

Adsorption of Pb²⁺ using corn cob activated carbon as an adsorbent: operating conditions

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Abstract

According to the United Nations World Water Development Report, wastewater is the main source of water pollution, with around 80% of the world's wastewater not receiving proper treatment. Therefore, wastewater treatment is essential to maintain water quality and it is necessary to use appropriate processes to remove pollutants present in industrial wastewater, such as metal ions. In this work, the use of corn cob activated carbon (CCAC) as an adsorbent for the removal of lead ions (Pb²⁺) from aqueous media was evaluated. For this purpose, the effects of the initial pH of the solution, adsorbent mass/volume of solution (m/V) ratio and stirring speed on the adsorption process were investigated. The results showed that the conditions that gave the best results for the adsorptive capacity (*q*) were: initial pH of the solution of 3, m/V ratio of 2 g·L⁻¹ and stirring speed of 200 rpm, with an adsorptive capacity of 0.423 mmol·g⁻¹ (84,6%). In this way, it was possible to verify the efficiency of using corn cob as a precursor in the preparation of activated carbon for the removal of Pb²⁺ ions, thus giving a new use to a waste product and contributing to the reintroduction of an agro-industrial waste into the production chain.

Keywords: Biochar; Agro-industrial waste; Lead.

1. Introduction

The presence of various pollutants harmful to human health from industrial effluents in receiving bodies is observed worldwide and is a public health problem. Among the main pollutants are heavy metals [1].

Heavy metals such as lead are widely used in paint and battery industries, which can cause its presence in wastewater in the form of the metal ion Pb²⁺. Due to its bioaccumulative capacity, the presence of Pb²⁺ in water sources, even at low concentrations can cause damage to humans (neurological and cardiovascular problems, anemia and organ failure) and plants (inhibition of root development) [2,3].

In order to remove these pollutants from aqueous media, the adsorption process has been demonstrated to be a highly effective and frequently utilized method. The adsorptive process is highlighted by its easy-of-operation, low maintenance requirements, and the possibility of using biomass as an adsorbent or as a precursor in the production of activated carbon [4].

The use of biomass is an environmentally friendly alternative, once it can be obtained from agro-industrial wastes. In addition, it is highly available, accessible and renewable with no added value [5]. One of the agro-industrial wastes that can be used is the corn cob.

Corn cob represents about 20-30% of the maize crop and, although it can be used as a source of ruminant feed or energy, it is usually inappropriately disposed of by burning, since its production is greater than consumption [6]. Thus, the use of corn cob in the adsorptive process as a precursor in the preparation of adsorbents contributes to the environmental perspective by using one waste product to treat another.

In light of these considerations, the objective of this work was to evaluate the use of corn cob activated carbon as an adsorbent for the removal of lead ion (Pb²⁺) from aqueous media. To this end, studies were carried out to verify the effects of the initial pH of the solution, the adsorbent mass/volume of solution ratio and the stirring speed on the adsorption process.

2. Methodology

2.1 Preparation and quantification of solutions

The working solutions were obtained by diluting stock solutions of Pb²⁺ ions prepared from lead (II) nitrate [Pb(NO₃)₂]. The metal ion content was quantified using a flame atomic absorption spectrometer (brand: Varian; model: Spectr AA 240 FS; carrier gas: air-acetylene mixture) at a wavelength of 261.4 nm.

The analytical curve with linear range of 0.05-1.50 mmol·L⁻¹, constructed for the quantification of the metal ion in solution, obtained a good linear fit and precision in reading the results, as it showed: Limit of Detection (LOD) = 0.004 mmol·L⁻¹, Limit de Quantification (LOQ) = 0.014 mmol·L⁻¹, $r = 0.9999$, CV = 2.66%. The adsorptive capacity (q) was calculated from Eq.1.

$$q = \frac{(C_i - C_f) \times V}{m} \quad (1)$$

where q [mmol·g⁻¹] is the adsorptive capacity; C_i and C_f [mmol·L⁻¹] are the initial and final concentration, respectively; V [L] is the solution volume and m [g] is the mass of the adsorbent.

2.2 Preparation of the adsorbent

Corn cobs were purchased from a commercial source, washed, crushed, and dried to obtain in natura corn cobs (IN). The IN material was chemically activated with phosphoric acid (H₃PO₄; brand: VETEC; purity: 85%) in a ratio of 5:3 (mass of adsorbent/volume of acid). Then, the material was dried in an oven (brand: Splabor; model: SP-100A) at 110°C for 16 hours and was placed in a muffle furnace (brand: Quimis; model: Q318M21) at 500°C for 1 hour.

After reaching room temperature, the material was washed with a solution of 1% sodium bicarbonate (NaHCO₃; brand: VETEC) and distilled water to remove the residual acid present, thus obtaining corn cob activated carbon (CCAC).

At the end of the washing process, CCAC was dried again in an oven, followed by granulometric classification using Tyler series sieves in 0.2-1.0 mm.

Based on characterization tests carried out in previous work [7], CCAC presented the following characteristics: surface area = 948 m²·g⁻¹; pore diameter = 2.49 nm; pore volume = 0.59 cm³·g⁻¹; pH

of point zero charge (pH_{PZC}) = 6.0; presence of acid groups on material surface (carboxylic, phenolic and lactonic groups).

2.3 Definition of operating conditions

In order to define the ideal working condition for the removal of Pb²⁺ from aqueous media by batch studies, the influence of the initial pH of the solution, the m/V ratio and the stirring speed were evaluated.

To evaluate the influence of the initial pH of the solution on the adsorption process, 0.1g of CCAC was placed in contact with 50 mL of the working solution (1 mmol·L⁻¹) at pH 2 to 7 and kept under constant stirring at 300 rpm for 2 h. In addition, to determine the effect of Pb²⁺ precipitation, tests were performed at the same conditions without the adsorbent. At the end of the experiment, the samples were filtered and the Pb²⁺ ion content was quantified.

The influence of m/V ratio was evaluated for 0.5, 1.0, 2.0, 4.0, 8.0 e 16.0 g·L⁻¹. To perform the experiments, 0.1g of CCAC was brought into contact with 50 mL of the solution containing Pb²⁺ at 1 mmol·L⁻¹ at 300 rpm for 2 h. The samples were filtered and the content of Pb²⁺ ions was quantified. It is noteworthy that the experiments were conducted in triplicate.

Finally, to verify the influence of the stirring speed, 0.1g of CCAC was placed in contact with 50 mL of Pb²⁺ ion solution (1 mmol·L⁻¹) for 2 h, at stirring speeds of 100, 200 and 300 rpm, in triplicate. The studies were also conducted without stirring. The samples were then filtered and the metal ion content was quantified.

3. Results and discussion

To achieve the highest possible removal, the operating conditions for the removal of Pb²⁺ ions from aqueous media using CCAC were evaluated. To this end, studies were conducted to analyze the effect of the initial pH of the solution, the mass/volume ratio, and the stirring speed.

3.1 Effect of initial pH of the solution

The pH of the solution is an essential parameter in adsorption studies, as changes in the distribution of chemical species in the solution can affect the process [8]. Therefore, the effect of the initial pH of

the solution, in the range of 2 to 7, was evaluated for the Pb²⁺ ions, as illustrated in Fig.1.

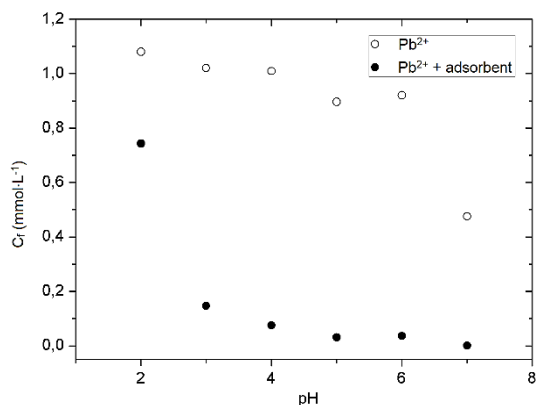


Fig.1. Evaluation of the effect of the initial pH of the solution on the adsorption of Pb²⁺ ions by CCAC. Conditions: $C_i = 1 \text{ mmol}\cdot\text{L}^{-1}$, m/V ratio = $2 \text{ g}\cdot\text{L}^{-1}$, stirring speed = 300 rpm and time = 2 h.

As illustrated in Fig.1, at pH values higher than or equal to 5, the final concentration of the metal ion exhibits a variation in the absence of the adsorbent, which can be attributed to the precipitation effect. This result corroborates with the chemical speciation diagram for Pb²⁺ in solution obtained by Cerino-Córdova et al. (2013) [9].

Fig.1 also shows that, from pH 2 to 4, the presence of the adsorbent results in an increase in the Pb²⁺ removal, with q of 0.20, 0.50 and 0.53 $\text{mmol}\cdot\text{g}^{-1}$, respectively. This is due to the fact that at lower pH values, there is a greater quantity of H⁺ ions, resulting in competition between H⁺ and Pb²⁺ ions to occupy the adsorbent's active sites [10].

Therefore, in order to avoid the precipitation region and based on q value, pH 3 was selected to work in the following studies. It is noteworthy that at pH 4, turbidity was observed in the solution upon contact with the adsorbent, prompting the decision to work at pH 3.

3.2 Effect of the mass of the adsorbent/volume of the solution ratio

The m/V ratio allows for the evaluation of the adsorptive capacity obtained for the different relations under study. This is an important parameter for the adsorption process, since it prevents the usage of unnecessary amount of adsorbent and facilitates the identification of the ideal ratio between percentage removal (%R) and q . The effect of the m/V ratios on the adsorption process of Pb²⁺ ion by CCAC is shown in Fig. 2

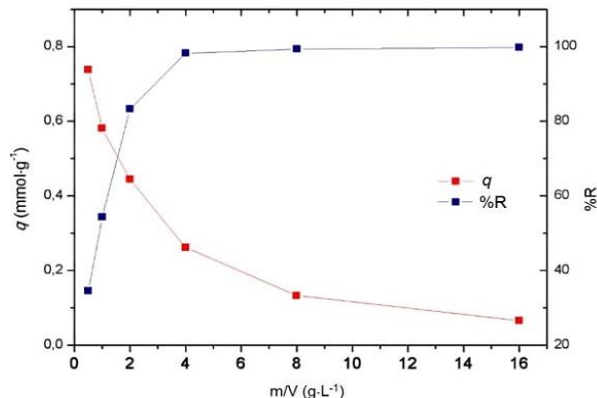


Fig.2. Evaluation of the adsorbent mass/solution volume ratio for the adsorption of Pb²⁺ ions by CCAC. Conditions: $C_i = 1,1 \text{ mmol}\cdot\text{L}^{-1}$, pH = 3, stirring speed = 300 rpm and time = 2 h.

Fig.2 illustrates that for higher m/V ratios, the %R increases and the q decreases. This is due to the fact that cause for higher ratios, a greater amount of the adsorbent is used, resulting in the presence of more active sites to be filled by the adsorbate, which cause greater removal. However, the inversely proportional relationship between q and m results in a decrease in q as the m/V ratio increases [11].

Fig.2 also indicates that %R increases from 35 to 100% and q decreases from 0,74 to 0,07 $\text{mmol}\cdot\text{g}^{-1}$. In order to establish a better relation between %R and q , the m/V ratio closest to the intersection of the curves was selected, which was $2 \text{ g}\cdot\text{L}^{-1}$.

3.3 Effect of the stirring speed

The stirring speed is important to consider in the adsorption process, since it is related to mass transfer within the system and influences diffusion. The values of q obtained for the stirring speed studied are shown in Table 1.

Table 1. Effect of stirring speed on the adsorption of Pb²⁺ ions by CCAC. Conditions: $C_i = 1 \text{ mmol}\cdot\text{L}^{-1}$, pH = 3, $m/V = 2 \text{ g}\cdot\text{L}^{-1}$ and time = 2 h.

Stirring speed (rpm)	q (mmol·g ⁻¹)
0	0.376
100	0.378
200	0.423
300	0.424

Table 1 shows that there was no significant difference in the q value for the essay without agitation and at 100 rpm, as well as between 200 and 300 rpm, with q varying by 12% from 0 to 300 rpm.

It can be posited that increasing the agitation speed can may facilitate more effective contact between the adsorbent and the adsorbate, causing an increase in the diffusion rate and more effective mass transfer, thus resulting in higher q values [12].

Therefore, due to the lower energy expenditure, a stirring speed of 200 rpm was selected for future work to evaluate de kinetic evolution and equilibrium of adsorption.

4. Conclusion

In view of the above, it was possible to define the following operating conditions for the adsorption of Pb^{2+} using CCAC: pH 3, m/V ratio of 2 g·L⁻¹ and stirring speed of 200 rpm.

In addition, the present work has also contributed to the discussion on environmental issues by providing a useful agro-industrial waste with no added value, proving its efficiency as a precursor in the preparation of activated carbon with viability in the removal of Pb^{2+} ions from aqueous media.

Acknowledgements

The authors would like to thank the FACEPE, the CNPq, the NUQAAPE/FACEPE (process APQ-0346-1.06/14) and the FADE/UFPE. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) - Código de Financiamento 001.

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