Binary Mixture of Copper-Cobalt Ions Uptake by Zeolite using Neural Network

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Abstract—In this study a neural network (NN) was proposed to predict the sorption of binary mixture of copper-cobalt ions into clinoptilolite as ion-exchanger. The configuration of the backpropagation neural network giving the smallest mean square error was three-layer NN with tangent sigmoid transfer function at hidden layer with 10 neurons, linear transfer function at output layer and Levenberg-Marquardt backpropagation training algorithm. Experiments have been carried out in the batch reactor to obtain equilibrium data of the individual sorption and the mixture of copper-cobalt ions. The obtained modeling results have shown that the used neural network has better adjusted the equilibrium data of the binary system when compared with the conventional sorption isotherm models.

Keywords—Adsorption isotherm, binary system, neural network; sorption

I. INTRODUCTION

HEAVY metals are well known for toxicity and their disposal is a significant industrial waste problem. Their amount in the environment not only increases every year, but also they are not biodegradable and tend to accumulate in living organisms [1]. Treatment processes for the removal of heavy metals ions from wastewater include coagulation, carbon adsorption, ion exchange, precipitation, reverse osmosis, etc. [2]. The sorption processes are probably the most attractive among these methods, since their application is simple, and they require relatively mild operating conditions, although the cost of substrate materials and regeneration is the limiting factor [3]. For this reason it is important to look for low-cost sorbents that could replace synthetic ion exchange resins [4, 5].

Natural zeolites are the most important inorganic cation exchangers that exhibit high ion exchange capacity, selectivity and compatibility with the natural environment [6]. They are naturally occurring alumina-silicate based minerals. Clinoptilolite is the most abundant natural zeolite that occurs in relatively large minable sedimentary deposits in sufficiently high purity in many parts of the world [7, 8]. For the effective utilization of a natural zeolite as an ion exchanger it is essential to have chemical models that help to describe accurately heavy metals exchange equilibria [1]. Originally, by analogy with the sorption process, empirical equations such as Freundlich or Langmuir were adjusted to experimental data. These approaches were successfully applied by Polzer et al. [9] to interpret transport of radionuclides in volcanic tuff media and by Zheng et al. [10] to explain transport of cesium ion in a hydrous sodium crystalline silicocitrate, labelled TAM-5. The present models proposed in the literature describe the process either as phase equilibrium, where deviation from the ideal adsorption behavior is explained in terms of energetic heterogeneity [11, 12], or in terms of the law of mass action. In the latter case, non-ideal behavior of the liquid and solid phase results from the interaction among counterions [13]. The thermodynamic model for ion exchange based on the Pitzer or Bromley equations used for calculation of the activity coefficients in liquid phase and the Wilson equation for the same in zeolite phase are excellent in prediction ion exchange equilibrium between aqueous solutions and clinoptilolite. However, sufficiently good results for binary systems are obtained assuming ideal behavior of the zeolite phase. The resulting average is lower than 8%. It should be emphasized that estimation of activity coefficients in the liquid phase is connected with the introduction into the equilibrium model two additional equations with two unknown Wilson’s parameters, which significantly complicates the mathematical calculations. On the other hand, the calculated binary interaction parameters are very useful for estimation of equilibrium constants for multicomponent solutions. The target metal pollutants in this study were Cu (II) and Co (II) which is frequently found in industrial effluents. The modeling of binary adsorption equilibrium is still a challenging task. Several isotherms have been proposed to describe the equilibrium of such system but it was found that the mathematical description of sorption isotherms of the analyzed ions in the presence of one or two additional ions the solution is complicated from the theoretical point of view [14]. In this case the application of Neural Networks was proposed.
II. EXPERIMENTAL

A. Preparation of the adsorbent and synthetic solution

The clinoptilolite used in this study was sourced from the Vulture Creek, KwaZulu-Natal Province of South Africa [14]. The clinoptilolite was crushed and milled into powder with average particle sizes of approximately 75μm. The powder was then examined using an X-ray powder diffractometer (XRD) Phillips X’pert Model 0993 to determine its composition. Its elemental composition was determined using X-ray fluorescence spectroscopy (XRF, Phillips Magix Pro) while the surface area was analyzed using BET (Tristar 3000) [14]. The measurements were done under a nitrogen atmosphere. Prior to porosity and surface area analysis, 2g of sample was first degassed and nitrogen gas was flushed through for 4h at the solutions of Cu and Co were prepared by dissolving CuSO₄·5H₂O and CoSO₄·7H₂O respectively in deionizer water at pH 6.5. The synthetic wastewaters were prepared at five different Cu²⁺ and Co²⁺ ion concentrations, at 0.361, 1.099, 1.969 and 2.748 g/l. The solutions were assayed using atomic adsorption spectroscopy (AAS), (Model Varian Spectra (20/20)) [14].

B. Batch adsorption studies

The Cu and Co ion-exchange processes on the clinoptilolite were conducted at room temperature. Glass columns of 2cm diameter and 30cm of length were pre-loaded with 25g of either natural clinoptilolite (as received) or HCl-activated clinoptilolite [14]. Aliquots of 25 ml of the prepared Cu-bearing solutions of desired concentrations were passed through each of the two types of zeolites. These were afforded the same solution-zeolite contact time. After passing through the zeolite-packed column the resultant solutions were assayed using AAS in order to ascertain the zeolite’s removal efficiency [14]. The flame type used was air-acetylene and the adsorption wavelengths for the metal were cu (324.7nm). Standards of 1000 mg/l, 2000mg/l and 300mg/l were then adsorption wavelengths for the metal were cu (324.7nm). Standards of 1000 mg/l, 2000mg/l and 300mg/l were then adsorbed onto clinoptilolite. As the sites are gradually filled up, adsorption proceeds slower and the kinetics becomes more dependent on the rate at which the adsorptive is transported from the bulk phase to the actual micropores of the clinoptilolite structure with ease.

A. Effect of pH

The metal ions removal was increased gradually with the increase in solution pH, as expected. The variation in the removal of metal ion with respect to pH can be explained by considering the surface charge of the adsorbent material. The difference of the adsorption capacity of clinoptilolite for heavy metal ions may be due to a number of factors which include hydration diameter and solubility of cations. The hydrated radii of Cu (II) and Co (II) are 0.419 and 0.423 nm, respectively [15]. The Cu (II) particles should ideally be adsorbed in larger quantities compared to the Co (II) particles, since the smaller particles can pass through the micropores of the clinoptilolite structure with ease.

B. Effect of contact time and temperature

The effect of contact time on the adsorption of Cu (II) and Co (II) ions onto clinoptilolite was studied at various temperatures, i.e., 25, 35, 45 and 60. It was observed that the initial uptake rate for two metals was very high, as a large number of adsorption sites are available for adsorption at the onset of the process. It was established that at 25°C within the first hour of contact, almost 70% and 80% of Cu (II) and Co (II) ions, respectively, were adsorbed onto clinoptilolite. As the sites are gradually filled up, adsorption proceeds slower and the kinetics becomes more dependent on the rate at which the adsorptive is transported from the bulk phase to the actual adsorption sites. In the case of Cu-Clino system, 2h was found to be sufficient to attain equilibrium at room temperature, whereas in the case of Cu-Clino system equilibrium was established within almost 1h. It was also found that the amount of adsorption decreases with increasing temperature in both systems.

Adsorption of metal ion on Clino adsorbent shows similar behaviour with respect to increase in temperature. The equilibrium adsorption capacity of Cu (II) and Co (II) ions onto Clino was favoured at lower temperatures. The decrease in the uptake of heavy metal ions with increase in temperature may be attributed to the increase in the average kinetic energy of the metal ions. The attractive forces between metal ions and Clino surface sites will become insufficient to retain the metal ion at the binding site of Clino. Therefore, increase in temperature may be associated with decrease in the stability of metal ion-adsorbent interaction.

C. Effects of initial metal ion concentration

The amount of metal ions adsorbed per unit mass (qₐ) of Clino increases gradually with an increase in metal concentration, whereas the extent of radiation (%) decreases with increasing metal ion loading. At low concentration of the metal ions, a unit mass of the Clino is exposed to small number of metal ions and consequently the adsorption is independent of the initial metal ion concentration. The extent of adsorption comes down for a fixed adsorbent content at high metal ions concentration due to decreased number of available adsorption sites on Clino surface. Similar observations have been reported earlier on montmorillonite [17], Sawdust [18] and boron waste [19].

D. Single Component Isotherms

The mathematical expression that represents the Langmuir isotherm can be written as follows:

\[
\% \text{Uptake} = \left( \frac{C_o - C_f}{C_o} \right) \times 100
\]
The Langmuir isotherm constant is given by:

\[ q^*_i = \frac{q_m b_i C^*_i}{1 + b_i C^*_i} \]  (2)

Where \( q_m \) and \( b_i \) are Langmuir isotherm constants. These constants have a physical meaning and \( b_i \) parameter represents the ratio between sorption and desorption rates. Therefore, the high \( b_i \) values indicate high affinity of the ion for the site of adsorbent material, while the \( q_m \) parameter represents the total number of available sites of the sorbent. When \( b_i C^*_i > 1 \), the isotherm is favourable, if \( b_i C^*_i = 1 \) the isotherm is quasi linear [20].

The Freundlich isotherm is given by:

\[ q^*_i = a_i (C^*_i)^n \]  (3)

Where \( a_i \) and \( n \) are Freundlich isotherm constants.

The Freundlich isotherm does not predict the sorbent saturation. Thus, the model allows the existence of an infinite superficial covering. The Freundlich isotherm is frequently used to model the limited segments of experimental data [21].

The maximum adsorption capacity and affinity obtained for individual adsorption of Cu and Co ions by clinoptilolite has presented the following order Cu > Co. Ma and Tobin [22] have justified this order of preference/affinity as a function of ionic radius, reducing it sorption in comparison with other ions.

**E. Binary Component Isotherms**

The multi-component Langmuir model was the most frequently used to fit the binary sorption data. The mathematical expression that represents the model of the Langmuir isotherm for a binary mixture can be written as follows:

\[ q^*_i = \frac{q_m b_i C^*_i}{1 + b_i C^*_i + b_2 C^*_2} \]  (4)

Where \( q_m, b_1 \) and \( b_2 \) are the binary Langmuir isotherm constants.

Chong and Volesky [23] and Sanchez et al. [24] have applied a model originally developed by Bailey and Ollis [25] to represent the binary data of biosorption equilibrium.

The original model was developed to describe the non-competitive inhibition during enzymatic kinetic studies. This model is represented by (5):

\[ q^*_i = \frac{q_{m0} b_i C^*_i}{1 + b_i C^*_i + b_2 C^*_2 + 2kC^*_i C^*_2} \]  (5)

Where \( q_{m0}, b_1, b_2 \) and \( K \) are model constants.

Chong and Volesky [23] and Sanchez et al. [24] have used modified models of the Langmuir isotherm to represent the biosorption equilibrium data in binary mixtures. These models have been developed through the incorporation of the new parameters to the original model of the Langmuir isotherm in (2).

Incorporating the new constants \((k_1, k_2)\) in the exponential form to the denominator of the Langmuir isotherm concentration, the following expression was achieved:

\[ q^*_i = \frac{q_m b_i C^*_i}{[1 + b_i (C^*_i)^{k_1} + b_2 (C^*_2)^{k_2}]} \]  (6)

Adding the constants \((k_1, k_2)\) in the exponential form to the numerator and the denominator of the Langmuir isotherm concentration, the Langmuir-Freundlich isotherm [26] was obtained, which can be represented by the following mathematical expression:

\[ q^*_i = \frac{q_m b_i C^*_i^{k_1} + b_2 (C^*_2)^{k_2}}{[1 + b_i (C^*_i)^{k_1} + b_2 (C^*_2)^{k_2}]} \]  (7)

Sag and Kutsal [27] have used the empirical Freundlich model to describe the biosorption equilibrium in binary systems, whose mathematical representation can be written as follows:

\[ q^*_i = a_i (C^*_i)^{n_1} + a_2 (C^*_2)^{n_2} \]  (8)

Where \((a_1, n_1)\) and \((a_2, n_2)\) are the Freundlich isotherm constants obtained from the individual compounds equilibrium data. The other constants are determined using the equilibrium binary data.

In the original Langmuir isotherm model, the chemical species 1 and 2 compete for the occupation of the same site in adsorbent. Jain and Snowyink [28] have proposed an adsorption model for the binary mixtures based on the hypothesis that a part of adsorption occurs without competition, where \( q_{m1} \neq q_{m2} \). The model representation is given by the following equations:

\[ q^*_1 = |(q_m1 - q_m2) b_i C^*_1|/(1 + b_i C^*_1) + |(q_m1 - q_m2) b_i C^*_2|/(1 + b_i C^*_2) \]  (9)

The first term at the right-hand side of Eq. (10) is the expression of the Langmuir isotherm for the molecule number of chemical species 1 that adsorb without a competition and it is proportional to the numbers of sites \((q_{m1} - q_{m2})\). The second term represents the molecule number of chemical species 1 that adsorb on the sites \( q_{m1} \) with a competition based on the Langmuir adsorption model. The molecule number of species 2 that adsorb on the sites \( q_{m2} \) with the competition of species 1 can be calculated by (11).

**Nomenclature**

- \( a_i \): Freundlich mono-component isotherm constant
- \( b_i \): Langmuir isotherm constant (m-equiv./L)
- \( C^*_j \): concentration in the fluid phase (m-equiv./L)
- \( C^*_0 \): initial concentration in the fluid phase (m-equiv./L)
- \( k_1, k_2, k \): multi-component Langmuir-type constants
\( n \)  Freundlich mono-component isotherm constant

\( m \)  dry mass of zeolite (g)

\( q_{\text{in}} \)  Langmuir constant related to the capacity of adsorption (\( \text{mequiv./g} \))

\( q^*_j \)  concentration at equilibrium in the biosorbent (\( \text{mequiv. /L} \))

\( V \)  solution volume (L)

Subscripts: subscript \( j \) metal species.

\( \alpha_{12}, \alpha_{21}, \alpha_{11}, \alpha_{22} \)  Freundlich binary isotherm constant

\( F. \text{Modelling using the neural networks} \)

In this study, Neural Network Toolbox was used to develop the NN model. A three-layer NN with tangent sigmoid transfer function (\texttt{tansig}) at hidden layer and a linear transfer function (\texttt{purelin}) at output layer was used. The data gathered from batch experiments was divided into input matrix and target matrix. The optimum architecture of the NN model and its parameters variation were determined based on the minimum value of the mean squared error of the training and prediction set. The training was stopped after 167 iterations for the Levenberg-Marquardt algorithm (LMA) because the differences between training and validation error started to increase. Fig. 1 illustrates training, validation and test mean squared errors for the LMA.

![Fig. 1 Training, validation and test mean squared errors for the Levenberg-Marquardt algorithm.](image1)

The optimal architecture of the NN model showed in Fig. 2 was determined based on minimum value of mean squared error of training and prediction set. The determination of neurons weights was carried out minimizing the objective function. The data sets were used to feed the optimized network in order to test and validate the model. Fig. 2 shows a comparison between predicted and experimental values of the output. For a search of the objective function minimum a simplex method was used originally developed by Nelder and Mead [15, 29]. This is a direct search method where only information about the objective function current values is used. To simulate the equilibrium data using NN, a data set including information about the equilibrium concentrations of each ion in the fluid phase like entrance net variables and ions adsorbed concentrations as exit net variables were used.

![Fig. 2 The optimal architecture of NN](image2)

Different net structures with one hidden layer have been tested in a search of the best combination of connection weights to be achieved a smaller objective function values and average error. The absolute average deviation (AAD) and the objective function values for the architectures different types of the investigated net were used to represent the sorption equilibrium values of the Cu and Co binary system. The AAD was also proposed by Fagundes-Klen et al., [20] to simulate the equilibrium data of a binary stem Zn-Cd.

![Fig. 3 Comparison between predicted and experimental values of the output](image3)

![Fig. 4 Comparison of experimental and calculated data](image4)
Fig. 4 presents experimental versus calculated data for copper and cobalt. The modelling results of the equilibrium data of a binary system Cu-Co by using NN have better fitted experimental data compared to that one’s obtained by using the adsorption isotherms [20].

IV. CONCLUSIONS

In this study, the adsorption equilibrium experimental data of the single-component system and the binary mixture of copper and cobalt ions were found to fit well using several isotherm models. However, it did not accurately predict the adsorption in a binary mixture. The NN technique was used to fit the experimental data and it was shown that this technique is more efficient comparing with the one using the adsorption isotherms models.

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REFERENCES


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