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Breakthrough curves modelling of liquid-phase biosorption of Cu^{++} on Helianthus Annuus particles

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Abstract

A continuous fixed bed study was carried out by using shells of Helianthus Annuus as a biosorbent in the uptake of Cu++. The effect of operating parameters such as inlet Cu++ concentration, flow rate, pH and par-ticle size on Cu++ uptake was investigated. Adam's-Bohart, Thomas, Clark and Yoon-Nelson models were applied to experimental data to predict the most suitable breakthrough curves in a fixed bed column. In this study, average percent error (APE) analysis and correlation coefficient (R^2) were used to define the most suitable model for the tracing of breakthrough curve at different experimental conditions. The Fixed bed column model studies indicated that Thomas model (R^2 0.97) and APE (%) (6.4) was suitable to de-scribe the adsorption equilibrium of Cu++.

Keywords: Adsorbent, Copper, Helianthus Annuus, Fixed Bed, Thomas Model

INTRODUCTION

Basic metals such as aluminum, cadmium, chromium, copper, mercury, nickel, and zinc have been classified as the metals of primary importance for recovery from industrial wastewater [1,2]. Wastewater containing metal ions has to be recovered using conventional methods based on electrochemistry, precipitation, solvent extraction or ion exchange resins [3]. The adsorbents such as fly ash [4], blast furnace slag [5], PAC [6, 7] have been used. Materials of agricultural and biological origin have led to the investigation of low cost and easily available adsorbents [8, 9]. Biosorption, an alternative process, is the uptake of heavy metals from aqueous solutions by biological materials. This novel approach is competitive, effective and cheap [10]. Biosorption of metals by biomass has been much explored in recent years. Different form of inexpensive, non-living plant material such as rice husk [11], sawdust [12], and pine bark and canola meal [13, 14] have been used widely and Scots pine cones [15, 16] newly investigated as potential biosorbents for heavy metals. The aim of the present work is to identify the most suitable model in the removal of Cu^{++} from aqueous solutions using a fixed bed column. For this purpose, four different models such as Thomas, Adams-Bohart, Clark and Yoon-Nelson models were used to predict breakthrough curves and biosorption capacities. Error analysis and correlation coefficient (R^2) were determined to test the adequacy and accuracy of the model equations.

MATERIAL and METHODS

The shells of Helianthus Annuus were used in this investigation. Fresh shells of Helianthus Annuus were dried in outdoors for 72 h, and cut into small pieces, ground in a blender to granulate and sieved to get it separated for different particle sizes (0.25-0.5, 0.5-1 and 1-2 mm). 0.6, 1.27, 2.54 and 3.81 g portions of the sample were taken for biosorption column studies. Cu^{++} solutions were prepared by diluting 400 mg/L of $CuSO_4.5H_2O$ (Merck) stock solution with deionized water to a desired concentration range between 20 and 60 mg/L. The initial concentration of the Cu^{++} in the solution and samples after biosorption process were complexometrically determined [17]. Continuous flow biosorption experiments were conducted in teflon columns of 1 cm i.d. and 5, 10 and 15 cm heights. Cu^{++} solution having an initial concentration of 40 mg/l was pumped upward through the column at a desired flow rate by a peristaltic pump. Samples were collected from the exit of the column at different intervals. Operation of the column was stopped when the effluent Cu^{++} concentration equals influent Cu^{++} concentration.

Mathematical description

The performance of a fixed-bed column is described through the concept of the breakthrough curve. The loading behavior of Cu^{++} biosorbated from solution in a fixed-bed is usually expressed in term of Ct/Co as a function of time. The value of qtotal for a given feed concentration and flow rate is equal to the area under the plot of the adsorbated Cu^{++} concentration (Cad=Co-Ct) (mg/l) vs. t (min) and can be calculated from Eq. (1):

$$q_{total} = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} C_{ad}\,dt \qquad (1)$$

Where Co is influent Cu^{++} Con. (mg/L), Cad is adsorbated Cu^{++} Con. (mg/l), Ct is effluent Cu^{++} Con. (mg/l)

Thomas model

The maximum biosorption capacity of an biosorbent is also needed to design a fixed bed. Traditionally, Thomas model is used to fulfill the this purpose. The data obtained from a column in continuous mode studies were used to calculate the maximum solid phase concentration of Cu^{++} on biosorbent and the biosorption rate constant using the kinetic model developed by Thomas. The expression by Thomas for an column is given Eq. (2).

$$\frac{c_t}{c_o} = \frac{1}{1+\exp(k_{TH} q_e \frac{x}{Q} - k_{TH} C_o t)} \qquad (2)$$

Adams-Bohart model

Adams-Bohart model assumes that the biosorption rate is proportional to both the residual capacity of the biosorbent and the concentration of the adsorbing species. Adams-Bohart model is used for the description of the initial part of the breakthrough curve, expressed in Eg(3). From this equation, values describing the characteristic operational parameters of the column were determined from a plot of Ct/Co against t at a given bed height and flow rate using the nonlinear regressive method.

$$\frac{c_t}{c_o}=\frac{\exp(k_{AB}\,\mathrm{c_o t})}{\exp(k_{AB}N_o\,{}^{Z}\!/_{F})-1+\exp(k_{AB}\,\mathrm{c_o t})} \qquad (3)$$

Yoon-Nelson model

Yoon-Nelson is based on the assumption that the rate of decrease in the probability of adsorption for each biosorbate molecule is proportional to the probability of biosorbate biosorption and the probability of biosorbate breakthrough on biosorbent. Yoon-Nelson model not only is less complicated than other models, but also requires no detailed data concerning the characteristics of biosorbate, the type of biosorbent, and the physical properties of the biosorption bed. The Yoon-Nelson equation for a single component system is expressed by Eq (4).

$$\frac{c_t}{c_{o-}c_t}=\exp(k_{YN}t-\tau k_{YN}) \qquad (4)$$

The approach involves a plot of Ct/(Co–Ct) vs sampling time (t) according to Eq. (4). The parameters of kYN and τ can be obtained using the nonlinear regressive method.

Clark model

The Clark defined a new simulation of breakthrough curves. The model developed by Clark was based on the use of a mass-transfer concept in combination with the Freundlich isotherm.

$$\frac{c_t}{c_o}=\left(\frac{1}{1+A\exp^{-rt}}\right)^{\frac{1}{(n-1}} \qquad (5)$$

From a plot of Ct/Co against t, at a given bed height and flow rate using nonlinear regressive analysis, the values of A and r can be obtained.

Error analysis

As different formulas used to calculate R^2 values would affect the accuracy more significantly during the linear regressive analysis, the nonlinear regressive analysis can be a better option in avoiding such errors [18]. So the parameters of different kinetic models were obtained using nonlinear analysis. In order to confirm which model was better, Average Percent Error (APE) analysis was performed. The (APE) calculated according to Eq. (6) indicated the fit between the experimental and predicted values of Ct/Co used for plotting breakthrough curves.

$$APE(\%)=\frac{\sum_{i=1}^{N}\left[\frac{({}^{c_t}\!/_{c_o})_{\exp erimental}-({}^{c_t}\!/_{c_o})_{theoritical}}{2}\right]}{N}x100$$

(6)

RESULTS

Determination of the most suitable model for the breakthrough curves in the removal of Cu^{++} using a fixed bed column

The effect of operating parameters such as inlet Cu^{++} concentration, flow rate, pH and particle size on Cu^{++} uptake was investigated. Adam's-Bohart, Thomas, Clark and Yoon-Nelson models were applied to experimental data to predict the most suitable breakthrough curves in a fixed bed column. In this study, APE (%) analysis and R^2 were used to define the most suitable model for the tracing of breakthrough curve at different experimental conditions. The R^2 and APE (%) of Adam's-Bohart, Thomas, Clark and Yoon-Nelson models were determined as (0.970, 0.960, 0.965 and 0.940) and (6.4, 7.69, 6.9 and 9.39), respectively. The general model concerning Thomas equation as a function of flow rate, pH, concentration and particle size was given in Fig.1

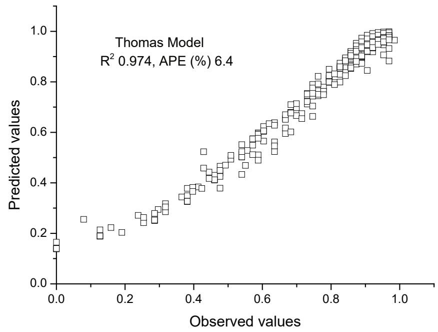

Figure 1. General Model concerning Thomas

The fixed bed column model studies indicated that Thomas model (R^2 0.97) and APE (%) (6.4) was suitable to describe the biosorption equilibrium of Cu^{++}.

Effect of flow rate on the breakthrough curve

The breakthrough curves at various flow rates are shown in Fig. 2 where it can been seen that the breakthrough generally occurred faster with a higher flow rate. Breakthrough time increased significantly with a decrease in the flow rate. At a low rate of influent, Cu^{++} had more time to be in contact with adsorbent, which resulted in a greater uptake of Cu^{++} ions in the fixed bed.

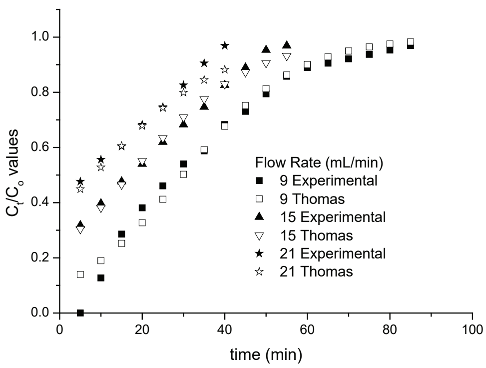

Figure 2. Breakthrough curves: the effect of different flow rates on Cu^{++} adsorption in the fixed bed.

The observed and predicted biosorption capacities (from Thomas model) in the breakthrough (Ct/Co) of 98% for the F. rates of 9, 15 and 21 mL/min were defined as (17.9, 18), (17.4, 16.58) and (15.6, 8.24) mg/g, respectively.

Effect of influent Cu^{++} concentration on the breakthrough curve

The effect of influent Cu^{++}concentration on the shape of the breakthrough curves is shown in Fig. 3. It is illustrated that the breakthrough time decreased with increase of influent Cu^{++} concentration. The observed and predicted biosorption capacities (from Thomas model) in the breakthrough (Ct/Co) of 98% for the inlet concentration of 20, 40 and 60 mg/L were defined as (15.2, 15.18), (17.97, 17.9) and (23.98, 25.9) mg/g, respectively. At lower influent Cu^{++} concentrations, breakthrough curves were dispersed and breakthrough occurred slowly. As influent concentration increased, sharper breakthrough curves were obtained. These results demonstrate that the change of concentration gradient affects the saturation rate and breakthrough time. This can be explained by the fact that more biosorption sites were being covered with the Cu^{++} ions.

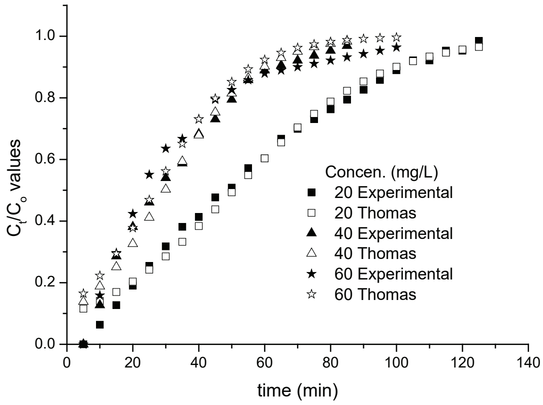

Figure 3. Breakthrough curves: the effect of influent Cu^{++} concentations on Cu^{++} biosorption in the fixed bed.

Effect of the pH of solution on the breakthrough curve

The pH value of solution influences both the biosorbent surface metal binding sites and the metal chemistry in water. The pH of feed solution was changed from 3 to 5.6. The highest experimental and theoretical biosorbent capacity and the longest breakthrough time was received at pH 5.6 as seen in Fig. 4.

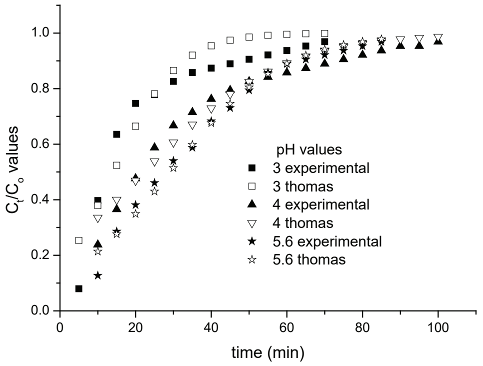

Figure 4. Breakthrough curves: the effect of different pH values on the Cu^{++} adsorption in the fixed bed.

The observed and predicted biosorption capacities (from Thomas model) in the breakthrough (Ct/Co) of 98% for the pH values of 3, 4 and 5.6 cm were defined as (9.7, 8.5), (14.64, 16.40) and (17.97, 17.9) mg/g, respectively.

The slope of the breakthrough curve decreased with increase of pH value, which resulted in a broadened mass transfer zone. High uptake was observed at the pH 5.6.

Effect of the particle size on the breakthrough curve

The particle sizes of biosorbent were 0.25-0.5, 0.5-1 and 1-2 mm, while bed depth, influent Cu^{++} concentration and pH were kept constant at 5 cm, 40 mg/l and 5.6, respectively.

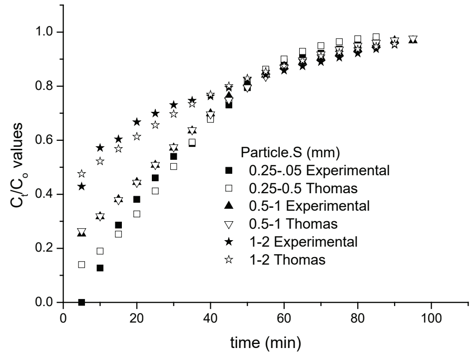

Figure 5. Breakthrough curves: the effect of different particle sizes on the Cu^{++} adsorption in the fixed bed.

The breakthrough curves of concerning with particle size are given in Fig. 5. The observed and predicted biosorption capacities (from Thomas model) in the breakthrough (Ct/Co) of 98% for the particle sizes of 0.25-0.5, 0.5-1 and 1-2 mm were defined as (17.9, 17.97), (7.5, 6.89) and (5.7, 2.47) mg/g, respectively. An increase in the particle size appeared to increase the sharpness of the breakthrough curve. Furthermore, the biosorption capacity for the larger particle size is lower than that for smaller one. A rapid decrease in the column biosorption capacity with an increase in particle size was observed. That is mainly true due to the higher surface area of the smaller particle size, hence a higher biosorption capacity is expected and also the mean intraparticle diffusion paths are shorter.

CONCLUSIONS

The R^2 and APE (%) of Adam's-Bohart, Thomas, Clark and Yoon-Nelson models were determined as (0.970, 0.960, 0.965 and 0.940) and (6.4, 7.69, 6.9 and 9.39), respectively. The fixed bed column model studies indicated that Thomas model (R^2 0.97) and APE (%) (6.4) was suitable to describe the adsorption equilibrium of Cu^{++}.The observed and predicted adsorption capacities (from Thomas model) in the breakthrough (Ct/Co) of 98% for the flow rates of 9, 15 and 21 mL/min were defined as (17.9, 18), (17.4, 16.58) and (15.6, 8.24) mg/g, respectively. The observed and predicted adsorption capacities (from Thomas model) in the breakthrough (Ct/Co) of 98% for the inlet concentration of 20, 40 and 60 mg/L were defined as (15.2, 15.18), (17.97, 17.9) and (23.98, 25.9) mg/g, respectively. The observed and predicted adsorption capacities (from Thomas model) in the breakthrough (Ct/Co) of 98% for the pH values of 3, 4 and 5.6 cm were defined as (9.7, 8.5), (14.64, 16.40) and (17.97, 17.9) mg/g, respectively. The observed and predicted adsorption capacities (from Thomas model) in the breakthrough (Ct/Co) of 98% for the pH values of 0.25-0.5, 0.5-1 and 1-2 mm were defined as (17.9, 17.97), (7.5, 6.89) and (5.7, 2.47) mg/g, respectively.

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