of 99% was obtained in the current study, which is comparable to the percentages reported in previous studies. Khattab *et al.* (2013) used a packed-bed cell consisting of graphite particles for electrochemical removal of copper from dilute wastewater. The cell was found to be effective in reducing metal ion concentration to less than 0.05% of the initial concentration, although they reported no data on the energy consumption. Rabbani *et al.* (2012) studied the performance of an electrochemical system with iron electrodes for removing copper and achieved 95% removal rate, while they used much higher current intensities (1 A) in comparison with this research (0.25 A). Basha *et al.* (2008) evaluated the performance of cathodic reduction in removing heavy metals from copper smelting effluent. The removal percentages of copper using a stainless steel cathode were in fluctuation between 96 and 98.8%. Davoudi *et al.* (2014) also removed 63.42% of heavy metal chromium simultaneously with phenol and ammonia from tannery effluent using an electrochemical reactor divided by a cellulosic separator.

In the polynomial function assigned for the removal of copper, the linear effect of electrolysis time  $x_2$  ( $p$ -value  $< 0.0001$ ) and current intensity  $x_3$  ( $p$ -value = 0.0008) on the removal percentage of copper was significant. It can be seen from Equation (7) that the removal efficiency of copper is very influenced by the time of electrolysis, and the coefficient of +4.88 shows the direct relationship between this variable and the studied response. The percentage of copper removal increased almost 10% when the retention time went from level -1 (34.19 min) to level +1 (75.81 min) provided that the two other variables were constant at central levels. In line with this study, the decrease of copper ions with increasing time of electrolysis was observed by Pak *et al.* (2001), Rabbani *et al.* (2012), and Khattab *et al.* (2013). Regarding the reaction time, there is a significant curved effect with the coefficient of -3.04. The negative sign of the square effect suggests that longer time of electrolysis ( $> 75.81 \text{ min}$ ) will not result in greater efficiencies. As reported in Table 2 under similar operating conditions, when reaction time increased from 55 min to

90 min (except run number 12) the process efficiency decreased about 1.8% on average. The reduction of removal efficiency at higher reaction time could be related to the dissolving of green color deposits of copper oxides formed on the surface of solution and their re-entry into the electrolyte (Kakakhel *et al.* 2007).

The positive effect of current intensity with the coefficient of +2.21 also shows the contribution of this parameter to the increase of copper removal, which is in agreement with the studies of Pak *et al.* (2001), Rabbani *et al.* (2012), and Khattab *et al.* (2013). But it must be noted that the behavior of the system regarding different values of current intensity was not linear. In central values of initial copper concentration ( $3 \text{ mg L}^{-1}$ ) and retention time (55 min), increased from level -1 (0.16 A) to level +1 (0.34 A), the increased copper removal was observed only when current intensity went from level -1 (0.16 A) to level 0 (0.25 A), and higher current intensities not only did not yield greater removal percentages, but also led to the reduced efficiency. This can be explained by the fact that the production of hydrogen gas near the surface of the cathode can loosen Cu-containing precipitates attached to the cathode surface and their re-dissolution in the solution (Kakakhel *et al.* 2007). The significant quadratic term  $x_3$  (coefficient of -7.29,  $p$ -value  $< 0.0001$ ) also confirms the curve effect of current intensity on the response in the perturbation plot of Figure 2.

### The role of cellulosic separator

In this study, a layer of cellulose fibers fixed at the middle of the cell was used to separate anolyte from catholyte contents to achieve the benefits of electrolysis in a divided cell. This physical layer could successfully create two distinct environments in the two sides of the separator, i.e. in the anodic and cathodic compartments. The alkaline pH in the cathodic compartment was essential for the reduction and separation of copper ions in accordance with the purpose of this study. The layer of cellulose fibers, opposite to some alternatives such as asbestos that was used in our preliminary study, could also establish a constant electric flux between anode and cathode electrodes. However, the cellulosic separator does not have the ion selectivity feature and hence it cannot be used for purposes such as separation of chlorine and sodium hydroxide in the chloralkali process.

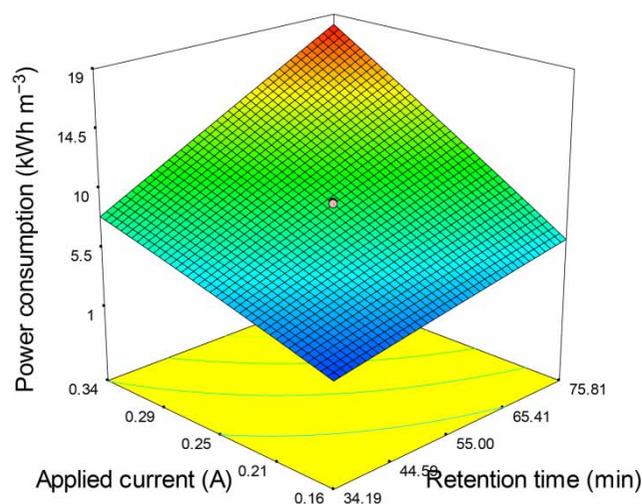
### Energy consumption

Electrical energy consumption due to the imposing operating costs is known as a weakness of electrochemical

treatment methods. The amount of energy consumed in each experiment was calculated through the equation:

$$\text{Electrical energy consumption (kWh m}^{-3}\text{)} = \frac{VIT}{V_s} \quad (9)$$

where  $V$  is the applied voltage (V),  $I$  is the current intensity (A),  $T$  is the time of electrolysis (h), and  $V_s$  is the solution volume ( $\text{m}^3$ ). The constant term of Equation (8) indicates that 8.97 kWh of energy is used for treating  $1 \text{ m}^3$  of synthetic solution of copper when values of variables were constant at central points. Equation (8) also reveals the significant main and interaction effects ( $p$ -value  $< 0.0001$ ) of applied current and time of electrolysis on the energy consumption. The synergistic effect of mentioned variables is depicted in the 3D surface plot of Figure 3. In the displayed response surface plot, the predicted values of energy consumption are shown as a function of variations in applied current and time, while the solution concentration is constant at the central level. As can be inferred from Figure 3, at constant level



**Figure 3** | Response surfaces for energy consumption as a function of electrolysis time and current intensity.

of residence time (34.19 min), about 2.787-fold more energy was consumed when current intensity increased from level  $-1$  to level  $+1$ . By conducting the experiments at constant level of current intensity (0.16 A), when electrolysis increased from level  $-1$  to level  $+1$ , energy consumption became 2.19-fold greater. These results suggest that the treatment process will be less costly if the lower levels of current intensity are applied. Under such conditions, the current-induced deficiencies can be compensated for by increasing the residence time of solution in the reactor.

### Optimization of experimental conditions

Design-Expert software was used to optimize the experimental results. The desired goal for each response and factors affecting the response was chosen from five options including none, maximize, minimize, target, or in range. Since various concentrations of copper tested in this study did not alter the removal efficiency of copper remarkably, this parameter was targeted at the central value. To adopt a cost-driven approach and also to save energy, current intensity was minimized. But to compensate for reduced efficiency due to the decreased current intensity and to achieve the maximum rate of copper removal, residence time was maximized. Accordingly,  $3 \text{ mg L}^{-1}$  copper concentration, 75.8 min electrolysis time, and 0.16 A current intensity (as minimized goal) were selected as numerical optimization option of RSM to achieve the best removal efficiency in the range of 69.9–99% (the goal was maximized) by consuming the least possible amount of energy in the range of  $1.78\text{--}18 \text{ kWh m}^{-3}$  (the goal was minimized). After determining the favorable criteria for factors and responses, RSM proposed four solutions to achieve the optimization goals. Table 4 presents the combinations of the factors optimized for satisfying the requirements placed on factors and responses. After numerical optimization, the point prediction option of RSM, which had predicted responses under optimal experimental conditions of each solution, was

**Table 4** | Optimization conditions predicted by CCD to achieve maximum rate of copper removal using least probable energy

Solution	$X_1$ : Copper conc. ( $\text{mg L}^{-1}$ )	$X_2$ : Time of electrolysis (min)	$X_3$ : Current intensity (A)	$Y_1$ : Copper removal (%)	$Y_2$ : Consumption of energy ( $\text{kWh m}^{-3}$ )
1	3	75.81	0.18	91.42	7.28
2	3	75.81	0.17	91.315	7.235
3	3	75.81	0.18	91.548	7.335
4	3	75.81	0.19	92.882	7.94

applied to verify optimization results. The program predicted 91.42% copper removal efficiency (corresponding importance: 5) and 7.28 kWh m<sup>-3</sup> energy consumption (corresponding importance: 3) under optimal values of variables: 3 mg L<sup>-1</sup> copper concentration, 75.81 min reaction time, and 0.18 A current intensity suggested in the solution number 1. In the point prediction option of the program, a prediction interval at confidence level of 95% was determined for every response. The low and high prediction intervals of responses were 87–95.8% for copper removal and 6.78–7.77 kWh m<sup>-3</sup> for energy consumption. To validate the suggested optimum values, an extra experiment was performed under conditions proposed by the solution number 1. The experiment showed 91% copper removal and 7.05 kWh m<sup>-3</sup> energy consumption; both values were quite close to the estimated values and were also between the foreseen ranges by point prediction. Based on the optimization results, only 0.27 mg L<sup>-1</sup> copper remained in the final effluent, which is much less than what is permitted by the USEPA (1.3 mg L<sup>-1</sup>) for the presence of copper in industrial treated effluents.

### SUGGESTIONS FOR FURTHER STUDIES

Since the metal removal occurs only through cathodic reactions, it is proposed for further research to put both input and output in the cathodic compartment and fill the anolyte with a neutral electrolyte. Thereby, we can even increase the residence time in the reactor to have improved removal rates.

### CONCLUSIONS

This study showed that electrochemical reduction in an electrolysis cell divided by a cellulosic separator is able to reduce copper concentrations far below strict discharge limits. Depending on various operational conditions, Cu ion removal was obtained of between 69.93 and 99%. Electrical energy was consumed in the range of 1.78 to 18.1 kWh m<sup>-3</sup>. The optimal current intensity and electrolysis time for treating a solution containing 3 mg L<sup>-1</sup> copper were 0.18 A and 75.8 min, respectively. Under such conditions, the removal efficiency and energy consumption were 91% and 7.05 kWh m<sup>-3</sup>, respectively. This study proved the ability of the electrochemical process using graphite anodes and steel cathodes for copper removal from aqueous solutions, which was facilitated under alkaline conditions prevailing

in the cathodic compartment due to applying a cell divided by a cellulosic separator.

### DISCLOSURE STATEMENT

No potential conflict of interest is reported by the authors.

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### REFERENCES

- Awual, M. R., Ismael, M., Yaita, T., El-Safty, S. A., Shiwaku, H., Okamoto, Y. & Suzuki, S. 2013 Trace copper(II) ions detection and removal from water using novel ligand modified composite adsorbent. *Chemical Engineering Journal* **222**, 67–76.
- Bagastyo, A. Y., Batstone, D. J., Kristiana, I., Escher, B. I., Joll, C. & Radjenovic, J. 2014 Electrochemical treatment of reverse osmosis concentrate on boron-doped electrodes in undivided and divided cell configurations. *Journal of Hazardous Materials* **279**, 111–116.
- Basha, C. A., Bhadrinarayana, N., Anantharaman, N. & Begum, K. M. S. 2008 Heavy metal removal from copper smelting effluent using electrochemical cylindrical flow reactor. *Journal of Hazardous Materials* **152**, 71–78.
- Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S. & Escalera, L. A. 2008 Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta* **76** (5), 965–977.
- Bilal, M., Shah, J. A., Ashfaq, T., Gardazi, S. M. H., Tahir, A. A., Pervez, A., Haroon, H. & Mahmood, Q. 2013 Waste biomass adsorbents for copper removal from industrial wastewater – a review. *Journal of Hazardous Materials* **263** (2), 322–333.
- Chang, N.-B., Houmann, C., Lin, K.-S. & Wanielista, M. 2016 Fate and transport with material response characterization of green sorption media for copper removal via desorption process. *Chemosphere* **154**, 444–453.
- Cudennec, Y. & Lecerf, A. 2003 The transformation of Cu(OH)<sub>2</sub> into CuO, revisited. *Solid State Sciences* **5** (11–12), 1471–1474.
- Danilov, F., Protsenko, V. & Butyrina, T. 2001 Chromium electrodeposition kinetics in solutions of Cr(III) complex ions. *Russian Journal of Electrochemistry* **37** (7), 704–709.
- Davoudi, M., Gholami, M., Naseri, S., Mahvi, A. H., Farzadkia, M., Esrafil, A. & Alidadi, H. 2014 Application of electrochemical reactor divided by cellulosic membrane for optimized simultaneous removal of phenols, chromium, and

- ammonia from tannery effluents. *Toxicological & Environmental Chemistry* **96** (9), 1310–1332.
- Del Rfo, A. I., Molina, J., Bonastre, J. & Cases, F. 2009 Influence of electrochemical reduction and oxidation processes on the decolourisation and degradation of CI Reactive Orange 4 solutions. *Chemosphere* **75** (10), 1329–1337.
- El-Ghenymy, A., Cabot, P. L., Centellas, F., Garrido, J. A., Rodríguez, R. M., Arias, C. & Brillas, E. 2013 Electrochemical incineration of the antimicrobial sulfamethazine at a boron-doped diamond anode. *Electrochimica Acta* **90**, 254–264.
- Gong, J.-L., Wang, X.-Y., Zeng, G.-M., Chen, L., Deng, J.-H., Zhang, X.-R. & Niu, Q.-Y. 2012 Copper (II) removal by pectin-iron oxide magnetic nanocomposite adsorbent. *Chemical Engineering Journal* **185–186**, 100–107.
- Hastie, J., Bejan, D., Teutli-Leon, M. & Bunce, N. J. 2006 Electrochemical methods for degradation of Orange II (sodium 4-(2-hydroxy-1-naphthylazo) benzenesulfonate). *Industrial & Engineering Chemistry Research* **45** (14), 4898–4904.
- Hossain, M., Ngo, H. H., Guo, W. & Nguyen, T. 2012 Removal of copper from water by adsorption onto banana peel as bioadsorbent. *International Journal of Geomate* **2** (2), 227–234.
- Jiang, W., Wang, W., Pan, B., Zhang, Q., Zhang, W. & Lv, L. 2014 Facile fabrication of magnetic chitosan beads of fast kinetics and high capacity for copper removal. *ACS Applied Materials & Interfaces* **6** (5), 3421–3426.
- Kakakhel, L., Lutfullah, G., Bhangar, M. I., Shah, A. & Niaz, A. 2007 Electrolytic recovery of chromium salts from tannery wastewater. *Journal of Hazardous Materials* **148** (3), 560–565.
- Khattab, I. A., Shaffei, M. F., Shaaban, N. A., Hussein, H. S. & Abd El-Rehim, S. S. 2013 Electrochemical removal of copper ions from dilute solutions using packed bed electrode. Part II. *Egyptian Journal of Petroleum* **22**, 205–210.
- Kutty, S., Ezechi, E., Khaw, S., Lai, C., Isa, M. & Salihi, I. 2016 Copper removal from biological treatment system using modified adsorbent derived from groundwater treatment plant sludge and rice husk. *Jurnal Teknologi* **78**, 53–57.
- Lee, J.-C., Son, Y.-O., Pratheeshkumar, P. & Shi, X. 2012 Oxidative stress and metal carcinogenesis. *Free Radical Biology and Medicine* **53** (4), 742–757.
- Ma, A., Hadi, P., Barford, J., Hui, C.-W. & McKay, G. 2014 Modified empty bed residence time model for copper removal. *Industrial & Engineering Chemistry Research* **53** (35), 13773–13781.
- Maljaei, A., Arami, M. & Mahmoodi, N. M. 2009 Decolorization and aromatic ring degradation of colored textile wastewater using indirect electrochemical oxidation method. *Desalination* **249** (3), 1074–1078.
- Méndez-Martínez, A. J., Dávila-Jiménez, M. M., Ornelas-Dávila, O., Elizalde-González, M. P., Arroyo-Abad, U., Sirés, I. & Brillas, E. 2012 Electrochemical reduction and oxidation pathways for Reactive Black 5 dye using nickel electrodes in divided and undivided cells. *Electrochimica Acta* **59**, 140–149.
- Pak, D., Chung, D. & Ju, J. B. 2001 Design parameters for an electrochemical cell with porous electrode to treat metal-ion solution. *Water Res* **35**, 57–68.
- Rabbani, D., Mostafaei, G., Roozitalab, N. & Roozitalab, A. 2012 Application of electrochemical process for removal of chromium and copper from Kahrizak leachate. *World Applied Sciences Journal* **17**, 442–446.
- Sadiq, R. & Rodriguez, M. J. 2004 Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: a review. *Science of the Total Environment* **321** (1–3), 21–46.
- Sala, M. & Gutierrez-Bouzan, M. C. 2012 Electrochemical techniques in textile processes and wastewater treatment. *International Journal of Photoenergy* **2012** (1), 1–12.
- Schaefer, C. E., Andaya, C., Urtiaga, A., McKenzie, E. R. & Higgins, C. P. 2015 Electrochemical treatment of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) in groundwater impacted by aqueous film forming foams (AFFFs). *Journal of Hazardous Materials* **295**, 170–175.
- Sharma, K., Sharma, S., Sharma, S., Singh, P., Kumar, S., Grover, R. & Sharma, P. 2007 A comparative study on characterization of textile wastewaters (untreated and treated) toxicity by chemical and biological tests. *Chemosphere* **69**, 48–54.
- Shawabkeh, R., Al-Harabsheh, A. & Al-Otoom, A. 2004 Copper and zinc sorption by treated oil shale ash. *Separation and Purification Technology* **40** (3), 251–257.
- Wen, Y., Ma, J., Chen, J., Shen, C., Li, H. & Liu, W. 2015 Carbonaceous sulfur-containing chitosan-Fe(III): a novel adsorbent for efficient removal of copper (II) from water. *Chemical Engineering Journal* **259**, 372–380.
- Zhang, Z., Xu, Y., Shi, W., Wang, W., Zhang, R., Bao, X., Zhang, B., Li, L. & Cui, F. 2016 Electrochemical-catalytic reduction of nitrate over Pd-Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in cathode chamber: enhanced removal efficiency and N<sub>2</sub> selectivity. *Chemical Engineering Journal* **290**, 201–208.

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