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Adsorption of the drugs paracetamol and propranolol using biochar produced from peanut shells: definition of operational conditions

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Abstract

Drugs that are not completely eliminated during wastewater treatment can remain in the aquatic environment for prolonged periods, potentially causing adverse impacts on aquatic organisms and terrestrial species that depend on these resources. In response to the significant risks associated with the presence of pharmaceuticals in bodies of water, this study investigated the adsorption process using activated carbon derived from peanut shells as an adsorbent, aiming to remove the pharmaceuticals paracetamol and propranolol. This approach is considered as an alternative or complement to currently used conventional treatment methods. The operational parameters evaluated included the pH of the solution, the adsorbent dosage and the stirring speed. The results indicated that a dosage of 2 $mg \cdot g^{-1}$ of adsorbent was able to remove 97% of paracetamol and 98% of propranolol at the solution's natural pH condition (pH 5.5). Furthermore, when evaluating different stirring speeds, it was observed that a complete drug removal (100%) was achieved at 50 rpm, highlighting the ideal conditions for the efficiency of the adsorption process of these pharmaceutical compounds. These results demonstrate the potential of the prepared adsorbent for adsorption of the drug mixture under study.

Keywords: Biomass; Activated charcoal; Wastewater treatment.

1. Introduction

In recent years, it has become increasingly common to detect the presence of pharmaceuticals, such as paracetamol (analgesic/anti-inflammatory) and propranolol (antihypertensive), in surface waters around the globe. These medications are widely consumed by the world population [1, 2]. Several studies have already highlighted the adverse effects that chronic exposure to these compounds can cause to biota and human health [3].

Due to its high stability and recalcitrant nature, drugs persist after being subjected to conventional treatments Applied in wastewater treatment plants (WWTPs). As a result, these pollutants remain present in the treated effluent and are subsequently discharged into receiving water bodies [4].

To complement conventional treatments, several advanced techniques are proposed and studied, with adsorption being a prominent example. This process is distinguished by its simplified operation, high efficiency and the ability to use waste as precursors to obtain adsorbents [5].

The operating conditions in adsorption play a crucial role in the efficiency and overall success of the process. Factors such as solution pH, adsorbent dosage and stirring speed directly influence the adsorptive capacity and adsorption kinetics [6].

The pH of the solution affects the surface charge of the adsorbent and the ionization of the adsorbate, which can significantly change the adsorption efficiency. The adsorbent dosage determines the number of active sites available for adsorption and, therefore, the contaminant removal capacity. Furthermore, the stirring speed affects the mass transfer between the solution and the adsorbent, influencing the time required to reach adsorption equilibrium [7].

Therefore, optimizing these conditions is essential to maximize the efficiency of the adsorption process, ensuring effective removal of contaminants present in the liquid medium. Thus, the present work investigates the operational conditions in the adsorption process of the drugs paracetamol (PCM) and propranolol (PPN) using activated carbon based on peanut shells in a finite bath system.

2. Materials and methods

To carry out the study, activated carbon produced from peanut shells (CA) [8] was used, being a micro-meso porous material, with a surface area of

547 $m^2 \cdot g^{-1}$, with average pore diameter of 0.2 nm and volume of 0.020 $cm^3 \cdot g^{-1}$. Its surface has oxygenated functional groups such as O-H, C-O, C=O and has a point of zero charge (pH_{PZC}) of 4.35.

Aiming to define the operational conditions for the adsorption of the binary mixture of PCM and PPN drugs by CA, the following parameters were evaluated: pH of the solution, mass ratio of the adsorbent per volume of the solution (m/V) and stirring speed of the process.

The adsorptive tests were carried out in a 125 mL Erlenmeyer flask using a solution of the drug mixture at an initial concentration of 10 $mg \cdot L^{-1}$ each. The experiments were carried out in triplicate, for a period of 120 min, at 25°± 2ºC and placed in the Shake incubator (Brand: SPlabor, model: SP-223).

At the end of each analysis, the samples were filtered using blue filter paper and quantified by UV/Vis spectrophotometry (Brand: TermoScientific, model: Genesys 10S UV-Vis) at the wavelengths of maximum absorbance (λc) of the drug mixture, being 228 and 279 nm. For each λc, an analytical curve was built in the concentration range of 1 to 15 $mg \cdot L^{-1}$, with the analytical parameters determined according to the National Institute of Metrology, Quality and Technology (INMETRO) [9].

The efficiency criteria for the operational parameters were based on the values of the removal percentages (%R) and the AC adsorptive capacity (q).

Thus, in the study of the solution pH influence, 0.1 of CA was placed in contact with 50 mL of solution at pH 3.5; 4.5 and 5.5, using a stirring speed of 100 rpm, being previously adjusted with solutions of hydrochloric acid (HCl) and sodium hydroxide (NaOH), both at 0.1 $mol \cdot L^{-1}$.

To influence the *m/V* ratio, five different rations were used (1, 2, 4, 8, and 16 $g \cdot L^{-1}$). With the data, a graph of the m/V relationship was plotted as a function of q and %R. Finally, the impact was assessed of the stirring speed (50, 100, 150, 200 and 250 rpm), tests were also carried out without stirring.

3. Results and discussion

In order to obtain the best efficiency in drug removal, the influence of solution pH, m/V ratio and stirring speed was studied. Thus, it was evaluated how these parameters influenced the adsorptive process.

The pH of the solution plays a fundamental role in the adsorptive process, as in addition to changing the surface charge of the adsorbents, it indicates the degree of dissociation or protonation of the solute [10]. The results obtained on the effect of the pH of the solution are presented in Table 1.

Table 1 – Assessment of the effect of the pH of the solution.

pH	λ_c 228 nm		λ_c 279 nm	
	q ($mg \cdot g^{-1}$)	*%R*	*q* ($mg \cdot g^{-1}$)	*%R*
3.5	5.07±0.01	100%	5.33±0.01	100%
4.5	5.07±0.03	100%	5.33±0.60	100%
5.5	5.05±0.01	100%	5.33±0.05	100%

At the pH assessed in this study, these two drugs are protonated (positive charge) [11]. As CA has a pH_{PZC} of 4.35, meaning that the surface of the material is negatively charged for solutions with pH 4.5 and 5.5, favoring electrostatic attraction between the drugs and the charcoal surface, converging with the obtained results.

However, for 3.5 (positively charged surface) values of 100% were also obtained, possibly due to the presence of oxygenated groups on the biochar surface, identified by characterization analyses.

Therefore, a pH of 5.5 (natural pH of the solution) was selected for subsequent studies, reducing the operating cost as it does not require the use of agents to correct the pH, in addition to complying with Nº CONAMA Resolution Nº 430/2011.

The relationship between the mass of adsorbent used and the volume of the solution (*m/V*) determines the balance between the adsorbate (drugs) and the adsorbent. The results obtained for several tested relationships are presented in Figure 1.

Based on the results (Figure 1), it was observed that as the m/V ratio increases, the removal percentage (%R) increases and the adsorptive capacity (q) decreases. Initially, an increase in the m/V ratio provides more active sites available for adsorption, which explains the increase in %R. However, a greater number of active sites available

without filling promotes a reduction in adsorption capacity [12].

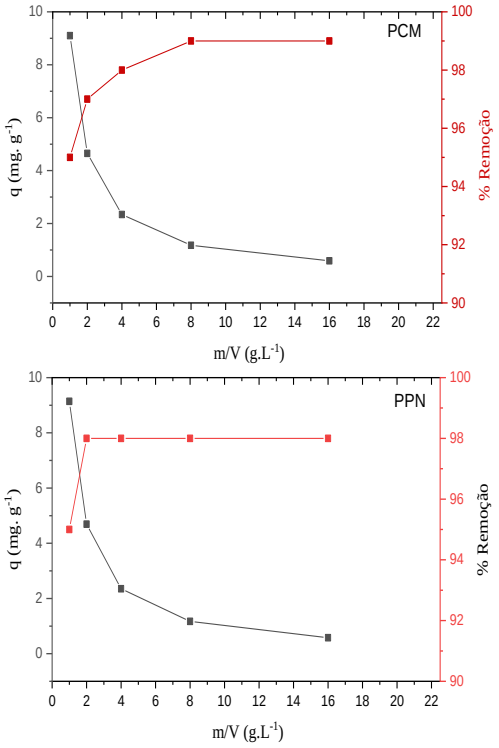

Fig. 1 – Influence of the adsorbent mass/solution volume ratio on the removal of PCM and PPN by CA.

The maximum %R achieved in the process for PCM removal was 99% with a dosage of 8 g·L^{-1} and *q* of 1.18 mg·g^{-1}. For PPN, the removal was 98% and *q* was 4.69 mg·g^{-1}, when 2 g·L^{-1} was used.

Considering that both *q* and *%R* are important in the adsorptive process, it is necessary to obtain the best performance of these two parameters simultaneously. To do this, the *m/V* ratio is chosen as the point closest to the intersection of the two curves. According to the curves in Figure 1, the dosage of 2 g·L^{-1} was the closest point to the intersection for both drugs, and this relationship was chosen for the following studies.

This choice should not significantly affect PCM removal, as at 2 g·L^{-1} it obtained an adsorptive capacity of 4.65 mg·g^{-1} and 97% removal. Combining the main characteristic of the adsorptive process, maximizing removal while using the minimum amount of adsorbent.

The stirring speed can affect the adsorption rate, since agitation can reduce the thickness of the boundary layer, in addition to keeping the particles suspended in the medium, factors that increase the speed of the adsorption process [13].

In Table 2 it is possible to observe the effect of stirring speed on the removal of drugs in the binary mixture by CA.

Table 2 – Influence of stirring speed on adsorption capacity.

Stirring speed (rpm)	*q* (mg·g^{-1})	
	PCM	PPN
0	4.607 ± 0.021	4.415 ± 0.053
50	4.672 ± 0.016	4.410 ± 0.033
100	4.518 ± 0.021	3.970 ± 0.013
150	4.642 ± 0.004	4.303 ± 0.004
200	4.607 ± 0.006	4.128 ± 0.002
250	5.027 ± 0.002	4.583 ± 0.009

According to the results observed in Table 2, stirring speed had a little influence on CA *q*. For PCM, *q* varied in the range of 4.6 mg·g^{-1} with a 10% difference between the lowest and the highest value. For PPN, q varied in the range of 4.0 mg·g^{-1} with a difference between the highest and lowest value of 13.4%.

Furthermore, the speed of 50 rpm achieved the second-best result, having a difference of 7% (PCM) and 4% (PPN) in relation to the highest value obtained at 250 rpm. In view of these results, the stirring speed selected for subsequent studies was 50 rpm, aiming to reduce the energy consumption of the process.

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Conclusion

Based on the results of this study on drug removal, the solution pH, *m/V* ratio and stirring speed were evaluated for their impact on the adsorptive process. pH 5.5 was selected because it offers good performance without the need for

adjustment, reducing operational costs. The *m/V* ratio showed that an initial increase benefits adsorption, but above a certain point saturation of the active sites occurs. Regarding the stirring speed, a moderate level did not affect significantly the adsorption capacity in systems with rapid adsorption and good internal diffusion. Thus, the study achieved ideal operating conditions, demonstrating the effectiveness of peanut shell AC in the adsorption of the mixture of analyzed drugs.

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