MODELING AND OPTIMIZATION OF IRON REMOVAL PROCESS FROM WASTEWATER

Petru BULAI¹, Elena-Raluca BULAI¹, Lăcămioara APETREI¹

¹ “Ştefan cel Mare” University, Faculty of Mechanical Engineering, Mecatronics and Management, Department of Mechanical & Technology, no. 13, Universităţii street, 720229, Suceava, Romania bulaipetru@yahoo.com

Abstract: The article presents the modeling and optimization of the conditions for the removal of iron ions from synthetic wastewater using ion exchange resins. Article contributes to the improvement of wastewater treatment by modeling the process using as process variables initial solution pH, initial metal ion concentration and resin dose. To study the combined effect of the process variables a 2³ orthogonal central composite design was used and for analysis of experimental data was used Response Surface Methodology (RSM).

Keywords: wastewater, iron ion removal, modeling, optimization

1. Introduction

The main source that contaminates natural water resources with iron ions is the discharge of insufficiently treated wastewater. Another important source is the pipes or other metal components corrosion [1], [2].

These ions can produce offensive taste of water that may affect the animal intake or treatment process in drinking water plant. Iron ions are not harmful but they may produce offensive tastes that will cause animals to limit or refuse intake of the water [3]. A higher concentration of iron ions in natural water resource may affect the resource aesthetics by iron precipitating as an orange coating on the resource bottom and on aquatic vegetation [3]. Concentration in iron above 0.3 mg/L may cause problems in irrigation operation by injury to plants [3].

To prevent occurrence of the previously mentioned aspects is necessary for iron ions to be removed from the wastewater before discharge to water resources. Ionic iron can be removed from wastewater by different processes: precipitation, sorption (ion exchange, biosorption), filtration (reverse osmosis, nanofiltration and ultrafiltration) or electrochemical processes [4].

This article presents the modeling and optimization of retention of iron ions from synthetic wastewater by ion exchange resins.

2. Experimental

2.1. Materials

In experimental sorption processes were used as sorbent the chelating resin Purolite S930 from International Limited (Hounslow, UK).

The main physical and chemical properties of the chelatic resin are presented in Table 1.

Table 1: Characteristic properties of the resin used*

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer matrix structure</td>
<td>Macroporous</td>
</tr>
<tr>
<td></td>
<td>styrene</td>
</tr>
<tr>
<td></td>
<td>divinylbenzene</td>
</tr>
<tr>
<td>Functional groups</td>
<td>Iminodiacetic acid</td>
</tr>
<tr>
<td>Ionic form (as shipped)</td>
<td>Na⁺</td>
</tr>
<tr>
<td>pH range (operating): H⁺ form, Na⁺ form</td>
<td>2 - 6; 6 - 11</td>
</tr>
<tr>
<td>Maximum operating temperature</td>
<td>70 °C</td>
</tr>
<tr>
<td>Particle size range</td>
<td>+ 1.0mm &lt;10%, -0.3mm &lt;1%</td>
</tr>
<tr>
<td>Total exchange capacity</td>
<td>≥ 1.9 meq/mL</td>
</tr>
</tbody>
</table>

* Manufacturer supplied.

In order not to exceed the maximum operating temperature of 70°C, recommended
by the manufacturer, the drying of resin was performed at 60 degrees using an oven.

For sample preparation was used a stock solution of iron (II), of 500 mg/L, from analytical-reagent grade iron sulphate (FeSO₄·7H₂O) in distilled water. To adjust the pH of the samples were used diluted solutions of sulfuric acid or sodium hydroxide.

2.2. Sorption experiments

For the study of iron ions retention on the hydrogen form of chelated resin the experiments were carried out in batch experiments using an amounts of 100 mL with different initial concentrations in Fe (II) and different amounts of resin. After adjusting the solution pH with acid or base, the Erlenmeyer flasks where mechanically shacked at constant temperature and at the rate of 120 cycles min⁻¹ using the Orbital Shaking Incubator GFL 3031. After equilibrium (24 hours) the resin and solution were separated by filtration.

Concentration of iron ions in the solution was determined using a spectrophotometric method with 1,10-phenanthroline and hydroxilaminochlorohidrat (λ=510nm) and Hach DR/2000 spectrophotometer [5].

To quantify the sorption process was calculated the amount of iron ions retained on resin, Q (mg/g), as shown in equation 1:

\[
Q = \frac{(C_0 - C_e)V}{m} \tag{1}
\]

where, \(C_0\) and \(C_e\) are the initial and the equilibrium concentrations of Fe (II) in the solution (mg/L), \(V\) is the volume of solution used in experiment (L), \(m\) is the mass of the resin (g) used in the experiment and \(Q\) is ion exchange capacity of the resin.

3. Results and discussions

3.1. Process modeling

For the experimental design was adopted a \(2^3\) orthogonal central composite design with 2 levels (±1 and ±\(\alpha\)) for each independent variables \((x_1\) - initial solution pH, \(x_2\) - initial metal ion concentration and \(x_3\) - resin dose) as presented in Figure 1.

Figure 1 Orthogonal central composite design for three independent variables and two levels [6]

A central composite design may contain only one observation at each of the \(n_f\) factorial points, two observation at each \(q\) axial points, and \(n_c\) observations at the center. This design is known as Khuri and Cornell orthogonal if \((n_f + 2\alpha^2)2 = n_f + n_c\), where \(n\) is the total number of observations and \(n = n_f + 2 + n_c\) and \(q\) is the number of independent variables [7].

Orthogonal central composite design with only one observation is achieved by appropriate choice of level \(a\) and \(n_c\), the number of the observations at the center. The value of level \(a\) would be:

\[
\alpha = \left(\frac{\sqrt{n_f \cdot n - n_f}}{2}\right)^{1/2} \tag{2}
\]

In order to encode the values of the independent variables was used the equation 3:

\[
x_i = \frac{Y_i - Y_0}{\Delta Y} \tag{3}
\]

where \(x_i\) is the coded value, \(Y_i\) is the corresponding natural value of the \(i^{\text{th}}\) test variable, \(Y_0\) is the natural value in the center point value and \(\Delta Y\) is the step change value [8], [9].

Experimental domain and the levels of independent variables for Fe (II) removal process from wastewater by Purolite S930 chelatic resin are given in Table 2.
To explain the behavior of the system, the quadratic and interaction effects of the process variables were calculated by using equation (4). The statistical significance of the regression model was tested by means of the Student’s “t” test.

\[
\hat{Q} = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j
\]  

(4)

where \( \hat{Q} \) is the measured response for each experiment (in this case – resin sorption capacity), \( \beta_0 \) is the intercept term, \( \beta_i, \beta_{ii} \) and \( \beta_{ij} \) are, respectively, the measures of the linear, quadratic and interaction effects of the process variables \( x_i, x_{ii} \) and \( x_i x_j \), and \( i = 1, 2, 3 \) and \( j = 1, 2, 3 \) (i ≠ j) [10],[11].

The regression coefficients of the empirical model (regression equation) were calculated by using equation 5 [12]:

\[
\beta = (X^T X)^{-1} X^T Q
\]  

(5)

where \( \beta \) is the column matrix of the regression coefficients, \( X \) is the matrix of coded variables and \( Q \) is the column matrix of ion exchange capacity of the resin (experimental values).

The regression coefficients, \( \beta \), obtained by solving equation 5 are presented in table 4. The quadratic model for exchange capacity fitted to the following regression equation 6.

The orthogonal central composite design of 2\(^3\) type was used as a design of experiments. The coded values and the natural values of the test variables as well as the experimental values of removal percent are presented in Table 3.

In order to explain the behavior of the studied system was used the second order polynomial equation (equation 4).

\[
\hat{Q} = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j
\]  

(4)

where \( \hat{Q} \) is the measured response for each experiment (in this case – resin sorption capacity), \( \beta_0 \) is the intercept term, \( \beta_i, \beta_{ii} \) and \( \beta_{ij} \) are, respectively, the measures of the linear, quadratic and interaction effects of the process variables \( x_i, x_{ii} \) and \( x_i x_j \), and \( i = 1, 2, 3 \) and \( j = 1, 2, 3 \) (i ≠ j) [10],[11].

The regression coefficients of the empirical model (regression equation) were calculated by using equation 5 [12]:

\[
\beta = (X^T X)^{-1} X^T Q
\]  

(5)

where \( \beta \) is the column matrix of the regression coefficients, \( X \) is the matrix of coded variables and \( Q \) is the column matrix of ion exchange capacity of the resin (experimental values).

The regression coefficients, \( \beta \), obtained by solving equation 5 are presented in table 4. The quadratic model for exchange capacity fitted to the following regression equation 6.

The statistical significance of the regression model was tested by means of the Student’s “t” test.

For this modeling process a design of 16 experiments was formulated consisting of 8 factorial points, 6 axial points (2 axial points on the axis of each design variable at a distance of \( \alpha \) from the design center) and one replicate at the center points. The coded values and the natural values of the test variables as well as the experimental values of removal percent are presented in Table 3.

### Table 2: Experimental ranges and levels of independent variables

<table>
<thead>
<tr>
<th>Independent variable</th>
<th>Code</th>
<th>Variable level</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>( x_1 )</td>
<td>-( \alpha )</td>
<td>-1</td>
</tr>
<tr>
<td>( C_0 ), mg Fe(II)/L</td>
<td>( x_2 )</td>
<td>2.8</td>
<td>3.0</td>
</tr>
<tr>
<td>Resin dose, g/L</td>
<td>( x_3 )</td>
<td>0.39</td>
<td>0.50</td>
</tr>
</tbody>
</table>

### Table 3: Orthogonal central composite design of \( 2^3 \) type

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>pH</th>
<th>( C_0 ), mg Fe(II)/L</th>
<th>Resin dose, a. g/L</th>
<th>( Q ), ion exchange capacity of the resin, mg Fe(II)/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Code (( x_i ))</td>
<td>Value (( Y_i ))</td>
<td>Code (( x_i ))</td>
<td>Value (( Y_i ))</td>
<td>Code (( x_i ))</td>
</tr>
<tr>
<td>1</td>
<td>+1</td>
<td>5</td>
<td>+1</td>
<td>300</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>3</td>
<td>+1</td>
<td>300</td>
</tr>
<tr>
<td>3</td>
<td>+1</td>
<td>5</td>
<td>-1</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>-1</td>
<td>3</td>
<td>-1</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>+1</td>
<td>5</td>
<td>+1</td>
<td>300</td>
</tr>
<tr>
<td>6</td>
<td>-1</td>
<td>3</td>
<td>+1</td>
<td>300</td>
</tr>
<tr>
<td>7</td>
<td>+1</td>
<td>5</td>
<td>-1</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>-1</td>
<td>3</td>
<td>-1</td>
<td>50</td>
</tr>
<tr>
<td>9</td>
<td>+1.215</td>
<td>5.22</td>
<td>0</td>
<td>175</td>
</tr>
<tr>
<td>10</td>
<td>-1.215</td>
<td>2.79</td>
<td>0</td>
<td>175</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>4</td>
<td>+1.215</td>
<td>326.88</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>4</td>
<td>-1.215</td>
<td>23.125</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>175</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>175</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>175</td>
</tr>
<tr>
<td>16</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>175</td>
</tr>
</tbody>
</table>
Table 4: The regression coefficients of the mathematical model

<table>
<thead>
<tr>
<th>Function</th>
<th>$\beta_0$</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
<th>$\beta_3$</th>
<th>$\beta_{12}$</th>
<th>$\beta_{13}$</th>
<th>$\beta_{23}$</th>
<th>$\beta_{11}$</th>
<th>$\beta_{22}$</th>
<th>$\beta_{33}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>48.41</td>
<td>6.39</td>
<td>14.09</td>
<td>-6.92</td>
<td>2.18</td>
<td>-2.37</td>
<td>1.33</td>
<td>0.85</td>
<td>-3.30</td>
<td>-2.91</td>
</tr>
</tbody>
</table>

$$Q = 48.41 + 6.39x_1 + 14.09x_2 - 6.92x_3 + 2.18x_1x_2 - 2.37x_1x_3 + 1.33x_2x_3 + 0.85x_1^2 - 3.3x_2^2 - 2.91x_3^2 \quad (6)$$

According to Student’s “t” test the effects of $x_1^2$ and $x_2x_3$ are non-significant and were excluded from the final regression equation (Equation 7).

$$Q = 48.41 + 6.39x_1 + 14.09x_2 - 6.92x_3 + 2.18x_1x_2 - 2.37x_1x_3 - 3.3x_2^2 - 2.91x_3^2 \quad (7)$$

The suitability between the model and experimental data was confirmed by the goodness-of-fit between calculated (predicted) values and experimental values of ion exchange capacity as shown in Figure 2. As one can see in figure 2, the regression model satisfactorily describes the experimental domain.

Likewise, the statistical F-test (Fisher's test) was performed in order to check the adequacy of empirical model. The F-test was done for a confidence level $\gamma = 0.05$ and degrees of freedom $f_1 = 6$ and $f_2 = 1$. In this respect, the calculated value of the Fisher's test ($F_C = 2.62$) was compared with the tabulated one ($F_T(f_1,f_2) = 238.883$). Since $F_C < F_T$, the mathematical model is adequate with a probability of 95 %, i.e. the agreement between the model and experimental data is statistically accepted for a confidence level $\gamma = 0.05$ [9].

The graphical representation of the regression equation (7) is called response surface and is used to describe the individual and cumulative effects of the design variables (factors) on the response. The Figures 3-5 shows the iron (II) sorption capacity of the resin as a function of designed variables.

Figure 2 Sorption capacity: experimental data versus predicted data given by regression model

Figure 3 Response surface plot and contour plots for the effect of solution pH ($x_1$) and resin dose ($x_3$)
The response surface from Figure 3-5 show that increasing of both \( x_1 \) (pH) and \( x_2 \) (initial metal concentration) variables would increase the sorption capacity. By contrast, the increasing in resin dose \( (x_3) \) has a negative effect on response and diminishes the sorption capacity of the resin.

### 3.1. Process optimization

For process optimization the Equation 7 was considered objective function. The optimization process consists in maximizing this equation taking into account the restrictions presented in Equation 8:

\[
\max \{ \dot{Q} (x_1, x_2, x_3) \} \quad \text{subject to} \quad -\alpha \leq x_i \leq +\alpha, \quad i = 1...3; \quad \alpha = 1.215
\]

The optimal solution was established by means of the gradient method [13]. The founded optimal point presented in Table 5 was verified experimentally with a precision 3.4172%. In accordance with the results presented in Table 5 the optimal solution is located into the valid region.

<table>
<thead>
<tr>
<th>pH</th>
<th>C_0</th>
<th>x_1</th>
<th>Y_1</th>
<th>x_2</th>
<th>Y_2(mg/L)</th>
<th>x_3</th>
<th>Y_3(g/L)</th>
<th>( \dot{Q} ) ion exchange capacity of the resin, mg Fe(II)/L</th>
<th>( Q ) ion exchange capacity of the resin, mg Fe(II)/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1845</td>
<td>5.18</td>
<td>1.1508</td>
<td>318.85</td>
<td>-0.7862</td>
<td>0.6069</td>
<td></td>
<td></td>
<td>76.67</td>
<td>74.05</td>
</tr>
</tbody>
</table>

### 4. Conclusions

Chelating resin Purolite S930 in hydrogen form can be used successfully to retain iron ions from wastewater.

The three parameters chosen in the modeling process as variables (initial solution pH, initial metal ion concentration and resin dose) shows an influence on the sorption process and also on the ion exchange capacity of the resin, \( Q \).
References


