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Ibuprofen Removal by Aluminum-Modified Activated Carbon (AC@Al) Derived from Coconut Shells

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Abstract: In this study, a new composite adsorbent consisting of aluminum-modified activated carbon (abbreviated hereafter AC@Al) was synthesized for the removal of the Ibuprofen compound (IBU), a non-steroidal anti-inflammatory drug (NSAID). Coconut shells were used as a source material for activated carbon, which was then modified with $AlCl_3$ to improve its properties. Adsorbent dosage, pH and initial IBU concentration, as well as contact time and temperature, are some of the factors affecting adsorption that were investigated in this work. Specifically, at pH 2.0 ± 0.1 with the application of 0.5 g/L of AC@Al in 100 mg/L of IBU, more than 90% was removed, reaching 100% with the addition of 1.0 g/L of the adsorbent. The IBU kinetic data followed the pseudo-second-order kinetic model. Non-linear Langmuir, Freundlich, Sips and Redlich–Peterson isotherm models were used to interpret the adsorption. According to the correlation coefficient (R^2), the Langmuir model was found to best match the experimental data. The maximum adsorption capacity (Q_{max}) according to the Langmuir model was found to be as high as 2053 mg/g. The positive values of ΔH^0 (42.92 kJ/mol) confirmed the endothermic nature of the adsorption. Due to the increasing values of ΔG^0 with temperature, the adsorption of IBU onto AC@Al proved to be spontaneous. Also, the adsorbent was regenerated and reused for five cycles. This study shows that AC@Al could be used as a cost-effective adsorbent.

Keywords: Ibuprofen; NSAIDs; adsorption; activated carbon; coconut shells; aluminum

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1. Introduction

Pharmaceuticals are continuously introduced into the influents of municipal wastewater treatment plants (WWTPs) from pollutants arising in both hospital and domestic wastewater. The World Health Organization (WHO) [1] emphasizes the importance of implementing an appropriate process for the elimination of pharmaceuticals from water solutions because of their widespread use by humans and their persistent presence, since the biological treatment methods used in WWTPs cannot effectively deconstruct them.

Analgesics and anti-inflammatories are among the most commonly used pharmaceuticals, and they are frequently found in wastewater and water samples. Ibuprofen (IBU) is a nonsteroidal anti-inflammatory drug (NSAID) that is the third most popular, prescribed and available pharmaceutical in the world. It is a colorless, crystalline solid with a characteristic odor, a derivative of propionic acid. It is considered an acid drug, and its chemical formula is 2-[4-(2-methylpropyl)phenyl]propanoic acid [2]. The toxicity and concentration of Ibuprofen in wastewater treatment plants is constantly increasing. NSAID use is primarily in the treatment of inflammation or musculoskeletal pain, and they can be released into water systems in a variety of ways, such as from hospitals or health centers or medicinal plants [3]. The concentrations at which they can be detected are low, ranging from ng/L to a few μg/L [4]. Despite the fact that these are low concentrations

and are difficult to detect, they have adverse impacts on human and environmental health. Due to the widespread use of these drugs in clinical practice and agriculture, they are very common in the aquatic environment due to their stability and hydrophilicity [5]. More specifically, Ibuprofen contains carboxyl and benzene groups, which are functional groups that contribute to its increased mobility while being easily soluble in organic solvents but poorly soluble in water [6,7]. A typical example is antibiotics, which are widely used for the treatment of various diseases and infections, as well as for aquaculture, food preservation, and some other industries. Global antibiotic consumption has been estimated at 1 ton to 2225 tons per year [8]. The structure of most antibiotics is complex and offers a higher resistance to biodegradation and increased accumulative occurrence in the environment [7]. The possibility of carcinogenesis, mutations, the toxicity of water recipients, and the growth of resistant bacteria, among other ecological effects, due to the presence of medically reactive compounds in aquatic systems is a serious issue. Therefore, the removal of pharmaceutical residues from drinking water and wastewater is particularly critical [8].

Numerous methods have been examined for the removal of pharmaceuticals from water and wastewater. These include ion exchange [9], several filtration methods [10,11], reverse osmosis [12], and the Fenton method [13]. The main disadvantages of these technologies is their cost and the need for the additional use of hazardous chemical reagents that are not environmentally friendly [5]. Of the available technologies for pharmaceutical removal, adsorption is preferred due to its ease of application, its simplicity, and the fact that it is one of the most economical technologies. A wide range of adsorbent materials are available and being considered for their application to pharmaceutical compounds. According to the literature, carbon-based adsorbents are among the best adsorbents for the uptake of IBU, exhibiting a high adsorption capacity [6].

In this research work, a new substantial composite (AC@Al) resulting from the modification of activated carbon (AC) with aluminum was formed and applied for the removal of IBU. Coconut shells were used to produce raw activated carbon, which was then modified with $AlCl_3$. The novelty of this study is the development of a sustainable and low-cost approach for the production of activated carbon derived from waste biomass, such as that of coconut shells, as a competitive adsorbent for the adsorption of Ibuprofen. To the best of our knowledge, there have been no recent studies in the literature using an aluminum-modified activated carbon of similar origin for the removal of this drug. However, a study conducted using bamboo-based activated carbons containing dispersed aluminum as an adsorbent for the removal of ciprofloxacin hydrochloride yielded positive results [14]. Similarly, in another study, the application of activated carbon commercially modified with aluminum chloride to clean anionic dye in wastewater was effective [15]. Adsorbent dosage, pH, initial IBU concentration, contact time and temperature were some of the factors affecting adsorption that were investigated in this study. Moreover, data were evaluated and modelled using kinetic and isothermal adsorption equations. Thermodynamics and adsorption–desorption research was also carried out.

2. Materials and Methods

2.1. Materials

Ibuprofen, which was the target contaminant, was purchased from Sigma-Aldrich, Merck KGaA, Darmstadt, Germany. We used 95% denatured ethanol to prepare the stock solutions, while all aqueous solutions were prepared with deionized water. $AlCl_3 \cdot 6H_2O$ (Sigma-Aldrich, Merck KGaA, Darmstadt, Germany) was used to modify the activated carbon. Also, 0.01–0.1 M of HCl (37% HCl (Panreac, AppliChem, Barcelona, Spain)) and NaOH solutions (≥97.0% ACS NaOH pellets (Sigma-Aldrich, Merck KGaA, Darmstadt, Germany)) were used for pH adjustment.

2.2. Synthesis of Aluminum-Based Activated Carbon

In this study, for the production of activated carbon, coconut shells were used [16,17], and AC was then impregnated with aluminum salts, such as aluminum chloride, according

to a method proposed by Tsoutsa et al. [15]. Specifically, in 25 mL of deionized water, 0.8 g of $AlCl_3$ was mixed with 5.0 g of AC. The contents were stirred for 60 min (1 h) at room temperature and placed in an ultrasonic bath for 120 min (2 h). Next, the blend was filtered and washed. Then, to obtain the AC@Al adsorbent, the mixture was dehydrated all night at a higher temperature (~333 K) and subsequently calcined for 300 min (5 h) at 773 K. Finally, to prepare for its use in the following experiments, the produced adsorbent was cooled to room temperature. It has to be noted that the characterization of AC@Al, including measurements of its BET surface area, Barrett–Joyner–Halenda (BJH) average pore size, and BJH pore volume, was already conducted [15] in previous research by the present group in which we tested the adsorbent for dye removal. Thus, AC@Al was known to have a surface area of 342 m^2/g.

2.3. Analytical Determinations

A UV–Vis spectrophotometer (WTW Spectroflex 6100, Weilheim, Germany) was used to determine the residual concentration of IBU at 222 nm [18] according to the standard calibration curve.

2.4. Adsorption Experiments

Several tests were conducted to examine the efficiency of AC@Al for IBU adsorption. First, 10 mL of the IBU solution was added to falcon tubes containing the appropriate amount of the adsorbent. IBU was added at several initial concentrations while maintaining a constant temperature. Then, the mixed compound was placed in a rotator at 80 rpm. While conducting the experiments, various parameters were kept constant or adjusted, such as pH level (2 to 10), initial concentration of IBU (20 to 1000 mg/L, as this is a common range used in the literature [6,19]), dosage (0.2, 0.5, 0.6, 0.8 and 1.0 g/L), and interaction time (2 to 240 min); equilibrium tests were set to 24 h. Upon the completion of adsorption, the collected samples were filtered through a 0.45 µm nylon filter and kept for the following measurements. The results shown are the averages of three experimental runs. The rate of IBU removed, expressed as R (%), is given by the following equation (Equation (1)):

$$R\ (\%) = \left(\frac{C_0 - C_f}{C_0}\right) \times 100\% \quad (1)$$

where C_0 is the initial IBU concentration (mg/L) and C_f is the residual IBU concentration (mg/L).

Equation (2) was used for adsorption capacity Q_e (mg/g) determination:

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where C_e (mg/L) is the equilibrium IBU concentration, V (L) is volume, and m (g) is the adsorbent's mass.

2.4.1. Equilibrium Experiments

For isothermal equilibrium tests, a fixed amount of the AC@Al adsorbent (g) was added to 15 mL falcon tubes containing 10 mL of the IBU solution (30 to 200 mg/L). For the evaluation of the results, Langmuir and Freundlich isotherm models were applied. Equation (3) is related to the Langmuir model [20]:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where Q_e is the concentration of IBU adsorbed in the solid phase (mg/g), Q_m is the maximum adsorption capacity (mg/g), and K_L is the relative energy for IBU adsorption(L/mg).

Adsorption isotherms were used to find out the mechanism of adsorption and to correlate the concentration of Ibuprofen with the adsorption capacity of the AC@Al adsorbent.

Initially, the Langmuir and Freundlich models were applied in this study. In the Langmuir model, the energy of adsorption is constant, as is the number of available adsorption sites on the surface of the adsorbent. Each site can only be occupied by one molecule, resulting in the formation of a monolayer with no interactions between the adsorbed molecules. Essentially, the adsorbent has a finite adsorption capacity (Q_m), that is, the maximum amount that the AC@Al surface can adsorb in equilibrium. The Freundlich model [21] deals with both monolayer and multilayer adsorption on heterogeneous surfaces. It describes the relationship regarding the concentration of IBU at equilibrium (mg/L) and the relative adsorption capacity of AC@Al, Q_e (mg/g), as stated in Equation (4).

$$Q_e = K_F C_e^{1/n} \tag{4}$$

where K_F is the adsorption's capacity constant and $1/n$ is the adsorption ability's or surface's heterogeneity constant.

In addition, as will be demonstrated by the experimental results, it was also necessary to apply the Langmuir–Freundlich (L–F) equation model (also known as the Sips isotherm model [22]) to the data of this study. The Sips isotherm, that is a combination of the Langmuir and Freundlich models, is a model that studies three parameters to adjust experimental results. It is represented by Equation (5):

$$Q_e = \frac{Q_m K_{LF} C_e^{1/n}}{1 + K_{LF} C_e^{1/n}} \tag{5}$$

where K_{LF} is the equilibrium constant of heterogeneous surfaces (L/g), Q_e is the adsorbed amount at equilibrium (mg/g), Q_m is the maximum adsorption capacity (mg/g), C_e is the adsorbate equilibrium concentration (mg/L) and n is the heterogeneity parameter ($0 < n < 1$).

Equation (5) is used for both high and low solution concentrations. In particular, at low concentrations, this isotherm follows the Freundlich isotherm, and at high concentrations, it follows the Langmuir isotherm, predicting monolayer adsorption capacity [23].

Finally, according to several researchers [24–26], the accuracy of the Redlich–Peterson (R–P) isotherm equation, including three adjustable parameters, is better than the Langmuir and Freundlich counterparts. Thus, the Redlich–Peterson model is widely used as the link between Langmuir and Freundlich isotherm models. The equation applied for this model is Equation (6):

$$Q_e = \frac{K_{RP} C_e}{1 + \alpha_R C_e^n} \tag{6}$$

where K_{RP} (L/g) and α_{RP} $(\text{L/mg})^n \cdot 10^3$) are the R–P constants and n reflects adsorbent heterogeneity.

2.4.2. Kinetics Experiments

Pseudo-first-order (PFO) (Equation (7)) and pseudo-second-order (PSO) (Equation (8)) kinetic models were used to study the effect of contact time in the adsorption process. The resulting values contributed to the estimation of adsorption, as well as to the determination of the proper rate terms for possible mechanisms. These calculations were conducted to better comprehend the IBU adsorption process.

$$Q_t = Q_e\left(1 - e^{-k_1 t}\right) \tag{7}$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \tag{8}$$

where Q_t and Q_e (mg/g) are the quantity of adsorbed IBU at time t (min) and equilibrium, respectively; the rate constants k_1 (L/min) and k_2 (g/mg min) denote to the rate of adsorption for the PFO and PSO models; and t is for the contact time measured in min.

2.5. Thermodynamics

For the thermodynamic evaluation and to better understanding of the adsorption process, the calculation of three thermodynamic factors at several temperatures (298, 308, 318 and 338 K) was required. These factors were the Gibbs free energy change (ΔG^0, kJ/mol), the entropy change (ΔS^0, kJ/mol·K), and the enthalpy change (ΔH^0, kJ/mol), and they were calculated with Equations (9)–(11) [27].

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

$$\Delta G^0 = -RT\ln(K_c) \quad (10)$$

$$K_c = \frac{C_s}{C_e} \quad (11)$$

Equation (9) was used to determine ΔG^0, and ΔH^0 and ΔS^0 were determined from the plot of ln(*Kc*) versus $1/T$ by analyzing the displayed slope and intercept calculated with Equation (12):

$$\ln(K_c) = \left(-\frac{\Delta H^0}{R}\right) + \frac{\Delta S^0}{R} \quad (12)$$

where R is the universal gas constant (8.314 J mol/K).

3. Results and Discussion

3.1. Effect of Adsorbent Dosage

Taking into account that the dosage of an adsorbent is one of the main parameters affecting the design and operation of an adsorption system, dosage was studied in our batch experiments to determine the ability of the tested material to remove Ibuprofen in aqueous solution, with an initial concentration of IBU 100 mg/L. Different concentrations of AC@Al from 0.2 to 1.0 g/L were used at specific acidic pH conditions [28], i.e., pH 3.0 ± 0.1, at a constant temperature of 298 K for 24 h. As presented in Figure 1, with growing adsorbent dosage, the percentage of IBU removal augmented from 85% with 0.2 g/L to 100% with 1.0 g/L.

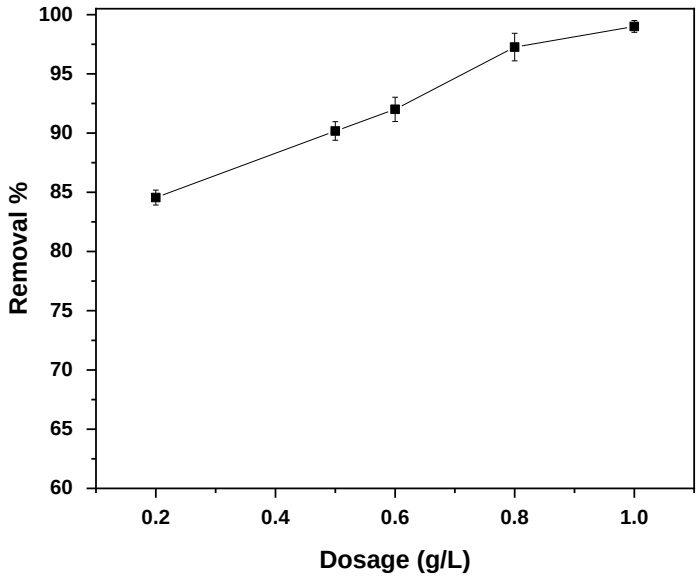

Figure 1. Effect of AC@Al dose on IBU adsorption; IBU C_0 = 100 mg/L, pH 3.0 ± 0.1, T = 298 K, t = 24 h.

3.2. Effect of pH

The influence of pH was examined in the pH range of 2.0–9.0 ± 0.1 with a static dosage of 0.8 g/L applied to 100 mg/L of IBU at T = 298 K for 24 h. The pH was checked and adjusted before the adsorbent's addition by adding appropriate low concentrations of NaOH or HCl. As shown in Figure 2, in acidic conditions, the removal of Ibuprofen was enhanced. Specifically, the highest removal rate was achieved at pH = 2.0 ± 0.1 (98.8%). Further increases in pH gradually reduced the absorbent capacity. As the pH values increased, the total surface charge of AC@Al became negative. Therefore, the overall negative value increased with further increases in pH, preventing negatively charged species from binding to the surface of the material due to the increasing repulsive forces between both the negatively charged IBU molecules and the surface [17].

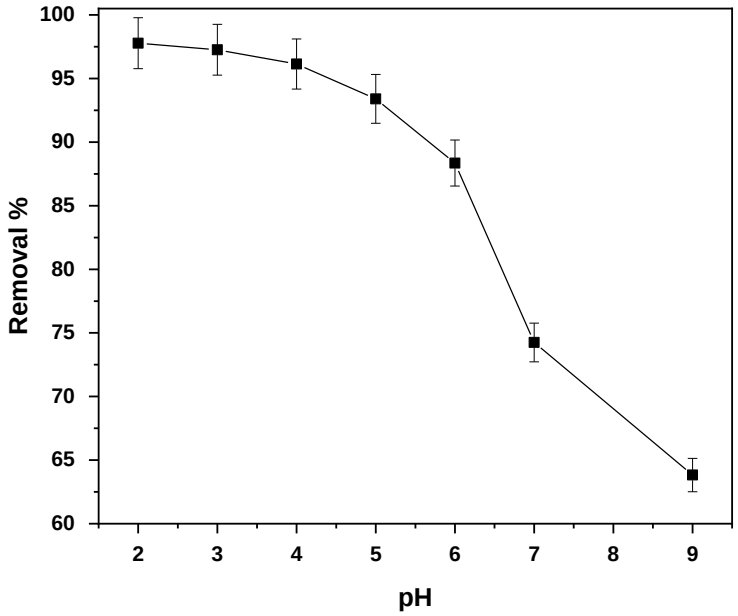

Figure 2. Effect of pH on the adsorption of IBU onto AC@Al; IBU C_0 = 100 mg/L, dose = 0.8 g/L, pH 2.0–9.0 ± 0.1, T = 298 K, t = 24 h.

The point of zero charge (pH_{pzc}) of AC@Al, which is the point at which a surface charge becomes neutral, was found by measuring it within a pH range of 2.0–10.0 ± 0.1. This was done by plotting ΔpH vs. $pH_{initial}$ using the pH drift method [29] (Figure 3) for pH_{pzc} calculation. The pH_{pzc} of AC@Al was determined in a pH range of 2.0–10.0 ± 0.1. For a pH lower than the point of zero charge (pH_{pzc} = 5.72) the surface of an adsorbent is positively charged due to protonation and the electrostatic repulsion between negatively charged Ibuprofen, while for higher values, there is a dissociation of the functional groups that creates a negative charge. As the pH increases, the effectiveness of adsorption decreases because of the repulsion occurring between the negative charge of the AC@Al surface and the Ibuprofen [15]. Ibuprofen is considered a weak acid, and its removal was advantageous at pH 2.0 ± 0.1 and unfavorable at pH > 7.0 [28]. IBU has a pKa = 5.2, and at the optimum pH of 2.0, which is <pKa, it occurs in the neutral form and is adsorbed via non-electrostatic interactions with the settling surface. With increases in pH, the relative rate of IBU removal decreased with the deprotonation of surface-active agents. Similar results have been reported in the literature regarding the optimum pH of 2.0 [30].

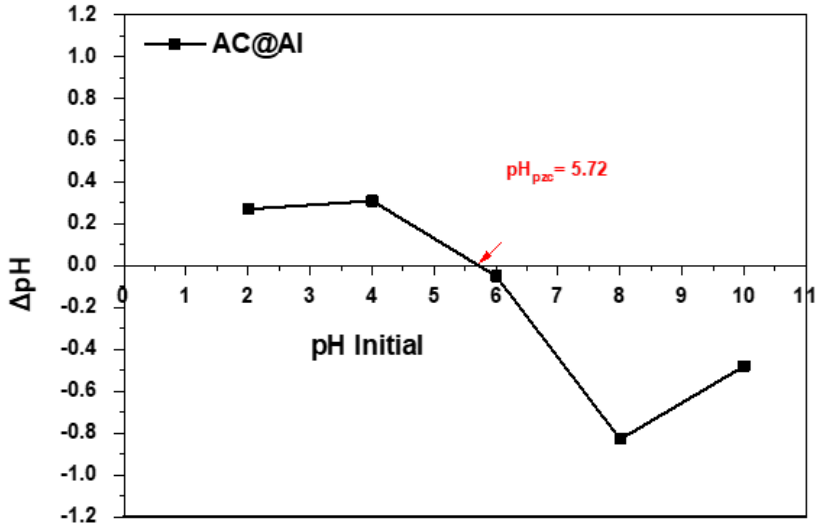

Figure 3. Identification of the pH_{pzc} of AC@Al (pH drift method [29]).

3.3. Effect of Contact Time

The kinetic behavior of adsorbent materials is a key factor in the adsorption process. In this study, the effects of interaction times between 2 and 240 min were studied, with the further parameters remaining constant (IBU C_0 of 100 mg/L, dose of 0.8 g/L, pH 2.0 ± 0.1, T = 298 K). According to the results (Figure 4), the percentage of IBU removal increased with increasing contact time and remained constant after 120 min (96%). It is worth noting that the reaction seemed to be extremely fast, as after 2 min, 44% of the Ibuprofen was already removed. In conclusion, in order to increase the correlation between cost and adsorption efficiency, 2 h (120 min) is as the optimal interaction time under these conditions.

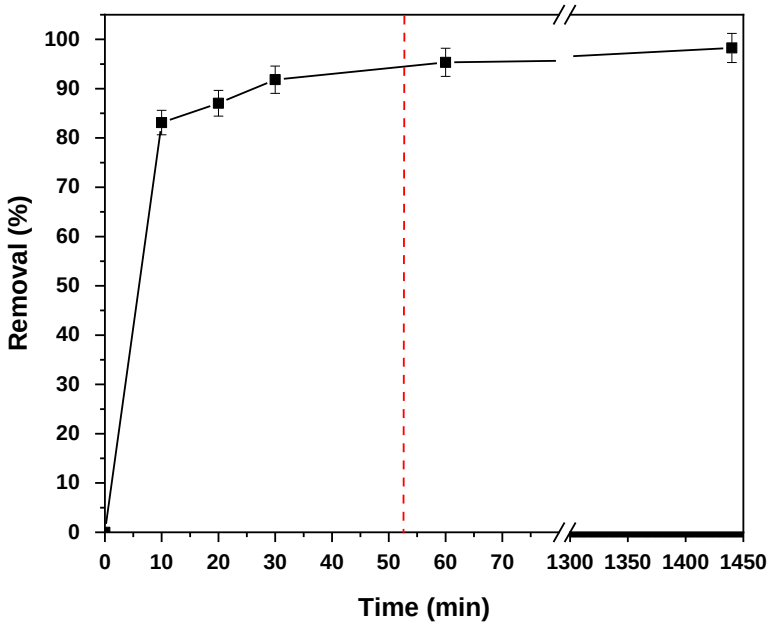

Figure 4. Effect of interaction time on the adsorption of IBU onto AC@Al; 100 mg/L of IBU C_0 and 0.8 g/L of adsorbent at pH 2.0 ± 0.1 and T = 298 K.

3.4. Adsorption Kinetics

In this research, the adsorption kinetics were evaluated through the use of pseudo-first-order (P*F*O) and pseudo-second-order (PSO) kinetic models. Figure 5 shows the pseudo-second-order kinetic model results, as they were better fitted to the adsorption of

IBU (100 mg/L) onto AC@Al at pH = 2.0 ± 0.1 when applying 0.8 g/L of AC@Al. Table 1 gives the constants of the pseudo-second-order model, as calculated with Equation (8).

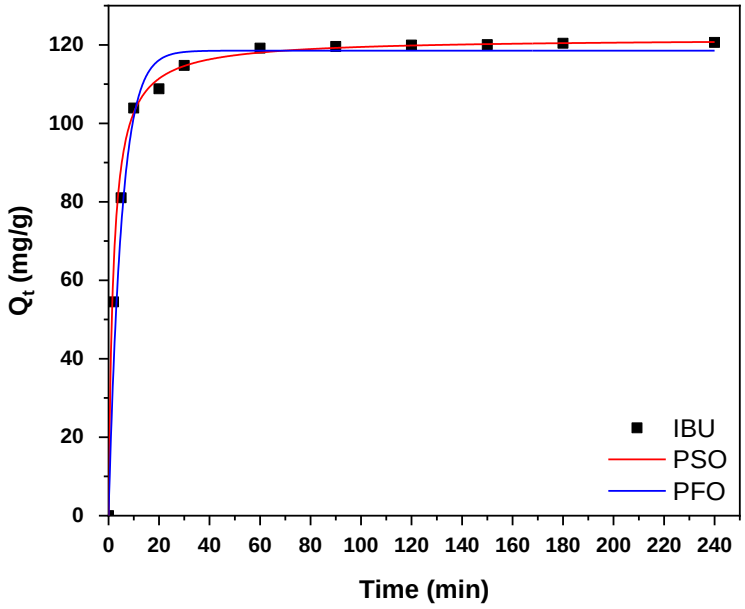

Figure 5. PFO and PSO kinetic models for the adsorption of IBU onto AC@Al; 100 mg/L of IBU C_0 and 0.8 g/L of adsorbent at pH 2.0 ± 0.1 and T = 298 K.

Table 1. Constants of PFO and PSO kinetic models for the adsorption of IBU onto AC@Al (0.8 g/L) at pH 2.0 ± 0.1 and T = 298 K.

Pseudo-First-Order Model (PFO)				Pseudo-Second-Order Model (PSO)		
$Q_{e\cdot exp}$ (mg/g)	k_1 (L/mg·min)	$Q_{e\cdot cal}$ (mg/g)	R^2	k_2 (L/mg·min)	$Q_{e\cdot cal}$ (mg/g)	R^2
122.8	0.1947	118.5	0.9914	0.00446	121.7	0.9991

The experimental adsorptivity ($Q_{e\cdot exp}$) was measured to be 122.8 mg/g, while the calculated adsorption capacity ($Q_{e\cdot cal}$) obtained with the PSO model was recorded as 121.7 mg/g and that obtained with the PFO model was recorded as 118.5 mg/g. The comparability of these values, combined with the high coefficient of determination for the PSO kinetic model (R^2 = 0.9991), indicates the excellent fit of the PSO model to the experimental data. This suggests that the adsorption process is mainly controlled by chemisorption mechanisms [31].

3.5. Adsorption Isotherms

The isotherms of IBU adsorption onto AC@Al were assessed by means of two models with two parameters, the Freundlich and Langmuir models, and two models with three adjustable parameters, the Sips and Redlich–Peterson models, using Origin software (OriginLab.OriginPro.v9.0.SR2). According to the correlation coefficient (R^2), all models demonstrated similar values. Particularly, the Langmuir model was shown to be much more tolerable (R^2 = 0.986) than the Freundlich model (R^2 = 0.981). Regarding the three-parameter models, the relative values were R^2 = 0.984 and R^2 = 0.985 for the Sips and Redlich–Peterson models, respectively. The isotherm parameters were calculated according to Equations (1)–(6) and are tabulated in Table 2. The relative fits are presented in Figure 6. Langmuir's declaration accepts [20] the existence of equivalent adsorption sites and a monolayer distribution of IBU onto the surface of the AC@Al adsorbent. Furthermore, as isotherms can contribute to the calculation of the possible maximum intake, in this study, according to the Langmuir model, the relative capacity was found to be very high, i.e.,

2053 mg/g, indicating that AC@Al is an effective adsorbent for IBU removal. In addition, the calculated isotherm parameters of the three-parameter Sips and two-parameter Langmuir models showed a partial agreement between the corresponding values of Q_m, with 2251 mg/g for Sips and 2053 mg/g for Langmuir, probably because these do not fully follow the Langmuir isotherm model. It is assumed that the adsorption capacity obtained with the Sips model could be more accurate than that obtained with the Langmuir equation [24]. Also, the R^2 values for the Redlich–Peterson and Langmuir models were found to be almost the same, confirming the literature findings that the Langmuir isotherm constitutes a subcase of the Redlich–Peterson isotherm [32]. In conclusion, the application of the four models confirmed that the adsorption mechanism is a mixture of the two models and does not follow an ideal and exclusively monolayer adsorption.

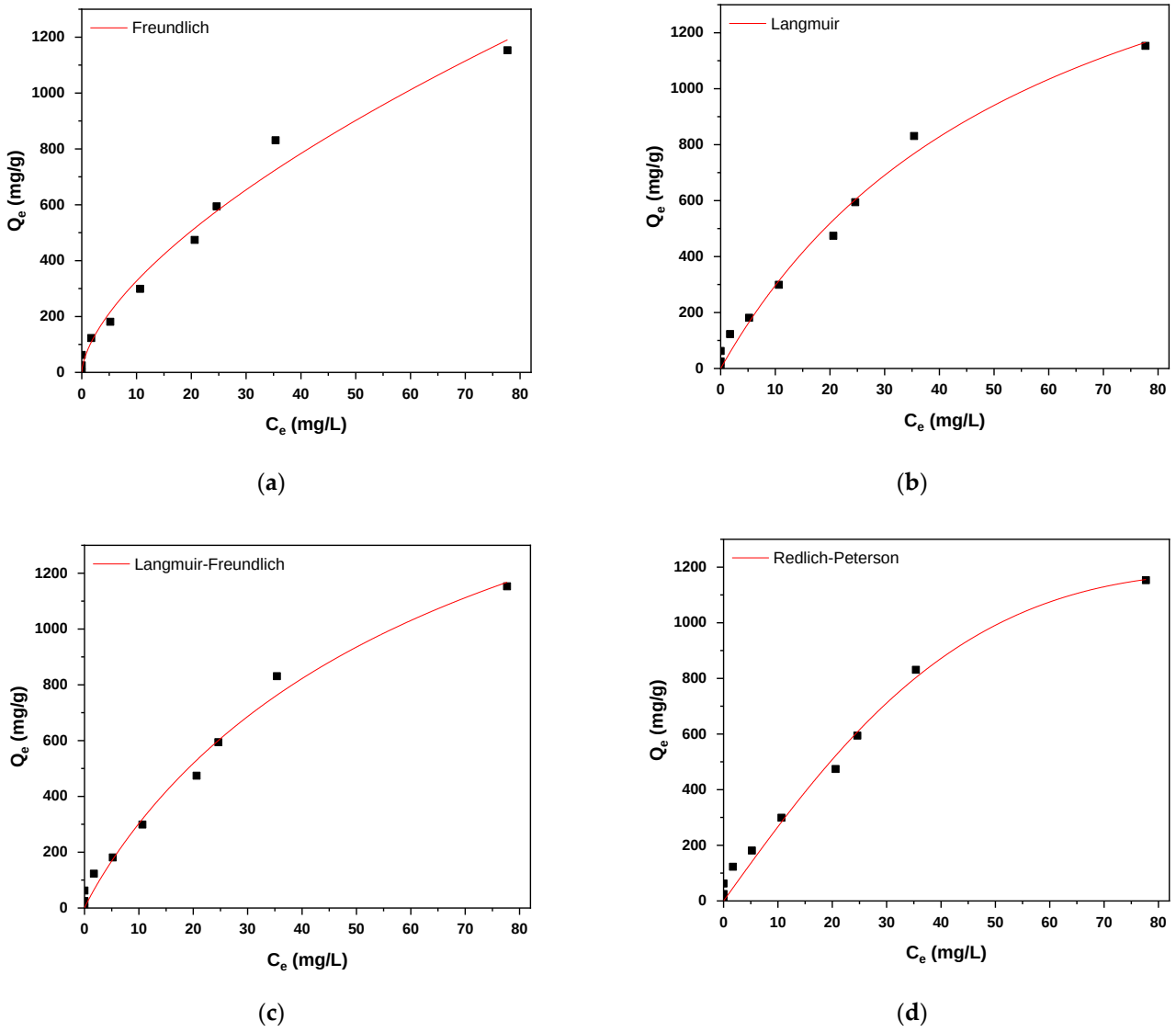

Figure 6. Isotherm models: (**a**) Langmuir, (**b**) Freundlich, (**c**) Langmuir and Freundlich (Sips), and (**d**) Redlich–Peterson isotherm models for the adsorption of IBU onto AC@Al; 20–1000 of IBU C_0 and 0.8 g/L of adsorbent at pH 2.0 ± 0.1 and T = 298 K for 24 h.

Table 2. Langmuir, Freundlich, Langmuir and Freundlich (Sips), and Redlich–Peterson isotherm model values.

Langmuir Isotherm Model			
Q_m (mg/g)	K_L (L/mg)		R^2
2053	0.017		0.986
Freundlich isotherm model			
$1/n$	K_F (mg/g)·(L/mg)$^{1/n}$		R^2
0.630	76.67		0.981
Langmuir–Freundlich (Sips) isotherm model			
Q_m (mg/g)	$1/n$	K_{LF} (L/g)	R^2
2251	0.944	0.0176	0.984
Redlich–Peterson (R–P) isotherm model			
$1/n$	K_{RP} (L/g)	α_{RP} (L/mg)^n·10^3)	R^2
0.552	27.22	0.31	0.985

3.6. Thermodynamics

The values of ΔH^0 and ΔS^0 were attained by examining the plot ln(K_c) vs. 1/T (R^2 = 0.947) [27]. When ΔG^0 is negative, the process is spontaneous, while when ΔG^0 is positive, the process is endothermic, that is, external energy is required to take place. In this study, the adsorption of IBU occurred spontaneously due to negative ΔG^0 values (Table 3). The ΔH^0 value for IBU was found to be 42.917 kJ/mol, demonstrating that the adsorption process was endothermic. The positive ΔS^0 value (0.1722 kJ/mol·K) for IBU was due to the increased randomness of the adsorbates at the interface between the solid and the solute during the adsorption process [33].

Table 3. Thermodynamic parameters for the adsorption of IBU onto AC@Al; 100 mg/L of IBU C_0 and 0.8 g/L of adsorbent at pH 2.0 ± 0.1 and T = 298 K for 1.5 h.

T (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol·K)	R^2
293	−7.525	42.917	0.1722	0.9446
303	−9.247			
313	−10.969			

3.7. Reuse Study

Recycling experiments were performed at optimum conditions (100 mg/L of IBU and 0.8 g/L of adsorbent at pH 2.0 ± 0.1) to examine the reusability of AC@Al for the removal of IBU from pharmaceutical wastewater. After the first cycle, the used AC@Al was treated with the addition of a 0.1 M NaOH solution for 1.5 h, and then it was washed with distilled water to remove the residual base. This procedure was followed for the next four cycles, and the results are provided in Figure 7. The relative percentage of IBU removal was about 96% in the first cycle and reduced to about 78% after the fifth cycle, confirming the reusability of AC@Al as an adsorbent for five cycles.

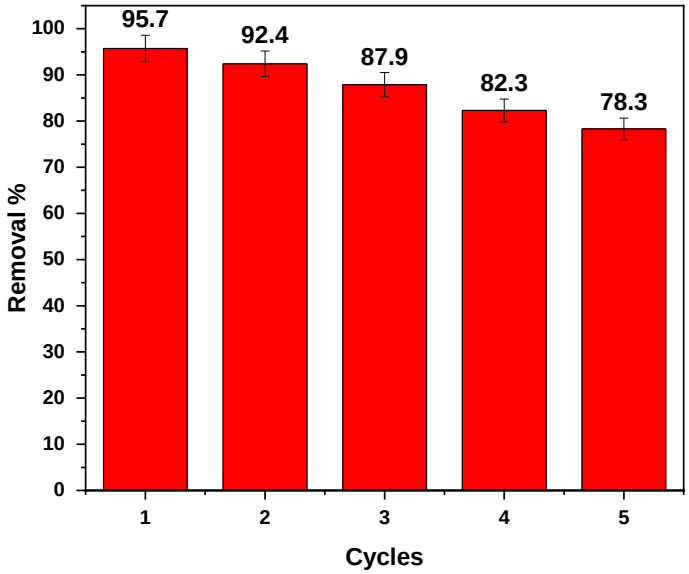

Figure 7. Adsorption of IBU onto AC@Al for 5 adsorption–desorption cycles after regeneration at alkalic pH using 0.1 M NaOH treatment; IBU C_o = 100 mg/L, dose = 0.8 g/L, pH = 2.0 ± 0.1, t = 1.5 h.

4. Conclusions

In this study, the application of hybrid, porous aluminum-modified coconut-shell-derived activated carbon (AC@Al) was evaluated for the removal of Ibuprofen (NSAID) from pharmaceutical wastewaters. The results showed that at pH 2.0 ± 0.1, a removal rate of around 99% was achieved when 0.8 g/L of AC@Al was added. Additionally, at pH 2.0, which is less than pH_{pzc} (5.72), the positively charged surface of AC@Al probably attracted negatively charged Ibuprofen molecules due to protonation and electrostatic repulsion. Langmuir, Freundlich, Sips and Redlich–Peterson isotherm models were applied to evaluate the adsorption. It was found that all isotherm models fit the adsorption well according to R^2 values, so the adsorption mechanism is a mixture that does not follow an ideal and exclusive monolayer adsorption. The PSO kinetic model was found to best fit the adsorption procedure, demonstrating that the adsorption of IBU onto AC@Al is close to chemisorption. The Langmuir maximum adsorption capacity was determined to be extremely high, reaching 2053 mg/g. According to kinetics calculations, equilibrium was reached at 90 min. Thermodynamics calculations showed that the adsorption was endothermic in nature (ΔH^0= 42.9 kJ/mol) and spontaneous ($\Delta G^0 < 0$) at all temperatures. The positive value of ΔS^0 (0.1722 kJ/mol·K) indicated that there was an increase in the random interaction between the solid and liquid interfaces. In conclusion, AC@Al as an adsorbent was effectively regenerated and reused for five cycles in the removal of IBU from pharmaceutical wastewater.

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