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Hardness and chloride removal in dewatering system: Modeling and optimization of electrochemical reaction

Ali Hasanzadeh-Sablouei[1], Seyed Morteza Moosavirad[2*]

[1] *Department of Mining Engineering, Higher education complex of Zarand, Kerman, Iran.*

[2] *Department of Environment, Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, Kerman, Iran.*

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ABSTRACT

The electrocoagulation (EC) process is a novel approach in the mining industry, especially to recycle water in the dewatering system of a mineral processing plant. In this research, the electrocoagulation process was studied to remove the hardness and chloride ions from concentrate thickener overflow water under different operating conditions: retention time (5–15 min), initial pH (4–10), current density (41.6–166.6 A/m^2) and electrode type (Fe, Fe-Al, Al). Four factors with three levels with the D-optimal response surface design were applied for optimization. As a result, the optimal situation for the electrocoagulation process was characterized by a retention time of 15 min, initial pH of 9.08, the current density of 139.59 A/m^2, and electrode type Fe-Al. In this situation, the maximum removal efficiency of hardness (60.11%) and chloride (98.38%) were yielded with a desirability value of 0.989. These results illustrated the effectiveness of the EC process as an influence method for the removal of hardness and chloride in terms of separation.

1. Introduction

The mining industry expends extensive amounts of water, and the process involved in the copper mining industry consumes more than 1.3 billion m^3 water [1]. Although, mine water consumption is considered as a tiny section of the total water applied worldwide. So that, in countries such as South Africa, Chile, and Australia, where mining consumes more human and mechanical energy, the utilization of mine water is contained to about 2 to 4.5% of the total national water quantity [2,3]. Mining requires equipment on a large scale with high energy consumption for the treatment system, pumping, and cooling the water systems. Therefore, it is necessary to decrease the rate of water consumption and the amount of energy. In order to attain a sustainable mining industry, improving the operational conditions and designing a water system are the main strategic elements in this field. Nevertheless, few studies

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*Corresponding author: Tel: +983432473788
Email address: s.m.moosavirad@kgut.ac.ir

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have been performed on the design of the water processes in industrial operations, especially mining [4]. In copper production, the ore is first extracted from the mine pit and then transferred to the mineral processing and beneficiation plant for concentrate production. Water is utilized in the mineral processing plant for various applications: comminution (crushing, grinding, and screening), neutralizing dust, water process, and flotation or other beneficiation processing. Nowadays, implementing mining policy enforces applying a maximum rate of water reuse and recycling. And there is much effort to recycle water for use in the mining sector [5]. The recycling process works to improve water quality, which cross-section includes solid-liquid separation by methods such as clarification or filtration. Solid-liquid separation involves the precipitation of solids in water using gravitational force that it exerts by thickeners and clarifiers [6-7]. Thickening is the most applicable method among dewatering systems such as filtration [8]. Thickeners are major processes for the separation of solids from liquid in the mining industry. Thickeners are based on two types, namely large-diameter conventional and high rate thickeners. Raw water consumption is reduced by reclaiming of thickener return water. The water overflow of the thickener is recycled back to the water process and decreases the use of raw water. In order to accelerate the precipitation in the thickeners, flocculants are mostly added to produce a series of interconnected solid particles to make them more compressive. The inlet combination of thickener is distributed into two flows: Water overflow that is used in the concentration plant and the underflow of the pulp which utilized as Cu concentrate [9,10]. The most applicable processes or the typical treatment methods of generated water from industrial effluent are membrane processes, ion exchange, coagulation, adsorption, and electrodialysis [11]. The reverse osmosis and ion exchange methods produce large volumes of reusable water from solutions with high amounts of acids or salts; as well, the regeneration of resin is considered a fundamental problem [12-15].In the coagulation method, the sedimentation of a chemical material reduces the total hardness from lime for softening, which generates an extensive volume of lime sludge [16]. One effective method that has been widely investigated is the electrochemical process [17]. The electrocoagulation method introduces an innovation that is applicable in the mining industry. It has more influence than conventional methods due to accelerating in separation and has competitive electrical characteristics (especially regarding maintenance time, reduction of wastewater production, and ordinary operation) [18]. The available concentration plant consists of five main sections: crushing, milling, flotation unit, beneficiation, and dewatering. The dewatering unit of a mine separates particles more vast than the usual size and the water is reused in the concentration plant. So far, no studies have been conducted on water recycling using electrocoagulation in mineral processing plants. Most studies have focused on hardness removal from industrial effluents. Among the many advantages of the electrocoagulation process, the following can be mentioned: high efficiency of particle separation, easy to use process (In reason, no coagulants are added to the water), requires small space and less equipment, and the possibility of full automation [19]. This process is different because of its minimal sludge production and short operation time [20]. The disadvantages of this system include hydrogen gas production (a possible safety hazard), anode corrosion, and sludge sedimentation on electrodes that can limit the process. Although, increasing the concentration of iron and aluminum ions in the water lead to high initial investment and high electricity consumption that can influence some areas [21]. Hardness and chlorine ions are two of the main factors that lower the quality of recycled water from the thickener overflow in a copper concentration plant. Hardwater, especially calcium ions, can notably affect the mining industry due to mineral accumulation in the water pipes and the reduction of heat transfer in the boiler and cooling tower [22,23]. Chloride is one of the most serious anions constituted in industry water. It usually compounds with calcium, magnesium, or sodium to form various salts. These salts are collectively called chlorides. Over time, chloride ions lead to high corrosivity that harms plumbing, transfer water equipment, and boilers [24]. Therefore, the present study investigated the removal of hardness and chloride via EC in the dewatering unit to improve the thickener's overflow water quality and recycle it. The operation time, initial pH, current density, and electrode type were specified as four inducing factors, and the percentage of removal was considered a response. The utilization of electrocoagulation technology has been considered as a new method to improve water quality in existing mining industries. This process includes the combined application of electricity current and air bubbles. In fact, this process, through the three mechanisms of electrode oxidation, production of gas bubbles, and flotation and settling of the formed clots, leads to the removal of contaminants in the water and improves water quality considerable. In the present study, this process (EC) by treating the effluent of the concentrate plant (return water) illustrates that this operation is a new and applicable method in industrial and mining units. Water plays a very important and vital role in the industries, considering that we are facing the problem of dehydration, the reuse and recovery of process water in the industries is very valuable and significant. Due to the fact that the concentration of chlorine ions is effective on corrosion behavior in industrial facilities and cooling towers, and on the other hand, high TH causes sediment in the inner wall of boilers and pipes in industrial units. Since there are different methods for removing water, such as ion exchange and filtration, which have the ability to remove all water quality parameters, and since the goal is only to Hardness and chloride removal in the water; Therefore, in this article, an efficient and modern method (EC) to improve the quality of returned water by removing these two parameters is discussed. Response-surface methodology executed on the D-optimal experimental design was used to evaluate the optimal condition. Then, a quadratic model correlating the hardness and chloride removal to four variables was expanded. RSM consists of mathematical and statistical approaches for making empirical models and assessing the influences of some factors to provide the best situations. In an accurate plan of experiments, the purpose is to consider the optimization of a response as the output variable that is affected by several independent variables as input variables. But the common methods take time and energy. Therefore, the use of RSM to optimize the experimental condition is purposed to decrease the expenditure of costly analysis methods and time [25]. The D-optimal design is an influence method of RSM for the optimization of complex processes. It is commonly utilized to improve the culture medium [26]. Much scientific research is investigated based on a foundation of the D-optimal design [27]. This work aimed to investigate the water recycling (removal of hardness and chloride) of the overflow of a copper concentration plant by EC and to optimize the effects of factors influencing the efficiency of the removal using RSM (D-optimal).

2. Materials and methods

2.2. Concentrate thickener processing wastewaters

In the concentrate thickener, the wastewater sample was collected from the outlet of the thickener overflow in a copper concentration plant. The wastewater sample was kept in the dark at 4 °C in a refrigerator and applied without any dilution. Table 1 shows the compound of thickener wastewater.

Table 1. Characteristics of thickener overflow wastewater.

Parameter	Value
pH	9.37
chloride (mg/l)	79
TH (mg/l)	295
TSS (mg/l)	558.8
Conductivity(μS/cm)	910

2.2. Experimental setup

The experimental setup for water recycling using the EC procedure is exhibited in Figure. 1. The reactor's volume was about 6 L (length of 30 cm; width of 10 cm, and height of 20 cm with an effective volume of 5 L) and included three sections: dewatering system, EC reactor, and the electronic control module (ECM). The EC procedure included four stages [28,29]: 1) reactions of electrolytic at electrode's surfaces; 2) the coagulation process in the phase of containing water; 3) the solution sorption or copper concentrate on coagulants; 4) settling or the accumulations' flotation. The copper concentrate composition in the EC procedure is separated in the treated water, exhibiting in the form of the floating layer, and some sludge remained as mineral-rich sediment. In addition, the electrodes consisted of iron as anode and aluminum as the cathode. Six iron and aluminum electrodes were created from 20 × 2 cm plates, and the effective area of the electrode in the outlet water from the thickener overflow was 90 cm2. The electrodes were connected in parallel form to each other, and the electrode distance was 2 cm. The total electrodes were linked to the outlets of the electric control unit. Electric power supplies provide the clean, stable DC power needed for controlling the applications. First, the residual solids on the electrodes were washed and dried before each run. Next, the pH was measured using a pH meter (ExStik, Extech, USA), and H_2SO_4 was used for adjusting pH in each run. The total hardness (TH) and chloride are the main parameters in the water cycle process. Therefore, the EC process was employed to reduce them to prevent corrosion in the equipment and water pipes. Finally, TH was measured according to the standard EDTA titration method, and chloride values were taken using the silver chloride turbidimetric method [30]. The efficiency of the EC process is given below [31]:

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

where the contents of C_0 and C_i display the concentration of hardness and chloride before and after the EC process.

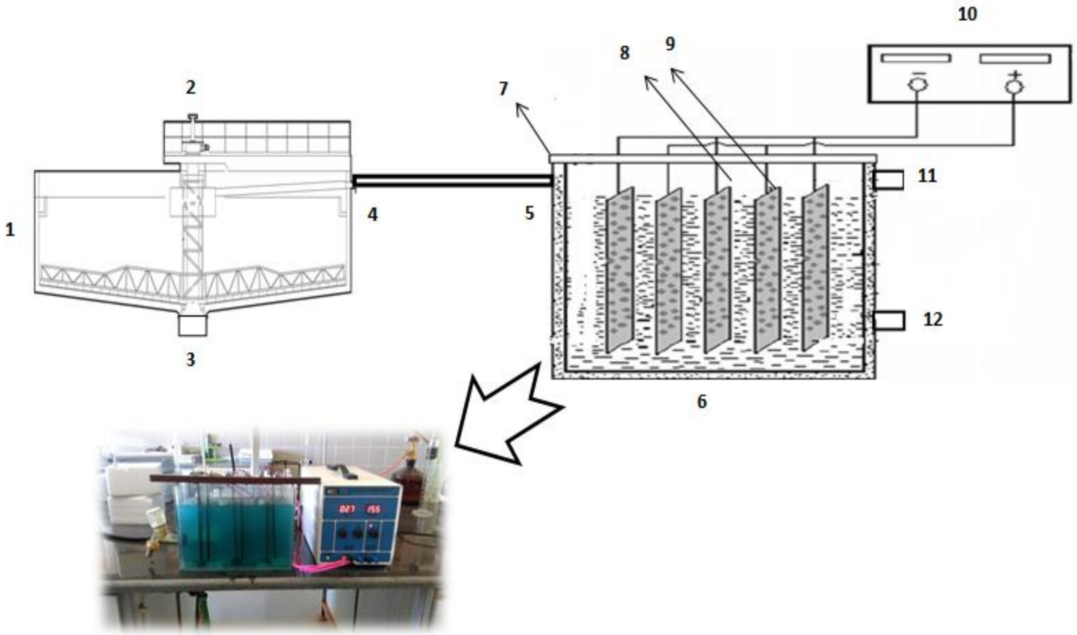

Fig. 1. Schematic diagram of the dewatering system, EC reactor and the electric control module. 1. Thickener; 2. Feed inlet; 3. Thickener underflow; 4. Thickener overflow; 5.Inlet for wastewater; 6. EC reactor; 7. PVC cover; 8. Cathode; 9. Anode; 10. DC power supply; 11. Sludge outlet; 12. Water recovery.

2.3. Analysis method

In this research, the selected parameters for the hybrid electrochemical reactions are optimized in statistical form by adopting RSM. RSM is considered an analysis of regression applied to present the content of a dependent variable based on the detected amounts of the independent ones. RSM has a high capability in the production of various compositions of parameters over a short time to create actual data in laboratory tests. According to the obtained data, a variable is selected that has the highest calculated value. Therefore, a researcher could consider the variables that are significant to yield acceptance [32]. The physical, chemical, and biological processes for modulation and optimization are handled by RSM [33,34]. The D-optimal indicator is one of the most important criteria for the choice of design points. D-optimal criteria can minimize the variance related to the evaluation of defined model coefficients [35]. In this study, the operation items in the EC system, including three numerical variables (pH, retention time, and current density) and a constant variable (electrode type), were optimized using RSM. In order to provide the optimum condition for operating variables, two dependent parameters were assessed as the responses: hardness% removal (Y_1) and chloride% removal (Y_2). To describe the behavior of the system, the analysis of the second-order multiple regression by the procedure of minimum squares regression was used to acquire the mathematical model [31,36]. The model represented by a quadratic equation for detecting the appropriate situation could be explained following Eq. (2):

$$\mathrm{Y} = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} {x_j}^2 + \sum \sum_{i<j=2}^{k} \beta_{ij} x_i x_j + e \qquad (2)$$

where Y represents the response; x_i and x_j are considered as variables (i & j in 1-k range); β_0 is a coefficient of intercept of the model; β_j, $\beta_{jj,}$ and β_{ij} are the linear, quadratic, and the second-order interaction coefficients, respectively; k represents the quantity of the independent parameters (k = 4 in the present research); and e represents the error in analyses. The assessment of the regression coefficient and analysis of variance (ANOVA) are carried out to prove the competence of the recommended polynomial model. In order to obtain the graphical analyses from the interactions made between the variables and responses, ANOVA was obtained using statistical analysis software (SAS) (the version of Design-Expert 7.0.0). The variables and experimental values of the process parameters are presented in Table 2.

Table 2. Coded and experimental values of process parameters.

Design matrix	**parameter values**	**Numerical variable**			**parameter levels**	**categorical variable**
		Retention time (min) (A)	**Effluent pH (B)**	**Current density(A/m^2) (C)**		**Electrode type (D)**
D-optimal matrix	Low level (-1)	5	4	41.66	level 1	Fe
	Center point (0)	10	7	104.1	level 2	Fe-Al
	High level (+1)	15	10	166.66	level 3	Al

3. Results and discussion

3.1. Analysis and Interpretation of the response

Twenty runs from the D-optimal experimental responses are shown in Table 3. The hardness removal percent varied from 8.16% to 44.89%, while the chloride removal percentage varied from 9.51% to 91.23%.

3.2. The conformation of the EC process and hardness and chloride removal's model by ANOVA

The ANOVA outcomes are displayed in the linear model for the hardness removal and the quadratic model for the chloride removal evaluation, respectively, in Tables 4 and 5. The F-values of the model is significant when the values are placed between 23.89 and 26.84. The probability of this wide model happening using a chance is 0.01%. When this model procedure is significant, the values of "Prob.>F" are less than 0.050 [37]. The point to be considered is that the correlation agent should be at least 0.80 for attaining appropriate adaptability. The "Predicted R-squared" of 0.9917 (R_1^2) is adaptable with the "Adjusted R-squared" of 0.9502 (R_1^2 adj).

Table 3. Process design layout using D-optimal design and test results.

Exp. no.	A (min)	B	C (A/m^2)	D	% Hardness removal	% chloride removal
1	10	7	104.1	Fe	23.80	73.09
2	5	7	104.1	Al-Fe	34.01	58.32
3	15	4	166.6	Fe	8.16	79.10
4	15	10	41.6	Fe	35.37	89.57
5	15	4	166.6	Al	37.07	77.10
6	15	7	104.1	Al-Fe	19.05	62.58
7	10	10	41.6	Al	43.54	81.23
8	10	7	104.1	Al-Fe	21.09	16.65
9	5	10	166.6	Al	42.86	83.35
10	5	4	41.6	Fe	19.05	68.71
11	5	4	166.6	Al-Fe	18.37	13.64
12	5	4	41.6	Al	17.01	83.48
13	5	10	166.6	Fe	35.39	72.89
14	15	4	41.6	Al-Fe	18.36	83.45
15	15	10	166.6	Al-Fe	40.48	91.24
16	15	10	104.1	Al	44.90	83.37
17	5	10	41.6	Al-Fe	29.93	66.58
18	10	10	104.1	Al-Fe	42.18	20.78
19	15	7	41.6	Al	37.41	87.46
20	10	4	104.1	Al-Fe	28.57	9.51

Table 4. Defluorination rate analysis of variance for response surface linear model.

Source	Sum of Squares	df	Mean Square	F-Value	p-value Prob > F	
Model	2245.64	15	149.71	23.89	0.0119	significant
A	1.65	1	1.65	0.26	0.643	
B	374.27	1	374.27	59.72	0.0045	
C	106.8	1	106.8	17.04	0.0258	
D	1	1	1	0.16	0.7166	
AB	13.11	1	13.11	2.09	0.2439	
AC	17.75	1	17.75	2.83	0.191	
AD	139.64	1	139.64	22.28	0.018	
BC	51.1	1	51.1	8.15	0.0648	
BD	54.16	1	54.16	8.64	0.0605	
CD	141.95	1	141.95	22.65	0.0176	
B^2	218.08	1	218.08	34.8	0.0097	
C^2	131.22	1	131.22	20.94	0.0196	
ABD	165.76	1	165.76	26.45	0.0142	
ACD	69.02	1	69.02	11.01	0.0451	
BCD	96.38	1	96.38	15.38	0.0295	
Residual	18.8	3	6.27		R_1^2	0.9917
Cor Total	2264.44	18			Adj. R_1^2	0.9502

The "Predicted R-squared" of 0.9931 (R_2^2) expressed in Table 5 has desirable compatibility with the "Adjusted R-squared" of 0.9561(R_2^2adj). Therefore, this model can be appropriately applied to conduct the design room. The coefficients and constants are taken using suitable data noted in Tables 4 and 5 of Eqs. (3) & (4), respectively:

$$\begin{aligned} \mathrm{Y}_1 = 21.66 &- 0.47\mathrm{A} + 6.75\mathrm{B} + 4.06\mathrm{C} - 0.56\mathrm{D} \\ &- 1.42\mathrm{AB} + 1.68\mathrm{AC}\ 24.53\mathrm{AD} \\ &+ 2.84\mathrm{BC}\ 15.02\mathrm{BD} + 27.24\mathrm{CD} \\ &+ 13.71\mathrm{B}^2 - 9.52\mathrm{C}^2 \\ &+ 35.44\mathrm{ABD} - 20.84\mathrm{ACD} \\ &- 24.99\mathrm{BCD} \end{aligned} \qquad (3)$$

$$
\begin{aligned}
Y_2 = 15.37 + 8.46A + 5.41B - 2.91C + 4.75D \\
- 8.38AB + 9.83AC + 11.16AD \\
+ 13.71 - 13.66BD + 27.95CD \\
+ 45.36A^2 - 19.43C^2 \\
+ 53.81D^2 + 22.50ABC \\
+ 34.99AB - 21.77ACD
\end{aligned}
\quad (4)
$$

It should be very accurate considering that the choice model creates a moderate approximation to arrive at the actual system. The model competence can be determined by the diagnostic layout containing normal probability versus standardized residuals and the predicted value versus the actual one [37,38]. Figure. 2 shows the plots with normal probability in the standardized residuals for the percentage of hardness and chloride removal. The plot with normal probability demonstrates the normal diffusion of the residuals. Also, it demonstrates that the points of the figure follow a fairly straight line. This can confirm the valuable data and the reliability of the empirical data. As shown in Figure 3, the actual response values are obtained from the experimental data and the predicted response values are obtained by approaching the functions. The predicted values are of a desirable compromise with the experimental values. It can be argued that the model is valid and has acceptable compatibility with experimental data.

Table 5. Defluorination rate analysis of variance for response surface quadratic model.

Source	Sum of Squares	df	Mean Square	F-Value	p-value Prob > F	
Model	13869.97	16	866.87	26.84	0.01	significant
A	902.95	1	902.95	27.96	0.0132	
B	335.61	1	335.61	10.39	0.0484	
C	80.59	1	80.59	2.5	0.2123	
D	195.03	1	195.03	6.04	0.0911	
AB	665.97	1	665.97	20.62	0.02	
AC	920.56	1	920.56	28.51	0.0128	
AD	834.73	1	834.73	25.85	0.0147	
BC	1623.19	1	1623.19	50.27	0.0058	
BD	261.97	1	261.97	8.11	0.0652	
CD	682.52	1	682.52	21.14	0.0193	
A^2	2489.55	1	2489.55	77.09	0.0031	
C^2	401.37	1	401.37	12.43	0.0388	
D^2	2730.98	1	2730.98	84.57	0.0027	
ABC	1130.63	1	1130.63	35.01	0.0096	
ABD	842.04	1	842.04	26.08	0.0145	
ACD	542.89	1	542.89	16.81	0.0262	
Residual	96.88	3	32.29		R_2^2	0.9931
Cor Total	13966.84	19			Adj. R_2^2	0.9561

The influence of practical parameters resulting from the response surface analysis is assessed by measuring the maximum hardness and chloride removal by considering each variable. In the electrochemical processes, the retention time, pH, and density of current can be referred to as highly significant parameters to adjust the rate of reaction [39,40]. Hence, the impact of the three principal parameters on the hardness and chloride removal was evaluated through RSM. The influences of each variable on the hardness and chloride removal are explained below and represented in Figures. 4-6.

(i). Retention time

In EC processes, retention time is considered one of the most important operating parameters [29]. The retention time ranged from 5 to 15 min and was investigated to comprehend how time influenced the removal efficiencies. The other parameters of pH, current density, and electrode type were kept constant at 7, 104.10, and Fe-Al, respectively. As underscored in Figure. 4a and b, a raised removal rate resulted from an increase in the retention time. As shown in Figure 4, although chloride removal is reduced in the time interval of 5 to 7.5 min, after 7.5 minutes it increases. The influence of retention time is the main parameter that adjusts the rate of reaction in the EC process. According to Faraday's Law, the content of iron transferred to the hybrid mode by Fe electrodes can influence residence time, extending the ions of Fe transferred to the system [32]. Whereas the content of dissolved material is increased by Fe electrodes, enhancing the percentage of removal efficiency. One can express this using an adequate value of iron electrode as a coagulant, which effectively decreases double-layered from the hydroxides of the suspended metallic and unstable particles [41]. Hydroxide flocs are created from hydroxyl and ferric ions that are released from the electrodes' surface. The flocs that have been produced adsorb the particles with more pollutants [29,42].

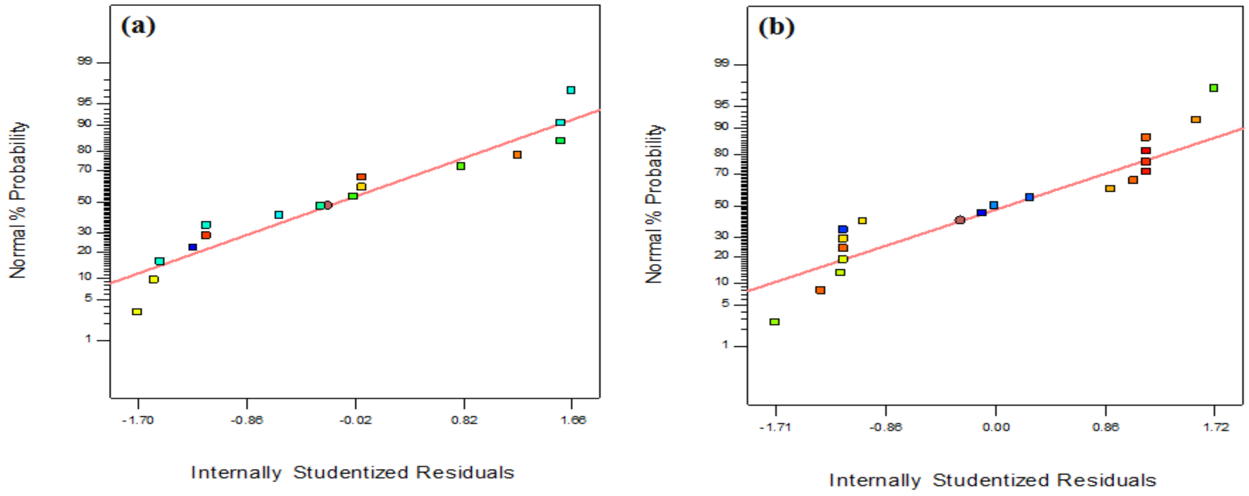

Fig. 2. Normal probability plots of internally studentized residuals: (a) %Hardness removal; (b) % chloride removal.

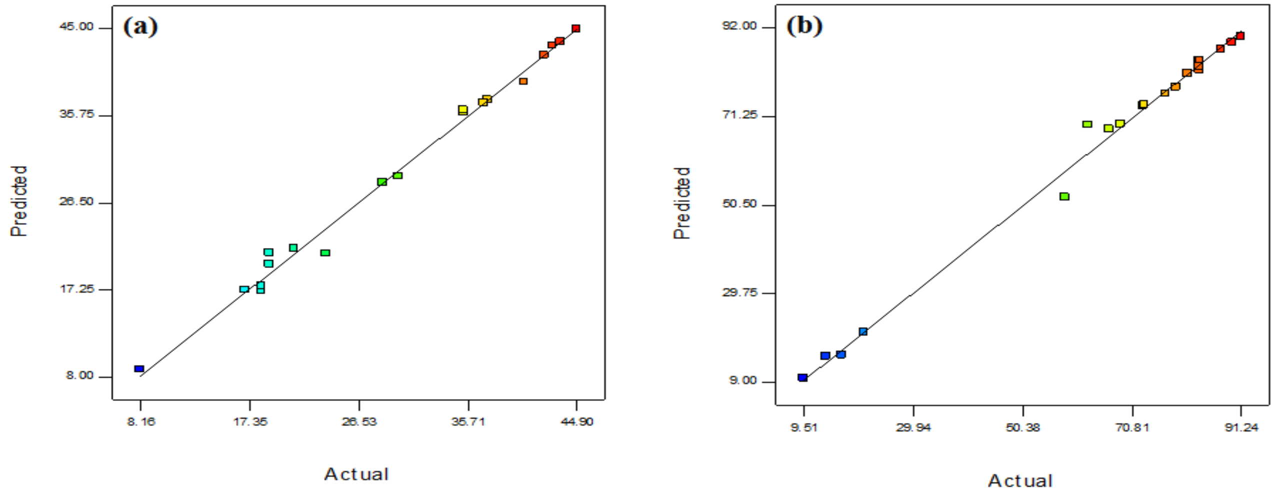

Fig. 3. Linear correlation between actual and predicted rates: (a) Hardness removal (%); (b) Cl removal (%).

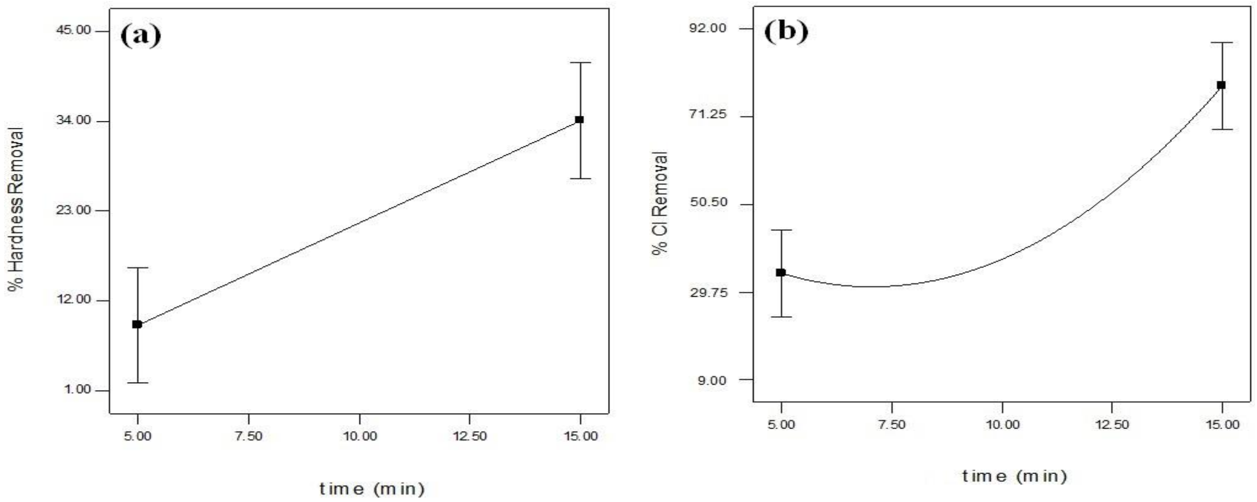

Fig. 4. Effect of retention time a) on hardness removal (%) and b) on Cl removal (%) (Initial pH: 7; current density: 104.10; electrode type: Fe-Al), One factor plot.

(ii). Initial pH

Initial pH is one of the major parameters that effectively implements the EC process [43]. A varied range from pH 4 to 10 was investigated to distinguish the influences of initial pH on the efficiency of hardness and chloride removal. The constituting chemical reactions are represented in Eqs. (4)- (6) [44]:

Reaction 1 (acid pH):

$$2\mathrm{Fe}_{(s)} + 6\mathrm{H_2O}_{(l)} \leftrightarrow \mathrm{O}_{2(g)} + 4\mathrm{H}_{2(g)} + 2\mathrm{Fe(OH)}_{2(S)} \quad (4)$$

Reaction 2 (neutral pH):

$$3\mathrm{Fe}_{(s)} + 8\mathrm{H_2O}_{(l)} \leftrightarrow \mathrm{Fe(OH)}_{2(S)} + 2\mathrm{Fe(OH)}_{3(S)} + 4\mathrm{H}_{2(g)} \quad (5)$$

Reaction 3 (alkaline pH):

$$2\mathrm{Fe}_{(s)} + 6\mathrm{H_2O}_{(l)} \leftrightarrow 2\mathrm{Fe(OH)}_{3(S)} + 3\mathrm{H}_{2(g)} \quad (6)$$

The pH variations were probed for several types of flocs. Reaction 1 (Equation 4) yielded green $Fe(OH)_{2(S)}$ flocs with acid pH; reaction 2 (Equation 5) pointed to green $Fe(OH)_{2(S)}$ and colloids of yellow $Fe(OH)_{3(S)}$ with neutral pH, and reaction 3 (Equation 6) represented flocs of brown $Fe(OH)_{3(S)}$ with alkaline pH. Regarding the obtained results, for increasing the yield of the Ec system, it is recommended to apply it at alkaline conditions.In this situationthere is a lower yield in $Fe(OH)_{2(S)}$ than $Fe(OH)_{3(S)}$ of sweep flocculation [44]. The initial pH and retention time influence on hardness and chlorine removal percent are exhibited in Figure 5(a,b). The outcomes demonstrate that the percentage of removal efficiencies tend to increase whenever the initial pH increase to the alkaline condition. With increasing pH from the acidic to alkaline form, the amount of hardness and chloride to intensity is reduced. For example, the removals of hardness and chloride were 43.23 and 83.48 in a pH of 9, respectively. Figure 5(c,d) illustrates the initial pH and current density influence on hardness and chloride removal. Increasing the pH cannot confirm a consecutive reduction of hardness and chloride, which is not a notable change; but, the hardness and chlorine removal are enhanced with increasing the current density. Whenever the pH went from 9 to 10, the removal of hardness and chloride increased to 35.17% and 82.55, respectively. This condition caused sedimentation of hardness around the cathode, as expressed in the following equations [29]:

$$\begin{aligned}
&\mathrm{HCO_3}^{-} + \mathrm{OH}^{-} \leftrightarrow \mathrm{CO_3}^{2-} + 4\mathrm{H}_{2(g)} + \mathrm{H_2O}\\
&\mathrm{CO_3}^{2-} + \mathrm{Ca}^{2+} \leftrightarrow \mathrm{CaCO_3} \qquad (7)\\
&\mathrm{SO_4}^{2+} + \mathrm{Ca}^{2+} + 2\mathrm{H_2O} \leftrightarrow \mathrm{CaSO_4.2H_2O}.
\end{aligned}$$

The intense reduction of hardness is ascribed to more sweep flocculation in alkaline situations. Based on reaction 3 (equation (6)), the most iron hydroxide was produced in the alkaline condition. Also, more flocs would be formed, and most carbonated salts would be included. Water softening reduces calcium, magnesium, and other metal cations in water with high hardness. Hard water causes limescale buildup, which can destroy plumbing and lead to the corrosion of pipes. Therefore, hardness should be reduced as much as possible. Malakootian et al. (2010) found that hardness reduction occurred at a pH of 7.0 and 10.0, and the presence of calcium decreased by 95.4% and 97.4%, respectively. The production of H_2 and OH^- in the cathode promote sequential pH increments for all experimental runs, which is similar to the trend of the hardness removal. But in neutral pH conditions, this rising trend happens with lesser intensity. One reason is that in alkaline pH conditions, a lesser amount of OH^- is produced, which can originate from the abundant content of OH^- formerly available in the solution. Based on reaction 3 (Equation 6), the reversible reaction was disposed to the left side with increasing pH and to the right side with reducing pH. The results show that the pH would increase remarkably when the initial pH was fairly low. The conditions were clear, but different conclusions were yielded in some cases; but, the initial pH was higher than the final pH that originated from the alkaline pH condition with a group of different complex reactions of electrodes [28,45,46]. Also, according to the outcomes, increasing the initial pH from 4 to10 improved the removal yield of chloride. This is certainly due to the fact that when pH is in the neutral condition and alkaline level, the formation of amorphous $M(OH)_3$ species is dominant. The newly-organized amorphous $M(OH)_3$ species have a large surface area, which can be useful for the removal of hardness and chloride by sweep coagulation pursued by the precipitation process. Although, an initial pH of more than six caused a reduction in removal efficiency due to the production of monomeric $M(OH)_4$ species [43,47]. However, these outcomes showed that the EC system represented several buffering pH capacities, particularly in the alkaline pH condition. In this investigation, the pH of the generated water was approximately 9-10, which was suitable to apply to the water cycle in the copper mine concentration plant. The most removal of hardness and chloride occurred in this pH area. Hence, the following experiments were carried out on raw water (overflow thickener) with a constant pH.

(iii). Current Density

The current density is one of the most significant parameters affecting the EC process [43]. It is distinguished with the coagulant amount and production ratio of the bubble. However, Thea's agents as intensity affect the parameters of the solution admixture and mass transfer in the electrode's surface [48]. Based on Faraday's electrolysis laws, the amount of coagulant produced in the anode is balanced with the entire electric loading passing in this field, which is called current density. Massive content of $Fe(OH)_3$ coagulants are generated in order to unstable of colloidal particles by raising the current density, which leads to more sedimentation and accelerates the reaction [49]. In other words, with increasing current density, a considerably content of H_2 is produced from the cathode electrodes; it can be noted that bubble size is reduced by raising the current density [50]. Therefore, it causes an increase in bubble agglomeration and also a strong upper current. It has been observed that smaller size bubbles produce a wider surface for connecting to more particles, providing higher removal efficiency [51]. The removal of hardness and chloride are derived by flocs that tend to shift using the huge contents of small bubbles by the flotation process. All of the above explanations show that with increased current density, a better reduction in hardness and chlorine is achieved [29]. As shown in Figures 6a and b, hardness and chloride removal efficiency are raised rapidly in the current density of 104.1 A/m^2. It is based on the fact that the coagulation process improves in the electrodes of the cathode and anode with increasing current density.Thus, flock formation of the metal hydroxide$(M(OH)_3)$ increases in the experiments, and consequently, leads to an upgrade in the removal efficiencies. However, the removal efficiency of hardness and chloride in the current density (104.1–166.6 A/m^2) is approximately invariable.

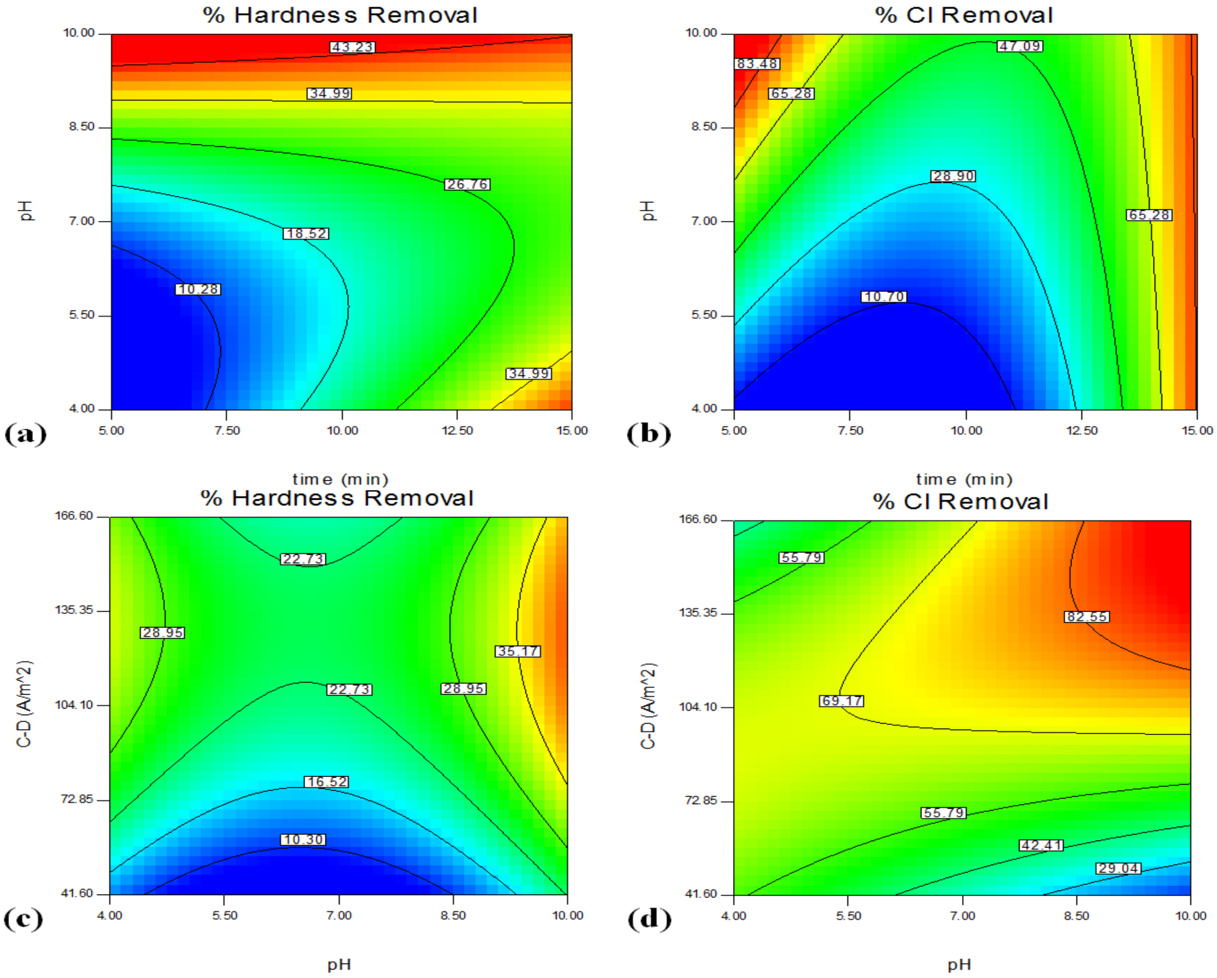

Fig. 5. Effect of a) Initial pH and retention time (electrode type: Fe-Al; current density: 104.10) on hardness removal(%), b) Initial pH and retention time (electrode type: Fe-Al; current density: 104.10 A/m^2) on chloride removal (%); c) Initial pH and current density (electrode type: Fe-Al; retention time: 10 min) on hardness removal(%) and d) Initial pH and current density (electrode type: Fe-Al; retention time: 10 min) on chloride removal(%); 2D contours.

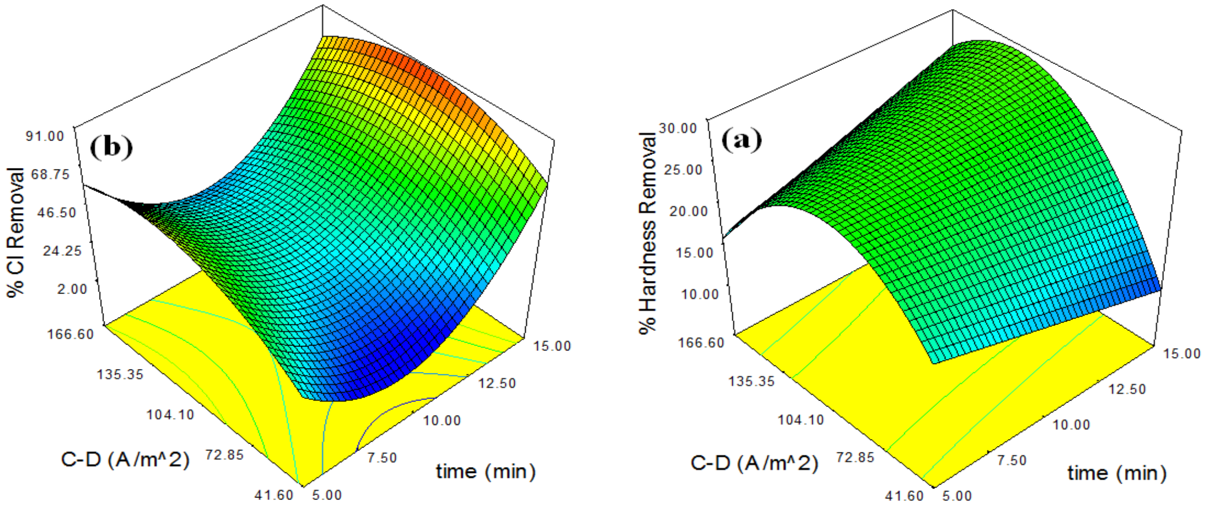

Fig. 6. Effect of current density and retention time on a) Hardness removal (%), b) On chloride removal (%) (initial pH:7; electrode type: Fe-Al); 3D surface plots.

3.4. Optimal status and confirmation of the model

The improvement and optimization of all the influence parameters are significant in the growth of the coagulation process [52]. The purpose of this investigation was to assay the values of the impressive factors (retention time, Initial pH, current density and electrodes type) via RSM that result in the utmost removal of hardness and chloride [33]. Based on the D-optimal results, the optimal situation for the EC process was characterized as follows: a retention time of 15 min, an initial pH of 9.08, the current density of 139.59 A/m^2, and the electrodes type Fe-Al. In this situation, the maximum removal efficiency of hardness (60.11%) and chloride (98.38%) are obtained in a condition with a desirability value of 0.989. Since the aim of the study is to achieve optimal conditions, triple trials were executed with optimal conditions and the mean values of actual tests, indicating the validation of the optimal situations [40]. This confirms that the D-optimal design and the utility functions can be utilized to optimize the experiments design for the removal of hardness and chloride by the EC process [31]. Mousavirad and Hassanzadeh-Sablouei [18,53] considered the operating costs of the electrocoagulation process. The results show that using an aluminum electrode in the electrocoagulation treatment system is quite economical in terms of operating costs.

4. Conclusions

In this research, D-optimal was used to assay and optimize the process variables, including the time of electrolysis, initial pH, current density, and electrode type, on the removal of hardness and chloride from the thickener overflow by using the EC process in the mineral processing plant. The outcomes indicated that in electrochemical processes, the electrolysis time, initial pH, and current density are the significant parameters that control the ratio of reaction. The F-values were significant when the values were between 23.89 and 26.84. The quadratic and linear models may be applied to evaluate design conditions. The coincidence of the experimental values and data points set near the diagonal line was proven by the model predictions. The plot with normal probability demonstrated the normal diffusion of the residuals. Also, it demonstrated that the points of the figure followed a fairly straight line. This confirmed the valuable data and reliability of the empirical data. The retention time ranged from 5 to 15 min and was investigated to comprehend how time influenced the removal efficiencies. A raised removal rate resulted from an increase in the retention time. Although chloride removal was reduced in the time interval between 5 to 7.5 min, after 7.5 minutes, the chlorine removal increased. The outcomes demonstrated that the percentage of removal efficiencies tend to increase whenever the initial pH increased to the alkaline condition. With increasing pH from acidic to alkaline, the amount of hardness and chloride to intensity was reduced. The removal of hardness and chloride were 43.23 and 83.48 in a pH of 9, respectively. The increase in pH cannot confirm a consecutive reduction of hardness and chloride, which was not a notable changed; but, the hardness and chlorine removal was enhanced with increased current density. Whenever the pH went from 9 to 10, the removal of hardness and chloride increased to 35.17% and 82.55, respectively. Also, the removal yield of chloride improved by increasing the initial pH from 4 to10. The efficiency of hardness and chloride removal increased rapidly to the current density of $104.1 A/m^2$. Based on the D-optimal results, the optimal situation for the EC process was characterized as follows: retention time of 15 min, initial pH 9.08, the current density of 139.59 A/m^2, and electrode type Fe-Al. The maximum removal efficiency of hardness (60.11%) and chloride (98.38%) are yielded in a condition with a desirability value of 0.989. This investigation recommends the use of RSM in the EC process as an influence method for assessing the reaction between the effecting parameters and also optimization on a large scale. The EC process is a novel approach that can be used in the mining industry, especially for water recycling in the dewatering system of mineral processing plants.

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