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Computer-aided Modeling and Evaluation of a Packed Bed for Chromium (vi) Removal using Residual Biomass of *Theobroma Cacao* L.

Ángel Darío González-Delgado[a], Candelaria Tejada-Tovar[b,*], Angel Villabona-Ortíz[b]

[a]Chemical Engineering Department, Nanomaterials and Computer-Aided Process Engineering Research Group (NIPAC), Universidad de Cartagena, Avenida del Consulado St. 30, Cartagena de Indias 130015, Colombia
[b]Chemical Engineering Department, Process Design and Biomass Utilization Research Group (IDAB), Universidad de Cartagena, Avenida del Consulado St. 30, Cartagena de Indias 130015, Colombia
ctejadat@unicartagena.edu.co

The use of residual biomass in environmental applications continues gaining attention of the scientific community, the presence of heavy metals in the environment represents a problem of interest due to their toxicity, accumulation, and persistence. Bio-adsorption allows the use of agricultural or industrial waste, it is an efficient and non-destructive method for the removal of heavy metals, making it a viable method due to its low cost and easy implementation, however, the behaviour at large scale of these biomass-based emerging technologies is unknown; in this work, the modeling and computer-aided scaling up of an industrial scale column for the adsorption of Cr (VI) present in aqueous solution on an adsorbent based on *Theobroma cacao* L. was performed using Aspen Adsorption V10 software. The parameters for the modeling were obtained from experiments performed by the authors and scientific literature. Results show parameters as flowrate of feedstock, bed diameter and bed length showed sensitivity in the performance of the breakthrough column.

1. Introduction

Heavy metals in water bodies could be concentrated in the living tissues of organisms due of bioaccumulation and magnification; thus, caused by the increase in polluted effluents product of industrial activities such as battery manufacturing, mining, smelting, refining, tanneries and soldering (Jencarova and Luptakova, 2012). Usually, Cr (VI) is found in water environments as chromate ions (CrO_4^{2-}) o dichromate ($Cr_2O_7^{2-}$), which easily crosses biological barriers, being carcinogenic, moreover, Cr (VI) is 500 times more toxic than Cr (III). Due to its toxicity, chromium causes respiratory problems, lung cancer and affects the male reproductive system (Hedberg et al., 2019). In addition, the concentration of chromium in industrial wastewater usually exceeds the threshold limit set by governing institutions, thus those effluents need to be treated in order to reduce the concentration before being discharged. Several processes are being implemented for this issue, such as membrane filtration, chemical precipitation, ion-exchange, oxidative techniques, filtration and ultrafiltration (Jencarova and Luptakova, 2012).
Adsorption is an economic process widely used to separate heavy metal at low concentrations from aqueous solution, considering it is a simple and highly efficient operation without toxic sludge generation. The use of adsorbents of agricultural and agro-industrial origin are extensively used due to their high availability and high selectivity for heavy metals (Khalil et al., 2021). Adsorption studies using agricultural and agro-industrial materials as adsorbents for removing heavy metals in a batch system, have allowed to have comprehensive isotherm data, in order to understand the interactions mechanisms between the pollutant and the adsorbent (Al-Ghouti and Da'ana, 2020). Yet, experimental approaches are costly and time-consuming and restricts the evaluation of operating variables desirable to design a packed bed column. From the isotherm equilibrium data, a viability study can be explored to prove their scalability onto a bigger proportion (Chatterjee et al., 2018).

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Packed bed columns are devices stuffed with adsorbent, in which the polluted solution flows through the bed containing the contaminant to be removed into the adsorbent surface. Then, continuous packed bed systems are preferred for industrial wastewater treatment due of their capacity for handling large volumes of polluted solution (Jafari and Jamali, 2016). It also provides information on breakthrough and exhaustion times, which are important to evaluate the feasibility of adsorbents, considering the packed beds operate until the saturation of adsorbents (Elabbas et al., 2016). The breakthrough curves information can be used for design adsorption columns, because provide information about the change of the concentration as a function of the time (Shahid et al., 2019). Nevertheless, the experimental work at big scale in continuous systems is expensive and require large intervals of time. In this sense, few studies have reported the challenge to scale, model and simulate the system for future transition from laboratory to industrial application (Igberase and Osifo, 2019; Upadhyay et al., 2021). Hence, in this present work, simulation of packed bed adsorption of Cr (VI) ion onto cocoa husk was carried out using Aspen Adsorption simulator tool to solve sets of equations of the model. Factors affecting the dynamic column performance were investigated, including the effect of as flowrate of feedstock, bed diameter, porosity and, bed length.

2. Methodology

The system of chromium (VI) ion–contaminated stream flowing through the cacao husk packed fixed bed adsorption column was simulated on the software Aspen Adsorption® V10.0. Physical properties that are crucial for execution of these simulation-based experiments were taken from data base of the investigation line, as well as bulk density, particle density, and particle size of cocoa husk. For the application of response surface methodology, software Statgraphics V19 was used.

2.1 Data collection

The data required for the simulation of the properties of the adsorbent and the adsorption isotherm were obtained from research group data collection. The Bulk density and particle size of the cocoa husk, were determined by experimentation, and are equal to 518 kg/m^3 500 µm, respectively. Freundlich parameters are shown in Table 1:

Table 1. Freundlich isotherm parameters

Model	Parameter	Value
Freundlich	K_F [(mg g^{-1})(mg L^{-1})$^{-1/n}$]	8.69
	1/n	1.53
	R^2	0.9974
	SS	0.5782

2.2 Aspen adsorption assumptions and mathematical background

Using Aspen Adsorption® V10, liquid adsorption system was used to developed the simulations, taking intoaccount the below assumptions: The behaviour of fluid across the column was assumed to be without axial dispersion; ideal mixing in the liquid phase, so molar concentrations are calculated from molar volumes; Isotherm model used was Freundlich; with an isothermal energy Balance; lumped mass-transfer rate, with a solid-film linear resistance; the film model wasfluid; there is no pressure drop through the column; constant superficial velocity; and mass transfer coefficient was assumed constant. Figure 1a shows the adsorption process as designed in Aspen Adsorption for simulation. The discretization method used in all the simulations was based on the first-order Taylor series expansion, by assuming a volume of control (V_c), considering that the column has a cylindrical configuration with an area A and height Δz. Then, the partial differential mass balance equation which was used to express the chromium ion concentration in a small control volume inside the adsorbent bed is presented in Eq(1):

$$\varepsilon \Delta Z \frac{\delta C_i}{\delta t} = (\mu_0 \varepsilon C_i)_z - (\mu_0 \varepsilon C_i)_{z+\Delta z} - \left(\varepsilon D_{L_i} \frac{\delta C_i}{\delta z}\right)_z + \left(\varepsilon D_{L_i} \frac{\delta C_i}{\delta z}\right)_{z+\Delta z} - \rho_s \Delta Z \frac{\delta Q_i}{\delta t} \quad (1)$$

In Eq(1), D_{Li} is the axial dispersion coefficient (m^2/s), ρ_s is the bed column density (kg/m^3), μ_0 is the interstitial velocity (m/s),z is the axial position (m), t is the process time (s), C_i is the concentration of pollutant in liquid-phase (kg/m^3), and Q_i is the solid-phase concentration of pulutan (g/kg) (Biswas et al., 2020).

For simulation, linear lumped resistance kinetic model was assumed, which indicates that the initial concentration is a driving force for mass transfer during adsorption process. In addition, the adsorption of chromium ions onto cocoa husk process is represented by Freundlich model as it gives a much higher R^2 value (equal to 0.99), as well as the adjustment of experimental points was closer.

2.3 Experimental design

The experiments were designed by using a Response Surface Central composite design: 2^3 + star, made in Statgraphics V.19. The independent variables and their ranges are presented in Table 2. Simulation experiments were developed for the 17 experiments in Aspen Adsorption, and the response variables, namely saturation time and exhaustion C/C_o, were obtained.

Table 2. Parameters used for simulation

Parameter	-1	0	1
Inlet flowrate, m^3/s	7.5×10^{-7}	2.88×10^{-6}	5×10^{-6}
Bed height, m	0.30	0.45	0.60
Bed diameter, m	0.06	0.072	0.084

3. Results and discussion

3.1 Establishment of the base simulation breakthrough

A base simulation for the adsorption of Cr (VII) onto cocoa husk was established as a reference point, prior to the studies on the affecting parameters. The initial values specifications are presented in Table 3, and these values will remain the same throughout the study except for the manipulated variable.

Table 3. Parameters used for base case simulation

Parameter	Value
Inlet flowrate, m^3/s	7.5×10^{-7}
Inlet concentration, mg/L	30 mg/L
Bed height, m	0.3
Bed diameter, m	0.06
Bed porosity, m^3 void/m^3 bed	0.25
Bulk density, kg/m^3	518
Constant mass transfer coefficient, 1/s	3.2×10^{-10}
Freundlich isotherm	
K_F, (mg g^{-1} (mg $L^{-1})^{1/n}$	8.69
1/n	1.53

The plot of the base-case simulation breakthrough curve is shown in Figure 1b. The plot indicates that the column achieves breakthrough time at about 118.65 s, under the conditions stated in Table 2. It is observed a common “S” shape on the simulated breakthrough.

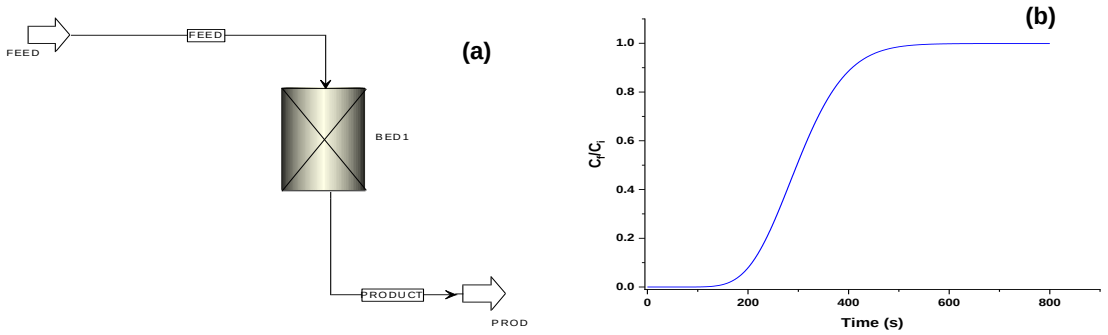

Figure 1. (a) Adsorption process flowsheet in Aspen Adsorption®, (b) Concentration ratio profile of the stream exiting from the cacao husk for the base simulation case

3.2 Analysis of variance and factors and response interactions

The regression analysis of experimental data obtained in Table 4 led to the conclusion that breakthrough time of the bed for this system can be expressed as a function of inlet flowrate, bed height and breakthrough time, via Eq(2). The same, for the case of saturation time of the bed, can be modeled by Eq.(3). In addition, the description of exhaustion C/C_o ratio, can be described by Eq(4). The predicted R^2, values were found to be very close to 1 in case of all models which indicates that the suggested models can be good predictors of the experiment results.

Table 4. Parameters used for simulation and responses

Factors				Responses		
Run	Inlet flowrate, m^3/s	Bed height, m	Bed diameter, m	Breakthrough time, s	Saturation time, s	Exhaustion C/C_o
1	2.88×10^{-6}	0.60	0.075	97.21	372.87	0.9590
2	2.88×10^{-6}	0.45	0.075	76.01	273.92	0.9503
3	5×10^{-6}	0.3	0.084	37.25	149.66	0.9791
4	7.5×10^{-7}	0.3	0.06	118.65	442.64	0.9475
5	5×10^{-6}	0.3	0.06	15.82	68.26	0.9533
6	5×10^{-6}	0.45	0.075	42.96	165.17	0.9648
7	5×10^{-6}	0.60	0.084	79.89	273.92	0.9649
8	7.5×10^{-7}	0.60	0.084	521.66	1703.49	0.9503
9	7.5×10^{-7}	0.60	0.06	252.74	883.15	0.9560
10	2.88×10^{-6}	0.3	0.075	76.02	277.79	0.9533
11	2.88×10^{-6}	0.45	0.075	73.96	279.62	0.9560
12	2.88×10^{-6}	0.45	0.084	92.34	343.	0.9503
13	2.88×10^{-6}	0.45	0.075	76.01	279.62	0.9560
14	7.5×10^{-7}	0.3	0.084	248.79	853.10	0.9503
15	5×10^{-6}	0.60	0.06	35.20	138.03	0.9503
16	7.5×10^{-7}	0.45	0.075	301.19	1023.94	0.9533
17	2.88×10^{-6}	0.45	0.06	48.88	180.67	0.9560

Table 5 show the analysis for the three evaluated responses for the breakthrough time, saturation time, exhaustion C/C_o ratio. While it was observed that, for breakthrough time and saturation time, as well as all three evaluated factors, i.e., inlet flowrate (A), bed height (B), and bed diameter (C), as well as their interaction such as AA, AB and AC, with significant factors (with P-value <0.005); for Exhaustion C/C_o ration time, there was not any significant variable. Thus, might be because, the increase of the bed height enhance the adsorption due to the growth of the amount of active sites that allow the union of the ions with the functional groups, this effect is evident in the adsorption of Cr(VI) with bed heights as shown in Figure 2.

Table 5. ANOVA for evaluated factors over response

Response	Source	Sum of square	F-Ratio	P-Value
Breakthrough time, s	A: Inlet flowrate, m^3/s	146241.0	123.22	0.0000
	B: Bed height, m	23118.1	19.48	0.0031
	C: Bed diameter, m	25891.3	21.82	0.0023
	AA	21979.5	18.52	0.0036
	AB	14890.0	12.55	0.0094
	AC	13941.3	11.75	0.0110
	BB	78.8	0.07	0.8041
	BC	2519.97	2.12	0.1884
	CC	11.78	0.01	0.9234
	Total error	8307.71		
Saturation time, s	A: Inlet flowrate	1.63×10^6	163,99	0,0000
	B: Bed height	241180.0	24,21	0,0017
	C: Bed diameter	259537.0	26,05	0,0014
	AA	227331.0	22,82	0,0020
	AB	150546.0	15,11	0,0060
	AC	129208.0	12,97	0,0087
	BB	1428.5	0,14	0,7162
	BC	20679.1	2,08	0,1928
	CC	0.11	0,00	0,9975
	Total error	69733.5		
Exhaustion C/C_o	A: Inlet flowrate, m^3/s	0,000105177	1,87	0,2142
	B: Bed height, m	0,0000133722	0,24	0,6411
	C: Bed diameter, m	0,000124238	2,20	0,1812
	AA	0,0000352913	0,63	0,4548
	AB	0,0000365513	0,65	0,4472
	AC	0,0000365513	0,65	0,4472
	BB	0,00000710613	0,13	0,7330
	BC	0,000105851	1,88	0,2129
	CC	0,0000594573	1,05	0,3386
	Total error	0,000394616		

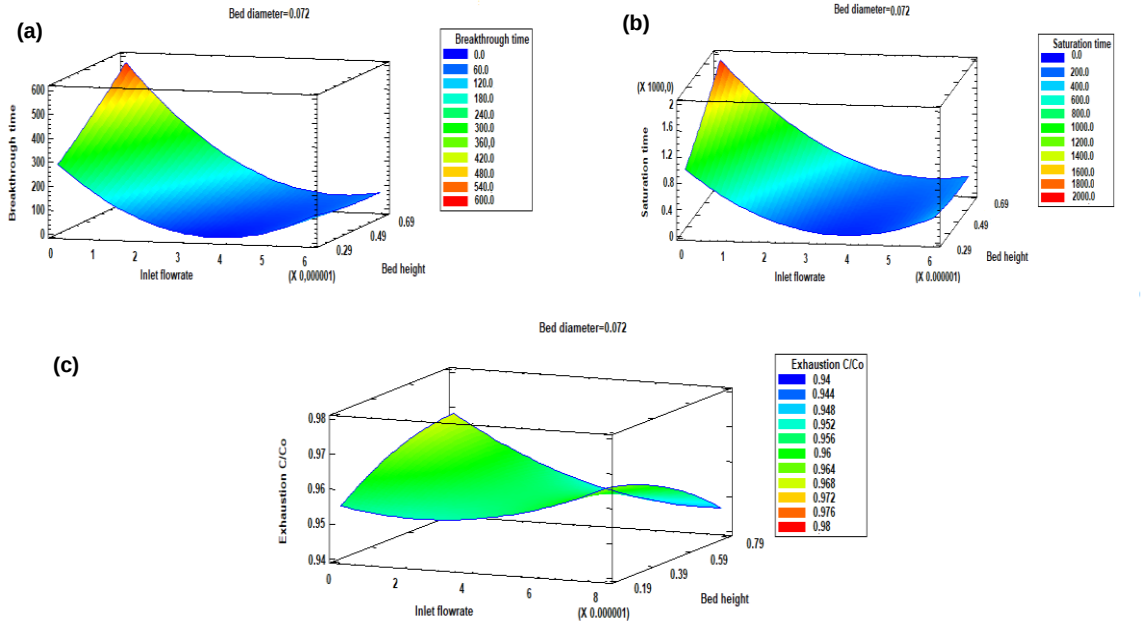

Figure 2. Three-dimensional contour plots to examine the relationship between the factors and (a) breakthrough time, (b) saturation time and (c) exhaustion C/C₀

In addition, the diminution in exhaustion C/C₀ caused by increasing in inlet flowrate and bed height, which leads to minimal change in exhaustion capacity. With respect to flow rate, it was found that increasing the inletflow rate results in the decrease in both saturation and breakthrough time, as the result of reduction in residence time of the chromium ions inside the bed which ceases the opportunity for the exchange between the ions and active adsorption centers into the micro- and mesopores of the adsorbent particles, as reported by cadmium and copper adsorption onto water hyacinth (Soriano et al., 2016). Meanwhile, the diminution of the breakthrough time with the augmentation in flowrate is related with the early exhaustion of adsorption sites, since a greater number of ions are entering into the system per unit time in addition to higher number of ions being adsorbed due to lower mass transfer resistance (Upadhyay et al., 2021). 3D contours of Figure 2, visually illustrates the behavior of response variables while varying factors.

$$BT = -118.37 + 5.71\times10^{6}F - 212.29H + 2252.48D + 2.01\times10^{13}F^{2} - 1.35\times10^{8}F\times B - 1.63\times10^{9}F\times D + 241.03H^{2} + 97.99.01H\times D + 15664.4D^{2} \quad (2)$$

$$ST = -572.41 - 1.11\times10^{7}F - 670.47H + 15250D + 6.45\times10^{13}H^{2} - 4.30\times10^{8}F\times B - 4.95\times10^{9}F\times D + 1026.24H^{2} + 28070.5H\times D - 1506.95D^{2} \quad (3)$$

$$C/C_{0} = 0.89 + 5494.02F - 0.088H + 1.88D + 3.92F^{2} - 6705.88F\times H - 83823F\times D - 0.035H^{2} + 2.02H\times D - 15.95D^{2} \quad (4)$$

4. Conclusions

The analysis of breakthrough curves by simulation in Aspen Adsorption® V10, was found that chromium removal onto cocoa a packed bed of cocoa husk shows higher performance both influent flow rate and bed height. Through the application of response surface methodology, the effect of variation in column bed height, inlet flowrate and bed diameter over the breakthrough time, saturation time time and exhaustion C/C₀ ratio of the cocoa husk packed bed was evaluated, finding great influence by all the evaluated variables and their interactions over the system.

Nomenclature

A– cross-sectional area of the packed bed, m^2
BT – the breakthrough time, s
C/C₀ – exhaustion C/C₀
D – bed diameter, m
F – inlet flowrate, m^3/s
F-ratio–relates the variances of independent samples
H – bed height, m

T – temperature, °C
P – pressure, bar
P-value–probability of obtaining the observed results
Q_i – cocoa husk adsorption capacity, mg/g
ST – the saturation time, s
w – fin width, m
z – bed axial position, m

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