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Simulation of a packed column for the removal of Pb(II) from solution using *Theobroma cacao L.* as a bioadsorbent

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Abstract: Water bodies contaminated with heavy metals have generated significant concern worldwide due to their toxicity, persistence, bioaccumulation, and non-biodegradability. Among these pollutants is Pb (II), which enters water sources primarily as a result of anthropogenic activities. Prolonged exposure to this contaminant can cause neurological disorders, as well as respiratory and urinary issues. This research aims to model an industrial-scale packed column using Computer-Aided Process Engineering (CAPE) to remove Pb (II) from an aqueous solution, using *Theobroma cacao L.* as bioadsorbent. Using Aspen Adsorption, several simulations were bperformed on adsorption columns with varying configurations at an industrial scale, evaluating the parametric sensitivity to bed height, inlet flow rate, and initial concentration. The results showed that the simulated adsorption columns achieved removal efficiencies of up to 99%. The optimal simulation conditions for the column simulation included a bed height of 5 m, an initial concentration of 3000 mg/L, and an inlet flow rate of 50 m³/day. It was observed that increasing the inlet flow rate reduced the breakthrough and saturation times of the process, while increasing the bed height extended these times. These findings demonstrate the potential of computational tools as valuable alternatives for predicting the performance of adsorption columns packed with biomass.

Introduction

Nowadays, the world faces significant challenges caused by various organic and inorganic pollutants in water bodies, which negatively affect the environment. Among these pollutants are heavy metal ions, which enter water sources primarily due to anthropogenic activities. These metals are toxic, peresistent, non-biodegradable, and carcinogenic in nature (Chakraborty et al., 2022; Vaiškūnaitė, 2024). Lead (Pb) is one such toxic heavy metal that typically enters the human body through the respiratory and digestive systems. Exposure to this contaminant can cause various adverse health effects, including neurological, respiratory, urinary, and cardiovascular disorders (Balali-Mood et al., 2021). Pb can be found in various sources, such as dust, battery vents, lead-based paints, and Pb-contaminated food. Notably, the canned food industry contributes to lead exposure due to the leaching properties of canned food (Raj & Das, 2023). In Colombia, Law 41 of 2020 stipulates that the maximum allowable concentration of lead in water is 0.0005 mg/L (Amini et al., 2005).

To recover and improve the quality of contaminated water, several methods have been developed for the removal of heavy metals from solution, including ion exchange, coagulation/flocculation, photocatalysis, electro-remediation, membrane technology, and adsorption (Znad et al., 2022). Although each method has its own advantages and limitations, adsorption has emerged as an attractive and effective option for treating wastewater contaminated with heavy metals, due to its feasibility, low cost, and high efficiency (Adegoke et al., 2022). Various adsorbent materials have been developed from agricultural residues, such as plantain peels (Mohamed et al., 2020), coconut shells (Abdul Rahim et al., 2020), and sugar cane bagasse (Yogeshwaran & Priya, 2021), among others. Among these, cocoa husks have been identified as a promising adsorbent material due to their availability, renewability, and low cost (Tejada-Tovar et al., 2022). On the other hand, computational tools have been increasingly used to model and scal treatment processes, with platforms such as Aspen Plus (Gündüz Han et al., 2023) and ChemCAD (Sánchez et al., 2019) playing a significant role. However, the modeling of packed columns remains at a preliminary stage of development.

Therefore, this research aims to model an industrial-scale packed column using *Theobroma Cacao L.* as an adsorbent, using computational tools and parametric evaluation to simulate the adsorption of Pb (II) from solution, based on experimental data previously obtained by the authors. The study demonstrates the potential of CAPE in predicting the performance of adsorption columns and provides quantitative insights for scaling and parameterizing industrial-scale packed columns using *Theobroma Cacao L.*

Methodology

Parametric evaluation of the adsorption column.

Using Aspen Adsorption as a tool to simulate the adsorption column for removing Pb (II) from wastewater, a parametric evaluation was carried out to assess the impact varying initial concentration levels (100 mg/L, 500 mg/L, 1000 mg/L, 2000 mg/L, 3000 mg/L) (Murthy et al., 2012), column height (3 m, 4 m y 5 m), and inlet flow rate (50 m^3/day, 100 m^3/day, 150 m^3/day, 200 m^3/day and 250 m^3/day) (Upadhyay et al., 2021).

Adsorption Column Configuration

Configuring the adsorption column in Aspen Adsorption involves several tabs where the column configuration is defined: General, Material/Momentum Balance, Kinetic Model, Isotherms, and Energy Balance. In the General tab, the discretization method for the simulation was specified. For this study, the UDS1 method was used with a node count of 10, as it offers excellent overall performance, reasonable accuracy, and relatively low computational time. In the Material/Momentum Balance tab, it was specified that there is no pressure drop, only convection in the liquid phase, and a constant velocity. Since only convection is considered, the UDS 1 method functions as a scheme based on a first-order Taylor expansion, described by the following equation (Soriano et al., 2017):

$$\frac{\delta \Gamma_i}{\delta z} = \frac{\Gamma_i - \Gamma_{i-1}}{\Delta z} \quad (1)$$

In the Kinetic Model tab, the Linear Driving Force (LDF) model was selected. This model assumes that mass transfer is governed by a function of the concentration, describing the rate at which the pollutant is adsorbed (Nikam et al., 2022). This model is represented by the following equation:

$$\frac{\partial w_k}{\partial_t} = MTC_{sk}(w_k^* - w_k) \quad (2)$$

MTC represents the mass transfer coefficient (m/s), and denotes the instantaneous equilibrium adsorbate loading on the adsorbent (mg/g). In the Isotherm tab, the Freundlich isotherm model was selected to describe the adsorption process, which occurs on a homogeneous surface with multiple layers (Hu et al., 2022). This model is represented by the following equation:

Table 1. Column simulation results.

Freundlich -LDF		Flow rate (m^3/day)														
		250			200			150			100			50		
		Bed height (m)														
Concentration (mg/L)	**Results**	3	4	5	3	4	5	3	4	5	3	4	5	3	4	5
3000	**R.T (min)**	563	749	935	702	935	1167	935	1244	1554	1399	1864	2328	2793	3722	4617
	S.T (min)	1223	1609	1971	1500	1971	2404	1971	2560	3134	2842	3696	4543	5343	6932	8308
200	**R.T (min)**	294	393	492	368	492	617	492	658	824	741	990	1239	1488	2015	2520
	S.T (min)	1371	1823	2253	1718	2253	2733	2253	2936	3581	3275	4228	5242	6201	7823	9642
1000	**R.T (min)**	351	469	587	439	587	734	587	784	980	882	1177	1472	1788	2383	2975
	S.T (min)	1355	1747	2132	1642	2132	2630	2132	2796	3412	3109	4042	4964	5673	7423	9171
500	**R.T (min)**	440	586	733	550	733	916	733	977	1221	1099	1466	1831	2197	2929	3661
	S.T (min)	1286	1667	2042	1568	2042	2508	2042	2647	3254	2956	3637	4501	5348	7039	8671
100	**R.T (min)**	529	685	856	660	856	1071	856	1143	1432	1287	1722	2158	2594	3468	4342
	S.T (min)	1183	1291	1645	1441	1645	2072	1645	2208	2754	2493	3313	4101	4879	6347	7802

$$q_e = k_f C_e^{1/n} \quad (3)$$

Where is the Freundlich constant, indicating the adsorption capacity ((mg/g) (ml/g)^n), is the equilibrium concentration of the contaminant in solution, and n reflects the effect of the initial concentration on the adsorption capacity. In the Aspen Adsorption, this equation is represented as follows:

$$w_i = IP_{1i} * c_i^{IP_{2i}} \quad (4)$$

By comparing the theoretical equation with the one used in the software, the following equivalences can be established: $IP_{1i} = k_f$, $IP_{2i} = 1/n$ y C_e. In the Energy Balance tab, an isothermal process was assumed. Subsequently, the necessary parameter specifications were entered to complete the configuration of the adsorption column. These values were based on studies of similar column processes for the removal of heavy metals from industrial wastewater, as well as on experimental data from studies involving the biomass Theobroma Cacao L used as the adsorbent material. The column was configured with a diameter of 1 m (Agarwal et al., 2022), a bed porosity of 0.67 m^3 vacuum/ m^3 of bed, a total void porosity of 0.4 (Benyahia & O'Neill, 2005; Dixon, 1988). The bulk density was set at 0.0365 g/cm^3, and the mass transfer coefficient was defined as 1.88*10^{-7} s^{-1} (Koua et al., 2019). The Freundlich equation constants (IP_1) and (IP_2) were set to 0.453 and 1.476, respectively (Tejada-Tovar et al., 2018).

Results and discussions

Data obtained from the simulation of the adsorption column

Aspen Adsorption was used to simulate a Pb (II) adsorption column under various configurations of column height, initial concentration, and inlet flow rate. The rupture time (R.T) and saturation time (S.T) obtained from the simulations are presented in Table 1. It was observed that both R.T. and S.T. increase with column height but decrease with higher flow rates. This behavior is attributed to the fact that, at lower flow rates and greater column hights, the fluid spends more time in contact with the adsorbent bed. This extended residence time enhances the adsorption process, resulting in longer rupture and saturation times.

Evaluation of the impact of changing the column height

The effect of varying the column height (3, 4, and 5 meters) was evaluated while keeping the initial concentration fixed at 3000 mg/L and an inlet flow rate at 50 m^3/day. As shown in Figure 1, both rupture time and saturation time increased with column height. However, the overall efficiency of the adsorption process was negatively affected. This decrease in efficiency is attributed to the longer residence time required for the fluid to pass through a taller column, which may lead to early saturation of the adsorbent near the inlet and underutilization of the lower sections of the bed (Fran Mansa et al., 2021).

Evaluation of the impact of changing the inflow rate

The effect of varying the inlet flow rate was evaluated over a range of 50 m^3/day, 100 m^3/day, 150 m^3/day, 200 m^3/day,

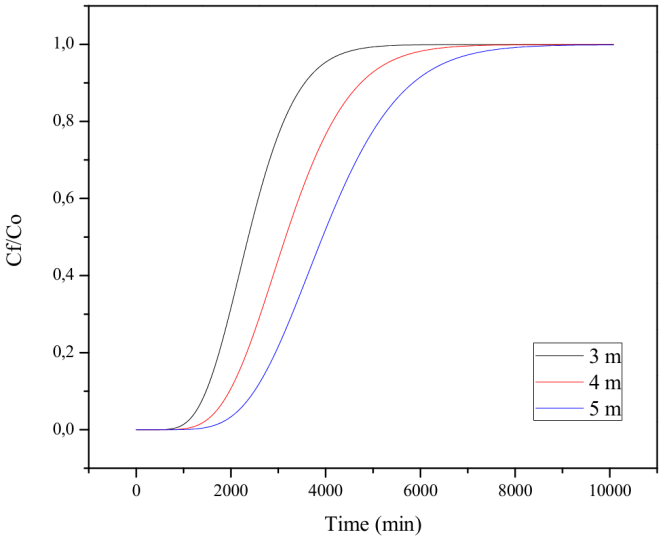

Figure 1. Rupture curves at different column heights at an initial concentration of 5000 mg/L and an input flow rate of 50 m^3/day.

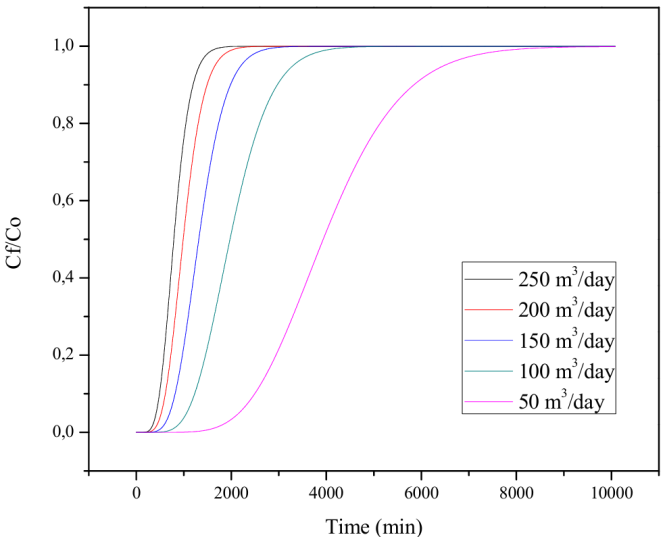

Figure 2. Rupture curves at different inlet flow rates at an initial concentration of 3000 mg/L and 5 m head

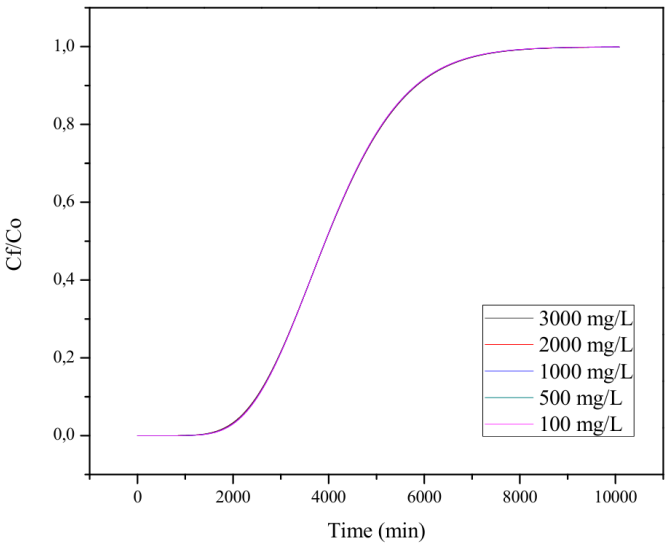

Figure 3. Rupture curves at different initial concentrations with a head of 5 m and an inlet flow rate of 50 m^3/day.

and 250 m^3/day, while keeping the column height and initial concentration fixed at 5 m and 3000 mg/L, respectively. Figure 2 shows that as the flow rate increased, both the rupture time and saturation time decreased, and the efficiency of the adsorption process also decreased. This decrease in efficiency is due to the reduced residence time at higher flow rates, which limits the contact time between the adsorbate and the adsorbent. Although increased flow enhances mass transfer rates, the insufficient interaction time prevents complete adsorption, thereby decreasing overall process efficiency (Zhang et al., 2019).

Evaluation of the impact of changing the initial Pb (II) concentration.

The effect of varying the initial concentration of Pb(II) was evaluated across a range of 100 mg/L, 500 mg/L, 1000 mg/L, 2000 mg/L, and 3000 mg/L, while maintaining a fixed column height of 5 m and an inlet flow rate of 50 m^3/day. As shown in Figure 3, changes in initial concentration did not significantly impact the rupture time, saturation time, or overall process efficiency. . This suggests that the adsorption process was not strongly influenced by variations in the initial concentration under these conditions. A possible explanation is that the number of active sites available on the adsorbent was sufficient to accommodate the varying pollutant loads, or that the high affinity between the adsorbent and adsorbate allowed the system to rapidly reach adsorption equilibrium (Villabona-Ortíz et al., 2022).

In the various configurations of the adsorption column packed with Theobroma cacao L biomass for Pb(II) removal, the Freundlich isothermal model and LDF kinetic model used in this study exhibited better performance compared to results reported in the literature for other heavy metals and biomasses (Hardyianto Vai Bahrun et al., 2021; Lubiano et al., 2023), . Based on these results, the efficiency of the process is influenced by the parameters in the following order of significance: inlet flow rate > bed height > initial concentration.

Conclusion

In this study, the use of the Freundlich-LDF model across various configurations of an adsorption column packed with *Theobroma cacao L.* biomass demonstrated Pb (II) removal efficiencies of up to 99%, highlighting the potential of this material for pollutant removal. Through a parametric evaluation, the influence of inlet flow rate, initial concentration, and bed height on the rupture time (R.T.), saturation time (S.T.), and overall process efficiency was assessed. When column heights of 3, 4, and 5 meters were tested, an increase in rupture time and saturation time was observed with greater height, accompanied by a decrease in process efficiency. For inlet flow rates of 250, 200, 150, 100, and 50 m3/day, higher flow rates led to increased efficiency and reduced R.T. and S.T.. Finally, varying the initial concentration across 50, 1000, 2000, 3500, and 500050 mg/L showed a significant effect on process efficiency, indicating its sensitivity to concentration changes. These findings demonstrate the value of computational modeling, as it enables prediction and optimization of adsorption column performance using agricultural waste materials under various industrial-scale configurations.

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