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Diclofenac Removal in Fixed Bed Adsorption Using Hydrochar from Coffee Grounds: Performance Evaluation

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Abstrair

The adsorption of diclofenac using coffee grounds biochar in adsorption process has been recently considered as a promising approach for the wastewater treatment in contaminations with this emerging pollutant. Biochar produced from coffee grounds has a surface rich in functional groups such as carboxyls and hydroxyls, which would facilitate the adsorption of several organic contaminants. Therefore, in this work was synthesized hydrochar using hydrothermal methodology, and experiments were conducted in fixed bed adsorption at different heights (1 cm and 3 cm) revealed that the removal efficiency of diclofenac is significantly influenced by the column height and the amount of available adsorbent. In a 3 cm bed height, the adsorption efficiency reached approximately 70%, indicating a good removal capacity for diclofenac. In contrast, When using a 1 cm bed, the efficiency was reduced to approximately 20%, indicating that a lower amount of adsorbent leads to faster saturation and less efficient adsorption. The analysis of the breakthrough curves obtained during the process showed that the increase of the column height and the adsorbent mass are would be essential to maximize the process efficiency. Despite the predictions observed in the smaller columns, coffee grounds biochar stands out as a sustainable and low-cost alternative for the removal of diclofenac from wastewater, with potential for application in long-scale treatments after optimization of operational conditions.

Keywords: Emerging Pollutants; Thomas Model; Activated Adsorbents; Hospital Effluents.; Hydrothermal synthesis.

1. Introduction

Emerging Pollutants (EP) are groups of substances with a high potential to harm ecosystems and human health, since conventional effluent treatment methods are not effective in their complete removal [1]. Among these EPs stands out diclofenac sodium (DS), that is an anti-inflammatory commonly used in the treatment of pain and inflammation of various causes. Its presence has been detected both in aquifers and in soils irrigated with conventionally treated water [3]. These detections indicated the need to study different methods for the purification of effluents containing DS, and among these, adsorption has proven to be an effective solution [2, 4].

Adsorption is attractive not only for its efficiency, but also for its low energy and production costs, in addition to the possibility of using residual biomass as raw material, such as waste from agro-industrial products, which made it an environmentally friendly technique. In this context, biochars produced from plant residues have been widely studied for this purpose [5], with coffee grounds appearing as an example of biomass with high availability for the production of these materials. Coffee biochar has been shown to be effective in adsorbing several contaminants, such as heavy metals, dyes, organic compounds and emerging pollutants such as diclofenac. The combination of physical interactions (such as capture in pores) and chemical interactions (such as binding with functional groups on the surface) explains its adsorbent characteristics [6]. To analyze the adsorption processes in a more realistic manner, the fixed bed approach with continuous flow was used, employing the breakthrough curve as a methodology for evaluating the performance of the adsorbent and the process [7].

Based on this, this work aimed to produce and activate a hydrochar derived from coffee grounds for the removal of DS from synthetic effluents in a fixed bed column, seeking future applications for decontamination of hospital effluents. Pollutant concentration and bed height conditions were varied.

2. Experimental

2.1 Synthesis of hydrochar

The coffee grounds were obtained after consumption of local commercial coffees and were washed with hot water and dried in an oven at 60 ºC for 24 hours. Afterwards, they were placed in a hydrothermal reactor at 180ºC for 24 hours, followed by a new wash and thermal activation at 300 ºC for 2 hours.

2.2 Adsorption study

Preliminary batch tests were performed with the objective of evaluating the affinity of DS with the produced adsorbent. With stirring at 150 rpm and 30 ºC, approximately 0.1 g of adsorbent was applied in 20 mL of diclofenac solution at 10 mg/L. For the adsorption study in a continuous flow fixed bed, synthetic effluent containing DS was used, varying the concentration (5, 50 and 100 ppm) and bed height (1 and 3 cm), setting the flow rate at 20 mL/min in a 15 cm height and 1.5 cm in internal diameter glass column, interspersed with 2 mm glass microbeads.

The adsorption capacity (qt, mg/g) and the percentage of DS removal (%) were calculated by equations (1) and (2), respectively:

$$q_t = \frac{(C_0 - C_t)}{m} * V \qquad \text{Eq.(1)}$$

$$\%_{removal} = \frac{C_0 - C_t}{C_0} * 100 \qquad \text{Eq.(2)}$$

Where C_0 is the initial adsorbate concentration (mg/L), C_t is the adsorbate equilibrium concentration (mg/L), V is the solution volume (L) and m is the adsorbent mass (g). UV-Vis spectrophotometry was used to measure the concentrations. The mathematical model of Thomas Eq. (3) was applied to adjust the kinetic data.

$$\frac{C}{C_0} = \frac{1}{C_0\, e^{K_{Th}(q_0 m C_0 V)}} \qquad \text{Eq.(3)}$$

Where, C is the concentration of the contaminant in the effluent, C_0 is the initial concentration of the contaminant in the effluent, kTh is the Thomas rate constant (L/min mg), q_0 is the maximum adsorption capacity of the adsorbent (mg/g), m is the mass of the adsorbent (g), V is the volume of treated solution (L).

3. Results and discussions

With the batch affinity test, it was noted that the adsorbent and the adsorbate had a strong affinity. At natural pH, the pollutant removal was greater than 40%. The breakthrough curve for the 1 cm bed and 5 ppm, Figure 1(A), showed an adsorption of 33.35%, for 50 ppm, Figura 1(B), 34% and for 100 ppm, Figure 1(C), only 10.36%.

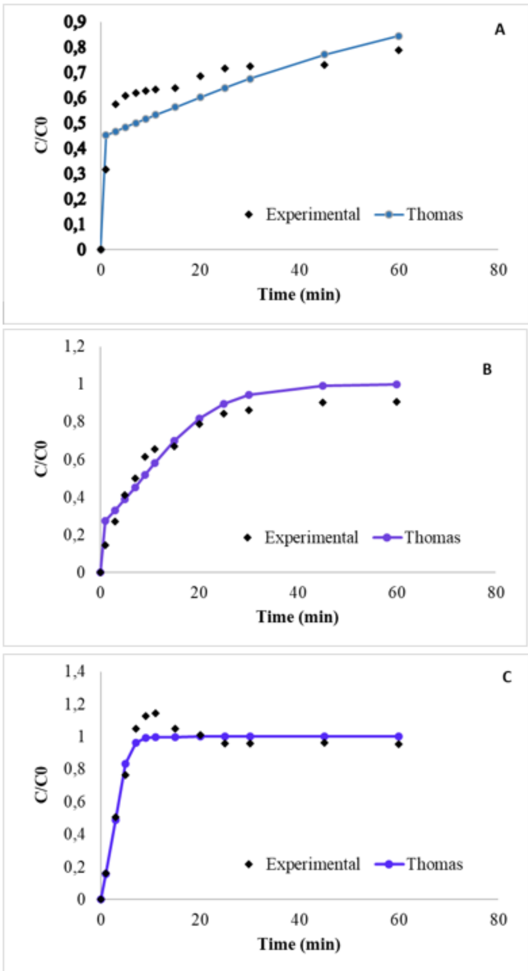

Fig 1: Adsorption breakthrough curve in a 1 cm fixed bed of adsorbent and DS at concentrations of [A] 5ppm, [B] 50ppm and [C] 100 ppm.

This result indicated that at a bed height of 1 cm, high concentrations very quickly saturate the main sites of the adsorbent, generating possible electrostatic repulsion of the incoming pollutant to form other layers. It was also noted that for 5 and 50 ppm the column did not saturate completely. The breakthrough curve obtained for the column with 3 cm of coffee grounds hydrochar at 5 ppm concentration, Figure 2(A), shows an adsorption efficiency of 100%, indicating that the spine did not even reach its breaking point in 60 minutes of treatment.

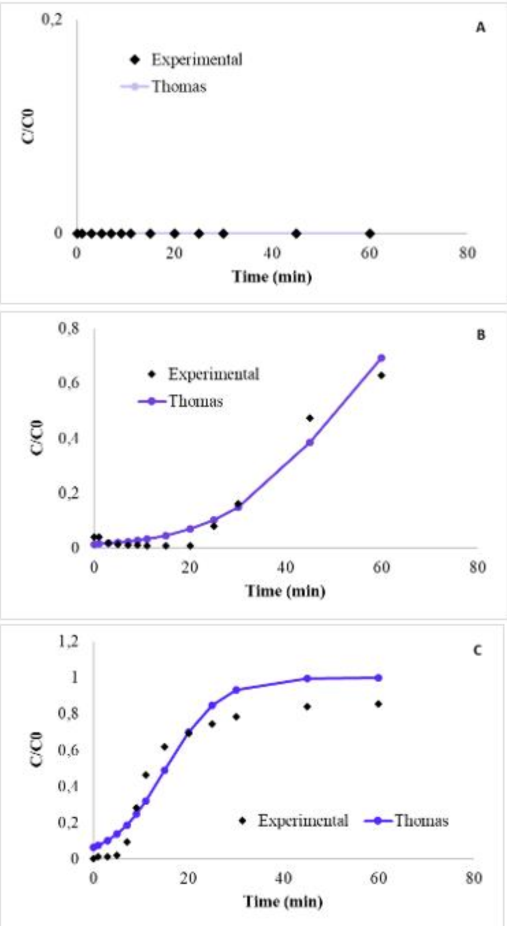

Fig 2: Adsorption breakthrough curve in a 3 cm fixed bed of adsorbent and DS at concentrations of [A] 5ppm, [B] 50ppm and [C] 100 ppm.

For Figure 2(B), at 50 ppm, it was reached close to 23 minutes, but without exhaustion point and removing 81,1%. Treating a 100 ppm solution, Figure 2(C), the breakthrough point was reached at 9 minutes and also without exhaustion observed, and a 50.6% removal recorded suggesting ample potential for fixed bed adsorption with this hydrochar. The greater bed height also reduced the problematic effect when using 1 cm, that is, without accumulation of pollutants in the reduced quantity of sites, in addition to presenting a more compacted bed, reducing the potential for material losses due to dragging, which was also observed in the system with 1 cm. The kinetic fitting with the Thomas model provided a good fit to the experimental data, with a rate constant (kTh) of 0.00211 L/min mg and predicted adsorption capacity at equilibrium of up to (q0) 44.5699 mg/g. These results suggest that, although column height is a limiting factor, larger or series conformations of columns could further improve the removal efficiency of diclofenac. Thus, the work showed that coffee grounds hydrochar would be an efficient option also in fixed bed operation mode, with potential for optimization in practical wastewater treatment applications.

4. Conclusions

Analysis of the results indicates that coffee grounds hydrochar demonstrated a strong affinity for the adsorbate, evidenced by pollutant removal efficiencies that ranged from 10.36% to 100%, depending on the concentration and column height. In a 1 cm column, the rapid saturation of the adsorption sites at higher concentrations generated a lower removal efficiency, while a 3 cm column allowed a much higher removal efficiency, with 100% efficiency for 5 ppm and 81.1% for 50 ppm, without reaching the saturation point in 60 minutes. Kinetic modeling by the Thomas model showed a good fit, suggesting a significant adsorption capacity. These results demonstrate that, despite the limitations imposed by the column height, coffee grounds hydrochar has considerable potential for practical hospital effluents treatment applications

5. Acknowledgements

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6. References

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