Optimization of boron removal from water by electrodialysis using response surface methodology

Fatma Guesmi, Islem Louati, Chiraz Hannachi and Béchir Hamrouni

ABSTRACT

Boron removal from water containing 5 mg L\(^{-1}\) of boron using electrodialysis (ED) was studied as a function of several parameters such as flow rates, initial pH, coexisting anions and ED time. An ED cell, equipped with three cation exchange membranes (fumasep FKB) and two anion exchange membranes (fumasep FAB), was applied. The central composite design, which is the standard design of response surface methodology, was used to evaluate the effects and interactions of studied factors on boron removal efficiency. The effectiveness of the considered design parameters was well examined to find the optimum condition. The experimental data obtained were analyzed by analysis of variance for the polynomial model with 95% confidence level. Boron removal by ED showed to be independent of the electrodialysis time, whereas flow rate as well as the pH of the feed solution and also the coexisting anions on the feed solution play a significant role on the deboronation efficiency. According to the desirability function, the maximum response of 43.5% was predicted for boron removal at a pH equal to 10, a flow rate of 10 L h\(^{-1}\), a ratio between sulfates and that of boron equal to 2 and a reaction time of 25 minutes.

Key words | boron removal, electrodialysis, factorial design, optimization, response surface methodology

INTRODUCTION

Boron is a trivalent metalloid which is very abundant in the environment. It is an essential micronutrient for plants, humans and animals. However, it is harmful at higher concentrations and can cause several problems (Kabay et al. 2008; Kheriji & Hamrouni 2016; Miller et al. 2016). In 1993, the World Health Organization (WHO) included boron on a list of drinking water standards and set a limit of 0.5 mg L\(^{-1}\) for boron in drinking water. In the same year the European Union determined the risk caused by boron to the environment and human health. At that time, however, there was no known technology that allowed such a level of boron content to be achieved. Due to this, in 1998 the WHO raised the value to 0.5 mg L\(^{-1}\) (Wyness et al. 2003; Kabay et al. 2006; Wolska & Bryjak 2013). This value was revised to 2.4 mg L\(^{-1}\) in 2011 due to the positive effect of boron for human health (WHO 2011). On the other hand, the EU still suggests the maximum boron concentration in drinking water as 1.0 mg L\(^{-1}\).

Conventional methods suggested for boron removal from water include membrane process (Kheriji et al. 2015; Kheriji & Hamrouni 2016; Kheriji et al. 2016), electrocoagulation (Isa et al. 2014; Can et al. 2016), adsorption (Köse et al. 2011), ion exchange (Wolska & Bryjak 2015) and electrodialysis (Oren et al. 2006; Kabay et al. 2008). However, adsorption is effective for boron removal only under high boron concentration. Various sorbents are used for boron removal by adsorption such as activated carbon, fly ash, clays, natural minerals, layered double hydroxides and biological materials. During the last few decades, electrochemical water treatment technologies such as electrocoagulation have undergone rapid growth and development. The application of a chelating ion exchange resin seems to be one of the most effective methods for boron removal from aqueous solutions. It was found that chelating resins containing ligands having three or more hydroxyl groups present high selectivity to boron, although these groups are not reactive to ordinary metals and other elements. In the case of the reusability of the ion exchange process, the post-regeneration process causes cost increases.

Electrodialysis (ED) is an electrochemical separation process based on the transfer of ions through ion exchange membranes under the influence of an electrical potential difference as a driving force. ED is usually applied in desalination of brackish water, recovery of sodium chloride from sea water, recovery of metal or acid from steel industries, etc. (Strathmann 2010; Lee 2011).

Boron removal by ED has been investigated by several researchers (Melnik et al. 1999; Turek et al. 2005; Yazicigil & Oztekin 2006; Kabay et al. 2008; Turek et al. 2008; Dydo 2013). It was shown that boron removal depends on the type of membrane, boron concentration in the feed, electrical current density, the types of the salts in the same solution and the pH of the solution, which is the critical factor for boron removal. Melnik et al. (1999) studied boron removal by ED using homogeneous type MK-100 and MA-100 membranes and heterogeneous type MK-40 and MA-40 membranes. They found that boron removal reached a maximum value at pH > 10. Dydo (2013) and Yazicigil & Oztekin (2006) carried out studies on boron removal using ED. They reported that the transport of boron was affected by the types of salt in the solution. Results showed that sulfate ions have more influence on boron transfer than nitrates or chlorides. According to Turek et al. (2008) higher boron removal efficiency was obtained at pH 12. A similar finding was observed by Kabay et al. (2008). It was found that boron transfer occurred at pH of 10.5. This finding due to the formation of $\text{B(OH)}_4^-$ ions in the solution at high pH as shown in Figure 1.

The performance of ED for boron removal depends on several factors. Most of the reported researches on boron removal were usually carried out using conventional methods by varying one of the independent parameters while keeping all other factors at fixed levels. These methods are often time consuming and require a number of experiments, which are unreliable to determine optimum levels. They are usually unable to determine the true optimal conditions because interaction among variables is not taken into consideration. Response surface methodology (RSM) is one of the multivariate techniques that can deal with experimental design and statistical modelling.

Therefore, the aim of this investigation is to study the influence of the ED parameters (flow rates, initial pH, coexisting anions and ED time) on boron removal. The effect of operating parameters on boron removal by ED was investigated and optimized using central composite design (CCD) under RSM, which was used for the first time to optimize the boron removal process. In addition, this methodology was utilized to predict the optimum values for these operating variables in order to obtain the maximum value of boron removal by ED.

**MATERIALS AND METHODS**

**Electrodialysis equipment and membrane**

In this investigation, ED experiments were conducted using an FT-EDR-40-x ED unit supplied by Fumatech Funktionelle Membranen und Anlagentechnologie. The ED cell is equipped with three cation exchange membranes (fumasep FKB) and two anion exchange membranes (fumasep FAB), and a pair of electrodes made of platinum/iridium-coated titanium and spacers. The active surface of each membrane is 36 cm$^2$. The simplified schematic of the ED unit working in continuous mode is presented in Figure 2.
Reagent

Analytical grade salts of boric acid, sodium chloride and sodium sulfate are used in all experiments to prepare synthetic solutions with known amount of salts and the electrode rinse solution.

Experimental procedure

The ED experiments were carried out with synthetic boron concentration of 5 mg L$^{-1}$ at room temperature and an electrolyte solution of 2.5 g L$^{-1}$. The applied current density across the ED cell was fixed at a value below the limiting current.

In this study continuous operation mode was used for boron removal by ED. When an electrical potential difference is formed between electrodes, borate ions migrate towards the anode. Borate ions leave the dilute compartment and move through the anion exchange membrane and are retained by the cation exchange membrane in the concentrated compartment (Kabay et al. 2008).

After each experiment, solutions of 0.1 mol L$^{-1}$ HCl, 0.1 mol L$^{-1}$ NaOH and ultrapure water were circulated through the ED cell for 30 min in order to remove any deposits.

Analytical method

In this study the electrical conductivity of samples was measured using a 912 Conductometer (Metrohm AG, Switzerland). Solutions pH were determined by a pH-meter (780 pH-meter, Metrohm AG, Switzerland).

Boron concentration was determined spectrophotometrically using the azomethine-H method. A TOMOS V-1100 model spectrophotometer was used for the measurements.

Determination of the limiting current

Limiting current density (LCD) is a significant parameter in the ED process. Indeed, when operated at above the limit current density a higher electrical resistance or lower current can be shown. This can cause some problems such as water dissociation or salt precipitation. So it becomes necessary to determine the LCD in order to prevent problems and operate the electrodialyzer successfully (Ben Sik Ali et al. 2010). The method of Cowan and Brown was used to determine the limit current density. The methodology has already been described in our previous paper (Guesmi et al. 2016).

Experimental design and optimization

In this investigation, the CCD for the RSM was mainly applied to optimize boron removal using the ED process. This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with minimum number of experiments, as well as to analyze the interaction between parameters (Behbahani et al. 2011). The CCD is the most frequently used five-levels fractional factorial design for the construction of a second-order response surface model (Soleymani et al. 2015). Generally, this design includes three points: cube points that come from the factorial design, axial and center points. Therefore, the number of runs N can be determined by:

$$N = 2^k + 2k + n_c$$  \hspace{1cm} (1)

where k is the number of factors and $2^k$, $2k$ and $n_c$ are the factorial, axial and center point runs, respectively.

The studied parameters in this study were the initial pH of the treated solution, the flow rate, the electrodialysis time and the ratio of equivalent concentration of sulfate ions as the variables. Each of the variables was examined at five different levels ($-\alpha$, $-1$, 0, $+1$, $+\alpha$) and their levels and ranges are shown in Table 1.

In the present work the experimental data were analyzed using Statistica v.10 software.

RESULTS AND DISCUSSION

Determination of the limiting current

The limiting current ($I_{lim}$) was determined by measuring the potential (E) and the cell resistance (E/I) as a function of the applied current (I). The method of Cowan and Brown was

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Experimental factors and levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factors and units</td>
<td>Symbols</td>
</tr>
<tr>
<td>pH</td>
<td>X$_1$</td>
</tr>
<tr>
<td>Flow rate (L h$^{-1}$)</td>
<td>X$_2$</td>
</tr>
<tr>
<td>[SO$<em>4^{2-}$]$</em>{C_{Boron}}$</td>
<td>X$_3$</td>
</tr>
<tr>
<td>ED time (min)</td>
<td>X$_4$</td>
</tr>
</tbody>
</table>
used to determine the limit current density. This method consists of plotting the electric resistance versus the reciprocal of the current (1/I).

The effects of the electrolyte concentration and the flow rate on the LCD were investigated. The NaCl concentration in the solution was varied from 0.5 to 2.5 g L\(^{-1}\) and the experiments were conducted in a constant flow rate of 15 L h\(^{-1}\). Table 2 displays the variation of the LCD with NaCl concentrations.

Results show that the LCD increases with the NaCl concentration. The limiting current density for an ED system operating at a constant NaCl concentration (2.5 g L\(^{-1}\)) is proportional to the concentration of ions in the diluate and to the mass transport coefficient (Greiter et al. 2004). In addition, it has been shown that the limiting current density is proportional to the concentration of ions in the diluate and to the mass transport coefficient (Greiter et al. 2002). Indeed, the higher the ion supply rate of the stationary layer, the less the diffusion through the membranes will be slowed down. This results in a minimization of the polarization of the concentration, which would increase the current density to accelerate the process.

The effect of the flow rate on the LCD was determined in this study with constant NaCl concentration (2.5 g L\(^{-1}\)). Obtained results are given in Table 3.

It was shown from Table 3 that the LCD is proportional to the increase of the flow rate. According to Lee (2011) the thickness of the diffusion boundary layer decreases with the increase of flow rate, which gives rise to the reduction of ionic mass transfer resistance on the membrane surface.

In all experiments the applied current was fixed at a value below the limiting current (\(I = 80\%I_{\text{lim}}\)).

### Application of RSM to optimize boron removal by ED: analysis of CCD

The design matrix consisting of 50 sets of experiments in coded terms along with their values for the response are given in Table 4.

<table>
<thead>
<tr>
<th>Run</th>
<th>(X_1)</th>
<th>(X_2)</th>
<th>(X_3)</th>
<th>(X_4)</th>
<th>Observed</th>
<th>Predicted</th>
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<td>1</td>
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<td>(-1)</td>
<td>(-1)</td>
<td>(+1)</td>
<td>18.50</td>
<td>20.85</td>
</tr>
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<td>(-1)</td>
<td>(+1)</td>
<td>(-1)</td>
<td>1.99</td>
<td>2.47</td>
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<td>(-1)</td>
<td>5.45</td>
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<td>(+1)</td>
<td>(+1)</td>
<td>0.71</td>
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<td>(-1)</td>
<td>(-1)</td>
<td>35.60</td>
<td>34.54</td>
</tr>
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<td>(+1)</td>
<td>(+1)</td>
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<td>(+1)</td>
<td>(-1)</td>
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<td>14.50</td>
<td>14.50</td>
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<td>0</td>
<td>0</td>
<td>0</td>
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<td>14.50</td>
</tr>
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<td>12</td>
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<td>(-1)</td>
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<td>2.76</td>
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<tr>
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<td>(-1)</td>
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<td>(+1)</td>
<td>(+1)</td>
<td>(-1)</td>
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<td>15</td>
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<td>(-1)</td>
<td>(-1)</td>
<td>(+1)</td>
<td>40.90</td>
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<tr>
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<td>(-1)</td>
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<td>(+1)</td>
<td>(+1)</td>
<td>(+1)</td>
<td>0.99</td>
<td>0.58</td>
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<td>0</td>
<td>14.50</td>
<td>14.50</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>14.50</td>
<td>14.50</td>
</tr>
<tr>
<td>21</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0.12</td>
<td>0.09</td>
</tr>
<tr>
<td>22</td>
<td>(+2)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.16</td>
<td>3.71</td>
</tr>
<tr>
<td>23</td>
<td>0</td>
<td>(-2)</td>
<td>0</td>
<td>0</td>
<td>35.10</td>
<td>34.95</td>
</tr>
<tr>
<td>24</td>
<td>0</td>
<td>(+2)</td>
<td>0</td>
<td>0</td>
<td>1.70</td>
<td>3.37</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td>0</td>
<td>(-2)</td>
<td>0</td>
<td>27.70</td>
<td>26.98</td>
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<tr>
<td>26</td>
<td>0</td>
<td>0</td>
<td>(+2)</td>
<td>0</td>
<td>0.24</td>
<td>0.49</td>
</tr>
<tr>
<td>27</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(-2)</td>
<td>4.50</td>
<td>5.89</td>
</tr>
<tr>
<td>28</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(+2)</td>
<td>8.80</td>
<td>8.93</td>
</tr>
<tr>
<td>29</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>14.50</td>
<td>14.50</td>
</tr>
<tr>
<td>30</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>14.50</td>
<td>14.50</td>
</tr>
</tbody>
</table>

### Table 2 | LCD values as function of NaCl concentration

<table>
<thead>
<tr>
<th>NaCl concentration (g L(^{-1}))</th>
<th>(I_{\text{lim}}) (A)</th>
<th>LCD (A m(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.40</td>
<td>11.1</td>
</tr>
<tr>
<td>1</td>
<td>0.11</td>
<td>30.5</td>
</tr>
<tr>
<td>1.5</td>
<td>0.13</td>
<td>36.11</td>
</tr>
<tr>
<td>2</td>
<td>0.17</td>
<td>47.2</td>
</tr>
<tr>
<td>2.5</td>
<td>0.24</td>
<td>66.7</td>
</tr>
</tbody>
</table>

### Table 3 | Effect of flow rate on the limiting current density

<table>
<thead>
<tr>
<th>Flow rate (L h(^{-1}))</th>
<th>(I_{\text{lim}}) (A)</th>
<th>LCD (A m(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.12</td>
<td>33.3</td>
</tr>
<tr>
<td>15</td>
<td>0.13</td>
<td>36.1</td>
</tr>
<tr>
<td>20</td>
<td>0.13</td>
<td>36.1</td>
</tr>
<tr>
<td>25</td>
<td>0.14</td>
<td>38.8</td>
</tr>
<tr>
<td>30</td>
<td>0.15</td>
<td>41.6</td>
</tr>
</tbody>
</table>
Development of regression model equation

Based on the data analysis, the second order quadratic model for boron removal efficiency in terms of coded factors is given by Equation (2):

\[
R_B(\%) = 14.50 + 3.10X_1 - 7.89X_2 - 6.12X_3 + 0.76X_4 \\
- 3.15(X_1)^2 + 1.17(X_2)^2 - 0.06(X_3)^2 - 1.77(X_4)^2 \\
- 4.27(X_1X_2) - 0.93(X_1X_3) + 0.19(X_1X_4) \\
+ 3.06(X_2X_3) - 0.36(X_2X_4) - 0.64(X_3X_4)
\]

(2)

In Equation (2) the positive signs of the term indicate a synergistic effect, while the negative sign indicates an antagonistic effect.

This model equation was used to estimate the influence of the factors studied on boron removal by ED. The statistical significance of the model was examined through analysis of variance (ANOVA) for the polynomial model with 95% confidence level, and an adequacy plot was used to justify the goodness of model fit. ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation, for the purpose of testing hypotheses on the parameters of the model (Maran & Priya 2015).

Results of the ANOVA study are shown in Table 5. Generally, a highly significant regression model is justified by higher Fischer’s F-value, with P-value (probability) as low as possible (Chaudhary & Balomajumder 2014). It can be seen from Table 5 that the model F-value of 16.600 for boron removal efficiency is higher than the critical value of 2.73 (F0.05,4,27) which implies that the model is significant. Also, the low P-value (10^-6 < 0.05) of the model proves the ability of the model and indicates the statistical significance and adequacy at 95% confidence level. The value of the determination coefficient, R², of the quadratic regression model (0.965) and the value of adjusted determination coefficient (0.933) are very high and confirmed that the model was highly significant.

Student’s t-test

The Pareto analysis (Figure 3) was used to determine the main significant factors on the response variable. This can be demonstrated by a graphical representation of the Pareto diagram. This graphic contains a bar for each factor, classified from the most significant to the least significant. A vertical line (reference line) is drawn at the location of the 0.05 critical values. Any bars that extend to the right of that line indicate effects that are statistically significant at the 5% significance level (Mahmoud & Hoadley 2012).

Based on the graphical analysis of the Pareto diagram, the flow rate of the feed solution is the most influential factor on boron removal by ED, followed by the coexistence of sulfate ion, then the pH of the solution and finally the electrodialysis time. According to the sign of the coefficient, it is observed that the pH of the solution has a positive effect on boron removal by ED. This behavior can be attributed to the presence of B(OH)₄⁻ ions in the solution at high pH. A similar finding was observed by others researchers (Melnik et al. 1999; Kabay et al. 2008; Turek et al. 2008). In contrast, the flow rate of the feed solution had a negative effect on boron removal. This result is due to the fact that the increase in flow rate limits the retention time of boron inside the different compartments, of the cell and some ions were taken out of ED without crossing the membrane. Moreover, the increase in flow rate could increase the hydraulic pressure between membranes, thereby damaging the membranes and shortening their lives (Gherasim et al. 2014). On the other hand, the electrodialysis time and the coexistence of sulfate ions have also a negative effect on boron removal. The transfer of boron is prevented by increasing the number of coexisting ions. Indeed, in the presence of monovalent and divalent ions set in the ion exchange membrane, monovalent ion can be transferred with a usual fixed ion. Thus, it can move more easily from one functional group to the next. In contrast, bivalent ions move less easily because their movement is interfered with by the coexistence of monovalent ions. The same result was
found by Dydo (2015) and Yazicigil & Oztekin (2006). They reported that the order of boron transfer was found to be $\text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$.

**Three-dimensional response surface plots**

The three-dimensional (3D) response surfaces (Figure 4) were studied in order to gain a better comprehension of the boron removal process using ED. These plots are a graphical representation of a 3D response surface as a function of two independent variables, maintaining all other variables at central level (0) (Ghosh et al. 2015). The curvatures of plots may be attributed to interaction between the variables.

Figure 4 shows some curvatures, which proves that there are interactions between the factors as we saw in the Pareto diagram. In fact, the most important curvature that can be observed is that of the graph (c), which allows us to deduce the presence of a strong interaction between electrodialysis time and pH factors. A smaller curvature can be seen on the graph (b) representing an interaction between the concentration ratio and the pH.

**Optimization of CCD by desirability function for boron removal by ED**

The desirability profile for predicted values was obtained by using the Statistica 8.00 software for the optimization of the ED process for boron removal (Figure 5). The scale in the range of 0.0 (undesirable) to 1.0 (very desirable) was used to obtain a global function that should be maximized according to efficient selection and
optimization of designed variables. The CCD matrix shows the minimum (0.12%) and maximum (40.9%) for boron removal percentage. According to this result, the values of desirability function for the dependent variables of removal percent (Figure 5) indicate that the desirability of 1.0 was assigned to maximum removal (40.9%), 0.0 for minimum (0.12%). Obtained results show that the optimal conditions for the removal of boron are: a pH equal to 10, a flow rate of 10 L h\(^{-1}\), a ratio between the concentration of sulfates and that of boron equal to 2 and a reaction time of ED of 25 minutes. A desirability value of 1 corresponds to an optimal boron removal percentage of 43.506%.

**CONCLUSION**

In summary, ED was investigated for boron removal from aqueous solution. The RSM has been successfully applied to evaluate the effect of operating parameters on boron removal. The CCD for the RSM was performed for the removal of boron by ED. The statistical significance of the model was examined through ANOVA for a polynomial model with 95% confidence level. Obtained results show that the flow rate, the pH of the solution and the coexistence of sulfate ion are the most influential factors on boron removal by ED.

**REFERENCES**


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