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Production and Characterization of Groundnut Shell as an Absorbent for Removing Heavy Metals from Local Dye Effluent in Rafin Dutse Stream water, Azare, Bauchi

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ABSTRACT:
Cleanandsafedrinkingwaterisabasicneedforhumans and animal world over.Togetgoodwaterquality, severalwatertreatment methodsarebeingused.Thispaperadoptsgroundnut shellassourceof activatedcarbon fordrinkingwater treatment.The groundnutshellwas separated frompeelsusing threshing methodandwashedtheshell repeatedly withtapwaterinordertoremoveallthedirt'sandotherco ntaminant. It was furtherwashedwithdistilledwaterandsundriedforthre e(3)days.Thedriedsamplewasgroundtoobtainapowd erforms. It wassievedwitha500µmmeshandstoredin airtightcontainer,300gof thepowdered sample.The groundnutshellwastreatedwith 1 Msolutionof K_2CO_3, $ZnCl_2$and KOH. A certain amount of powder was placed in a crucible muffle furnace carbonized at temperature of400^0C for 2 hours, cooled and then stored in a sealed bag.Thereafter,itwascleanedwithdistilledwateruntili tspHvaluewas5.7.Theapplication of theactivatedcarbondevelopedwason rawwater fromunprotectedRafinDuste stream water nearcharachar,Azare Area of Bauchi State, Nigeria. Theselected heavymetals levelsin the digestswereanalyzedusingatomicabsorptionspectro meter(AAS),whiletemperature and pHwereanalyzedusingtheappropriate equipment.Testswerecarriedoutbeforeand aftertreatmentwiththeactivatedcarbon.The parameters testedwere, temperature, turbidity, color, salinity, odor and, pH were shown in table 1.Thewaterqualitychangesnoticed includedthereductioninturbidity,colorofthewater,an dpH(decreasedfrom6.91 to 6.5), the color of water is blue after adsorption of activated carbon turn to colorless. Assessment of heavy metals, physical and chemical properties of the stream water, chemical parameters before and after adsorption of activated carbon werecarriedouttoidentifythelevel ofthepollutantsdischargedtotheenvironment.The heavymetals presents before water treatments were;(Pb,Cu, Zn,Cd,Cr,Mn,Fe, Hgand Ni)with high concentrations of (0.01mg/L, 0.98mg/L, 0.05mg/L, 0.002mg/L, 0.03mg/L, 0.04mg/L, 0.02mg/L,0.021mg/L and 0.20mg/L)while As was not detected and were shown in table 2 respectively.All the heavy metal concentrations reduces drastically after the application of activated carbon were ;(Pb, Cu, Zn, Cd, Cr, Mn, Fe, Hg, and Ni) and (0.001mg/L,0.53mg/L, 0.20mg/L, 0.0001mg/L, 0.02mg/L, 0.03mg/L, 0.01mg/L, 0.011mg/L and 0.13mg/L) respectively.The characterization of groundnut shell ash as activated carbon were also determine and shown in table 3 were the ; yield 68%, fixed carbon 81.56%, ash content 3.10%, moisture content 2.58% and pH of 5.7. The comparisons of means concentration of heavy metals were within the reference limit of WHO and FEPA standard and shown in table 4. GSACwassynthesizedandcharacterizedby differenttechniquesincluding FESEMandEDX. The groundnut shell activated carbon (GSAC)showedhighmethyleneblue adsorptionefficiency onBatch.The groundnut shells investigated in this study exhibited high potential for the removal of Cu, Mn, Hg, Cr, Fe,Ni, Pb etc. were analyzed and reduces drasticallyfrom aqueous solution even without physical or chemical modification. Theadsorptionofheavy metal was

highly dependentoncontacttime,pH,adsorbentdose,initialmetal ionconcentrationandtemperature.Theadsorptionof heavy metalswasfoundtobeoptimumatacontacttimeof120min;pH5.7adsorbentdoseof2.0g/L;metalionconcentrationof25 mg/L; and temperature of 41.5 °C. For all the isotherm modelstested. ThesurfaceareasofBETandLangmuirwere395.5and1005m^2/g,respectively.Itclearlyshowsthat theobtainedsurfaceareaandporesizearedependingontheamountofintroduced$ZnCl_2$andactivation temperature. Well-developedporoussurfaceofGSAC wasobservedviaFESEMmicrograph(2500×)which isconsideredas channels to themicroporousnetwork (Figure.3a).Itshowedthattheadsorbenthaveroughtexturewith heterogeneoussurfaceand avariety ofrandomly distributedporesize.EDXanalysisofGSAC (Figure.3b) showed the presence of four elements–carbons (88.62%), oxygen (15.30%), Zinc (0.72%) and Chloride (0.36%). Presenceofoxygenmaybeattributedtothelittleamount ofmoistureinthecarbon. Very lowlevelof ZincandChloridewereobserved,becauseoftheusageof$ZnCl_2$asanimpregnatingchemicaltoactivationof carbon. TheFTIRspectraintherange400to4000cm^{-1} ofGSACwaspresentedin(Figure3c).

Keywords: Water treatment, Groundnut shell, activated carbon, Heavy metals, and Effluent.

I. INTRODUCTION

Waterisvitaltoalllivingthingsand,ispresentinalmost allfoods,unlessstepshavebeentakentoremove it,even thoughitcontributesnocaloriestothedietHanjraet al., (2019).Waterisessentialforlifeandlivelihoods;itisalsoacoreinfrastructure sectoroftheeconomy.Fouroutofeveryfivepeoplearound theworldareserved byrenewablefreshwaterservices.But becausethedistribution offreshwaterisuneveninspace andtime,morethanonebillionpeoplelive underwater stressandonly15%oftheworld's population liveswith relativewaterabundance. Itiswellestablishedthatvast changeswithgreatgeographicvariabilityoccur infresh waterresourcesandtheirprovisioning ofecosystemservices inallscenarioconsideredundertheMillenniumEcosystem Assessmentcarriedoutbetween2018and2022MillenniumEcosystemAssessment Report (2022).

Wastewateris the liquid end-product,or by-product,ofmunicipal,agricultural, andindustrial activity.Assuch,the chemicalcomposition ofwastewater naturallyreflectsthe originfromwhichitcame. Wastewater (inthesenseof the effluent)is composedof 99%waterand1%suspended, colloidalanddissolvedsolids.Wastewater hasbeende-scribedasboth"aresourceandaproblem" Qadiret al., (2018).Potential problemsprincipallyrelatestothepresenceoftoxicchemicals(fromindustrial sources ofeffluent) andthepresence of pathogenicmicroorganisms.Irrigationwitheven treated wastewatercanleadtoexcessnutrients,pathogens, heavy metalsandsaltsbuilding upontheirrigated land,unless careistaken.Theseparation ofindustrialanddomestic wastewaterwillfacilitatethelikelihoodof safe reusesPatil(2019).

Industrialwastewaterisoneoftheimportantsourcesofpollutants leadingtothepollution ofthewaterenvironment. Duringthelastcenturylargeamountsofindustrial wastewaterwasdischargedintorivers,lakesandcoastal areas.This hasresulted inseriouspollutionprobleminthewaterenvironment andcausednegative effectstotheecosystemand humanlife.Thesewastes oftencontainawiderange of contaminantssuchaspetroleum hydrocarbons,chlorinated hydrocarbons,heavymetals,variousacids,alkalis,dyesand otherchemicalswhichgreatlychangethephysico-chemical propertiesofwater.Allthesechemicalsarequiteharmful orevenfatallytoxictotheaquaticecosystem Ado et al., (2019).

Heavy metalpollutionhasbecomeoneofthemostseriousenvironmentalproblemstoday. Wastewaterscontainingheavymetalsareproducedeach yearbytextileindustriesand otherprocesses.Mostofthechemicalmethodsusedincleaningupoftheseheavymetals arenoteffective.Microorganismshavebeenusedextensively incleaningofheavymetals intheenvironmentbutplanthasnotbeenusedextensively inremovingheavymetalsfrom wastewater.Thisnecessitatestheuseofgroundnutshell foradsorptionofheavymetals. Nickelandchromiumwhicharewidelyused andextremelytoxicinrelativelylowdosages, themainpathway throughwhichnickelandchromiumentersthewaterbodiesviawastes fromindustrialprocesses.Heavy metalsare toxic and harmful water pollutant. Their present not only affects the human being but also affects the animal and vegetation because of their versatility in aqueous ecosystem, heavymetal pollutionhasbecomeoneof themostseriousenvironmentalproblemstodayand cancausedifferentalimentlikecancer, hypertension,kidney tumorsandreproductive difficulties.Thisstudyissettoaddress thechallenge toenvironmentalpollutionbyproviding theactivatedcarbon from groundnut shell thatmediatedadsorption bestamong thevariousdyeremovalprocesses. Adsorptionprocessusingcommercialactivated ishighcost,thisprovidethesearchfor alternativeandlow-costadsorption,renewableand easily availablematerialfromthe surrounding areas,alsoforlargeeconomic-scaleproductionto dyeremoval processes.Inthis case, agricultural wastes are available and an excellent option in the purification of contaminantfromliquidand gasstreamsthat evolvefromindustrialanddomesticsources Alluri,(2017).

Activatedcarbon (AC)isaneffectivefetteringmaterial,highlyporouswithimmensesurface area. Themostcommondescribedactivatedcarbonisthatitactslikeasponge,sucking contaminatesfromliquidsandgases. Activatedcarbonremovesmanyorganicandsome specific inorganicsubstances suchaschlorine, cadmium, nicked,leadandchromiumfrom commonindustrial pollutants. Activated carbon mediated adsorption is the best amongst various dye removal processes;itjustbecauseof its simplicity, low costand reusabilityofnon-toxicadsorbentIdris, (2020).

GroundnutbotanicallybelongstoAracheshypo GaeaLinnofleguminous family. Groundnutisaself-pollinated;annualand herbaceouslegumecrop.Theshellconstitute about 25-35%ofthepod. Theseedaccountsfortheremainingportion(65-75%)Sada, etal.,(2018).Theworldcountries,Nigeriais amongtheforemostproducers ofgroundnut, withanannual production rate of about 2.699 millionmetrictonnesin2002and1.55 milliontonnesin2008Sada,et al., (2018). Ithasthepotential to producehightonnesinfutureduetohighdemandfrom groundnutsproductssuchasgroundnutoil, spread, paste andconcentrate. Overtheyears,palmkernel,coconut andgroundnut shells are amongthemajor solid waste especiallyinthedeveloping countries oftheworld.Their potential as a very useful engineering material hasnot been fullyinvestigated and utilized.Theutilizationoftheseshellswillreducewaste management cost,leadstoclean environment asresultof pollution reduction and the increase in financialbaseofthe farmer when such waste are sold as rawmaterials.Theyareusedintheabatement of hazardouscontaminationofthe environment.

Hendersonetal.,(2019) investigatedwastewatersfromtextileandtanneryeffluentsattract attentionofenvironmentalprotectionagenciesallovertheworld.Theynotonlydeface thelookofnaturalwaters,butarealsohighlytoxicChu,(2017).Somedyesarereported toharmmammaliancellsbycausingkidneytumorsand reproductivedifficulties.These dyesarealsopotentially carcinogenic,genotoxic,mutagenicinmanyanimalspecies Adsorptionprocess isconsideredveryeffectiveintextileandtannerywaste watertreatment. Itprovessuperiortotheotherprocesses bybeingsludgefreeandcancompletely remove evenveryminuteamountsofdyesinwastewaterNigarn etal.,(2016). Adsorptionprocess using commercial activated carbons is very effective for removal of dyes from wastewater but its high cost has provided the search for alternatives and low-cost adsorptionsNimratet al.,(2019).

ToyinOmotoso,(2017)investigatetheadsorptionoftoxicwaterpollutantsusing modified groundnutshelltoexamineinadsorptionofheavy metalssuchascopper(Cu),magnesium (Mg),Iron(Fe)andChromium(Cr)inanindustrialeffluentdischarge. Theresultofthe capacitywasfoundtobeFe>Cr>Mgformodifiedgroundnutshellintheorderof100%,98%,70%and9% respectively.Thisstudy isaprognosisintocapacityofplantsubstratein bioremediationofpollutedsoilandgroundwater,reducingdifferentheavy metalsinthe streameffluent.GroundnutshellisagoodabsorbentofFeandMg.However,theeffectof pHconcentrationontheadsorptionofmetalswas notinvestigated.

Isah,(2020)investigateonadsorptionofleadionsongroundnutshellactivatedcarbon.Thisworkfocuses ontheutilizationofactivatedcarbonpreparedfromgroundnutshellforthe

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removalofleadfromwater.Theeffectsof temperature, contact time, and initial concentration of lead on the adsorption process have been investigated. Groundnutshellactivatedcarbonisproventobecapable ofremovingleadfromwaterwithaveryhighefficiency underambientconditions.Adsorptionofleadontogroundnutshellactivatedcarbonisbestdescribedby thepseudo secondorderkineticmodelandtheLangmuiradsorption isothermmodel.

II. MATERIALS AND METHODS

2.1Materials

The materials, equipmentandinstrumentsused inthis studywereall calibrated tochecktheirstatus beforeandinthemiddleof theexperiments. AllGlasswareswerecleanedwith10% concentratedHNO_3inordertooxidizeandremove impurities tiesonthecontainersurfaces. Groundnut, $ZnCl_2$, KOH, H_3PO_4.Apparatussuchasvolumetric flasks,samplebottles,funnel, watchglass,burette,beaker, measuring cylinder,andpipettewerethoroughlywashed withdetergentsandtapwater,andthenrinsedseveraltimes withdeionizedwater. Crucible furnace, Threshing machine and grinding machine, sieve andfilterpaperwere used.

2.2 Sample Collection

Thewastewater sample ofRafinDutsewascollectedfrom charachar near Azare, Katugum Local Government Area of Bauchi State. Nigeria.The watersamples werecollectedbya stratifiedsamplingmethodfromdifferent spot which was shown in figure 1.The sampleswere used to determine their physical and chemical characteristics before adsorption of activated carbon, the following tests were conducted and shown in table 1 and elements of heavy metals presents such as Cu, Zn, Cd, Pb,Mn, Ni, Fg.etc where determined and shown in table 1.

Figure: 1 Sample of Water Collected from RafinDutse Stream WaterCharachar, Azare

2.3 Sample Collection Preparations of Activated Carbon

Thegroundnutwasobtained fromAlkaleriMarket,AlkalerilocalGovernmentArea of BauchiS t a t e ,Nigeria.The groundnut sample wasseparated frompeelsusing threshing methodandwashedtheshell repeatedly withtapwaterinordertoremoveallthedirt'sandothercontaminant. It was furtherwashedwithdistilledwaterandsundriedforthree(3)days.Thedriedsamplewasgroundtoobtainapowderforms. It wassievedwitha500µmmeshandstoredin airtightcontainer,300gof thepowdered sample.The groundnutshellwastreatedwith 1 M solutionofK_2CO_3, $ZnCl_2$and KOH. A certain amount of powder was placed in a crucible muffle furnace carbonized at temperature of400^0C for 2 hours, cooled and then stored in a sealed bag. Thereafter,itwascleanedwithdistilledwateruntilitspH valuewas5.7 and the samples of the groundnut, ground shell and activated carbon were shown in figure 2(a), 2(b) and 2 (c)

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Figure 2(a): Groundnut

Figure 2(b): Groundnut Shell Powder

Figure 2(c): Ground Shell Ash (Activated Carbon)

2. 4 Application of Activated Carbon

Activated carbonpreparedfrom groundnut shells was used for the treatmentofopenwaterfromRafinDutseCharachar, Azare. Theexperimentswerecarriedout in triplicate. Samplesoftherawwater (100 ml)weremixed withcarbon (0.1g) in250 mlErlenmeyer flasks. Themixtureswereshakenat200rpmin a temperature-controlledshakerat (25 ±2^{0}C)for2 hours then filteredusing aWhitmanfilterpaper size15 to remove thecarbon.Fullchemicaland bacterialanalysiswas doneto checkthewater parametersaftertreating withactivatedcarbon. Thechemicalanalysis includeddetermination chemicaloxygen demand, thermal conductivity, yield, porosity, pore size, pore volume, volatile matter, fixed carbon, ash content, BET surface area, FETSEM, EDX and FTIR spectra test. Heavy metals such as Cd, Mg, Cr, Ni etc. were shown in table 3, 4 and figures 3(a), 3(b) and3(c) respectively.

III. RESULTS AND DISCUSSION

3.1 Physical Characteristics of Water Sample before and after Absorbent of Activated Carbon

Table 1: Physical Characteristics of Water Sample for PH, Temperature, Salinity, Colour and Odour Test Before and After Applications of Activated Carbon Treatment

S/N0	Characterization of Water	pH		Temperature (^{0}C)		Turbidity (NTU)		Salinity (ppm)		Colour		Odour(TON)	
	(Trials)	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
1	Firs reading	6.93	6.41	73.0	43.0	2.00	1.70	196	267	blue	Nil	2.00	1.00
2	Second reading	6.89	6.52	72.5	42.9	1.95	1.71	215	224	blue	Nil	2.3	1.01
3	Third reading	6.92	6.58	74.0	43.0	2.00	1.73	106	204	blue	Nil	2.1	1.00
4	Average	6.91	6.50	73.2	42.9	1.98	1.71	172	231	blue	Nil	2.1	1.00

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(a) Theanalysisofwastewaterforheavymetalco ntamination isanimportant stepinensuringhumanandenvironmental healthsafety.Excess levelsofheavymetals mightcause severalshorttermandlongtermeffectstohuman.TheWHO standardsforthepHofthedrinking waterrangesfrom6.5to7.5. ThetestsforthepH of the waterwas carried out based on average value before the application of carbon is 6.91 and after applying activated carbon it reduces to 6.50. The pH is ok, but if its less than 6.50 are most likely to be contaminated with pollutants, making it unsafe to drink, it can also corrode (dissolve) metal pipes,which may also beacidic. However, the activated carbons raise the pHof water near the neutral value when injected into water system.

(b) The effect of temperatures was performed at three different readings with thermostatic shaker machinewhilekeepingallotherparametersconstant, with average of 73.2^{0}C before applying activated carbon, after applying activated carbon it reduces to 42.9^{0}C. There was a change in the temperature of water before and after application of the activated carbon, which means that it has effect on the temperature of the drinking water. From the WHO 2019 guideline for other key housing risk factors value for drinking water quality, wherever possible, water temperatures should be kept outside the range of 25-50^{0}C to prevent the growth of the organism.

(c) There was a little change on the average value of turbidity before and after the application of the activated carbon from 1.98 to 1.71NTU. According to WHO 2019, turbidity most be less than 1, if not will caused by suspended chemical and biological particles, can have both water safety and aesthetic implications for drinking-water supplies.

(d) Color and Odor; the color before and after the application of the activated carbon from blue color to nil was observed, the dissolve elements or suspended impurities may give water a different color.However, after activation of carbon it reduces the contaminated particles to colorless as its physical characteristics. Odor of water is expressed in terms of a unit called threshold odor number, which signifies the dilution ratio at which taste and odor in the apparatus called osmoscope was utilized. The acceptable limit is 1 TON and causes of rejection limit 3 TON. The result for an average before and after the application of activated carbon is from 2.1 to 1.0, the effect of adsorption fall within the accepted limit.

Table 2: Chemical Characteristics of Water Sample: Percentage of Water Quality Parameter beforeAbsorbent Treatment

S/No	Element of heavy metals before Absorbent Treatment	Concentration o(mg/L) of sample First reading	Concentration o(mg/L) of sample second reading	Concentration o(mg/L) of sample third reading	Mean Concentration (Mg/L)
1	Pb	0.01	0.01	0.01	0.01
2	Cu	0.98	0.98	0.98	0.98
3	Zn	0.50	0.50	0.50	0.50
4	Cd	0.002	0.002	0.002	0.002
5	Cr	0.03	0.03	0.03	0.03
6	Mn	0.04	0.04	0.04	0.04
7	Fe	0.02	0.02	0.02	0.02
8	Hg	0.021	0.021	0.021	0.021
9	As	Not detected	Not detected	Not detected	Not detected
10	Ni	0.20	0.20	0.20	0.20

Table 3: Chemical Characteristics of Water Sample: Percentage Change in Water Quality Parameter after Absorbent Treatment with Groundnut Shell Ash Activated Carbon

S/No	Element of Heavy metals After Absorbent Treatment	Concentration o(mg/L) of sample First reading	Concentration o(mg/L) of sample second reading	Concentration o(mg/L) of sample third reading	Mean Concentration (Mg/L)

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1	Pb	0.001	0.001	0.001	0.001
2	Cu	0.53	0.53	0.53	0.53
3	Zn	0.20	0.20	0.20	0.20
4	Cd	0.0001	0.0001	0.0001	0.0001
5	Cr	0.02	0.02	0.02	0.02
6	Mn	0.03	0.03	0.03	0.03
7	Fe	0.01	0.01	0.01	0.01
8	Hg	0.011	0.011	0.011	0.011
9	As	Not detected	Not detected	Not detected	Not detected
10	Ni	0.13	0.13	0.13	0.13

Table4:Comparisonofthemeanconcentration ofheavy metalswithsomeinternationalwaterstandards

Elements	**Mean concentration (mg/L)**	**WHO (2019) (mg/L)**	**FEPA (2019)**
Pb	0.01	0.01	0.01
Cu	0.98	2.0	1.0
Zn	0.50	-	-
Cd	-	0.003	0.003
Cr	0.03	0.05	0.05
Mn	0.04	0.05	-
Fe	0.02	0.05	0.01

Theanalysisofwastewaterforheavymetalcontamination isanimportant stepinensuringhumanandenvironmental healthsafety.Excess levelsofheavymetals mightcause severalshorttermandlongtermeffectstohuman.Table 2 illustratesthedistributionofmetalsconcentrationin an average value of wastewatersamplesbefore adsorbent treatment, the levels ofPb, Cu, Zn, Cr, Mn and Fe, while Cd was not detectedintheeffluentsamplesanalyzed and was compared with table 4 of comparable mean concentration for WHO and FEPA standard.Pb was 0.01 mg/L which agree with WHO and FEPA standard with concentration of heavy metal, while Cu was 0.98mg/L which was close to 1.0 and far from 2.0 of the WHO and FEPA value respectively.Cr was 0.03mg/L which is within the range to 0.05 of WHO and FEPA standard with concentration of heavy metal. Mn was 0.04mg/L which is close to 0.05 of WHO and FEPA standard with concentration of heavy metal. Fe was 0.02mg/L which is within the reference limit for 0.05 and 0.01of WHO and FEPA standard with concentration of heavy metal. Theconcentrations ofheavy metalspresent intheRafindutsecharachar stream water effluentsampleswerefoundtovary significantly.Theconcentrationof activated carbon for Pb, Cu,Zn,Cr,Mn,Fe, Hg and Ni obtainedwere reduces drastically shown in table 3, with the following values; 0.001mg/L,0.53mg/L,0.20mg/L,0.0001mg/L,0.02mg/L,and0.03mg/L,0.03mg/L, 0.01 and 0.13mg/Lrespectively, whileAswasnotdetectedintheeffluentsamplesanalyzed. ThelevelsofCu,Zn,Cr, Mn, Hg, Fe and Niwerebelowthemaximumlimitsset by WHOandFEPA whilethenon-detected levelsof Ascouldbeduetoits absence intherawmaterials inuseatthetimeofsample collectionSankpal, (2012). Thehigher concentrationsofFeandZncouldbeattributedtotheuse of brass as cleaningmaterial.SecondlyZnisaconstituentofgalvanizedsteelincludingwaterdistribution pipesanditspresencemightbe due tocorrosion,the metalmay findits way tothewastewaterandsubsequentlytotheenvironment Pawlowski, (2013).WhencomparedwiththeFEPAandWHOstandardsinTa- ble3,theCrconcentration of0.03mg/Lishigherthan the permissible limits of 0.05 mg/L set by FEBA and WHO standards.PossiblesourcesofCrinindustrialeffluentcould belinkedtochromeplatingandalloysforcorrosionprev entionOliveira,(2012).Cuconcentration of0.98mg/LislessthanreferencelimitsasshowninTable4,andWHOstandardsof2.0and1.0mg/Lrespectively WHO(2019) and FEPA (2019).TheconcentrationofPbobtained was0.01mg/Lwhichiscorresponded to theFEPA andWHOacceptablelimitsof 0.01mg/L.ElevatedPbconcentrationsinstreameffluentscouldbemuchassociated withmetallurgy andmetalprocessingamongothersHarrison, (2018). Theconcentration ofFewas0.02mg/L,thisisabove WHOandless limitsof FEPAof0.05mg/L, 0.01mg/L.Fe isoneofthe mostabundantelementintheearthcrustFrey,(2012) andcanbedischargedtoenvironment throughvariousindustrialprocessesAdo,(2015).Theconcentrationsofthepollutantsreported inthisstudywerenotalarming, because it was proved from the results.

Table 5: Characterization of Groundnut Shell Ash as Activated Carbon

S/No	Parameter/ Characteristics	Results
1	Yield (%)	68
2	Fixed carbon(%)	81.56
3	Volatile Matter(%)	16.62
4	Ash content (%)	3.10
5	Moisture content (%)	2.58
6	Bulk density (g/cm^3)	0.48
7	Iodine number (mg/g)	1007
8	BET surface area (m^2/g)	1005
9	Pore volume (cm^3/g)	0.77
10	Pore size(mm)	0.79
11	Porosity (%)	96.31
12	PH	5.7
13	Langmuir surface area (m^2/g)	395.5
14	Thermal conductivity at 25^0 C	0.155
15	Density ((cm^3/g)	1.46

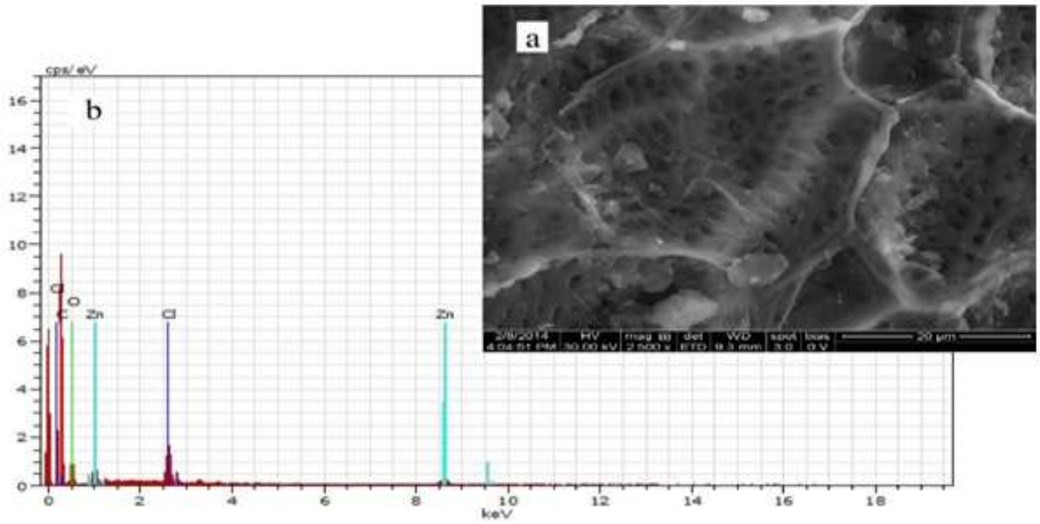

Figure3:AnalysisofGSAC(a)FESEM and (b)EDX.

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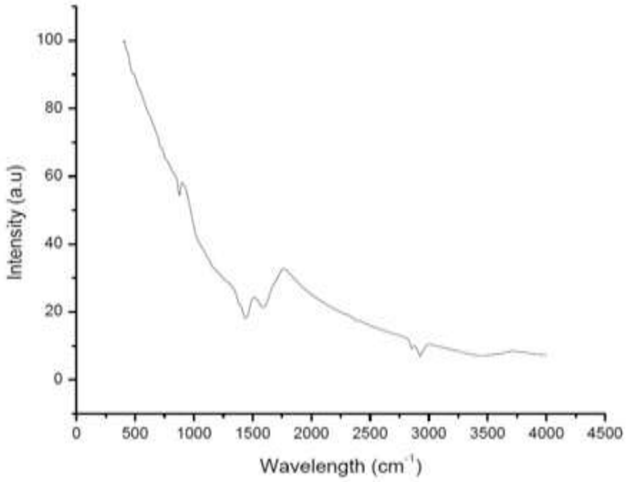

Figure3: FTIR spectra ofGSAC (c)

Literaturepertainsdue to theincreasing demandof activated AC;there is astrong need for thesortoflow-cost,easy availability,highly efficientandeco-friendly precursorsfor thepreparationofACthatshouldbecost-effective withcommercially availableACIdris, (2020).Onthecontrary,groundnutshellhasreceivedmuchlessattentionasa precursorforthepreparationofAC. So,thisstudywasanotherattempttoexploregroundnutshellasan inexpensive precursorforthe preparation ofAC.

3.2CharacterizationofActivated Carbon

TheyieldandbasiccharacterizationofGSACareaspresentedinTable5.Fromtheresultitcanbeobserved thattheobtainedyield was (68.%)ofGSACmaybeduetotarformationandliberationofvolatileparticles,andweight ofthe sample increased after chemical activation because ofimpregnated $ZnCl_2$thatusedduring chemicalactivation Asadullah, (2007). ThesurfaceareasofBETandLangmuirwere395.5and1005m^2/g,respectively.Itclearlyshowsthat theobtainedsurfaceareaandporesizearedependingontheamountofintroduced$ZnCl_2$andactivation temperatureMolina-Sabio, (2014).Similarresultshavebeenexplainedinvariousstudieswithdifferent typesofprecursorsalong with$ZnCl_2$ activationKalilet al (2000) andQian, (2007).Itisanevidentthatmovementofthevolatilesubstancesthroughporepassages wasnothinderedandwerereleasedfromthecarbonsurfacewiththeactivationof$ZnCl_2$.Themechanismof poreformationinGSACby$ZnCl_2$ activationisnotwidelyknown.However,$ZnCl_2$ mainlydegradescellulosebydehydration during pyrolysiswhichcauses aromatization ofthe carbonaceous skeleton.

Well-developedporoussurfaceofGSAC wasobservedviaFESEMmicrograph(2500×)which isconsideredas channels to themicroporousnetwork (Figure.3a).Itshowedthattheadsorbenthaveroughtexturewith heterogeneoussurfaceand avariety ofrandomly distributedporesize.EDXanalysisofGSAC (Figure.3b) showed the presence of four elements– carbons (88.62%), oxygen (15.30%), Zinc (0.72%) and Chloride (0.36%). Presenceofoxygenmaybeattributedtothelittleamount ofmoistureinthecarbon. Very lowlevelof ZincandChloridewereobserved,becauseoftheusageof$ZnCl_2$asanimpregnatingchemicaltoactivationof carbon.TheFTIRspectraintherange400to4000cm^{-1} ofGSACwaspresentedin(Figure3c).Thistypeofanalysis usedforidentificationoforganicfunctionalgroupspresentedonthesurfaceNamasivayam, (2006). IntheFTIRspectruma significantpeakat1453cm^{-1}isassignedtothecharacteristicCH_2bendingvibrationsandisprobablyascribable tocarbonylgroupswhicharehighly conjugatedin the graphemelayer.Thisisconsistentwiththebasicnatureof thecarbon.Peaklocatedat1602cm^{-1} are duetoConjugatedC=CStretchingVibrations. The peak located at 2923cm^{-1} is due to CH_2 stretching vibrations.

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3.3 EffectofContactTime and InitialDyeConcentration

Effectofcontacttimeonadsorptionofmethylene blueonGSACispresentedin(Figure3).Resultsindicated thatrateofdyeremovalprogressivelyincreasedastheagitationtimeincreased.Toincreasetherateofcolor removalwithagitationtimemaybeattributedtodecrease eindiffusionlayerthicknesssurrounding theadsorbent particles. The equilibrium time increased with dye concentration and it was dependent on initial dye concentrationfortherangeofconcentrationusedforthe study.Themaximum equilibrium timeofmethylene blue by GSAC (500 mg) was recorded as 20 h.Further,it revealedthatwith increasein dyeconcentration,percentageremovalofdyedecreased whereastheamountof thedyeadsorbedunitweightofthe adsorbent(mg/g)increased in the rangeof concentration tested suggesting that, dye removal using adsorption technique is concentration dependent. Similarresults have been reported byseveralauthors foradsorption ofdyesusinglowcostmaterialsRajasekharet al., (2009).

3.4 EffectofpHon DyeAdsorption

TheeffectofpHon adsorptionofmethyleneblueonto GSACwasinvestigated in differentpH rangeof3.0, 5.0, 7.0,9.0and11.0withfixeddyeconcentration(10ppm)andfixedGSACdose(500mg/50mL)at6h. The removalcapacity ofGSACshowednodiscerniblepatternoverentirepH range.Maximummethylene blueuptake(99.45%)occurredatpHof9.0withaadsorptionloadingof500mg/50mLandlowestadsorption (71.12%)occurredataninitialpHof3.0.Similarlyremovalpercentagewasmeasuredas90.23%,98.35%and93.87%forpHlevelof5.0,5 . 7.and11.0respectively.The resultsobtainedareincloseagreementwith previously reported studiesAgarwal, (2006) and Barkat et al., (2009).

3.5 Chemical Composition of the Groundnut Shell Powder

The chemical composition of groundnut shell powder consists of the following element oxide shown in table 6, after carbonization in crucible furnace it produces the final activated carbon for water treatment.

Table 6: Chemical Composition of the Groundnut Shell Powder

S/No	Element Oxide	(wt %)
1	SiO_2	5.92
2	Al_2O_2	2.41
3	Fe_2O_3	6.05
4	CaO	2.1
5	MgO	0.3
6	LOI	80.56

IV. CONCLUSION

Thisstudy used the ground nut shell as carbon adsorbent in removing toxic metal. The physiochemical properties of carbon were determined in table 3, the chemical characteristics of the present heavy metals in theRafinDutse stream water were determine ; Pb, Cu, Zn, Cd, Cr, Mn, Fe, Hg and Ni with high concentrations, (0.01mg/L, 0.98mg/L, 0.05mg/L, 0.002mg/L, 0.03mg/L, 0.04mg/L, 0.02mg/L,0.021mg/L and 0.20mg/L)while As was not detected and were treated with activated carbon, it reduces drastically shown in table 2 and 3 respectively. The characterization of groundnut shell ash as activated carbon were also determine and shown in table 3 ; yield were 68%, fixed carbon 81.56%, ash content 3.10%, moisture content 2.58% and pH of 5.7.The comparison of means concentration of heavy metals was within the reference limit of WHO and FEPA standard which were shown in table 4.GSACwassynthesizedandcharacterizedby differenttechniquesincluding FESEMandEDX. GSACshowedhighmethyleneblue adsorptionefficiency onBatch.The groundnut shells investigated in this study exhibited high potential for the removal of Cu, Mn, Hg, Cr, Fe,Ni, Pb etc. were analyzed and reduces drasticallyfrom aqueous solution even without physical or chemical modification. Theadsorptionofheavy metal washighly dependentoncontacttime,pH,adsorbent dye,initialmetal ionconcentrationandtemperature.Theadsorptionof heavy metalswasfoundtobeoptimumatacontacttimeof120min;pH5.7adsorbentdoseof2.0g/L;metalionconcentrationof25 mg/L; and temperature of 41.5 °C. For all the isotherm modelstested. ThesurfaceareasofBETandLangmuirwere395.5and1005m^2/g,respectively.It is therefore concludedthatgroundnut shellactivatedcarbon can berelied on in drinking watertreatment and this study significantly emphasizes that ground shell activated carbon GSAC would be effective adsorbent to remove heavy metals.

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