Original Article

A Study of Cadmium Removal from Aqueous Solutions by Sunflower Powders and its Modeling Using Artificial Neural Network

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Abstract

Background and purpose: Cadmium is hazardous and non-biodegradable material entering the food chain. In this paper, the removal of cadmium from aqueous solutions by sunflower powder (the natural biosorbent) was investigated.

Materials and Methods: The experiments were performed in a batch system. The effect of parameters such as contact time, pH, cadmium concentration and adsorbent dose were evaluated.

Results: The results showed that increasing of pH, contact time and adsorbent dose caused increasing efficiency of removal cadmium from aqueous solutions. The results were modeled using biosorption kinetics and a neural network with four hidden neurons, including bias which was able to predict the concentration dependency of data very accurately.

Conclusion: On the basis of the results, could be used from sunflower residues as a cost and efficient biosorbent for treatment of wastewater with Cadmium. The prediction of the artificial neural network model fit the experimental data very precisely.

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Key words: Sunflower Powder, Aqueous Two Phase, Biosorption, Cadmium, Biokinetics, Neural Network

1. Introduction

Heavy metals are highly toxic and considered as a serious threat to human health and the environment. The increase of heavy metals in the environment is largely as a result of industrialization. As a result of this problem, the need to remove and recovery these heavy metals have been on the increase (1). Cadmium is highly toxic at low concentrations and widely used in various applications. If the metal is used by humans, in addition to osteoporosis, it accumulates in the kidneys causing the kidneys to malfunction. Cadmium is a contaminant that is among the priority pollutants of American Environmental Protection Agency (USEPA) (2). The proposed maximum contaminant level (MCL) and maximum contaminant level goals (MCLG) values for cadmium is 0.005mg/l (2). The maximum permitted concentration by the World Health Organization (WHO) is determined 0.001mg/l. The main sources of cadmium to the aquatic environments are via wastewaters of some industrial processes such as plating, pottery, tiles, plastics, metals, mining and smelting, paint, Cd- Ni batteries, industries which produce chemical fertilizers and pesticides (2). The surrounding soils of agricultural lands are one of the important areas which have been contaminated with cadmium due to phosphate fertilizers or sewage sludge used to improve soil. Different methods such as chemical precipitation, ion exchange, electro-dialysis and adsorption etc. have been studied and used for removal of heavy metals where in each method has its own disadvantages (3). Adsorption by organic matters such as algae, bacteria, fungi, leaves, trees and agricultural wastes have been widely studied in recent years as a convenient and inexpensive method for heavy metals removal (to maintain high efficiency at low to medium concentrations). Agricultural residues contain lignin and cellulose, which usually constitute the main structure of it. There are compounds such as hemi-cellulose, lipids, proteins, glucose, starch, water, hydrocarbons and other compounds in their structure. These groups have the ability to link with heavy metals in solution by replacing hydrogen ions or giving pair of electrons of these groups to form complexes with metal ions. Sunflower waste can be considered as a low-cost adsorbent for the removal of heavy metals due to fiber characteristics, porosity and low molecular weight. Carboxylic and hydroxyl groups on the surface structure of sunflower waste have a great affinity for heavy metal ions (4). In addition, sunflower waste is inexpensive, available and easy to prepare, it can be considered as an effective biosorbent which is used in water and wastewater treatment (5). Agriculture biosorbent as grape skin (6), apple peels, apple kernel (6), orange waste (7), olive stone (8), medlar peels (9) coconut shell powder (10), pine sawdust (11) and papaya wood (12) have been used for the removal of heavy metals from aqueous solutions. The aims of this study are: (i) to determine maximum removal of cadmium in different concisions such as pH, contact time, adsorbent dose and initial concentration of cadmium, (ii) to determine the biosorption kinetics to fit the behavior for conventional models and (iii) to compare the experimental data with neural network.

2. Materials and Methods
2.1. Preparation of biosorbent
This is an experimental study in which the sunflower waste is used as biosorbent in the removal of cadmium from aqueous solution. The wastes from sunflower were collected in the agricultural lands at harvesting season. The wastes were washed with purified water to remove dust. Then wiped dry out completely in the sun. The dried matter was crushed into fine particles with an electric mill. In order to eliminate color and contamination, fine particles had been mixed to distilled water with ratio of 1 to 5 and then heated for 5 hours. Next, the samples were filtered by Whatman membrane filter (0.45 microns) and washed several times with distilled water and placed in oven (at 80 centigrade) to remove moisture. After drying, the absorbent was milled again to smaller particles. The ASTM sieve was used for particle sizing that was approximately below than 200 micron and then was placed into impermeable plastic bags (13, 14).

2.2. Reagents
In this study, stock solution of cadmium (1000 mg/ l) was prepared by dissolving of cadmium nitrate ($CdN_2O_6.4H_2O$) in deionized water and then the desired concentrations were provided with diluting the stock solution.

2.3 .Experimental plan
Experiments were conducted in Batch system in the laboratory scale. This study investigated some factors such as pH (2, 4, 6, 7), contact time (5, 10, 15, 30, 45, 60, 120 minutes), the initial concentration of cadmium (15, 30, 60 mg/l) and the amount of adsorbent (0.2, 0.6, 1 g /100 ml). The nitric acid and Na OH 0.1N were used to adjust the pH of the solution.

In order to increase the accuracy and precision of results, 200 samples were carried out in triplicate and averaging was used. A shaker (Model FL 83) by speed of 120 rpm was used in order to mix the samples. The samples were filtered by Whatman 0.45 microns. The filtrates were transmitted to polyethylene containers and pH was kept in acidic condition with nitric acid. Cadmium concentrations in the storage samples were measured by using atomic adsorption spectrophotometer (PG-instrument 990). The measurement was performed according to the standard methods for water and wastewater examination.

2.4. Artificial neural network
Artificial neural networks (ANNs) are highly flexible mathematical constructs that have been inspired in the workings of the biological nervous system. ANNs have a natural tendency for storing experiential knowledge and making it available for use (15). ANNs can simply be viewed as general nonlinear models which have the ability to encapsulate the underlying relationship that exists between a series of inputs and outputs of a system. There are many different ANN structures like MLP (multi layer perception), RNN (recurrent neural network) and RBF (radial basis function). Each of these structures has been used for modeling of different case studies. Feed forward neural networks (FFNN) are undoubtedly the most commonly neural network structure used in engineering applications. It has been shown that a three-layer FFNN can represent any function provided that sufficient number of neurons are present (16). A FFNN normally consists of three layers: an input layer, a hidden layer, and an output layer. The feed forward neural networks that have been used in this examination are presented in Fig. 1.
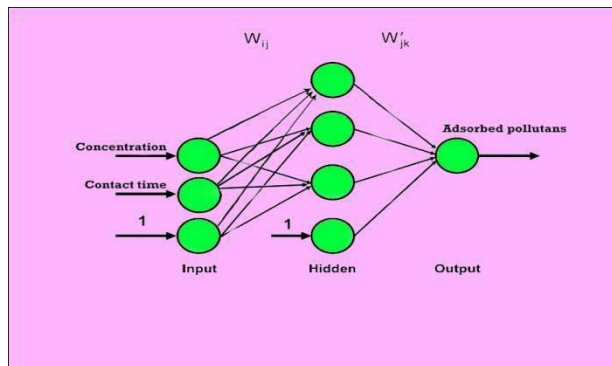
Figure 1. Feed forward neural networks used to represent adsorbed pollutants isotherm data sets

The input layer receives the process inputs and fans out this information to all functional neurons of the hidden layer. Each neuron of the hidden layer essentially accomplishes two works: (1) a weighted summation of all process inputs; and (2) a non-linear transformation, via a neuron transfer function of the weighted summation to produce the output of each neuron of the hidden layer which then serves as inputs to the neurons of the output layer. The output layer performs the same task as the neurons of the second layer to produce the final output of the FFNN. The typical transfer functions that are used in the hidden and output layers are linear, sigmoid or hyperbolic tangent. The input and output to the FFNN are usually scaled between 0.1 and 0.9.

3. Results
3.1. Influence of pH on the biosorption
Usually wastewater containing cadmium is acidic to neutral pH, so in this study the samples were investigated in pH 2, 4, 6, and 7. The results showed that the efficiency of cadmium removal by sunflower adsorbent was raised by increasing pH.

3.2. Influence of initial cadmium concentration on the biosorption
The effect of initial cadmium concentration on adsorption efficiency showed that increasing initial concentration decreased the adsorption rate, but the efficiency is committed high. For the initial concentrations of 15, 30, and 60 mg/l, removal efficiencies was 90, 93 and 99 percent respectively.
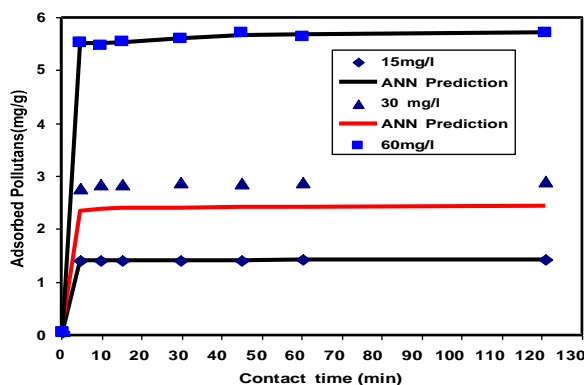

Figure 2. Effect of initial cadmium concentration on cadmium removal (pH = 6, adsorbent dose 1 g in 100 cc) and comparison with ANN

3.3. Influence of adsorbent dose on the biosorption
The effect of adsorbent mass (0.2, 0.6 and 1 g) in cadmium concentration of 60 mg/l at pH =6 was determined in different contact times (Figure 3). The results indicate that by increasing the dose of adsorbent, the removal rate generally increases, so removal of cadmium in amounts of 0.2, 0.6 and 1 g of adsorbent in 120 minutes was 64, 92 and 95 percent, respectively.
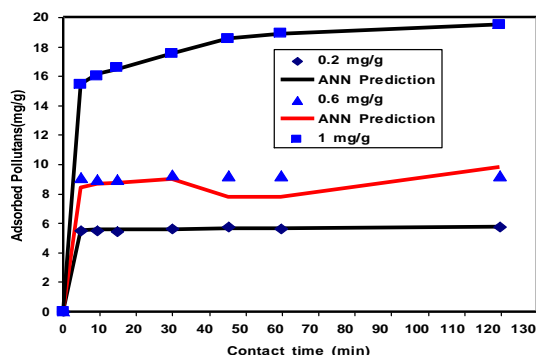
Figure 3. Effect of adsorbent dose on cadmium removal (Cadmium concentration= 60 mg/l, pH = 6) and comparison with ANN

3.4. ANN modeling

The results were modeled by neural network with four hidden neurons, including bias. In this modeling, contact time and initial concentration were input variables and an adsorbed pollutant was output variable. For each series of adsorption data, upper and lower initial concentrations were used as the training data set to fit the initial concentration dependent neural network and the remaining series (intermediate initial concentration) was used as the validation data set to assess the performance of the neural network predictions for the data that were not used during the fitting process. As can be seen from Figures 2 and 3, the neural network model is able to predict very well the observed data points for both the training and validation data sets.

3.5. Biosorption kinetics

Kinetics models were suggested for clarifying the mechanism of adsorption and evaluation of adsorbent performance which depends on the physical and chemical properties of absorbent and mass transfer process (18). The kinetics of adsorption followed from pseudo first and second models (equation 1 and 2) (18).

$$\ln(q_e - q_t) = \log(q_e) - kt \qquad (1)$$

$$\frac{t}{q_t} = \frac{1}{k} + \frac{t}{q_e} \qquad (2)$$

In this work, pseudo first and second models are investigated for the kinetics of cadmium removal by sunflower plant waste. Considering figure 4 it indicates that the correlation coefficient (R^2) in pseudo first model is relatively low, therefore this model is inappropriate. As can been seen from figure 5, the correlation coefficient is very high in the pseudo second model. Then, this model provides the appropriate cadmium adsorption on sunflower plant waste ($R^2 = 0.999$). In addition, the retention of a metal ion (cadmium) by biosorbent can be evaluated by a simple mass balance following the logic that the metal removed from the solution is found in or on the solid biomass

$$q = \frac{V(C_i - C_{eq})}{M} \qquad (3)$$

Where C_i and C_{eq} (mg/l) are the initial and equilibrium concentration of the solute, respectively, q is metal retention by the biosorbent (mg / g), V(L) is the volume of liquid phase, $M(g)$ is mass of adsorbent and q_t is metal adsorbed at time t(min).
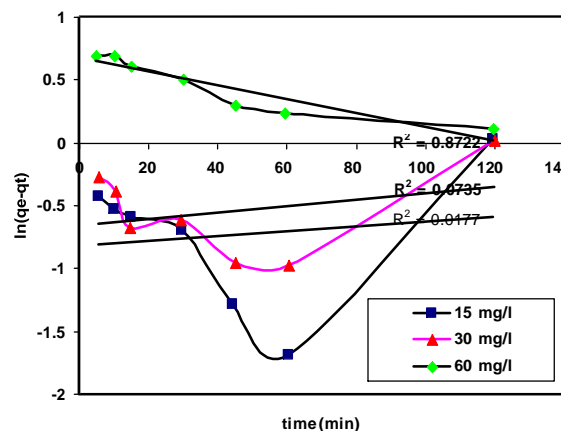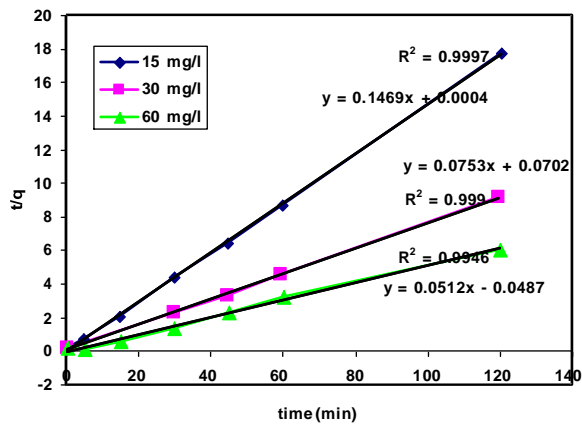

Figure 4. Pseudo first order kinetic model

Figure 5. pseudo-second kinetic model

4. Discussion

4.1. Influence of pH on the biosorption

The results showed that the efficiency of Cadmium removal by sunflower adsorbent in pH=6 was maximum. With increasing pH due to the release of hydroxide ion is reduced Cd uptake and maximum removal occurred at ph=6. This result is consistent to studies in Cadmium removal by sugarcane and rice paddy residues (19, 20).

4.2. Influence of initial cadmium concentration on the biosorption

The effect of initial cadmium concentration on adsorption efficiency showed that increasing initial concentration decreased the adsorption rate, but the efficiency is committed high. This phenomenon is due to the saturation of the active sites of the adsorbent. Higher initial concentration can create a significant driving force that can overcome the mass transfer resistance. The results in this step are compatible with the results of Mahvi and et al. (17). For the initial concentrations of 15, 30, and 60 mg/l, removal efficiencies was 90, 93 and 99 percent respectively.

4.3. Influence of adsorbent dose on the biosorption

The results indicate that by increasing the dose of adsorbent, the removal rate generally increases, so removal of cadmium in amounts of 0.2, 0.6 and 1 g of adsorbent in 120 minutes was 64, 92 and 95 percent, respectively. Zazouli et al showed that removal Cadmium increased with increasing amount of adsorbent due to availability of larger surface area to absorb (21). The efficiency of cadmium removal from aqueous solution by sunflower plant residues as a natural biosorbent was evaluated. The effect of parameters such as contact time, pH, cadmium concentration and adsorbent doses were analyzed. In general, the best efficiency of cadmium removal by sunflower residues was obtained at pH=6, dose adsorbent of 1 mg/ g and initial concentration of cadmium of 60 mg/l. The second order model described the sorption kinetics in removal of cadmium from aqueous solution by sunflower residues. Neural network with four hidden neurons, including bias, was able to predict very accurately the concentration dependency of data and the predictions of the artificial neural network model fit the experimental data very accurately.

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