Abstract: Zinc (II) removal using low-cost sorbents requires a proper process parametric study to determine its optimal performance characteristics. In this respect, the present study proposes a new modeling and simulation procedure for heavy metal removal system and is carried out to optimize input variables such as initial pH, adsorbent dosage, and contact time for biosorption of Zinc (II) by using bentonite. The proposed experimental system is cost-effective and requires less calculation for determining optimal values, i.e., input variables and their related removal capacity, $R_{\text{rem}}\%$. To optimize the adsorption process, cubic spline curve fitting and numerical differentiation techniques are used for required calculations. According to the proposed calculations, the removal capacity is calculated as 98.66%, while the optimal values are calculated as initial pH – 6.76, adsorbent dosage – 1.14 g L$^{-1}$, contact time – 13 minutes. To evaluate the results, full factor experimental design and 3 way ANOVA test are used for comparison.

INTRODUCTION

The contamination of water by heavy metals through the discharge of industrial waste water is a worldwide environmental problem. Heavy metals, such as Pb, Cd, Cu, Hg, Cr, Ni and Zn are the main heavy metals that are of greatest concern. Among these contaminants, zinc is usually considered to be non-toxic for human at lower concentration ranges. The World Health Organization (WHO) recommended the maximum acceptable concentration of zinc in drinking water as 5.0 mg/L [11, 18]. Beyond the permissible limits, zinc is a toxic element [21]. Ingestion of excess concentration of zinc causes in humans such toxic symptoms as fever, diarrhea, gastrointestinal tract irritation etc [16]. With regard to industrial exposure, zinc fume fever resulting from inhalation of freshly formed fumes presents the most significant effect. The plants grown on zinc enriched soil also show various abnormalities and disorders like reduction of growth, inhibition of photosynthesis and respiration together with interruption of metabolism linked to the transport processes [2]. High concentration level of Zn(II) ions contamination in the industrial wastewaters must be reduced to acceptable levels before discharging them into the environment [21].

Major sources of zinc in the environment are the manufacturing of brass and bronze alloys and galvanization [22]. Different methods such as adsorption, chemical precipitation, membrane filtration, ion-exchange, and electrochemical deposition are used to treat
wastewaters containing heavy metals [3, 4, 5]. Of all these methods, adsorption appears to be the most effective, especially for effluents with moderate and low concentrations. Since the volume of water to be purified is generally large, the adsorbent required in the process should possess high selectivity with respect to the heavy metal ions, it should be non-toxic, regenerable, easily recoverable from filters, relatively cheap and readily available [12].

Natural adsorbents such as soil, clay and mineral have the advantage of easy availability and low-cost [6, 13, 17]. Bentonite has a 2:1 layer structure and it consists of alumina octahedral layer sandwiched between two silica tetrahedral layers [9]. It has a defective structure because of the isomorphic substitution of the Mg or Fe atoms for the Al atoms (octahedra) and the Al atoms for the Si atoms (tetrahedra) so that the negatively charged aluminosilicate layers accommodate exchangeable cations such as Na⁺, Ca²⁺ and/or Mg²⁺ in the interlayered-spacing for the sake of charge compensation [1]. Bentonite exhibits an enormous surface area when it is hydrated. It consists of numerous microscopic platelets; each with negative charges on flat surfaces and positive charges on edges. Hydration causes these platelets to separate into a porous structure containing both positive and negative charges [7]. These properties of bentonite make it a potential adsorbent for heavy metal adsorption from aqueous solutions.

In this study, the removal of Zn(II) from an aqueous solution by bentonite is investigated. The study is based on the traditional one factor at a time experiments, which are relatively cost effective rather than full or fractional factor experimental designs. In order to optimize the adsorption process, Cubic Spline Curve Fitting (CSCF) and Numerical Differentiation (ND) techniques are applied to investigate the individual effects of the initial pH, adsorbent dosage and contact time for Zn(II) removal efficiency.

**MATERIAL AND METHODS**

*MATERIALS USED IN EXPERIMENTAL STUDY*

Bentonite was obtained from Bensan Mining Industry in Çanakkale, Turkey. The chemical composition of the bentonite was evaluated by using X-ray Fluorescence techniques and the results have been presented in Table 1.

<table>
<thead>
<tr>
<th>Component</th>
<th>B</th>
<th>IW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>1.80</td>
<td>2.04</td>
</tr>
<tr>
<td>MgO</td>
<td>4.00</td>
<td>1.85</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>17.00</td>
<td>3.01</td>
</tr>
<tr>
<td>SiO₂</td>
<td>61.00</td>
<td>23.18</td>
</tr>
<tr>
<td>CaO</td>
<td>2.50</td>
<td>11.21</td>
</tr>
<tr>
<td>ZnO</td>
<td>-</td>
<td>14.15</td>
</tr>
<tr>
<td>CuO</td>
<td>-</td>
<td>0.71</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.50</td>
<td>0.37</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.00</td>
<td>39.17</td>
</tr>
<tr>
<td>SO₃</td>
<td>-</td>
<td>7.09</td>
</tr>
</tbody>
</table>

B: Bentonite, IW: Industrial waste
The sample was washed with distilled water to remove any non-adhesive impurities and small particles and then dried at 70°C for 24h to remove moisture. Fig. 1 shows the scanning electron microscope (SEM) image of the adsorbent.

![Fig. 1. SEM micrograph of the waste](image)

The industrial waste used in this study was obtained from the Elektrosan Elektro-copper Industry & Trade Co. Ltd. in Samsun, Turkey. The chemical composition of the sample is presented in Table 1. As seen in Table 1, the industrial waste contains significant levels of Fe$_2$O$_3$ (39.17%) and SiO$_2$ (23.18%). Fig. 2 shows the SEM image of the waste.

**Experimental procedure**

ASTM test methods were used to evaluate the leaching potentials of heavy metal in the waste in this study. Standard 1:4 w/w mixtures were performed using the deionized water in a Teflon bottle. Bottles were shaken for 48 h at 25°C on an end-over-end rotary shaker rotating at 200 rpm. Leachates were filtered (0.22-µm openings) and used as leaching solution in the adsorption experiments.

The adsorption of Zn(II) from leaching solution on bentonite was performed using the batch equilibrium technique. The influence of parameters such as initial pH, adsorbent dosage and contact time was investigated. The effect of pH was studied by changing the pH between 2.0 and 8.0 and by keeping the amount of bentonite and contact time. The effect of adsorbent dosage was investigated by using different bentonite amounts ranging from 0.2 g/L to 2 g/L. Then contact time was determined at optimum pH and adsorbent dosage values for increasing periods of time from 5 mins to 120 mins. Zn(II) concentrations of aqueous leachate were analyzed by atomic absorption spectrometric procedure using a flame atomic absorption spectrophotometer (UNICAM model 929) with an air-acetylen flame and a hollow cathode lamp. Each experiment was performed in duplicate.
to observe the reproducibility and increase of the reliability, and the mean values were used for each set of values.

The sorption efficiency of the system ($R_{em} \%$) is calculated in Eq. (1).

$$R_{em} \% = \left( \frac{C_i - C_e}{C_i} \right) \cdot 100$$  \hspace{1cm} (1)

where $C_i$ is the initial concentration of metal ions in solution (mg L$^{-1}$), and $C_e$ is the final concentration of metal ions in solution (mg L$^{-1}$).

**Cubic Spline Curve Fitting (CSCF)**

Cubic spline curve fitting technique is used because it is easy to implement and produce a curve that appears to be seamless. Least square curve fitting approach tends to build in distortions near the first and last samples of the data. However, cubic splines avoid this phenomena, but they are only piecewise continuous, meaning that a sufficiently high derivative (third) is discontinuous.

The experiments, which are used for calculating adsorption capacity in percent ($R_{em} \%$) by changing pH level, adsorbent dosage and contact time, are repeated 2 times and the average values are taken into account. Data points of $R_{em} \%$ are then interpolated by using cubic spline curve fitting technique. The main purpose of using CSCF technique is to increase data points between minimum $R_{em} \%$ and maximum $R_{em} \%$. The data points (experiments related to one factor at a time) consist of 9 to 11 samples (Fig. 3, Fig.4 and Fig. 5).
Fig. 3. The effect of initial pH on adsorption capacity (R\textsubscript{em} \%) 

Fig. 4. The effect of adsorbent dosage (d\textsubscript{o}) on adsorption capacity (R\textsubscript{em} \%)

Fig. 5. The effect of contact time (c\textsubscript{t}) on adsorption capacity (R\textsubscript{em} \%)
The number of samples is reproduced to 100, which is required for numerical differentiation technique. Then 1\textsuperscript{st} order numerical differentiation technique is applied to each interpolated Rem\% curve to calculate optimum levels of pH level, adsorbent concentration and contact time.

In this section, cubic spline interpolation will be described as mathematical background to generate Rem\% data points. Since the curve fitting technique is called “cubic”, the fitted equation is in the 3\textsuperscript{rd} order (Eq. 2). Spline theory is relatively simple. Over \( n \) intervals, the routine fits \( n \) equations subject to the boundary conditions of \( n + 1 \) data points. The assumed form for the cubic polynomial curve fit for each segment is defined in (2).

\[
y = a_i (x - x_i)^3 + b_i (x - x_i)^2 + c_i (x - x_i) + d_i
\]

where the spacing between successive data points is defined in (3).

\[
h_i = x_{i+1} - x_i
\]

The function \( y \) is called a cubic spline and states the \( y \) consists of piecewise cubics. The cubic spline constrains the function value, 1\textsuperscript{st} derivative and 2\textsuperscript{nd} derivative. The routine must ensure that \( y(x), y'(x) \) and \( y''(x) \) are equal at the interior node points for adjacent segments. Substituting a variable \( S \) for the polynomial’s second derivative reduces the number of equations from \( a, b, c, d \) for each segment 1-1 to only \( S \) for each segment. For the \( i \)\textsuperscript{th} segment, the \( S \) governing equation is defined in (4).

\[
h_{i-1} S_{i-1} + (2h_{i-1} + 2h_i) S_i + h_i S_{i+1} = 6 \left( \frac{y_{i+1} - y_i}{h_i} - \frac{y_i - y_{i-1}}{h_{i-1}} \right)
\]

Finally, the cubic spline properties are found by substituting into the following equations. These \( a, b, c \) and \( d \) values correspond the polynomial definition for each segment (Thant and Aye 2009; Mathews and Fink 2004).

\[
a_i = (S_{i+1} - S_i)/6h_i \\
b_i = S_i/2 \\
c_i = \frac{y_{i+1} - y_i}{h_i} - \frac{2h_i S_i + h_j S_{i+1}}{6} \\
d_i = y_i
\]

The following Figures show experimental data points and curve fitted values for pH, adsorbent dosage and contact time. The number of points, \( n \), is selected 100, which is quite suitable for numerical differentiation approach to get optimum levels.

The slopes of line1, line2 and line3 shown in Figs 3–5 are defined by using numerical derivative technique after CSCF technique.

**Numerical Differentiation (ND)**

Numerical differentiation is not only an elementary issue in numerical analysis, but also a very useful tool in applied sciences. In practice, numerical approximations to derivatives are used mainly in two ways. First, the derivatives of a function at specified points
within its domain can be computed. The function is given to user either in the form of a discrete set of argument and function values, or in a continuous analytical form. Second, the numerical differentiation formula is used in deriving numerical methods for solving ordinary differential equations (ODEs) and partial differential equations (PDEs) (Li 2005; Tachev 2009). The first approach is used in this proposed work.

A ripe application area for numerical differentiation is discontinuity analysis for nonlinear systems. The problem of numerical differentiation is well-known to be ill posed in the sense that small perturbations of the function to be differentiated may lead to large errors in the computed derivative. However, in many applications it is necessary to estimate the derivative of a function given to the noisy values of this function.

The derivative of a function \( f(x) \) is defined as:

\[
f'(x) = \frac{df(x)}{dx} = \lim_{\Delta x \to 0} \frac{f(x + \Delta x) - f(x)}{(x + \Delta x) - x}
\]  

(6)

\( f'(x) \) is regarded as derivative of adsorption capacity in the text and three derivative functions are calculated for pH, adsorbent dosage and contact time.

Numerical algorithms for computing the derivative of a function require the estimate of the slope of the function for some particular range of x values. Three common approaches are the backward difference, forward difference, and the central difference. In this study, forward difference is used for required calculations as in Eq. (6).

RESULTS AND DISCUSSION

Several laboratory experiments have been done to increase the efficiency of the proposed techniques. The experiments, which are used for calculating adsorption capacity in percent (\( R_{em} \)) by changing pH level, adsorbent dosage and contact time (regarded as input variables), are repeated 2 times and the average values are taken into account. The data used in this paper are shown in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>Adsorption capacity, ( R_{em} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pH</td>
<td>2–10</td>
</tr>
<tr>
<td>Adsorbent dosage (g/L)</td>
<td>0.2–2</td>
</tr>
<tr>
<td>Contact time (min)</td>
<td>5–120</td>
</tr>
</tbody>
</table>

In this study, optimum adsorption capacity (\( R_{em} \)) is simply calculated by numerical derivative technique. As seen in Fig. 3, Fig. 4 and Fig. 5, the slopes of the lines (1 to 3) are calculated by 1st order derivatives.

The derivative of \( f(x) \) at \( a \) is the slope of the line tangent to \( f(x) \) at \( a \) as shown in Fig. 6 [14].

Taking into account Fig. 6, the following outcomes can be drawn:

a) points where the derivative of \( f(x) \) is equal to zero are known as critical points,

b) the function may be horizontal in this region or may have reached a so-called
extrema point, a point where \( f(x) \) is at a local (global) maximum or local (global) minimum.

Global maximum and minimum points are used for determining optimal initial pH, adsorbent dosage and contact time values. In order to refrain from local maximum and minimum points, numerical differentiation is calculated through \( n - 1 \) points.

The following Fig. 7 shows the numerical differentiation curve for \( R_{em} \% \) with respect to pH.

As seen in Fig. 7, there are two minimum points, one for local and the other for global. Global minimum point is the value which is regarded as optimum pH level. According to Fig. 5, the optimum pH level is calculated as 6.76.

The following Fig. 8 shows the numerical differentiation curve for \( R_{em} \% \) with respect to adsorbent dosage.

As seen in Fig. 8, there are two minimum points, one for local and the other for global. Global minimum point is the value which is regarded as optimum dosage level. According to Fig. 6, the adsorbent dosage is calculated as 1.14 g L\(^{-1}\).

The following Fig. 9 shows the numerical differentiation curve for \( R_{em} \% \) with respect to contact time.
As seen in Fig. 9, there are again two minimum points, one for local and the other for global. According to Fig. 9, the optimum contact time is calculated as 13 mins. These optimum values obtained are summarized in Table 3.

Table 3. Optimum calculated input values according to the first order numerical differentiation and related adsorption capacities

<table>
<thead>
<tr>
<th>Various parameters</th>
<th>Optimum values</th>
<th>Adsorption capacities (Rem%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pH</td>
<td>6.76</td>
<td>98.20</td>
</tr>
<tr>
<td>Adsorbent dosage (g/L)</td>
<td>1.14</td>
<td>98.80</td>
</tr>
<tr>
<td>Contact time (min)</td>
<td>13</td>
<td>99.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>98.66 (Average)</td>
</tr>
</tbody>
</table>
This study is based on the traditional one factor at a time experiments, which are relatively cost effective rather than full or fractional factor experimental designs. In order to optimize the adsorption process, CSCF and ND techniques are applied to investigate the individual effects of the initial pH, adsorbent dosage and contact time. If interaction effects among variables, which are scarcely considered in many adsorption studies, are needed to be studied, a statistical experimental design can be applied. For this purpose, full factor experimental design and fractional experimental design based on Box-Behken approach are applied to evaluate the proposed CSCF and ND techniques.

Experimental design methods give a mathematical model that demonstrates the influence of each variable and their interactions on the process efficiency [15, 23].

In order to evaluate the influence and interactions of the initial pH, adsorbent dosage and contact time on the removal of Zn(II), a $3^3$ full factorial design is used. The conditions of the 27 experiments are required by this design. In order to increase the reliability the experiments are repeated twice and the average values of $R_{em\%}$ is used. The levels (-1, 0, 1) are chosen for each of the three parameters. Table 4 shows the selected levels of the three parameters.

<table>
<thead>
<tr>
<th>Parameters/Levels</th>
<th>-1</th>
<th>0</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pH</td>
<td>3</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>Adsorbent dosage</td>
<td>0.4</td>
<td>0.8</td>
<td>1.4</td>
</tr>
<tr>
<td>Contact time</td>
<td>10</td>
<td>20</td>
<td>40</td>
</tr>
</tbody>
</table>

The levels are selected so that the optimum calculated values by CSCF and ND techniques are within these ranges. Using Matlab™ Statistics Toolbox, a regression analysis is performed to determine the coefficients of a first and second degree polynomial of the form:

$$ R_{em\%} = \beta_o + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j $$

where: $R_{em\%}$ is the removal capacity in percent so called as response variable, $\beta_o$ is the intercept, $\beta_i$ are coefficients and $x_i$ are processing variables – contact time, dosage and initial pH, respectively. In Eq. (7), the first summation represents linear terms, while the second one represents interaction effects. For regression analysis, four types of models are tested. Among them, linear model includes constant and linear terms, interaction model includes constant, linear, and interaction terms, quadratic model includes constant, linear, interaction, and squared terms, and finally pure quadratic model includes constant, linear, and squared terms. The following equations show the related coefficients of the models.

$$ R_{em\_linear\%} = 92.19 - 0.0317x_1 + 2.44x_2 + 5.28x_3 $$

$$ R_{em\_interaction\%} = 92.19 - 0.0317x_1 + 2.44x_2 + 5.28x_3 + 0.0275x_1x_2 + 0.0275x_1x_3 - 0.0275x_2x_3 $$
Fig. 10 and Fig. 11 show the main and interaction effects, respectively. As seen from Fig. 10 and Fig. 11, interactions and contact time do not have substantial effects on removal capacity ($R_{em}$%), while initial pH and adsorbent dosage have noteworthy effect on E%.

\[
R_{em - quadratic} \% = 95.42 - 0.0317x_1 + 2.44x_2 + 5.28x_3 + 0.0275x_1x_2 + 0.0275x_1x_3 - 0.0275x_2x_3 - 0.035x_1^2 - 1.51x_2^2 - 3.28x_3^2
\]

\[
R_{em - pure - quadratic} \% = 95.42 - 0.0317x_1 + 2.44x_2 + 5.28x_3^2 - 0.035x_1^2 - 1.51x_2^2 - 3.28x_3^2
\]
Besides, equations from (8)–(11) prove this statement. According to the linear regression form of Eq. (8), the removal capacity is predicted between 84.47% and 99.91%, while the calculated removal capacity is 98.66% by the proposed method. Regarding to Fig. 10, it can be concluded that contact time has less effect on removal capacity and the first level (10 mins) can be selected for an optimum value. The third levels of adsorbent dosage and initial pH have the maximum effects on removal capacity, which are already defined as 1, 4 and 8, respectively. These predicted levels of the main factors are quite close to calculated values by the proposed algorithm.

Table 4 shows the results of the 3-way ANOVA test of main and interaction effects. Table 5 also proves that the adsorbent dosage and initial pH have significant effect on removal capacity of Zn(II), while interaction effects have no significant contribution on removal capacity, $R_{\text{em}}\%$. In Table 5, $x_1$ represents contact time, $x_2$ represents adsorbent dosage, and $x_3$ represents initial pH.

### Table 5. 3-way ANOVA test for main and interaction effects

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum Sq.</th>
<th>d.f.</th>
<th>Mean Sq.</th>
<th>F</th>
<th>Prob &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_1$</td>
<td>0.025</td>
<td>2</td>
<td>0.013</td>
<td>3.14</td>
<td>0.0985</td>
</tr>
<tr>
<td>$x_2$</td>
<td>121.632</td>
<td>2</td>
<td>60.816</td>
<td>15036.94</td>
<td>0</td>
</tr>
<tr>
<td>$x_3$</td>
<td>566.875</td>
<td>2</td>
<td>283.438</td>
<td>70080.75</td>
<td>0</td>
</tr>
<tr>
<td>$x_1 \times x_2$</td>
<td>0.017</td>
<td>4</td>
<td>0.004</td>
<td>1.05</td>
<td>0.4415</td>
</tr>
<tr>
<td>$x_1 \times x_3$</td>
<td>0.016</td>
<td>4</td>
<td>0.004</td>
<td>1</td>
<td>0.4621</td>
</tr>
<tr>
<td>$x_2 \times x_3$</td>
<td>0.017</td>
<td>4</td>
<td>0.004</td>
<td>1.05</td>
<td>0.4415</td>
</tr>
<tr>
<td>Error</td>
<td>0.032</td>
<td>8</td>
<td>0.004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>688.615</td>
<td>26</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### CONCLUSION

In this work, the removal of Zn(II) ions from aqueous solution is carried out using bentonite. The highest sorption capacity and optimal values of initial pH, adsorbent dosage, and contact time are calculated effectively by using numerical differentiation method. The proposed calculation techniques in this study have been found to be relatively fast and cost-effective. Furthermore, these techniques can easily be implemented for many kinds of biosorption studies. According to the evaluation techniques, such as experimental design and 3 way ANOVA test results, the suggested calculation techniques present an efficient way of determining sorption capacity.

### REFERENCES


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