Bioresource Technology 151 (2014) 406–410

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Short Communication

The use of NARX neural network for modeling of adsorption of zinc ions using activated almond shell as a potential biosorbent

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HIGHLIGHTS

- The removal increased with the increasing adosorbant amount, pH and contact time.
- The percentage of removal decreased with increasing concentration.
- The values of optimum input parameters and efficiency are close to each other.
- Activated almound shell can be effectively used for the removal of zinc ions.

ARTICLE INFO

Article history:
Received 24 July 2013
Received in revised form 30 September 2013
Accepted 6 October 2013
Available online 12 October 2013

Keywords:
Zinc
Biosorption
Almond shell
Isotherm
NARX neural network

ABSTRACT

In this study, nonlinear autoregressive model processes with exogenous input (NARX) are applied for the prediction of percentage adsorption efficiency for the removal of zinc ions from wastewater by activated almond shell. The effect of operational parameters such as pH, dosage, particle size and initial metal ions concentration are studied to optimize the conditions for maximum removal of zinc ions. The model is first developed using a two layer NARX network. A comparison between the model results and experimental data showed that the NARX model is able to predict the removal of zinc ions from wastewater. The outcomes of suggested NARX modeling were then compared to batch experimental studies. The results show that activated almond shell is an efficient sorbent and NARX network, which is easy to implement and is able to model the batch experimental system.

1. Introduction

Heavy metals have become major surface water and groundwater contaminants. Electroplating, metal finishing, textile, storage batteries, mining, ceramic and glass industries discharge wastewater with high heavy metal content. The release of heavy metals such as Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Co^{2+} into the environment is a potential threat to water and soil quality as well as to plant, animal and human health (Cheung et al., 2000; El-Kamash et al., 2005; Aziz et al., 2008). One of the most important heavy metal is zinc. Various traditional methods, such as chemical precipitation, electrolyte reduction, solvent extraction, ion exchange, complexation/sequestration, cementation, electrochemical operation, coagulation–flocculation, biological treatment, and adsorption are used to remove these heavy metal ions, but their applications are largely limited by harsh reaction conditions, high cost and secondary pollution. Several novel methods for removing heavy metal ions have been developed and explored, such as biosorption (Babel and Kurniawan, 2003; Aziz et al., 2008; Ding et al., 2012). Biosorption is the natural capability of the biomass to immobilize dissolved components, e.g. heavy metal ions, on its surface. Biomass is composed mostly of polysaccharides, proteins and fats, and has many functional groups able to bind heavy metal ions (Doulati et al., 2008; Kazemipour et al., 2008; Witek-Krowiak et al., 2011). A wide variety of materials derived from natural resources, plant wastes or industrial by-products such as peat, wood, barley, rice husk, plant straw, rice bran, peanut shell, almond shell, hazelnut shell, algal biomass, fruit stones, plum kernels, banana pith, soybean, cottonseed hulls, humic acids, corn stalk, tree bark, sugar beet pulp, leaves, green algae, activated carbon fibers, coconut, fly ash, pine bark, black cumin, sawdust are being used as low cost alternatives to expensive adsorbents (Bulut and Tez, 2007; Kazemipour et al.,

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http://dx.doi.org/10.1016/j.biortech.2013.10.019

2008; Bingöl et al., 2012; Ding et al., 2012; Sundaram and Sivakumar, 2012).

Artificial neural networks (ANNs) offer a powerful tool of mapping a given set of inputs into their desired outputs. Multi Layer Perceptron (MLP) network, widely used, is organized in layers, with the user having access to the input and the output layers while the rest of layers are hidden (Haykin, 1999). The ability of an ANN to learn and generalize the behaviour of any complex and non-linear process makes it a powerful modeling tool. In the past, ANNs have been successfully employed in the modeling of several processes (Yetilmezsoy and Demirel, 2008; Prakash et al., 2008; Sadrzadeh et al., 2009; Bingöl et al., 2012). NARX neural network is a recurrent neural network. Researchers have demonstrated that a NARX network model is well suited for modeling nonlinear systems such as heat exchangers (Chen et al., 1990), waste water treatment, catalytic reforming systems in a petroleum refinery (Su et al., 1992), nonlinear oscillations associated with mutli-legged locomotion in biological systems (Venkataraman, 1994), and various artificial nonlinear systems (Chen et al., 1990). NARX networks also converge much faster and generalize better than these other networks (Lin et al., 1996). In this study, activated almond shell, which is a very cheap and readily available material has been investigated for the removal of Zn(II) ions from aqueous solution. The effects of adsorbent dosage, particle size, initial metal ions concentration and initial pH on the removal of zinc ions were investigated and the experimental data obtained were evaluated and fitted using adsorbent equilibrium isotherms, and kinetic models. A NARX neural network is proposed to model the experimental system and predict the removal efficiency. The suggested technique is compared to batch experimental designs. To the authors' knowledge, NARX neural network is first used for adsorption studies. The results indicate that activated almond shells are good adsorbents for Zn^{2+} in aqueous solutions.

2. Methods

2.1. Material

This section describes the use of almound shells as a biosorbent. Almound shells were ground in a ball mill and the resulting crumbs were sieved to obtain size of smaller than 90 μm. Before using them, all the sorbents were washed thoroughly with deionized water and dried in air oven at 100 °C for 24 h. The acid treatment was performed by agitation for 30 min of 15 g of almond shells and 15 ml of H_2SO_4 1.86% at room temperature. Then, the sample was washed with distilled water and soaked in 1% $NaHCO_3$solution to remove any remaining acid. All chemicals used were analytical grade reagents of the highest quality available and deionized water was used. Stock zinc solution for all experimental studies was prepared in deionized water using the analytical reagent grade $ZnSO_4 \cdot 7H_2O$.

2.2. Methods

2.2.1. Experimental studies

The samples were broken and sieved into the following particle sizes (mm): −2.0 + 1.19, −1.19 + 0.84, −0.84 + 0.50, −0.50 + 0.35, and −0.35 + 0.23. They were washed thoroughly with deionized water to remove the dirt and other foreign matter and dried at 105 ± 5 °C for 2 h. The effect of pH on the zinc adsorption was investigated using 30 mg/L Zn(II) containing solution over the pH range 2–10. Batch mode adsorption isotherm studies were carried out 23 °C. Adsorption isotherms were performed for initial Zn(II) concentrations of 15, 30, 50, 70 and 100 mg/L. Adsorption experiments were performed by shaking 0.125–4.0 g of activated almond shell samples in a 100 mL of aqueous solutions of Zn(II). After the adsorption period, the mixtures were filtered with 0.45 μm filter and acidified with HNO_3 to decrease the pH to below 2 before the AAS measurement.

2.2.2. Modeling approach

Considering the nonlinear nature of the real word problems a dynamic recurrent ANN methodology was also considered. The NARX neural network is a dynamic recurrent network that encloses several layers with feedback connections (Chen et al., 1990). The reason for choosing a NARX network is that it converges much faster and generalizes better than other network and it is a powerful modeling and validation tool.

2.2.2.1. The NARX model. A NARX network output during training can be mathematically expressed by Eq. (1).

$$y(t) = f(u(t-n_u), \ldots u(t-1), u(t), y(t-n_y), \ldots y(t-1) \qquad (1)$$

where f is a nonlinear function describing the system behaviour (obtained via ANNs), $u(t)$ and $y(t)$ represent input and output of the network at time t, n_u and n_y are the input and output order. While training, the network output is regressed on the actual target values since they are available. These actual target values are feedback to the network during the training process. This essentially renders better training and learning and the network behaves as a feed forward network that is always stable. In another words, when the function f can be approximated by a Multi Layer Perceptron, the resulting system is called a NARX network (Chen et al., 1990).

In this study, a two-layer NARX network given in Fig. 1 is used to predict the adsorption efficiency. The network, an input layer including recurrent unit with 4 neurons (pH, adsorbent dosage, particle size and initial metal ions concentration) and an output layer with 2 neurons (R and absorbent capacity), is established. In Fig. 1, z is the delay element and w_{ij} and b_k show neural network's weight and bias values, respectively.

3. Results and discussion

3.1. Experimental results

3.1.1. Effect of particle size

The adsorption characteristics of activated almond shell with respect to particle sizes show that decreasing in particle size of activated almond shell causes an increase adsorption loading and adsorption efficiency. The difference between the minimum and maximum values of the removal efficiencies obtained for Çankırı-Çorum and Manisa-Gördes clinoptilolites samples of −1.19 + 0.84 and −0.35 + 0.23 mm were 1.87% and 6.01%. Therefore, increase in removal efficiency with decrease in particle size of natural clinoptilolites is not significant. Generally, the finer particle yields a higher adsorption capacity than the coarse one due to the higher specific surface area of the former (Babel and Kurniawan, 2003; Witek-Krowiak et al., 2011).

3.1.2. Effect of adsorbent dosage

The removal efficiency of zinc ions increased with the increase adsorbent dosage, but the amount of Zn ions adsorbed by unit weight of the adsorbed decrease. The removal efficiency for 2.5 g/L of activated almond shell sample was found to be 23.3% but as the activated almond shell amount was increased to 20 and 40 g/L removal efficiencies were found to be 77.3% and 79.4%, respectively. This result was anticipated because of for a fixed initial solute concentration, increasing amount of adsorbent provides greater surface area. The shell is composed of cellulose,