Efficient removal of pharmaceutical contaminants using laccase immobilized on activated coal derived desde cashew nut shells: Thermodynamic, Kinetic and Calorimetry study

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Abstract

This study details the removal of diclofenac, amoxicillin, and carbamazepine using granular activated carbons (ACs) derived from cashew nut shells. Laccase enzyme impregnation was achieved using three activating agents (KOH, NaOH, $ZnCl_2$), resulting in bioadsorbents labeled as LAC-x. Fourier transform infrared spectroscopy (FTIR) confirmed enzyme immobilization. Optimal conditions were pH 5, 30°C, and a laccase content of 2.5 mg mL^{-1}. Laccase immobilization increased from 10°C to 30°C, with values of 63.3 to 53.4 U g^{-1}, respectively. Decreased immobilization at 40-50°C was observed due to restricted enzyme access in porous structures. Immersion interactions exhibited spontaneous exothermic behavior following Langmuir isotherms and pseudo-first-order kinetics. This enzymatic removal system offers scalable potential, representing a significant advancement in pharmaceutical disposal research.

Keywords: Pharmaceutical contaminants, Thermodynamics, Adsorption, Immersion Calorimetry, Enzyme Laccase.

1. Introduction

The presence of emerging compounds poses a significant threat to global environmental and human health equilibrium. These compounds, spanning pharmaceuticals, personal care products, pesticides, and industrial byproducts, infiltrate ecosystems via various pathways including wastewater discharge, agricultural practices, and improper disposal [1–13]. Their impact on aquatic organisms, ecosystems, and human health is well-documented, ranging from disruptions in biological processes to hormonal disorders [14–21].

Numerous removal methods, encompassing physical, chemical, and biological approaches, have been developed to mitigate this issue, with biological methods like biodegradation and bioadsorption gaining traction due to their efficacy and eco-friendliness [22–28]. Among bioadsorbents, activated carbon derived from cashew nut shells shows promise, leveraging the fruit's abundant waste to produce a material with high surface area and porosity, ideal for adsorbing organic pollutants [29–45].

Immobilizing laccase on activated carbon further enhances contaminant degradation, but thorough kinetic, thermodynamic, and calorimetric studies are needed to understand this interaction fully and optimize removal processes. Therefore, this research aims to address emerging compound contamination by employing bioadsorbents based on laccase-immobilized activated carbon, focusing on amoxicillin, diclofenac, and carbamazepine as probe molecules (AMO, DFC, CBZ). The study also intends to explore the broader applications and benefits of this approach while emphasizing the necessity for future research to develop sustainable solutions for emerging contaminant removal.

2. Methodology and materials

The chemical activation method was used with three different activating agents to explore the capacity to retain the laccase enzyme and its subsequent effectiveness in the adsorption-degradation of the emerging compounds used in this research: KOH, NaOH and $ZnCl_2$.

2.1 Activation methods [46-59]

The activated carbons from cashew nut shells were prepared by chemical activation using KOH (ACK), NaOH (ACN), and $ZnCl_2$ (ACZ) under the conditions suggested in the literature and by our laboratory experience.

2.1.2 Textural characterization of activated carbons

The characterization of the specific surface area and pore texture of the synthesized activated carbons was carried out by nitrogen adsorption-desorption analysis at -196 °C, using the AutosorbiQ St equipment (Anton Paar, Boynton Beach, FL, US). The specific surface area related to micropores, S_{BET} (m^2g^{-1}), was determined using the BET (Brunauer-Emmett-Teller) method for calculation [60]. The mesoporous pore size distribution, PSD, was estimated using the Barret-Joyner-Halenda (BJH) calculation method [60,61]. To estimate the PSD of the micropores, the nonlocal density functional theory (NLDFT) calculation method was employed using the SAIEUS® software [62]. In addition, the surface area, S_{NLDFT} ($m^2\ g^{-1}$), the total pore volume, V_{tot} ($m^3\ g^{-1}$), and the micropore volume, Vmic ($m^3\ g^{-1}$), were also determined using the NLDFT method integrating the PSD over the entire range of pore sizes. Finally, the mesopore volume, $V_{mesopore}$ (m^3g^{-1}), was calculated as the difference between V_{tot} and V_{mic}.

2.2 Fixation of laccase on activated carbon

The experimental procedure followed established methodologies with slight modifications based on prior research and laboratory experience. In summary, activated carbon (AC) was mixed with a laccase enzyme solution and incubated at 30°C and 250 rpm for six hours. After centrifugation and rinsing steps to remove unbound enzyme, immobilized laccase activity was determined by subtracting initial activity. Further analyses, including pH, temperature, stability, enzyme concentrations, and optimal parameters for contaminant removal, were conducted on resulting samples [63-65].

2.2.1 Enzymatic Assay

Enzymatic activity was assessed by monitoring the oxidation of ABTS, a substrate for laccase, for both free and immobilized enzyme forms. Absorbance increase at 425 nm, using an extinction coefficient of ε = 36,000 $M^{-1}\ cm^{-1}$, was recorded at room temperature with a double-beam Aligent Cary 3500 Compact UV-Vis spectrophotometer. One laccase activity unit was defined as the enzyme amount oxidizing one micromole of ABTS per minute under standard assay conditions: pH = 5 buffer, 0.5 mM ABTS, and 2 mg mL^{-1} enzyme concentration. The color change to blue during the process indicated successful ABTS oxidation [63-65].

$$Free\ laccase\ activity\ (U.mL^{-1}) = \frac{\Delta abs\ x\ D_f\ x\ R_v}{\epsilon\ x\ t\ xE_v} \quad (1)$$

$$Immobilized\ laccase\ activity\ (Ug^{-1}) = \frac{\Delta abs\ x\ D_f\ x\ R_v}{\epsilon\ x\ t.x\ M_{carrier}} \quad (2)$$

The variables in the above equations are defined as follows: Δabs represents the absorbance of $ABTS^+$, D_f is the dilution factor, Rv represents the reaction volume in milliliters, ε denotes the extinction coefficient of $ABTS^+$, t represents the duration of the reaction in minutes, $M_{carrier}$ indicates the mass of the carrier used for laccase immobilization in grams and E_v represents the volume of the enzyme in milliliters.

2.3 FTIR, Boehm titrations

The chemical structure of the prepared solids was determined using FTIR, specifically a Nicolet™ iSTM 5 FTIR instrument coupled to iD7 ATR. IR spectra were obtained with a resolution of 2 cm-1 (400 to 4000 cm^{-1}). To assess laccase enzyme fixation effectiveness, Boehm titrations were performed to quantify surface functional groups, including phenolic (–OH), carboxylic (–COOH), and carbonyl (C– O) groups typical of activated carbons. Basic

and acidic sites were evaluated using $NaHCO_3$, Na_2CO_3 , and NaOH solutions (0.05 M), mixed with activated carbon and stirred for 72 hours. Subsequently, excess solution was quantified by back-titration using NaOH (0.025 M) for basic sites and HCl (0.025 M) for acidic sites [66-67].

2.4 Determination of the point of zero charge (pH_{PZC}).

Activated carbon surfaces exhibit varying acidity levels based on precursor origin and activation method. The point of zero charge (pH_{PZC}) was determined to assess this property, as shown in Fig 1. Results indicate acidic pH_{pzc} values of 5.0, 4.5, and 6.0 for KOH, NaOH, and ZnC_{l2} activated carbons, respectively. Chemical activation produces acidic oxygenated surface groups.

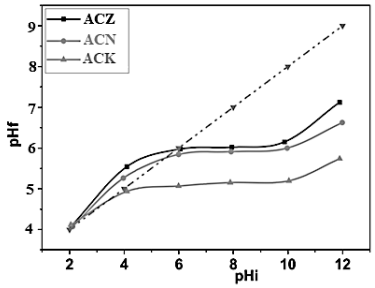


Fig 1. Results obtained in the determination of pH_{pzc} for ACK, ACN and ACZ

2.5 HPLC measurements

In this study, diclofenac (DCF), carbamazepine (CBZ), and amoxicillin (AMO) were used as probe molecules to investigate adsorption-degradation. High-performance liquid chromatography (HPLC) using a Merck-Hitachi D-7000 instrument determined pharmaceutical degradation. Zorbax SB-Aq column (150 mm × 4.6 mm, 5 µm) with gradient elution was employed. Sample volume injected was 10 µL. Mobile phase consisted of 0.1% trifluoroacetic acid in MQ water (eluent A) and methanol (eluent B), with a gradient program from 40% to 100% B over 1 to 5 minutes. Flow rate was 1 mL min^{-1}. Calibration showed linearity between 5 and 100 µg mL^{-1} for DCF, AMO, and CBZ. Degradation of these compounds involved adding 250 mg of LAC-x to 0.075 L matrix containing 100 mg L^{-1} of pharmaceutical molecules, stirring continuously at 150 rpm. Supernatant samples were collected every 30 minutes for analysis by HPLC. Additionally, adsorption experiments without immobilization were conducted under similar conditions [66-70]

2.6 Adsorption, kinetics and thermodynamics studies.

Several models have been employed to describe adsorption processes, using variables like q_e (amount adsorbed per gram of adsorbent at equilibrium, mgg^{-1}) and Ce (solute concentration in solution at equilibrium, mgL^{-1}) to determine adsorption characteristics. Langmuir and Freundlich models were utilized, each with its non-linear and linear equations. These models were applied to interpret the adsorption of pharmaceutical molecules from aqueous solution on bioadsorbents, with fitting parameters determined from original adsorption data. Subsequently, adsorption kinetics of DCF, AMO, and CBZ were analyzed using pseudo-first order (PFO), pseudo-second order (PSO), and intraparticle diffusion (IPD) models. The suitability of each model was assessed using the coefficient of determination (R^2). In kinetic experiments, 200 mg of each adsorbent was added to 50 mL of solution containing the molecules, stirred at 250 rpm. Concentrations were measured at specific intervals, and the amount adsorbed at equilibrium (q_e) was calculated. Additionally, the Elovich model was applied. Thermodynamic parameters including Gibbs free energy change (ΔG^o), enthalpy change (ΔH^o), and entropy change (ΔS^o) were calculated to understand the adsorbate-adsorbent interaction. These parameters were determined using the classical equations of thermodynamics, with ΔG^o related to the thermodynamic adsorption equilibrium constant (Kc^o), universal gas constant (R), and temperature (T). The relationship between ΔH^o, ΔS^o, and $K_c{}^o$ was established using the linearized van't Hoff equation [71-75].

2.7 The immersion enthalpy of the bioadsorbents synthesized in this research.

DFC, CBZ, and AMO were analyzed for their relationship with bioadsorbents using a locally constructed microcalorimeter equipped with thermopiles, recording thermal changes during interaction with solvents. Electrical calibration was performed [76-82].

3. Results

FTIR results for activated carbons without laccase showed different molecular vibrations. It was established that impregnation with the laccase enzyme caused subtle changes in some of the FTIR bands. Electrostatic and hydrophobic interactions facilitate the adsorption of enzymes on activated carbon under certain conditions. Generally, the laccase enzyme tends to have a basic character, which complemented the acidic nature of the prepared carbons, favoring the fixation of enzymes [65, 83].

Textural characterization

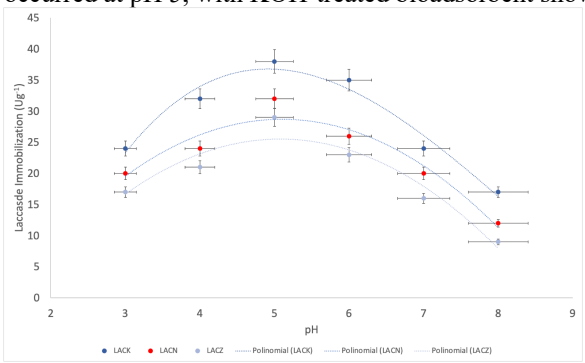
Textural parameters in Table 1 demonstrate KOH activation yields highest surface area and pore volume compared to NaOH and $ZnCl_2$. KOH-treated carbons display well-developed specific surface and micropores, evident from micropore volume exceeding total volume and S_{NLDFT} exceeding S_{BET}. $ZnCl_2$ activation produces a deeper microporous structure with lower pore volume and surface area. The average pore diameter of KOH-treated carbon is smaller, confirming mainly microporous nature. PSD analysis reveals varied pore sizes, with KOH and NaOH showing concentrated micropores. These findings validate activation efficiency and the impact of activating agents. Notably, $ZnCl_2$ maintains good N_2 adsorption capacity while preserving microporosity, crucial for practical applications.

Table 1. Textural characterization by N_2 adsorption isotherms at − 196 ° C

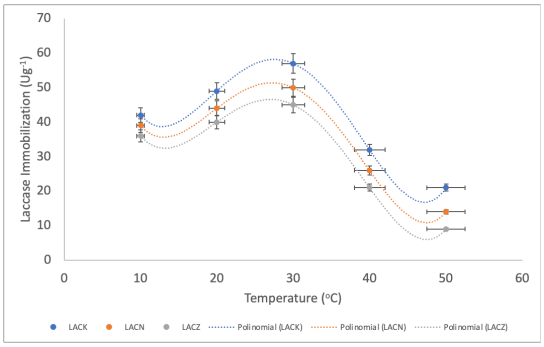
Sample	S_{BET} $m^2 g^{-1}$	S_{NLDFT} $m^2 g^{-1}$	Average Particle nm	Size Total Pore $cm^3 g^{-1}$	Volume Mesopore $cm^3 g^{-1}$	Volume Micropore $cm^3 g^{-1}$	Volume Microporosity (%)
ACK	1300.	1343	1.9	1.46	0.42	0.99	70.2
ACN	1100	1054	2.2	1.09	0.31	0.88	74.0
ACZ	800	775	2.5	0.45	0.06	0.31	83.8

Enzymatic immobilization

The adsorption method immobilized laccase enzyme on activated carbons (AC's) prepared in this study. To optimize immobilization, pH and temperature effects were studied. Figs 2a-d illustrate pH, temperature, enzyme concentration, and immobilization performance. Laccase immobilization increased progressively from pH 3 to 5, reaching maxima at pH 5. Temperature between 10°C to 30°C favored immobilization, with a decline at higher temperatures [63-65]. Enzyme concentration between 1.0 to 2.0 mg mL^{-1} showed increased immobilization, but higher concentrations had no effect due to limited surface sites. Optimal immobilization occurred at pH 5, with KOH-treated bioadsorbent showing the highest yield at 77.5%.



(a)



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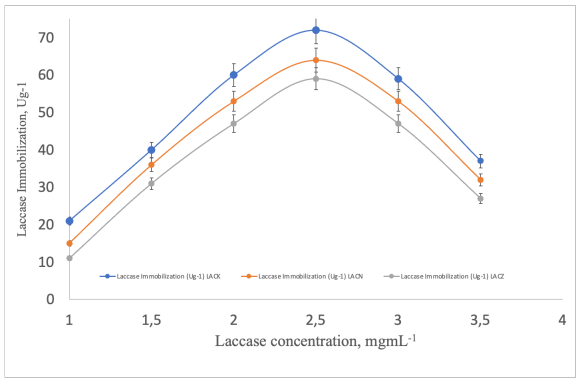
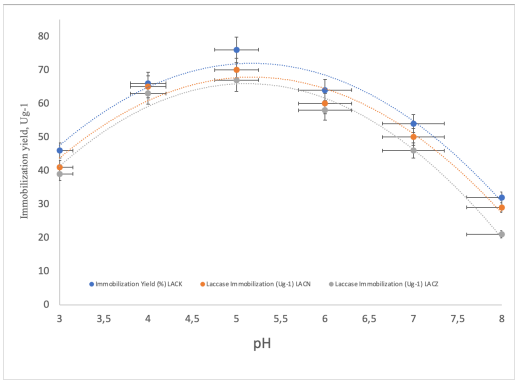


(c)



(d)

Fig 2. Effect of varying the pH level (a), temperatures (b) and concentrations of the laccase enzyme (c) on the immobilization and efficiency of the process (d).

Adsorption studies: isotherms, kinetics and thermodynamics.

The experimental data of fitting probe molecules (amoxicillin, diclofenac and carbamazepine – AMO, DCF, CBZ) in bioadsorbents (carbons activated with laccase enzyme – LAC-x) used Langmuir and Freundlich isotherms, as shown in the results reported. in Table 2a, 2b and 2c. The Langmuir model showed superior fit with high correlation coefficients (around 0.99) for all bioadsorbents. The Freundlich models had R^2 values further from unity, indicating monolayer formation. LACK showed the highest sorption capacity, with DCF being the most adsorbed (387.7 mg g^{-1}), followed by CBZ (344.3 mg g^{-1}) and AMO (324.6 mg g^{-1}). R_L values ($0 < R_L < 1$) indicate favorable adsorption, while high K_L values suggest a strong affinity between pharmaceutical molecules and bioadsorbents. Finally, it is worth highlighting that the data obtained here are in total agreement taking into account the chemical characteristics of the bioadsorbents and the corresponding chemical characteristics of the emerging compound.

Table 2a Fitting experimental data to amoxicillin (AMO) adsorption models

	Langmuir				Freundlich		
Samples	R_L	q_{max}	$K_L(Lmg^{-1})$	R^2	K_F $_{[(mg.g^{-1})(mg.L^{-1})\ 1/n]}$	n_F	R^2
LACK	0.794	324.6	0.7564	0.999	312.2	10.432	0.968
LACN	0.753	309.3	0.6845	0.993	287.4	8,432	0.953
LACZ	0.654	267.1	0.5313	0.996	212.8	7.982	0.934

Table 2b. Fitting experimental data to diclofenac (DCF) adsorption models

	Langmuir				Freundlich		
Samples	R_L	q_{max}	$K_L(Lmg^{-1})$	R^2	K_F $_{[(mg.g^{-1})(mg.L^{-1})\ 1/n]}$	n_F	R^2
LACK	0.898	387.7	0.9657	0.991	312.2	16.546	0.929
LACN	0.876	342.3	0.8721	0.992	287.4	13.432	0.976
LACZ	0.865	301.4	0.6542	0.997	212.8	11.954	0.959

Table 2c. Fitting experimental data to carbamazepine (CBZ) adsorption models

	Langmuir				Freundlich		
Samples	R_L	q_{max}	$K_L(Lmg^{-1})$	R^2	K_F $_{[(mg.g^{-1})(mg.L^{-1})\ 1/n]}$	n_F	R^2
LACK	0.843	344.3	0.8725	0.998	312.2	12.983	0.978
LACN	0.804	321.7	0.7821	0.996	287.4	10.231	0.967
LACZ	0.786	287.3	0.5987	0.992	212.8	9.432	0.945

Another hand, Pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetics were utilized to explore adsorption mechanisms and intermolecular forces, including covalent and ion exchange. PFO describes

reversible physical adsorption, while PSO involves chemical bonds. Intraparticle diffusion (IPD) model elucidates rate-limiting steps. Figs 3 depicts fits to PFO, PSO, IPD, and Elovich models for tested pharmaceutical compounds. Results align with PFO kinetics, indicating physisorption limits adsorption. Three linear segments observed in IPD modeling suggest multi-stage adsorption, involving external diffusion, lower diffusion into porous structure, and subsequent saturation of reactive sites. Overall, adsorption of pharmaceuticals on bioadsorbents involves physisorption and chemisorption mechanisms, with IPD revealing three sequential steps: film diffusion, gradual adsorption, and equilibrium [70-81].

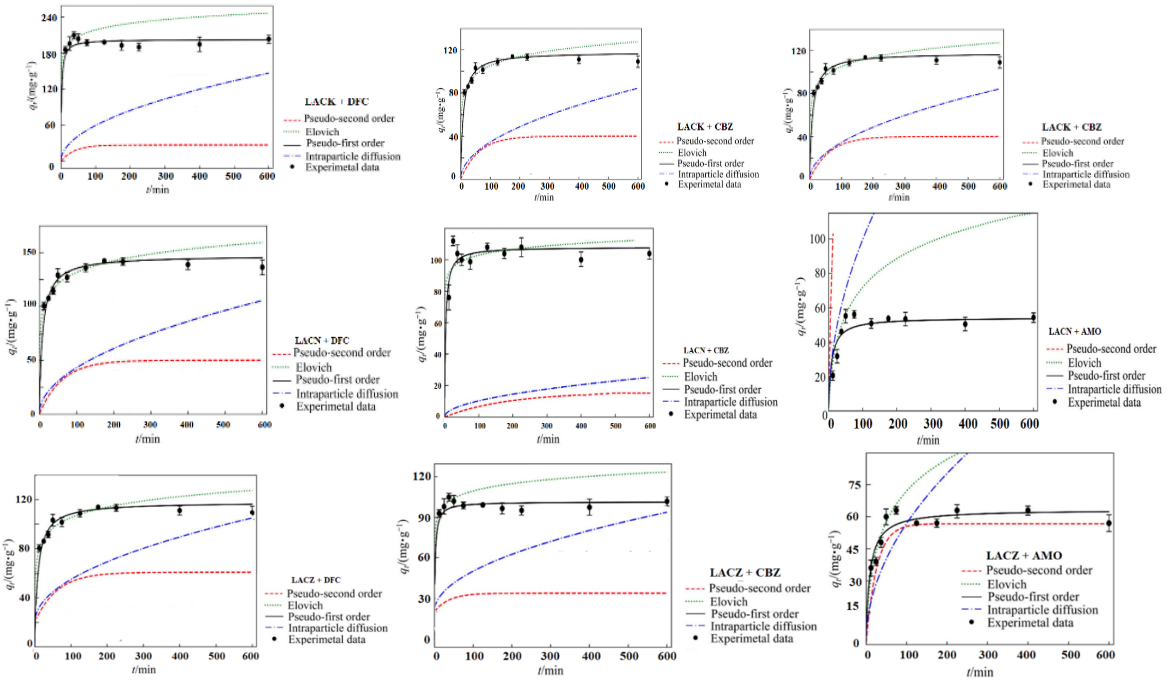


Fig 3. Kinetic models applied to the adsorption isotherms of PFO, PSO, IDF and Elovich: comparative analysis and adjustment.

The evaluation of the thermodynamic parameters of the pharmaceutical compounds in the bioadsorbents were evaluated. The results showed that the ΔG^{o} values decrease with increasing temperature, indicating a beneficial influence of temperature on the adsorption efficiency. Negative ΔG^{o} values measured at four different temperatures indicate spontaneous adsorption of pharmaceutical compounds and all biosorbents. Positive values of ΔH^{o} suggest an endothermic adsorption process. Positive values of ΔS^{o} indicate a stable and random adsorption process [75, 82].

Calorimetric results analysis

Calorimetric studies were performed to explore the interactions between the bioadsorbents and the pharmaceutical molecules used in the study. The immersion enthalpy, a thermodynamic parameter correlated with pore structure and surface chemistry, was analyzed. The enthalpies of immersion in water and various solutions. These values varied depending on the type of interaction established between the bioadsorbent and the pharmaceutical molecules. In particular, the LACK biosorbent system exhibited the highest values for the thermodynamic variables, indicating greater compatibility with the tested pharmaceutical molecules [82-84].
The immersion calorimetric curves of LACK, LACN and LACZ in DFC, CBZ, AMO, benzene and water at 100 ppm (potential vs. time) were determined. The area under the curve represents the amount of heat produced by the solid-liquid contact. The thermograms facilitated the evaluation of immersion enthalpies for DFC, CBZ, AMO, benzene, and water in the synthesized bioadsorbents. Immersion enthalpies were predominantly

negative, indicating an exothermic process. LACN showed a hydrophilic nature, evidenced by the Hf factor exceeding unity and high enthalpies of immersion in water. This behavior was attributed to the -OH groups introduced during the chemical activation process and reinforced by the fixation of enzymes on the surface of the bioadsorbent.

The enzyme laccase, with various functional groups including $-NH_2$, -COOH, and -OH, could influence the surface of activated carbon when attached to carbon treated with KOH or NaOH. This could introduce a localized polarity, reinforcing the hydrophilic behavior. The hydrophilic factor was correlated with the structure and characteristics of the molecules. Diclofenac sodium, carbamazepine, and amoxicillin interacted primarily through ion-dipole interactions, hydrogen bonding, and dissolution in aqueous solutions.

The interaction between LACK and DFC exhibited the highest immersion enthalpies, followed by the LACK-CBZ and LACK-AMO interactions. This trend aligned with findings from previous research. LACK acid-type activated carbon showed stronger interactions with pharmaceutical molecules compared to other bioadsorbents.

4. Conclusions

In this study, activated carbon was derived from cashew nut shells using KOH, NaOH, and ZnCl2 as activating agents, with laccase enzyme immobilization to create bioadsorbents. These were tested for adsorption capacity of diclofenac sodium, carbamazepine, and amoxicillin, alongside kinetics, thermodynamics, and calorimetric analysis. Results indicate all bioadsorbents conform well to the Langmuir model, with LACK exhibiting the highest adsorption capacity: 387.7 mgg^{-1} for DFC, 344.3 mgg^{-1} for CBZ, and 3245.6 mgg^{-1} for AMO, surpassing values reported in literature. Adsorption followed the PFO model, with IPD analysis revealing a three-step process, likely involving some chemical interaction. Thermodynamic evaluation, particularly Gibbs free energy, affirmed spontaneity. Calorimetric data confirmed exothermic enthalpy, with LACK-DFC exhibiting the highest value at 158.7 $kJmol^{-1}$, followed by LACK-CBZ at 137.4 $kJmol^{-1}$, and LACK-AMO at 125.8 $kJmol^{-1}$. Overall, the research highlights the potential of agricultural waste-derived bioadsorbents in efficiently removing emerging compounds, with spontaneous adsorption demonstrated via calorimetric analysis, supporting scalability.

Acknowledgments

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