



Optimization of Adsorption Parameters for Polycyclic Aromatic Hydrocarbon (PAH) Removal Using Acid-Activated Carbon Derived from Crustacean Shell Waste

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ABSTRACT

The aim of this study was to demonstrate the potential of acid-activated carbons derived from shell waste as sustainable and efficient adsorbents for PAH removal from contaminated water. Activated carbon was synthesized from periwinkle shells, clam shells, whelk shells, and a 1:1 composite of clam and whelk shells. The precursor materials were carbonized at 450 °C under limited-oxygen conditions and chemically activated using H_2SO_4 at 750 °C. The resulting adsorbents—Periwinkle Shell Acid-Activated Carbon (PSAAC), Clam Shell Acid-Activated Carbon (CSAAC), Whelk Shell Acid-Activated Carbon (WSAAC), and Clam-Whelk Shell Acid-Activated Carbon (CWSAAC)—were characterized using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) and physicochemical analysis. Among the synthesized materials, CSAAC exhibited the highest surface area (1277 m^2/g), indicative of enhanced adsorption potential. Batch adsorption experiments were conducted to evaluate the influence of adsorbent dosage and contact time on PAH removal efficiency. CWSAAC demonstrated the highest removal efficiency, achieving 98.93% at a 1 g dosage. The removal efficiency of the adsorbents followed the trend: CWSAAC (98.93%) > CSAAC (98.92%) > PSAAC (98.77%) > WSAAC (96.62%). Adsorption isotherms were modeled using Langmuir, Freundlich, Henry, Elovich, and Janovich models. The Freundlich and Langmuir models best described PAH adsorption for PSAAC, CSAAC, and CWSAAC, with CSAAC exhibiting the highest Langmuir monolayer adsorption capacity (23.995 mg/g). In contrast, WSAAC adsorption was best described by the Henry isotherm, indicating a preference for low-concentration adsorption. Kinetic studies revealed that PAH adsorption followed a pseudo-second-order model, suggesting that chemisorption was the dominant mechanism. These findings highlight the potential of acid-activated carbons derived from crustacean shell waste as cost-effective and sustainable adsorbents for PAH remediation in contaminated water systems.

Keywords: Polycyclic aromatic hydrocarbons (PAHs); crustacean shells; H2SO4 activation; periwinkle shells; clam shells; whelk shells; composite shells; Freundlich isotherm; Langmuir isotherm; Henryisotherm; Elovich isotherm; Janovich isotherm.

1. Introduction

The contamination of water bodies by toxicants has become a critical environmental issue, prompting widespread public discourse and concern across many nations [1]. Among these pollutants, polycyclic aromatic hydrocarbons (PAHs) have attracted significant attention due to their persistent presence in the environment and their detrimental effects on ecosystems and human health. PAHs are recognized as some of the most carcinogenic, mutagenic, and toxic organic contaminants [2]. These organic pollutants originate from both natural processes, such as volcanic eruptions and forest fires, and anthropogenic activities linked to industrialization and urbanization [3]. Over the past few decades, increasing regulatory and scientific focus has been placed on 16 PAHs classified as priority pollutants by the United States Environmental Protection Agency (U.S. EPA) due to their widespread occurrence and severe toxicological properties, including mutagenicity, teratogenicity, and

carcinogenicity [4]. Like heavy metals, PAHs bioaccumulate in human and animal tissues, posing significant health risks. These compounds have been linked to both carcinogenic and mutagenic effects, ranging from non-cancerous conditions-such as skin disorders and adverse impacts on the lungs and blood in both humans and animals-to severe cancer-related outcomes, including respiratory tract tumors, leukemia, lung cancer, and bladder cancer [5]. Additionally, PAHs have been shown to negatively affect multiple organ systems, including the reproductive, developmental, cardiovascular, nervous, and immune systems [6].Human exposure to PAHs primarily occurs through oral ingestion, dermal absorption, and inhalation. For non-smokers and individuals without occupational exposure, the predominant route of contamination is via the consumption of contaminated food and water. This underscores the critical importance of addressing PAH contamination in water sources as part of broader efforts to

protect public health [7]; [8].

With the growing emphasis on environmentally friendly and sustainable approaches to water pollution remediation, adsorption using eco-friendly and low-cost materials has gained significant attention. This has led to increased research into the utilization of abundant and inexpensive carbon precursors for effective pollutant removal. Traditionally regarded as waste, crustacean shells have long contributed to environmental pollution. However, recent studies highlight their potential as a renewable and costeffective alternative to conventional materials, with applications spanning from construction to environmental protection. This shift not only reduces manufacturing costs but also mitigates environmental burdens. Research attributes the versatility of crustacean shells to chitin, a nitrogen-rich polysaccharide composed of N-acetyl glucosamine (GlcNAc) [9]. Chitin exhibits exceptional chemical resistance and mechanical strength, making it a promising precursor for activated carbon [10]. Through pyrolysis, chitin can be converted into biochar, which has shown significant potential for water treatment applications [9]. This study evaluates the effectiveness of chemically modified activated carbon from crustacean shells for PAH removal, highlighting its adsorption capacity, kinetics, isotherms, and thermodynamics as a sustainable water treatment solution.

2. Materials and Methods

2.1 Preparation of the adsorbent

Periwinkle shells (Tympanotamusfuscatus), West African clam shells (Galatea paradoxa), and whelk shells (Buccinumundatum) were sourced from the Creek Road Market in Borokiri, Port Harcourt, Rivers State, Nigeria. To eliminate residual organic matter, dust, and soluble impurities, the shells were soaked in a cleansing solution with warm water for three days, followed by rigorous washing with tap water under continuous agitation. The cleaned shells were sun-dried for three days before undergoing thermal carbonization at 450 °C for 3 hours under limited oxygen conditions. The resulting biochar was finely ground, and a composite mixture was prepared before chemical activation. The powdered carbon was impregnated with 0.5 M H₂SO₄ and mixed to form a uniform paste. The mixture was subsequently thermally activated in a muffle furnace at 750 °C for 2 hours to enhance porosity and surface functionality. After cooling, the activated carbon was thoroughly washed with deionized water until a near-neutral pH (~6) was attained. The final adsorbent samples were oven-dried at 105°C for 6 hours and stored in air-tight containers for subsequent characterization and adsorption experiments.

2.2 Characterization of Adsorbents

The structural and chemical characteristics of the prepared adsorbents were analyzed using Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDX), and the Sear method [11] for surface area estimation.Surface morphology and elemental composition were examined using a Phenom Pro X SEM (Serial No: MVE0224651193, Model No: 800-07334) under high vacuum at an accelerating voltage of 15 kV. Prior to analysis, samples were mounted on adhesive carbon stubs and coated with a 20 nm carbon layer using a Quorum Q150R ES mini sputter coater to enhance conductivity. Elemental composition was determined using an Oxford XMax 50 Silicon Drift Energy Dispersive X-ray (EDX) detector. The specific surface area of the adsorbents was estimated using the Sear method, providing a quantitative assessment of their adsorption capacity and surface properties.

2.3 Collection of contaminated water

The groundwater study was taken from Site X in RumuekpeEmuoha Local Government Area, Rivers State Nigeria which has geographical coordinates of longitude 6° 41'25" E and latitude 5° 01' 41"N. The area hosts a few oil processing facilities and a substantial collection of crude oil pipelines. Several oil spill incidents have been reported generally in this area due to pipeline vandalization, pipeline ruptures and illegal activities of oil militants. Five wells with a depth of 8 meters each were constructed and groundwater samples collected and analysed.

2.4 Batch Adsorption studies

2.4.1 Effect of Adsorbent Dosage

Specified adsorbent doses of 0.2, 0.4, 0.6, 0.8, and 1.0 g were added to 50 mL water samples with an initial PAH concentration of 50 mg/L at pH 6. The mixtures were agitated at 150 rpm using a mechanical shaker for optimal contact times of 90 minutes (PSAAC), 60 minutes (CSAAC and CWSAAC), and 120 minutes (WSAAC). Equilibrium studies were conducted at room temperature (25°C). After agitation, the mixtures were filtered using Whatman No. 542 filter paper, and the residual PAH concentrations in the filtrates were analyzed using GC-MS. The equilibrium adsorption capacity (qe) was calculated using Equation (1).

$$q_e = \frac{(c_o - c_e)v}{M}$$
(1)

Where: qe = quantity adsorbed (mg/g)

 C_o and C_e = initial and equilibrium concentrations (mg/l)

V = Volume (L)

M = mass of adsorbent (g)

2.4.2 Effect of Contact Time

The relationship between contact time and the adsorption capacity of the activated carbon samples was investigated. In this experiment, 1 g of each activated carbon sample was added to 50 mL of a PAH standard solution with an initial concentration of 50 mg/L in a conical flask. The samples were collected at 10-minute intervals from 10 to 120 minutes at room temperature. Residual PAH concentrations in the solution were then extracted and analyzed.

2.4.3 PAHs Extraction Method

The liquid-liquid extraction technique described by [12] was employed to extract PAHs from the sampled solutions. Analytical-grade dichloromethane (DCM) (99.0% purity, Loba Chemie) was used as the extraction solvent. A 25 mL volume of DCM was added to the solution, followed by vigorous shaking for approximately 2 minutes to facilitate phase separation, with intermittent venting to release pressure. The extraction process was repeated twice to maximize PAH recovery. The mixture was then left to evaporate at room temperature for six hours. To eliminate any remaining water, 1 g of anhydrous sodium sulfate was introduced before 1 mL of the extract was transferred into a vial for injection into an Agilent 7890N GC/MS gas chromatograph.

2.4.4 Sample Analysis Using GC-MS

A 1 mL aliquot of the extracted analyte was introduced into the heated injector of the gas chromatograph, where it was vaporized and carried by helium gas through a capillary separation column (30 m length, 250 μ m internal diameter, and specific film thickness). The temperature program commenced at 80°C (held for 2 minutes) and increased at a rate of 30°C per minute until reaching a maximum of 310°C. The separation of PAH components was governed by their solubility in the stationary phase, the carrier gas flow rate, and the temperature gradient. As each component traveled at a distinct rate, the sample was fully separated before reaching the detector for quantification.

2.4.5 Equilibrium Modeling

The adsorption performance of the activated carbons was assessed using various isotherm models, including the Henry, Langmuir, Freundlich, Elovich, and Jovanovic models. The XLSTAT 2014 software was utilized to estimate model coefficients via nonlinear optimization. The Henry isotherm was modeled as a single-parameter system, while the Langmuir, Freundlich, Elovich, and Jovanovic models were treated as two-parameter isotherms. Parameter estimation was performed using an iterative direct optimization method to minimize errors.

2.4.6 Adsorption Kinetics

Kinetic studies were conducted at varying time intervals to evaluate the adsorption behavior of PAHs. The experimental procedures mirrored those of the equilibrium tests, with 1 g of each activated carbon sample (PSAAC, CSAAC, WSAAC, and CWSAAC) added to 50 mL of PAH solution (50 mg/L) in plastic containers. The mixtures were agitated at 150 rpm using a mechanical shaker. Samples were withdrawn at predetermined time intervals (5, 10, 20, 30, 40, 50, 60, 70, 80, 100, and 120 minutes) and filtered. The residual PAH concentrations were analyzed, and the adsorption capacity at each time point (qt) was determined using Equation (2). At time t, q.(mg/g) was calculated using Equation 2

$$q_t = (C_o - C_t) \frac{v}{m} (2)$$

qt: uptake capacity of the material at time t (mg/g) C_0 and C_t are the initial and final concentrations of the contaminated solution (mg/l) m: mass of adsorbent material (g) V: volume of treated solution (l)

3. Results and Discussion

3.1 Results of the Adsorbent Characterization Experiments

3.1.1 SEM-EDX and Surface Area of the Activated Carbon Prepared

Activated carbon samples generally possess a surface area between 500 and 1500 m²/g, contributing to their high efficiency in adsorption processes [13]. As presented in Table 1, the prepared carbon samples exhibited surface areas ranging from 960 to 1277 m²/g, indicating their suitability for PAH adsorption. Among them, CSAAC demonstrated the highest surface area at 1277 m²/g.

Table 1: Specific Area of activated crustacean shells

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Parameter/Sample	PSAAC	CSAAC	WSAAC	CWSAAC
Specific Surface Area (m2/g)	1193	1277	960	1256

The elemental analysis obtained from Energy Dispersive Xray spectroscopy, as presented in Table 2, reveals the composition of various elements present in the adsorbents. The analysis confirmed the presence of calcium (Ca) and oxygen (O) across all tested materials. Notably, the treated activated carbons exhibited a high calcium content due to activation and mineralization, with a consistent calcium-tooxygen weight ratio of 1:1 in all samples [14][15]. The results further indicated a significant presence of calcium oxide (CaO) in all samples, enhancing their porosity and adsorption capacity. As shown in Table 2, the activated carbon samples had higher atomic concentrations of oxygen than calcium, with CSAAC exhibiting the highest oxygen concentration at 78.16 cm⁻¹.

Table 2 Elemental analysis of the acid-activated carbon from crustace an shells by $\ensuremath{\mathsf{EDX}}$

Sample/ band (cm ⁻¹)	Element	Atomic concentration	Weight concentration
CSAAC	0	78.16	58.83
	Са	21.84	41.17
DSAAC	0	67.37	45.18
PSAAC	Са	32.63	54.82
WSAAC	0	74.43	53.75
	Са	25.57	46.25
CWSAAC	0	75.50	55.15
	Са	24.50	44.85

The SEM micrograph of CSAAC (Figure 1A) revealed a welldeveloped porous and rough structure with interconnected micropores, likely resulting from chemical activation and carbonization. The presence of these well-defined pores suggests its suitability as an effective adsorbent [16].

Similarly, PSAAC exhibited surface heterogeneity with a diverse range of pore sizes, aligning with the findings of [17], which associate high pore density and varied pore structures with enhanced adsorption capacity. WSAAC displayed a rough, porous, and irregular surface, further reinforcing its potential as an efficient adsorbent.

The SEM micrograph of CWSAAC (Figure 1D) showed a rough and heterogeneous surface with open spaces and large pores of varying sizes. The presence of these well-defined open pores indicates a strong adsorption potential, consistent with the observations of [18] regarding the effects of sulfuric acid activation on activated carbon.





Figure 1: SEM Micrographs (at 150 μm) of CSAAC (A), PSAAC (B), WSAAC (C), and CWSAAC (D)

3.2.1 Effect of Adsorbent Dosage on Adsorption Efficiency

Figure 2 illustrates the relationship between adsorbent mass and the percentage removal of the adsorbate for the activated carbons. As the adsorbent mass increases from 0.2 g to 1 g, the percentage removal of the adsorbate also rises across all samples. Specifically, for CSAAC, the removal efficiency improves from approximately 84.63% at 0.2 g to 98.92% at 1 g. Similarly, CWSAAC increasedfrom 82.02 to 98.93%, PSAAC from 82.18 to 98.77%, and WSAAC from 78.79 to 96.62%. The observed trend suggests that higher adsorbent masses provide more surface area and adsorption sites, enhancing removal efficiency [19].

A steep increase in removal efficiency at lower adsorbent masses (0.2–0.4 g) suggests a significant improvement in adsorption due to a greater availability of active sites [20]. However, beyond 0.4 g, the slope flattens, indicating a diminishing increase in removal efficiency as equilibrium is approached. This suggests that adsorption sites become increasingly saturated or that the concentration of available adsorbate decreases, thereby reducing removal efficiency [21].

Figure 3 presents the effect of adsorbent mass on adsorption capacity. Unlike percentage removal, adsorption capacity decreases with increasing adsorbent mass. For instance, CSAAC exhibits the highest adsorption capacity at 0.2 g, approximately 10.6 mg/g, which declines to around 2.47 mg/g at 1 g. Similarly, CWSAAC and PSAAC follow the same trend, reducing from about 10 mg/g at 0.2 g to 2.5 mg/g at 1 g. WSAAC, starting at 9.85 mg/g at 0.2 g, decreases to 2.42 mg/g at 1 g. This inverse relationship can be attributed to the dilution effect, where increasing adsorbent mass leads to a greater number of adsorption sites, but the adsorbate concentration remains constant, causing a reduction in adsorption capacity per unit mass [22]. Consequently, while the overall amount of adsorbate removed increases, the adsorption efficiency per gram of adsorbent diminishes [23].

A comparative analysis of the four types of acid-activated carbons indicates that CSAAC, CWSAAC, and PSAAC exhibit similar trends in both percentage removal and adsorption capacity, demonstrating comparable adsorption efficiencies. In contrast, WSAAC consistently shows lower adsorption capacities and percentage removals, making it less effective. For example, at 0.2 g, CSAAC, CWSAAC, and PSAAC achieve over 80% removal, whereas WSAAC attains only 78.79%. This disparity persists across all tested masses, with WSAAC requiring a higher mass to reach the same removal efficiency as the other adsorbents. At 1 g, while CSAAC, CWSAAC, and PSAAC achieve around 98.9% removal, WSAAC lags at approximately 96.62%. These findings support the conclusions of [24],

which emphasize that selecting an optimal adsorption medium can enhance PAH removal efficiency to nearly 100%.

Overall, the results highlight a trade-off between adsorbent mass and adsorption capacity. While increasing adsorbent mass improves overall removal efficiency, it reduces adsorption capacity per unit mass due to site saturation. This balance is essential for optimizing adsorption processes. Among the tested adsorbents, CSAAC, CWSAAC, and PSAAC demonstrate superior efficiency and cost-effectiveness compared to WSAAC, as they achieve higher removal efficiencies with lower adsorbent doses.



Figure 2: Effect of adsorbent mass on percentage removal for acid-activated carbon



Figure 3: Effect of adsorbent mass on adsorption capacity for acid-activated carbon

3.2.2 Effect of Contact time on adsorption capacity

At the start of the adsorption experiment, as illustrated in Figure 4, PSAAC, CSAAC, and CWSAAC exhibited higher adsorption capacities compared to WSAAC within the first 10 minutes. At this point, PSAAC, CWSAAC, and CSAAC recorded adsorption capacities of 2.269, 2.296, and 2.358, respectively, while WSAAC had a lower adsorption capacity of 1.994. The rapid adsorption observed can be attributed to the physicochemical properties of both the adsorbent and the adsorbate, which facilitate van der Waals interactions [25].

These results indicate that after 10 minutes, WSAAC had adsorbed the least amount of PAH per gram of adsorbent, whereas CSAAC demonstrated the highest adsorption capacity within the same period.

As contact time increased, all adsorbents exhibited a general upward trend in adsorption capacity, although the rate of increase varied among them. This pattern aligns with thefindings [26]. WSAAC displayed a steady but continuous increase, reaching approximately 2.37 after 100 minutes. In contrast, CSAAC and CWSAAC achieved their peak adsorption capacities around 60 minutes, while PSAAC plateaued at approximately 90 minutes. This suggests that, beyond these respective durations, the adsorption sites became saturated, making further adsorption negligible [27]. Among the adsorbents, CWSAAC attained the highest adsorption capacity at approximately 2.473, followed closely by PSAAC at 2.469 and CSAAC at 2.3. These findings indicate that while WSAAC exhibited a slower adsorption rate and lower overall capacity. CSAAC, CWSAAC, and PSAAC reached their saturation points more quickly and maintained higher adsorption performance.

The results from the Analysis of Variance (ANOVA), presented in Table 3, confirmed significant differences in adsorption capacities among the four acid-activated carbons over contact time (F(3,31)=11.667,p<0.0001)(F(3,31) = 11.667, p < 0.0001)(F(3,31)=11.667,p<0.0001). This statistical evidence supports the conclusion that adsorption capacities varied significantly across the different adsorbents.

Further insights from Tukey's HSD test in Table 4 indicate that CSAAC, PSAAC, and CWSAAC belong to group A, meaning their adsorption capacities are statistically similar. However, WSAAC falls into group B, signifying its adsorption capacity is significantly lower than the others. The combined findings from ANOVA and Tukey's test highlight clear differences in adsorption performance, reinforcing that CSAAC, PSAAC, and

CWSAAC are superior in adsorption efficiency. The lower performance of WSAAC suggests that either its activation process or inherent structural properties are less effective for adsorption applications [28].



Figure 4: Adsorption Capacity against the contact time

Table 3: Analysis of Variance of the Adsorption Capacity based on Contact Time for the different Acid activated carbon.

Source	DF	Sum of squares	Mean squares	F	Pr> F
Model	3	0.329	0.110	11.677	< 0.0001
Error	31	0.291	0.009		
Corrected Total 34 0.619					
Сотрі					

Table 4: Tukey Test

Category	LS means	Standard error	Lower bound (95%)	Upper bound (95%)	Gro	ups
CSAAC	2.416	0.034	2.346	2.485	Α	
PSAAC	2.397	0.032	2.331	2.463	А	
CWSAAC	2.384	0.034	2.314	2.454	Α	
WSAAC	2.186	0.031	2.123	2.248		В

3.2.3 Adsorption Isotherm Models

The result from the isotherm models for Henry, Langmuir, Freundlich, Elovich and Janovich constants for PAH adsorption in Table 5 indicated that the equilibrium data fitted the Freundlich isotherm better for PSAAC, CSAAC, and CWSAAC while Henry Isotherm was a better fit for WSAAC. The resultant Freundlich exponent values n for PSAAC, CSAAC, and CWSAAC were noted as 1.528,1.503, and 1.632 respectively. This signifies high adsorption rate as the ideal values for the exponent n lying between 0 and 10 suggest favorable adsorption [29][30]. The Freundlich constant KL indicates the adsorption capacity and it is noted that CSAAC presented the maximum adsorption capacity for the isotherm at a value of 2.590mg/g. The Henry isotherm model best described the adsorption behaviour of WSAAC with an R^2 value of 0.816 and a Henry constant (K_{HE}) of 0.800 respectively. This suggests that the adsorption process for WSAAC follows a linear isotherm, indicative of low-concentration adsorption states or infinite dilution, where the adsorbate molecules do not interact with each other, and the surface sites are uniformly available [31]. The results from Table 5 also indicated that the Coefficient of determination (R^2) for Freundlich isotherm for PSAAC, CSAAC and CWSAAC were 0.970, 0.952, and 0.971; Langmuir Isotherm were 0.941,0.923, and 0.937 while Janovich were 0.939,0.922, and 0.934, respectively. The results indicate that the adsorption patterns for PAHs followed the Langmuir and Freundlich isotherms (as Janovich isotherm is established on the assumptions contained in the Langmuir model). According to [32] any adsorption system which obeys both the Freundlich and Langmuir isotherms shows that the solute forms a homogenous monolayer on the adsorbate. This implies that the adsorption of PAHs onto PSAAC, CSAAC, and CWSAAC obeyed both Freundlich and Langmuir isotherms signifying that the PAHs formed a monolayer on the surfaces of the adsorbents.

Number of parameters	Isotherm Model Type	Model Parameters	Activated samples			
			PSAAC	CSAAC	WSAAC	CWSAAC
One Barameter	Henry	K _{HE}	1.232	1.438	0.800	1.234
one-rai anietei		R ²	0.908	0.909	0.816	0.890
	Langmuir	Qm	21.247	23.995	8.864	18.719
		b	0.099	0.095	2.144	0.126
		R ²	0.941	0.923	0.812	0.937
	Freundlich	Kf	2.374	2.590	0.970	2.587
Two-Parameters		n	1.528	1.503	1.099	1.632
		R ²	0.970	0.952	0.797	0.971
	Elovich	β	0.364	0.366	0.299	0.385
		α	7.324	8.818	3.008	8.300
		R ²	0.797	0.767	0.591	0.805
	Jovanovic	Qm	14.214	16.059	10.970	12.976
		K _f	0.137	0.132	0.005	0.164
		R ²	0.939	0.922	0.812	0.934

 $\begin{array}{l} Q_{m} = \mbox{ Maximum monolayer adsorption capacity (mg/g), } K_{HE} = \mbox{ Henry's adsorption constant, } b = \mbox{ Langmuir constant (L/mg), } R^{2} \\ = \mbox{ Correlation Coefficient, } K_{F} = \mbox{ Affinity factor (mg/g)*(L/mg)^{1/n}, } n \\ = \mbox{ Freundlich exponent, } \alpha = \mbox{ initial rate constant (mg/g * min), } \\ \beta = \mbox{ desorption constant (mg/g)} \end{array}$

3.2.4Adsorption Kinetics

Table 6 presents the kinetic parameters for the adsorption process using different activated carbons. For CSAAC, the equilibrium adsorption capacity (qe) was 2.4327 in the first-order model and 2.4672 in the second-order model. The rate constants (K), representing the adsorption rate, were 0.5842 for the first-order model and 1.0626 for the second-order model, with the higher value in the second-order model indicating a more rapid adsorption process. The coefficient of determination (R^2) was exceptionally high, at 0.9997 for the first-order and 0.9999 for the second-order model, demonstrating an excellent fit for both models. However, the slightly higher R^2 value in the second-order model suggests a marginally better description of CSAAC's adsorption kinetics.

For CWSAAC, the equilibrium adsorption capacity was 2.4054 in the first-order model and 2.4522 in the second-order model. The corresponding rate constants were 0.5399 and 0.7927, respectively, with the higher second-order rate constant suggesting a more efficient adsorption process. The R^2 values of 0.9994 for the first-order and 0.9998 for the second-order model indicate a superior fit for the second-order model.

PSAAC exhibited qe values of 2.4159 in the first-order model and 2.4779 in the second-order model. The rate constants were 0.2707 for the first-order and 0.3661 for the second-order model, with the latter indicating a faster adsorption process. The R^2 values were 0.9995 for the first-order and 0.9998 for the second-order model, further confirming the better fit of the second-order model.

For WSAAC, the equilibrium adsorption capacities were 2.2163 in the first-order model and 2.3251 in the second-order model. The rate constants were 0.2095 for the first-order and 0.1879 for the second-order model. Although the second-order rate constant was comparatively lower, the R^2 values (0.9975 for the first-order and 0.9989 for the second-order model) indicate that the second-order model provides a better fit.

Overall, the pseudo-second-order model consistently demonstrated a superior fit across all activated carbons, as indicated by higher values compared to the first-order model. This aligns with previous studies by [33], which reported that the pseudo-second-order model more accurately describes adsorption kinetics. The higher rate constants in the secondorder model further reinforce its suitability for modeling the adsorption process. Additionally, the findings support the conclusion of [24] that. This suggests that chemisorption is the dominant adsorption mechanism the pseudo-second-order model is typically applicable to chemisorption processes with a high degree of correlation observed in this study.

Table 6: Kinetic Models

Carbon Activator	Model Parameters	First-Order	Second Order
	qe	2.4327	2.4672
CSAAC	К	0.5842	1.0626
	R ²	0.9997	0.9999
	qe	2.4054	2.4522
CWSAAC	К	0.5399	0.7927
	R ²	0.9994	0.9998
PSAAC	qe	2.4159	2.4779
	К	0.2707	0.3661
	R ²	0.9995	0.9998
WSAAC	qe	2.2163	2.3251
	К	0.2095	0.1879
	R ²	0.9975	0.9989

4. Conclusion

This study demonstrated the potential of acid-activated carbons derived from shell waste as sustainable and efficient adsorbents for PAH removal from contaminated water. CWSAAC exhibited the highest removal efficiency (98.93%), while CSAAC had the largest surface area, enhancing adsorption potential. Adsorption followed the Freundlich and Langmuir isotherms for PSAAC, CSAAC, and CWSAAC, while WSAAC aligned with the Henry isotherm. Kinetic studies indicated a pseudo-secondorder model, suggesting chemisorption as the dominant mechanism. These findings underscore the environmental benefits of utilizing shell waste-derived activated carbons as cost-effective and eco-friendly solutions for water purification.

Disclaimer (Artificial Intelligence)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during the writing or editing of this manuscript.

Competing Interests

Authors have declared that no competing interests exist.

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