Assessing the Performance of Heavy Cu2+ Metal Sorption by Immobilized Biosorbent in Fixed-bed Column Reactor Based on Breakthrough Curves

by Astri Rinanti

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Abstract. This research was conducted to determine the best performance of Cu^{2+} metals biosorption contained in electroplating effluent based on the values of breakthrough curve parameters. This involved the formation of biosorbents from a biomass consortium immobilized by an alginate polymer at a ratio of 0.5 gram of biomass/gram of alginate while the kinetics of the Cu^{2+} metal absorption was studied using the Thomas model. The biosorption performance was assessed by varying the bed heights at 2.5, 5, and 7.5 cm, at pH 4, and room temperature of 26˚±1 in a continuous laboratory scaled fixed-bed column reactor system which was built of glass, with a volume of 1.5 L, and equipped with a peristaltic pump at a flow rate of 15 mL/min. An increase in the biosorption performance was observed due to the increment in the bed height and the best value was obtained at 7.5 cm, based on the shape of the sloping curve, maximum capacity (q_e) of 0.118 mg of Cu^{2+}/g of biosorbent, and breakthrough time of 20.6 minutes. Therefore, the kinetic studies showed the Thomas model has the ability to describe a good biosorption process with a maximum value of r^2 reaching 0.985.

Introduction

It is possible to use both live and dead biomass in studying biosorption but dead ones have been discovered to be more beneficial due to their ability to ensure the toxic properties of the dissolved heavy metals do not affect absorption capacity, work without the continuous supply of nutrients, and can be regenerated and reused for several cycles [1, 2, 3]. However, they are not applicable on a large scale and for continuous processes [4]. Moreover, dead biomass is generally in the form of dry powder, therefore, it has small particle size, low mechanical strength, low density, mass loss during regeneration and there is also difficulty in separating it from waste [5, 6]. It can, however, be modified through physical processes including autoclaving, steam and thermal drying, chemical processes such as pre-treatment with acids, alkalis or other chemicals, and chemical absorption of biomass to form membranes, beads, pellets or granular biosorbents to increase its adsorption capacity [7]. The chemical absorption of biomass commonly called biomass immobilization was reported to have the capability to offer better potential to produce adequate particle sizes, ensure easy separation of biomass and effluent, regeneration ability, as well as the ability to avoid high biomass loading and clogging in continuous systems [8, 9].

The use of biomass immobilization as a heavy metal biosorbent has attracted the attention of researchers due to its several advantages over free suspended cells. Some of these include its ability to increase cell stability, reuse, stronger mechanically, facilitate maintenance, and cause more minimal clogging in a continuous system [10]. The research conducted by [11] proved the temperature stability and re-use of immobilized *Saccharomyces cerevisiae* cells were better than the free suspended cells and this means it successfully maintained its activity at high temperatures and could be reused up to 7 times. In addition, the mechanical strength of immobilized biomass was greater than free suspended cells because it has the ability to prevent cells from spreading widely to the surrounding areas [12].

Initially, some researches were conducted on heavy metal biosorption to study batch equilibrium and the absorption capacity of biosorbents was found to be useful in providing basic information about the effectiveness of metal-biosorbent systems. However, it is not possible to apply the findings to all systems such as column due to the insufficient contact time to attain equilibrium [13]. In addition, [14] reported that large-scale biosorption processes were conducted continuously, generally through the use of a Fixed-Bed Column Reactor which has a tubular structure with a silent catalyst and feed solution continuously flowing into it. It is important to note that the silent catalyst is a granular biosorbent densely packed to allow the free flow of feed solution through the column [13]. Therefore, the process involves allowing liquid waste containing heavy metals to flow at a constant rate through a column filled with biosorbent in order to ensure heavy metal ions are continuously removed from the waste and accumulated on the solid phase surface of the biosorbent. This is expected to continue until the concentration of the solute in the waste reaches the same value as the feed solution, and the column is considered saturated because it cannot absorb any more. However, it is possible to describe this process through the Breakthrough Curve which has been reported to be a useful tool for calculating the absorption capacity of a particular column [15].

Based on this description, this research was conducted in the field of environmental biotechnology to obtain the best performance of the biosorption of Cu^{2+} metals contained in electroplating wastewater by immobilized biosorbent based on the characteristics and values of the breakthrough curve parameters.

Material and Methods

Cultivation, Production, and Biomass Immobilization

The biomass used as the biosorbent was obtained from a microbial consortium consisting of *Saccharomyces cerevisiae* and 3 species of microalgae - *Chlorella sp*, *Ankistrodesmus braunii*, and *Scenedesmus quadricauda*. The cultivation was conducted in a 10 L Vertical Column Photobioreactor containing artificial growth media of *Provasoli Haematococcus* Media [16] while the biomass was harvested by centrifugation and dried for immobilization. Moreover, the dry biomass was mixed with a 2% Na-Alginate solution and stirred using a magnetic stirrer for 3 hours to ensure complete dissolution of the mixture. The biosorbents were immobilized into beads by dripping the mixture under gravity using a 20 mL syringe into a 0.1 M CaCl$_2$ solution [9]. However, the effluent with an initial concentration of Cu^{2+} at 15 mg/L was used as an adsorbate of heavy metal biosorption.

Effect of Bed Height

The immobilized biosorbents in the form of beads were arranged in a Fixed Bed Reactor to reach bed heights of 2.5, 5.0, and 7.5 cm and the feed solution with a concentration of Cu^{2+} of 15 mg/L was flowed into the reactor from the bottom with a discharge of 13 ml/min at 25°C and a pH value of 4. The adsorbate in the effluent solution was observed periodically to determine the change in concentration of Cu^{2+} (C_e/C_o) towards time (t) at different bed heights and a graph was plotted to form the breakthrough curve.

Analysis of the Breakthrough Curve

The breakthrough curve for the biosorption of Cu^{2+} using different biosorbent concentrations and bed heights was analysed to determine the Fixed Bed Column Reactor parameters such as breakthrough time (t_b), effluent volume (V_{eff}), total heavy metal mass removed (q_{total}), total heavy metal mass passing through the column (m_total), biosorption capacity (q_e), and metal removal efficiency (R) [17]. Breakthrough time (t_b) is the time the Cu^{2+} concentration in the effluent (C_e) reaches 10% from the initial value (C_0) and it is usually obtained by using the linear interpolation method to estimate the intermediate value of two data points assumed to be in a straight line after which mathematical calculations would be conducted using the TREND formula in Excel. Moreover, the effluent volume, V_{eff} (mL), was calculated using Eq. 1:

$$\mathbf{V_{eff} = Q \times t_{total}} \tag{1}$$

The total mass of metal ($\boldsymbol{q_{total}}$) absorbed by the immobilized biosorbent in the column at a given flow rate ($\boldsymbol{Q}$) and initial concentration of waste was obtained by integrating the plot of the concentration removed ($\boldsymbol{C_{ad}}$) on the flow time ($\boldsymbol{t_{total}}$) to form Eq. 2:

$$\mathbf{q_{total} = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} C_{ad}\,dt = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} (C_0 - C_e)\,dt} \tag{2}$$

Integrating Eq. 2 leads to Eq. 3 :

$$\mathbf{q_{total} = \frac{Qt_{total}(C_0 - C_e)}{1000}} \tag{3}$$

By using Eq. 1 where the effluent volume through column $\left(\boldsymbol{V_{eff}}\right) = \boldsymbol{Q} \times \boldsymbol{t_{total}}$, Eq. 3 was rearranged to have Eq. 4:

$$\mathbf{q_{total} = \frac{(C_0 - C_e)V_{eff}}{1000}} \tag{4}$$

The total mass of the metal passing through the column ($\boldsymbol{m_{total}}$) was determined using the following Eq. 5:

$$\mathbf{m_{total} = \frac{C_0 Q t_{total}}{1000}} \tag{5}$$

Biosorption **capacity was** calculated **using Eq.** 6:

$$\mathbf{q_e = \frac{q_{total}}{M}} \tag{6}$$

Where $\boldsymbol{M}$ is the weight of the immobilized biosorbent (g).

It is possible to obtain the value of $\boldsymbol{q_{total}}$ from Eq. 2 and 3 as well as through the calculation of the area under the curve ($\boldsymbol{A}$). This involves determining the amount/concentration of substances entering the column, $\boldsymbol{A_{1t}}$, and those coming out as effluent, $\boldsymbol{A_{2t}}$.

$$\mathbf{A_{1t} = C_0 \times t_n} \tag{7}$$

$$\mathbf{A_{2t} = (A_{2t})_{n-1} + \left\{\left(\frac{C_n + C_{n-1}}{2}\right) \times (t_n - t_{n-1})\right\}} \tag{8}$$

By using Eq. 7 and 8, the value of $\boldsymbol{q_e}$ is obtained through the equation:

$$\mathbf{q_e} = \frac{\mathbf{Q(A_{1t}-A_{2t})}}{\mathbf{M}} \tag{9}$$

The total removal or removal efficiency can, therefore, be calculated based on the ratio of the total mass of the adsorbed metal ($\boldsymbol{q_{total}}$) to the total metal mass sent through the column ($\boldsymbol{m_{total}}$) as shown in Eq. 10:

$$\textbf{Total Removal (R)} = \frac{\mathbf{q_{total}}}{\mathbf{m_{total}}} \times \mathbf{100}\ \% \tag{10}$$

Analysis of Isotherm Adsorption in Fixed Bed Column Reactor

The column performance on Fixed Bed Column Reactor was analysed using the Thomas Model involving the use of experimental data to predict breakthrough curves, kinetic rate constants, and column adsorption capacity [18, 19]. This is one of the most common and widely used models in describing the behaviour of the biosorption process in a Fixed Bed Column Reactor compared to other prediction models [17, 20, 21]. It assumes the adsorption equilibrium occurs following the Langmuir isotherm and that there is no axial dispersion by assuming the rate of driving force follows the kinetics of second-order reciprocal reactions [18, 19, 22 - 25]. The Thomas model form is as follows:

$$\mathbf{ln}\left(\frac{\mathbf{C_o}}{\mathbf{C_e}} - \mathbf{1}\right) = \frac{\mathbf{k_{Th} q_T M}}{\mathbf{Q}} - \frac{\mathbf{k_{Th} C_0}}{\mathbf{Q}} \tag{11}$$

$\boldsymbol{C_o}$ = initial influent concentration (mg/L), $\boldsymbol{C_e}$ = concentration of solute in effluent (mg/L), $\boldsymbol{k_{Th}}$ = Thomas rate constant (L/mg.minute), $\boldsymbol{Q}$ = volumetric flow rate (L/min), $\boldsymbol{q_T}$ = maximum absorption (mg/g), $\boldsymbol{M}$ = mass of adsorbent (g), $\boldsymbol{V}$ = processed volume (L), Kinetic coefficient, $\boldsymbol{k_{Th}}$ and maximum adsorption capacity, while the $\boldsymbol{q_T}$ was obtained by plotting $\boldsymbol{ln}[(\boldsymbol{C_o}/\boldsymbol{C_e}) - \mathbf{1}]$ on $\boldsymbol{t}$.

Results and Discussion

The biosorption characteristic parameters such as breakthrough time (t_b), total adsorbed metal weight (q_{total}), total weight of metals passing through the column (m_{total}), biosorption capacity (q_e) and percentage of heavy metal that can be removed (R) as listed in Table 2 are shown in the breakthrough curve in Fig. 1. Moreover, the bed height was discovered to affect immobilized biosorbent's adsorption ability in fixed-bed column reactors based on the breakthrough curve formed. This was observed with the increment in the adsorption ability as the bed height increased. Furthermore, the curve was found to become steeper as the bed height increased from 2.5 to 5 and then to 7.5 cm.

Fig. 1 also shows the initial concentration of adsorbate (C_e/C_o) increased over time (t) to reflect the biosorption event occurring during the passage of the feed solution through the column containing the immobilized biosorbent. It is important to note that the adsorbate absorption started at the beginning of the column while the adsorption reaction zone increasingly moved with the biosorbent saturation at the bottom as shown in Fig. 3. Furthermore, the breakthrough concentration of 10% C_0 was obtained when the adsorption zone reached the effluent point. The time required to attain the breakthrough point (t_b) is an important parameter in this research.

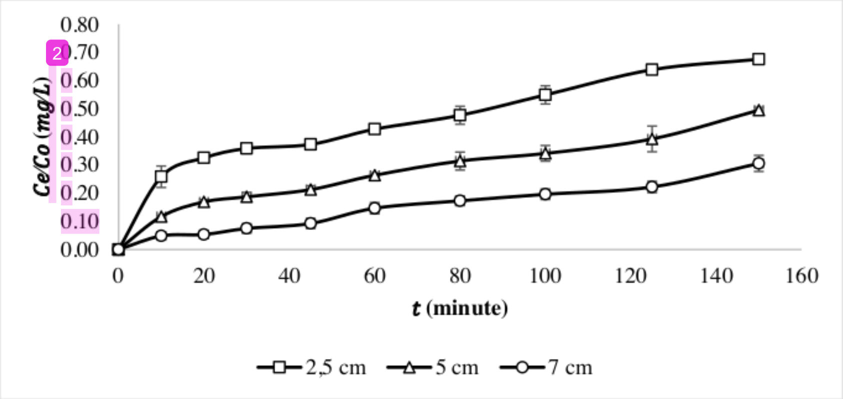

Fig. 1. Breakthrough curve for biosorption of Cu^{2+} metal ion by immobilized biosorbent with bed height variation

Table 1. Breakthrough curve parameters for biosorption of Cu^{2+} metals with a biosorbent concentration of 0.5 g/g of polymer

Bed Height (cm)	***M*** (g)	t_b (minute)	m_{total} (mg)	q_{total} (mg)	q_e (mg/g)	***R*** (%)
2.5	99	3.87	29.348	15.752	0.0940	53.67
5.0	192	8.53	29.348	20.962	0.1095	71.43
7.5	297.5	20.6	29.348	24.830	0.1180	84.61

Different results were obtained for the breakthrough time of each reactor while varying the bed height as shown in the curve. This means a steeper curve shape indicates a faster time (t_b) is required to reach the breakthrough concentration. This is evidenced by the results of the data calculated in Table 2 that showed a bed height of 2.5 cm requires 3.87 minutes to achieve concentration ($C_e/C_0 = 0,1C_0$). This is faster compared to 5 cm requiring 8.53 minutes, and 7.5 cm that needed 20.6 minutes. This is an important parameter in analysing biosorption performance due to its ability to show how fast a bed column gets saturated and a higher value means the bed column is better because it takes a longer time to saturate.

Table 1 also shows the total mass of Cu^{2+} metals entering the column (m_{total}) has a fixed value of 29.348 mg. This means all the variations of concentration have the same total mass entering the column and the values were obtained by multiplying the initial concentration of Cu^{2+} metal with the total reactor operating time of 150 minutes.

Based on Table 1, the total mass of Cu^{2+} adsorbed (q_{total}) was observed to be increasing from 15.752, 20.962, to 24.83 mg for 2.5, 5. and 7.5 cm respectively. In addition, the biosorption capacity (q_e) also changed along with the increase in the total mass of the adsorbed metal (q_{total}) in accordance with the relationship provided in equation (6). Table 2 further shows the value was increasing from 0.094, 0.1095, to 0.118 mg/g for each bed height of 2.5, 5, and 7.5 cm respectively.

Table 1 also indicates the removal efficiency (%R) of heavy metal Cu^{2+} increased as observed in the values for 2.5, 5, and 7.5 cm which was 53.67%, 71.43%, and 84.61% respectively. This means an increase in the bed heights led to the increment in the removal efficiency of the metal.

The analysis of these data showed a greater bed height has the more sloping breakthrough curve and this consequently led to an increase in the breakthrough time, the total mass of absorbed adsorbate, and biosorption capacity. This was evident in the fact that the highest biosorption capacity was 0.118 mg/g at a bed height of 7.5 cm followed by 0.1095 mg/g while the lowest was recorded in the 2.5 cm with 0.094 mg/g. The same was observed with the removal efficiency as well as other parameters mentioned.

This relationship could be due to several things, for example, the increase in adsorbate absorption ability is associated with the increasing number of immobilized biosorbents used and this is in line with previous studies that showed these are required to reach a certain height [26] such that the desire for higher bed requires more biosorbent and, consequently, more biomass which further causes increased adsorbate adsorption capacity.

The improvement in the biosorption capacity because of the increase in bed height has also been reported to be due to the increment in the contact time between the feed solution and the immobilized biosorbent at the same flow rate. At 7.5 cm, the longer contact time was observed to bind the adsorbate contained in the feed solution compared to 2.5 cm and 5 cm and this was reported to have caused more absorption.

In addition to affecting the biosorption capacity of Cu^{2+} metals, bed height variations also affected the column saturation. At the same influent concentration and flow rate, a lesser bed height has the tendency of making the column saturate quickly as shown in Fig. 1 where 2.5 cm has a greater increase in concentration towards the initial value in comparison with 5 and 7.5 cm. Moreover. The saturation occurred because immobilized biosorbents were no longer able to absorb the adsorbate contained in the feed solution. This, therefore, means a higher bed requires more time to saturate and that sorption capacity is very dependent on the amount of biosorbent available for absorption.

Similar research was conducted by [14] on the effect of bed height on adsorption capacity by the mobile biosorbent of *Sargassum tenerrimum* with the bed heights varied at 15, 20 and 25 cm to absorb adsorbate at an initial concentration of 100 mg/l and a flow rate of 5 ml/min. Even though the same results were obtained with this study regarding the parameters, the absorption capacity was found to be higher with 67.96, 68.46, and 68.76 mg/g, respectively. This means the absorption of metals in fixed-bed columns is strongly influenced by the amount of biosorbent and the differences in the values obtained are associated with their mobile and immobile natures. This research proves beads made from a microbial consortium consisting of *Saccharomyces cerevisiae* and 3 species of microalgae, *Chlorella sp, Ankistrodesmus braunii, and Scenedesmus quadricauda*, have an active side of metal binder which is more effective to increase the metal absorption capacity compared to the findings of previous studies.

The kinetics of Cu^{2+} metal absorption in this research were studied using the Thomas model and it involved applying the data from bed height optimization to describe biosorption events in the Fixed Bed Column Reactor. This model has the ability to predict the operating time with a known concentration of metal ions [20]. However, the bed heights were optimized based on the changes in the concentration of Cu^{2+} metal contained in the effluent over a period of time as shown in Table 2.

Table 2. Determination of the optimum bed height is based on changes in the concentration of Cu^{2+} metal in the effluent

Operating time, t_s (minute)	Concentration of Cu^{2+} metal in effluent, C_e (mg/L)		
	$Z = 2.5$ cm	$Z = 5$ cm	$Z = 7.5$ cm
0	0.000	0.000	0.000
10	3.880	1.758	0.728
20	4.884	2.538	0.801
30	5.383	2.809	1.123
45	5.602	3.193	1.389
60	6,413	3,958	2,200
80	7,152	4,717	2,595
100	8,239	5,123	2,944
125	9,580	5,893	3,334
150	10,137	7,427	4,587

Based on the data in Table 2, $ln(C_0/C_e - 1)$ was plotted on the operating time (t_S) at a flow condition of 13 ml/min and an initial waste concentration of 15 mg/L to form the data distribution. Moreover, a linear regression analysis was conducted to draw a straight line between the distributed data at different variations of the biosorbent concentration as shown in Fig. 2.

The figure, therefore, indicates the distribution of points $\ln(C_0/C_e - 1)$ has a value that decreases with operating time (t_S). The closeness of the relationship between the linear regression line and the distribution point is shown by the coefficient of determination (R^2). Moreover, an equation was produced from the linear regression line to determine the kinetic parameters of the Thomas model in the form of the Thomas rate constant (K_{Th}) and the maximum metal concentration in the adsorbent (q_T) from the slope and intercept of the equation respectively and the values obtained are presented in Table 3.

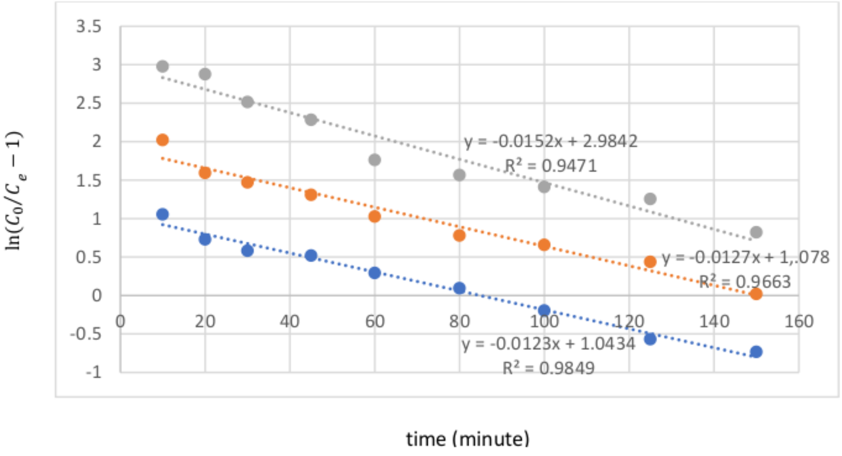

Fig. 2. Plot of $ln(C_0/C_e - 1)$ towards operating time (T_S) on bed height variation

According to Table 3, the maximum adsorption capacity obtained from the Thomas Model ($q_{e_{kal}}$) was increasing with the bed height from 2.5 to 7.5 cm. This, therefore, further confirms a higher bed leads to greater adsorption capacity for the column since the highest value of 1,734 mg/g was recorded for 7.5 cm. However, Thomas's kinetic rate constant shows a decrease in value while the bed height was increased.

Table 3. Thomas model parameters and comparison
between calculated maximum adsorption capacity ($\boldsymbol{q_{e_{kal}}}$) and research results ($\boldsymbol{q_{e_{eks}}}$)

Bed Height	M (g)	Equation y = ax +b	K_{Th} ($\times 10^{-5}$)	$q_{e_{kal}}$	$q_{e_{eks}}$	R^2
2.5	99	y = 0.0123x + 1.0434	19.66	0.0552	0.0069	0.985
5.0	192	y = - 0.0127x + 1.9078	8.91	0.9905	0.0078	0.966
7.5	297.5	y = - 0.0152 + 2.9842	3.69	1.7346	0.0122	0.947

The maximum adsorption capacity of the Thomas model ($q_{e_{kal}}$) is not much different from the value obtained from the research while the increase in the model's values for columns with 2.5 to 7.5 gr/gr of polymer heights is the same with those observed with the bed height optimization. This means the Thomas model has the ability to predict biosorption events in the Fixed Bed Column Reactor. Furthermore, the R^2 at 2.5, 5, and 7.5 cm were 0.985, 0.966, and 0.947, respectively and this indicates biosorption was most effective at least height.

The prediction of breakthrough curves at different bed heights was conducted using Thomas model parameter data as shown in Fig. 3.

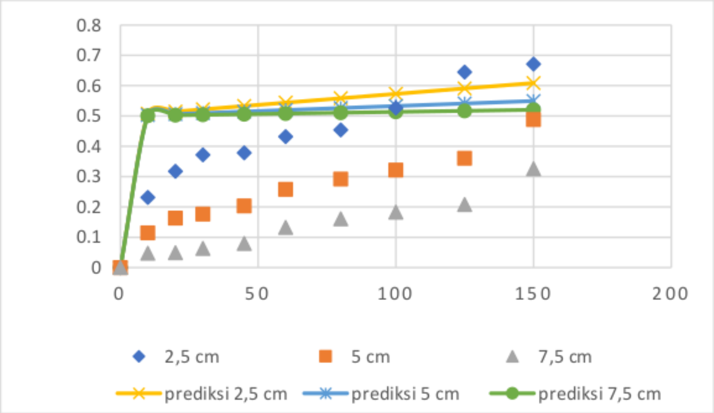

Fig. 3. Comparison between the breakthrough curve of research result
and thomas model prediction (*symbol: research data; line: model calculation results*)

A good closeness is observed between the breakthrough curve predicted by Thomas model and actual results for all heights as shown in Fig. 3. This is, however, applicable to the range of $(C_e/C_0) > 0{,}5$ while the difference in the results is more obvious with $(C_e/C_0) < 0{,}5$. This, therefore, means the model only has the ability to predict the performance at the end of the breakthrough curve but unable to properly act on the beginning.

Conclusion

The best biosorption column performance was shown by biosorbents formed by 0.5 g of biomass per g of the polymer at a bed height of 7.5 cm. This was observed from the t_b and q_{total} values of 7.34 minutes and 19,474 mg of Cu^{2+} for the 0.5 g/g of polymer and 20.6 minutes and 0.118 mg/g for 7.5 cm, respectively. This is supported by the sloping breakthrough curve showing this condition is the longest to be saturated. Moreover, Thomas's model was applied to describe the biosorption events in the columns and predict the appropriate designs. The biosorption kinetics were found to have a coefficient of determination (r^2) of 0.985, 0.966, and 0.947 for 2.5, 5, and 7.5 respectively. However, the model only has the ability to describe the end of a good breakthrough curve $(C_e/C_0 > 0{,}5)$. Therefore, further research should focus on studying the biosorption kinetics using other models to predict better initial performance of the breakthrough curve.

Acknowledgments

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