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Computational prediction of packed-bed reactor performance for hexavalent chromium removal from aqueous solution

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Abstract: Adsorption is a surface-based process employed for the removal of contaminants. The process uses organic materials as bioadsorbents. Most adsorption studies have been conducted at the laboratory scale; therefore, few studies have aimed to predict process behaviour and the efficiency of bioadsorbents at an industrial scale. Therefore, the objective of this study is to model a column for the removal of hexavalent chromium from aqueous solution using cocoa residues as an adsorbent material on an industrial scale. To this end, Aspen Adsorption was used to stimulate the column at large scale, evaluating the effects of variations in the inlet flow rate, bed height, and initial concentration of Cr(VI) on the adsorption. The Langmuir and Freundlich isotherm models were applied, with the linear driving force (LDF) used as the kinetic model. The results showed removal efficiencies of up to 94.73% for the Langmuir–LDF model and up to 95.85% for the Freundlich–LDF model. The adsorption column simulation conditions that yielded the best results for both models included a bed height of 5 m, an initial concentration of Cr(VI) of 5,000 mg·dm^{-3}, and an inlet flow rate to the adsorption column of 100 m^3·day^{-1}. This study represents as a novel approach within the field of engineering, demonstrating how computational tools can effectively predict the performance of adsorption columns packed with organic waste-based biomasses.

Keywords: adsorption, biomaterials, hexavalent chromium, industrial scale-up, process simulation, water treatment

INTRODUCTION

Water pollution has become a significant global concern, as clean water is essential for life. However, contamination of water resources has had serious repercussions on both human health and the environment. Various anthropogenic activities, such as industrial operations, primarily use water to carry out various stages of processing, consume large volumes of water and generate wastewater containing pollutants. Wastewater is frequently discharged into natural water bodies (Babuji *et al.*, 2023). Among these pollutants, heavy metals are particularly hazardous due to their non-biodegradable nature, toxicity, and high persistence, and tendency to bioaccumulate (Pandiyan *et al.*, 2021). Heavy metals enter water bodies through several industrial sources, including electroplating (Gupta *et al.*, 2021), tanneries (Genawi *et al.*, 2020), and other industrial processes. Chromium is one such contaminant, naturally present in volcanic debris, rocks, and the earth's crust. It can exist in various oxidation states due to its high redox capacity; these states can range from (–II) to (IV), but it can also be found in more stable forms, namely chromium in states (III) and (VI). Human activity is the main factor in the formation of Cr(VI).

This ion is highly soluble, toxic, mutagenic, and carcinogenic (Selimin *et al*., 2021), necessitating its removal from water bodies to mitigate a range of adverse health effects, such as immune suppression, nasal irritation, dermatitis, respiratory problems, and internal bleeding (Sharma *et al*., 2022). Given the urgent need to remove heavy metals from water bodies, several techniques have been developed to remove heavy metals from water. These include: (1) electrocoagulation, which destabilises and removes contaminants present in solution via the application of electric current (Das, Sharma and Purkait, 2022), (2) flotation, which separates solid or liquid contaminants by introducing fine bubbles into a treatment cell (Pooja, Kumar and Indraganti, 2022), and (3) adsorption, which is widely used in wastewater treatment due to its cost-effectiveness, simplicity, efficiency, and environmental sustainability (Wang and Guo, 2020). Several studies have explored the use of agricultural residues as adsorbents for the removal of contaminants, with high levels of efficiency reported for materials such as yam husk (Villabona-Ortíz, González-Delgado and Tejada-Tovar, 2022) and banana peels (Villabona-Ortíz *et al.,* 2022). Among these alternatives, cocoa waste (from *Theobroma cacao* L.) stands out as a promising adsorbent. In Colombia, cocoa cultivation generates significant quantities of residual biomass, composed of cocoa pod husk, bean husk, and pulp – representing approximately 80% of the fruit's dry mass. Cocoa husk, in particular stands out as a promising adsorbent material due to its abundance, low cost, and renewable nature. Its composition, which is rich in cellulose, hemicellulose, and, is abundant, low cost, and renewable. Its composition, rich in cellulose, hemicellulose, and lignin – confers a high adsorption capacity, making it a sustainable alternative for the removal of contaminants from aqueous environments (Villabona-Ortiz, Tejada-Tovar and Gonzáles-Delgado, 2021). However, most studies using such bioadsorbents have been limited to the laboratory scale. Therefore, efforts have focused on scaling up adsorption processes using computational tools. These simulations aim to predict the performance of industrial-scale systems based on findings. Aspen Adsorption, developed by AspenTech, enables the modelling and simulation of adsorption processes under various conditions, with the primary objective of predicting and understanding the behaviour of contaminant removal processes. This line if research is aligned with the broader global commitment to preserving water quality, protecting the environment, and safeguarding the planet as a whole. In this regard, the United Nations has developed and established 17 Sustainable Development Goals (SDGs) to address the wide range of global challenges. Among these are SDG 6 and SDG 14 – Clean Water and Sanitation, and Life Below Water – which seek to prevent and reduce pollution of aquatic ecosystems through various strategies, such as reducing the volume of untreated wastewater discharged. Thereby, they intend to improve water quality and maintain this vital resource free from contaminants and waste (NU, 2018). Therefore, this study aims to model an industrial-scale packed adsorption column using computational tools and parametric evaluation to remove Cr(VI) from aqueous solution using cocoa waste as an adsorbent. It seeks to demonstrate the potential of computational tools to predict the performance of adsorption columns, while also providing quantitative insights into the scale-up of a column packed with *Theobroma cacao* L.

MATERIALS AND METHODS

PHYSICAL PROPERTIES, PARAMETERS AND MATHEMATICAL MODELS REQUIRED FOR ASPEN ADSORPTION

To initiate the packed column simulation process, it is first necessary to input the list of components and select the appropriate physical property package for the removal of the chosen contaminant, using the Aspen Properties® database. The ELECNRTL property package was selected due to its suitability for modelling systems at both low and high pollutant concentrations in solution. After defining the components and their physical properties, the packed column was configured to simulate the adsorption process. This required to specify several parameters within the software. To this end, relevant literature on industrial-scale adsorption using packed columns for heavy metal removal was consulted.

The column configuration requires the following: a column diameter of 1 m, a column porosity of 0.670 m^3 of voids per m^3 of bed, a total void porosity of 0.400, a bulk density of the adsorbent of 0.036 $g{\cdot}cm^{-3}$; and a mass transfer coefficient of $1.370 \cdot 10^{-4}$. In addition, it is necessary to determine the isothermal models to be employed in the simulation, as the constants associated with these models are required for the proper configuration of the column. Therefore, in this study, the Langmuir and Freundlich isotherm models were adopted. The Langmuir model assumes monolayer adsorption onto a heterogeneous surface (Sultana *et al*., 2022) and is described in the literature by the following equation:

$$q_e = \frac{q_{\max} \cdot b \cdot C_e}{1 + b \cdot C_e} \tag{1}$$

where: q_e = adsorption capacity of contaminant ($mg{\cdot}g^{-1}$), $q_{\max}$ = maximum amount of solute ($mg{\cdot}g^{-1}$), b = Langmuir constant that expresses the affinity of the active sites with the contaminant ($dm^3{\cdot}mg^{-1}$), C_e = concentration of the contaminant at equilibrium in solution ($mg{\cdot}dm^{-3}$).

According to the software documentation, the Langmuir equation is presented as follows:

$$w_i = \frac{IP_{1i} \cdot IP_{2i} \cdot c_i}{1 + IP_{2i} \cdot c_i} \tag{2}$$

where, a comparison between the equations determined that $q_{\max} = IP_{1i}$, $b = IP_{2i}$, and $C_e = c_i$. Whereas Freundlich assumes that adsorption is generated on a heterogeneous multilayer surface (Fouad, 2023). Its version in the literature is described by the following equation:

$$q_e = K_F \cdot C_e^{1/n} \tag{3}$$

where: K_F = Freundlich constant of the adsorption capacity $(mg{\cdot}g^{-1}){\cdot}(mg{\cdot}dm^{-3})^{1/n}$, n^{-1}= impact of the initial concentration on the adsorption capacity.

Looking up the Freundlich equation in the software, it is expressed as follows:

$$w_i = IP_{1i} \cdot c_i^{IP_{2i}} \tag{4}$$

Comparison of the equations showed that $K_F = IP_{1i}$, $n^{-1} = IP_{2i}$, and $C_e = c_i$. The values used for the models needed to configure the adsorption column are listed in Table 1.

Table 1. Parameters of the Langmuir and Freundlich models

Model	Parameter	Value
Langmuir	q_{max} (mg·g^{-1})	227.348
	b (dm^3·mg^{-1})	0.011
Freundlich	K_F (mg·g^{-1})·(mg·dm^3)$^{1/n}$	8.693
	n^{-1}	1.530

Explanations: q_{max} = maximum amount of solute, b = Langmuir constant that expresses the affinity of the active sites with the contaminant, K_F = Freundlich constant of the adsorption capacity, n–1 = impact of the initial concentration on the adsorption capacity.
Source: own elaboration.

It is also necessary to establish the kinetic model used to describe the rate of the adsorption process. In this study, the Linear Driving Force (LDF) model, as implemented in the software, was adopted to represent the adsorption rate through the overall mass transfer coefficient. This model assumes that mass transfer is governed by a linear relationship between concentration and time, either in the liquid or solid phase (Durán, Rubiera and Pevida, 2022). The model is expressed by the following equation:

$$\frac{\partial w_k}{\partial_t} = MTC_{sk}\left(w_k^* - w_k\right) \quad (5)$$

where: w_k = instantaneous equilibrium adsorbate loading on the adsorbent (mg·g^{-1}), t = time (s), w_k^* = amount that should be adsorbed if the system were in instantaneous equilibrium with the fluid phase (mg·g^{-1}), MTC_{sk} = coefficient for mass transfer overall (m·s^{-1}).

PARAMETRIC EVALUATION

To evaluate the effect of parameter variations on the adsorption process, a parametric analysis was carried out, considering three scenarios: variation in column height, variation in inlet flow rate, and variation in initial concentration. Therefore, to assess the impact of column height on process time and performance the simulation was conducted using a height range of 4 to 5 m, while keeping the initial concentration and inlet flow rate constant. Similarly, the inlet flow rate was evaluated while maintaining the column height and initial concentration fixed, using flow rates of 100 and 200 m^3·day^{-1} (Upadhyay *et al.*, 2021). Finally, the effect of varying initial concentration was analysed at levels of 2,000 and 5,000 mg·dm^{-3}, with constant column height and inflow rate (Gupta *et al.*, 2021).

RESULTS AND DISCUSSION

EVALUATION OF THE IMPACT OF THE VARIATION OF PARAMETERS ON THE ADSORPTION PROCESS

The impact of varying adsorption parameters on the removal of Cr(VI) from aqueous solution was assessed using Aspen Adsorption for the modelling of the adsorption column. A combination of the selected isotherm models with the chosen kinetic model was employed. The residence time (*R.T.*) and saturation time (*S.T.*) results obtained from the simulations are presented in Table 2.

Table 2. Data obtained from simulations

Model	Initial concentration (mg·dm^{-3})	Inlet flow rate (m^3·day^{-3})	Bed height (m)	*R.T.*	*S.T.*
				min	
Langmuir	2,000	200	4	214	1,732
			5	271	2,105
		100	4	441	3,186
			5	553	3,865
	5,000	200	4	184	1,878
			5	233	2,294
		100	4	381	3,474
			5	480	4,242
Freundlich	2,000	200	4	214	1,732
			5	271	2,111
		100	4	441	3,201
			5	555	3,885
	5,000	200	4	184	1,884
			5	233	2,294
		100	4	381	3,499
			5	480	4,264

Explanations: *R.T.* = rupture time, *S.T.* = saturation time.
Source: own study.

IMPACT OF BED HEIGHT VARIATION ON ADSORPTION

Variations in column height – from 4 to 5 m – were used to evaluate their impact on the absorption process, with the initial Cr(VI) concentration of 5,000 mg·dm^{-3} and an inlet flow rate of 100 m^3·day^{-1}. The results indicated that reducing the column height had a positive effect on the efficiency of the adsorption process; however, both breakthrough time and saturation time decreased. This behaviour was consistent across both case studies: the Langmuir–LDF (Fig. 1a) and Freundlich–LDF model (Fig. 1b). This is attributed to the fact that a shorter column allows the fluid to pass through the system in less time, resulting in a reduction in residence time (Ronda *et al.*, 2018). The adsorption efficiencies for the Langmuir–LDF model were 90.00% at 4 m and 87.34% at 5 m. In contrast, the Freundlich–LDF model achieved efficiencies of 91.00% at 4 m and 88.46% at 5 m. These findings indicate that both the Freundlich–LDF and Langmuir–LDF models yield similar results, suggesting that either model is suitable for describing the adsorption process.

IMPACT OF INLET FLOW RATE VARIATION ON ADSORPTION

The effect of varying inlet flow rate was analysed at 100 and 200 m^3·day^{-1}, using a fixed bed height of 5 m and an initial contaminant concentration of 5,000 mg·dm^{-3}. It was observed that as the inlet flow rate increased, both residence time (*R.T.*) and saturation time (*S.T.*) decreased, while adsorption efficiency improved. This behaviour was observed in both case studies, i.e. Langmuir–LDF (Fig. 2a) and Freundlich–LDF (Fig. 2b). This can be attributed to an enhanced mass transfer rate and reduced mass transfer resistance at higher flow rate. The greater volume of influent per unit of time shortens the contact time and increases adsorption efficiency (Upadhyay *et al.*, 2021). The adsorption efficiencies for the Langmuir–LDF model were 93.61% at an inlet flow rate of 200 m^3·day^{-1} and 87.73% at 100 m^3·day^{-1}, while the Freundlich–LDF model achieved efficiencies of 94.00% at 200 m^3·day^{-1} and 88.46% at 100 m^3·day^{-1}. It is evident that these models produce comparable results, indicating that either model is suitable for describing the adsorption process.

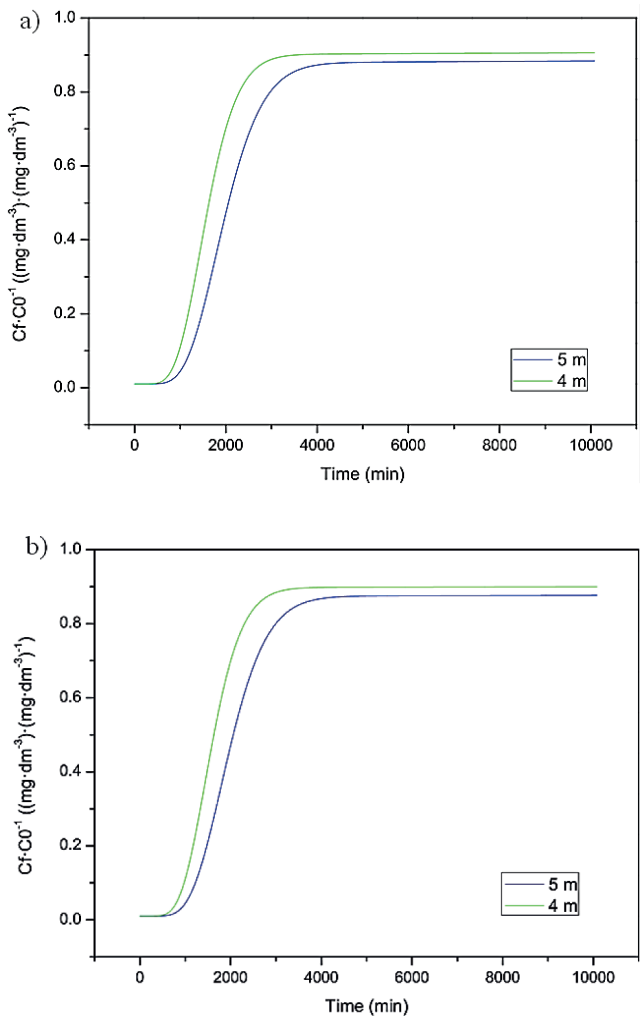

Fig. 1. Breakthrough curves of bed height variation for: a) Langmuir-LDF, b) Freundlich-LDF; LDF = linear driving force, *Cf* = concentration of Cr(VI) at the outlet of the column (mg·dm^{-3}), C_0 = concentration of Cr(VI) at the inlet of the column (mg·dm^{-3});
source: own study

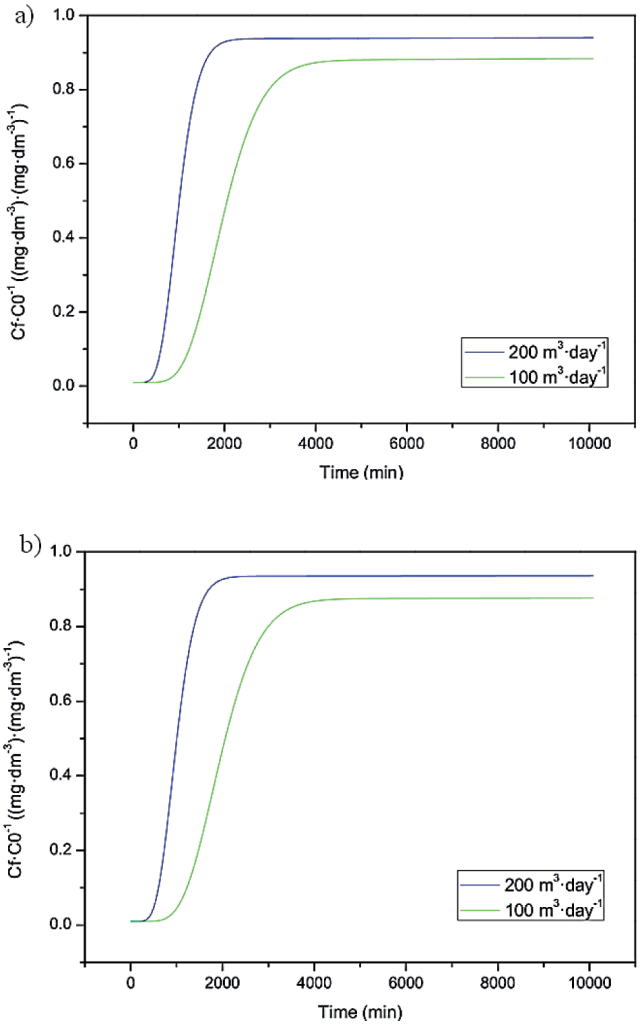

Fig. 2. Breakthrough curves of inlet flow variation for: a) Langmuir-LDF, b) Freundlich-LDF; LDF, *Cf* = concentration of Cr(VI) at the outlet of the column (mg·dm^{-3}), C_0 = concentration of Cr(VI) at the inlet of the column (mg·dm^{-3}) as in Fig. 1;
source: own study

IMPACT OF INITIAL Cr(VI) CONCENTRATION VARIATION ON ADSORPTION

The variation of initial concentration was analysed at 2,000 and 5,000 mg·dm^{-3}, with a fixed bed height of 5 m and an inlet flow rate of 100 m^3·day^{-1}. It was observed that changes in the initial concentration had no significant effect on either the adsorption efficiency or the breakthrough and saturation times for both models employed (Fig. 3). This outcome may be attributed to the number of active sites available on the adsorbent or to the strong adsorbent–adsorbate affinity, which may have facilitated the rapid attainment of adsorption equilibrium. However, a slight difference was observed between the efficiencies obtained for each model: the Langmuir–LDF model yielded 87.73% at 5,000 mg·dm^{-3} and 87.83% at 2,000 mg·dm^{-3}, while the Freundlich–LDF model achieved 88.46% at 5,000 mg·dm^{-3} and 88.28% at 2,000 mg·dm^{-3} (Patel, 2020). It is evident that these models produce comparable results, indicating that either model is suitable for describing the adsorption process.

These findings demonstrate the impact of the evaluated parameters, with the inlet flow rate having the greatest impact, followed by packed column height, and finally initial concentration, which – as previously discussed – had the least effect on the Cr(VI) adsorption.

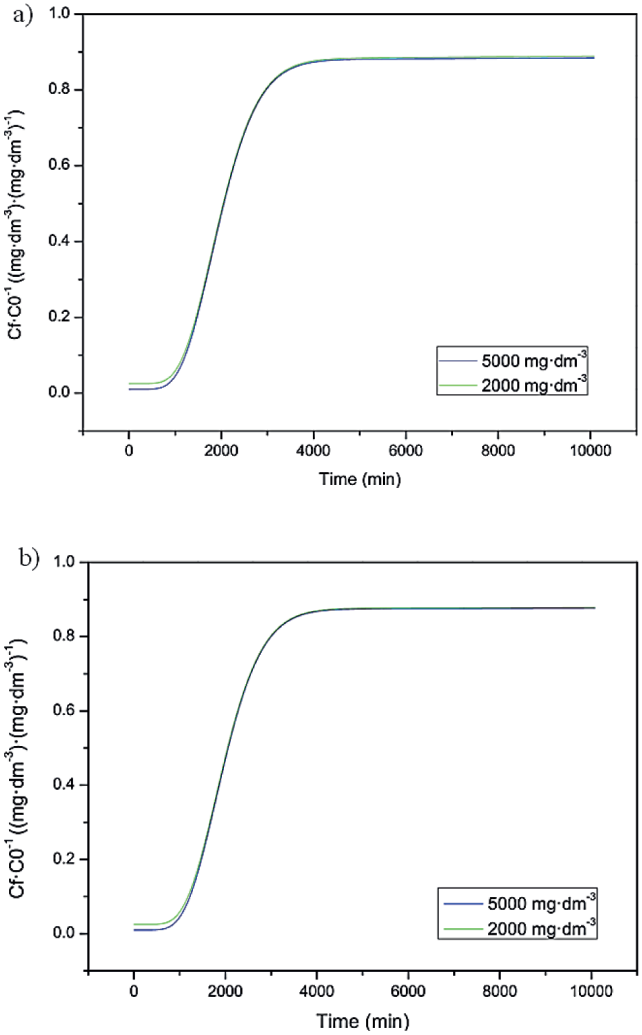

Fig. 3. Breakthrough curves for initial concentration variation: a) Langmuir–LDF, b) Freundlich–LDF; LDF, *Cf* = concentration of Cr(VI) at the outlet of the column (mg·dm^{-3}), C_0 = concentration of Cr(VI) at the inlet of the column (mg·dm^{-3}) as in Fig. 1;
source: own study

COMPARISON OF THE RESULTS WITH SCIENTIFIC LITERATURE

The results obtained from the industrial-scale simulation of the packed bed using *Theobroma cacao* L. were compared with findings from previous studies. However, this comparison should be considered relative, as each study employed different flow conditions, initial concentrations, bed heights, and types of adsorbent biomaterials. The findings indicate that *Theobroma cacao* L., when used in an industrial packed bed, is effective for the removal of Cr(VI) from aqueous solutions. A comparison of these results with values reported in the scientific literature is presented in Table 3.

Table 3. Comparison of result with literature

Specification	Contaminant		
	Pb(II)	Cd(II)	Cr(VI)
Adsorbent	olive tree pruning	dolochar	*Theobroma cacao* L.
Initial concentration (mg·dm^{-3})	100	55	5,000
Inlet flow rate (m^3·day^{-1})	128.04	75	100
Bed height (m)	2.26	0.65	5
Rupture time (min)	201.6	666	480
Saturation time (min)	530	1,140	4,264
Source	Ronda *et al.* (2018)	Upadhyay *et al.* (2021)	this study

Source: own elaboration.

CONCLUSIONS

In this research, an industrial-scale simulation of an adsorption column packed with *Theobroma cacao* L. was developed using Aspen Adsorption, offering a novel approach to predicting the behaviour and performance of the system. The effect of varying initial concentration, inlet flow rate, and bed height on process efficiency, breakthrough time, and saturation time were evaluated through a parametric analysis. The bed height was evaluated at 4 and 5 m, while the higher value resulted in an increase in residence time (*R.T.*) and saturation time (*S.T.*), but a decrease in adsorption efficiency. For inlet flow rate, values of 100 and 200 m^3·day^{-1} were tested. The higher flow rate reduced both breakthrough and saturation times but improved adsorption efficiency. Additionally, initial concentrations of 2,000 and 5,000 mg·dm^{-3} were assessed, showing minimal impact on breakthrough or saturation times. These results demonstrate a novel approach to predicting the potential performance of a packed column filled with *Theobroma cacao* L. residues for Cr(VI) adsorption at industrial scale.

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CONFLICT OF INTERESTS

All authors declare that they have no conflicts of interest.

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