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Removal Continuous Studies of Chromium (VI) Using Sugar Cane Bagasse

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In this work was studied the behavior of biosorption process of chromium from aqueous solutions onto modified sugar cane bagasse packed bed columns. The performance of packed beds is described through the concept of the breakthrough curve. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of a biosorption column. Four mathematical models; Adams–Bohart, Thomas, Dose-answers and Yoon–Nelson models were applied to experimental data to predict the breakthrough curves and to determine the characteristic parameters of the column useful for process design. The experimental data show the breakthrough increased meanwhile the feed flow decreased and the packed bed lengths. The breakthrough curve study show the Adams–Bohart model could be used for the description of the initial part of the breakthrough curve. The dose-answers models reproduced the entire breakthrough curve.

1. Introduction

Industrial effluents are the major sources for contamination of water resources by heavy metals. Chromium (Cr) compounds are widely used by many industries such as electroplating, leather tanning, paint and pigments, metal finishing, resulting in a large quantity of this element being discharged into effluent industrial wastewaters (Singh et al., 2001).
According to Kaimbi and Chirwa (2015), most of the anthropogenic Cr discharged to the environment is in the hexavalent state since most human activities oxidise chromium ore (Cr(III)) to chromates and dichromates (Cr(VI)). The detoxification of Cr therefore involves reduction of Cr(VI) to Cr(III). However, for in situ bioremediation systems, this causes accumulation of the Cr(III) precipitate, $Cr(OH)_3(s)$. Cr(VI) easily combines with oxygen to form water soluble, negatively charged oxyanions such as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) which adsorb to positively charged species in contrast to cationic metal species (Scialdone et al., 2014).
Compounds of Cr(VI) are very mobile, so they readily enter into underground waters and make them poisonous. Moreover, the hexavalent form Chromium, is generally considered more toxic than the trivalent form, since its salts are very soluble and can be easily absorbed and accumulated in the human body, causing skin irritation, lung cancer, and kidney, liver or gastric damage (Marrugo et al., 2015). The recommended limit of Cr(VI) in potable water is 0.1 mg/L (Zghida et al., 2003) and removal of Cr(VI) from water and wastewater has been a great challenge for environmental scientists (Arivoli et al., 2007).
The most common method is chemical precipitation; this method requires relatively high amount of chemical usage, accumulation of concentrated sludge with obvious disposal problems, and expensive plant requirements or operational costs. Other processes include chemical coagulation/flocculation, oxidation, ion

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exchange, precipitation, evaporation, reverse osmosis, electrodialysis, membrane separation and solvent extraction (Chen et al., 2010). According to Gavrilescu (2004) these methods are relatively expensive, with high costs of operation and energy requirements.
The removal of metal ions from effluents is of importance to many countries of the world both environmentally and for water re-use. The application of low cost sorbents such as carbonaceous materials, agricultural products and waste by-products has been investigated (Nguyen and Do, 2001). In recent years, agricultural by-products have been widely studied for metal removal from water. These include peat (Ho and McKay, 2000), pine bark (Al-Asheh and Duvnjak, 1997), banana pith (Low et al., 1995), rice bran, soybean and cottonseed hulls (Marshall and Johns, 1996), peanut shells (Wafwoyo et al., 1999), olive stone (Blázquez et al., 2011). The mechanism of binding by inactivated biomass may depend on the chemical nature of pollutant (species, size and ionic charge), type of biomass, its preparation and its specific surface properties and environmental conditions (pH, temperature, and ionic strength, existence of competing organic or inorganic ligands in solution). In this work has been study the biosorption of Chromium (VI) using packed bed column using chemical modified bagasse (BMC) and it been applied several mathematical models to describe the breakthrough curve to obtain the parameters to define this biosorption behavior.

2. Material and methods

2.1 Preparation of biosorbent

Sugar cane bagasse (SCB) is a waste byproduct from sugar milling. The SCB used in this work was supplied by the pilot plant “Jose´ Marti” located in Central University “Marta Abreu” of Las Villas, Cuba. For the modification process, H_2SO_4 was used to try to increase the proportion of active surfaces and to eliminate soluble components, such as tannins, resins, reducing sugars, and colorings agents. For this treatment, the sugarcane bagasse was suspended during 3 h with 0.5 M sulphuric acid with a solid–liquid relation of 0.025 g/mL at 25 °C, and agitated on a shaker at 240 rpm. After treatment, the biomass was separated and washed with Milli-Q water until the pH of the washings reached neutrality. After washing, the biomass (BMC) was dried in a hot air oven at 40 °C and used in characterization experiments and tested for chromium biosorption capacity (Martín-Lara et al., 2010).

2.2 Preparation of chromium (VI) solutions

Analytical reagent grade of $K_2Cr_2O_7$ was used by preparing the synthetic wastewater. It was prepared by diluting the $K_2Cr_2O_7$ with distilled water to desired concentrations. The pH of the solution was adjusted to 2 by addition of NaOH (0.1 mol/L) or HCl (0.1 mol/L) solutions (Aloma, 2012).

2.3 Process simulation

The use of software "PSI", which allowed model, simulate and scale the chemical reaction stages, were developed mathematical methods and procedures for evaluating and predicting the behavior of dangerous reactions; achieving integrated designs of the reactors that minimize the consumption of material resources, reduce waste disposal to the environment and ensure more security when working with hazardous substances. The column was a simple glass column reactor with an inner diameter (ID) = 15 cm, length (L) = 50 cm, length of the biosorbent packed bed (L’) = 20 cm, biomass particle size = 0.5 -1 mm.
The Chromium (VI) solution at a known concentration and flow rate was passed continuously through the stationary bed of biosorbent. Samples were taken from the effluent at timed intervals and analyzed for Chromium (VI) as described below. The experiment was continued until a constant concentration of Chromium (VI) was obtained.

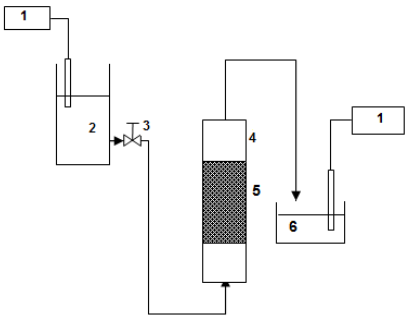

Figure 1: Experimental arrangement for operating the biosorption packed-bed column: (1) pH measurement, (2) stock container with $K_2Cr_2O_7$-solution (20 L), (3) one-way-valve, (4) glass column, (5) packed biosorbent, (6) stock collector

The studies were performed at a constant temperature of 25 °C to be representative of environmentally relevant conditions. All the experiments were carried out in duplicates and the average values were used for further calculations. Column effluent samples were collected and the pH was recorded (Aloma, 2012). The chromium concentrations to determine the removal percent in column were determined using Atomic Absorption Spectrophotometer SpectrAA 220 SS Varian. Figure 1 illustrates the experimental arrangement.

3. Results

3.1 Optimal conditions of the wastewater treatment process

A column study was conducted for 450 min, an influent pH of 2 and a flow rate of 2 mL/min. The plots of the ratio of effluent to influent copper ion concentration (C/C_0) versus time (breakthrough curves) for BMC are shown in Figure 2.

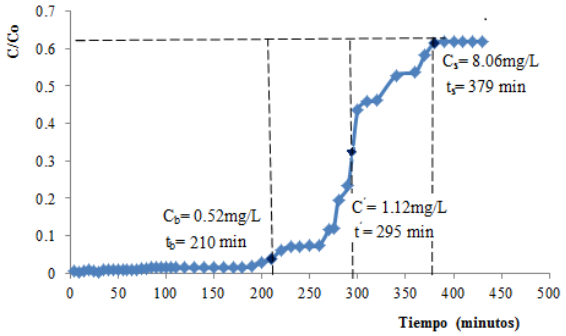

Figure 2: Obtained breakthrough curve for the biosorption of Cr (VI) to the exit of the packed-bed column

The main parameters of the column were breakthrough time (t_b), total quantity of metal removal (q_{total}), total quantity of metal that passes through the column (m_{total}), biosorption capacity (q_e), and percentage of metal removal (%R), calculated and reported in Table 1.

*Table 1: Characteristic parameters of the breakthrough curves for Cr (VI) in packed-bed column using BMC**

Metal	C_o (mg/L)	t_b (min)	LUB (cm)	C_b (mg/L)	q_{total} (mg)	m_{total} (mg)	%R	q_e (mg/g)	C_e (mg/L)
Cr (VI)	13.0	210.0	9.45	0.52	4.9	5.2	96.0	0.98	7.5×10^{-4}

*C_0: initial concentration; C_b: concentration in rupture point; t_b: time of rupture point; LUB: length of unused bed.

The volume of the effluent, V_{ef} (mL), can be calculated through the following Eq(1):

$$V_{ef} = Q \cdot t_{total} \quad (1)$$

where t_{total} is the total time in min, Q is the flow rate which circulates through the column in mL/min. The area under the breakthrough curve represents the total mass of metal biosorbed, q_{total}, in mg, for a given feed concentration and flow rate and it can be determined by integration of the Eq(2).

$$q_{total} = \frac{Q}{1{,}000} \int_{t=0}^{t=t_{total}} C_R . dt \quad (2)$$

where C_R is the concentration of metal removal in (mg/L).
The total amount of metal ions sent to the column, in mg, can be calculated from the following expression:

$$m_{total} = \frac{C_0 \cdot Q \cdot t_{total}}{1{,}000} \quad (3)$$

and the total metal removal (%) can be calculated from the ratio of metal mass biosorbed (q_{total}) to the total amount of metal ions sent to the column (m_{total}) as appear in Eq(4):

$$\%R = \frac{q_{total}}{m_{total}} . 100 \quad (4)$$

The amount of metal biosorbed at equilibrium or biosorption capacity, q_e (mg of sorbated metal/g of sorbent), and the equilibrium metal concentration, Ce (mg/L) can be determined using the Eq(5) and Eq(6) as follow:

$$q_e = \frac{q_{total}}{m} \quad (5)$$

$$C_e = \frac{m_{total} - q_{total}}{V_{ef}} \quad (6)$$

where *m* is the mass of sorbent (g).
The calculation of the not used bed surface obtained by the Eq(7) constitutes a method to evaluate the capacity of biosorbents adsorption in packed bed suggested by Ruthven (1985).

$$\mathrm{LUB} = \mathrm{H}.\left(\frac{t_s - t_b}{t_s}\right) \quad (7)$$

where L_0, represents the height of the bed, (cm); t_s, represents the time at which the saturation of the bed is reached, (min); and tb, represents the time to breakthrough point of the bed is reached, (min).
The breakthrough point was choose 0.52 mg/L, considering the concentration establish by standard spilled (Cr (VI) standard spilled: 0.5 mg/L), following the criteria establish by Tenorio (2006) which establish to select an arbitrary low level of concentration like a breakthrough point.

3.2 Determination of kinetic parameters

The dynamic behavior of the column was predicted with the Bohart-Adams, Yoon-Nelson, and Thomas models. The breakthrough curves showed the superposition of experimental results and the theoretical calculated points. The experimental data's were processed and adjusted by Software MATLAB 2007 (Figure 3).

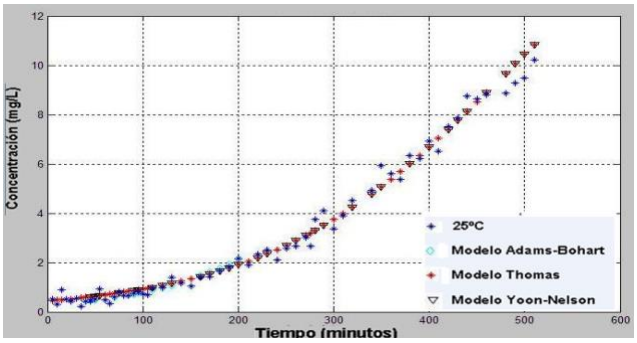

Figure 3: Experimental and predicted breakthrough curves obtained according to the Adams–Bohart; Thomas; Dose-answer and Yoon-Nelson models (Temperature: 25 ºC, C_o: 13 mg/L, initial pH: 2)

3.3 Application of the Adams–Bohart model

The Adams–Bohart sorption model was applied to experimental data for the description of the initial part of the breakthrough curve. The mass transfer rates obey the following equations:

$$\frac{dq}{dt} = -k_{AB} \cdot q \cdot C_b \quad (8)$$

$$\frac{dC_b}{dZ} = \frac{-k_{AB}}{U_o} \cdot q \cdot C_b \quad (9)$$

where k_{AB} is the kinetic constant (L/mg·min). Some assumptions are made for the solution of this differential equation systems:

- The concentration field is considered to be low, e.g. effluent concentration $C < 0.15C_o$.
- For $t \rightarrow \infty$, $q \rightarrow No$, where No is the saturation concentration (mg/L).

When the differential equation systems solved, the following equation Eq(10) is obtained with parameters k_{AB} and N_o:

$$ln\frac{C}{C_0} = -k_{AB}.C_o.t - k_{AB}.N_o.\frac{Z}{U_o} \quad (10)$$

where C_o and C are the inlet and effluent Chromium concentrations (mg/L), respectively. From this equation values describing the characteristic operational parameters of the column can be determined from a plot of ln C/C_o against t at a given bed height and flow rate.
After applying Eq(10) to the experimental data for 2 mL/min flow rates and inlet Chromium concentration 13 mg/L, a linear relationship between ln C/C_o and t was obtained for the relative concentration region up to 0.5, i.e. up to 50 % breakthrough, for all breakthrough curves (R^2 = 85.9). Respective values of N_o and k_{AB} were

calculated from the ln C/C_o versus t plots; the flow rate and inlet Chromium concentration studied are presented in Table 2 join with the correlation coefficient.

3.4 Application of the Tomas model

Successful design of a column adsorption process requires prediction of the concentration–time profile or breakthrough curve for the effluent. The maximum adsorption capacity of an adsorbent is also needed in design. Traditionally, the Thomas model is used to fulfill the purpose. The model has the following form:

$$\frac{C}{C_o} = \frac{1}{1+exp\left[\frac{K_{Th}}{Q}.(q_o.X - C_o.V_{eff})\right]} \quad (11)$$

where k_{Th} is the Thomas rate constant (mL/min·mg) and q_o is the maximum solid-phase concentration of the solute (mg/g).

Application of this model to the data at C/Co ratios higher than 0.08 and lower than 0.97 with respect to flow rate and inlet Chromium concentration enabled the determination of the kinetic coefficient in this system.

A linear regression was then performed on each set of transformed data to determine the coefficients from slope and intercept. Inspection of each of the regressed lines indicated that they were all acceptable fits with linear regression coefficient of 92.76. The values of k_{Th} and q_o are presented in Table 2. The Thomas model is suitable for adsorption processes where the external and internal diffusions will not be the limiting step.

3.5 Application of the Yoon and Nelson model

A simple theoretical model developed by Yoon–Nelson was applied to investigate the breakthrough behavior of Chromium on immobilized BMC. The values of k_{YN} (a rate constant) and τ (the time required for 50 % adsorbate breakthrough) were determined from ln[C/(Co − C)] against t plots, at 2 mL/min and 13 mg/L inlet Chromium concentration. The values of k_{YN} and τ are also listed in Table 2; the data indicate that τ values (τ 194.6 min) is to close to the experimental result (t = 200 min). The theoretical curve is compared with the corresponding experimental data in Figure 3. The experimental breakthrough curve was very close to that predicted by the Yoon–Nelson model. From the experimental results and data regression (R^2 = 92.8), the model proposed by Yoon–Nelson provided a good correlation of the effect of inlet Chromium concentration and flow rate.

3.6 Application of the Dose-answer model

The dose-response model has been commonly used in pharmacology to describe different processes; nowadays it is used to describe the behavior of biosorption using fixed bed columns (Yan et al., 2001) and (Senthilkumar et al., 2006). The model has the following form:

$$Y = b_o - \frac{b_o}{1+\left(\frac{X}{b_2}\right)^{b_1}} \quad (12)$$

where X and Y represented the dose and answer in high percentage of possible answer; b_0 is the expecting answer at saturated concentration; b_1 is the slope of the function and b_2 is the concentration which gain the half of the maximum answer. The linearized form of the Dose-answer model is as follows:

$$ln\left(\frac{C}{C_i - C}\right) = a.\ln V_{eff} - a.\ln\left(\frac{q_o.m}{C_i}\right) \quad (13)$$

After applying Eq(13) to the experimental data for 2 mL/min flow rates and inlet Chromium concentration 13 mg/L, a linear relationship between ln (C/Ci - C) versus Volume or time was obtained the models parameters *a* and q_o represented in Table 2. The results show that this model reproduces the breakthrough curves in an acceptable way (R^2 = 95.8). This model reproduces the complete breakthrough curves quite well in general.

Table 2: Parameters predicted from the Adams–Bohart; Thomas; Yoon-Nelson and Dose-answer models[*]

Me-tal	C_o (mg/L)	Bohart-Adams			Thomas			Yoon-Nelson			Dose-answer		
		R^2	k_{AB} (L/mg ·min)	N_o (mg /L)	R^2	K_{Th} (mL/mg ·min)	q_o (mg /g)	R^2	k_{YN} (L/mg ·min)	τ (min)	R^2	a	q_o (mg /g)
Cr(VI)	13	85.9	0.005	59.5	92.76	0.96	2.57	92.8	0.013	194.6	95.9	3.31	2.33

[*]Temperature: 25 ºC; C_o: 13 mg/L; pH: 2

4. Conclusions

The biosorption of Chromium (VI) from aqueous solution on chemical modified bagasse was investigated in a continuous packed bed column. The Adams–Bohart; Thomas; Yoon–Nelson and Dose-answer models were applied to experimental data obtained from dynamic studies performed on fixed column to predict the

breakthrough curves and to determine the column kinetic parameters. The initial region of breakthrough curve was defined by the Adams–Bohart model and Dose-answer model reproduces the complete breakthrough curves with R^2 of 95.9. The model constants belonging to each model were determined by linear regression techniques and can be used in column design.

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