

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:

Clean and safe drinking water is a basic need for humans and animal world over. To get good water quality, several water treatment methods are being used. This paper adopts groundnut shell as source of activated carbon for drinking water treatment. The groundnut shell was separated from peels using threshing method and washed the shell repeatedly with tap water in order to remove all the dirt's and other contaminant. It was further washed with distilled water and sun dried for three (3) days. The dried sample was ground to obtain a powder forms. It was sieved with a 500 μ m mesh and stored in airtight container, 300g of the powdered sample. The groundnut shell was treated with 1 M solution of K_2CO_3 , $ZnCl_2$ and KOH. A certain amount of powder was placed in a crucible muffle furnace carbonized at temperature of 400⁰C for 2 hours, cooled and then stored in a sealed bag. Thereafter, it was cleaned with distilled water until its pH value was 5.7. The application of the activated carbon developed was on raw water from unprotected Rafin Duste stream water near charachar, Azare Area of Bauchi State, Nigeria. The selected heavy metals levels in the digests were analyzed using atomic absorption spectrometer (AAS), while temperature and pH were analyzed using the appropriate equipment. Tests were carried out before and after treatment with the activated carbon. The parameters tested were, temperature, turbidity, color, salinity, odor and, pH were shown in table 1. The water quality changes noticed included the reduction in turbidity, color of the water, and pH (decreased from 6.91 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 were carried out to identify the level of the pollutants discharged to the environment. The heavy metals presents before water treatments were; (Pb, Cu, Zn, Cd, Cr, Mn, Fe, Hg and 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. GSAC was synthesized and characterized by different techniques including FESEM and EDX. The groundnut shell activated carbon (GSAC) showed high methylene blue adsorption efficiency on Batch. 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 drastically from aqueous solution even without physical or chemical modification. The adsorption of heavy metal was highly dependent on contact time, pH, adsorbent dose, initial metal ion concentration and temperature. The adsorption of heavy metals was found to be optimum at a contact time of 120 min; pH 5.7 adsorbent dose of 2.0 g/L; metal ion concentration of 25 mg/L; and temperature of 41.5 ⁰C. For all the isotherm models tested. The surface areas of BET and Langmuir were 395.5 and 1005 m²/g, respectively. It clearly shows that the obtained surface area and pore size are depending on the amount of introduced $ZnCl_2$ and activation temperature. Well-developed porous surface of GSAC was observed via FESEM micrograph (2500 \times) which is considered as channels to the micro porous network (Figure. 3a). It showed that the adsorbent have rough texture with heterogeneous surface and a variety of randomly distributed pore size. EDX analysis of GSAC (Figure. 3b) showed the presence of four elements–carbons (88.62%), oxygen (15.30%), Zinc (0.72%) and Chloride (0.36%). Presence of oxygen may be attributed to the little amount of moisture in the carbon. Very low level of Zinc and Chloride were observed, because of the usage of $ZnCl_2$ as an impregnating chemical to activation of carbon. The FTIR spectra in the range 400 to 4000 cm^{-1} of GSAC was presented in (Figure 3c).

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

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I. INTRODUCTION

Water is vital to all living things and, is present in almost all foods, unless steps have been taken to remove it, even though it contributes no calories to the diet Hanjra *et al.*, (2019). Water is essential for life and livelihoods; it is also a core infrastructure sector of the economy. Four out of every five people around the world are served by renewable freshwater services. But because the distribution of freshwater is uneven in space and time, more than one billion people live under water stress and only 15% of the world's population lives with relative water abundance. It is well established that vast changes with great geographic variability occur in fresh water resources and their provisioning of ecosystem services in all scenario considered under the Millennium Ecosystem Assessment carried out between 2018 and 2022 Millennium Ecosystem Assessment Report (2022).

Wastewater is the liquid end-product, or by-product, of municipal, agricultural, and industrial activity. As such, the chemical composition of wastewater naturally reflects the origin from which it came. Wastewater (in the sense of the effluent) is composed of 99% water and 1% suspended, colloidal and dissolved solids. Wastewater has been de- scribed as both "a resource and a problem" Qadir *et al.*, (2018). Potential problems principally relates to the presence of toxic chemicals (from industrial sources of effluent) and the presence of pathogenic microorganisms. Irrigation with even treated wastewater can lead to excess nutrients, pathogens, heavy metals and salts building up on the irrigated land, unless care is taken. The separation of industrial and domestic wastewater will facilitate the likelihood of safe reuses Patil (2019).

Industrial wastewater is one of the important sources of pollutants leading to the pollution of the water environment. During the last century large amounts of industrial wastewater was discharged into rivers, lakes and coastal areas. This has resulted in serious pollution problem in the water environment and caused negative effects to the ecosystem and human life. These wastes often contain a wide range of contaminants such as petroleum hydrocarbons, chlorinated hydrocarbons, heavy metals, various acids, alkalis, dyes and other chemicals which greatly change the physico-chemical properties of water. All these chemicals are quite harmful or even fatally toxic to the aquatic ecosystem Ado *et al.*, (2019).

Heavy metal pollution has become one of the most serious environmental problems today. Wastewaters containing heavy metals are produced each year by textile industries and other processes. Most of the chemical methods used in cleaning up of these heavy metals are not effective. Microorganisms have been used extensively in cleaning of heavy metals in the environment but plant has not been used extensively in removing heavy metals from waste water. This necessitates the use of groundnut shell for adsorption of heavy metals. Nickel and chromium which are widely used and extremely toxic in relatively low dosages, the main pathway through which nickel and chromium enters the water bodies via wastes from industrial processes. Heavy metals are 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, heavy metal pollution has become one of the most serious environmental problems today and can cause different aliment like cancer, hypertension, kidney tumors and reproductive difficulties. This study is set to address the challenge to environmental pollution by providing the activated carbon from groundnut shell that mediated adsorption best among the various dye removal processes. Adsorption process using commercial activated is high cost, this provide the search for alternative and low-cost adsorption, renewable and easily available material from the surrounding areas, also for large economic-scale production to dye removal processes. In this case, agricultural wastes are available and an excellent option in the purification of contaminant from liquid and gas streams that evolve from industrial and domestic sources Alluri, (2017).

Activated carbon (AC) is an effective fettering material, highly porous with immense surface area. The most common described activated carbon is that it acts like a sponge, sucking contaminates from liquids and gases. Activated carbon removes many organic and some specific inorganic substances such as chlorine, cadmium, nicked, lead and chromium from common industrial pollutants. Activated carbon mediated adsorption is the best amongst various dye removal processes; it just because of its simplicity, low cost and reusability of non-toxic adsorbent Idris, (2020).

Groundnut botanically belongs to Araches hypo Gaea Linn of leguminous family. Groundnut is a self- pollinated; annual and herbaceous legume crop. The shell constitute about 25-35% of the pod. The seed accounts for the remaining portion (65-75%) Sada, *et al.*,(2018). The world countries, Nigeria is among the foremost producers of groundnut, with an annual production rate of about 2.699 million metric tonnes in 2002 and 1.55 million tonnes in 2008 Sada, *et al.*, (2018). It has the potential to produce high tonnes in future due to high demand from groundnuts products such as groundnut oil,

spread, paste and concentrate. Over the years, palm kernel, coconut and groundnut shells are among the major solid waste especially in the developing countries of the world. Their potential as a very useful engineering material has not been fully investigated and utilized. The utilization of these shells will reduce waste management cost, leads to clean environment as result of pollution reduction and the increase in financial base of the farmer when such waste are sold as raw materials. They are used in the abatement of hazardous contamination of the environment.

Henderson *et al.*, (2019) investigated wastewaters from textile and tannery effluents attract attention of environmental protection agencies all over the world. They not only deface the look of natural waters, but are also highly toxic Chu, (2017). Some dyes are reported to harm mammalian cells by causing kidney tumors and reproductive difficulties. These dyes are also potentially carcinogenic, genotoxic, mutagenic in many animal species Adsorption process is considered very effective in textile and tannery wastewater treatment. It proves superior to the other processes by being sludge free and can completely remove even very minute amounts of dyes in wastewater Nigarn *et al.*, (2016). Adsorption process 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 adsorptions Nimrat *et al.*, (2019).

Toyin Omotoso, (2017) investigate the adsorption of toxic water pollutants using modified groundnut shell to examine in adsorption of heavy metals such as copper (Cu), magnesium (Mg), Iron (Fe) and Chromium (Cr) in an industrial effluent discharge. The result of the capacity was found to be Fe>Cr>Mg for modified groundnut shell in the order of 100%,98%, 70% and 9% respectively. This study is a prognosis into capacity of plant substrate in bioremediation of polluted soil and groundwater, reducing different heavy metals in the stream effluent. Groundnut shell is a good absorbent of Fe and Mg. However, the effect of pH concentration on the adsorption of metals was not investigated.

Isah, (2020) investigate on adsorption of lead ions on groundnut shell activated carbon. This work focuses on the utilization of activated carbon prepared from groundnut shell for the removal of lead from water. The effects of temperature, contact time, and initial concentration of lead on the adsorption process have been investigated. Groundnut shell activated carbon is proven to be capable of removing lead from water with a very high efficiency under ambient conditions. Adsorption of lead onto groundnut shell activated carbon is best described by the pseudo second order kinetic model and the Langmuir adsorption isotherm model.

II. MATERIALS AND METHODS

Materials

The materials, equipment and instruments used in this study were all calibrated to check their status before and in the middle of the experiments. All Glass wares were cleaned with 10% concentrated HNO₃ in order to oxidize and remove impurities ties on the container surfaces. Groundnut, ZnCl₂, KOH, H₃PO₄. Apparatus such as volumetric flasks, sample bottles, funnel, watch glass, burette, beaker, measuring cylinder, and pipette were thoroughly washed with detergents and tap water, and then rinsed several times with deionized water. Crucible furnace, Threshing machine and grinding machine, sieve and filter paper were used.

Sample Collection

The wastewater sample of Rafin Dutse was collected from charachar near Azare, Katugum Local Government Area of Bauchi State, Nigeria. The water samples were collected by a stratified sampling method from different spot which was shown in figure 1. The samples were 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 Rafin Dutse Stream Water Charachar, Azare

Sample Collection Preparations of Activated Carbon

The groundnut was obtained from Alkali Market, Alkali local Government Area of Bauchi State, Nigeria. The groundnut sample was separated from peels using threshing method and washed the shell repeatedly with tap water in order to remove all the dirt's and other contaminant. It was further washed with distilled water and sun dried for three (3) days. The dried sample was ground to obtain a powder forms. It was sieved with a 500 μ m mesh and stored in airtight container, 300g of the powdered sample. The groundnut shell was treated with 1 M solution of K_2CO_3 , $ZnCl_2$ and KOH. A certain amount of powder was placed in a crucible muffle furnace carbonized at temperature of 400 $^{\circ}$ C for 2 hours, cooled and then stored in a sealed bag. Thereafter, it was cleaned with distilled water until its pH value was 5.7 and the samples of the groundnut, ground shell and activated carbon were shown in figure 2(a), 2(b) and 2 (c)



Figure 2(a): Groundnut



Figure 2(b): Groundnut Shell Powder



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

Application of Activated Carbon

Activated carbon prepared from groundnut shells was used for the treatment of open water from Rafin Dutse Charachar, Azare. The experiments were carried out in triplicate. Samples of the raw water (100 ml) were mixed with carbon (0.1 g) in 250 ml Erlenmeyer flasks. The mixtures were shaken at 200 rpm in a temperature-controlled shaker at $(25 \pm 2)^{\circ}$ C for 2 hours then filtered using a Whitman filter paper size 15 to remove the carbon. Full chemical and bacterial analysis was done to check the water parameters after treating with activated carbon. The chemical analysis included determination chemical oxygen 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) and 3(c) respectively.

III. Results and Discussion

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 / N O	Characterization of Water	pH		Temperature (°C)		Turbidity (NTU)		Salinity (ppm)		Colour		Odour(TON)	
		Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
	(Trials)												
1	First 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

- The analysis of wastewater for heavy metal contamination is an important step in ensuring human and environmental health safety. Excess levels of heavy metals might cause several short term and long term effects to human. The WHO standards for the pH of the drinking water ranges from 6.5 to 7.5. The tests for the pH of the water was 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 be acidic. However, the activated carbons raise the pH of water near the neutral value when injected into water system.
- The effect of temperatures was performed at three different readings with thermostatic shaker machine while keeping all other parameters constant, with average of 73.2°C before applying activated carbon, after applying activated carbon it reduces to 42.9°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°C to prevent the growth of the organism.
- 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 must 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.
- 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 before Absorbent 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)
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

Table 4: Comparison of the mean concentration of heavy metals with some international water standards

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

The analysis of wastewater for heavy metal contamination is an important step in ensuring human and environmental health safety. Excess levels of heavy metals might cause several short term and long term effects to human. Table 2 illustrates the distribution of metals concentration in an average value of wastewater samples before adsorbent treatment, the levels of Pb, Cu, Zn, Cr, Mn and Fe, while Cd was not detected in the effluent samples analyzed 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. The concentrations of heavy metals present in the Rafin dutse charachar stream water effluent samples were found to vary significantly. The concentration of activated carbon for Pb, Cu, Zn, Cr, Mn, Fe , Hg and Ni obtained were reduces drastically shown in table 3, with the following values; 0.001 mg/L, 0.53 mg/L, 0.20 mg/L,0.0001 mg/L, 0.02mg/L, and 0.03 mg/L, 0.03 mg/L, 0.01 and 0.13mg/L respectively, while As was not detected in the effluent samples analyzed. The levels of Cu, Zn, Cr, Mn, Hg, Fe and Ni were below the maximum limits set by WHO and FEPA while the non-detected levels of As could be due to its absence in the raw materials in use at the time of sample collection Sankpal, (2012).

The higher concentrations of Fe and Zn could be attributed to the use of brass as cleaning material. Secondly Zn is a constituent of galvanized steel including water distribution pipes and its presence might be due to corrosion, the metal may find its way to the wastewater and subsequently to the environment Pawlowski, (2013). When compared with the FEPA and WHO standards in Ta- ble 3, the Cr concentration of 0.03 mg/L is higher than the permissible limits of 0.05 mg/L set by FEBA and WHO standards. Possible sources of Cr in industrial effluent could be linked to chrome plating and alloys for corrosion prevention Oliveira, (2012). Cu concentration of 0.98 mg/L is less than reference limits as shown in Table 4, and WHO standards of 2.0 and 1.0 mg/L respectively WHO (2019) and FEPA (2019) . The concentration of Pb obtained was 0.01 mg/L which is corresponded to the FEPA and WHO acceptable limits of 0.01 mg/L. Elevated Pb concentrations in stream effluents could be much associated with metallurgy and metal processing among others Harrison, (2018). The concentration of Fe was 0.02 mg/L, this is above WHO and less limits of FEPA of 0.05 mg/L, 0.01 mg/L. Fe is one of the most abundant element in the earth crust Frey, (2012) and can be discharged to environment through various industrial processes Ado, (2015). The concentrations of the pollutants reported in this study were not alarming, 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 ^o C	0.155
15	Density ((cm ³ /g)	1.46

Figure 3: Analysis of GSAC (a) FESEM and (b) EDX.

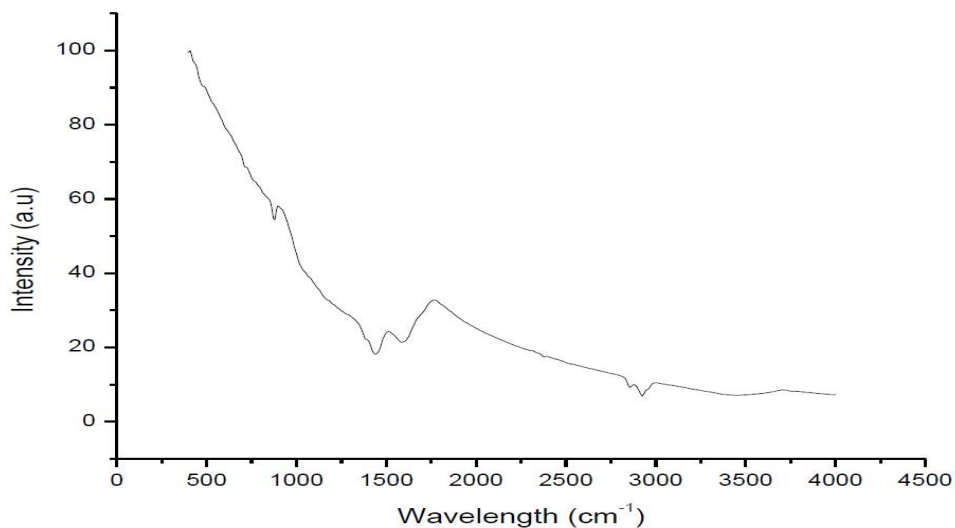
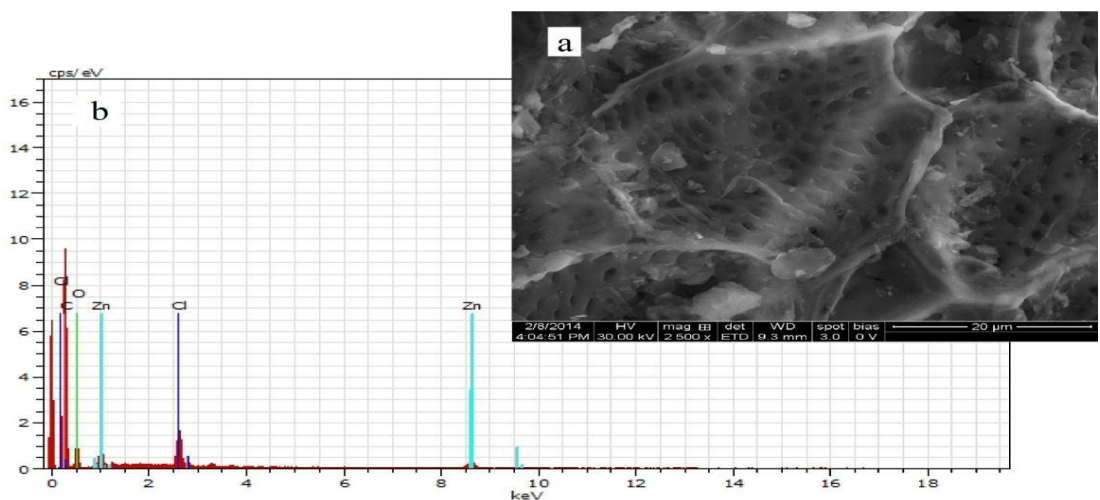


Figure 3: FTIR spectra of GSAC (c)

Literature pertains due to the increasing demand of activated AC; there is a strong need for the sort of low-cost, easy availability, highly efficient and eco-friendly precursors for the preparation of AC that should be cost-effective with commercially available AC Idris, (2020). On the contrary, ground nut shell has received much less attention as a precursor for the preparation of AC. So, this study was another attempt to explore groundnut shell as an inexpensive precursor for the preparation of AC.

Characterization of Activated Carbon

The yield and basic characterization of GSAC are as presented in Table 5. From the result it can be observed that the obtained yield was (68.%) of GSAC may be due to tar formation and liberation of volatile particles, and weight of the sample increased after chemical activation because of impregnated $ZnCl_2$ that used during chemical activation Asadullah, (2007).

The surface areas of BET and Langmuir were 395.5 and 1005 m^2/g , respectively. It clearly shows that the obtained surface area and pore size are depending on the amount of introduced $ZnCl_2$ and activation temperature Molina-Sabio, (2014). Similar results have been explained in various studies with different types of precursors along with $ZnCl_2$ activation Kalil *et al* (2000) and Qian, (2007). It is an evident that movement of the volatile substances through pore passages was not hindered and were released from the carbon surface with the activation of $ZnCl_2$. The mechanism of pore formation in GSAC by $ZnCl_2$ activation is not widely known. However, $ZnCl_2$ mainly degrades cellulose by dehydration during pyrolysis which causes aromatization of the carbonaceous skeleton.

Well-developed porous surface of GSAC was observed via FESEM micrograph (2500 \times) which is considered as channels to the micro porous network (Figure. 3a). It showed that the adsorbent have rough texture with heterogeneous surface and a variety of randomly distributed pore size. EDX analysis of GSAC (Figure. 3b) showed the presence of four elements—carbons (88.62%), oxygen (15.30%), Zinc (0.72%) and Chloride (0.36%). Presence of oxygen may be attributed to the little amount of moisture in the carbon. Very low level of Zinc and Chloride were observed, because of the usage of $ZnCl_2$ as an impregnating chemical to activation of carbon. The FTIR spectra in the range 400 to 4000 cm^{-1} of GSAC was presented in (Figure 3c). This type of analysis used for identification of organic functional groups presented on the surface Namasivayam, (2006). In the FTIR spectrum a significant peak at 1453 cm^{-1} is assigned to the characteristic CH_2 bending vibrations and is probably ascribable to carbonyl groups which are highly conjugated in the grapheme layer. This is consistent with the basic nature of the carbon. Peak located at 1602 cm^{-1} are due to Conjugated C=C Stretching Vibrations. The peak located at 2923 cm^{-1} is due to CH_2 stretching vibrations.

Effect of Contact Time and Initial Dye Concentration

Effect of contact time on adsorption of methylene blue on GSAC is presented in (Figure 3). Results indicated that rate of dye removal progressively increased as the agitation time increased. To increase the rate of color removal with agitation time may be attributed to decrease in diffusion layer thickness surrounding the adsorbent particles. The equilibrium time increased with dye concentration and it was dependent on initial dye concentration for the range of concentration used for the study. The maximum equilibrium time of methylene blue by GSAC (500 mg) was recorded as 20 h. Further, it revealed that with increase in dye concentration, percentage removal of dye decreased whereas the amount of the dye adsorbed unit weight of the adsorbent (mg/g) increased in the range of concentration tested suggesting that, dye removal using adsorption technique is concentration dependent. Similar results have been reported by several authors for adsorption of dyes using low cost materials Rajasekhar *et al.*, (2009).

Effect of pH on Dye Adsorption

The effect of pH on adsorption of methylene blue onto GSAC was investigated in different pH range of 3.0, 5.0, 7.0, 9.0 and 11.0 with fixed dye concentration (10 ppm) and fixed GSAC dose (500 mg/ 50 mL) at 6 h. The removal capacity of GSAC showed no discernible pattern over entire pH range. Maximum methylene blue uptake (99.45%) occurred at pH of 9.0 with a adsorption loading of 500 mg/50mL and lowest adsorption (71.12 %) occurred at an initial pH of 3.0. Similarly removal percentage was measured as 90.23%, 98.35% and 93.87% for pH level of 5.0, 5.7. and 11.0 respectively. The results obtained are in close agreement with previously reported studies Agarwal, (2006) and Barkat *et al.*, (2009).

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 ₂ O ₂	2.41
3	Fe ₂ O ₃	6.05
4	CaO	2.1
5	MgO	0.3
6	LOI	80.56

IV. Conclusion

This study 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 the Rafin Dutse 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. GSAC was synthesized and characterized by different techniques including FESEM and EDX. GSAC showed high methylene blue adsorption efficiency on Batch. 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 drastically from aqueous solution even without physical or chemical modification. The adsorption of heavy metal was highly dependent on contact time, pH, adsorbent dye, initial metal ion concentration and temperature. The adsorption of heavy metals was found to be optimum at a contact time of 120 min; pH 5.7 adsorbent dose of 2.0 g/L; metal ion concentration of 25 mg/L; and temperature of 41.5 °C. For all the isotherm models tested. The surface areas of BET and Langmuir were 395.5 and 1005 m²/g, respectively. It is therefore concluded that groundnut shell activated carbon can be relied on in drinking water treatment and this study significantly emphasizes that ground shell activated carbon GSAC would be effective adsorbent to remove heavy metals.

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