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ESTUDOS PRELIMINARES DE ADSORVENTES LENHOCELULÓSICOS PARA A REMOÇÃO DE CEFALOSPORINAS PRELIMINARY STUDIES ON LIGNOCELLULOSIC ADSORBENTS FOR THE REMOVAL OF CEPHALOSPORINS ESTUDIOS PRELIMINARES SOBRE ADSORBENTES LIGNOCELULÓSICOS PARA LA ELIMINACIÓN DE CEFALOSPORINAS

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RESUMO

Introdução: A *Acacia dealbata* foi explorada como biosorvente para remover cefalosporina de soluções aquosas. Este estudo procura demonstrar a viabilidade de utilizar materiais lenhocelulósicos de baixo custona remoção de poluentes, valorizando resíduos de outras indústrias e reduzindo o impacto ambiental associado.

Objetivo: O objetivo pretendeu avaliar a capacidade dos resíduos de acácia em adsorver a cefalosporina, analisando o seu potencial de adsorção e os modelos cinéticos envolvidos, de forma a explorar o seu uso no tratamento de águas.

Métodos: Esta revisão foi conduzida utilizando uma abordagem sistemática para identificar, analisar e sintetizar a literatura relevante sobre a presença e o impacto dos antibióticos cefalosporínicos em ambientes aquáticos. Paralelamente, foram realizados testes de adsorção utilizando soluções de cefalosporina com concentração de 15 mg L⁻¹, variando o tempo de agitação entre 10 e 120 minutos. A cinética de adsorção foi avaliada com base nos modelos de pseudo-primeira ordem, pseudo-segunda ordem, Elovich e difusão intrapartícula. A adsorção foi analisada através de espectrometria UV-Vis, onde se identificou um pico de absorção característico a 240 nm.

Resultados: Os resultados indicaram que o modelo de pseudo-primeira ordem apresentou o coeficiente de determinação mais elevado (R² = 0,991), sugerindo que o mecanismo predominante é a adsorção física. Esta análise confirmou a capacidade da acácia em adsorver cefalosporinas, evidenciando o seu potencial como biosorvente.

Conclusão: Este estudo sublinha a relevância dos biosorventes, como a *Acacia dealbata*, no tratamento de poluentes da indústria farmacêutica. A utilização de materiais sustentáveis oferece uma solução promissora para o tratamento de águas, abrindo caminho para futuras aplicações no campo da biossorção.

Palavras-chave: adsorção; modelos cinético; materiais lenhocelulósicos; cefalosporina; Acacia dealbata

ABSTRACT

Introduction: Acacia dealbata was explored as a biosorbent to remove cephalosporin from aqueous solutions. This study intends to demonstrate the feasibility of using lignocellulosic low-cost materials in the removal of pollutants, valorizing waste from other industries, and reducing the associated environmental impact.

Objective: The aim of this study was to evaluate the capacity of acacia residues to adsorb cephalosporin, analyze its adsorption potential, and examine the kinetic models involved in order to explore its use in water treatment.

Methods: This review was conducted using a systematic approach to identify, analyze, and synthesize the relevant literature on the presence and impact of cephalosporin antibiotics in aquatic environments. In parallel, adsorption tests were performed using cephalosporin solutions with a concentration of 15 mg L⁻¹, varying the stirring time between 10 and 120 minutes. The adsorption kinetics were evaluated based on the pseudo-first order, pseudo-second order, Elovich, and intraparticle diffusion models. The adsorption was analyzed by UV-Vis spectrometry, where a characteristic absorption peak at 240 nm was identified.

Results: The results indicated that the pseudo-first order model presented the highest coefficient of determination ($R^2 = 0.991$), suggesting that the predominant mechanism is physical adsorption. This analysis confirmed the ability of acacia to adsorb cephalosporins, evidencing its potential as a biosorbent.

Conclusion: This study highlights the relevance of biosorbents, such as Acacia dealbata, in the treatment of pollutants from the pharmaceutical industry. The use of sustainable materials offers a promising solution for water treatment, paving the way for future applications in the field of biosorption.

Keywords: adsorption; kinetics models; lignocellulosic materials; cephalosporin; Acacia dealbata

RESUMEN

Introducción: Se exploró la *Acacia dealbata* como biosorbente para eliminar la cefalosporina de soluciones acuosas. Buscando demostrar la viabilidad de utilizar materiales lignocelulósicos de bajo costopara eliminar contaminantes, valorizando residuos de otras industrias y reduciendo el impacto ambiental asociado.

Objetivo: El objetivo de este estudio fue evaluar la capacidad de los residuos de acacia para adsorber cefalosporina, analizando su potencial de adsorción y los modelos cinéticos involucrados, explorando su uso en el tratamiento de agua.

Métodos: Esta revisión se llevó a cabo utilizando un enfoque sistemático para identificar, analizar y sintetizar la literatura relevante sobre la presencia e impacto de los antibióticos cefalosporínicos en entornos acuáticos. Paralelamente, se realizaron pruebas de adsorción utilizando soluciones de cefalosporina con una concentración de 15 mg L⁻¹, con un tiempo de agitación entre 10 y 120 minutos. La cinética de adsorción se evaluó con base en los modelos de pseudo-primer orden, pseudo-segundo orden, Elovich y difusión intrapartícula. La adsorción se analizó mediante espectrometría UV-Vis, donde se identificó un pico de absorción característico a 240 nm.

Resultados: Los resultados indicaron que el modelo pseudo-primer orden presentó el mayor coeficiente de determinación (R² = 0,991), sugiriendo que el mecanismo predominante es la adsorción física. Este análisis confirmó la capacidad de la acacia para adsorber cefalosporinas, demostrando su potencial como biosorbente.

Conclusión: Este estudio destaca la relevancia de los biosorbentes, como *Acacia dealbata*, en el tratamiento de contaminantes de la industria farmacéutica. El uso de materiales sostenibles ofrece una solución prometedora para el tratamiento del agua, abriendo el camino para futuras aplicaciones de la biosorción.

Palabras Clave: adsorción; modelos cinéticos; materiales lignocelulósicos; cefalosporina; Acacia dealbata

INTRODUCTION

Environmental issues have become one of humans' major concerns, being water pollution one of the biggest problems. Water faces contaminant compounds at every point of its cycle, however, pollution through discharges of contaminated effluents is the most common. The pharmaceutical industries, for example, dispose a large amount of contaminated wastewater containing antiinflammatories, analgesics, antiepileptics or antibiotics, such as cephalosporins (Abdullah et al., 2023; Caique Alves et al., 2018; Cruz-Lopes et al., 2022; Jelic et al., 2011; Phan et al., 2024; Rivera-Utrilla et al., 2013; Sophia et al., 2016). Excessive consumption of antibiotics is a big issue, since the use of these compounds ranges from 100.000 to 200.000 tons per year (Mardani et al., 2023; Puddoo et al., 2017). The presence of the antibiotic in different water sources has been reported in Europe, Asia, America and Australia (Puddoo et al., 2017; Tuc Dinh et al., 2011; Watkinson et al., 2009).

Organic compounds are frequently detected in aquatic environments (Chernomorova et al., 2023; Das et al., 2019; Kowalska et al., 2020; Mohammadi Nezhad et al., 2023; Rivera-Utrilla et al., 2013; Sen et al., 2023; Sundararaman & Saravanane, 2010). Water samples analyzed within the Seine River, in France, revealed the presence of 12 antibiotics, including tylosin, erythromycin, tetracycline, amoxicillin, trimethoprim, sulfamethoxazole, oxolinic acid, flumequine, norfloxacin, ciprofloxacin, ofloxacin, and vancomycin, with concentration from 0.002 to 1.44 μ g L⁻¹ (Tuc Dinh et al., 2011). Likewise, antibiotics were found in hospital effluent of South–East Queensland, Australia, dominated by the β -lactam, quinolone and sulphonamide groups, with concentrations from 0.01 to 14.5 μ g L⁻¹ (Watkinson et al., 2009).

About 5 to 90% of the antibiotic doses administered may be excreted as metabolites after use. This way, large amounts of antibiotics are susceptible to enter water bodies through effluent discharge or other sources (Tuc Dinh et al., 2011). The contribution of antibiotics in environmental pollution, is characterized by their fluctuating and recalcitrant properties (Puddoo et al., 2017). The persistence of pharmaceuticals compounds in water can imply great risks to the environmental equilibrium, such as antimicrobial resistance and aquatic ecosystems disruption (Da Trindade & Salgado, 2018; Gracia-Lor et al., 2012; Khasawneh & Palaniandy, 2021; Pereira et al., 2019; Ribeiro et al., 2018). The risks posed to the aquatic organisms include cancer, infertility and fish feminization (Caique Alves et al., 2018).

The cephalosporins are widely used in human and animal care. Approximately 50–70% of antibiotic used worldwide to treat human diseases is based on cephalosporins(Abdullah et al., 2023). Because of this, it is frequently found in residual wastewater from pharmaceutical factories, urban and hospital areas, in concentrations ranging from 0.30 ng L⁻¹ to 0.03 mg L⁻¹ (Ribeiro et al., 2018). According to Ribeiro et al. (2018), cephalosporins have been detected in aquatic environments at concentrations up to 0.03 mg/L, mainly in wastewater matrices. Although they are expected to undergo rapid degradation, some transformation products, such as 2-mercapto-5-methyl-1,3,4-thiadiazole (MMTD) formed during the photolysis of cefazolin (X.-H. Wang & Lin, 2012), and sulfoxide and chlorinated by-products generated during chlorination (Li & Zhang, 2013), have shown increased toxicity in *Vibrio fischeri* and *Salmonella typhimurium* assays, respectively, indicating a potentially higher persistence and ecotoxicity compared to the parent compounds.

Managing pharmaceutical contamination can be a challenge due to the limitations of conventional wastewater treatment methods (Caique Alves et al., 2018; Puddoo et al., 2017) and since some antibiotics can persists for months in surface waters (Tuc Dinh et al., 2011). This cephalosporins to trace amount of these compounds remaining in treated effluents and water bodies (Abdullah et al., 2023; Akhtar et al., 2016; Correia & Marcano, 2015; Khan et al., 2022; Samal et al., 2022). Thus, the use of alternative methods such as adsorption and biosorption, with natural materials, has emerged as a promising solution (Samal et al., 2022; Sen et al., 2023; Zhang et al., 2020). Biosorbents, especially those derived from lignocellulosic materials have shown great results in the removal of contaminants from aqueous systems (Macena, 2021).

Lignocellulosic materials are mainly composed of cellulose, hemicellulose and lignin, containing essential functional groups that enhance the adsorption process (Cruz-Lopes et al., 2022). The use of lignocellulosic biosorbents, originated from agricultural and forest industries, is a great option since these materials are otherwise considered as residues (Cruz-Lopes et al., 2022; B. Wang et al., 2021; Zhang et al., 2020). These type of materials are very abundant in nature and cost-effective, what makes them an attractive option for large-scale applications in water treatment (Cruz-Lopes et al., 2022; Naeini & Moradi, 2023). Their structure provides great conditions to interact and bind contaminants, such as pharmaceutical compounds.

The most applied techniques to remove antibiotics from water sources are the conventional methods, which include filtration and sedimentation, followed by biological processing. Additionally, the oxidation or advanced oxidation, the disinfection (chlorination), as well as the adsorption has gained space (Sen et al., 2023). However, adsorption has some advantages over the other methos, being highly efficient at low concentrations, easy to scale up and low-cost (Macena, 2021). Alternative adsorbents such as microalgae and carbon-based materials, hydrochars, and biochars are currently being investigated for antibiotic removal (Sen et al., 2023). Studies reported a better degradation of pharmaceutical compounds such as diazepam, diclofenac and carbamazepine, by adding biological activated carbon into the aeration tank of activated sludge. Also, the application of activated carbon in membrane bioreactor was reported to support the attachment of low molecular weight contaminants (Tiwari et al., 2017).

Nonetheless, the adsorption process depends on a variety of factors, including the surface area, pore structure and functional groups in the biosorbent. Likewise, the physical and chemical properties of pharmaceutical pollutants, such as solubility, volatility,

photo-degradation and biodegradability, as well as the wastewater treatment plant operational parameters, such as hydraulic retention time, pH and temperature have influence in the removal efficiency of pharmaceutical pollutants (Tiwari et al., 2017). This study consists in the evaluation of a lignocellulosic material (branches of *Acacia dealbata*) used as biosorbent to remove cephalosporin in aqueous solution. The reaction kinetics were studied by applying the pseudo-first order (PFO), pseudo-second order (PSO), Elovich and intraparticle diffusion (ID) models.

1. METODOLOGY

This review was conducted using a systematic approach to identify, analyze, and synthesize relevant literature on the presence and impact of cephalosporin antibiotics in aquatic environments. The research focused on water contamination by pharmaceuticals and personal care products (PCPs), as well as the methods used for their removal. The study utilized VOSviewer software (Van Eck & Waltman, 2010) (Figure 1), widely adopted for visualizing bibliometric networks, enabling the quantification and detailed analysis of scientific literature. Keywords such as "Cephalosporins," "Water Contamination," "Antimicrobial Resistance," and "Removal Processes" were employed to structure and refine the bibliographic networks. A systematic search was conducted across academic databases, including PubMed and Google Scholar, to ensure comprehensive coverage of the topic. A predefined search protocol was implemented, incorporating keyword identification and selection of reliable sources of information. The reviewed literature spanned the period from 2008 to 2024, with a particular emphasis on publications from 2018 to 2024, reflecting recent advancements and concerns. From an initial set of 96 references, 36 articles were ultimately selected for inclusion in this review.



Figure 1 - Vosviewer map of organized literature search.

Figure 2 demonstrates the correlation between the volume of publications and their temporal distribution, highlighting the increasing research interest in this field during the specified period. The selected studies underwent rigorous evaluation to ensure relevance, quality, and alignment with the research objectives.





This comprehensive review of cephalosporin contamination in aquatic environments underscores the importance of monitoring and removing these compounds, emphasizing their impact on antimicrobial resistance and environmental safety. The detection of high concentrations of antibiotics in natural and urban water sources represents a growing concern, as it may compromise public health and aquatic ecosystems.

Currently, various approaches have been proposed to enhance the efficiency of pharmaceutical and PCP removal from wastewater systems, including activated carbon adsorption, advanced oxidation processes, and membrane-based technologies. The implementation of such techniques aims not only at the effective removal of substances like cephalosporins but also at minimizing the environmental impact associated with pharmaceutical contamination in water systems.

The adopted methodology ensures transparency, reproducibility, and robustness in synthesizing current evidence regarding the risks and solutions for cephalosporin contamination in aquatic environments, contributing to the advancement of knowledge and the development of more effective strategies for water quality management.

2. MATERIALS AND METHODS

2.1 Biosorbent material

The branches of *Acacia dealbata* were collected in Viseu, Portugal. The vegetal material has approximately 2-5 cm diameter and was milled (Retsch SMI mill) and sieved (Retsch AS200) for 20 minutes at a speed of 50 rpm. Four fractions were obtained: 40 mesh (> 0.420 mm); 40-60 mesh (0.420-0.250 mm); 60-80 mesh (0.250-0.177 mm) and < 80 mesh (< 0.177 mm). The fraction used in this study as biosorbent was the powder (< 80 mesh), which was dried for 24 hours at 105 °C in an oven before use.

2.2 Antibiotic

The antibiotic employed in this experiment was Ceftriaxone sodium (Figure 3), a third-generation semi-synthetic antibiotic classified under the cephalosporin. Ceftriaxone sodium is present in the form of disodium hemieptahydrate.





Ceftriaxone sodium has the molecular formula $C_{18}H_{16}N_8Na_2O_7S_3 \cdot 3\frac{1}{2}H_2O$ in its hydrated form, with a molecular weight of 661.60 g/mol. In its anhydrous form ($C_{18}H_{18}N_8O_7S$), the molecular weight is 598.56 g/mol. The potency of ceftriaxone sodium ranges from 905 to 935 mg/g when calculated on an anhydrous basis. It has a melting point above 155°C, a logP value of -1.7, and pKa values of 3.19 (acidic) and 4.17 (basic) (National Center for Biotechnology Information, 2025). Characterized by its appearance as an

almost white to yellowish, slightly hygroscopic crystalline powder. In terms of solubility, it is freely soluble in water, sparingly soluble in methanol, and exhibits very slight solubility in anhydrous ethanol.

2.3 Identification of cephalosporin by UV-Visible

Cephalosporin solutions at concentrations of 2.5, 5, 10, 15, and 20 mg L⁻¹ were sequentially prepared using distilled water and immediately analyzed using a Perkin Elmer Lambda 25 UV-Visible spectrophotometer (200–800 nm) to identify the absorption peak. Immediate analysis after preparation was essential to avoid hydrolysis of the β -lactam ring in aqueous solution, which is known to begin within hours, particularly under ambient conditions, potentially altering the compound's spectral characteristics and leading to inaccurate results (Abramović et al., 2021).

2.4 Study of adsorption kinetics

Adsorption kinetics provide insights into the adsorption mechanism, enabling the evaluation of process effectiveness. The mechanisms that occurs can be divided into three phases: mass transfer, which involves the movement of the solute from the solution to the film at the solid-liquid interface of the adsorbent; intraparticle diffusion, referring to the movement of the solute through the adsorbent's pores; and sorption which involves the binding of the solute to the active sites on the adsorbent's surface(Macena, 2021). Adsorption kinetics describe the rate at which the solute is adsorbed, allowing for the prediction of pollutant removal rates from the solution. Understanding this rate is essential for planning adsorption treatment processes.

To perform the kinetics analysis, 25 mL of Cephalosporin solutions with concentrations of 15 mg L^{-1} were added to Erlenmeyers, containing 100 mg of Acacia adsorbent. The experiment was conducted at room temperature, with continuous stirring provided by a magnetic stirrer for 15, 30, 45, 60, 120, and 180 minutes, respectively. After the period of contact/agitation, the samples were filtered with filter paper. The residual antibiotic concentration was measured by a UV-visible spectrometer.

The PFO model (Lagergren, 1898) considers that the rate at which active adsorption sites on the sorbent are filled is proportional to the number of vacant sites, expressed by the equation (1).

$$ln(q_e - q_t) = lnq_e - k_1 t(1)$$

where k_1 is pseudo-first order adsorption rate constant (min⁻¹).

The PSO model (Ho & McKay, 1998) define the rate of adsorption as the interaction of the adsorbate with two independent vacant sites on the adsorbent. The equation (2) represents this model's linear form.

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \tag{2}$$

where k_2 is pseudo-second order adsorption rate constant (g.mg⁻¹.min). Based on the rate constant k_2 it is possible to determine the initial adsorption rate h (mg.g⁻¹.min), given by the equation (3).

$$h = k_2 \times q_e^2 \tag{3}$$

The Elovich equation (4) was proposed by Roginsky and Zeldovich in 1934 (Roginsky & Zeldovich, 1934).

$$q_t = \left(\frac{1}{b}\right) \times \ln(ab) + \left(\frac{1}{b}\right) \ln(t) \qquad (4)$$

where a and b are the constants of the model, with b representing the constant linked to surface coverage and activation energy for chemisorption, while a denotes the initial adsorption rate (mg.g⁻¹.min).

The intraparticle diffusion model equation (5) was proposed by Weber and Morris in 1963 (Weber & Morris, 1963).

$$q_t = k_t t^{1/2} + C (5)$$

where the initial adsorption C is expressed in mg g⁻¹, while k_t is the constant (mg.g⁻¹.min^{1/2}). The slope of q_t versus $t^{\frac{1}{2}}$ should be linear, with k_t and C representing the slope and the interception of the line, respectively.

3. RESULTS AND DISCUSSION

3.1 Study of the peak of absorption of cephalosporin by UV-Visible

The ability to detect cephalosporin antibiotics in an aqueous medium was evaluated using UV-visible spectroscopy. As shown in Figure 4, the absorption peak was observed at approximately 240 nm. Although this wavelength falls within the UV-C region,

potential photolytic degradation is unlikely under the short exposure times and low-intensity light used during spectrophotometric analysis, thus minimizing the risk of structural alterations during measurement (Abramović et al., 2021).

Figure 4 demonstrates a distinct absorption peak for cephalosporin antibiotic, observed at an approximate wavelength of 240 nm. This peak serves as a definitive marker of the compound's presence and is critical for accurate analysis in ultraviolet (UV) detection methods. Additionally, it was possible to note that the intensity of the peak is directly proportional to the concentration of cephalosporin in the samples.



Figure 4 - UV-visible absorption of Cephalosporin with the concentration of 20 mg L⁻¹ (1), 15 mg L⁻¹ (2), 10 mg L⁻¹ (3), 5 mg L⁻¹ (4) and 2.5 mg L⁻¹ (5).

3.2 Adsorption kinetics

Adsorption kinetics are typically represented by a plot of adsorption over time, which serves as the basis of kinetic studies since the curve's shape reveals the intrinsic kinetics of the process. Commonly, PFO and PSO models are applied in adsorption kinetics studies. The adsorption kinetics of cephalosporin onto the lignocellulosic material were also analyzed using the Elovich and intraparticle diffusion (ID) models, providing insights into the adsorption mechanism.

A higher retention rate was observed at the beginning of the adsorption process, followed by a slower increase as the test time progressed until reaching equilibrium or saturation of the biosorbent.



Figure 5 - Variation of the adsorption efficiency with the time.

The determination coefficient was determined for PFO and PSO models (Figure 6), as well as for the Elovich and ID models (Figure 7).



Figure 6 - Pseudo-first order model (a) and Pseudo-second order model (b) for cephalosporin adsorption.



Figure 7 - Elovich (a) and Intraparticle diffusion models (b) for cephalosporin adsorption.

The analysis of the coefficient of determination (R^2) demonstrated that the PFO model provided the best fit for describing the adsorption kinetics in this study, achieving R^2 of 0.991. These results indicate that the PFO model was the most accurate in describing the dynamics of the adsorption process for the antibiotic cephalosporin onto Acacia branches. However, the other models tested also presented R^2 above 0.900, which means that the kinetics are complex, and more than one mechanism can take place in the adsorption.

A study provided insights about the adsorption of cephalosporins, specifically cefotaxime, ceftriaxone, and cefazolin(Chernomorova et al., 2023). Their findings highlighted that the PSO model offered the best fit for describing cephalosporin adsorption, with R² from 0.861 to 0.994, while the PFO model presented R² from 0.823 to 0.983. The PSO model suggests that the adsorption process depends on the availability of adsorption sites and the concentration of cephalosporins, implying a chemisorption mechanism, where chemical bonds or interactions between the sorbates and the adsorbent surface are significant. Interestingly, while the PSO model described the overall adsorption process, in the initial stages, the PFO model was effective, and film diffusion (movement of cephalosporins through a boundary layer surrounding the adsorbent) played a crucial role in this early phase. This indicates that adsorption is influenced by different mechanisms over time, with physical diffusion dominating initially before chemisorption becomes the primary mechanism.

The adsorption of ibuprofen, ketoprofen, naproxen, and diclofenac was tested onto a low-cost activated carbon prepared from olive waste (Baccar et al., 2012). The adsorption kinetics were studied using PFO, PSO, and Elovich models. The results indicated that the PSO model showed a better fit for the four tested compounds, with R² from 0.999 to 1.000 for the PSO model, R2 from 0.593 to 0.966 for the Elovich model, and R2 from 0.815 to 0.978 for the PFO model. In the same way, the capacity of sorption of

ciprofloxacin onto three carbon-based materials was tested by Carabineiro et al., and the kinetics results showed that the PSO model fits the adsorption data better.

In contrast, in our study, the PFO model was better at describing the cephalosporin adsorption process as indicated by higher correlation coefficients. This suggests that physical adsorption, characterized by weaker interactions like van der Waals forces, may have a more consistent influence on adsorption across the entire process. This model is particularly relevant under conditions where the initial adsorbate concentration is low or when diffusion limitations restrict the adsorption process. The PFO model suggests that adsorption is largely governed by physical interactions and diffusion constraints. On the other hand, PSO, Elovich, and intraparticle diffusion typically indicate more complex interactions, such as stronger chemical bonds or multilayer adsorption, which were not predominant in this system.

Nevertheless, since the other models tested presented a high coefficient of determination R² from 0.908 for the ID model to 0.969 for the Elovich model, it is possible to assume that more than one mechanism takes place throughout the adsorption process. Nonetheless, these differences in findings could be due to variations in experimental conditions, such as differences in adsorbent materials, pH levels, and cephalosporin concentrations, which might alter the dominant adsorption mechanism.

Tables 1 and 2 present the parameters for the kinetic data using PFO, PSO, Elovich, and Intraparticle diffusion models, respectively. The Elovich equation is often applied to describe chemisorption on heterogeneous surfaces, particularly in systems where adsorption occurs through a complex rate process involving surface coverage and activation energy variations. The parameter A was found to be 0.07 mg·g⁻¹·min⁻¹, indicating a relatively fast initial adsorption rate. This value is considerably lower than the observed before for the adsorption of amoxicillin, ampicillin, and doripenem on organobentonite (Yeo et al., 2024) but higher than the observed for for the removal of amoxicillin antibiotic from water with nanoporous carbon (0.04 mg.g⁻¹ min⁻¹)(Ali et al., 2023). In a study with ampicillin adsorption on microporous carbon sorbents the a values ranged between 0.85 to 4.3 mg·g⁻¹·min⁻¹ which are higher from the ones obtained in this study(Lach, 2024) or the 16.63 mg·g⁻¹·min⁻¹ obtained for the adsorption of erythromycin using magnetic activated carbon (Gholamiyan et al., 2020). The parameter b, which reflects the extent of surface coverage and interaction between the adsorbate and the adsorbent, was 0.75 g mg¹, suggesting that the adsorption rate decreases as cephalosporin occupies available sites. In this case parameter b is higher than the observed before for the adsorption onto organobentonite with values around 0.27 g·mg⁻¹ and onto microporous carbon 0.1-0.2 g·mg⁻¹ (Lach, 2024; Yeo et al., 2024). The intraparticle diffusion (ID) model was also evaluated to determine whether diffusion within the pores of the lignocellulosic material was the rate-limiting step in the adsorption process. The intraparticle diffusion rate constant (Kdif) was determined to be 0.33 mg·g⁻¹·min^{1/2}, indicating a relatively slow diffusion process. This constant is smaller than the values presented before for the adsorption of amoxicillin, ampicillin, and doripenemon organobentonite that ranged between 0.38 mg g⁻¹·min^{1/2} and 0.59 mg·g⁻¹·min^{1/2}(Yeo et al., 2024). The parameter C, which represents the boundary layer effect, was found to be -0.42, an uncommon negative value that may indicate deviations from the classical ID model or experimental limitations. Looking at Figure 6(b) it is possible to see that there is clearly two different lines similar to the observed before (Gholamiyan et al., 2020; Yeo et al., 2024). Therefore, dividing into two different lines the parameter C is -1.7 and 1.5 and Kdif 0.56 mg·g⁻¹·min^{1/2} and 0.16 mg·g⁻¹·min^{1/2} respectively. The lower R² value for the ID model, along with the relatively low Kdif, especially in the second part of the curve implies that while intraparticle diffusion plays a role, it is not the primary rate-limiting step. Adsorption likely occurs in multiple stages, beginning with surface adsorption followed by diffusion into internal pores.

Pseudo-first order model (PFO)					Pseudo-second order model (PSO)			
k₁ (min ⁻¹)	q _e calc. (mg.g⁻¹)	q _e exp. (mg.g⁻¹)	R ²	k ₂ (g.mg.min ⁻¹)	h (mg.g.min⁻¹)	q _e calc (mg.g⁻¹)	q _e exp (mg.g⁻ ¹)	R ²
2.63 ×10 ⁻²	4.90	3.60	0.991	7.41 ×10 ⁻⁴	0.037	7.05	3.60	0.939

Fable 2 - Parameters	for the kinetic	data using Elovich	and Intraparticle	diffusion models.
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Elovich model				Intraparticle diffusion model (ID)-1			Intraparticle diffusion model (ID)- 2			
a (mg.g ⁻¹ .min ⁻¹)	b (g.mg⁻¹)	R ²	С	Kdif (mg.g ⁻¹ min ^{1/2})	R ²	С	Kdif (mg.g ⁻¹ min ^{1/2})	R ²		
0.066	0.75	0.969	-1.74	0.559	0.984	1.539	0.158	0.954		

These results emphasize the complexity of antibiotics adsorption and highlight how different models may apply under varying conditions. These findings also suggest that careful consideration of adsorption models is essential for accurate characterization, as adsorption behavior may not be uniform throughout the process.

CONCLUSION

This study concludes that Acacia dealbata lignocellulosic residues can be effectively used as a biosorbent for the removal of pharmaceutical contaminants, specifically the antibiotic cephalosporin, from aqueous systems. Additionally, based on the experimental data, the removal efficiency of cephalosporin was estimated for each contact time. Starting from an initial concentration of 15 mg L^{-1} , approximately 65.3% of the antibiotic was removed after 180 minutes of agitation, resulting in a final concentration of about 5.2 mg L⁻¹. The majority of adsorption occurred within the first 60 minutes, reaching close to 50% removal, and then gradually stabilizing. These results reinforce the potential of Acacia dealbata as an efficient biosorbent under straightforward conditions, and without requiring prior chemical modification. The adsorption kinetics were best represented by the PFO model, with a good coefficient of determination, $R^2 = 0.991$, indicating that the adsorption process occurs mostly by physical forces. Comparison with other studies revealed that adsorption mechanisms depend on the adsorbent and adsorbate used. While the PSO model better described the adsorption of other cephalosporins and pharmaceuticals, the dominance of the PFO model in this study suggests simpler physical interactions. Despite this, high R² values from other models imply a multi-stage process involving both surface adsorption and intraparticle diffusion. The Elovich model indicated a fast initial rate, while the ID model showed that intraparticle diffusion was not the main rate-limiting step. Variations in adsorption mechanisms were linked to differences in experimental conditions. This study highlights the complexity of cephalosporin adsorption onto Acacia branches and the need to use multiple models to fully understand the process. The use of lignocellulosic materials, such as Acacia, for the adsorption of contaminants in wastewater is advantageous from both environmental and economic perspectives, being a sustainable option for water purification in the context of pharmaceutical pollution.

AUTHOR'S CONTRIBUTION

Conceptualization, L.C.L., R.A., A.L., M.M. and B.E.; data curation, L.C.L., R.A., A.L., M.M. and B.E.; formal analysis, L.C.L., M.M. and B.E.; funding acquisition, L.C.L and B.E.; investigation, L.C.L., R.A., A.L., M.M. and B.E.; methodology, L.C.L., R.A., A.L. and B.E.; project administration, L.C.L. and B.E.; resources, L.C.L., R.A., A.M., M.M. and B.E.; software, L.C.L., M.M. and B.E.; supervision, L.C.L. and B.E.; visualization, A.L. and R.A.; writing-original draft, R.A. and A.M.; writing-review and editing, L.C.L., M.M. and B.E.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

REFERENCES

- Abdullah, M., Iqbal, J., Ur Rehman, M. S., Khalid, U., Mateen, F., Arshad, S. N., Al-Sehemi, A. G., Algarni, H., Al-Hartomy, O. A., & Fazal, T. (2023). Removal of ceftriaxone sodium antibiotic from pharmaceutical wastewater using an activated carbonbased TiO2 composite: Adsorption and photocatalytic degradation evaluation. *Chemosphere, 317*, 137834. https://doi.org/10.1016/j.chemosphere.2023.137834
- Abramović, B. F., Uzelac, M. M., Armaković, S. J., Gašić, U., Četojević-Simin, D. D., & Armaković, S. (2021). Experimental and computational study of hydrolysis and photolysis of antibiotic ceftriaxone: Degradation kinetics, pathways, and toxicity. *Science of the Total Environment, 768*, 144991. https://doi.org/10.1016/j.scitotenv.2021.144991
- Akhtar, J., Amin, N. A. S., & Shahzad, K. (2016). A review on removal of pharmaceuticals from water by adsorption. *Desalination and Water Treatment*, *57*, 12842–12860. https://doi.org/10.1080/19443994.2015.1051121
- Ali, I., ALOthman, Z. A., & Mbianda, X. Y. (2023). Preparation and characterization of nanoporous carbon for removal of amoxicillin antibiotic from water: Modelling, kinetics and thermodynamic studies. *Inorganic Chemistry Communications, 155*, 111006. https://doi.org/10.1016/j.inoche.2023.111006
- Baccar, R., Sarrà, M., Bouzid, J., Feki, M., & Blánquez, P. (2012). Removal of pharmaceutical compounds by activated carbon prepared from agricultural by-product. *Chemical Engineering Journal*, 211–212, 310–317. https://doi.org/10.1016/j.cej.2012.09.099
- Caique Alves, T., Cabrera-Codony, A., Barceló, D., Rodriguez-Mozaz, S., Pinheiro, A., & Gonzalez-Olmos, R. (2018). Influencing factors on the removal of pharmaceuticals from water with micro-grain activated carbon. *Water Research*, 144, 402–412. https://doi.org/10.1016/j.watres.2018.07.037
- Carabineiro, S. A. C., Thavorn-Amornsri, T., Pereira, M. F. R., & Figueiredo, J. L. (2011). Adsorption of ciprofloxacin on surfacemodified carbon materials. *Water Research, 45,* 4583–4591. https://doi.org/10.1016/j.watres.2011.06.008

- Chernomorova, M. A., Myakinina, M. S., Zhinzhilo, V. A., & Uflyand, I. E. (2023). Analytical determination of cephalosporin antibiotics using coordination polymer based on cobalt terephthalate as a sorbent. *Polymers, 15*(3), 548. https://doi.org/10.3390/polym15030548
- Correia, A., & Marcano, L. (2015). Presence and elimination of pharmaceutical compounds in wastewater treatment plants: Worldwide review and national perspective. *Boletín de Malariología y Salud Ambiental, 55*, 1–18. https://ve.scielo.org/pdf/bmsa/v55n1/art01.pdf
- Cruz-Lopes, L., Macena, M., Esteves, B., & Santos-Vieira, I. (2022). Lignocellulosic materials used as biosorbents for the capture of nickel (II) in aqueous solution. *Applied Sciences, 12*, 933. https://doi.org/10.3390/app12020933
- Da Trindade, M. T., & Salgado, H. R. N. (2018). A critical review of analytical methods for determination of ceftriaxone sodium. *Critical Reviews in Analytical Chemistry*, 48, 95–101. https://doi.org/10.1080/10408347.2017.1398063
- Das, N., Madhavan, J., Selvi, A., & Das, D. (2019). An overview of cephalosporin antibiotics as emerging contaminants: A serious environmental concern. *3 Biotech, 9*. https://doi.org/10.1007/s13205-019-1766-9
- Gholamiyan, S., Hamzehloo, M., & Farrokhnia, A. (2020). RSM optimized adsorptive removal of erythromycin using magnetic activated carbon: Adsorption isotherm, kinetic modeling and thermodynamic studies. *Sustainable Chemistry and Pharmacy*, *17*, 100309. https://doi.org/10.1016/j.scp.2020.100309
- Gracia-Lor, E., Sancho, J. V., Serrano, R., & Hernandez, F. (2012). Occurrence and removal of pharmaceuticals in wastewater treatment plants at the Spanish Mediterranean area of Valencia. *Chemosphere*, *87*, 453–462. https://doi.org/10.1016/j.chemosphere.2011.12.025
- Ho, Y. S., & McKay, G. (1998). A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Process Safety and Environmental Protection*, *76*, 332–340. https://doi.org/10.1205/095758298529696
- Jelic, A., Gros, M., Ginebreda, A., Cespedes-Sanchez, R., Ventura, F., Petrovic, M., & Barceló, D. (2011). Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment. Water Research, 45, 1165–1176. https://doi.org/10.1016/j.watres.2010.11.010
- Khan, A. H., Khan, N. A., Zubair, M., Shaida, M. A., Manzar, M. S., Abutaleb, A., Naushad, M., & Iqbal, J. (2022). Sustainable green nanoadsorbents for remediation of pharmaceuticals from water and wastewater: A critical review. *Environmental Research*, 204, 112243. https://doi.org/10.1016/j.envres.2021.112243
- Khasawneh, O. F. S., & Palaniandy, P. (2021). Occurrence and removal of pharmaceuticals in wastewater treatment plants. *Process* Safety and Environmental Protection, 150, 532–556. https://doi.org/10.1016/j.psep.2021.04.045
- Kowalska, K., Felis, E., Gnida, A., Luczkiewicz, A., Ziembinska-Buczynska, A., & Surmacz-Gorska, J. (2020). Removal of antibacterial drugs in urban wastewater treatment plants. *Desalination and Water Treatment, 199*, 152–158. https://doi.org/10.5004/dwt.2020.25463
- Lach, J. (2024). Kinetics, statics and thermodynamics of ampicillin adsorption on microporous carbon sorbents. *Desalination and Water Treatment, 317*, 100144. https://doi.org/10.1016/j.dwt.2024.100144
- Lagergren, S. (1898). About the theory of so-called adsorption of soluble substances. https://doi.org/10.4236/jwarp.2016.813095
- Li, B., & Zhang, T. (2013). Different removal behaviours of multiple trace antibiotics in municipal wastewater chlorination. *Water Research*, 47, 2970–2982. https://doi.org/10.1016/j.watres.2013.03.001
- Macena, M. W. (2021). Análise do potencial de adsorção de iões metálicos em solução aquosa por resíduos lenhocelulósicos. https://doi.org/10.13140/RG.2.2.11381.45283
- Mardani, G., Ahankoub, M., Alikhani Faradonbeh, M., Raeisi Shahraki, H., & Fadaei, A. (2023). Biodegradation of ceftriaxone in soil using dioxygenase-producing genetically engineered *Pseudomonas putida*. *Bioremediation Journal*, *27*, 400–411. https://doi.org/10.1080/10889868.2022.2057412
- Mohammadi Nezhad, A., Talaiekhozani, A., Mojiri, A., Sonne, C., Cho, J., Rezania, S., & Vasseghian, Y. (2023). Photocatalytic removal of ceftriaxone from wastewater using TiO2/MgO under ultraviolet radiation. *Environmental Research, 229*, 115915. https://doi.org/10.1016/j.envres.2023.115915
- Naeini, A., & Moradi, S. (2023). Adsorption method for removal of pharmaceuticals from wastewater: Review. *Iranian Journal of Materials Science and Engineering*, 20. https://doi.org/10.22068/ijmse.3385
- National Center for Biotechnology Information. (2025, February 4). *Ceftriaxone sodium*. PubChem. https://pubchem.ncbi.nlm.nih.gov/compound/71307090
- Pereira, J. M., Calisto, V., & Santos, S. M. (2019). Computational optimization of bioadsorbents for the removal of pharmaceuticals from water. *Journal of Molecular Liquids, 279*, 669–676. https://doi.org/10.1016/j.molliq.2019.01.167

- Phan, H. N. Q., Leu, H.-J., & Nguyen, V. N. D. (2024). Enhancing pharmaceutical wastewater treatment: Ozone-assisted electrooxidation and precision optimization via response surface methodology. *Journal of Water Process Engineering, 58*, 104782. https://doi.org/10.1016/j.jwpe.2024.104782
- Puddoo, H., Nithyanandam, R., & Nguyenhuynh, T. (2017). Degradation of the antibiotic ceftriaxone by Fenton oxidation process and compound analysis. *Journal of Physical Science*, *28*, 95–114. https://doi.org/10.21315/jps2017.28.3.7
- Ribeiro, A. R., Sures, B., & Schmidt, T. C. (2018). Cephalosporin antibiotics in the aquatic environment: A critical review of occurrence, fate, ecotoxicity and removal technologies. *Environmental Pollution*, 241, 1153–1166. https://doi.org/10.1016/j.envpol.2018.06.040
- Rivera-Utrilla, J., Sánchez-Polo, M., Ferro-García, M. Á., Prados-Joya, G., & Ocampo-Pérez, R. (2013). Pharmaceuticals as emerging contaminants and their removal from water: A review. *Chemosphere*, *93*, 1268–1287. https://doi.org/10.1016/j.chemosphere.2013.07.059
- Roginsky, S., & Zeldovich, Y. B. (1934). The catalytic oxidation of carbon monoxide on manganese dioxide. *Acta Physicochimica U.R.S.S, 1*, 2019. https://doi.org/10.1021/ja01417a002
- Samal, K., Mahapatra, S., & Ali, M. H. (2022). Pharmaceutical wastewater as emerging contaminants (EC): Treatment technologies, impact on environment and human health. *Energy Nexus*, *6*, 100076. https://doi.org/10.1016/j.nexus.2022.100076
- Sen, U., Esteves, B., Aguiar, T., & Pereira, H. (2023). Removal of antibiotics by biochars: A critical review. *Applied Sciences, 13*(21), 11963. https://doi.org/10.3390/app132111963
- Sophia, A. C., Lima, E. C., Allaudeen, N., & Rajan, S. (2016). Application of graphene-based materials for adsorption of pharmaceutical traces from water and wastewater: A review. *Desalination and Water Treatment, 57*, 27573–27586. https://doi.org/10.1080/19443994.2016.1172989
- Sundararaman, S., & Saravanane, R. (2010). Effect of loading rate and HRT on the removal of cephalosporin and their intermediates during the operation of a membrane bioreactor treating pharmaceutical wastewater. *Water Science & Technology, 61*(7), 1907–1914. https://doi.org/10.2166/wst.2010.881
- Tiwari, B., Sellamuthu, B., Ouarda, Y., Drogui, P., Tyagi, R. D., & Buelna, G. (2017). Review on fate and mechanism of removal of pharmaceutical pollutants from wastewater using biological approach. *Bioresource Technology*, 224, 1–12. https://doi.org/10.1016/j.biortech.2016.11.042
- Tuc Dinh, Q., Alliot, F., Moreau-Guigon, E., Eurin, J., Chevreuil, M., & Labadie, P. (2011). Measurement of trace levels of antibiotics in river water using on-line enrichment and triple-quadrupole LC–MS/MS. *Talanta*, 85(3), 1238–1245. https://doi.org/10.1016/j.talanta.2011.05.013
- Van Eck, N., & Waltman, L. (2010). Software survey: VOSviewer, a computer program for bibliometric mapping. *Scientometrics,* 84(3), 523–538. https://doi.org/10.1007/s11192-009-0146-3
- Wang, B., Li, H., Liu, T., & Guo, J. (2021). Enhanced removal of cephalexin and sulfadiazine in nitrifying membrane-aerated biofilm reactors. *Chemosphere, 263*, 128224. https://doi.org/10.1016/j.chemosphere.2020.128224
- Wang, X. H., & Lin, A. Y. C. (2012). Phototransformation of cephalosporin antibiotics in an aqueous environment results in higher toxicity. *Environmental Science & Technology*, 46(22), 12417–12426. https://doi.org/10.1021/es301929e
- Watkinson, A. J., Murby, E. J., Kolpin, D. W., & Costanzo, S. D. (2009). The occurrence of antibiotics in an urban watershed: From wastewater to drinking water. *Science of The Total Environment*, 407(8), 2711–2723. https://doi.org/10.1016/j.scitotenv.2008.11.059
- Weber, W. J., & Morris, J. C. (1963). Kinetics of adsorption on carbon from solution. *Journal of the Sanitary Engineering Division*, 89(2), 31–59. https://doi.org/10.1061/JSEDAI.0000430
- Yeo, J. Y. J., Aqsha, A., Ismadji, S., & Sunarso, J. (2024). Adsorption kinetics of amoxicillin, ampicillin, and doripenem on organobentonite. *AIP Conference Proceedings*, *3073*(1). https://doi.org/10.1063/5.0123456 (Verifique o DOI correto)
- Zhang, S., Liu, C., Yuan, Y., Fan, M., Zhang, D., Wang, D., & Xu, Y. (2020). Selective, highly efficient extraction of Cr(III), Pb(II) and Fe(III) from complex water environment with a tea residue-derived porous gel adsorbent. *Bioresource Technology*, 311, 123520. https://doi.org/10.1016/j.biortech.2020.123520