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Waste Leather Treated with Acid as a Crucial Adsorbent for Celecoxib Removal

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Abstract

The study investigated the adsorption properties of celecoxib from acid-digested waste leather (ADCL) under various physicochemical conditions. The batch method was used to assess the effects of particle size, adsorbent dose, pH, temperature, initial concentration, and contact time. Results showed that the smallest particles, with the largest surface area, exhibited the highest adsorption capacity. Celecoxib exhibited 90.85% adsorption at pH 2, and the isotherm model demonstrated its adsorption behavior at different temperatures. Adsorption occurred at a pH of 2, with the amount of celecoxib adsorbed depending on the dose, contact time, and its initial concentration. The pseudo-second-order kinetics classified the process as physicochemical adsorption, and the results were supported by FT-IR, SEM data, XRD spectra, and thermodynamic analysis.

1. Introduction

Pharmaceutical contamination of water has become a serious environmental issue, as many drugs persist in aquatic ecosystems, posing significant risks to both human health and the environment [1-2]. Among these, celecoxib sodium, a widely used nonsteroidal anti-inflammatory drug (NSAID), has been detected in water systems due to improper disposal and the inefficiency of conventional wastewater treatment methods in its complete removal [3]. Therefore, developing an effective and economical strategy to eliminate such pharmaceutical contaminants is crucial. Adsorption is widely regarded as one of the most effective methods for water purification due to its simplicity, cost-effectiveness, and high efficiency. In this context, carbon-based adsorbents, such as activated carbon and its derivatives, have been extensively studied for their effectiveness in removing organic pollutants from water [4].

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This study aims to evaluate the potential of commercial carbon sorbents as effective adsorbents for the removal of celecoxib sodium from aqueous solutions. This study highlights the impact of pharmaceuticals on the biosphere and strategies for their mitigation. Drugs such as beta-blockers, painkillers, antibiotics, female hormones, cholesterol medications, and antiepileptic drugs are commonly detected in water due to human consumption and disposal [5-6]. These chemicals pose significant risks to living organisms and persist in water for extended periods. Celecoxib, a widely used pharmaceutical, has been detected in surface waters across several countries due to inadequate treatment processes [7]. This study aims to evaluate the feasibility of using commercial carbon sorbents as adsorbents to remove celecoxib sodium from water, while investigating the kinetics, statics, and process parameters influencing its adsorption [8]. The absence of guidelines for acceptable medication levels in water after treatment in sewage plants underscores the importance of close monitoring and regulation.

2.Materials and methods

The tests involved using a solution of HCl and NaOH at 30°C to modify its acidic and basic properties. The adsorbing material and substance were kept in contact for a specific duration, and their quantities were recorded. The mixture was shaken for 180 minutes

at 100–300 rpm using a machine, then filtered through Whatman 40 filter papers. The filtrate was analyzed using a UV light machine to determine its content, with 50 ml used for optimal size and amount. Equation 1 was applied to evaluate the adsorbate degradation results.

$$\text{Adsorption (\%)} = (C_o - C_e) \times 100 / C_o \quad (1)$$

Here, C_o represents the initial concentration, and C_e denotes the final concentration of the drug adsorbate at equilibrium.

3.Results and discussion

The crystalline structure of ADCL was determined using XRD analysis. **Fig.1**(a) shows sharp, narrow diffraction peaks. After acid (H_2SO_4) activation during the pyrolysis of ADCL, a prominent diffraction peak emerged, indicating the formation of a microcrystalline structure. Additionally, the peak near 750 exhibits a microcrystalline structure similar to that of graphite, facilitating the rapid adsorption of celecoxib from synthetic solutions. This adsorption is physical in nature and governed by weak Van der Waals forces [9–11].

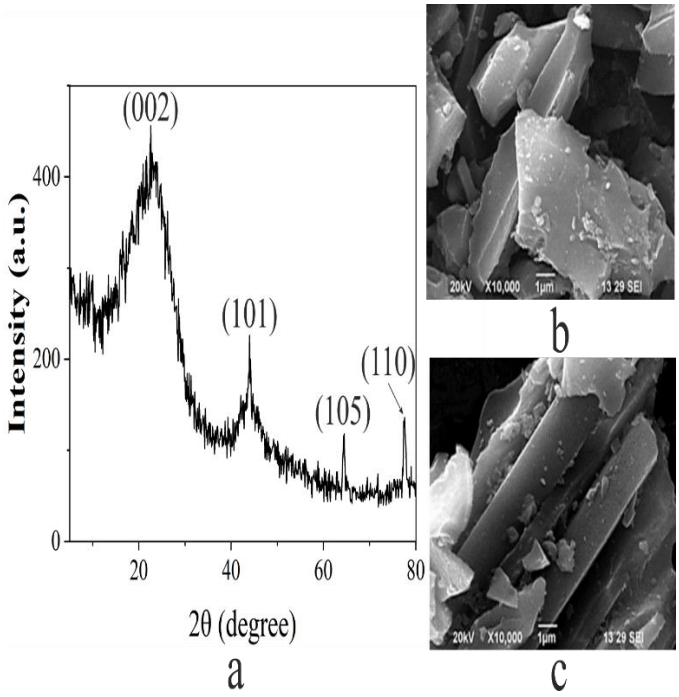

Fig.1. (a) XRD Spectrum; SEM image (b) before (c) after adsorption.

Through SEM analysis [12–15], the surface morphology of synthetic ADCL was examined both before and after the injection of celecoxib. **Fig.1**(b, c) illustrates the significant differences in the adsorbent's porosity and textural characteristics before and after the accumulation of celecoxib molecules on its surface. The micrograph revealed that the material contains numerous tiny pores, facilitating the adhesion of the medicine in an aqueous solution. Artificial modifications also induced changes in the cell structure of ADCL. The results demonstrated that the synthesized ADCL possesses a large, porous structure with a high surface area and an average pore size. These findings indicate that synthetic ADCL has a high carbon content due to chemical activation with H_2SO_4, whereas celecoxib-loaded carbon exhibits a lower carbon content. This reduction is attributed to the attraction of celecoxib ions to the carbon surface, resulting from the celecoxib acid-loaded adsorbent.

3.1 Effect of Particle Size

The study investigated the adsorption of celecoxib using acid-digested waste leather (ADCL) categorized into three distinct particle size ranges: 0–63 μm, 63–125 μm, and 125–200 μm. The ADCL was divided accordingly, and the adsorption performance for each particle size was evaluated. The results of the adsorption efficiency are presented in **Fig.2**(a).

3.2 Effect of pH

The pH level of the solution significantly influences the bio-surface adsorbent, enhancing its ability to remove celecoxib from aqueous solutions. The study utilized ADCL to examine the effect of varying the pH from 1 to 6 on celecoxib adsorption. The results indicate that the efficiency of drug adsorbate removal decreases with increasing pH. An acidic medium with a pH of 2 was found to be optimal for celecoxib adsorption, as illustrated in **Fig.2**(b). This is attributed to the strong electrostatic attraction between ADCL and celecoxib, which limits the adsorption of drug adsorbate solution ions onto ADCL's surface. The highest removal efficiency was observed at a pH of 1, due to the increased positive charges at the solution interface and the more strongly charged surface of ADCL.

3.3 Effect of Adsorbent Dosage

A wide range of ADCL adsorbent doses was investigated to evaluate their impact on the removal of celecoxib from aqueous solutions. The adsorbent dose plays a crucial role in determining the binding capacity of drug molecules in the solution. As shown in **Fig.2**(c), the efficiency of celecoxib removal from the solution increased from 71.23% to 93.46% as the adsorbent dose was increased from 50 mg to 200 mg. Adsorption peaked at 200 mg or higher, with 150 mg identified as the optimal adsorbent dose. The adsorption sites on the surface of ADCL significantly enhance removal efficiency.

3.4 Effect of Initial Concentration

Celecoxib's initial concentration significantly influences its removal efficiency. Equilibrium tests were performed to evaluate the effect of the initial concentration on the drug's adsorption. As the initial celecoxib concentration in the aqueous solution increased, the removal efficiency of the drug adsorbate decreased. As shown in **Fig.2**(d), the efficiency of celecoxib removal dropped from 94.88% to 83.68%, likely due to the limited availability of adsorption sites. This suggests that celecoxib favors active sites, with fewer surface sites available for adsorption as the number of adsorbing species increases at higher initial concentrations.

3.5 Effect of Contact Time

The adsorption of celecoxib was studied using ADCL, a natural adsorbent, at 30°C. The substance was left in contact with celecoxib for durations ranging from 30 to 180 minutes, with maximum efficiency observed at 180 minutes, achieving 66.09% removal of water ions, as shown in **Fig.2**(e). The bio-adsorbent's surface contains numerous active sites for capturing celecoxib

ions. However, when the contact time increased to 210 minutes, the adsorption efficiency decreased due to the accumulation of unfavorable molecules on the material, which hindered further adsorption of celecoxib.

3.6 Effect of Temperature

Using the bio-adsorbent (ADCL), alizarin yellow celecoxib was optimally adsorbed at temperatures ranging from 30 to 60°C, as illustrated in **Fig.2**(f). The percentage of celecoxib adsorbed increased with rising solution temperature, ranging from 87.11% to 93.21%. This may be attributed to the faster diffusion of celecoxib molecules across the internal pores and external boundary layer of ADCL, leading to an enhanced adsorption rate in the aqueous solution. This observation is consistent with the fact that a temperature increase supplies the endothermic adsorption process with the necessary energy to proceed more rapidly [16].

3.7 Kinetic, Isothermal, and Thermodynamic Study

The sum of squared error (SSE, %) is used alongside the R^2 value to evaluate the accuracy of kinetic models. Various concentrations of celecoxib were tested to analyze their impact on the adsorption rate by ADCL. SSE is calculated using the formula SSE (%) = $(qe_{exp} - qe_{cal})^2$ N, where N is the number of data points. It helps measure how well each model fits the data. A better fit means a higher R^2 value and a lower SSE[17]. The results are shown in **Error! Reference source not found.**. I t was found that the second-order kinetic model is the most accurate for explaining how celecoxib sticks to ADCL [18,19].

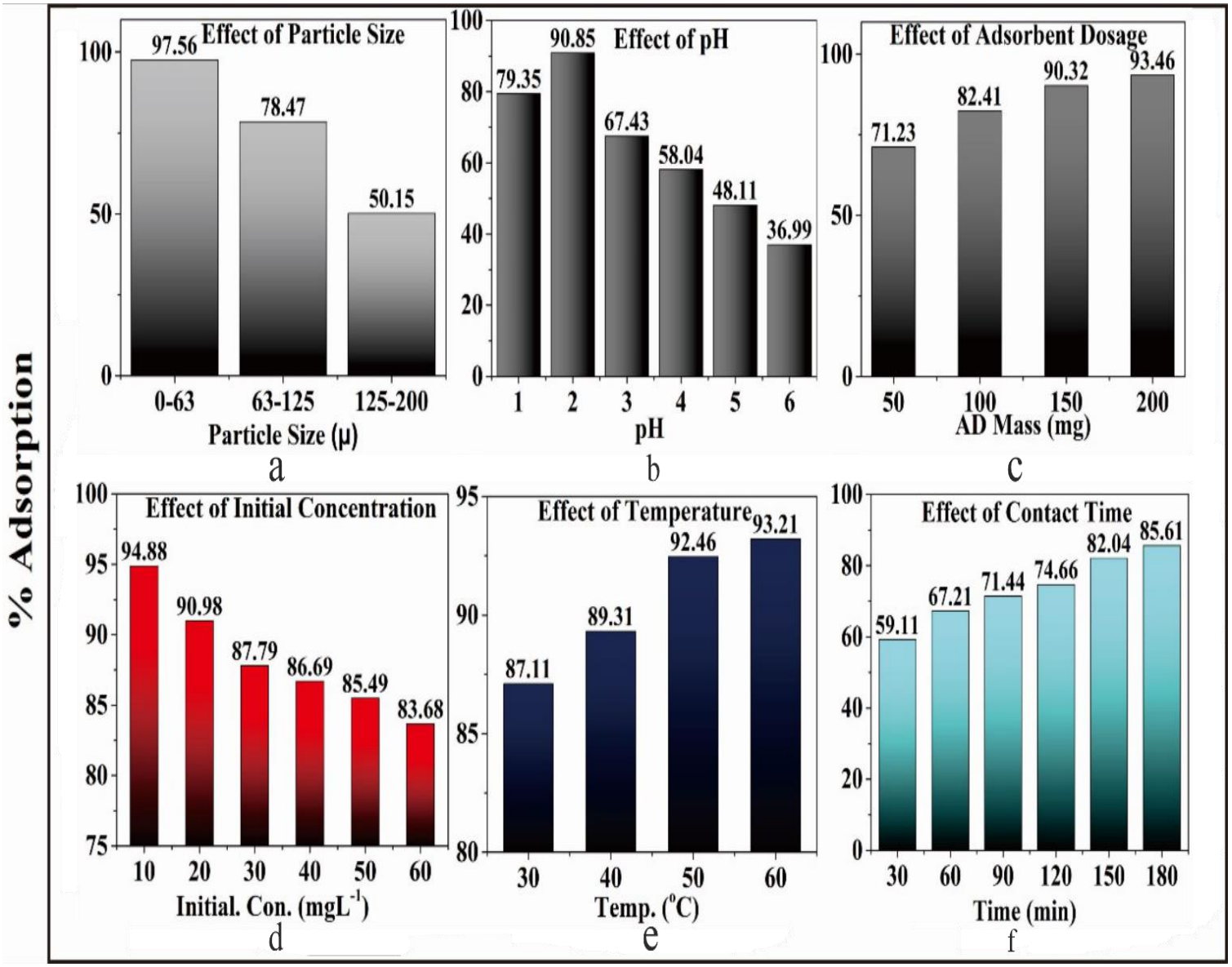

Fig.2. Effect of (a) particle size, (b) pH, (c) adsorbent dosage, (d) initial concentration, (e) temperature, and (f) contact time on ADCL adsorption performance.

Table 1. Kinetic, isothermal, and thermodynamic parameters for the adsorption of celecoxib

Kinetic						
I Order	K_1	0.006909	q_e	1.212883	R^2	0.882
II Order	q_e	3.236246	K_2	0.016556	R^2	0.987
Int part diff	K_p	0.096	c	1.685	R^2	0.94
Elovich model	β	0.423	α	0.736	R^2	0.917
Isothermal						
L Isotherm	K_L		q_0		b_L	R^2
	4.878049		23.80952		0.204878	0.916
F Isotherm	K_F		n		-	R^2
	4.466836		1.538462		-	0.996
DKR	β		b		q_0	R^2
	2.55633		1.1398		25.00345	0.967
RP	β		b_R		K_R	R^2
	0.122		8.196721		1.844262	0.977
Thermodynamic						
ΔG^0		ΔH^0	ΔS^0		$\text{Log}_{10} K_a$	1/T
-2046.827		38.29428	61.27085		0.352694	0.0032987
-2666.515		-	-		0.444801	0.0031934
-3782.673		-	-		0.611461	0.0030945
-4212.303		-	-		0.660471	0.0030017

Studying adsorption isotherms, such as Langmuir and Freundlich, helps to better understand how celecoxib is adsorbed [20,21]. The Langmuir isotherm describes how a single layer of molecules attaches to a surface with specific binding sites. Celecoxib demonstrated good adsorption ability, with a sorption equilibrium constant (KL) value of 4.878049. On the other hand, the Freundlich isotherm accurately represents the experimental data, showing a maximum adsorption capacity of 4.466836. The Redlich-Peterson isotherm, with an R^2 value of 0.967, effectively explains the experimental results. The DKR model, which uses sorption energy to differentiate between chemisorption and physisorption, was applied to study the adsorption process. The Langmuir model fit the experimental data well, suggesting that the ADCL carbon surface is uniform, leading to a single-layer adsorption of celecoxib molecules on the ADCL carbon. The positive enthalpy change values indicate that the adsorption process is endothermic. Since the entropy factor ($T\Delta S^o$) outweighs the enthalpy factor (ΔH^o), the process is likely spontaneous, as evidenced by the negative Gibbs free energy (ΔG^o) [22–24]. The activation energies for celecoxib adsorption on the adsorbent were calculated using the Arrhenius equation and are presented in **Table 1**. The activation energy observed suggests that physical factors play a significant role in determining the sorption mechanism and the feasibility of adsorption.

Conclusion

The study explores the adsorption of celecoxib, a pharmaceutical compound, onto waste leather carbon. The smallest particles (0–63 μm) exhibit the highest surface area, making them the most effective at attracting other substances. Adsorption is most efficient at lower pH levels, where hydroxide ions are formed. At pH 2, 90.85% adsorption is achieved. The amount of celecoxib adsorbed depends on the quantity of adsorbent used, the contact duration, and the initial concentration of celecoxib. The adsorption process follows pseudo-second-order kinetics, indicating physisorption, with the Freundlich and Langmuir isotherm models providing a suitable fit. The research demonstrates that adsorption is feasible, spontaneous, and physical, as indicated by negative ΔG^o , and positive ΔH^o and ΔS^o Values. These findings suggest

that celecoxib contamination can be effectively removed from water and industrial waste.

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