Assessing the Sustainable Potential of Chemically Activated Crustacean Shells for Pilot-ScaleRemovalofPersistentOrganicPollutantsinContaminatedWater:APathTowards Environmental Sustainability

Abstract: Activated Carbon Samples were produced from periwinkle shells, clamshells, whelk shells, and a 1:1 composite of clam/whelk shells at a carbonization temperature of 450°C under limited-oxygen conditions and then activated using KOH at an activation temperature of 650°C. This produced Periwinkle, clam, whelk, and clam/whelk composite base activated carbons noted PSBAC,CSBAC,WSBAC,andCWSBACrespectively. Thepropertiesoftheseadsorbentswere characterized by scanning electron microscopy energy dispersive X-ray analysis (SEM-EDX), FourierTransformInfraredspectrometry(FTIR),andphysicochemicalanalysis.Theexamination indicatedthatCSBAChadthehighestsurfaceareaat1288m^2/g.Theeffectoftheactivatedcarbon dosagesandcontacttimesontheadsorptionofPAHswasstudiedinbatchadsorptionexperiments and the results indicated that CSBAC had the highest removal efficiency at 1g of 98.94%. The adsorption of PAHs was modeled using Langmuir, Freundlich, Henry, Elovich, and Janovich isotherms.TheFreundlichand Langmuirmodels welldescribedthesorptionequilibrium datafor PSBAC, CSBAC, and CWSBAC with PSBAC having a Langmuir maximum monolayer adsorption capacity of 31.688mg/g. Henry Isotherm best described the sorption equilibrium data for WSBAC. Kinetic studies indicated that the adsorption processes of PAHs agreed well with a pseudo-second-order kinetic model.

Keywords: Persistent organic pollutants (POPs), Polycyclic Aromatic Hydrocarbons (PAHs), Crustacean Shells, KOH Activation, Periwinkle Shells, Clam Shells, Whelk Shells, Composite Shells, Freundlich Isotherm, Langmuir Isotherm, Henry Isotherm, Elovich Isotherm, Janovich Isotherm.

1. Introduction

Persistentorganicpollutants(POPs)posesignificantthreatstotheenvironmentandhumanhealth due to their long-lasting nature and potential for bioaccumulation. Polycyclic Aromatic Hydrocarbons(PAHs),asubsetofPOPsarepressingissuesthatdemandsustainableandefficient solutionsasthesecompoundsareamongthemostcarcinogenic,mutagenic,andtoxiccontaminates [1] PAHs generally enter water sources through road runoff, Industrial wastewater, petroleum spills,andfossilfuelscombustion[2].Duringthelasttwodecades,specialattentionhasbeenpaid to 16 polycyclic aromatic hydrocarbons (PAHs) listed by the United States Environmental Protection Agency (U.S EPA) as priority pollutants due to their widespread environmental presence and their potential mutagenicity, teratogenicity, and carcinogenicity [3]. PAHs bioaccumulate in human and animal tissue and have been noted to have carcinogenic and mutageniceffectsonhumansrangingfromnon-cancereffects (skindisorders,effectsonlungand blood in both humans and animals) to Cancer effects (respiratory tract tumors, leukemia, lung cancer, and bladder cancer) [4]. They can adversely affect various reproductive, developmental, cardiovascular,nervous,andimmuneorgans[5].ExposurestoPAHsduringpregnancyhavebeen linked to decreased birth weight and impaired child development [6]. In recent years, many methods such as chemical oxidation, photocatalytic advanced oxidation, and biological degradation have been used to remove PAHs from wastewater [7] These treatment processes are chosenmainlybased on the initialqualityofthewater, parameters establishedbyregulations and proposed use [8]. Most methods have limitations, including the high operation and maintenance cost and Incomplete removal of the organic pollutants. Adsorption is a widely used method for environmental protection, separation processes, gas purification, and wastewater treatment because it plays an important role in sustainable development [9]. Several adsorbent media such as activated carbon, biochar,and modified clayminerals have beenlargely used to remove PAHs from aqueous solution[10]. The choiceofsuitable absorbent varies dependingon its application. Cost,Kinetics,compatibility,selectivity,capacity,andregenerabilityareimportantcharacteristics that affect the choice of adsorbents [8].

Materials used as adsorbents should be environmentally friendly, inexpensive, and simple to fabricate, exhibit high sorption capacity to remove the highest amount of pollutants, demonstrate high selectivity for specific contaminants, and be reusable and recyclable [11]. Activated carbon as a precursor for adsorption dates back to Ancient Egypt, where it was used to treat intestinal ailments, absorb unpleasant odours and tastes in water and write on papyrus. Hippocrates was documentedasusingwoodchartofilterwatertopreventbadtasteandodourbesidesastreatment for diseases such as anthrax, epilepsy, and Chlorosis [12]. Due to the high cost of available Commercial Activated Carbon, various studies focus on developing new low-cost Activated Carbon with properties comparable to that of commercial ones [13]. This has given rise to extensive studies on low-cost adsorbents ranging from plant seeds, stems, and husks to animal biomass.Activatedcarbonderivedfrombiomasshasgainedwideacceptanceinrecenttimesas

theyhave been widelyused in the removal of hazardous substances from the environment due to their nonhazardous nature and ability for regeneration [14]. [15] noted that 6 to 8 million tonnes of valuable crustacean shell waste are produced globally every year which makes it an environmentallyabundantresourceasprecursorsforactivatedcarbon.Crustaceanshellshavevast amounts of chitin, a carbohydrate-based polymer that shows exceptional features such as biodegradability and biocompatibility and has been utilized as renewable, energy-efficient, cost-effective, and sustainable alternative materials. This study explores the feasibility and efficiency ofchemicallyactivatedcrustaceanshellsforpilot-scaleremediationofpolyaromaticHydrocarbon (PAHs)incontaminatedwater,withafocusonassessingtheirsustainablepotentialasithighlights the potential of these shells as a green and sustainable solution for tackling emerging environmental challenges.

2. MaterialsandMethods

2.1 Preparation of the adsorbent

Periwinkle shells (Tympanotamus fuscatus), West African Clamshells(Galateaparadoxa),andWhelkshells(BucciumUndatum)werepurchasedfromTown Market in Borokiri, Port Harcourt, Rivers State in Nigeria. They were soaked for four days in cleansing agents and warm water to remove dust, remaining organic particles, and soluble impurities. The shells were thoroughly washed in tap water and continuously agitated to remove theremainingimpurities.Theshellswere driedin thesun forthreedays, carbonized at450^{o}Cfor 3 hours, and then powdered. The composite was prepared before chemical activation.

The samples were then soaked in 0.5 M KOH and mixed until a paste was formed then heated in a muffle furnace for 650^{0} for 2 hours. The resultant samples were cooled, and washed with deionized water to a pH of 6. The samples were then dried in the oven at 105^{o}C for 6 hours and stored in air-tight containers.

2.2 Characterization

AttenuatedTotalReflectanceFourierTransform InfraredSpectroscopy(ATR-FTIR)wasperformedusingAGILENTTECHNOLOGIESCARY630FTIRCARY630ZnSe. PARTNO:-G804364002,MODELNO:-MY19322004.Thesamplesspectrawerecollectedby placing the samples onto the ATR crystal and applying pressure to ensure good contact with the crystal.Thespectrawerethencollectedbyshininganinfraredbeamontothecrystalandmeasuring the reflected light as a function of wavelength. The collected spectra were typically processed using software to remove any remaining baseline drift or noise. Scanning electron microscopy- energy dispersive X-ray analysis was performed using a PHENOM PRO X Serial no: MVE0224651193Modelno:800-07334Thesampleswereмountedonstubswithadhesivecarbon and coated in 20 nm Carbon with aQUORUM Q150R ESmini sputter coater, and thenanalyzed withaPhenomPRO-XSEMequippedwith anOxfordXMax 50Silicon DriftEnergyDispersive X-ray detector at 15KV underhighvacuum. The specific surface area of the adsorbent was estimated according to the Sear method [16].

2.3 Preparation of PAHs contaminated water

Analytical-grade PAHs and high-performance liquid Chromatography–grade-acetone(HPLC)fromLoba(LO)chemicewithdistilledwaterwereused for the adsorption experiments. This was done in batches using 100ml volume flasks

2.4 BatchAdsorptionstudies

2.41 Effect of Adsorbent Dosage

Specified adsorbent doses of 0.2, 0.4, 0.6, 0.8, and 1.0g at pH of 9 were added to 50ml water samples of 50mg/l initial PAH's concentration and attached to a mechanicalshakerandthemixtureswereagitatedat150rpmfordifferentoptimalperiod(90mins for PSBAC, 60mins for CSBAC and CWSBAC and 120 mins for WSBAC). Equilibrium studies were performed at room temperature (25^{o}C). At the end of the agitation time, the mixtures were filtered through no. 542 Whatman filter paper. The filtrates were then separately analyzed for residualconcentrationsofPAHsusingtheGCMSgaschromatograph.Theequilibriumadsorption capacity (qe) was obtained by using Equation (1).

$$\square_e = \frac{(C_o - C_e)V}{M} \quad (1)$$

Where:qe=quantityadsorbed(mg/g)

CoandCe=initialandequilibriumconcentrations(mg/l) V =

Volume (L)

M=massofadsorbent (g)

2.4.2 Effect of Contacttime

The experiment wasconducted to model the relationship betweencontact time and the adsorption capacity of activated samples. In a conical flask, 1 g of activated carbon sample was added to 50 ml PAHs standard solution at a concentration of 50 mg/L and was collected at 10-minute intervals from 10 minutes to 120 minutes at room temperature. PAH residues in the solution were extracted and analyzed.

2.4.3 PAHs Extraction method

The Liquid-Liquid extraction Technique used by [17] was used for extractingselectedPAHsfromsampledsolutions.Dichloromethane(DCM)byLoba(LO)chemice analytical grade with 99.0% Purity was used for the extraction. Twenty-five (25) ml of dichloromethanewas added, shaken vigorouslyfor about 2 minutesto separate the organic layer, andventedoccasionallytoreleasepressure.Theextractedmixtureisdecantedandrepeatedtwice to ensure maximum PAH extraction. The solution waited six hours at room temperature for evaporationofDCM.1gofsodiumsulphatewasintroducedtoadsorbanytracewaterbefore1ml of solution was decanted into the vial and ready for injection into Agilent 7890N GC/MS gas chromatography.

2.5 Sample Analysis Using GC-MS

1 ml of the analyte was introduced into the heated injector tube, vaporized, and mixed with a carrier gas. As the sample vapor is carried through the separation capillarycolumnof30metresandfilmthicknessandinternaldiameterof250umbythecarriergas (helium), the analyte partitions between the gas and liquid phases according to the analyte components' solubility in the liquid at the column operating temperature which starts at 80^{o}C for 2minutes and increases at a rate of 30^{o}C per minute until it peaks at 310^{o}C. The rate of travel through the column is determined bythe sample solubilityin the stationary phase, the carrier gas flow rate, and the temperature. Each component travels at a characteristic rate. The sample

completely separated before arriving at the detector.

2.6 Equilibrium modeling

The adsorption performanceoftheactivated carbons wasevaluated using the Henry, Langmuir, Freundlich, Elovich, and Jovanovic isotherm models.XLSTAT 2014 program wasusedforestimatingcoefficientsbasedonanonlinearoptimizationtechnique.Direct optimization method for nonlinear equations using iteration was used to minimize error in estimatingmodelparameters.Oneoftheisotherm models(HenryIsotherm) was aone-parameter model while the other four (Langmuir, Freundlich, Elovich, and Jovanovic isotherms) were two-parameter isotherm models.

2.7 Adsorption kinetics The adsorption kinetics were processed at varying time intervals using an initial concentration (50mg/l) of PAHs. The procedures of kinetic experiments were identical to thoseoftheequilibriumtest.1gofcrustacean-activatedcarbons(PSBAC,CSBAC,WSBAC,and CWSBAC)weremixedwith50mlofPAH'ssimulatedsolutionintoplasticcontainerswhichwere then attached to a mechanical shaker at150 rpm. Thesamples weretakenat preset timeintervals (5, 10, 20, 30, 40, 50, 60, 70, 80, 100 and 120mins) and filtered. The concentrations of PAHs at thesetimeintervalsweremeasured.Theadsorptioncapacityofthe adsorbents atpresettimet, qt, was calculated from Equation 2:

Attimet,q_t(mg/g)wascalculatedusingEquation2

$$\square_t = (\square - \square_o)^V \quad t_m \quad (2)$$

qt:uptakecapacityofthematerialattimet (mg/g)

$C_0$and$C_t$aretheinitialandfinalconcentrationsofthecontaminatedsolution(mg/l) m:mass of adsorbent material (g)

V:volumeoftreatedsolution(l)

3. **ResultsandDiscussion**

3.1 Results of theAdsorbent Characterization Experiments

3.1.1 The FTIR, SEM-EDX, and Surface Area oftheActivatedCarbonPrepared

TheresultinTable1indicatedthattheKOH-activatedcarbons displayed a large surface area for effective adsorption. [18] stated that the typical surface area of activated carbon samples ranges from 500 to 1500 m²/g. CSBAC had the highest surface area of 1288 m²/g

Table1:SpecificAreaofactivatedcrustaceanshells

Parameter/Sample	PSBAC	CSBAC	WSBAC	CWSBAC
SpecificSurfaceArea (m2/g)	1275	1288	986	1270

TheresultsoftheFTIRinTable2andFigure1showthatthespectraalignwithfunctionalgroups that were assigned to O-H, C-H, esters C=O, and amides C=O groups respectively indicating surfacechemistry duetotheactivatingagentwithKOH.Italsoindicateslowpeakintensitiesof

theO-H, C-H,andC-Ovibrationswhichis alsoconsistentwithKOHactivation.Thisconformto similar work by [19

Table2:FT-IRspectradataoftheactivatedcrustaceanshells

Sample/band(cm^{-1})	O-H	C-H	C=O	C-O	C-O-C	M-O	Ar-H
CSBAC	3553	3345	1797	1122	1398	873	713
PSBAC	3518	3358	1789	1135	1389	864	704
WSBAC	3576	3389	1793	1135	1393	869	713
CWSBAC	3523	3336	1789	1126	1397	869	713

TheSEM-EDXinFigure2indicatedabroadlyopenporestructuredemonstratingwell-developed micropores.Thisis consistentwiththeactivationofpotassiumhydroxide (KOH)whichproduces well-defined micropores to show the high adsorption capacity of the activated sample [20]. The elemental analysis in Table 3 confirmed a balanced ratio of oxygen and calcium, with CSBAC showing an oxygen concentration of 61.77 cm^{-1} and calcium at 38.23 cm^{-1}. The EDX analysis demonstrated that active carbons' calcium oxides(CaO) exist. CaO is a strong dehydrator, which absorbs water from the environment and increases the porosityof the treated activated materials, as observed in SEM studies.

Table3: ElementalanalysisoftheactivatedcrustaceanshellsbyEDX

Sample/band(cm^{-1})	Element	Atomic concentration	Weight concentration
CSBAC	O	61.77	39.21
	Ca	38.23	60.79
PSBAC	O	70.97	49.39
	Ca	29.03	50.61
WSBAC	O	71.45	49.97
	Ca	28.55	50.03
CWSBAC	O	74.34	53.63
	Ca	25.66	46.37

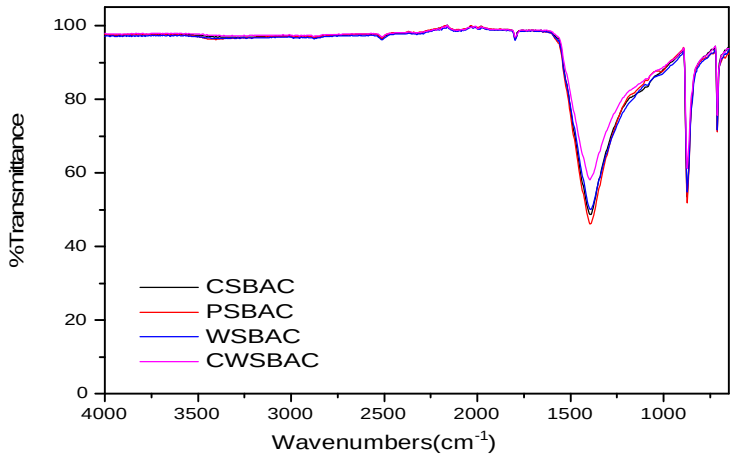

Figure1: StackedFT-IRspectraofKOH-treatedactivatedcarbons

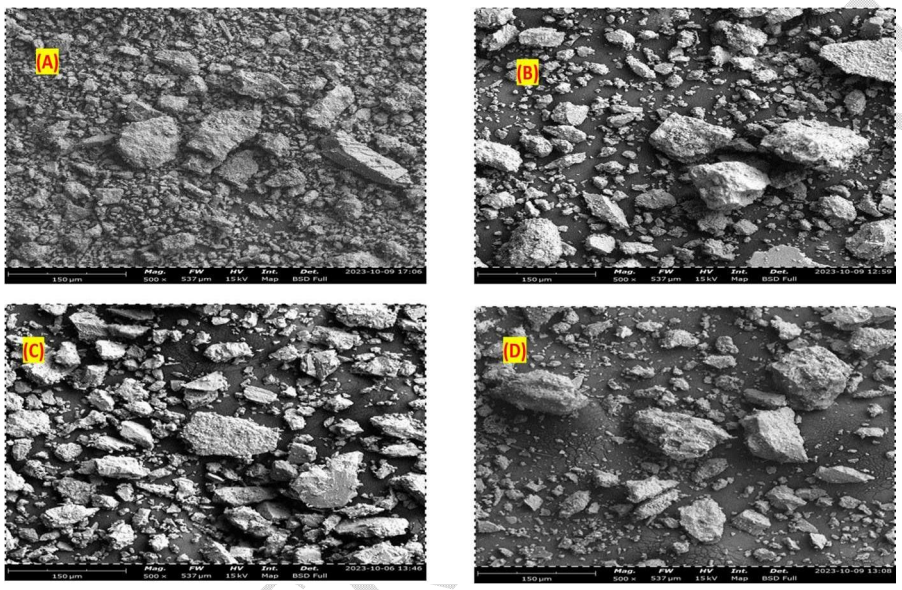

Figure2:SEMMicrographs(at150µm)ofCSBAC(A),PSBAC(B),WSBAC(C),andCWSBAC (D)

3.2 ResultsofBatchAdsorptionstudies

3.2.1 EffectofAdsorbentDosageonAdsorptionEfficiency

ThegraphicalandTabularrepresentationof the results obtained of the relationship between the mass of the adsorbent and the percentage removaloftheadsorbate(Figure3andTable4)revealedtheincreaseinthemassoftheadsorbent increased the percentage removal of the adsorbate. CSBAC indicated a percentage removal of approximately84.14%at0.2gto98.94%at1g.Similarly,CWSBACincreasesfrom83.14%to 98.91%, PSBAC from 82.03% to 98.54%, and WSBAC from 79.90% to 97.20%. This trend indicates that a higher mass of adsorbent provides more surface area and adsorption sites, enhancingtheremovalefficiency[21].Thesteepslopeobservedatalowermassofadsorbent(0.2 to0.4g)suggeststhatatloweradsorbentmasses,theadditionofadsorbentsignificantlyimproves theremovalefficiencyduetotheincreasedavailabilityofadsorptionsites[22].Beyond0.4g,the

slope tends to flatten, suggesting that the rate of increase in percentage removal becomes less effective as the system approaches equilibrium and the available adsorption sites become increasingly saturated [23].

3.3 Results of Equilibrium Concentration on Adsorption Capacity

The result in Figure 4 showed an increaseinadsorptioncapacityindirectproportiontoanincreaseintheequilibriumconcentration for all adsorbents. It was observed that at an equilibrium concentration of approximately 2mg/l, the adsorption capacities of all activated samples were at 3mg/g with a slight disparity with WSBAC which was reported at 2mg/g. Further increase in equilibrium concentration revealed a wider disparity in the adsorption capacities of the activated samples. At an equilibrium concentration of approximately 7mg/l, CSBAC had the highest adsorption capacity of 9.2mg/g withCWSBACandPSBACshowingaslightlyloweradsorptioncapacityofapproximately9mg/g and8.6mg/grespectively.TherewasawidedisparityintheadsorptioncapacityofWSBACwhich was noted to be approximately 4.5mg/g. This suggests that WSBAC is less favorable for the adsorption of PAHs. Analysis of Variance (ANOVA) in Table 5 indicated that there was no significant difference in the adsorption capacities of all the activated carbons subjected to investigationdespitetheloweradsorptioncapacityofWSBAC(F-value(3,16)=0.008,p-value= 0.999)

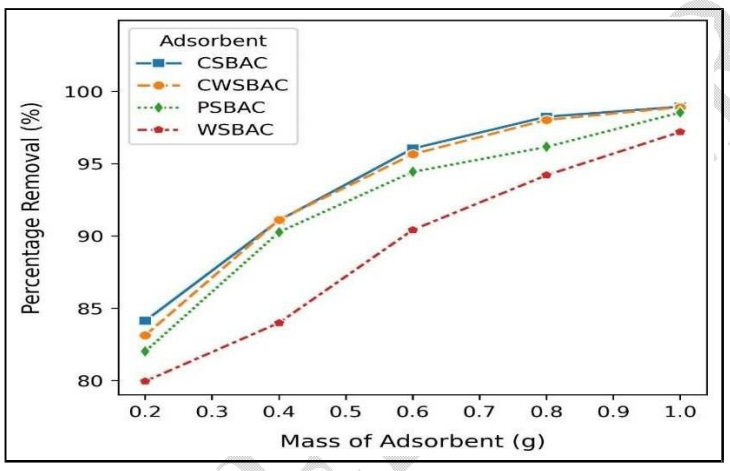

Figure3: Effectofadsorbentmassonpercentageremoval.

Table4: Efficiencyofadsorption(PercentageRemoval)atadsorbentdosageof1g

Sample	Efficiency(%)	Ranking
CSBAC	98.94	1
CWSBAC	98.91	2
PSBAC	98.54	3
WSBAC	97.20	4

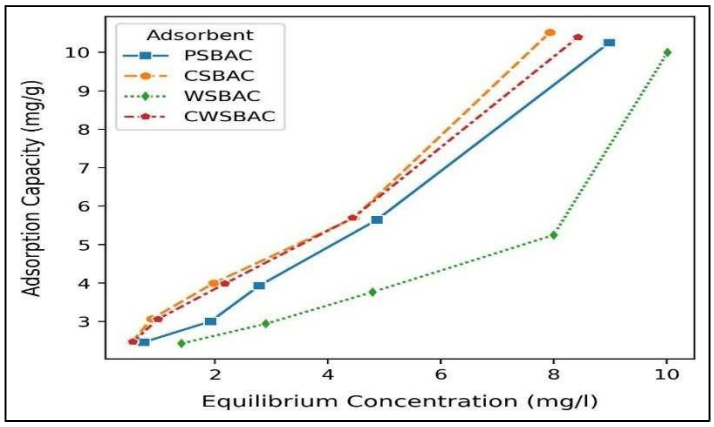

Figure4: AdsorptionCapacityagainsttheequilibriumconcentration

Table5: ANOVAforAdsorptionCapacity.

Source	DF	Sumofsquares	Meansquares	F	Pr >F
Model	3	0.226	0.075	0.008	0.999
Error	16	159.421	9.964		
CorrectedTotal	19	159.648			

ComputedagainstmodelY=Mean(Y)

3.3.1 Effect of Contact time on adsorption capacity

The result from Figure 5 showed that all four adsorbents exhibited increasing adsorption capacities as the contact time increased. As contact time increases, a general upward trend in adsorption capacity is observed for all adsorbents, although the rate of increase varies among them [24]. WSBAC showed a steady, continuous increase in adsorption capacity reaching approximately 2.362 mg/g after 100 minutes without attaining equilibrium adsorption capacity. In contrast, CSBAC, CWSBAC, and PSBAC exhibit quickeradsorptionratesinitially,plateauingaround60to90minutes.Theresultindicatesthatthe adsorption sites for CSBAC, CWSBAC, and PSBAC may become saturated, as extending the contact time beyond this period does not significantly increase their adsorption capacities. This result indicates that a progression in contact time resulted in a decrease in active sites, and the formation of strong bonds between the adsorbate and adsorbent, leading to a slowdown in the process before equilibrium [25]. CSBAC achieves the highest adsorption capacity of approximately 2.49 mg/g, followed by CWSBAC with a capacity of around 2.473 mg/g, and PSBACwithabout2.263mg/g.TheanalysisofVariance(ANOVA)inTable6showssignificant differencesintheadsorptioncapacitiesforthefourbase-activatedcarbons(F-value(3,31)=9.408, p-value <0.0001). Thisprovidedsufficient evidencetostatethat theadsorptioncapacitiesforthe fourbase-activatedcarbonsweredifferentoverthecontacttime.TheTukeytestresultsinTable7 revealed that CSBAC, CWSBAC, and PSBAC belong to group A, indicating no significant differences in their adsorption capacities among these three adsorbents. However, WSBAC belongstogroupB,indicatingitsadsorptioncapacityissignificantlylowercomparedtotheother three adsorbents.

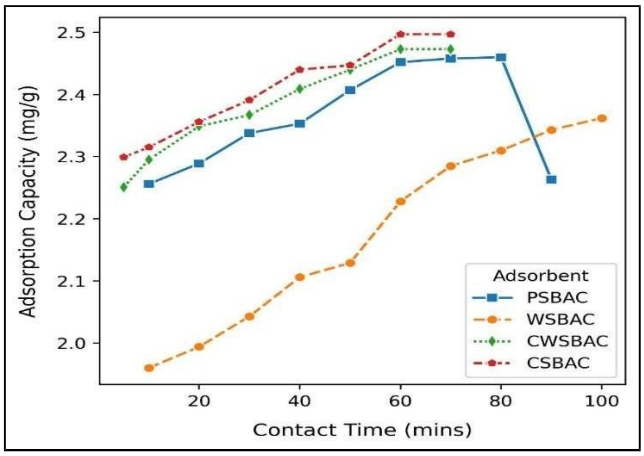

Figure5: AdsorptionCapacityagainstthecontacttime

Table 6: Analysis of Variance of the Adsorption Capacity based on Contact Time for the different Base activatedcarbon.

Source	DF	Sumof squares	Mean squares	F	Pr >F
Model	3	0.313	0.104	9.408	0.000
Error	31	0.344	0.011		
Corrected Total	34	0.657			

ComputedagainstmodelY=Mean(Y)

Table7:TukeyTest

Category	LSmeans	Standard error	Lower bound (95%)	Upper bound (95%)	Groups	
CSBAC	2.405	0.037	2.329	2.481	A	
CWSBAC	2.382	0.037	2.306	2.458	A	
PSBAC	2.364	0.035	2.292	2.436	A	
WSBAC	2.176	0.033	2.108	2.244		B

3.4 Regression Modeling

The regression modeling results indicate a highly effective model for predicting percentage removal based on the mass of the adsorbent used. The goodness of fit, ANOVA, and model parameters for base-activated carbon reveal significant findings. The goodnessoffitfortheregressionmodelinTable8showsanR^2valueof0.921andanadjustedR^2 of 0.900, indicating that the model explains 92.1% of the variability in percentage removal. The adjusted R^2, which accounts for the number of predictors, confirms the model's robustness. The Mean Squared Error (MSE) is 3.976, and the Root Mean Squared Error (RMSE) is 1.994, both demonstratinghighaccuracyinthemodel'spredictions.TheDurbin-Watsonstatistic(DW)of 1.432suggestsnosignificantautocorrelationintheresiduals,supportingthemodel'sreliability.

TheANOVAresultsinTable9furthervalidatethemodel'ssignificance,withamodelF-valueof 43.662andap-valueoflessthan0.0001.ThishighF-valueindicatesthattheregressionmodel is

highly significant, and at least one of the predictors (mass of adsorbent or type of adsorbent) significantly explains the variation in percentage removal. The model parameters for activated carboninTable10providedetailedinsightsintotheeffectsofeachpredictor.Theinterceptis 77.251withastandarderrorof1.300andat-valueof59.427($p<0.0001$),indicatingasubstantial baselinepercentageremoval.Thecarbondosageparameterhasavalueof19.847,withastandard errorof1.576andat-valueof12.590($p<0.0001$),indicatingastrongpositivecorrelationbetween themassofadsorbentandpercentageremoval.Thetypeofadsorbentalsosignificantlyaffectsthe percentage removal. CSBAC increases percentage removal by 4.533 units, CWSBAC by 4.212 units, and PSBAC by 3.129 units compared to the reference adsorbent (WSBAC), which has a coefficient of 0.000. The standard errors for these parameters are 1.261, with t-values indicating significant effects (p-values of 0.003 for CSBAC, 0.004 for CWSBAC, and 0.025 for PSBAC).

Table8: Goodnessof fit

Observations	20.000
Sum of weights	20.000
DF	14.000
R^2	0.945
AdjustedR^2	0.925
MSE	0.631
RMSE	0.794
DW	2.218

Table9:ANOVA

Source	DF	Sumof squares	Mean squares	F	Pr >F
Model	5	150.813	30.163	47.798	<0.0001
Error	14	8.835	0.631		
Corrected Total	19	159.648			

ComputedagainstmodelY=Mean(Y)

Table10: ModelParameters(BaseactivatedCarbon)

Source	Value	Standarderror	t	Pr >|t|	Lower bound(95%)	Upper bound (95%)
Intercept	-2.138	2.397	-0.892	0.387	-7.279	3.002
CarbonDosage	1.782	2.136	0.834	0.418	-2.799	6.363
Ce	1.097	0.206	5.333	0.000	0.656	1.538
Adsorbent-CSBAC	2.760	0.685	4.027	0.001	1.290	4.231
Adsorbent-CWSBAC	2.555	0.663	3.851	0.002	1.132	3.978
Adsorbent-PSBAC	1.898	0.597	3.182	0.007	0.619	3.178
Adsorbent-WSBAC	0.000	0.000				

3.5 AdsorptionIsothermModels

FromtheresultsfromTable11,Themaximumadsorptioncapacity for monolayer $Q_m$was compared between Langmuir and Janovich isotherms, and it was noted that Langmuir Isotherm presented the highest adsorption capacities for PSBAC, CSBAC and CWSBAC with values of 31.688, 18.335 and 18.743 mg/g respectivelywhile Janovich Isotherm presented a higher maximum capacity for WSBAC at 10.362 mg/g.

It can be noted that the resultant Freundlich exponent values n for PSBAC, CSBAC, and CWSBAC were 1.329, 1.633, and 1.621 respectively. This signifies high adsorption rate as the ideal values for the exponent n lying between 0 and 10 suggest favorable adsorption [26] [27]. This implies that the activated samples are heterogeneous with sites of varying affinities, and have a varied surface with multiple adsorption sites, each with different adsorption energies whichisbettercapturedbytheFreundlichmodelthanbyothermodels[28].TheHenryisotherm model best described the adsorption behavior of WSBAC with R^2 values of 0.835 and a Henry constant (K_{HE}) of 0.871. This suggests that the adsorption process for WSBAC follows a linear isotherm, indicative of low-concentration adsorption states or infinite dilution, where the adsorbatemoleculesdonotinteractwitheachother,andthesurfacesitesareuniformlyavailable [29].

Table11:IsothermModels

Numberof parameters	Isotherm ModelType	Model Parameters	Activatedsamples			
			PSBAC	CSBAC	WSBAC	CWSBAC
One-Parameter	Henry	K_{HE}	1.187	1.376	0.871	1.301
		R^2	0.939	0.886	0.835	0.892
Two-Parameters	Langmuir	Q_m	31.688	18.335	9.133	18.743
		b	0.051	0.144	2.131	0.131
		R^2	0.951	0.898	0.834	0.917
	Freundlich	Kf	1.901	2.770	0.908	2.649
		n	1.329	1.633	1.020	1.621
		R^2	0.966	0.940	0.831	0.956
	Elovich	□	0.339	0.380	0.317	0.380
		α	5.867	9.306	3.406	8.664
		R^2	0.742	0.787	0.512	0.799
	Jovanovic	Q_m	19.316	13.416	10.362	13.322
		K_f	0.082	0.170	0.000	0.163
		R^2	0.951	0.897	0.834	0.915

Q_m = Maximum monolayer adsorption capacity (mg/g), K_{HE} = Henry's adsorption constant, b = Langmuir constant (L/mg), R^2 = CorrelationCoefficient, K_F= Affinityfactor (mg/g)*(L/mg)$^{1/n}$, n= Freundlichexponent, α=initial rate constant (mg/g * min), β=desorption constant (mg/g)

3.5.1 AdsorptionKinetics Table12indicatedthatacrossallactivatedcarbons,thesecond-orderkinetic modelgenerallyprovidedabetterfitfortheadsorptiondata,asevidencedbyhigherR^2values

comparedtothefirst-ordermodel.Thisconformswithpreviousfindingsreportedby[30]and[31]. Therateconstants inthesecond-ordermodel,despitevarying, generallysuggestedmoreaccurate andfasteradsorptionprocesses,reinforcingthesuitabilityofthesecond-ordermodelindescribing thekineticsofadsorptionfortheseactivatedcarbons.Thereviewofsorptionkineticsdoneby[32] concluded the pseudo-second-order equation might be applied to chemisorption processes with a high degree of correlation. This indicates that chemisorption is the mechanism identified in this research.

Table12:KineticModels

CarbonActivator	ModelParameters	First-Order	SecondOrder
CSBAC	qe	2.4231	2.4662
	K	0.5770	0.8937
	R^2	0.9994	0.9997
CWSBAC	qe	2.4044	2.4513
	K	0.5333	0.7822
	R^2	0.9995	0.9998
PSBAC	qe	2.3797	2.4248
	K	0.2881	0.4946
	R^2	0.9992	0.9993
WSBAC	qe	2.2119	2.3306
	K	0.1959	0.1677
	R^2	0.9972	0.9987

4. Conclusion

This study provides valuable insights into the potential use of Chemically activated crustacean shells as a viable option for addressing PAH contamination in water. The experimental analyses established that the activated carbons prepared from periwinkle shells, clamshells, whelk shells, and composite clam/whelk shells have good morphology and physicochemical properties for adsorption. The removal of PAHs was influenced by the operational parameters which were contact time and adsorbent dosage. Freundlich isotherm adequately described the sorption for CSBAC, CWSBAC, and PSBAC, while the sorption using WSBAC was adequately interpreted byHenryisotherm. Furtheranalyses into the adsorption kinetics revealed the processes followed pseudo-second-orderkinetics.Ithasshownthatmodified Crustaceanshellsareexcellentandeco-friendlyalternativesfortheremovalofPAHsfromtheaquaticenvironmentwithemphasisonthe importance of sustainability in pollution management practices.

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