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Effect of bed height on fixed-bed adsorption in the removal of Cu^{2+} ions using corn cob activated carbon

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Abstract

The presence of heavy metals, such as copper, in aqueous media is a concern due to the effects on the environment and the human health. To ensure water quality, various processes are used to remove heavy metals from solutions, such as adsorption. Therefore, this work evaluated the effect of bed height on the adsorption of Cu^{2+} ions in a continuous system using carbon chemically activated with phosphoric acid with corn cob as the precursor material. Hence, three different heights (10 cm (9g); 20 cm (1.8g); 30 cm (7g)) were evaluated. From the results, it could be verified that increasing the height resulted in longer breakthrough and saturation times due to the amount of active sites available to be occupied. It was also found that, despite the inversely proportional relationship between the mass of adsorbent (m) and the adsorptive capacity (q), q was 0.346 and 0.393 mmol·g^{-1} at 10 and 30 cm, respectively. In addition, an increase in the mass transfer zone (MTZ) from 9.68 to 21.65 was observed, making possible to treat a larger volume of the solution.

Keywords: Heavy metal; Agro-industrial waste; Biomass.

1. Introduction

Copper, which is widely used in steel alloys, mining, electroplating and pulp and paper industries, can be found in wastewater if it is not properly treated before discharged into receiving bodies. Its presence can cause damages to human health (cancer, kidney and gastrointestinal diseases) as it is considered toxic even at low concentrations [1].

In view of these harmful effects, the Conselho Nacional do Meio Ambiente (CONAMA) through Resolution n° 430/2011 established standards for effluent discharges into receiving bodies, with a maximum value for dissolved copper of 1.0 mg·L^{-1}. [2].

In order to attend the requirements of the legislation, adsorption has emerged as an efficient and easy-to-operate process, capable of removing metal ions from aqueous media [3].

The adsorption process can occur in two distinct systems: batch and continuous fixed-bed. Most of the works found in the literature employ batch studies, indicating a need for further investigation in continuous system.

The study of batch systems provides pertinent information about the adsorbent-adsorbate system that can be applied in a continuous process. It should be noted that the continuous process allows more effective control of the process, optimization of residence time and more effective contact between the adsorbent and adsorbate [4].

Furthermore, fixed-bed adsorption enables the treatment of larger volumes of solution and obtaining information on important parameters, such as bed height, which can be employed to optimize column operation. This factor is essential for the successful implementation of the system on an industrial scale [5].

Blagojev et al. (2021) [6] carried out a study in a continuous system on the removal of Cu^{2+} ions using wheat straw as an adsorbent, in particle size of 0.425-0.600 nm. The experiments were conducted in a 50 cm column with an internal diameter of 2.2 cm. The following conditions were employed: initial solution concentration was 1.57 mmol·L^{-1} at a pH of 4.5; a flow rate of 12 mL·min^{-1}; adsorbent mass equal to 6 g. The studies were conducted in triplicate and at the end an adsorption capacity of 0.17 mmol·g^{-1} was obtained.

In view of the above, the objective of this study was to evaluate the effect of bed height in the fixed-bed adsorption process on the removal of Cu^{2+} ions from aqueous media using activated carbon derived from corn cob.

2. Methodology

2.1 Preparation and quantification of solutions

The working solutions were prepared by diluting stock solutions of 10 mmol·L^{-1} of the Cu^{2+} ions, obtained from copper (II) nitrate trihydrate [$Cu(NO_3)_2 \cdot 6H_2O$]. The metal contents were quantified before and after adsorption in a Flame Atomic Absorption Spectrometer (brand: Varian; model: AA 240 FS; carrier gas: air-acetylene mixture; wavelength = 218.2 nm).

To quantify the ion (Cu^{2+}), an analytical curve was built in the range of 0.05 to 1.5 mmol·L^{-1}, showing the following values for figures of merit: limit of detection (LD) = 0.003 mmol·L^{-1}; limit of quantification (LQ) = 0.012 mmol·L^{-1}; linear correlation coefficient (r) = 0.9999; coefficient of variation (CV) = 2.15%. These values demonstrate that the method is accurate for quantifying the metal ion. Finally, the adsorptive capacity (q) was calculated using Equation 1.

$$q = \frac{C_i Q}{1000 m_s} \int_0^t \left(1 - \frac{C_f}{C_i}\right) dt \qquad (1)$$

where: q [mmol·g^{-1}] is the adsorptive capacity; C_i and C_f [mmol·L^{-1}] are de initial and final concentration of the metal ion, respectively; Q [mL·min^{-1}] is the fluid flow rate; m [g] is the mass of the adsorbent and t [min] is the time.

2.2 Preparation of the adsorbent

The methodology for obtaining corn cob activated carbon (CCAC) involves two main stages: 1. producing in natura corn cob (IN) by washing and drying the residue; 2. heat treatment followed by activation with phosphoric acid. These steps are described below.

Initially, to obtain IN, the raw corn cobs were washed with distilled water, dried at 110 °C for 1 h in an oven (brand: Splabor; model: SP- 100A) and ground in a knife mill (brand: CIENLAB; model: CE-430).

The IN material was placed in contact with phosphoric acid (H_3PO_4; brand: VETEC; purity: 85%) in a 5:3 ratio (mass of IN/volume of acid), followed by drying in an oven for 16 hours at 110°C and carbonization in a muffle furnace (brand: Quimis; model: Q318M21) for 1 hour at 500°C. To remove any residual acid, the material was washed with a 1% sodium bicarbonate solution ($NaHCO_3$; brand: VETEC) and distilled water.

Finally, the CCAC was dried again in an oven at 60°C for 1 hour and classified in a series of Tyler sieves with particle sizes of 0.2-1.0 mm.

Based on characterization tests conducted by CCAC in previous works [7], the following characteristics were identified: surface area of 948 m²·g^{-1}; pore diameter of 2.49 nm; pore volume of 0.59 cm³·g^{-1}; and pH of point of zero charge (pH_{pzc}) equal to 6.0.

It is noteworthy that the pH_{pzc} value is due to washing with $NaHCO_3$. Despite this value, acid activation resulted in an increase of acid groups, which favored the adsorption of metallic ions in previous batch studies. These results were corroborated by Fourier transform infrared spectra and Boehm titration.

2.3 Evaluation of the effect of bed height in a fixed bed column

For the fixed-bed column studies, a 34 cm borosilicate column with an internal diameter of 0.45 cm was utilized. The column was packed with the adsorbent and the lower and upper portions of the columns were filled with glass wool to ensure uniform inflow and outflow.

The solution was pumped through a Tygon tube with flow rate control coupled to a peristaltic pump (brand: Gilson; model: MINIPLUS 3) into the column by an upward flow. The samples were collected at the top of the column.

Thus, the effect of bed height was evaluated in a continuous system (10 cm (0.9g), 20 cm (1.8g), 30 cm (2.7g)) and the experiments were carried out in the following conditions: C_i = 1.25 mmol·L^{-1}, Q = 8 mL·min^{-1}, t = 8 h. It should be noted that the operating conditions defined for this work were based on previous finite batch studies [7].

Furthermore, the mass transfer zone (MTZ) was obtained according to the methodology developed by Geankoplis (2003) [8], which employs the calculation of the time equivalent to the total capacity, the time which the effluent concentration reaches the maximum permissible level, total bed length and the length of the bed used up to the break point.

3. Results and discussion

In order to better understand the fixed-bed column adsorption, it is necessary to evaluate the effects of different parameters on the adsorption process, including bed height. Therefore, the breakthrough curves obtained for Cu^{2+} removal when evaluating the effect of the bed height are shown in Fig. 1.

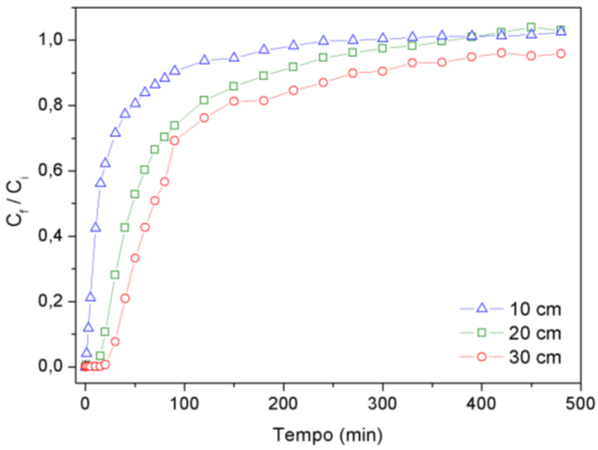

Fig.1. Effect of bed height on the removal of Cu^{2+} by CCAC. Conditions: C_i = 1.25 mmol·L^{-1}, Q = 8 mL·min^{-1} e t = 480 min.

Fig.1 shows that as the bed height decreases, the breakthrough curves shift to the left, resulting in shorter breakthrough (t_b) and saturation times (t_s). This behavior indicates the occurrence of the greatest mass transfer (region with 100% removal of the adsorbate) in a shorter period of time. Based on the results obtained from the breakthrough curves, the values of t_b, t_s, q, MTZ and the volume of solution treated (V) were obtained and are shown in Table 1.

Table 1. Parameters obtained from the study of the effect of bed height on the removal of Cu^{2+}.

Bed Height (cm)	**t_b (min)**	**t_s (min)**	**q (mmol·g^{-1})**	**MTZ**	**V (mL)**
10	1	150	0.346	9.68	1200
20	15	240	0.395	15.95	1920
30	30	420	0.393	21.75	3360

Table 1 shows longer values for t_b and t_s with increasing bed height. This is due to the fact that the increase in the bed results in the use of a greater amount of adsorbent, resulting in a greater number of active sites available to be filled [9]. Another factor that may have increased t_s was the contact time between the adsorbent and the solution, since the residence time of the solution in the column is longer.

Table 1 also indicates that as the height of the bed increases, the MTZ presents higher values, which enables the treatment of a greater quantity of solution. A similar result was observed by Payel, Hashem e Hasan (2021) [10], who utilized biochar derived from tannery sludge to adsorb chromium in a fixed-bed column.

Furthermore, Table 1 does not show a proportional relationship between the q values for the bed heights under investigation, resulting in relatively close values, differing from the expected result since the mass shows an inversely proportional relationship with q, as illustrated in Eq.1. This indicated that the increasing of the bed height would tend to decrease the material's adsorptive capacity. However, this behavior was no observed in the adsorption of Cu^{2+} by CCAC, which is a positive aspect of using this adsorbent.

4. Conclusion

The present study shows that the breakthrough curves obtained for the fixed-bed adsorption tests provide valuable insights into the performance of CCAC as an adsorbent for the removal of Cu^{2+}. It was observed that even with an increase in the mass of the adsorbent used in the column, there was no significant decrease in the adsorptive capacity, which is a highly encouraging outcome for the utilization of the CCAC as an adsorbent. It is also noteworthy that the utilization of agro-industrial waste as an adsorbent contributes to the reduction of the environmental impact of waste generation, returning the material to the production cycle.

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