Characterizationand OptimizationofCrustaceanShell-DerivedActivatedCarbonforWastewaterTreatmentApplications

Abstract

Comparative studies of the Surface Chemistry, morphology, and physicochemicalproperties of crustacean shells activated chemically using acid (H_2SO_4) and base (KOH) wereinvestigated.Theresultantactivationyielded Acidandbaseactivatedsamplesfor Periwinkleshells(PSAACandPSBAC),Clamshells(CSAACandCSBAC),whelkshells(WSAACandWSBAC),and a 1:1 Clam/Whelk composite Shells (CWSAAC and CWSBAC) respectively. The propertiesinvestigated were moisture content, specific gravity, surface area, porosity, ash content, Carbonyield,Fixedcarbon,FTIR,andSEM-EDX.Fromtheresultsobtained,theacidandbaseactivationof activated carbons from Periwinkle, Clams, Whelks, and Clam/Whelk composite shells showsgood physicochemical properties for wastewater treatment. Although Clam Acid activated shell(CSAAC) with a surface area of 1277 (m^2/g), % moisture content, ash content, carbon yield, andfixed carbon of 1.4, 8.3,87, and 63.7% respectively displayed better physicochemical properties,the Clam Shellbase activated Carbon (CSBAC) had a better porosity of 0.88which is an indicationofbetteradsorptionpropertyofalow-costactivatedsampleforwastewateradsorptionexperiments. The % Ash Content of acid and base activated samples was comparably low withWhelk Shell Base activated carbon (WSBAC) displaying the highest ash content of 12.3%. Thedifferenceinbulkdensities(g/cm^3)ofacid-activatedandbaseactivatedcarbonswasinfinitesimal.Theorderofdecreasingbulkdensitiesis CSBAC> CSAAC>CWSBAC>CWSAAC>PSBAC >PSAAC>WSBAC>WSAACwithcorrespondingvaluesof0.687>0.653>0.543>0.530> 0.524>0.502>0.476>0.454(g/cm^3).Theporosityofactivatedsampleswasarrangedindescendingorder :CSBAC>PSBAC>CSAAC>CWSAAC>PSAAC=CWSBAC>WSAAC >WSBACwithcorrespondingvaluesof0.88>0.86>0.83>0.81>0.80=0.80>0.62>0.59.FTIR andSEM-EDXindicatedthatallsampleswere successfullyconvertedtoactivatedcarbon.

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Keywords: Surface Chemistry, Morphology, Physicochemical Properties, Crustacean Shells,Acid Activation, Base Activation, Periwinkle Shells, Clam Shells, Whelk Shells, CompositeShells, Wastewater Treatment, surface area, Bulk Density, Porosity, Ash Content, Carbon Yield,FTIR,SEM-EDX

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1. Introduction

Activated carbon has been globally recognized as the oldest, most widely used, and popularadsorbentinthewaterandwastewatertreatmentindustries[1]

Activated Carbon is "char", which has been subjected to a reaction with gases and/or chemicalsduring or after carbonization to increase its adsorption capacities. [2] described Char as "acarbonization product of a natural or synthetic organic material, which has not passed through afluidstageduringcarbonization".Activatedcarbonreferstoawiderangeofcarbonizedmaterialswitha highdegreeofporosityandhighsurfacearea[3].

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DuetothehighcostofavailableCommercialActivatedCarbon,variousstudiesfocusondevelopingnewlow-costActivatedCarbonwithpropertiescomparabletothatofcommercialones[4].Thishasgivenrisetoextensivestudiesonlow-costadsorbentsrangingfromplantseeds,stems,and husks to animal biomass. Carbon adsorbents derived from biomass (agricultural and householdresidues)havebeenwidelyusedintheremovalofhazardoussubstancesfromtheenvironmentduetotheirdistinctivequalitiesoflargeinternalsurfacearea,mechanicalintegrity,andregeneration [5]Thechoiceofprecursorforlow-costactivatedcarbonshouldbepreferablefreelyavailable,inexpensive,andnonhazardousfornature[6]. [7]reportedthatanestimated globalquantityofcrustaceanshellwastediscardedrangesbetween6 and 8 million tonnes every year.Due to the immense nature of crustacean shells, they occupyvaluablespacewhendiscardedinlandfills,therebypotentiallynecessitatingtheformationofnew landfill sites, which can have substantial economic and environmental implications. Recentadvancement in Research has found that Chitin, found in shells is an invaluable resource as itaccounts for its versatility for use in various industries. It is estimated that approximately 80% ofchitin production comes from crustacean shells [8]. Chitin is the second most abundant naturalbiopolymer after cellulose and is widely used due to its abundance, renewability, and low cost[8].These have become a new source of raw material for various industries that have foundvalueintheotherwise wasteproduct.Theutilizationofwasteshellsas arenewable and cheap alternative to traditional materials in industries which include the cosmetic,food, and feed industries as well as materials for various applications, including heterogenouscatalysts, blended cement manufacture, concrete aggregate, ceramics and plastics additives,biofilter medium, and biomedical applications are available in literature [9]; [10]. Nigeria has a coastline of 853km whichlies between Latitude 4^{o} 10' to 6^{o}20'N and longitude 2^{o} 45' to 8^{o} 5' E which stretches from theWestern border with the Republic of Benin to the eastern border with the Cameroon Republic[11].ThisvastcoastlineoffersawiderangeofcrustaceansIndigenoustothecountryincluding

Periwinkles(Tympanotamusfuscatus),WestAfricanClams (Galateaparadoxa),andWhelks(BucciumUndatum).

These crustacean shells have also been used as renewable, energy-efficient, cost-effective, andsustainable alternative materials. These include the use of Oyster and pyramidella shells asheterogeneouscatalystsforthemicrowave-assistedbiodieselproductionfromJatrophacurcasoil[10]; the use of periwinkle shells in carburization, specifically in improving the surface hardnessof low carbon steel contributing to the improvement of mechanical properties in mild steel [12]andtheuseofgroundperiwinkle shellasafillerinbrakefriction[13].Chitincanbetransformedintobiocharthroughpyrolysis,andtheresu ltingchitin-biocharhaspotentialapplicationsinwater treatment [8]. Activated carbon has been utilized as an adsorbent material for the removalof target contaminants from aqueous environments as well as in solid-gas experiments, tomeasure the adsorption capacities and selectivity toward Carbon (IV) oxide [14]. It is expectedthatmoreresearchwillexploretheirpotential as veryusefulengineering materials. This studytherefore aims to compare the Morphology and Physicochemical properties of Acid and Baseactivatedcrustaceanshellsaseffectivelow-costadsorbentsforwastewatertreatment.

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2. MaterialsandMethods

2.1 Sample Collection, Preparation, and Carbonization

Periwinkle shells (Tympanotamusfuscatus), West African Clamshells (Galatea paradoxa), and Whelk shells (BucciumUndatum)were purchased from Town Market in Borokiri, Port Harcourt, Rivers State in Nigeria. Theyweresoakedwith cleansingagentandwarm waterforfourdaystoremovedust, remnant organicparticles as well as soluble impurities. The shells were thoroughly washed with tap water withcontinuous agitation to loosen remnant impurities. The shells were sun-dried for three daysbefore carbonization at 450^{o}C for 3 hours and then pulverized to powder. The Composite waspreparedbeforechemicalactivation.Thesamples weredividedintotwoequalpartsforchemicalactivationbyacidandbase.

2.1.1 ChemicalActivation

i) AcidActivation: Thesampleswaresoakedin0.5MofH$_2$SO$_4$andmixeduntilapastewasformedthen heated in a muffle furnace for 750^{0}C for 2 hours. The resultant sample was then cooled, andwashedwithdeionizedwatertoapHof6.Thesampleswerethendriedintheovenat105^{o}Cfor6hoursand storedinair-tightcontainers.

ii) Base Activation: The samples were soaked in 0.5 M KOH and mixed until a paste was formedthen heated in a muffle furnace for 650^{0} for 2 hours. The resultant sample was then cooled, andwashedwithdeionizedwatertoapHof6.Thesamples werethendriedintheovenat105^{o}Cfor6hoursandstoredinair-tightcontainers.

2.2 Surface Chemistry and Morphology Determination

Attenuated Total Reflectance FourierTransform Infrared Spectroscopy (ATR-FTIR) was performed using AGILENTTECHNOLOGIESCARY630FTIRCARY630 ZnSe.PARTNO:-

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G804364002,MODEL
NO:-MY19322004.The
samplesspectrawerecollectedbyplacingthesamplesontotheATRcrystalandapplyingpressuretoensur
egoodcontactwiththecrystal.Thespectrawerethen

collected by shining an infrared beam onto the crystal and measuring the reflected light as afunctionofwavelength.Thecollectedspectraweretypicallyprocessedusingsoftwaretoremoveanyremainingbaselinedriftornoise.

Scanning electron microscopy-energy dispersive X-ray analysis was performed using aPHENOM PROXSerialno:MVE0224651193Modelno: 800-07334. Thesampleswereremountedon stubs with adhesive carbon and coated in 20 nm Carbon with a QUORUM Q150R ES minisputter coater, and then analyzed with a Phenom PRO-X SEM equipped with an Oxford XMax50SiliconDriftEnergyDispersiveX-raydetectorat15KVunderhighvacuum.

2.2.1 DeterminationofPhysicochemicalProperties

2.2.1.1 Carbon yield

Carbon yield for the activated carbon samples was determined using the [15]technique.Thistechniqueinvolvedmeasuringtheweightofeachcarbonsamplebefore and aftercarbonizationandtheyieldcalculatedusingEquation1

$$CarbonYeild = \frac{W_f}{W_o} \times 100 \quad (1)$$

Where:W_f=massofcarbonretrievedfrom thefurnace

W_o=massofoven-driedsamplebeforecarbonization

2.2.1.2 Moisture Content

The moisture content was measured using the air oven method. A knownmass of each activated carbon sample was weighed and dried in an oven at a temperature of105^{o}Cfor6hoursandthesampleswerere-weighedafterdryingandthenewweightrecorded.The moisture content was then calculated as the ratio of the change in weight to the originalweightexpressedasapercentage.ThisisrepresentedinEquation2.

$$\frac{W_o - W_d}{W_o} \times 100\% \quad (2)$$

Where:

W_o=originalweight(g)

Wd=weightafterdrying(g).

Thetestwasperformedtwiceoneachactivatedcarbonsample andtheaveragevaluewasobtained.

2.2.1.3 Ashcontent

Theashcontentwasdeterminedusingthestandardtestmethodforashcontent[16].Acrucible waspre-heatedina furnacetoabout500^{o}Candthencooledinadesiccator.1.0gofthe activated sample was transferred into the crucible and re-weighed (oven-dry weight). Thecrucible and sample were then placed in the furnace and the temperature was raised to 630^{o}C for6 hours. The sample was then removed and allowed to cool in a desiccator to room temperatureandre-

weighed(ashweight).TheAshcontentofthesamplewascalculatedfromEquation3.

$$\%AshContent = \frac{\text{Ashweight}}{\text{Ovendryweigh}} \times 100 \quad (3)$$

2.2.1.4 SpecificSurfaceArea

ThespecificsurfaceareaoftheadsorbentwasestimatedaccordingtotheSear method [17]. About 1.5g of each prepared adsorbent was mixed with 30 g NaCl anddissolved in 100 mL of distilled water using a 250 mL conical flask. The mixtures were stirredfor 5 minutes. Then, the pH of solution was adjusted to 4 by the addition of HCL. The solutionwas then titrated by 0.1 M NaOH until pH of the solution attained a pH to 9. The volumes ofNaOH required to change pH value from 4 to 9 were recorded. The specific surface area ofsamplewasfoundusingEquation4:

specificsurfacearea(S)(m^2/g)-=32V−25; (4)

whereVisthevolumeof0.1MNaOHrequiredtoraisethepHfrom4.0to9.0.

2.2.1.5 Bulk Density

The bulk density was measured by utilizing the method of [18]. A measuringcentrifuge tube of 10 cm^3 volume was first zeroed on the weighing balance. The lump-freesample of each activated carbon of known weight was then taken and poured into the measuringcentrifuge tube to the 10 cm^3 mark tapping the cylinder for 1 to 2 minutes to ensure no void wascreated.Theweightwasthennotedandrecorded.Thebulkdensitywasthencalculatedusingthe Equation5

$$\text{BulkDensity} = \frac{\text{Weightogcarbon(g)}}{\text{Volumeofdrysample}(cm^3)} \quad (5)$$

2.2.1.6 Specific Gravity

A pycnometer was used for the determination of the specific gravity of theactivatedcarbonsamples.Themassoftheemptypycnometer(M1)wasfoundusingaweighingbalance. Then, a sample of oven-dried AC was placed inside and the combined mass (M2) wasfound. Water was then added to the activated carbon and agitated to remove all air pockets afterwhich the pycnometer filled up and its mass (M3) was measured. Finally, the pycnometer wasemptied, cleaned, and filled with water and its new mass (M4) was found. The specific gravity,GswascalculatedfromEquation6

$$G_s = \frac{M_2 - M_1}{(M_2 + M_4) - (M_1 + M_3)} \quad (6)$$

2.2.1.7 Porosity

Porosityorvoidfractionisameasureofthevoidspacesintheactivatedsample,andisa fraction of the volume of voids over the total volume, between 0 and 1, or as a percentagebetween0%and100%.Theporosityof theactivatedsampleswascalculatedusingEquation7

$$n = \frac{(1 - p)p_w G_s(1 + w)}{} \quad (7)$$

Where:n=Porosity

ρ=BulkdensityofActivatedCarbonsampleρw
=Densityofwater,
Gs=SpecificgravityofActivatedCarbonsamplew=

Moisturecontent.

3. ResultsandDiscussion

The results of the research carried out on the comparative studies of the surface chemistry,morphology,andphysicochemicalpropertiesof acidandbasechemicallyactivatedcarbonfromcrustaceanshellshavebeencarefullydetailedinTables1-5andFigures1-4.

Table1: PhysicochemicalCharacteristicsofChemicalActivatedCarbonsofCrustaceanShells

Parameter/Sample	PSAAC	CSAAC	WSAAC	CWSAAC	PSBAC	CSBAC	WSBAC	CWSBAC
%Moisture	1.4	1.4	2.3	1.6	1.8	2.0	2.4	1.8
%Ash	7.9	8.3	11.8	9.8	8.9	9.3	12.3	9.9
%CarbonYield	86.2	87	72.1	86.8	84.2	85.2	71.6	86.3
%FixedCarbon	60.2	63.7	53.7	60.8	61.8	62.1	52.8	59.8
SpecificSurfaceArea (m^2/g)	1193	1277	960	1256	1275	1288	986	1270
BulkDensity(g/cm^3)	0.502	0.653	0.454	0.530	0.524	0.687	0.476	0.543
SpecificGravity	1.27	2.07	0.97	1.98	1.12	2.01	0.91	1.91
Porosity	0.80	0.83	0.62	0.81	0.86	0.88	0.59	0.80

Table2:FT-IRspectradataoftheacid-activatedcrustacean shells

Sample/band(cm^{-1})	O-H	C-H	C=O	C-O	C-O-C	M-O	Ar-H
CSAAC	3540	3394	1797;1616	1122	1398	873	713
PSAAC	3540	3394	1789;1624	1135	1389	864	704
WSAAC	3553	3398	1797;1620	1135	1393	869	713
CWSAAC	3550	3398	1793;1616	1126	1397	869	713

Table3:FT-IRspectradataofthebase-activatedcrustaceanshells

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

Table4: Elementalanalysisoftheacid-activatedcrustacean shellsbyEDX

Sample/band(cm^{-1})	**Element**	**Atomicconcentration**	**Weightconcentration**
CSAAC	O	78.16	58.83
	Ca	21.84	41.17
PSAAC	O	67.37	45.18
	Ca	32.63	54.82
WSAAC	O	74.43	53.75
	Ca	25.57	46.25
CWSAAC	O	75.50	55.15
	Ca	24.50	44.85

Table5: Elementalanalysisofthebase-activatedcrustaceanshellsbyEDX

Sample/band(cm^{-1})	**Element**	**Atomicconcentration**	**Weightconcentration**
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

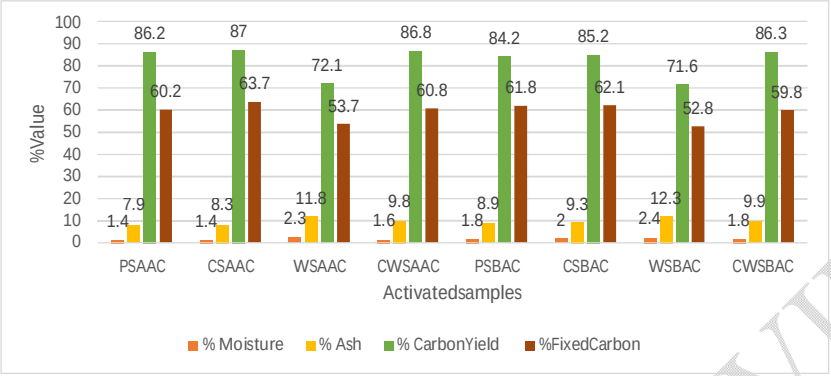

Figure1. Comparisonbetweenphysicochemicalpropertiesofacid-activatedcarbonand base-activatedcarbon.

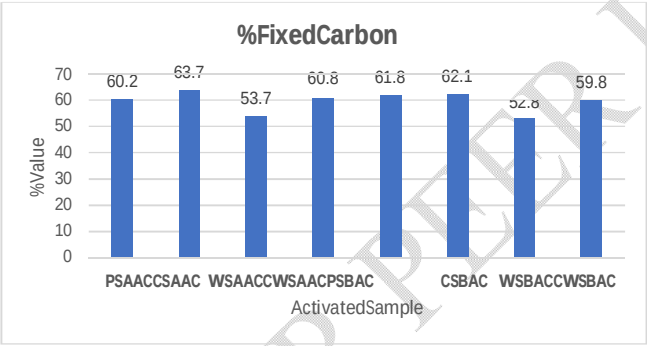

Figure2. Fixedcarbonyieldofacid-activatedcarbonandbase-activatedcarbon.

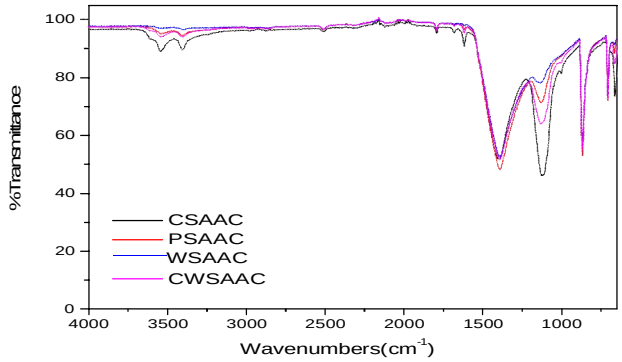

Figure3:StackedFT-IRspectraofacid-treatedactivatedcarbon

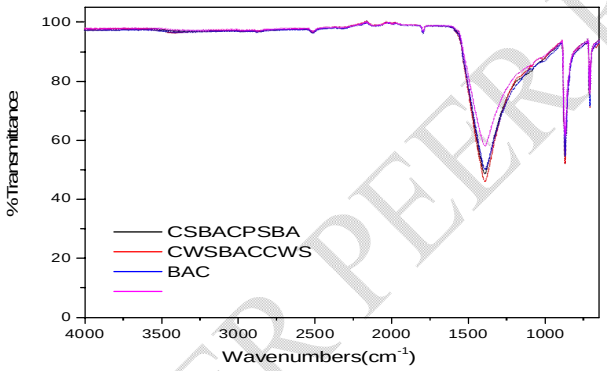

Figure4:StackedFT-IRspectraofbase-treatedactivatedcarbons

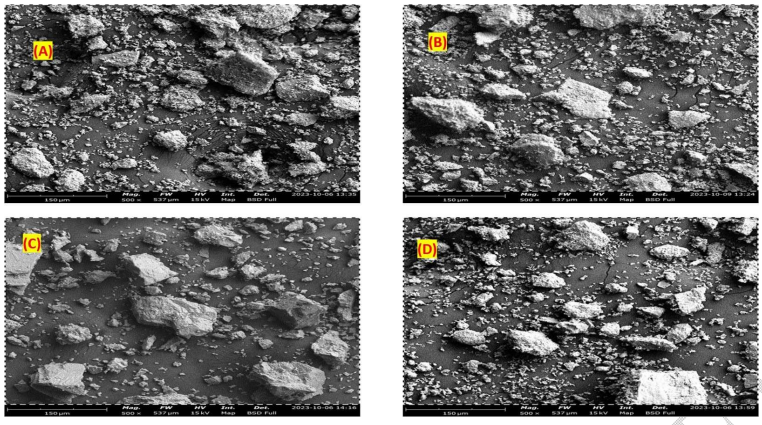

Figure5:SEMMicrographs(at150µm)ofCSAAC(A),PSAAC(B),WSAAC(C),andCWSAAC(D)

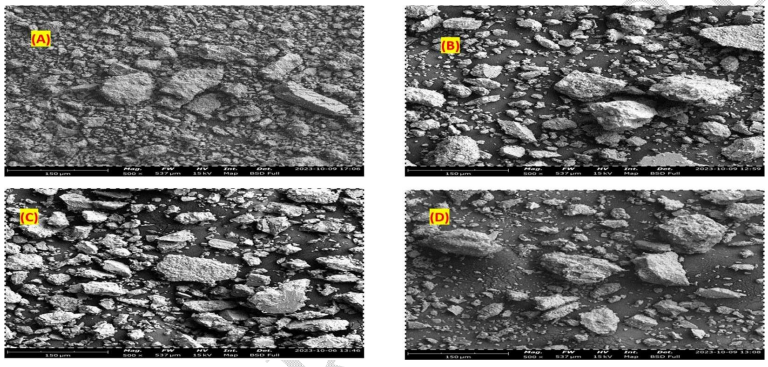

Figure6:SEMMicrographs(at150µm)ofCSBAC(A),PSBAC(B),WSBAC(C), andCWSBAC(D)

3.1 Surface Chemistry and Morphology

FT-IR analysis was performed to identify the functionalgroupspresentonthesurfaceoftheactivatedcarbons.TheFTIRspectraobtainedfortheprepar edacid- and base-treated activated carbon are presented in Figures 3 and 4 respectively. The spectradataforacid-activatedandbase-activatedsamplesaresummarizedinTables2and3,respectively.Acid-activated samples exhibited prominent absorption bands corresponding to O-H, C-H, C=O,andC-Ogroups,indicatingthepresenceofhydroxyl,aliphatic,ester,andcarboxylgroups.

Close observation of the spectra of the acid-treated samples, three prominent absorption bandsappeared in the functional group domain at ca. 3540, 3394, 1797, and 1616 cm^{-1} which wereassignedtoO-H,C-H,estersC=O,andamidesC=OgroupsrespectivelyforCSAAC.Thesebandswere observed to occur

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in similar positions in the spectra of PSAAC, WSAAC, and CWSAACwithonlyslightbathochromicorhypsochromicshiftswhichisanindicationofsimilarityinthe

surfacefunctionalityofthesematerials.Similarly,thebandsoccurringinthespectrumofCSAACat 1150, 1398, 873, and 713 cm^{-1} which have been attributed to C-O, C-O-C, M-O, and thearomatic C-H bending vibrations respectively were observed in similar regions in the other acid-treated samples. This evidence further rationalizes the similarity in these materials. The findingsherein conformwiththoseofpreviousstudiesfor similarkindsofmaterials[19];[20] and [21].

Base-activatedsamplesshowedsimilarfunctionalgroups,withslightvariationsinabsorptionbandintensities and positions, reflecting differences in surface chemistry due to the activating agent.Furthermore, the spectra of the base-modified samples showed the same absorption bands insimilar domains to those of the acid-treated materials with only two striking distinctions. Firstly,the peak intensities of the O-H, C-H, and C-O vibrations drastically decreased in their spectrawhichmaybecreditedtothetreatmentofthesematerialswithpotassiumhydroxide.Secondly,the peak associated with the amide C=O vibration in the spectra of the acid-treated samples iscompletely missing in the spectra of the base-treated materials. This observation can also beascribedtotheeffectofchemicaltreatmentbypotassiumhydroxide[22].

The SEM image for acid-activated samples inFigure 5shows that the activated carbon ischaracterizedbysurfaceheterogeneityandvariedstructureswithalargenumberofporesandporesizes. This is per findings from [23] that indicated that activated samples with a large number ofporesandporesizesandhighsurfaceareasdisplayedhighadsorptioncapacityandwerethereforegooda ctivatedcarbon.

TheSEMimageforbase-activated carbonsin Figure6indicatedabroadlyopenedporestructure,whichindicateswell-developedmicropores.ThisconformswithactivationwithPotassiumHydroxide(KOH)whichproduce swell-definedmicroporesthatmaketheactivatedsampledisplayhigh adsorption capacity [24]. When the micrographs from the two different sets of samples arecompared, a difference in particle size and shape is observed. The differences in particle size andshapeobservedonthesurfaceofactivatedcarbonsmaybeduetodepolymerizationandthereleaseof volatile substances from organic substances during the carbonization process and chemicaltreatments[25];[26]and[27].Interestingly,thesurfacemorphologyoftheacid-treatedmaterials;CSAAC,PSAAC,WSAAC,andCWSAACappearedtobesimilarbutdistinctfromtho seoftheirbase-treatedanalogues.Similarly,themicrographsoftheCSBAC,PSBAC,WSBAC,andCWSBACshowed similarfeaturesintheirsurface morphologybutatvariancewiththoseofacid-modified samples. This observation is in concomitance with the results from FTIR studies whichsuggestasignificantsimilarityinthesurfacecompositionofeachsetofmaterials.

Energy dispersive X-ray (EDX) analysis of the treated activated carbon materials was performedto estimate the composition of various elements present in the adsorbents. Tables 4 and 5 providethe atomic and weight concentrations of oxygen (O) and calcium (Ca) in the samples for both theacid and base-activated carbon respectively. Thus, the elemental analysis confirmed the presenceof Ca and O in all the materials under investigation. It can be observed

that the calcium weightpercentageishighinallthetreatedactivatedcarbonsasaresultofactivationandmineralization

with a calcium-to-oxygen weight concentration ratio of 1:1 in all the samples [28] and [29]. Theresultsindicatedasignificantpresenceofcalciumoxide(CaO)acrossallsamples,whichcontributest otheporosity andadsorptioncapacity of the activatedcarbons.Acid-activatedsamples, as presented in Table 4, showed higher atomic concentrations of oxygen compared tocalcium, with CSAAC having the highest oxygen concentration at 78.16 cm^{-1}. Conversely, base-activatedsamples,detailedinTable5,demonstratedamorebalancedratioofoxygenandcalcium,withCS BACshowinganoxygenconcentrationof61.77cm^{-1}andcalciumat38.23cm^{-1}.Consequently, the EDX analysis proved the presence of calcium oxide in the activated carbons.As CaO is a strong dehydrating agent, it adsorbs water from surroundings, thus increasing theporosityofthetreatedactivatedmaterials[29]asobservedintheSEMstudies.

3.1.1 Carbon Yield

The results from Table 1 showed a high carbon content ranging from 71.6 to 87%.Figure 1 presents the carbon yield percentages of the activated samples. High product yielddifference is a result of the origin of carbon material and activation processes [30].A goodactivated carbon should present a carbon yield of 60 to 98% [1]. The acid-activated samplespresented higher carbon yields compared to the base-activated samples. The highest carbon yieldwas observed in CSAAC at 87%, while WSBAC had the lowest at 71.6%. The high carbon yieldissimilartothefindingsof[31] witha95%carbon yieldfromactivatedcrustaceanshells.Ahighcarboncontentvalueisdesiredtoachieveahighsurfacearea becauseasthecarboncontentoftheactivated carbon increases, the surface area also increases [1]. A higher carbon yield indicates agreaterconversionofrawmaterialintoactivatedcarbon,whichisdesirableforeffectiveadsorption.

Fixed Carbon: Proximate analysis was used to calculate the fixed carbon content in the variousactivatedsamplesbyutilizingthe%ashandmoisturecontentderivedfromtheanalysis.It indicates the composition of the biomass regarding the moisture content, volatile matters, ashcontent,andfixedcarbon.[32]notedthemathematicalderivationoffixedcarboncontentandthisisex pressedinEquation8

$$\boldsymbol{Fixed\ Carbon = 100 - (\%Ash + \%\ Moisture + volatile matter)} \quad (8)$$

The fixed carbon content, illustrated in Figure 2, ranged from 52.8% to 63.7%. Acid-activatedsamples had slightly higher fixed carbon contents than the base-activated samples, except forWSAAC showing a low value at 53.7%. Among the base-activated samples, CSBAC had thehighestfixedcarboncontentat62.1%.Highfixedcarboncontentisindicativeofgreatercarbonization andlessvolatilematter,enhancingtheadsorbent'sstabilityandperformance.

3.1.2 Moisture Content

The moisture content of the activated samples is illustrated in Figure 1. Theresults indicated that the percentage moisture content ranged from 1.4% to 2.4%. This is inconformance with the results [33] obtained on the low moisture content of crustacean shells. Theacid-activatedsamples(PSAAC,CSAAC,WSAAC,CWSAAC)generallyexhibitedlowermoisturecontent

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thanthebase-
activatedsamples(PSBAC,CSBAC,WSBAC,CWSBAC).Specifically,CSAACandPSAAChadthel
owestmoisturecontentat1.4%,whileWSBAChad

the highest at 2.4%. A lower moisture content is preferable as it reduces the adsorbent's dilutioneffect,enhancingitsadsorptionefficiency.

3.1.3 AshContent

TheashcontentfortheactivatedsamplesinTable1variedbetween7.9%and12.3%.Acid-activated samples PSAAC, CSAAC, WSAAC, and CWSAAC with values of 7.9, 8.3, 11.8,and 9.8% respectively presented lower ash contents than base-activated samples, with PSAAChaving the lowest ash content at 7.9%. This is consistent with the results by [34] in a similarresearch.Incontrast,base-activatedsamplesPSBAC,CSBAC,WSBAC,andCWSBACpresentedslightly higher ash contents with values of 8.9, 9.3, 12.3 and 9.9% respectively against that of theacid-activatedsampleswithWSBACshowingthehighestat12.3%.Lowerashcontentisbeneficial for adsorbents as it increases the available surface area for adsorption and improvesoverallefficiency.

The activated samples indicate a relatively low percentage ash content which is an indication thatthesampleswillexhibithighadsorptivevalues.Thisisbecauseashisanimpuritythatreducestheover allactivityoftheactivatedcarbon.Theashcontentisveryimportantindeterminingthequalityof an adsorbent with a good adsorbent having as low ash content as possible (<15%) [35]. This isbecause high ash content reduces the adsorptive capacity of the adsorbent and lowers specificsurfacearea[36].Highashcontentalsoaffectstheefficiencyoftheactivatedsamplesasthehigher the ash content, the lower the efficiency of removal of toxic contaminants. This is supported by astudy by [37] that observed that activated carbon with high ash content adsorbed 4 times lesscontaminantsthanash-freeactivatedcarbon.

3.1.4 Specific Surface Area

The surface area of activated carbon samples typically has a surface arearanging from 500 to 1500 m^2/g, making it highly effective for adsorption processes [38]. Thecarbon samples had a resultant surface area ranging from 960 to 1288m^2/g making them suitableforadsorptionofPAHs.Comparisonbetweenacidandbase-activatedsamplesofeachcrustaceanshellsamplewasnotedtovaryslightlywiththebase-activatedsamplespresentingalargersurfacearea than acid-activated samples. The Surface area for CSBAC and CSAAC are 1288 and 1277m^2/g;PSBACandPSAACare1275and1193m^2/g;WSBACandWSAACare986and960m^2/g;whileCWSBACandCWSAACare1270and1256m^2/grespectively.Thepresenceofhighsurfaceareasinfluencesadsorptionasitpresentslargeactivesitesfortheadhesionofadsorbatesfromthesolution.

Carbonization and chemical activation improve the surface area of adsorbents as theyimprove adsorption sites allowing for more interaction sites between the activated carbon andadsorbate enhancing the adsorption capacity of the activated carbon [39]. [38] noted that thesurface area range of activated carbon can vary based on factors such as the activation methodused,theprecursormaterial,andtheactivationconditionsduringproduction.

3.1.5 Bulk Density

Bulk density, also known as apparent density is the mass of activated carbon perunit volume

(kg/m^3 or g/cm^3), including the voids between the particles. Typical powderedactivated carbon (PAC) may have a slightly lower bulk density of around 0.38g-0.45g/cm^3 thanthatofagranularactivatedsample.[40]notedthatanactivatedcarbonwithabulkdensityofabout0.5g /cm^3isadequateforadsorption.Thebulkdensitiesofallthecrustaceanshellsactivatedcarbonwerefoundt obewithintherangeof0.454g/cm^3to0.687g/cm^3.Thisissimilartoresultsfrom[41]

on the bulk density of low-cost precursors. Usually, adsorbents with high bulk density can holdmoreadsorbateperunitweightwhichmakeshighbulkdensityessentialforwastewatertreatmentpurposes.

3.1.6 Specific Gravity

The Specific gravity of the activated samples was noted to range from 0.97observed for WSAAC to 2.01 for CSBAC. This indicates that the activated carbon samples areeffectiveadsorbentsforthewastewatertreatmentprocessastheirrangesconformwiththeresearchconducted by [42] and [43] which stated that the values for the specific gravity of an activatedsampleliewithintherangesof0.8to2.1.

3.1.7 Porosity

Table 1 also shows the porosity of the activated carbon samples. Porosity describes thenumber of pores present in a sample [44].It can therefore be inferred from this that PorosityenhancestheadsorptioncapacityofanactivatedcarbonsampleThereforethehighertheporosity,the higher the adsorption capacity of the adsorbent. It is noted from Table 1 that the porosity oftheactivatedsamplesisintheorderCSBAC(0.88)>PSBAC(0.86)>CSAAC(0.83)>CWSAAC(0.81)>CWSBACandPSAAC(0.80)>WSAAC(0.62)>WSBAC(0.59).

4. Conclusion

A comparative study of the surface chemistry, morphology, and physicochemical properties ofchemically activated carbon from crustacean shells was carried out. The experimental analysesestablished that the activated carbons prepared from periwinkle shells, clamshells, whelk shells,and composite clam/whelk shells have good morphology and physicochemical properties foradsorption.ChemicalActivationmethodsusingbothacidandbaseactivationforcrustaceanshellsyielded activated carbons with high carbon yield, high fixed carbon, high bulk density, increasedsurface area, low ash content, low moisture content, and high porosity of carbon which indicatestheireffectivenessasadsorbentforindustrialtreatmentofwastewater.However,itcouldreasonablybeconcludedthatClamshellsactivatedwitheitherbaseoracidwithhighsurfaceareasof 1288 and 1277 m^2/g respectively have a better advantage to be used compared to Periwinkleshells, whelk shells, and the composite of clam/whelk shells. This Study revealed that ChemicalActivationofCrustaceanshellscanbeundertakenusingeitheracidorbasewithoutcompromisingon the efficiency of the resultant activated sample for the effective removal of adsorbates fromwastewatersamples.Thisthereforeexpandsthechoiceofactivationasthechoiceofprecursorsisabundanceinnature.

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Comment [u16]: Italize

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Comment [u18]: Must be consistent with writing name of journal ie shorten or in full, follow this journal's method, no page no. All colored red must be rectified, there are problems.

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