Chromium removal and water recycling from electroplating wastewater through direct osmosis: Modeling and optimization by response surface methodology

Zohreh Naghdali1,2, Soleyman Sahebi3, Reza Ghanbari1,2, Milad Mousazadeh1,2, Hamzeh Ali Jamali4,2*

1Student Research Committee, Qazvin University of Medical Sciences, Qazvin, Iran
2Department of Environmental Health Engineering, School of Health, Qazvin University of Medical Sciences, Qazvin, Iran
3Research and Technology Center of Membrane Processes (RTCMP), School of Chemical, Petroleum and Gas Engineering, Iran University of Science and Technology (IUST), Tehran, Iran
4Social Determinants on Health Promotion Research Center, Qazvin University of Medical Sciences, Qazvin, Iran

Abstract
Background: Considering the carcinogenic effects of heavy metals, such as chromium, it is essential to remove these elements from water and wastewater. Direct osmosis is a new membrane technology, which can be a proper alternative to conventional chromium removal processes.

Methods: The wastewater samples were collected from an electroplating unit, located in Alborz industrial city, Qazvin, Iran. Magnesium chloride was used as the draw solution, and a semipermeable membrane (Aquaporin) was used in this study. The experiments were designed, using response surface methodology (RSM) and central composite design (CCD) with draw solution concentration (0.5-1.5 M), feed solution concentration (4-12 mg/L), and experiment time (30-90 minutes) as variable factors. The chromium concentration and water flux were also measured, based on atomic absorption spectrophotometry and water flux equation, respectively.

Results: Direct osmosis was highly efficient in chromium removal and water recycling. Water flux and chromium removal efficiency were 15.6 LMH and 85.58%, respectively, under optimal conditions (draw solution = 1.27 mol/L, feed solution = 4 mg/L, and experiment time = 90 min). In terms of validity, the results predicted by the quadratic polynomial model were in good agreement with the responses reported in the laboratory.

Conclusion: In direct osmosis, the use of magnesium chloride as the draw solution resulted in the acceptable chromium removal from electroplating wastewater. Using this method, chromium concentration in wastewater reduced to a level lower than the discharge standards, established by Iran's Department of Environment.

Keywords: Direct osmosis, Chromium removal, Electroplating, Optimization

Introduction
In many countries, especially developing countries, significant amounts of heavy metals enter the environment through industrial activities either directly or indirectly (1,2). The most common heavy metals in industrial wastewater include arsenic, chromium, lead, cadmium, copper, nickel, and zinc, which are hazardous to human and environmental health (3-5). In terms of frequency, chromium is the seventh most abundant chemical element on the planet. Chromium is mostly found in the environment in two valence states, trivalent chromium (Cr III) and hexavalent chromium (Cr VI); the latter state is hazardous to both human and environment (6,7). Generally, the most important sources of chromium are leather, plating, tannery, and textile industries (8). In Iran, the standard chromium discharge from industrial wastewater into the environment is set at 0.5-1 mg/L (9). Therefore, chromium removal from wastewater seems essential. Currently, many physical, chemical, and biological processes, including chemical sequestration, air flotation, ion exchange, surface absorption, and membrane processes, have been proposed to remove heavy metals...
from industrial wastewater (10-13). Membrane filtration processes have various advantages, including low energy requirements, high separation efficiency, simple equipment requirements, and simple recycling of heavy metals (14). Today, membrane technologies, especially reverse osmosis, are the most extensively applied methods for water and wastewater treatment. However, in comparison with other membrane technologies, reverse osmosis requires more energy and costs, and results in severe membrane fouling (15). Recently, major attention has been paid to direct osmosis due to its various advantages, such as low energy requirements, low membrane fouling, simple reduction of membrane fouling, and increased water recycling. This technology, which is based on a natural phenomenon, is the process of spontaneous water diffusion across a semipermeable membrane. The driving force for the osmotic transfer of water from the feed solution into the draw solution is the osmotic pressure gradient between the solutions, without any need for external forces (16). In the conventional one-factor-at-a-time approach, only one factor or variable is examined at a time while keeping others fixed. This method is particularly valuable when the number of effective factors in the process is high, the duration of experiments is long, or costs are high (17). On the other hand, this method is unable to evaluate the interactive effects of factors and has a high error rate. Therefore, researchers employ the response surface methodology (RSM), which is a set of mathematical and statistical techniques (18,19) for designing experiments, modeling, optimization, and analyzing the interactive effects of different parameters. In addition, central composite design (CCD) is one of the most commonly used arrangements of RSM in the design of experiments (20,21). With this background in mind, the aim of this study was to optimize chromium removal and water recycling from electroplating wastewater, using direct osmosis process.

**Materials and Methods**

**Pilot-scale study of direct osmosis**

Figure 1 presents a general image of the pilot-scale process of direct osmosis in this study. This pilot study is a continuous system and consisted of a Plexiglas unit with two channels for the entry and exit of draw and feed solutions, an Aquaporin membrane (Aquaporin Asia Pte. Ltd, Singapore) with an effective area of 8 cm$^2$ (4 cm $\times$ 2 cm), and a two-way peristaltic pump (D500 model, Iran) for the transfer of solutions on the membrane sides. Due to the presence of proteins in the Aquaporin membrane structure, they have much more permeability than other membranes (22). The flow rate was set at 200 mL/min. Two Erlenmeyer flasks (100 mL) were used for the storage of draw and feed solutions. To measure the amount of permeate water through the membrane to the draw solution tank, a digital scale (0.01 g precision; Kern PCB 1000-2, Germany) was used.

**Materials**

Actual wastewater samples were collected from an electroplating unit, located in Alborz Industrial City, Qazvin, Iran. The baseline characteristics of the samples were as follows: chromium concentration, 14.51 mg/L; pH <2; turbidity, 21 NTU; and electrical conductivity, 4000 ms/cm. To prevent membrane fouling, the samples were passed through filters before use. The draw solution was prepared using magnesium chloride (MgCl$_2$; Merck). After each experiment, samples of draw solutions were analyzed to measure the amount of chromium passing through the membrane. The chromium concentration was measured using an atomic absorption spectrophotometer (BRAIC WFX-130).

**Experimental design**

The experiments were designed in Design Expert 7, based on CCD. Each independent variable (factor) was defined at five levels. The design points included factorial, axial, and central points. The independent variables were transformed into non-dimensional coded variables using Eq. (1):

$$x_i = \frac{X_i - X_0}{\Delta X}$$  

where $x_i$ represents the non-dimensional coded value of the variable, $X_i$ indicates the value of $x_i$ in the axial point, and $\Delta X$ is the difference in values. Experimental factors and their levels are presented in Table 1. To prepare the solution in these ranges, samples were diluted with tap water and their pH was adjusted in primary values. The $\alpha$ value was also measured ($\alpha= 1.68$) according to Eq. (2):

$$A = 2^{n/4} = 2^{3/4} = 1.68$$

where $n$ represents the number of independent variables. Water flux (L/m$^2$h or LMH) and chromium removal efficiency (%) were considered as the dependent variables (responses). With regard to the studied factors, a total of
20 experiments were designed, including eight factorial points, six axial points, and six central points, according to Eq. (3):

\[ N = 2^K + 2K + C_p \] (3)

where \( N \) represents the number of experiments, \( K \) indicates the number of factors, and \( C_p \) denotes the number of repeated points. The behavior of the system was studied using Eq. (4), which is a quadratic polynomial equation. All experiments were performed at laboratory temperature.

\[ Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \sum_{j=1}^{i} \beta_{ij} x_i^2 + \ldots + e \] (4)

where \( i \) is a linear constant, \( j \) is a quadratic constant, \( \beta \) is a regression constant, \( k \) indicates the number of investigated and optimized factors in the experiment, and \( e \) represents random error. After performing the experiments, data were analyzed using ANOVA and regression analysis. The models were modified by the omission of terms which were not significant at a confidence level of 95%. In order to optimize chromium removal and water recycling, in the optimization section of the program (numerical mode), the level of factors was selected to be “in range”, and responses were set at “maximized”.

### Analysis of water flux and chromium removal

Equation (5) was used to determine the amount of water flux during direct osmosis:

\[ J_w = \frac{\Delta m}{\rho A_{m} \Delta t} \] (5)

where \( J_w \) denotes the amount of water flux (LMH), \( \Delta m \) represents the weight of permeate water passing from the membrane to the draw solution (kg), \( \rho \) indicates the specific mass of water (1 kg/L), \( A_m \) is the effective membrane surface area (m²), and \( \Delta t \) is the experiment time (hours).

In addition, chromium removal efficiency was calculated using Eq. (6):

\[ R(\%) = \left(1 - \frac{C_p}{C_f}\right) \] (6)

where \( R \) indicates chromium removal by the membrane (%), \( C_p \) is chromium concentration in the draw solution (mg/L), and \( C_f \) is chromium concentration in the feed solution (mg/L).

### Results

Table 2 presents the experimental design with actual and predicted results. Based on the results, the highest removal rate of chromium and water flux were 100% and 17.4 LMH, respectively.

Table 3 presents the results of ANOVA test regarding chromium removal from wastewater and permeate water flux through the membrane. \( P \) value, probability of lack of fit (PLOF), \( R^2 \), adjusted \( R^2 \), adequate precision (AP), standard deviation (SD), coefficient of variance (CV), and predicted residual error sum of squares (PRESS) are also presented in this table.

Figures 2a and c present the normal probability plot of residuals and Figures 2b and d presents the plot of internally studentized residuals versus the run number in chromium removal and water flux by direct osmosis. According to Figures 2a-c, the residuals had a normal distribution because the points were almost located on a straight line. Also, in Figures 2b-c, the residuals were independent of each other and did not follow a particular pattern, therefore, the assumption of data independence was confirmed.

Figure 3 demonstrates the contour plots for the interactive effects of independent variables in chromium removal from wastewater and permeate water flux through the membrane (by keeping other independent variables in the mid-range).

### Discussion

Membrane processes have the potential to remove heavy metals from wastewater due to the inhibition of molecule and ion passage through the membrane. In this regard, ultrafiltration, nanofiltration, reverse osmosis, and electrodialysis methods have been applied to remove heavy metals (23). Direct osmosis, as a new membrane technology, allows water to pass through the semipermeable membrane due to the osmotic pressure difference. Unlike the reverse osmosis method, there is no need for extra energy in this technology (24). The results of ANOVA test revealed that the quadratic model was a good fit to the experimental data. The quadratic equations presented in Table 3 regarding chromium removal and water flux, show the significant

### Table 1.
The actual and coded values of independent variables

<table>
<thead>
<tr>
<th>Variables</th>
<th>Coded values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-α</td>
</tr>
<tr>
<td>Draw solution concentration (mol/L)</td>
<td>0.16</td>
</tr>
<tr>
<td>Feed solution concentration (mg/L)</td>
<td>1.27</td>
</tr>
<tr>
<td>Experiment time (min)</td>
<td>9.55</td>
</tr>
</tbody>
</table>
effects of feed solution concentration (A), initial concentration of draw solution (B), and experiment time (C). In addition, the interactive effects of these factors (AB, AC, and BC), as well as their quadratic effects (A², B², and C² for chromium removal and A² and C² for water recycling), were significant. The coefficient of determination (R²) is defined as the ratio of the explained variance to the total variance. The closer R² is to one, the higher is the model’s accuracy in predicting responses (25).

In this study, R² values were 0.94 and 0.97, respectively for chromium removal and A² and C² for water recycling. In addition, the adjusted R² coefficients (adj. R²), which are always lower than R² (26), were 0.88 and 0.94 for chromium removal and water flux, respectively, which indicates the good fit of the models. Lack of fit was 0.2 and 0.07 for water flux and Cr removal, respectively. According to the report of Khoshnamvand et al, lack of fit value: probability of error; PLOF: probability of lack of fit; AP: adequate precision; SD: standard deviation; CV: coefficient of variance; and PRESS: predicted residuals error sum of squares.

The ANOVA results of quadratic models for water flux and chromium removal are shown in Table 3. In this study, AP for chromium removal and water recycling was 16.50 and 23.91, respectively, which indicates the presence of good signals. In addition, the coefficient of variation (CV), which determines the repeatability of the model, is defined as the ratio of the estimated standard error to the mean response; the value of CV should not exceed 10% (29). In this study, CV values for water recycling and chromium removal were 7.9% and 4.98%, respectively, which indicates the models are repeatable. Similarly, the goodness of fit test was not significant for the responses (P ≥ 0.05), which also indicates the good fit of the models.

As shown in Figure 3a, by reducing the concentration of feed solution and increasing the experiment time, the water flux increased. The maximum water flux (18 LMH) was reported when chromium concentration was approximately 1.3 mg/L, and experiment time was
about 110 minutes. The interactive effect of experiment time and feed solution concentration on the removal efficiency of chromium is shown in Figure 3b. According to this figure, with an increase in the concentration of feed solution and experiment time, the removal efficiency of chromium increased. Maximum chromium removal from wastewater was observed at a feed solution concentration of 9.5 mg/L and experiment time of 73 minutes; chromium removal efficiency was reported to be above 95%. On the other hand, chromium removal efficiency decreased by increasing the concentration of feed solution and experiment time. It seems that the passage of chromium through the membrane pores reduces with time due to membrane fouling; consequently, chromium removal increases. However, water flux decreases over time due to membrane fouling and reduction of membrane pores. Water flux was not significantly affected by simultaneous changes in the concentration of draw solution and experiment time (Figure 3c). As shown in this figure, water flux increased due to increased osmotic pressure when higher concentrations of draw solution were used. However, water flux gradually decreased over time due to decreased osmotic pressure as a result of the dilution of draw solution. In this regard, Zhao et al (30) reported that by increasing the experiment time to five hours, water flux followed a decreasing trend when a cellulose triacetate membrane was used for nickel removal. However, by using a thin-film composite membrane, water flux was slightly increased over time. The time-dependent reduction of water flux may be due to the increased concentration polarization or membrane fouling due to the addition of nickel to the feed solution. As shown in Figure 3d, 100% of chromium was eliminated within 20 to 86 minutes at MgCl₂ concentrations below 0.8 mol/L. At higher concentrations, the removal efficiency of chromium decreased by increasing the concentration of draw solution and experiment time. The interactive effects of draw and feed solution concentrations on water flux and chromium removal are presented in Figures 3e and f. At low concentrations of feed solution, the water flux increased by increasing the concentration of draw solution. However, due to internal concentration polarization in the membrane, the increase in the concentration of draw solution does not always increase the water flux. On the other hand, chromium removal efficiency decreased by increasing the concentration of feed solution and experiment time. It seems that the passage of chromium through the membrane pores reduces with time due to membrane fouling; consequently, chromium removal increases. However, water flux decreases over time due to membrane fouling and reduction of membrane pores. Water flux was not significantly affected by simultaneous changes in the concentration of draw solution and experiment time (Figure 3c). As shown in this figure, water flux increased due to increased osmotic pressure when higher concentrations of draw solution were used. However, water flux gradually decreased over time due to decreased osmotic pressure as a result of the dilution of draw solution. In this regard, Zhao et al (30) reported that by increasing the experiment time to five hours, water flux followed a decreasing trend when a cellulose triacetate membrane was used for nickel removal. However, by using a thin-film composite membrane, water flux was slightly increased over time. The time-dependent reduction of water flux may be due to the increased concentration polarization or membrane fouling due to the addition of nickel to the feed solution. As shown in Figure 3d, 100% of chromium was eliminated within
flux also increased by increasing the concentration of draw solution, thereby, preventing the passage of As(V) from the membrane to the draw solution (32). On the other hand, when the concentration of feed solution exceeded 11 mg/L, changes in the draw solution had on significant effect on the removal of chromium; chromium removal also followed a downward trend. In addition, a study by Cui et al (10) reported similar results, despite a greater slope in the trend line compared to this study. At a draw solution concentration of 1 mol/L, removal of heavy metals reached 99.8% by increasing the concentration of feed solution to 2000 and 5000 mg/L, removal efficiency slightly decreased (99.6%). Conversely, Han reported that the removal rate of arsenic is not directly correlated with the concentration of draw solution (33). The results of numerical optimization in the used program showed the following optimal conditions: initial chromium concentration in the feed solution, 4 mg/L; draw solution concentration (MgCl\textsubscript{2}), 1.27 mol/L; and experiment time, 90 min. Under these conditions, the removal efficiency of chromium and flux of recycled water were 85.58% and 15.6 LMH, respectively. The suitability of the model was also 78.8%. In order to verify the predicted results by the model under the predicted optimal conditions, three additional experiments were performed in the laboratory, the results of which are presented in Table 4, along with the predicted results by the model. The results showed that the error rate and SD of the experimental and predicted data were low, and the model was a good fit to the experimental data. When there are several responses in a process, the optimal conditions can be graphically presented using an overlay plot of all contour plots. Graphical optimization represents the possible responses for each factor; areas that fit the optimal criteria are shaded. By selecting the minimum criteria for chromium removal and water flux (90% and 15 LMH, respectively), the optimal region is demonstrated in Figure 4. This region showed the optimal condition for chromium removal and water flux.

Conclusion
Considering the simplicity and cost-effectiveness of direct osmosis and its relatively high efficiency in water recycling and chromium removal from electroplating wastewater, membranes can be used in the treatment of wastewater. On the other hand, RSM and CCD can be applied to optimize the effective parameters in chromium removal and water flux in the treatment of electroplating wastewater. Based on the results, the optimal conditions include a feed solution concentration of 4 mg/L, draw solution concentration of 1.27 mol/L, and experiment time of 90 minutes; under these conditions, water flux and chromium removal efficiency were 15.6 LMH and 85.58%, respectively. Regarding removal efficiency, the amount of chromium in the effluent of the process was within the standard limits for the effluent discharge into the environment, established by Iran's Department of Environment.

It is recommended to investigate the effect of temperature, pH, and other types of draw solutions in future studies.

Acknowledgments
The authors would like to gratitude Research Vice Chancellor of Qazvin University of Medical Sciences for Financial support of this project (No. 14003407).

Ethical issues
The authors certify that all data collected during the study are as stated in this manuscript, and no data from the study has been or will be published separately elsewhere.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
All authors contributed equally to data collection and manuscript approval.

References


