Adsorption of the drugs paracetamol and propranolol using biochar produced from peanut shells: isotherm and kinetic studies

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Abstract

Drugs frequently detected in surface water, even at low concentrations, have the potential to cause significant adverse impacts on aquatic life. The long-term bioaccumulation of these compounds can result in chronic toxicity to aquatic organisms and pose a risk to the quality of drinking water. Given the serious risks associated with the presence of medicines in bodies of water, this study investigated the kinetics and isotherms of the adsorption process for the removal of the drugs paracetamol and propranolol, using activated carbon derived from peanut shells as an adsorbent. The results revealed that the kinetic evolution was rapid for both drugs, reaching equilibrium in 60 min. The experimental data were better represented by the pseudo-second order model. Furthermore, intraparticle diffusion is not a controlling step in the process. The maximum adsorptive capacity was 182 mg·g^{-1} for paracetamol and 173 mg·g^{-1} for propranolol. Therefore, the study was essential to obtain data that allows the optimization of the process, ensuring effectiveness in removing contaminants.

Keywords: Biomass; Activated charcoal; Wastewater treatment.

1. Introduction

The concern about the presence of pharmaceuticals in surface waters is justified by their considerable resistance to conventional wastewater treatment methods. This can result in bioaccumulation in organisms and cause harmful effects on the environment, especially in aquatic ecosystems[1].

Paracetamol (PCM) (analgesic/ antiinflammatory) and propranolol (PPN) antihypertensive) are examples of medicines frequently identified in surface waters. Normally found in low concentrations (ηg to μg·L^{-1}), recent studies have documented occurrence in the order of mg·L^{-1} [2].

N-acetylimidoquinone, a metabolite of PCM, is a toxic byproduct that causes damage to deoxyribonucleic acid (DNA), being classified as a carcinogen and mutagen. In the case of PPN, a significant harmful effect on green algal species was observed [1, 3].

In order to avoid this type of contamination, treatment processes have been studied. Among these processes, adsorption has stood out due to its simplified operation, high efficiency and ability to use waste as raw material in the production of adsorbents[4].

In this context, the present study investigates the kinetic evolution and adsorption equilibrium isotherms of PCM and PPN drugs by activated carbon derived from peanut shells.

2. Materials and methods

To conduct the study, activated carbon derived from peanut shells (CA) [5] was used, characterized as a micro-meso porous material, with a surface area of 547 m²·g^{-1}, average pore diameter of 2.2 nm and pore volume of 0.020 cm³·g^{-1}. The surface of CA contains oxygenated functional groups, such as O-H, C-O, C=O, and has a pH point of zero charge of 4.35.

After each analysis, the samples were filtered and analyzed by UV/Vis specrophotometry (TermoScientific, Genesys 10S UV-Vis) at the wavelenghths of maximum absorbance (λ_c) of the drug mixture (228 nm and 279 nm). For each λ_c, an aanalytical curve was constructed in the range of 1 to 15 mg·L^{-1}, and evaluated according to the Instituto Nacional de Metrologia, Normalização e Qualidade Industrial (INMETRO) [6].

Initially, the kinetic Evolution of adsorption of the binary mixture of PCM and PPN drugs (10 mg·L^{-1} each) by CA was investigated.

The experiments were carried out in 125 mL Erlenmeyer flasks and kept in a shaking incubator (SPlabor, SP-223). The operating conditions defined

in previous studies were used (pH 5.5, 2 g·L⁻¹ and 50 rpm) in contact times ranging from 0 to 120 minutes.

Then, the experimental data were fitted to pseudo-first order (PPO) (Equation 1) and pseudo-second order (PSO) (Equation 2) kinetic models using the *Origin Lab 7.5* software. The quality of adjustment of the models was evaluated based on the coefficients of determination (R^2) obtained in linear regression and the respective residual errors (RSS) [7]. Furthermore, the intraparticle diffusion kinetic models proposed by Weber-Morris (Equation 3) and Boyd (Equation 4) were investigated.

$$dq/\mathrm{dt} = K_f\,(q_{eq} - q_t) \qquad (1)$$

$$\mathrm{d}q/dt = K_s\,(q_{eq} - q_t)^2 \qquad (2)$$

$$q_t = K_d * t^{0,5} + \mathrm{C} \qquad (3)$$

$$F = 1 - 6/\pi^2 \sum_1^0 1/n^2 \exp\left(-n^2 B_t\right) \qquad (4)$$

being: q_{eq} and q_t the adsorptive capacity at equilibrium and at time t (mg·g⁻¹), respectively, K_f the PPO kinetic constant (min⁻¹), K_s the PSO kinetic constant (g·mg⁻¹·min⁻¹), K_d the intraparticle diffusion coefficient (mg·g⁻¹·min⁻⁰·⁵) and C is a constant related to the resistance to diffusion (mg·g⁻¹), reflecting the thickness of the boundary layer.

As F (q_t/q_{eq}) indicates the adsorption fraction at a time and B_t represents a mathematical function of F according to Equations 5 and 6.

$$F > 0,85,\ B_t = f(F) = -\,0,4977 - \ln(1 - F) \qquad (5)$$

$$\mathrm{F} < 0,85,\ B_t = f(F) = (\sqrt{\pi} - \{\sqrt{(\pi - [(\pi - F)/3])}\})^2 \qquad (6)$$

In the experiments to obtain the adsorption isotherms, initial concentrations of the binary mixture of drugs were investigated, ranging from 1 to 800 mg·L⁻¹ at 25 ± 1°C. The experimental data were fitted to the Langmuir (Equation 7), Freundlich (Equation 8) and Langmuir-Freundlich (L-F) (Equation 9) models. The models were adjusted and evaluated in a similar way to the procedures performed in the kinetic study [7].

$$q_{eq} = q_{máx}\,\mathrm{k}_L\,Ce\,/\,(1 + \mathrm{k}_L Ce) \qquad (7)$$

$$q_{eq} = \mathrm{k}_F\,Ce^{1/n} \qquad (8)$$

$$q_{eq} = q_{máx}\,\mathrm{k}_m\,Ce^c\,/\,(1 + \mathrm{k}_m Ce) \qquad (9)$$

In which: Ce is the concentration at equilibrium (mg·L⁻¹); $q_{máx}$ is the maximum adsorptive capacity (mg·L⁻¹); k_L is the equilibrium constant for the Langmuir model (L·g⁻¹); k_F is he equilibrium constant for the Freundlich model (mol⁻¹·L^(1/n)), where 1/n is the heterogeneity factor. The parameter c indicates which of the isotherms predominates in the system and k_m is the equilibrium constant for the Langmuir-Freundlich model.

3. Results and discussion

The kinetic study makes it possible to define when the system enters equilibrium and enables the investigation of the adsorption mechanism and identification of the controlling stage of the process. The experimental data on the adsorption of PCM and PPN drugs in mixture by CA, together with the adjustments to the PPO and PSO models, are presented in Figure 1.
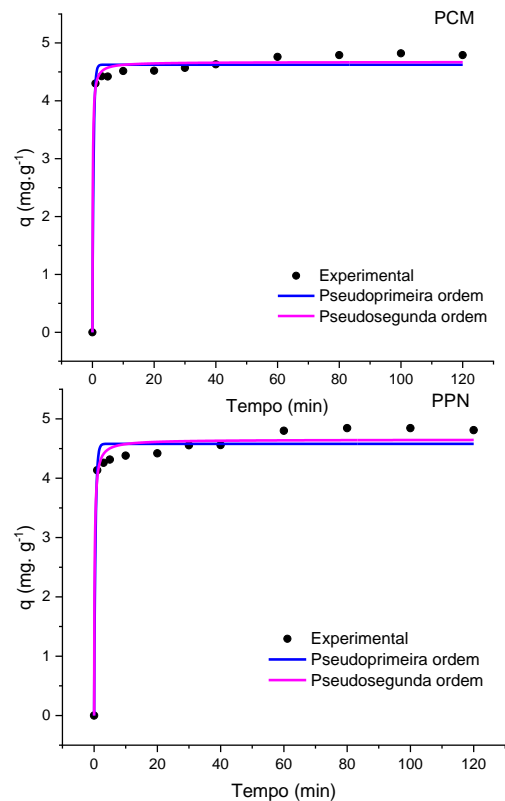

Figure 1 – Kinetic evolution of the adsorption of PCM and PPN drugs in mixture by CA.

In Figure 1, rapid adsorption is observed for both drugs in the initial minutes, followed by stabilization, reaching equilibrium after 60 min. The greater removal observed at the beginning of the process can be attributed to the high initial availability of active sites [5].

Although both models demonstrated a good fit to the experimental data, the adsorption of PCM and PPN was better represented by the PSO model, as it presented $R^2 > 0.98$ and the lowest residual residues (RSS) for both drugs. Therefore, this result suggests that the adsorption of drugs occurs preferentially on the surface of the material [7]. Furthermore, the experimental q_{eq} de 4.76 mg·g^{-1} (98% of removal) (PCM) and 4.80 mg·g^{-1} (99 % of removal) (PPN) were closer to the q_{eq} calculated by this model (4.67 and 4.65 mg·g^{-1} for PCM and PPN, respectively).

The adjustment of experimental data to the intraparticle models is shown in Figure 2.

In Figure 2A, it is observed that the data do not intersect the origin, suggesting that the adsorption mechanism of PCM and PPN on CA is complex and that intraparticle diffusion is not the step that determines the adsorption rate of the process. Furthermore, the graphs did not show linearity throughout the entire time interval, appearing to be divided into three distinct regions. The data presented a good fit to the Weber-Moris model ($R^2 > 0.90$), except for region III for PPN. It is also evident that the K_d diffusion coefficients (slope of the straight line) decrease over time, which is correlated with the reduction in drug concentration in the solution [8].

Figure 2B shows the fit of the experimental data to the Boyd model. Just like the previous model, the linear coefficient of the fitted curve is different from zero ($B_0 \neq 0$), confirming again that internal diffusion to the pores is not the controlling step of the process [7].

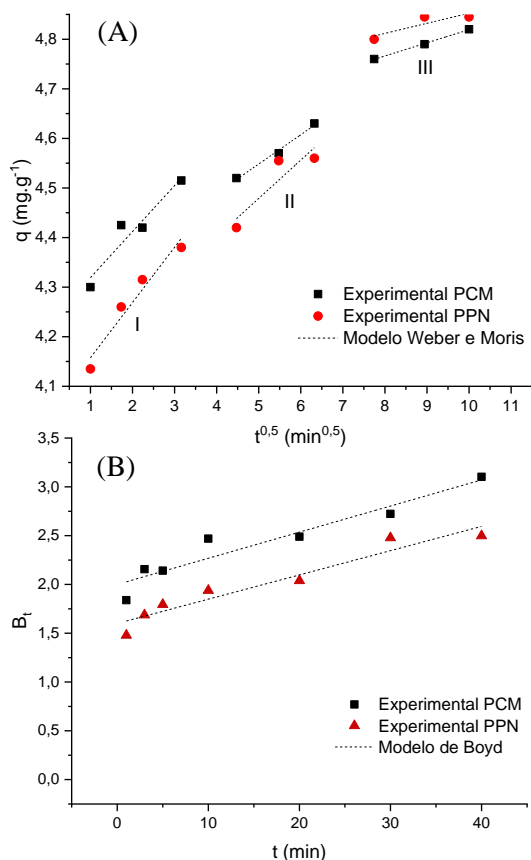The experimental data, as well as the adjustments to the isothermal models, are presented in Figure 3.

Figure 2 – Adjustment to intraparticle diffusion models of PCM and PPN drugs mixed by CA. Weber-Moris (A) and Boyd (B) model.
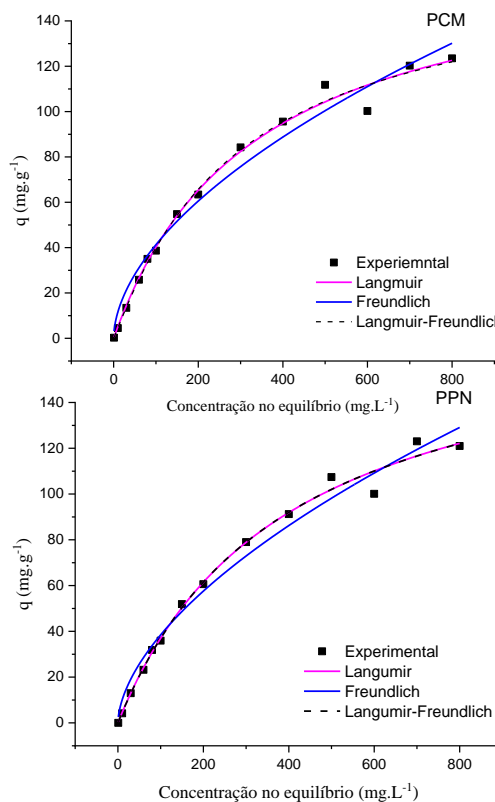

Figure 3 – PCM and PPN adsorption isotherms by CA.

The isotherms, Figure 3, are L1 type, indicating the great affinity of the drugs with CA. Despite the use of high initial concentrations (800 mg·L^{-1}), a plateau indicating equilibrium was not observed, which suggests an elevated availability of active sites in the adsorbent material [9].

The three models fit the experimental data well. The *c* parameter of L-F model was equal to 1, indicating a bias towards the Langmuir model. Furthermore, this last one demonstrated an R^2 > 0.99 and lower RSS, which best represented the experimental data.

Through this model, it was possible to calculate that CA presented a greater maximum adsorption capacity ($q_{máx}$ = 182 mg·g^{-1}) for PCM compared to PPN ($q_{máx}$ = 173 mg·g^{-1}). The PCM has a lower molar mass and less complex structure, this allows a greater number of molecules can be adsorbed per unit of adsorbent [10].

Conclusion

In the kinetic study, a satisfactory interaction between the drugs and the adsorbent was observed, evidenced by the rapid equilibrium achieved. The PSO model was the most appropriate to describe the experimental data, indicating that the drugs adsorption occurs preferentially on the surface of the adsorbent. The intraparticle diffusion models evaluated suggest that diffusion within particles is not the limiting step of the adsorption process. Furthermore, in the equilibrium study, it was observed that even with an increase in the initial concentration of drugs, adsorption continued to occur without reaching saturation of the adsorbent material. In this way, the study highlighted the complexity of the adsorbent-drug interaction and the material's ability to maintain high availability of active sites even in the face of high concentrations of contaminants.

Acknowledgements

References

[1] Melliti, A, Touihri, M, Kofronová, J, Hannachi, C, Sellaoui, L, Petriciolet, A B, Vurm, R. Sustainable removal od cadderine and acetaminophen form water using biomass waste-derived activated carbon: Synthesis, charecterization, and modelling. Chemosphere 2024; 355: 141787.

[2] Spaltro, A, Pila, M N, Colasurdo, D D, Grau, E N, Romam, G, Siminett, S, Ruiz, D L. Removal of paracetamol from aqueous solution by activated carbono and sílica. Experimental and computation study. J. of Con. Hyd. 2021; 236: 103739.

[3] Maszkowska, J, Stolle, S, Kumirska, J, Lukaszewicz, P, Mioduszewska, K, Puckowski, A, Caban, M, Wagil, M, Stepnowski, P, Bielinska, A B. Beta-clockrs in the environment: PartII. Ecotoxicity study. Science of The T. Env. 2014; 493: p. 1122-6.

[4] Michelon, A, Bortoluz, J, Raota, C S, Giovanela, M. Agro-industrial residues as biosorbents for the removal of anti-inflammatories from aqueous matrices: An overview. Environmental Advances 2022; 9: 100261.

[5] Santos, V. H, Nascimento, G E, Sales, D C S, Santos, J H L, Díasz, J M R, Duarte, M M M B. Preparation of adsorbents from agro-industrial wastes and theiir application in the removal of Cd^{2+} and Pb^{2+} ions from a binary misxture: Evoluation of ionic competition. Chemical Eng. Res. and Des. 2022; 184: p. 152-64.

[6] Instituto Nacional De Metrologia, Qualidade e Tecnologia (INMETRO). Orientação sobre validação de métodos analíticos (DOQ-CGCRE-008). Revisão 09, 2022: Acesso em 28 de maio de 2024.

[7] Nascimento, R F, Lima, A C A, Vidal, C B, Melo, D. Q.; Raulino, G. S. C. Adsorção: aspectos teóricos e aplicações ambientais. 2020; 2 ed, Fortaleza: UFC.

[8] Weber, W J, Morris, J C. Kinetics of adsorption on carbon from solution. J. of the Sanitary Eng. Divison 1963; 89.

[9] Laksaci, H, Belhamdi, B, Khelifi, O, Khelifi, A, Trari, M. Elimination of amoxicillin by adsorption on coffee waste based activated carbon. J. of Mol. Structure 2023; 1274: 134500.

[10] Streit, A F M, Collazzo. G C, Druzian, S P, Verdi, R S, Foletto, E L, Oliveira, L F S, Dotto, G L. Adsorption of ibuptofen, ketoprofen, and paracetamol onto activated carbon prepared from effluent treatment plant sludge of the beverage industry. Chemosphere 2021; 262: 128322.