Biosorption of Lead with *Turbinaria Conoides* and Neuro Fuzzy Modelling

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ABSTRACT

Many hazardous heavy metals are released into the environment by industrial technological activities into the food chain which become a serious threat to the environment. Lead is a common industrial metal that finds uses in storage batteries, gasoline additives and ammunition etc. and causes severe health effects even at relatively low levels in the body, including irreversible brain damage and injury to blood forming systems. In this paper, rigid biosorbents for the removal of lead has been identified and modeling of the sorption and desorption process is done with intelligent neuro-fuzzy system.

Keywords: Biosorption, Lead, *Turbinaria Conoides*, Neuro Fuzzy modeling

1. Introduction

The main goal today is to adopt appropriate methods and to develop suitable techniques either to prevent the metal pollution or to reduce it to acceptable levels. There are three principle advantages of biological technologies for heavy metal removal. First, biologically based processes can be carried out *in situ* at the metal contaminated site (Cheng et al 1998, Yu et al 2001). Second, bioprocess technologies are usually environmental benign. Third, the process is cost effective. The principal operating costs associated with bioprocesses are the generation of the biomass for treatment and the final segregation of the captured heavy metals from the biomass matrix. There are four major classes of bioprocess technologies for heavy metal ion removal: bioprecipitation, bioaccumulation, phytoremediation and biosorption.

The advantages of biosorption over other metal remediation methods include the following:

1. Biosorption of toxic heavy metals is well suited as a “polishing” water-treatment step because it is possible to reach drinking water quality of the treated water.

2. Metal biosorption process is cost effective. Biosorbent can either be a waste product from industry (e.g., fermentation by-product, crab shell, egg shell) or naturally abundant biomass (e.g., algae). Recent studies have shown that for certain types of seaweed biomass virtually no pretreatment may be necessary. For example, untreated *Sargassum* biomass was successfully applied in packed bed column for copper removal (Volesky et al 2003). This means that the sole costs of the seaweed–based biosorbent may be only those of collection and transport (Volesky and Schiewer 1999).
3. Biosorption can be operated under broad range of conditions (pH, temperature). Since the biosorbent used in the process is inert, the influences of environmental factors are usually less pronounced than that of living organisms.

4. Regeneration of the biosorbent is possible. This means that the biosorbent can be reused for a number of cycles, thereby decreasing process costs.

5. Possible metal recovery.

2. Literature Survey

Biosorption is a process that utilizes inactive biological materials to sequester toxic heavy metals and is particularly useful for the removal of contaminants from industrial effluents (Volesky and Holan 1995; Kratochvil and Volesky 1998). Biological materials that have been investigated for heavy metals uptake include bacteria (Brierley 1990), fungi (Tsezos and Volesky 1981), yeast (Volesky et al 1993), microalgae (Darnall et al 1986), macroalgae (Kuyucak and Volesky 1989a) and crab shell (Lee et al 1997).

Table 1: Biosorption of heavy metal ion Lead by various Bacterial species

<table>
<thead>
<tr>
<th>Organism</th>
<th>Uptake (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arthrobacter sp.</td>
<td>130</td>
<td>Veglio et al 1997</td>
</tr>
<tr>
<td>Streptomyces noursei</td>
<td>36.5</td>
<td>Mattuschka et al 1993</td>
</tr>
</tbody>
</table>

Table 2: Biosorption of heavy metal ion Lead by various fungal species

<table>
<thead>
<tr>
<th>Organism</th>
<th>Uptake (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absidia orchidis</td>
<td>351</td>
<td>Holan and Volesky 1995</td>
</tr>
<tr>
<td>Penicillium chrysogenum</td>
<td>116.0</td>
<td>Niu et al 1993</td>
</tr>
<tr>
<td>Rhizopus arrhizus</td>
<td>104.0</td>
<td>Tobin et al 1984</td>
</tr>
<tr>
<td>Rhizopus nigricans</td>
<td>166.0</td>
<td>Holan and Volesky 1995</td>
</tr>
</tbody>
</table>

Table 3: Biosorption of heavy metal ion Lead by various algal species

<table>
<thead>
<tr>
<th>Organism</th>
<th>Uptake (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascophyllum nodosum</td>
<td>270-360</td>
<td>Holan and Volesky 1994</td>
</tr>
<tr>
<td>Cladophora glomerata</td>
<td>75</td>
<td>Jalali et al 2002</td>
</tr>
<tr>
<td>Fucus vesiculosus</td>
<td>270-360</td>
<td>Holan and Volesky 1994</td>
</tr>
<tr>
<td>Gracilaria canaliculata</td>
<td>36</td>
<td>Jalali et al 2002</td>
</tr>
<tr>
<td>Gracilaria corticata</td>
<td>50</td>
<td>Jalali et al 2002</td>
</tr>
<tr>
<td>Padina pavonia</td>
<td>210</td>
<td>Jalali et al 2002</td>
</tr>
<tr>
<td>Polysiphonia violacea</td>
<td>100</td>
<td>Jalali et al 2002</td>
</tr>
<tr>
<td>Sargassum hystrix</td>
<td>265</td>
<td>Jalali et al 2002</td>
</tr>
<tr>
<td>Sargassum natans</td>
<td>220-270</td>
<td>Holan and Volesky 1994</td>
</tr>
<tr>
<td>Sargassum natans</td>
<td>224</td>
<td>Jalali et al 2002</td>
</tr>
<tr>
<td>Ulva lactuca</td>
<td>125</td>
<td>Jalali et al 2002</td>
</tr>
</tbody>
</table>

All these biomaterials have shown adequate heavy metal sorption capacity to be considered for process applications. The unique capabilities of certain types of biomass to concentrate and immobilize particularly heavy metals can be more or less selective. That depends, to a
certain degree on (Volesky 2001) (i) type of biomass, (ii) mixture in the solution, (iii) biomass preparation and (iv) environmental conditions.

Biosorption, like conventional sorption processes, involves inherently very fast sorption reaction mechanisms (Tsezos and Volesky 1981). In order to investigate the mechanism of sorption and the potential rate controlling steps such as mass transport and chemical reaction processes, kinetic models have been used by several investigators to examine the experimental data. These kinetic models included the Pseudo-first order and second order models (McKay et al 1999). A detailed literature on biosorption of heavy metal ion lead by various bacterial, fungal and algal species are provided in Table 1, 2 and 3 respectively.

3. Materials and methods

Continuous flow sorption experiments were conducted in a glass column. The column was designed with an internal diameter of 2 cm and 35 cm in length. Since the ratio of column diameter to particle diameter is high, the effects of channeling have a negligible effect. At the top of the column, an adjustable plunger was attached with a 0.5 mm stainless sieve. At the bottom of the column, a 0.5 mm stainless sieve was attached followed by glass wool. A 2 cm high layer of glass beads (1.5 mm in diameter) was placed at the column base in order to provide a uniform inlet flow of the solution into the column. Figure 1 shows the experimental set-up of column used in this research.

3.1 Sorption

A known quantity of biosorbent was placed in the column to get the desired bed height. Metal ion solution of known concentration and pH was pumped upward through the column at a
desired flow rate by a peristaltic pump (pp40, Miclins). Samples were collected from the exit of the column at different time intervals and analyzed for metal concentration using atomic absorption spectrophotometer.

3.2 Desorption

After the column reached exhaustion, the loaded biosorbent with metal ions was regenerated using a selected elutant. After elution, the distilled water was used to wash the bed until the pH in the wash effluent stabilized around 7.0. Then, the column was fed again with the metal solution and the sorption studies were carried out. After bed exhaustion, the elutant was fed into the column and the regeneration studies were conducted. These cycles of sorption followed by desorption were repeated several times to evaluate the biosorbent resorption capacity.

4. Modelling of Sorption and Desorption of Lead using Urbinaria Conoides

The experimental data will be more useful for scaled up industrial equipment if a suitable model is available. An adaptive neuro-fuzzy model for sorption and desorption of lead using seaweed algae Turbina conoides has been evolved with the obtained experimental input and output data.

A Fuzzy Inference System is a popular computing framework based on the concepts of fuzzy set theory, fuzzy if-then rules and fuzzy reasoning. It can be considered to be a parameterized nonlinear map (Jang 1993), called f based on the unified view of soft computing and expression of f is

\[ f(x) = \sum_{i=1}^{m} w_i b_i(x) \]

if Sugeno reasoning (Takagi and Sugeno 1985) is applied. The membership function \( \mu_{A_l}^{i_j}(x_i) \) corresponds to the input \( x_i \ldots x_n \) of the rule \( l \). The and connective in the premise is carried out by a product and defuzzification by the center-of-gravity method. This can be further written as

\[ f(x) = \sum_{i=1}^{m} w_i b_i(x) \]

where \( w_i = y^j \) and

\[ b_i(x) = \frac{\prod_{i=1}^{n} \mu_{A_l}^{i_j}(x_i)}{\sum_{i=1}^{m} \prod_{i=1}^{n} \mu_{A_l}^{i_j}(x_i)} \]

If F is a continuous, nonlinear map on a compact set, then there exists a fuzzy system f which can approximate F to any desired accuracy, i.e. \( F = \mathcal{F}_{FS} \).

To present the ANFIS architecture (Jang 1993), consider two-fuzzy rules based on a first-order Sugeno model.
**Rule 1:** if \((x \text{ is } A_1)\) and \((y \text{ is } B_1)\), then \((f_1 = p_1x + q_1y + r_1)\)

**Rule 2:** if \((x \text{ is } A_2)\) and \((y \text{ is } B_2)\), then \((f_2 = p_2x + q_2y + r_2)\)

The possible ANFIS architecture (Jang 1993) to implement the two rules has five layered architecture and is shown in Figure 2. \(x\) and \(y\) are the inputs and \(f\) is the required output. Note that a circle indicates a fixed node whereas a square indicates an adaptive node (the parameters are changed during training). In the following presentation \(O_{L,i}\) denotes the output of node \(i\) in a layer \(L\).

![ANFIS Architecture](image)

**Figure 2:** ANFIS Architecture

Layer 1: All the nodes in this layer are adaptive nodes and is the degree of the membership of the input to the fuzzy membership function (MF) represented by the node,

\[
O_{1,i} = \mu_{A_i}(x), \quad \text{for } i = 1,2, \text{ or}
\]

\[
O_{1,i} = \mu_{B_{i-2}}(y), \quad \text{for } i = 3,4,
\]

\(A_i\) and \(B_i\) can be any appropriate fuzzy sets in parameter form. For example, if bell MF is used then,

\[
\mu_{A_i}(x) = \frac{1}{1 + \left[\left(\frac{x - c_i}{a_i}\right)^2\right]^{b_i}} \quad i = 1,2
\]

where \(a_i, b_i\) and \(c_i\) are the parameters for the MF.

Layer 2: The nodes in this layer are fixed (not adaptive) and labeled \(\Pi\) to indicate that they...
play the role of a simple multiplier. The outputs of these nodes are given by
\[ O_{2,i} = w_i = \mu_{A_i}(x) \mu_{B_i}(y), \quad i = 1, 2 \] (7)

The output of each node is this layer represents the firing strength of the rule

Layer 3: Nodes in this layer are also fixed nodes. These are labeled N to indicate that these perform a normalization of the firing strength from previous layer. The output of each node in this layer is given by
\[ O_{3,i} = \bar{w}_i = \frac{w_i}{w_1 + w_2}, \quad i = 1, 2. \] (8)

Layer 4: All the nodes in this layer are adaptive nodes. The output of each node is simply the product of the normalized firing strength and a first-order polynomial.
\[ O_{4,i} = \bar{w}_i f_i = \bar{w}_i (p_i x + q_i y + r_i) \quad i = 1, 2 \] (9)

where \( p_i, q_i, \) and \( r_i \) are design parameters (consequent parameter since they deal with the then-part of the fuzzy rule)

Layer 5: This layer has only one node labeled \( \Sigma \) to indicate that it performs the function of a simple summer. The output of this single node is given by,
\[ O_{5,i} = \sum_i \bar{w}_i f_i = \sum_i \bar{w}_i f_i \quad i = 1, 2. \] (10)

The ANFIS architecture is not unique. Some layers can be combined and still produce the same output. In this ANFIS architecture, there are two adaptive layers (1 and 4). Layer 1 has three modifiable parameters (\( a_i, b_i, \) and \( c_i \)) pertaining to the input MFs. These parameters are called premise parameters. Layer 4 has also three modifiable parameters (\( p_i, q_i, \) and \( r_i \)) pertaining to the first-order polynomial. These parameters are called consequent parameters

The task of training algorithm for this architecture is to tune all the modifiable parameters to make the ANFIS output match the training data. Note here that \( a_i, b_i, \) and \( c_i \) describe the sigma, slope and the center of the bell MFs, respectively. If these parameters are fixed, the output of the network becomes
\[ f = \frac{w_1}{w_1 + w_2} f_1 + \frac{w_2}{w_1 + w_2} f_2 = \bar{w}_1 f_1 + \bar{w}_2 f_2 \] (11)
\[ f = \overline{w}_1 (p_1 x + q_1 y + r_1) + \overline{w}_2 (p_2 x + q_2 y + r_2) \] (12)
\[ f = \overline{w}_1 x p_1 + (\overline{w}_1 y q_1 + (\overline{w}_1 r_1) + (\overline{w}_2 x) p_2 + (\overline{w}_2 y) q_2 + (\overline{w}_2) r_2 \] (13)

This is a linear combination of the modifiable parameters. For this observation, the parameter set can be divided into two sets such as
\[ S = S_1 \oplus S_2 \] (14)

\( S \) = Set of total parameters
\( S_1 \) = Set of premise (non linear) parameters
\( S_2 \) = Set of consequent (linear) parameters.
\( \oplus \) = direct sum
For the forward path, least square method is applied to identify the consequent parameters. For a given set of values of $S_1$, training data can be plugged to obtain a matrix equation

$$A \Theta = y$$

where $\Theta$ contains the unknown parameters in $S_2$. This is a linear square problem, and the solution for $\Theta$, which minimizes $\|A \Theta - y\|^2$, is the least square estimator.

$$\Theta^2 = (A^T A)^{-1} A^T y,$$

For the backward path, the error signals propagate backward. The premise parameters are updated by the method (Jang 1993), through minimizing the overall quadratic cost function

$$J \Theta = \frac{1}{2} \sum_{k=1}^{N} [y(k) - \hat{y}(k, \Theta)]^2$$

in a recursive manner with respect to $\Theta_{(s2)}$. The update of the parameters in the $i^{th}$ node in layer L can be written as

$$\hat{\Theta}_i^L (k) = \hat{\Theta}_i^L (k-1) + \eta \frac{\partial^+ E(k)}{\partial \hat{\Theta}_i^L (k)}$$

where $\eta$ is the learning rate, and the gradient vector

$$\frac{\partial^+ E}{\partial \hat{\Theta}_i^L} = \varepsilon L_{i,i} \frac{\partial \hat{z}_{L,i}}{\partial \hat{\Theta}_i^L}$$

$\partial \hat{z}_{L,i}$ being the node’s output and $\varepsilon_{L,i}$ is the back propagated error signal.

When the number of rules is not restricted, a zero-order Sugeno model has unlimited approximation power for matching any nonlinear function arbitrarily well on a compact set.

5. Results and Discussions

Figure 3: Visualization of training dataset
Based on our experiments, the lead uptake of seaweeds decreased in the following sequence:

Turbinaria conoides > Turbinaria ornata > Ulva lactuca > Sargassum polycystium > Ulva reticulata > Gracilaria edulis. The whole process has been modeled with ANFIS.

The training dataset contains concentration, pH and time (hr) as input parameters and the amount of metallic ions removed as output parameter. Figure 3 shows the training dataset for continuous sorption lead Turbinaria conoides. Figure 4 shows the training curve and Figure 5 shows the output vs desired plot. The mean square error was found to be only 0.0001038. The model ANFIS structure evolved is shown in Figure 6. Figure 7 shows the training dataset for desorption of lead Turbinaria conoides. Figure 8 shows the testing of desorption of lead Turbinaria conoides on the training data and the average testing error was found to be 0.0875 only.

![Learning Curve](image1)

**Figure 4:** Learning Curve of network error convergence of ANFIS.

![Output vs. Desired Plot](image2)

**Figure 5:** Output vs desired plot for lead sorption
Biosorption of Lead with Turbinaria Conoides and Neuro Fuzzy Modelling

Figure 6: ANFIS model structure

Figure 7: Training dataset for desorption of lead Turbinaria conoides

Figure 8: Testing of desorption of lead Turbinaria conoides on the training data
6. Conclusion

This research suggests that biosorption is a viable process for the removal of lead from aqueous solutions. Due to the low M/G ratio, *T. conoides* performed very well in lead biosorption. Seaweeds are plentiful, fast growing and exist in many parts of world oceans and the biosorbent used in this research are inexpensive, effective and readily available. The whole process of sorption and desorption of lead has been modeled successfully with ANFIS to facilitate a successful reproduction of the biosorption process on a commercial level.

7. References


