

Modeling of Co-Cu elution from clinoptilolite using Neural Network

John Kabuba, Antoine Mulaba-Bafubiandi

Abstract—The elution process for the removal of Co and Cu from clinoptilolite as an ion-exchanger was investigated using three parameters: bed volume, pH and contact time. The present paper study has shown quantitatively that acid concentration has a significant effect on the elution process. The favorable eluant concentration was found to be 2 M HCl and 2 M H₂SO₄, respectively. The multi-component equilibrium relationship in the process can be very complex, and perhaps ill-defined. In such circumstances, it is preferable to use a non-parametric technique such as Neural Network to represent such an equilibrium relationship.

Keywords—Clinoptilolite, elution, modeling, neural network

I. INTRODUCTION

ION-exchange is gaining prominence as an efficient method for the removal of heavy metals from water and wastewater. The main advantage of this process is the possibility of replacing expensive synthetic ion-exchangers by low-cost sorbents such as natural zeolites [1].

Many researches has been undertaken to identify the ability of zeolites to remove certain pollutants as well as to understand the process mechanism [2, 3]. As ion-exchange process takes place in two stages: loading and elution. Most research on ion-exchange of Co and Cu has focused on the loading only, so that little quantitative information is available on the elution behavior. There is a need to study the behavior of Co and Cu metal during elution. In order to improve the performance of ion-exchange process, optimization and analysis of the process should be accomplished. Modeling is a tool to achieve the objectives. However, modeling of process covers a broad spectrum which lies on theoretical (or parametric) models based on fundamental knowledge of the process. Most of these models are obviously derived from physical descriptions and understanding of ion-exchange process under certain assumptions. These models are mathematically complex, computationally expensive and they ideally require a very detailed knowledge of the ion-exchange process. For this purpose, a non-parametric method of modeling such as a Neural Network will be used in this paper.

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II. MATERIALS AND METHODS

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. Clinoptilolite grains of sizes in the range of 1 mm to 2 mm were used for adsorption and elution studies. The clinoptilolite was treated in HCl at concentrations of 0.2 M at room temperature over a period of 8h [4]. The clinoptilolite was then washed in deionised water to remove the fine fractions and thereafter dried in the oven at 110°C for 24h [4].

The solution of Cu and Co was prepared by dissolving CuSO₄·5H₂O and CoSO₄·7H₂O respectively in deionised water at pH 6.5. These solutions were assayed using Atomic Absorption Spectroscopy (AAS), (model Varian Spectra (20/20)) [4].

B. Batch Cu and Co loading and elution

The Cu and Co ion-exchange process on the clinoptilolite was conducted at room temperature. Glass columns of 2cm diameter and 30 cm of length were pre-loaded with 5g of HCl-activated clinoptilolite. Aliquots of 25ml of the prepared Cu and Co bearing solution were passed through the clinoptilolite. There were afforded the same solution-zeolite contact time [4]. After passing through the zeolite-packed column the resultant solution was assayed using Atomic Absorption Spectroscopy (AAS) in order to ascertain the zeolite's removal efficiency. The flame type used was air-acetylene and the adsorption wavelengths for the two metals then prepared and a calibration curve was drawn using these standards. Dilution was applied stoichiometrically where the concentrations of the unknown solution of copper exceeded the standards concentration range of the standards [4].

All the elution experiments were carried out using glass columns. The elution solutions were prepared with hydrochloric acid, sulfuric acid and deionized water.

C. Definition of the Neural Network model

Neural networks (NN) are inspired by biological neural systems. In this approach weighted sum of inputs arriving at each neuron is passed through an activation function (generally non-linear) to generate an output signal [5]. An additional bias input is added to the weighted sum for increasing or lowering the net input to the activation function. Functions thus synthesized are largely determined by the network architecture and connections between the processing units.

Majority of NN architectures are feed-forward networks which are mostly trained from the input data using error back-propagation algorithm. Each input node represents an

independent variable while the output nodes give the dependent variables. Hidden layers are employed to perform non-linear transformations on the input space and are used for computation purpose. Hornik et al. [6] have shown that a three-layer NN with sigmoid transfer functions can map any function of practical interest and it has been confirmed by Bhatti et al. [7]. As we have chosen bed volume, pH, contact time as independent variables, and metal concentration as dependent variable; architecture with three neurons in the input layer, ten neurons in the hidden layer and one in the output layer was chosen. Each node in the input layer represents the value of one independent variable while the output nodes indicate the dependent variable.

II. RESULTS AND DISCUSSION

In order to investigate the elution behaviour of Co and Cu from the loaded clinoptilolite, elution experiments were conducted in which the acidity of the eluent was increased [8]. Elution of Co and Cu from the loaded clinoptilolite was carried out using sulphuric acid and hydrochloric acid.

A. The effect of H_2SO_4 and HCl on the elution of Co and Cu

The concentrations of H_2SO_4 and HCl in solution were varied from 0.2 M to 2 M. Fig. 1-4 illustrates the effect of acid concentration (H_2SO_4 , HCl) on the elution of metals (Co, Cu). Observing the plot one can see that HCl is best accomplished with concentration of 2 M which provided the sharpest elution curve. It was able to extract 40% of Cu and Co at 2 Bed volume. The other eluent were not so efficient, presenting a slower elution rate. As shown in Fig. 2 and 4, HCl was a very powerful metal-desorbing agent compare to H_2SO_4 in Fig. 1 and 3. The acid concentration higher than 2 M was not tested, as it was fear that the stability of the clinoptilolite might be affected [9]. Fig 2 shows that the Co is easily eluted when you compare to Cu in Fig. 4 due to his low charge density. Low charge density exhibits a high need for hydration. Therefore, their high affinity for the aqueous phase leads to a faster elution.

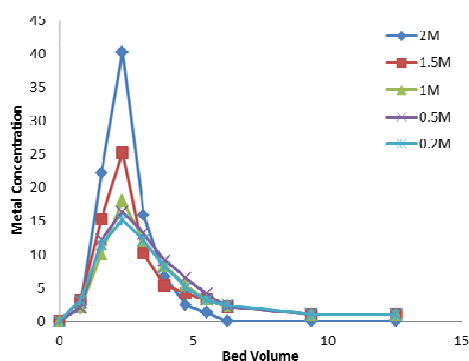


Fig. 1 Effect of H_2SO_4 concentration on the elution of Co

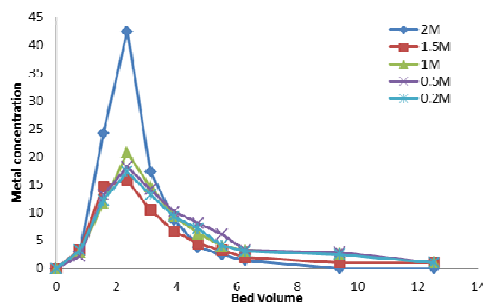


Fig. 2 Effect of HCl concentration on the elution of Co

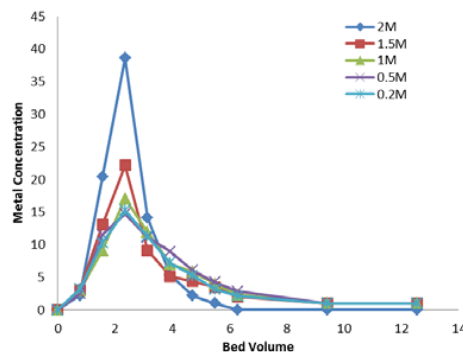


Fig. 3 Effect of H_2SO_4 concentration on the elution of Cu

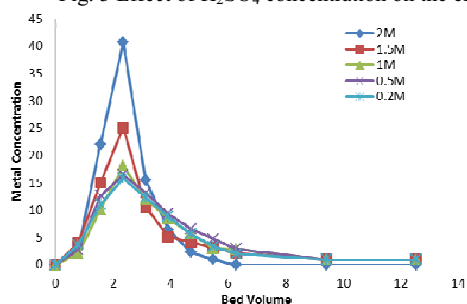


Fig. 4 Effect of HCl concentration on the elution of Cu

C. Neural Network model for elution

In a parametric method of equilibrium modeling such as the multi-component Freundlich isotherm, it is necessary to know the mathematical form of the expressions involved. Only in this way can the empirical parameters be estimated from batch equilibrium adsorption/desorption data, or from column data as described earlier [9, 10]. Inherent disadvantages of these parametric methods are that the selected mathematical forms of the equilibrium expressions are not necessarily valid. That all relevant variables are not necessarily included in the mathematical expressions, and that some related processes are ill-defined to such an extent that they defy explicit mathematical representation. For example, the pre-soaking step is still poorly understood [10], and the change in adsorptive of cobalt and copper due to the possible formation of a surface compound [11] cannot be modeled adequately by using explicit expressions.

Therefore, a non-parametric method such as a neural

network should be used instead to relate the equilibrium loading of a species to all the possible variables such as solution phase concentrations, temperature and the loading of the clinoptilolite. The main advantage is that no functional form needs to be specified a priori, and even semi-quantitative data such as the age of the clinoptilolite or the conditions of acid washing could be included as inputs. Especially in multi-component elution it becomes very difficult to estimate independently the dependence of the various metals on process conditions; when neural nets are used this step-wise estimation of parameters becomes unnecessary. Matlab computing environment was chosen to generate NN model using NN toolbox from the data. Hyperbolic tangent 'Tansig' (being a sigmoid transfer function) was chosen for the input to hidden layer mapping while a purely linear transfer function 'Purelin' was chosen for the hidden layer to the output layer mapping. A number of training runs were performed out to look out for the best possible weights in error back-propagation framework. The final selected network architecture was trained for 120 iterations. The trained network gave a mean squared error of 0.632 with regression coefficients of 0.99991 for training, 0.99993 for validation, 0.99998 for test and 0.99991 for all. The regression plots of the trained network are shown in Fig. 5. The results present in Fig. 6-9 illustrate that the NN model simulates satisfactorily the elution process of Co and Cu.

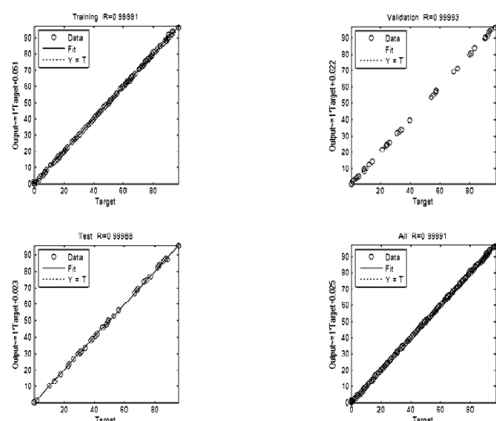


Fig. 5 Regression plot for the NN training

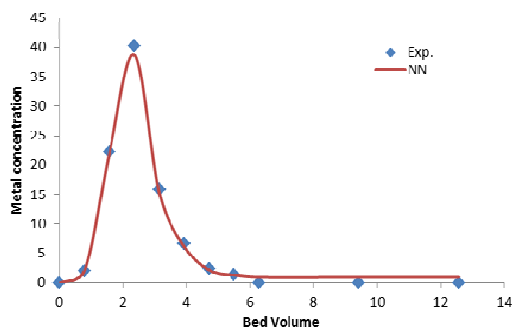
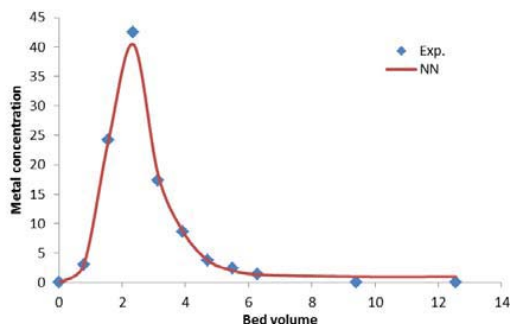
Fig. 6 Comparison of experimental data and NN model for Co using H_2SO_4 

Fig. 7 Comparison of experimental data and NN model for Co using HCl

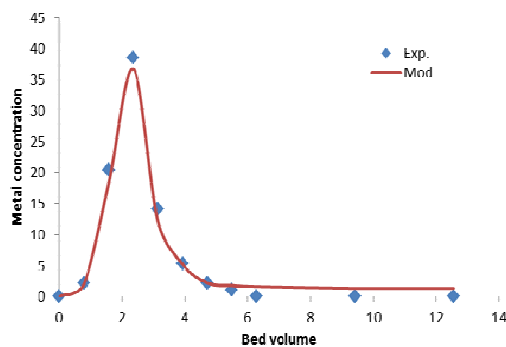
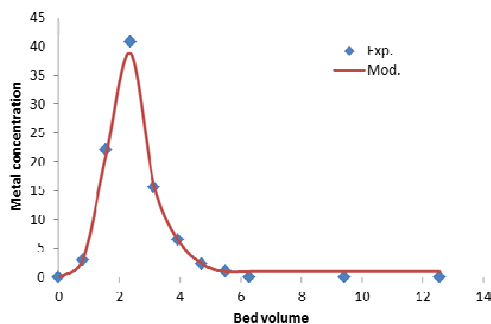
Fig. 8 Comparison of experimental data and NN model for Cu using H_2SO_4 

Fig. 9 Comparison of experimental data and NN model for Cu using HCl

III. CONCLUSIONS

The elution of Co and Cu from clinoptilolite with HCl and H_2SO_4 at the different concentration was investigated. It was found that the HCl at 2M has a high elution rate compare to the H_2SO_4 . An effort has been made to model the elution of Co and Cu process using NN approach. The NN model (3-10-1) developed from the limited experimental data scored fairly well on the validation experiments.

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