

Water recovery via the removal of Cl^- ion and total dissolved solids using electro dialysis in Gohar Zamin Iron Ore Concentrate Plant: modeling and simulation

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ABSTRACT

The desalination process consists of a set of multi-step actions, which are conducted on saline water in order to remove excess salts and other minerals. In the desalination process, water is recovered, so that it would be suitable for industrial usage. In the present study, electro dialysis (ED) was used for desalination, especially for removing chloride (Cl^-) ion and total dissolved solids (TDS), in Gohar Zamin Iron Ore Concentrate Plant. To optimize the influential factors in the removal of chloride and TDS in ED, the response surface methodology (RSM) was utilized. To this end, the D-optimal experimental design was applied to optimize the experiments. The effects of three independent parameters, including electrolysis time (A), consumption voltage (B), and initial concentration of chloride ion (C), were assessed for the removal of chloride and TDS from recovered water. In addition, interactive and linear models were applied to determine the responses of chloride and TDS removal rates, respectively. The optimal operating conditions for the removal of chloride with 51.46% efficiency were obtained at the runtime of 30 minutes, consumption voltage of 12 V, and initial concentration of 300 ppm. Similarly, optimal TDS removal with 48.03% efficiency was achieved at the runtime of 30 minutes, consumption voltage of 12 V, and initial concentration of 300 ppm. According to the findings, ED was a highly reliable method for the removal of salts from water, as well as the high-quality recycling of water from mineral industries, especially in mineral processing plants.

Keywords: D-optimal design, Iron ore effluent, Membrane process, Total dissolved solids

Introduction

Recognition of the concepts of water pollution, purification, and control is of utmost importance, which mostly depends on obtaining adequate knowledge regarding the resources, conveyance methods, and interaction of water pollutants and their outcomes. Another important issue in this regard is to control pollutants to be harmless and economical for industries and the environment.^{1,2}

The main concerns regarding water involve

its impurities, including the presence of suspended particle, gases, and soluble salts, and microbial contamination. Water-soluble salts are often found in two forms of cations and anions; the cations include calcium (Ca), magnesium (Mg), and manganese (Mn), and the anions include chloride (Cl^-), bicarbonate (HCO_3^-), carbonate (CO_3^-), and hydroxide (OH^-). Chloride in the form of chloride ion (Cl^-) is one of the main mineral anions found in water and wastewater. The combination of Cl^- and other elements is naturally found in all waters; such examples are sodium chloride (NaCl), calcium chloride (CaCl_2), and magnesium chloride (MgCl_2).

The salinity of Cl in water varies depending on its chemical composition. Cl in the proximity of sodium (Na) cation causes recognizable water salinity, depending on its chemical composition.

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The amount of water-soluble salts is often determined based on electrical conductivity and total dissolved solids (TDS).^{3, 4} Therefore, it is essential to remove salts, Cl^- ion (major role in water salinity), and TDS from water in order to enhance the quality of industry-consumed water, especially in the areas that are vulnerable to saline water.⁵

Gohar Zamin Iron Ore Concentrate Plant (GIOCP) is located at the distance of 35 kilometers from Sirjan city in Kerman province, Iran and has an annual capacity of four million tons. The capacity of this plant was expected to reach six million tons by implementing a developmental plan up until 2017. The plant is located in a hot and dry climate, where the rainfall rate is extremely low. Moreover, the water available in this area has high salinity and low volume; therefore, water recovery seems crucial in this active plant.

Using high-salinity water increases the concentration of Cl^- ion, thereby affecting the production of high-quality pellets and causing pitting corrosion in the air conditioning and thermal systems of GIOCP. This issue could be attributed to the release of Cl^- ion, as well as the high temperature and pressure and rapid dissolution of metals, especially stainless steels.^{6, 7} Under such circumstances, the study of the parameters associated with optimization seems inevitable. It is also notable that water constitutes 70-80% of the pulp volume in the flotation cycle. Nowadays, using waters with high concentrations of inorganic electrolytes in the flotation process has been on the rise due to the lack of water in numerous areas, especially in hot and dry climates. Therefore, providing effective solutions to remove or reduce the concentration of pollutants is of paramount importance.

The desalination process consists of a set of multi-step actions, which are conducted on saline water in order to remove excess salts and other minerals.⁸⁻¹⁰ In this process, water is recovered, so that it would be suitable for industrial usage. Water desalination methods, especially the removal of Cl^- ion and TDS, could be classified variably. The most common classification is based on the type of the system

function, such as thermal and membrane processes, as well as the processes that are based on chemical bonds (i.e., ion exchange) and other processes.^{11, 12} All these methods result in the production of high-quality water for industrial usage. Thermal technology encompasses techniques such as multi-stage flash distillation, multi-effect distillation, vapor-compression distillation, saline water evaporation using solar energy, evaporation using geothermal energy, and desalination using the excess energy of power plants with fossil and atomic fuels.¹³⁻¹⁵

In the mentioned methods, the distillation process is a simulation of water cycling in nature, in which saline water is heated, steamed, cooled, and converted into liquid again. Membrane processes include electrodialysis (ED), electrodialysis reversal, and reverse osmosis (RO). Membrane systems usually apply lower energies than thermal distillation energy, which have reduced the desalination costs within the past decade. In ED, the electrical potential of the membranes is applied to remove the salts between two membranes selectively. The final product is high-quality water, while in RO, pressure is applied to remove the salts, so that fresh water is passed through the membrane, and the salts remain behind the membrane.¹⁶⁻¹⁸

In the current research, we have investigated water desalination (removal of Cl^- ion and TDS) based on the membrane method of ED, where saline water is affected by direct current voltage as the driving force of the process. A stack of the ED process involves some cells, to which saline water is pumped for desalination. In addition, ions are separated through the membrane and affected by the electric field of the cells. Some of the membranes used in ED are permeable to positive ions (cations), and some are permeable to negative ions (anions). Concentrate and dilute compartments are formed due to the passing of the positive and negative ions through proper membranes. However, bacteria and non-ionic particles may not be separated from water. In such case, using supplementary processes is considered essential to obtaining optimal water.

An ED unit consists of several paired cells

and electrodes, which are located on their sides. The inlet water simultaneously passes through the parallel space of the cells, providing a continuous stream of saline and desalinated water. In the present study, we applied this technology for the desalination of the water samples containing various concentrations of Cl^- ion. Furthermore, several parameters affecting the ED process were investigated, and the optimal conditions for performing electrical desalination were determined, resulting in the removal of Cl^- ion and TDS from water. Design Expert 10 software was applied to design the experiments and determine the optimal conditions, and the investigated influential factors in the ED process were the power consumption voltage, initial concentration of the Cl^- ion, and process runtime.

Response surface methodology (RSM) is a set of mathematical and statistical techniques, which are employed for the making of experimental models to evaluate the effects of several factors and verify the optimal conditions. RSM is considered to be an important tool in data analysis software, especially Design Expert 10, which is mainly utilized for the modeling and simulation parameters of a process.¹⁹ With the accurate design of experiments and clarifying the objectives, RSM optimizes the response (output variable) with the influence of several independent variables (input variables).

Recently, RSM has covered the optimization of the processes used for the removal of metals and solids from industrial wastewater, such as chromium (Cr) procreation and electrolysis industries.^{20, 21} Moreover, RSM is applied as a technique based on statistical analysis for developing experiments, evaluating the unique and interactive effects of independent variables, and optimizing the parameters involved in the process with limited empirical experiments.²² Utilization of RSM has demonstrated that this model could be significantly influential in the optimization and prediction of electrochemical processes.²³ Unlike conventional approaches, which are mostly time-consuming and require high energy levels, RSM is an efficient tool for the design

and optimization of the target, as well as the reduction of research costs and time.²⁴

The D-optimal design is an effective RSM technique for the optimization of complex processes and is widely utilized to optimize experiments.²⁵ Since D-optimal design reduces the number of experiments, the optimal matrix is a remarkable method to investigate the effects of key parameters on the response. As a result, this method reduces energy consumption, time, and costs.²⁶

The application of RSM, especially the D-optimal design, has not been assessed for the removal of Cl^- ion and water-soluble solids using an ED system, and no details have been published in this regard. In the present study, the RSM has been conducted using the D-optimal design to optimize the influential factors in the removal of Cl^- ion and TDS from water in GIOCP. Parameters such as electrolysis runtime, the driving force applied to the system, and the initial concentration of the Cl^- ion was considered as the main influential factors, and the desired responses were considered in the removal of Cl^- ion and TDS.

Materials and Methods

Properties of Recycled Water to the Plant

The water samples recycled to the GIOCP that were utilized in the current research were collected from the output of the dewatering process. The samples were stored at the temperature of 4 °C and used without dilutions. The values of some qualitative parameters for the thickener overflow water are presented in Table 1.

The equipment required for the experiments included an ED system, a TDS meter, a 60-liter gallon, three pieces of transmission hose, a stop valve, an adapter for supplying the required voltage, and a pH meter. The materials required for the experiments included several water samples with various concentrations of Cl^- ion, TDS, and NaCl with 98% purity.

Table 1. Characteristics of thickener over flow water

Parameter	Value
pH	7.6-8.1
Cl^- (mg/l)	300-1000
TDS (mg/l)	1069-2670
Conductivity ($\mu\text{S}/\text{cm}$)	1894-4119

Experiment Description

One of the most cost-effective and practical methods for iron ore procreation is the use of direct and reverse flotation. Considering the objective of the current research regarding the optimization and increasing of the concentrate production, the effects of Cl^- ion and TDS on concentrate production were investigated to separate the valuable and invaluable (concentrate) materials. Moreover, ED was applied to decrease the concentration of the water salts.

Considering the mentioned effects of water on iron concentrate flotation, various samples were selected from the water recycled to GIOCP at various times, and their TDS was also measured using a TDS meter, which is used to estimate the TDS of a solution by measuring its conductivity. In addition, the quality of the water output from the purifier could be determined using a TDS meter. The filters of water purifiers wear out over time, and the health of water cannot be ensured without a proper tool to measure its quality. A TDS meter measures the TDS of a solution, which is the concentration of the solids that are dissolved in water. Since dissolved ionic solids (e.g., salts and minerals) increase the conductivity of a solution, the most accurate method for the

measurement of TDS in laboratory water samples is the evaporation of the water coming out of the dissolved salts in the form of sediments, followed by measuring the weight of the sediments.

After each experiment for the removal of Cl^- ion and TDS, one sample (500 ml) was filtered and analyzed. Additionally, the Cl^- ion content of the samples was calculated using the silver chloride (AgCl) turbidity method. During each experiment, the electrodes were connected to the positive or negative output of the power supply, and the voltage was adjusted based on its direct current (DC).

At the next stage, the ED reactor was washed twice with distilled water. After preparing the power supply, the recovered water sample was injected into the ED reactor. Before each experiment, the concentration of Cl^- ion in the samples was accurately adjusted with 98% NaCl . All the experiments were carried out at room temperature.

As is depicted in Figure 1, ED was used for the desalination of the collected water samples. In this method, several parameters were investigated, including the consumption voltage for setting up the ED apparatus and retention time at various concentrations of the Cl^- ion.



Fig. 1. Schematic diagram of ED apparatus

Analytical methods

The efficiency of the removal of Cl^- ions and TDS was calculated using the following equation:

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

Where C_0 and C_i represent the initial content of the materials and concentrations of

the Cl⁻ ion and TDS after the ED process, respectively.

Experimental design

Limited studies have been focused on the ED process for desalination in the mineral industry (mineral procreation) using the RSM.

As such, the research objective was to investigate the effects of the process parameters on the removal of the Cl⁻ ion and TDS using an ED system. The operating parameters that significantly affected the performance of the ED process included the initial concentration of the Cl⁻ ion, process runtime, and especially the consumption voltage. As a result, the effects of these operational parameters on the removal of pollutant ions were investigated and optimized using the RSM in the present study.

RSM is a statistical tool, which is generally implemented to optimize the main effects of the studied variables on some responses considering the current status of the process. On the other hand, RSM is a regression analysis used to predict the value of a dependent variable based on the controlled values of the independent variables. This could provide a set of empirical parameters in a short time, so that the desired experiments would be more efficient.²⁴ The variable resulting in the most predicted value could be determined using the estimated parameters, which enabled the researcher to identify the variables with the most significant effects on obtaining the desired response.^{27, 32}

The D-optimal design is a viable option for an experimental design since the considered design aimed to minimize the variance associated with the estimations of the desired model coefficients.³³ To investigate the independent and interactive effects of the variables of the process in the present study, the experiment was carried out using the D-optimal

design with four variables (one qualitative and three quantitative variables) at three levels. The variables involved in the process, including the runtime (A), consumption voltage (B), and initial concentration of the chloride ion (C), were assessed in order to determine the removal of the chloride (Y₁) ion and TDS (Y₂) from the water restored to the plant using ED (Table 2). In addition, second-order multiple regression analysis was performed to express the system behavior using the least square regression method to obtain the parametric estimation of the mathematical model.³⁴ Selection of the independent variables represented in the experiments was performed, as follows:

$$X_i = \frac{x_i - x_0}{\Delta x_i} \quad i=1, 2, \dots, k \tag{2}$$

where X_i is the partial value of an independent variable, x_i denotes the real value of an independent variable; x₀ represents the real value at the central point of an independent variable, and Δx_i shows the difference of the i variable and the real values. Accordingly, the data obtained from Equation 2 were applied to predict a model. To predict the optimal conditions, the linear and quadratic equation models were expressed in equations 3 and 4, respectively.

$$Y = \beta_0 + \sum_{j=1}^k \beta_j x_j \tag{3}$$

$$Y = \beta_0 + \sum_{j=1}^k \beta_j x_j + \sum_{j=1}^k \beta_{jj} x_j^2 + \sum_{i < j=2}^k \sum_{i=1}^k \beta_{ij} x_i x_j + e \tag{4}$$

Where Y represents the response, X_i and X_j denote the variables (i and j varies from one to k), β₀ is the constant, β_j is shows the linear coefficient, β_{ij} is the interaction factor, β_{jj} represents the quadratic factor, and k shows the number of the independent parameters (k=4).

Table 2. Range and levels of independent variables

Design matrix	Parameter values	Process runtime (min) (A)	Consumption voltage (B)	Initial concentration of chloride (C)	Parameter levels
D-optimal matrix	Low level (-1)	10	1.5	300	level 1
	Center point (0)	20	5.75	600	level 2
	High level (+1)	30	12	900	level 3

Results and Discussion

D-optimal design for the removal of TDS and Cl⁻ ion

The D-optimal design is provided by a computer algorithm. This auxiliary project could be beneficial only if the experimental design is not conventional.³⁵ Unlike standard, conventional designs (especially factorial designs), optimal matrix designs are generally non-orthogonal, and their estimations have a significant effect on the correlation. The expressed designs have optional features

regardless of the type of the required laboratory models (e.g., interactions, complete square, and cubic types) or the experiment target (e.g., screening and RSM). Therefore, the main reason for using the D-optimal designs as opposed to factorial designs was that the former does not require a large number of experiments and significant time and resources to analyze the process. In other words, this method turns the processes that are inaccessible or impractical due to the high number of experiments into practical and accessible ones.³⁶

Table 3. Experimental design matrix and response based on experiments conducted on Cl⁻ ion and TDS removal using D-optimal design

Run no	A: (min)	B: (v)	C: (ppm)	Cl ⁻ ion removal (%)	TDS removal (%)
1	10	12	900	28.98	28.61
2	29.6	6.2	570	28.22	14.02
3	19	11.7	570	41.1	35.69
4	10	8.1	300	28.03	27.22
5	29.6	6.2	570	23.31	19.58
6	10	1.5	300	5.6	7.39
7	15.5	6.2	570	17.79	18.95
8	20	11.4	870	38.73	35.82
9	15.5	6.2	570	18.72	21.25
10	30	12	900	27.53	26.66
11	30	12	300	53.26	48.64
12	30	1.5	900	16.05	2.99
13	19	11.7	570	38.64	43.54
14	22	7.5	300	34.57	30.3
15	29.6	6.2	570	19.01	21.87
16	19	6.2	888	19.64	15.55
17	22.6	1.5	300	6.53	4.49
18	22.1	1.5	648	8.13	2.73
19	10	1.5	675	6.36	4.16
20	19	6.225	888	17.85	14.16

Evaluation of the experimental results

Based on the design of the experiment in the current research, 20 experiments were carried out, and their detailed conditions have

$$\text{Cl}^- \text{ Ion Removal (\%)} Y_1 = 23.97 + 2.25*A + 15.78*B - 3.44*C - 0.62*AB - 0.90*AC - 5.74*BC \quad (5)$$

$$\text{TDS Removal (\%)} Y_2 = +21.16 - 0.33*A + 17.31*B - 4.54*C + 0.83*AB - 0.89*AC - 3.64*B \quad (6)$$

The data obtained from the D-optimal design were evaluated based on two indices, including the model sum of the squares and model summary statistics, in order to achieve valid regression models among various linear, interactive, quadratic, and cubic models. The results of Cl⁻ ion and TDS removal rates have

been presented in Table 3. The model equations of the quadratic regression of models five and six were verified using the Design Expert software version 10, as follows:

been shown in Tables 4 and 5.

Based on the results of the present study, it could be inferred that the quadratic and linear, R-squared (R²), adjusted R₂, and predicted R² models had a higher F-value and lower P-value. As such, the cubic model was proposed as an aliased model, and the experimental data could

not be utilized for its further modeling. Based on the aliased model, it could be stated that the experiments were not sufficient for independent evaluation; however, there were a few independent points in the design for the necessary modifications. In addition, some parameters could not be calculated independently. When a model is aliased, it is not considered appropriate for further investigation. Therefore, the quadratic model was selected to express the effects of the process

variables on the ED process for the removal of the Cl^- ion. Meanwhile, the model summary statistics indicated that after ignoring the aliased cubic model, a quadratic model was applied for the maximum adjusted R^2 and predicted R^2 values. TDS removal was analyzed simultaneously, and the obtained results are shown in Table 5. As a result, the linear model was selected to express the effects of the process variables on the efficiency of TDS removal in the ED process.

Table 4. Model sum of squares and summary statistics of Cl^- ion removal

Source	Sum of Squares	df	Mean square	F Value	p-value Prob > F	
Linear	374.34	11	34.03	3.58	0.0851	
2FI	157.03	8	19.63	2.06	0.2203	Suggested
Quadratic	110.04	5	22.01	2.31	0.1892	
Cubic	0	0				Aliased
Pure Error	47.53	5	9.51			
Model summary statistics						
Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	5.13	0.8674	0.8425	0.7534	784.64	
2FI	3.97	0.9357	0.906	0.7696	733.04	Suggested
Quadratic	3.97	0.9505	0.9059	0.6546	1098.76	
Cubic	3.08	0.9851	0.9432		+	Aliased

+ Case with the leverage of 1.00: PRESS statistic is not defined

Table 5. Model sum of squares and the model summary statistics of TDS removal

Source	Sum of Squares	df	Mean square	F Value	p-value Prob > F	
Linear	168.9	11	15.35	1.15	0.4705	Suggested
2FI	81.57	8	10.2	0.76	0.6526	
Quadratic	60.1	5	12.02	0.9	0.5461	
Cubic	0	0				Aliased
Pure Error	67.02	5	13.4			
Model summary statistics						
Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	3.84	0.9317	0.9189	0.8805	412.81	Suggested
2FI	3.38	0.957	0.9371	0.8479	525.43	
Quadratic	3.57	0.9632	0.9301	0.7664	806.78	
Cubic	3.66	0.9806	0.9263			Aliased

+ Case with the leverage of 1.00: PRESS statistic is not defined

Analysis of variance (ANOVA)

The accuracy and validity of the model were evaluated using the analysis of variance (ANOVA), and the obtained results are presented in Tables 6 and 7. ANOVA was also used to compare the variation sources with Fisher dissemination (F-test) to validate the reliability of the regression model. The F-values of 48.20 (Table 6) and 31.53 (Table 7) were acquired for the removal of the Cl^- ion and TDS,

respectively. Furthermore, a reasonable change was observed in their mean values. The prediction of the regression model was performed at 95% confidence interval, and the T-experiment was performed to assess the importance of each of the coefficients of the developed regression model (Equations 5 and 6).

The probability of error value (P-value) was applied to determine whether the

dependence between the response and each model variable was statistically significant. P-value was considered to be the lowest significant level, which ruled out unnecessary values, and the interactive effects were considered significant with the P-value of <0.05 .³⁴ Under such circumstances, the parameters with the P-values of >0.05 could be removed using the step-by-step removal method. On the other hand, the low values of 16.60 for the removal of the Cl^- ion and 15.96 for the removal of TDS confirmed the high

accuracy and validity of the experiments in the coefficient of variation. The acceptable accuracy value was a measure of the signal-to-noise ratio for the responses. The ratio values had to be more than four to determine whether the modeling was proper.³³ In the current research, the ratio was estimated at 21.02 and 23.56 for the removal of the Cl^- ion and TDS, respectively, indicating that the quadratic and linear models could be applied to improve the design conditions.

Table 6. Quadratic model of ANOVA for Cl^- ion removal efficiency in ED process

Source	Sum of Squares	df	Mean Square	F Value	p-value	Prob > F
Model	3305.13	6	550.86	48.20	0.0001	Significant
A	1.01	1	1.01	0.09	0.7713	
B	2815.83	1	2815.83	246.36	0.0000	
C	193.64	1	193.64	16.94	0.0012	
AB	3.81	1	3.81	0.33	0.5733	
AC	4.36	1	4.36	0.38	0.5474	
BC	78.16	1	78.16	6.84	0.0214	
Residual	148.58	13	11.43			
Lack of Fit	81.57	8	10.20	0.76	0.6526	
Pure Error	67.02	5	13.40			
Cor Total	3453.72	19				
Std. Dev.	3.97				R ²	0.9357
Mean	23.90				Adj R ²	0.9060
C.V. %	16.60				Pred R ²	0.7696
PRESS	733.04				Adeq precision	21.02

Table 7. Linear model of ANOVA for TDS removal efficiency in ED process

Source	Sum of Squares	df	Mean square	F Value	p-value	Prob > F
Model	2976.78	6	496.13	31.53	0.0001	Significant
A	46.49	1	46.49	2.95	0.1093	
B	2340.70	1	2340.70	148.75	0.0000	
C	111.32	1	111.32	7.07	0.0196	
AB	2.10	1	2.10	0.13	0.7208	
AC	4.46	1	4.46	0.28	0.6033	
BC	194.52	1	194.52	12.36	0.0038	
Residual	204.57	13	15.74			
Lack of Fit	157.03	8	19.63	2.06	0.2203	
Pure Error	47.53	5	9.51			
Cor Total	3181.35	19				
Std. Dev.	3.38				R ²	0.9570
Mean	21.18				Adj R ²	0.9371
C.V. %	15.96				Pred R ²	0.8479
PRESS	525.43				Adeq Precision	23.564

According to the information in Tables 6 and 7, the ANOVA results regarding the regression of the dependent parameters, the quadratic and linear models were respectively represented for the removal of the Cl^- ion and

TDS from water concerning the surface response prediction. Therefore, it could be inferred that the F-experiment with the low P-value ($P=0.0001$ for Cl^- ion removal, $P<0.0001$ for TDS removal) indicated the significant

regression models. The design of the model would be significant if the $\text{prob}>F$ values were less than 0.05.³⁷ The P-value in the present study was less than 0.05, indicating that the total ratio of the variance of the dependent variables was determined using the regression model.

The lack-of-fit F-value of 2.06 in the model explained the insignificance relative to pure error. Moreover, a high R^2 value confirmed that the linear model could express the total variations of the dependent variables. In the current research, the nominal coefficients of the model (R^2) demonstrated that the mentioned model could be utilized to obtain the total variations of 93.57% and 95.70% for the removal of Cl^- ion and TDS, respectively. Additionally, the nominal coefficient values (adjusted $R^2=0.9371$ and 0.9060) indicated the significance of the two responses for the removal of the Cl^- ion and TDS.

Assessment of the normal distribution of data

In the assessment of the normal distribution of data, the residual values determine the way by which the model could confirm the ANOVA assumptions, while the externally standardized residuals, along with the standard deviations, were evaluated to separate the actual and predicted values. In addition, the data were analyzed to determine their normal distribution, and the results have been shown in Figure 2-a and 2-b.

Figures 2-a and 2-b depict the rate of normal probability distribution compared to the standardized residuals for the removal rates of the Cl^- ion and TDS in the ED process. The normal distribution diagram illustrated whether the residuals followed the distribution normally; if they did, they could create straight line points. Some dissemination even closes to the normalized data; therefore, it could be inferred that the data were normally distributed based on Figures 2-a and 2-b.

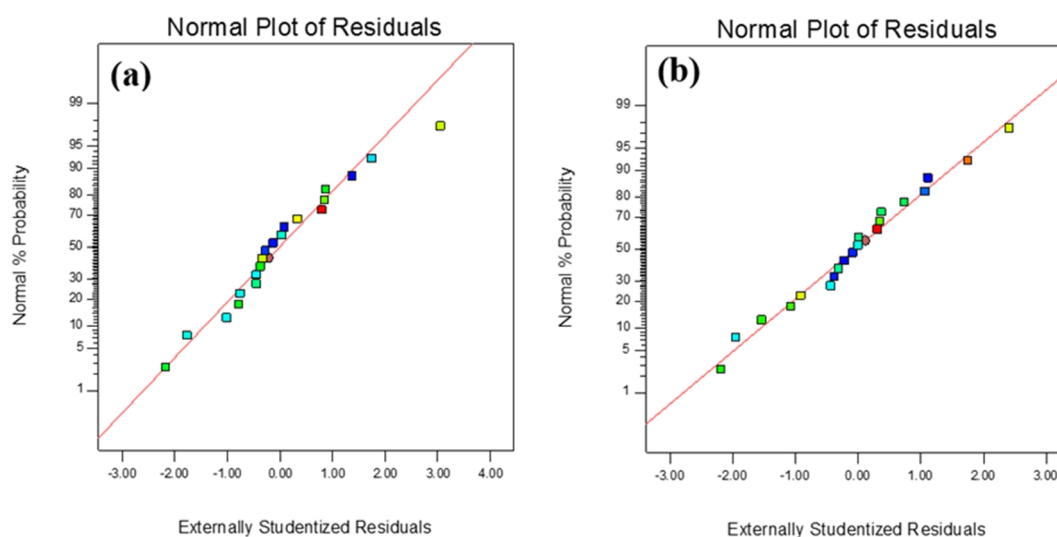


Fig. 2. Diagram of correlations between normal probability percentage and externally standardized residuals for a) Cl^- ion removal and b) TDS removal

Comparison of the experimental results and predicted values

Assessing the quality of the proposed model is essential to the analytical process. In the present study, the validity of the model indicated that it approached an accurate approximation to avoid weak or false analysis. The evaluation of the obtained and predicted experimental values of the model is

demonstrated in Figures 3-a and 3-b. Our findings confirmed that the model predictions were consistent with the experimental data, and the given points were adjacent to the diagonal line. Furthermore, the analysis showed that the application of these quadratic polynomial equations could be desirable for estimating the removal rates of the Cl^- ion and TDS using ED.

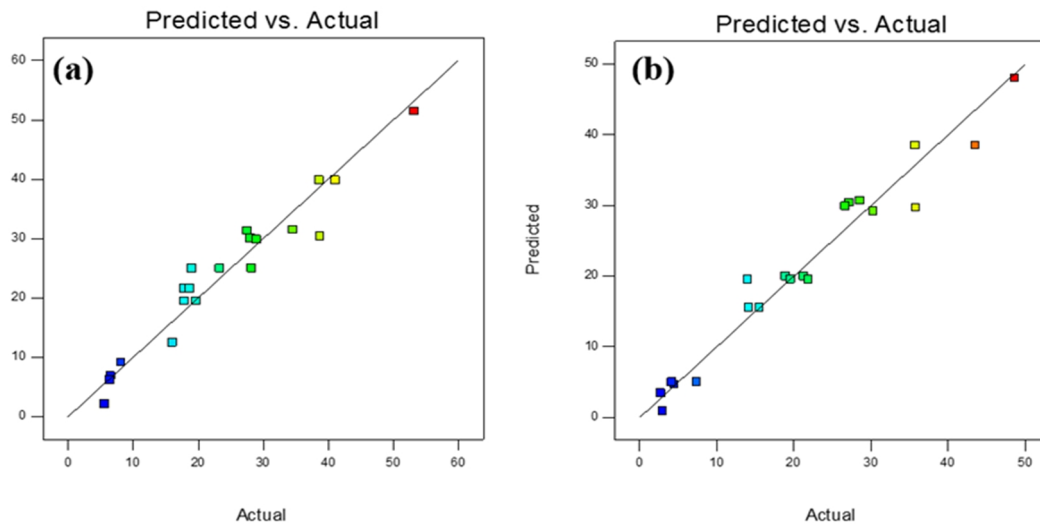


Fig. 3. Comparison of actual and predicted values for a) Cl⁻ ion removal and b) TDS removal

Evaluation of the effects of operating parameters on the process

Most ED processes are influenced by consumption voltage, initial Cl⁻ ion concentration, and process runtime. These are the most important parameters for adjusting the reaction rate. Therefore, the effects of these main parameters on the efficiency of increasing the removal rates of the Cl⁻ ion and TDS in the ED process were evaluated using the RSM. The main advantage of RSM, distinguishes this technique from other similar designs, is the interactive effects between the parameters.

Effect of consumption voltage

Experimental studies were carried out at the voltage range of 1.5-12 V so as to investigate the effects of the consumption voltage on the efficiency of Cl⁻ ion and TDS removal. The findings regarding the effect of voltage changes on the removal of the Cl⁻ ion and TDS from the water recycled to GIOCP using the ED systems are depicted in the form of a three-dimensional (3-D) plot in Figures 4-a and 4-b and 5-a and 5-b. As is depicted in Figure 4-a, the removal rate of Cl⁻ ion increased at higher voltages and increased process runtime, and the maximum efficiency of 50% was obtained. Meanwhile, the Cl⁻ ion removal efficiency increased to the

maximum value of 48% by increasing the voltage and reducing the initial concentration of the Cl⁻ ion (Figure 4a-b).

Figure 5-a depicts the effects of voltage and process runtime on TDS removal efficiency, confirming the increased removal efficiency at higher voltages. Although the removal efficiency of TDS increased at an increased process runtime, this trend was not considered significant, indicating the insignificant impact of the process runtime versus consumption voltage. Meanwhile, Figure 5-b shows that TDS removal efficiency increased to the maximum value and underwent a process similar to the trend of Cl⁻ ion removal through increasing the consumption voltage, as well as reducing the initial concentration of the Cl⁻ ion.

According to the findings of the current research, the separation rate also increased at higher voltages. Higher voltage was defined as applying of a higher driving force to the process, which in turn incremented the current intensity passing through the membrane. With a constant driving force, the feed concentration was higher, and the separation was more efficient. In addition, the separation rate decreased at higher concentrations due to the limited membrane load and concentration polarization.¹²

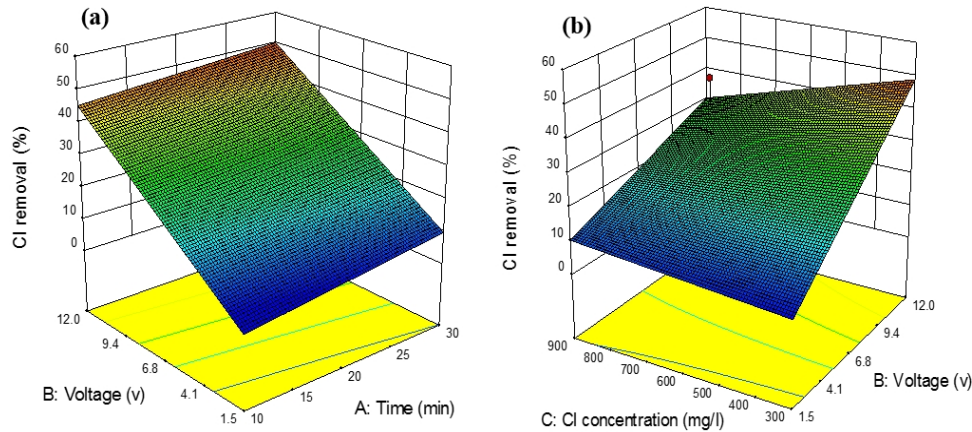


Fig. 4. 3-D Plots for effects of a) consumption voltage and process runtime (Cl^- ion initial concentration: 300 ppm) and b) consumption voltage and Cl^- ion initial concentration (process runtime: 30 minutes) on Cl^- ion removal rate

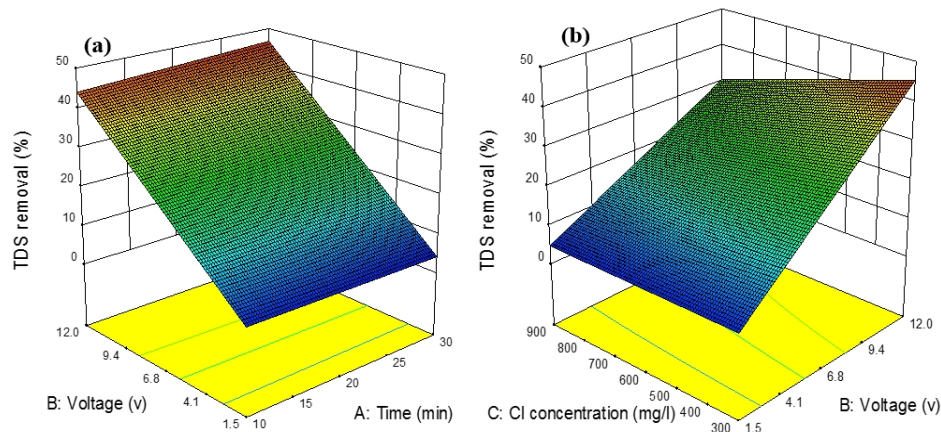


Fig. 5. 3-D Plots for effects of a) consumption voltage and process runtime (Cl^- ion initial concentration: 300 ppm) and b) consumption voltage and Cl^- ion initial concentration (process runtime: 30 minutes) on TDS removal rate

Effect of Cl^- ion initial concentration

The initial concentration of the Cl^- ion is considered to be a key parameter to improve the ED process.¹⁰ To determine this parameter, we employed various concentrations of soluble Cl^- ion (range: 300-900 ppm). Figures 6-a and 6-b and 7-a and 7-b shows the three- and two-dimensional contour plots for evaluating the effects of Cl^- ion initial concentration and ED process runtime on the removal rate of the Cl^- ion and TDS. According to the obtained results, the removal rate of the Cl^- ion decreased at higher initial concentrations. The similar overall and better separation. On the other hand, the limited membrane load and concentration

process was also obtained for TDS removal (Figures 7-a and 7-b), which demonstrated that the removal efficiency reduced at higher initial concentrations.

Based on the observations in the present study, it seems that the adsorption capacity and removal rate decreased at higher initial concentrations the Cl^- ion since the available adsorption sites decreased in order to be absorbed on the absorbent surface at higher concentrations.³⁸ In other words, the induction of a constant driving force led to the more significant reduction of the initial concentration polarization led to the reduced rate of separation at higher concentrations.¹²

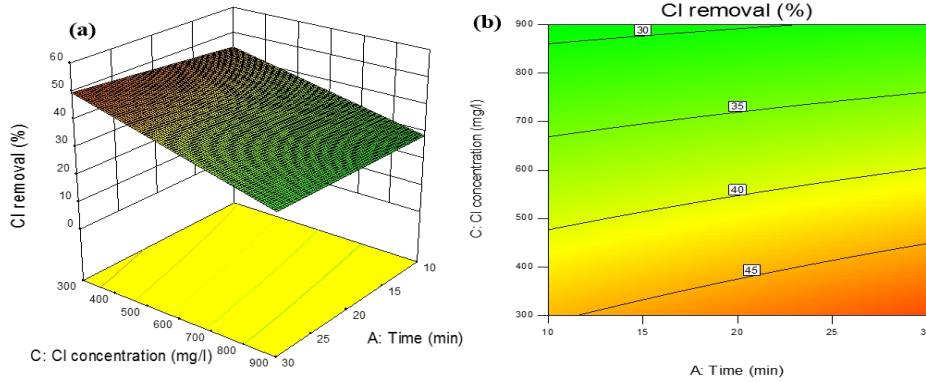


Fig. 6. Effects of Cl^- ion initial concentration and process runtime on Cl^- ion removal rate (%); a) 3-D plots, b) 2-D contour plots

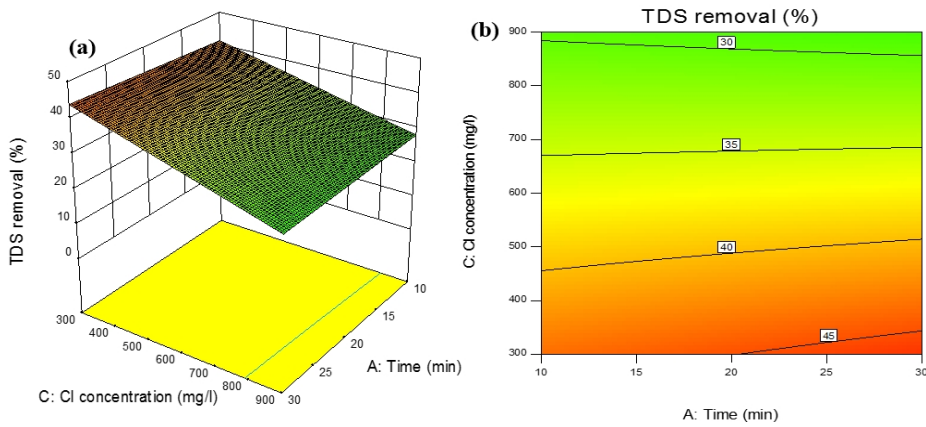


Fig. 7. Effects of Cl^- ion initial concentration and process runtime on TDS removal rate (%); a) 3-D plots, b) 2-D contour plots

Effect of process runtime

Process runtime is among the major parameters for the desalination of the water recycled to GIOCP. In the current research, the experiments were assessed based on the electrolysis time (A), which changed from 10 minutes to 30 minutes with the consumption voltage of 9 V and Cl^- ion initial concentration

of 412 ppm. As is depicted in Figure 8-a, the removal rate of the Cl^- ion increased gradually by increasing the electrolysis time since the process runtime influences the efficiency, and the average value of process separation would also increase by increasing the ED process runtime.

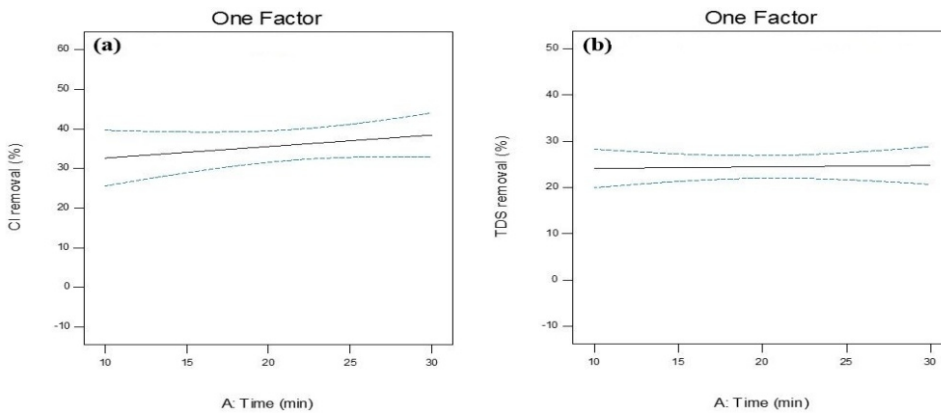


Fig. 8. Plots for effects of a time factor on a) Cl^- ion removal rate (%) (Consumption Voltage: 9 V; Cl^- Ion initial concentration: 412 ppm) and b) TDS removal rate (%) (Consumption Voltage: 9 V; Cl^- ion initial concentration: 412 ppm)

As is shown in Figure 8-b, the effect of the process runtime on the removal rate of TDS was not significant, which could be attributed to a trivial, reversed reaction in the other chemical parameters of water over time. In other words, it was expected that increasing the process runtime would increase TDS removal efficiency, while this hypothesis could not be confirmed practically, and only a slight rising trend was observed in the process of Cl^- ion removal.

Optimization and validation of the desalination process

One of the main objectives of the present study was to achieve the optimal conditions for the removal of the Cl^- ion and TDS from the thickener overflow water using the ED process in GIOCP. The values obtained from the RSM regression equations were applied based on the optimal design so as to optimize the process. In the optimization process, variables such as process runtime (A), consumption voltage (B), and Cl^- ion initial concentration (C) were applied within specified ranges, and responses such as the removal rates of Cl^- (Y1) and TDS (Y2) reached their maximum value.

According to the results of the present study, the removal values of Cl^- and TDS were confirmed through developing the desired conditions by conducting additional experiments in order to optimize the experimental conditions. In this regard, the optimal operating conditions for Cl^- ion removal with the efficiency of 51.46% was obtained at the process runtime of 30 minutes, consumption voltage of 12 V, and initial concentration of 300 ppm. Similarly, TDS removal with the efficiency of 48.03% was obtained at the process runtime of 30 minutes, consumption voltage of 12 V, and initial concentration of 300 ppm. Furthermore, the proper correlation between the actual and predicted results indicated that the reliability of the D-optimal experimental design was appropriate and could be applied effectively for the optimization of the ED process parameters in order to remove salts from the water restored to the iron ore procreation plant.

Conclusion

In the current research, the D-optimal experimental design was applied to evaluate and optimize the process variables, such as the process runtime, consumption voltage, and Cl^- ion initial concentration for the removal of the Cl^- ion and TDS, as well as the recycling of high-quality water to be restored to the production cycle of the iron ore processing plant through the ED process. The prediction of the regression model resulted in 95% confidence interval. In addition, the quadratic and linear models were utilized to improve the design conditions. According to the findings, the removal efficiency increased at higher voltages in the TDS removal process. Although the removal efficiency increased by increasing the process runtime, this trend was not considered significant, indicating the insignificant impact the process runtime versus consumption voltage. Meanwhile, TDS removal efficiency increased to the maximum value and underwent a process similar to the trend of Cl^- ions removal at higher consumption voltages and lower Cl^- ion initial concentrations. According to the results, it is perceived that the removal rate of the Cl^- ion would decrease by increasing its initial concentration, while the removal efficiency of the Cl^- ion would increase by incrementing the process runtime. A completely similar process was also achieved for TDS removal, in which the removal efficiency decreased at higher concentrations. Our findings demonstrated that the removal rate of Cl^- gradually increased by increasing the electrolysis time, and the average value of the separation process also increased by increasing the ED process runtime. On the other hand, the effect of the process runtime was negligible in the TDS removal process and had no significant effect on the removal efficiency. In general, the results of the present study indicated the possibility of the technical application of the ED system as a reliable method in the removal of the Cl^- ion and TDS in mineral industries, especially in mineral processing plants. The findings are hoped to lay the groundwork for further investigation regarding the other variables and comprehensive studies in this

regard. The ED process is essential to investigating the results to be utilized in the mineral industry and optimize on an industrial scale.

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