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Optimization of Variables in Fixed-Bed Column Using the Response Surface Methodology

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Abstract

Heavy metal removal technologies in industrial wastewater bodies are being implemented more frequently, due to the increasing demand for treatment of water contaminated with metals. Adsorption becomes important due to its profitability and use of organic waste. The objective of this research was to optimize the most incidental variables of the cadmium biosorption process with cocoa shell (*Theobroma cacao L.*) in fixed-bed column with the response surface methodology. The hypothesis of the study was that bed height is the most influential variable in the continuous adsorption process. The experimental design was 3^3 multilevel factorial , the information corresponds to the behavior of the bed and influence of feed flow, initial metal concentration in the solution and the height of the packed bed. A second-order polynomial model was generated with a correlation coefficient of 0.9072, which indicates that this makes a good adjustment of the experimental data. The theoretical and operational optimal conditions were determined. The optimal configuration of the actual and theoretical bed operating parameters were: 5 g biomass, 4.5 mL min^{-1} flow rate and 100 mg L^{-1} initial metal concentration for real conditions and 10.79 g, 4.50 mL min^{-1} flow rate and 40 mg L^{-1} for theoretical flow rate. It concluded that the height of the bed had a proportional influence on the removal rate, while the initial metal concentration in the synthetic solution and the increase in flow rate did not have a significant effect on the system.

Keywords: Biosorption, cadmium, surface response methodology, optimization, *Theobroma cacao L.*

1. Introduction

Heavy metals, such as mercury, nickel, copper, lead, chromium and cadmium, are in industrial wastes from oil refineries and paper, textile, metallurgy, plastics, electroplating and other industries [1]. In contrast to organic pollutants, heavy metals are persistent and can accumulate in the environment and living organisms, with adverse health effects [2, 3, 4, 5].

Biosorption has emerged as an alternative treatment of water contaminated with heavy metals due to the growing need for effective removal technologies, relatively low costs and environmentally friendly. Adsorption has been studied in continuous system with yam shells (*Goscorea rotundata*) and bagasse of African palm (*Elaeis guineensis*) as adsorbent has been studied. Thomas's kinetic model was the one that best adjusted the experimental data on Cr (VI) ion adsorption by palm bagasse; the maximum removal capacity was 32 mg g^{-1}, that of yam shells was 18 mg g^{-1}, with a break time of about 200 min and 5 min in the first and second cases [6].

Different authors have carried out adsorption works in continuous filler columns, using biosorbent materials in order to analyze and optimize the main operating variables [7], This is the case of the study on the optimization of the biosorption process variables Cr (VI) and Cr (III) in aqueous solution using a dry leaf biomass of the species Pinus densiflora, using Response Surface Methodology (RSM) as an optimization method [8].

The adsorption capacity of henna modified with Fe_3O_4 nanoparticles was studied in Cu (II) removal using the response surface method (RSM) and a central compound experimental design to optimize effective parameters. It was concluded that the elimination of Cu (II) increased from 0.73 % to 99.11% by increasing the pH from 2 to 5.2 (the maximum adsorption was at pH 5.2). The elimination was reduced to 66 % by the initial increase in the dilution concentration (10 - 100 mg L^{-1}). In addition, elimination increased from 41.65 % to 97.05 % by increasing the amount of adsorbent dose (from 0.1 to 1 g). Langmuir's model best adjusted the experimental adsorption data with a correlation coefficient R^2 = 1, while Freundlich's model confirmed that henna is a good Cu (II) adsorbent [9].

The objective of the present investigation was to optimize through surface response methodology (RSM) the variables with the most incidents in the biosorption process for the elimination of Cadmium in synthetic waters on a pilot scale using cocoa shell (*Theobroma cacao L.*) from the municipality of San Jacinto (Bolívar) as a biosorbent. Taking as a hypothesis of this research that bed height is the most influential variable in the Cadmium adsorption process in continuous system.

2. Methodology

2.1. Preparation of the biomass

The cocoa shell biomass was washed with water, followed by drying at 90 °C for 24 h in a Esco laboratory furnace, Model Isotherm® OFA-32-8, located in the Physicochemistry Laboratory of the University of Cartagena, followed by a reduction in size and sieving to obtain a particle size of 0.5 mm, which was selected due to the fact that in previous investigations by the IDAB research group it was the one that produced the best results. The resulting material was stored in airtight bags for later use as a biosorbent [10, 11].

2.2. Continuous system

A system consisting of an 1147.24 mL capacity feed tank, a peristaltic pump and a 30 cm high, 3.2 cm inner diameter acrylic filler column system was designed [12].

2.3. Synthetic water preparation and determination of the concentration of Cadmium

Synthetic waters were prepared at concentrations of 40, 100 and 160 mg L^{-1} of the ion Cd using Merck Chemicals branded Octahydrated Cadmium Sulfate ($3CdSO_4$-$8H_2O$), measuring the final concentration of contaminant by Atomic Adsorption Spectroscopy (AAS) analysis, using an iCE Model 3500 Series spectrometer from Thermo Scientific [13, 14].

2.4. Experimental design applied to the optimization of process variables

A complete 3^3 factorial design was used to determine the best combination of operational parameters, which led to an optimum response value using the Response Surface Methodology (MSR), thus obtaining a regression equation that adjusted all system data. Table 1 shows the three factors chosen and their experimental mastery. The response to be optimized was the percentage retained of cadmium (% R) [11, 15, 16].

Table 1. Factorial experimental design

Factors	**Experimental Domain**		
	(-1)	**(0)**	**(+1)**
X1: Feed flow rate mL min^{-1}	4.5	6.0	7.5
X2: Initial metal concentration mgL^{-1}	40.0	100.0	160.0
X3: Bed height (g biomass)	5.0	10.0	15.0

3. Results and Discussions

3.1. Influence of the feed rate

The adjustment equation, being a quadratic function, took the three experimental points (Figure 1); therefore, in the case of flow, the adjustment equation of the data generated a minimum. The flow rate has an effect of no more than 5% on the response variable, this is because, as the flow rate increased, the residence time decreased, so the contact time was shorter. This removal effect was a consequence of the chosen operating ranges, however, Hasan et al. [17], reported that when using wider ranges (2 to 10 mL min^{-1}) the influence of flow rate can be as high as 24.55%.

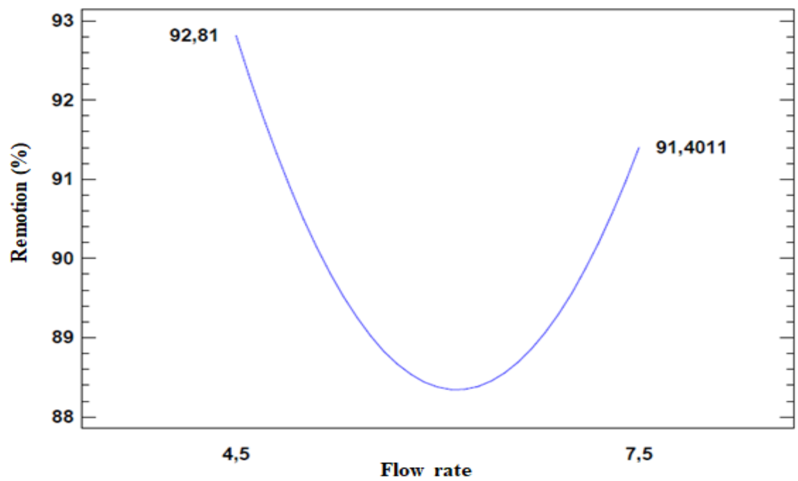

Figure 1. Influence of the flow (mL min^{-1}) on the removal rate

In the study carried out by Valencia-Ríos and Castellar-Ortega [18], they obtained similar results, since from the point of view of column operation the best results were obtained at small flows, since the metallic ions had enough time to diffuse inside the activated carbon, improving their adsorption capacity. Abdolali et al. [19], found that the increase in flow rate reduced the volume of effluent treated before bed was saturated and reduced bedtime and vice versa. The slower flow velocity provided more residence time for mass transfer in the pores, subsequently allowing metal ions to access more active sites within the adsorbent. On the other hand, Riazi et al. [20], assert that generally, column removal efficiency decreased as the flow rate increased and the mass transfer area decreased with the flow rate. These results are consistent with those reported in the present study.

3.2. Influence of initial metal concentration

The initial metal concentration had a negative effect on the removal percentage (Figure 2), where the highest removal percentages were achieved with the lowest value (40 mg L^{-1}). Also, Calero et al. [21] stated that saturation time decreased as the initial metal concentration increased. For the case of concentration, the system adjustment equation generated a minimum by trying to adjust all three experimental points.

The increase in input concentration means an early saturation of active sites, decreasing the efficiency of removal of metal ions present in synthetic water. Since, the diffusion process of metal removal is highly concentration dependent. The results of the influence of the initial concentration on the adsorption capacity of the metal ion confirm that the change of the initial concentration as the driving force affected the saturation velocity, at the time of penetration and the length of the adsorption zone [19, 22, 23].

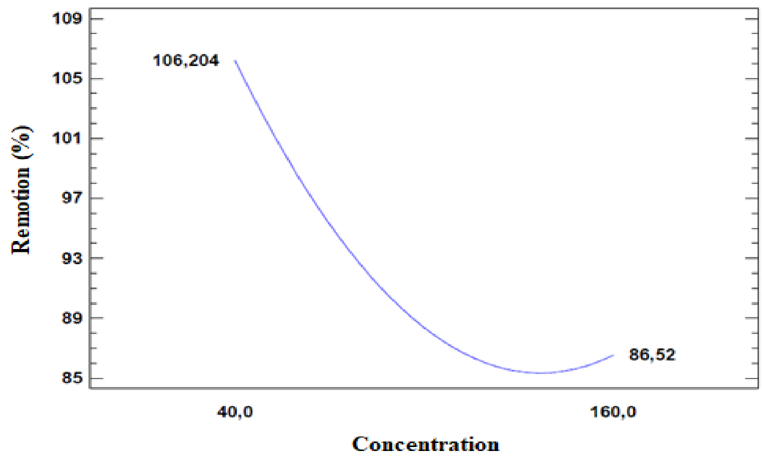

Figure 2. Influence of the concentration (mg L^{-1}) on the percentage of removal

3.3. Influence of filling height

The height positively affected the percentage of clearance (Figure 3), i. e., as the height increased, the percentage of clearance increased. This behaviour coincides with that reported in previous research with pine bark biomasses [13], Aeromonas hydrophila [17] and cocoa shells [12]. For height, the system adjustment equation generated a maximum by trying to adjust all three experimental points.

The results obtained and based on previous research, could be attributed to the fact that when the height of the bed is reduced axial dispersion predominates during mass transfer, therefore the metal ions do not have sufficient time to diffuse throughout the adsorbent. In addition, increasing bed height also increases the surface area of the adsorbent, with more active sites available for the ion exchange required during adsorption; consequently, the adsorption capacity of the bed at the breaking point is increased [24]. This is consistent with what Riazi et al. [20] and Acheampong et al. [25] who report that for better performance of a fixed-bed column, the height of the highest biosorbent bed would be more desirable if more active binding sites were provided.

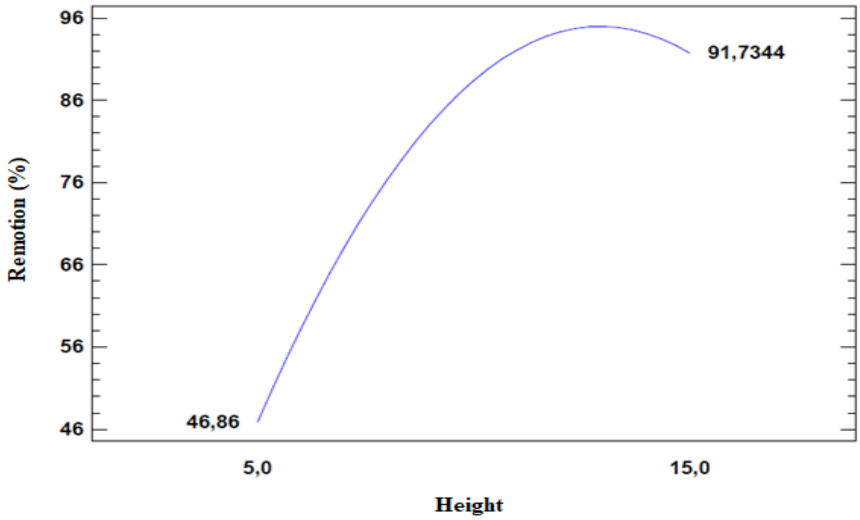

Figure 3. Influence of height (g of biomass) on removal percentage

3.4. Optimization of variables by Response Surface Method (RSM)

Once the 27 experiments were completed, the RSM was applied, a regression equation was obtained that adjusted all system data. The fit model equation was as follows:

$$\% R = 126.894 + 13.0942A - 21.6987B - 1.03441C - 0.763133A^2 + 0.265889AB + 0.0506056AC + 1.65778B^2 - 0.0132315BC + 0.00221852C^2 \quad (1)$$

The linear equation (1) was synthesized from previous experimentation to describe the relationship between removal percentage, bed height, flow and pollutant concentration, where % R is the removal percentage, A is the height (g biomass), B is the flow (mL min^{-1}) and C is the concentration (mg L^{-1}). With this equation a correlation coefficient was obtained, R^2 of 0.9072, which indicated that the model was adjusted by 90.7273 %. However, with this model, two types of optimal values were found: theoretical and operational [26].

3.5. Optimum theoretical removal value

The combination in the levels of the factors guaranteed a maximum percentage of removal (Table 2), this due to its high residence time in the bed, low concentration, and a greater height of biomass in the package, obtaining an optimal value of 109.77%. These factors represented the lower initial metal concentration, the lower flow rate, and a high bed height, but not the maximum, which indicated that beyond this point, there will not be a better performance of the system. Coinciding with previous research proposals [13, 17, 21].

Table 2. Factors for the theoretical optimum removal value

Factor	Unit	Low	High	Optimal
Height	g	5.0	15.0	10.8
Flow rate	mL min^{-1}	4.5	7.5	4.5
Concentration	mg L^{-1}	40.0	160.0	40.0

3.6. Optimum Operational Removal Value

Although a high percentage of removal was obtained, it is important to emphasize that the levels of the factors previously found are not operationally efficient, since they imply a very low capacity of the synthetic solution to pass through the packed column. With these considerations, the system was reshaped to obtain an optimum operational value of 53.29% (Table 3).

Table 3. Factors for optimum operational value

Factor	Low	High	Optimal
Height (g)	5.0	5.0	5.0
Flow rate (mL min^{-1})	4.5	7.5	4.5
Concentration (mg L^{-1})	100.0	160.0	100.0

3.7. Response Surface

The response surface graph (Figure 4) combined the three main factors and the value of the response variable in all resulting combinations.

Due to operational limitations, the only points admissible were those of the initial metal concentration line of 100 to 160 mg L^{-1} located in the 5 g high plane of the bed where the highest percentage of valid removal was at a concentration of 100 mg L^{-1}. It is confirmed that the most influential variable in the percentage of clearance was height, which affected positively. The second most influential variable was concentration, which affected negatively and to a lesser extent than height. The least influential variable was the flow rate, which negatively affected and has a confidence value of less than 95% (Figure 5).

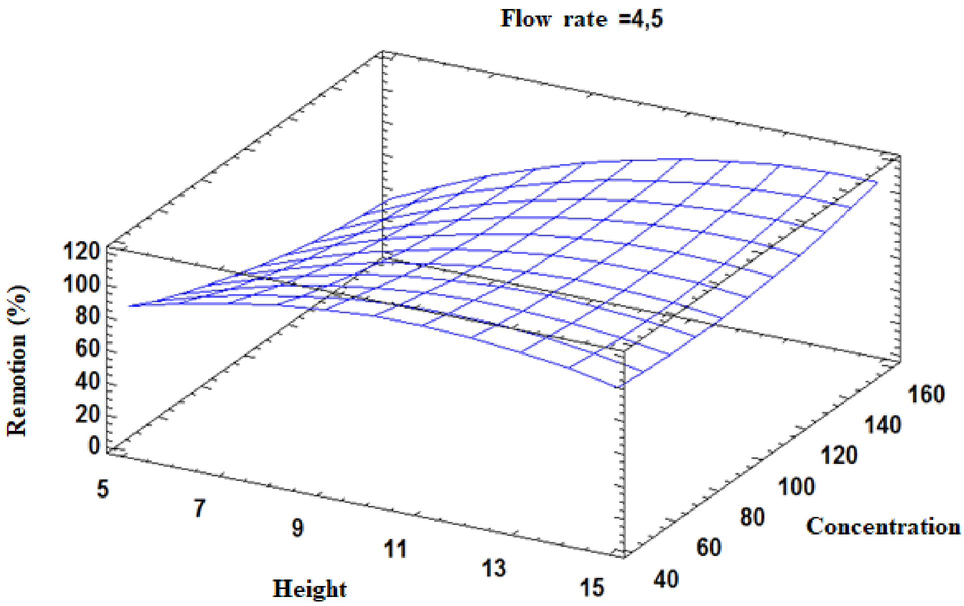

Figure 4. Response surface of the optimum operational value

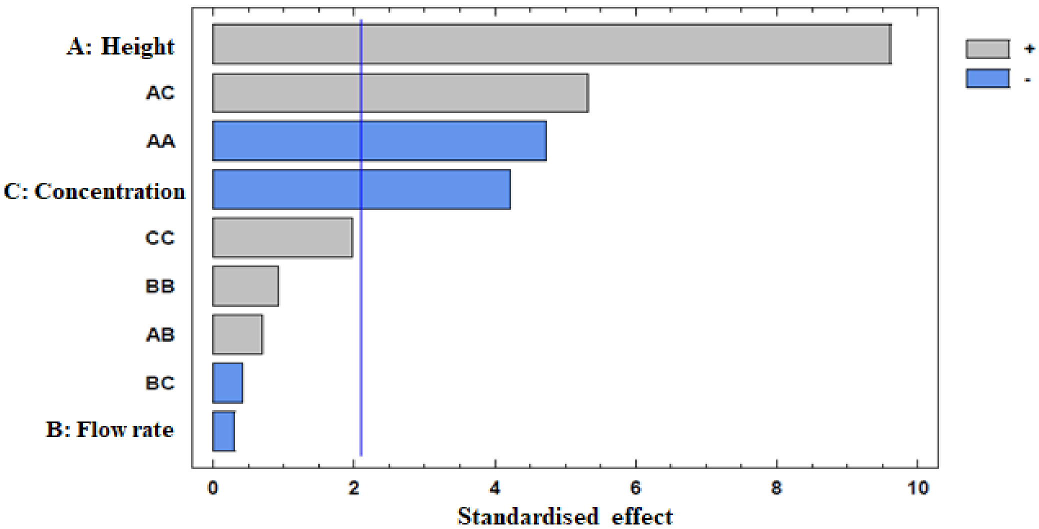

Figure 5. Pareto diagram of variables influencing the percentage of remotion

Sahu et al. [27] used the response surface methodology to optimize the elimination of lead (II) from aqueous solutions, finding that the variance analysis showed a high coefficient of determination (R^2 = 0.996) and a satisfactory second-order predictive regression model was obtained. In addition, it was found that the optimal adsorbent dose, temperature, initial lead concentration (II) and initial pH of lead solution (II) were 1.44 g L^{-1}, 50 ºC, 49.23 mg L^{-1} and 4.07, respectively. The contribution of significant effects on the amount of Cd ions removed (Figure 5). Effects with absolute values higher than the baseline were considered statistically significant in the polynomial equations [28, 29, 30].

3.8. Interaction of independent variables referring to the percentage of remotion

Independent variables interacted differently with different conditions (Figure 6). It was observed that high and low flow rates behaved similarly with respect to height, at lower altitude the flow rate of 4.5 mL min^{-1} offered a higher removal percentage, contrary to higher altitude conditions, where the flow rate of 7.5 mL min^{-1} offered a better result.

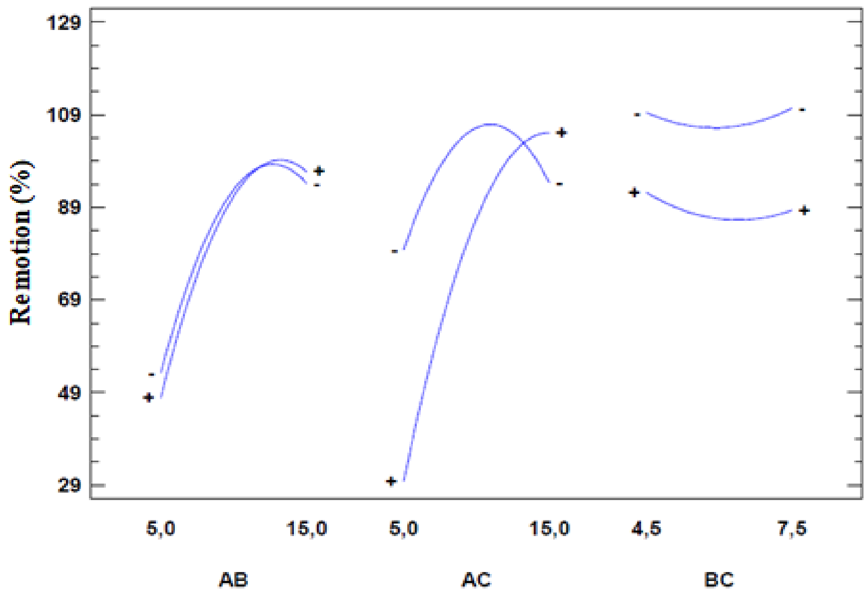

Figure 6. Interaction of variables (A: Height, B: Flow, C: Concentration).

With respect to initial concentration and bed height, it was evidenced that the best results were offered by the 40 mg L^{-1} concentration, while the 160 mg L^{-1} concentration required higher bed height to generate acceptable results. With respect to the initial concentration and the flow rate, high and low concentration values had a similar behavior when increasing the flow rate, where the lower concentration allowed a higher percentage of removal to be obtained. This can be attributed to the proportionality ratio between adsorbent mass and adsorbent percentage, due to the increase in the number of active sites available, thus increasing the adsorbent mass [30, 31].

4. Conclusions

The height of the bed has a proportional influence on the removal rate, while the initial metal concentration in the synthetic solution and the increase in flow rate have a negative effect. Se encontró que la cáscara de cacao es un buen precursor para la preparación de adsorbente de Cd en aguas residuales y que la metodología superficie de respuesta establece eficientemente las condiciones óptimas de adsorción.

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