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Chemical Synthesis and Characterization of Carbon Nanotube (CNT) from Rice Husk Wastes

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Abstract: the research work based on chemical synthesis of CNT using microwave method from rice husk waste materials. The carbon nanotube (CNT) synthesized was characterized using using XRD (X-ray diffraction), SEM (Scanning Electron Magnifier), EDX (Energy-dispersive X-ray) and FTIR (Fourier Transform Infrared Spectroscopy. The percentage yield of carbon nanotube (CNT) powder produced from the rice husk agriculture waste material was 50 g, which corresponded to 35% % yield. The Energy-dispersive X-ray (EDX) analysis reveals the presence of carbon, oxygen and sulphur is (65.60, 20.10 and 14.30) % respectively. The results confirm the high purity of carbon nanomaterial.at an atomic ratio of (6.7: 1.8: 1.3).The SEM results reveals a well-developed agglomeration with significant reduction in grain size and the particle size distribution fell in the range of 20 µm to 100 µm, with a mean particle size of 385 nm. The XRD pattern shows broad diffraction peaks that lies between 26.5º to 30.5º values of 2θ indicates pristine carbon (111), with little diffraction at 32.5º indicating (220). The presence of carbon demonstrated by the peak near to 2θ of 45º to 49.5º and peak near to 54° to 58.5º of 2θ value correspond to interlayer spacing of about 0.75nm (311) and indicate presence hydroxyl group in carbon powder. The FTIR results show that the peaks in the sample are analogous, C–H, C≡C, C=C and =C-H with medium stretching peaks were observed around 2898.29 cm^{-1}, 2156.07 cm^{-1}, 1580.4 $cm^{-1}$and 728.67 cm^{-1} respectively, which may be due to functional groups alkene for aromatic in the sample. As established from the characterization results, the carbon nanotube material has a good prospective potential for producing high valuable adsorbent product for reducing environmental pollution as well as other nano-materials based application.

1. Introduction

Carbon Nanoparticles such as graphene, nanodiamonds fullerene, nanotubes, and including activated carbon are the most attractive nanomaterials in the field of nanotechnology (Aadil *et al.* 2020; Aldwayyan *et al.* 2013). Due to their unique physical and chemical properties and their revolutionizing wide range of applications, resulting to extensive research interest (Greil, 2015). Among these, carbon nanotubes (CNTs) are the most interactive materials, made of hexagonal network of sp^2 hybridization of carbon atoms that is similar to graphene (Zhang *et al.* 2013; Rathinavel *et al.* 2021; Kolahdouz *et* *al. 2*013;). They are one of the strongest carbon nano-materials due to carbon-carbon σ bonds and can be mainly grouped into single wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs) (Asnawi *et al. 2*018).

Recently, the management of agriculture waste products such as rice husk, cocoa pod, sugarcane, and wood wastes have led to environmental pollution issue, because of their vast volume and slow decomposition rate (Olokoba and Mciver, 2024). For sustainable development process, underutilised resources such as rice husk waste can be easily converted into useful carbon sources such as hydrochar and highly porous carbon materials. A carbon-rich porous material is synthesized when biomass is subjected to a thermal and chemical process and can act as a precursor for carbon nanotubes (CNTs) synthesis, and this can be produced from a residue of paddy called rice husk (RH) (Adeola and Duarte, 2023). Rice husk (RH) is rich in cellulose and lignin which makes it as a good and economic source of carbon precursor, due to its very low processing costs if it disposal costs are included (Siddiqui *et al. 2*019). Apart from environmentally unfriendly disposal methods, current applications of rice husks are limited to produce low-value products. Synthesis of carbon nanotubes (CNTs) using agricultural waste material has received attention from researchers, carbon nanotubes (CNTs) can be applied in various fields of Nano-technology and science (Olokoba and Mciver, 2024), with variety of environmental potential applications such as the adsorption of organic pollutants, energy storage, heat and electrical conduction and removal of heavy metals from water (Hafez *et al.* 2024; Alshahateet *et al. 2*024; Asghar *et al.* 2024; Aaddouz *et al.* 2023; Athaib *et al.* 2022). Agricultural waste material such rice husks (RH) have been classified as the simple, cheap and eco-friendly sources for the preparation of carbon nanotubes (CNTs) (Chen *et al. 2*016).

The micro-structure and morphological characterization of carbon nanotubes (CNTs) using spectroscopy and scanning electron microscope (SEM) and as well as X-ray diffraction (XRD) analysis have confirmed the presence of carbon nanomaterials consisting of CNTs and other structures. Therefore, this study seeks to chemically synthesize and characterized carbon nanotubes (CNTs) produced from rice husks (RH) waste materials.

2. Materials and Method

2.1 Reagents and Chemicals

The analytical reagents were purchased from Merck (Darmstadt, Germany). Methanol, acetonitrile and formic acid were of HPLC grade and ultra-high pure water was used throughout the experimental runs. All other reagents and chemicals were of analytical grade. Working standard solutions were prepared by appropriate dilution with deionized water. Hydrochloric acid and sodium hydroxide solutions were used in adjusting the pH of the samples.

2.2 Green Synthesis of Carbon Nanomaterial from Rice Husk

Graphene was prepared from rice husk by using simple microwave furnace method which is been classified as top-down approach method. The production of graphene oxide (GO) from rice husk was realized by adapting the top-down approach from carbonized rice husk (CRH). The rice husk was purchased in a local paddy mill in Ilorin, Kwara State, Nigeria. Potassium hydroxide pellets (KOH, SigmaAldrich) was used as the activating agent. Rice husk is the primary raw material for this research work. The utilization of rice husk is crucial to reduce the waste through safe and sustainable approach.

2.3 Experimental Details

2.3.1 Synthesis of Carbon Nanomaterials.

Rice husks were washed vigorously using distilled water. This is been done manually by washing the rice husk severally and changing of water until the whole material turns clean without the trace of any unwanted materials for more than 1hr after which was spread and then dried in natural air at constant room temperature for 24hr. Thereafter, the dried rice husk was sieved before changing into powder by the use of mechanical method and using ferrocene $Fe(C5H5)2$ as a catalyst and then chemically activated by KOH using a ratio of 1:2.

The quantity of rice husk powder measured determines the quantity of the ferrocene to be used, that was why we measured 50g (RH) and then 10gm of ferrocene to start with. Ferrocene is been applied to rice husk powder according to the quantity of it. 50g of rice husk with 10gm of ferrocene is been applied +100 mL of ethanol and 40g of KOH in a round bottom flask while the simultaneously stirring the mixture for 30 min to get a homogeneous solution. Ordinarily ethanol cannot dissolve KOH, a small quantity of distilled water was added to it so as to dissolve before transferring it to the mixture of ethanol and ferrocene while stirring for 30 mins and then transfer into the rice husk powder with a continuous stirring for another 30min in order to get homogenous solution. Every 100 mL of ethanol was mixed with 10, 15 and 20gm of ferrocene in three stages (**Figure 1 and 2**) clearly demonstrates the schematic mechanism of the microwave synthesis of graphene.

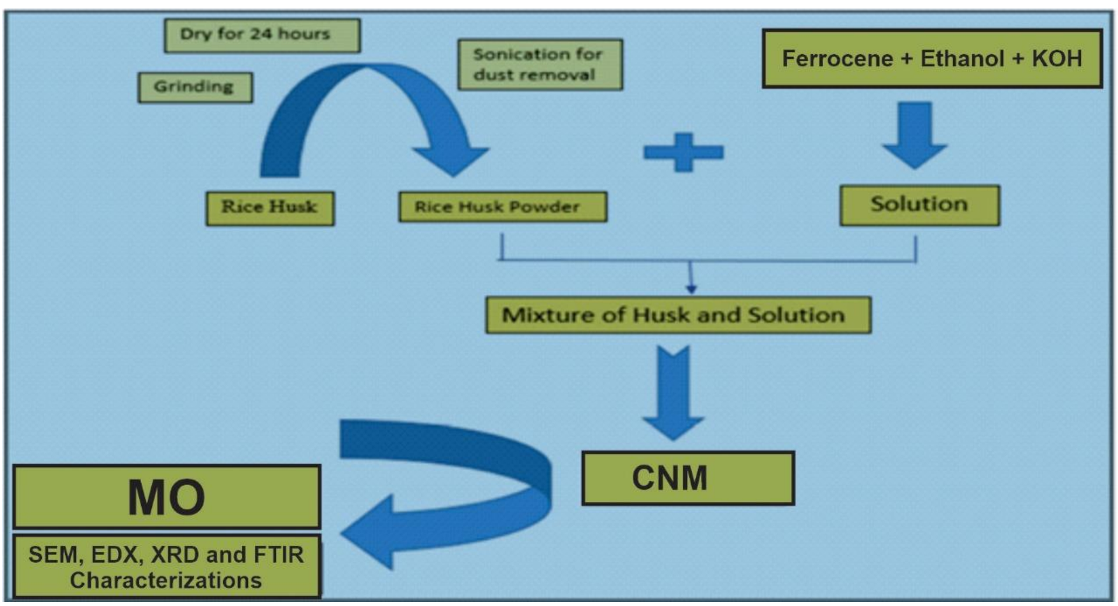

Figure 1. Schematic diagram of all steps included in the synthesis of graphene from rice husk by a simple microwave process. Reprinted from (Ismail *et al.* 2019).

The three resulting mixtures of ethanol and ferrocene (100 mL-10 gm, 100 mL-15 gm, 100 mL-20gm) were mixed with rice husk powder after which it transferred to the crucible and then covered with foil paper. It is important to label it one after the other to avoid mix up before inducing it into the microwave oven. It is observed when stirring that, it gives a choking smell and then gives the colour orange with the mixture of KOH, Ethanol and Ferrocene. The addition of Rice husk powder to the mixture then change the color to oily brownish color with a continuous stirring until the mixture become thick before transferring into crucible and then covered with foil paper before microwave at 400°C for 2hrs shows the presence of CNTs. Identification of the CNTs by selective method after the labelling have been heated off is been observed and then we removed it one after the other by the use of thong and then we leave it for cooling for at least 20min. Then, the samples were subjected to characterization methods.

Figure 2. Diagram showing the synthesis of CNT from rice husk.

2.4 Characterization Techniques

The material was studied using XRD (X-ray diffraction), SEM (Scanning Electron Magnifier), EDX (Energy-dispersive X-ray) and FTIR (Fourier Transform Infrared Spectroscopy. Energy-dispersive X-ray (EDX) analysis was used to determine the elemental composition of the synthesized carbon nanomaterial and the histogram representation (Ismail *et al.* 2019).

3. Results and Discussions

3.1 SEM-EDX analysis of carbon nanomaterial form rice husk

SEM micrographs (**Figures 3a-c**) revealed slightly irregular spherical CNP particles with a high degree of agglomeration and large pores. Carbon nanoparticle CNP size analysis was conducted using the SEM images, and the representative histogram was generated using EDX (**Figure 3d**). The particle size distribution fell in the range of 20 µm to 100 µm, with a mean particle size of 385 nm, as depicted in the figures which shows well-developed agglomeration growth with significant reduction in grain size. The grain size is ~20 µm, 50 µm and 100 µm for 10000x, 9000x and 8000x respectively. The possible reason for decreasing the grain size is that more crystal nucleus was formed with an increase in carbon content. It is well known that carbon nanomaterial contains a small amount of donor impurities, which yields the material fine-grained (Badapanda *et al.* 2012). The images from SEM of 50g samples show the formation of carbon nanomaterial structures. Surface morphology indicates a rough twisted and randomly oriented web-like network, coarse surfaces with various cracks and crevices, showing that the reduced powders retain the shape of the reduction vessel. Some of the particles may be onion-like carbon nanostructures, more agglomerated although from SEM photograph the differences between samples are not so clear. Depending on the nature and amount of the catalyst, some differences are revealed in SEM images.

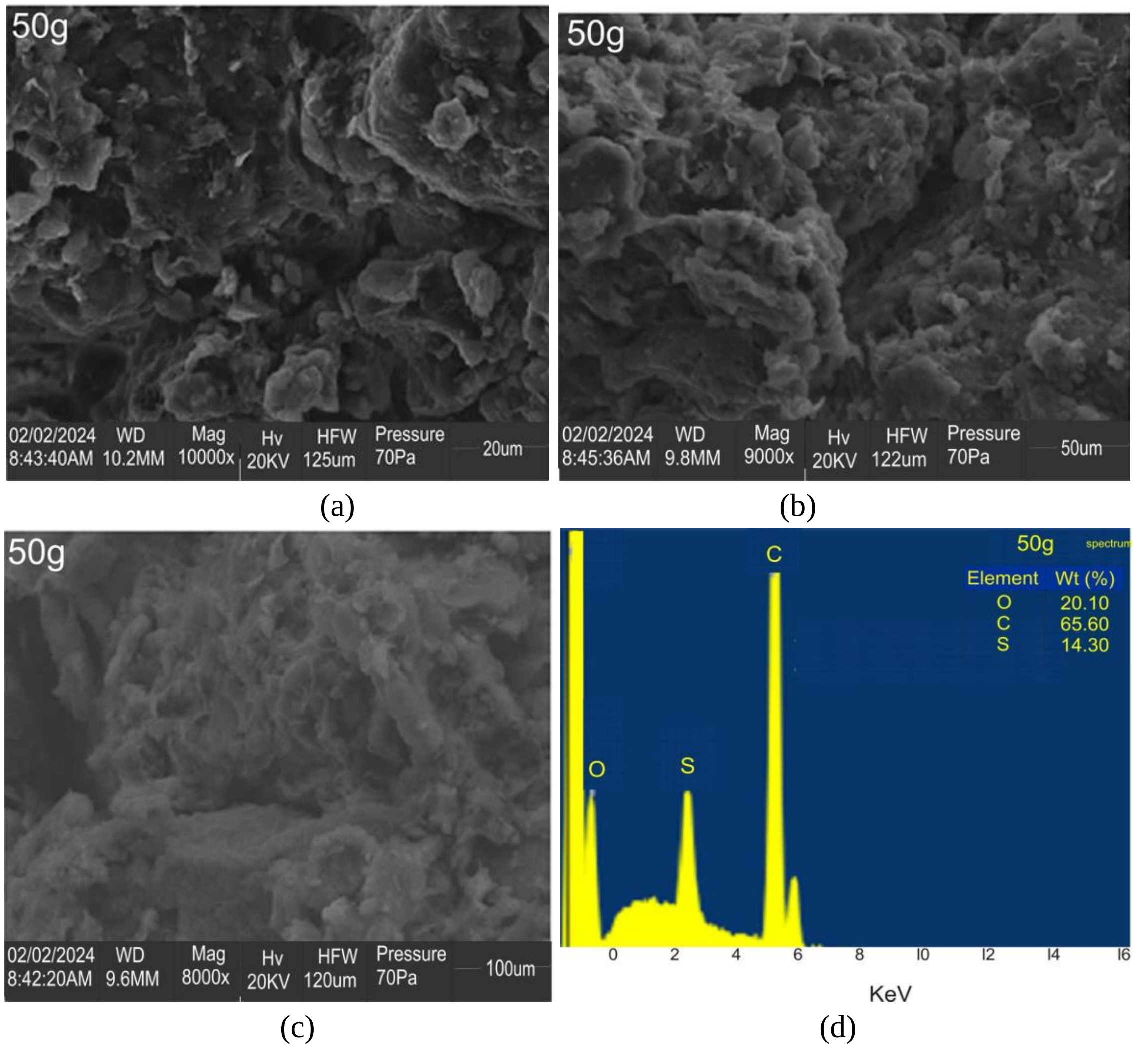

Figure 3. SEM Photograph of 50g carbon nanoparticle with variation of glucose of **a**) 20 µm M, **b**) 50 µm, **c**) 100µm and **d**) EDX

This can be explained by the removal of volatiles during the microwave process that created gaps and voids on the surface that may be caused by decarboxylation and dehydration during the degradation of rice husk biomass (**Fig. 3a-c**). When applied for adsorption and remediation, these developed pores could serve as the site for swallowing and trapping molecules. More so, the pores could also enhance the uninterrupted flow of adsorbate. The degree of devolatilization is an effective and important feature in achieving materials with specific density, higher porosity and unique pore structure (Ismail *et al.* 2013). The variation in the carbon nanomaterials structures from conventional to microwave synthesis is due to the overall heat transfer mechanism. Fig. 3 also gives the quantitative as well as qualitative information about the prepared carbon nanomaterial from rice husk, which were obtained by EDX technique. The presence of carbon, oxygen and sulphur is confirming from (see, **Table 1**) as the weight % of carbon, oxygen and sulphur is (65.60, 20.10 and 14.30) % respectively. The results confirm the high purity of carbon nanomaterial. The chemical composition of carbon powder was confirmed by EDX (**Figure 3d**), showing the presence of carbon, oxygen and sulphur atom at an atomic ratio of (6.7: 1.8: 1.3). The oxygen atom could be originated from the zinc oxide suspension used to place the specimen. The results have suggested high purity of carbon nanonamterial powder (Lou *et al.* 2014; Siddiqui, *et al.* 2018).

Table 1. shows composition of carbon nanoparticle measured by SEM-EDX.

Element	C	O	S
Wt (%)	65.60	20.10	14.30

3.2 XRD pattern analysis of carbon nanomaterial form rice husk

An XRD pattern in (**Figure 4**), shows broad diffraction peaks that lie between 26.5° to 30.5° values of 2θ indicates pristine carbon (111), with little diffraction at 32.5° indicating (220). The presence of carbon is demonstrated by the peak near 2θ of 45° to 49.5°. A peak near 54° to 58.5o of 2θ value corresponds to the interlayer spacing of about 0.75nm (311) and indicates the presence hydroxyl group in carbon powder (Rajan *et al.* 2018). A XRD pattern of 50g sample (Figure 4.6), the average crystallite size of carbon nanomaterial from the XRD data comes to be 120 µm.

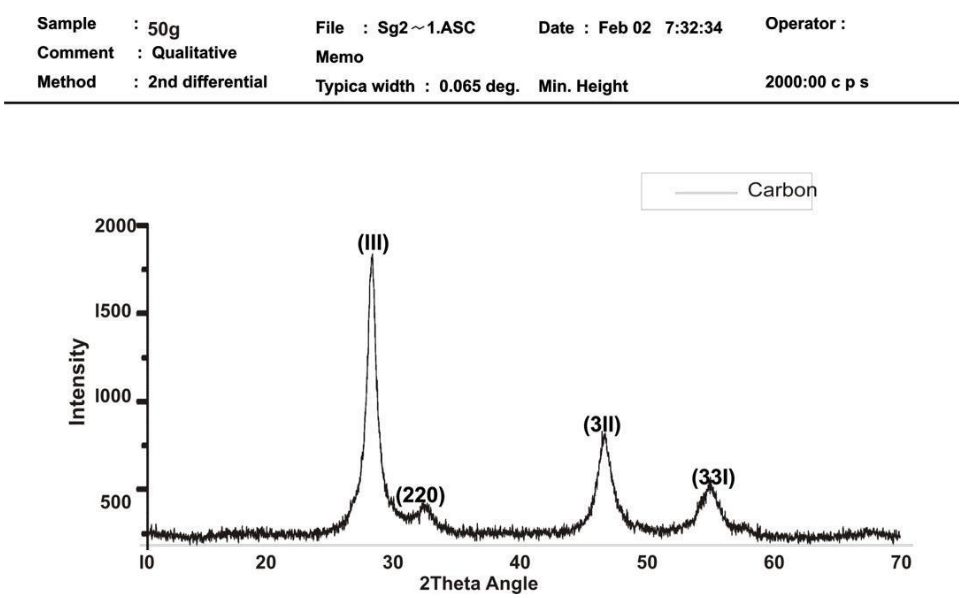

Figure 4. XRD pattern of 50g carbon nanomaterial

3.3 FTIR analysis of carbon nanomaterial form rice husk

CNT sample – FTIR (KBr, cm^{-1}): 3434.44 (O-H), 2898.29 (C-H), 2156.07 (C≡C), 1819.25 (C=O), 1580.4 (C=C) and 728.67 (=C-H).

FTIR spectra (**Figure 5**) were acquired to determine the surface functional groups, demonstrating peaks characteristic of carbon nanomaterial from rich husk synthesized by microwave process were compared. The results show that the peaks for all samples are analogous however, strong variation in transmittance data suggests that those bonds were broken. The O-H stretching, observed at a peak of 3434.44 cm^{-1} carbon nanomaterial, can be due to the presence of moisture or alcohols or their derivatives (Aliyev *et al.* 2019). Aliphatic C–H with medium stretching peaks was observed around 2898.29 cm^{-1} for the samples. Similarly, C≡C stretching was also found in rice husk carbon nanomaterial at 2156.07 cm^{-1} for the samples only, suggesting alkynes' presence. While the symmetric/asymmetric vibrations of carboxylates groups were identified at 1819.25 cm^{-1}. The peak at 1580.4 cm^{-1}in the sample represents the possibility of C=C stretch, possibly due to functional alkene groups for aromatic or esters (Lambert *et al.*1987). The band at 728.67 cm^{-1}, corresponds to =C-H out of plane bending vibrations (Packialakshmi *et al.* 2023), a significant difference was also found in carbon nanomaterials at 728.67 cm^{-1} peak, of the sample which is due to the presence of ZnO. This represents the bonding of zinc oxide in the composite and was confirmed by another study (Wang *et al.* 2011). All the FTIR analysis results indicated that the surface of CNP was rich in the hydrophilic group, consistent with previous reports (Lun *et al.* 2017). These functional groups originated from the breakdown of lignocellulose in the rich husk.

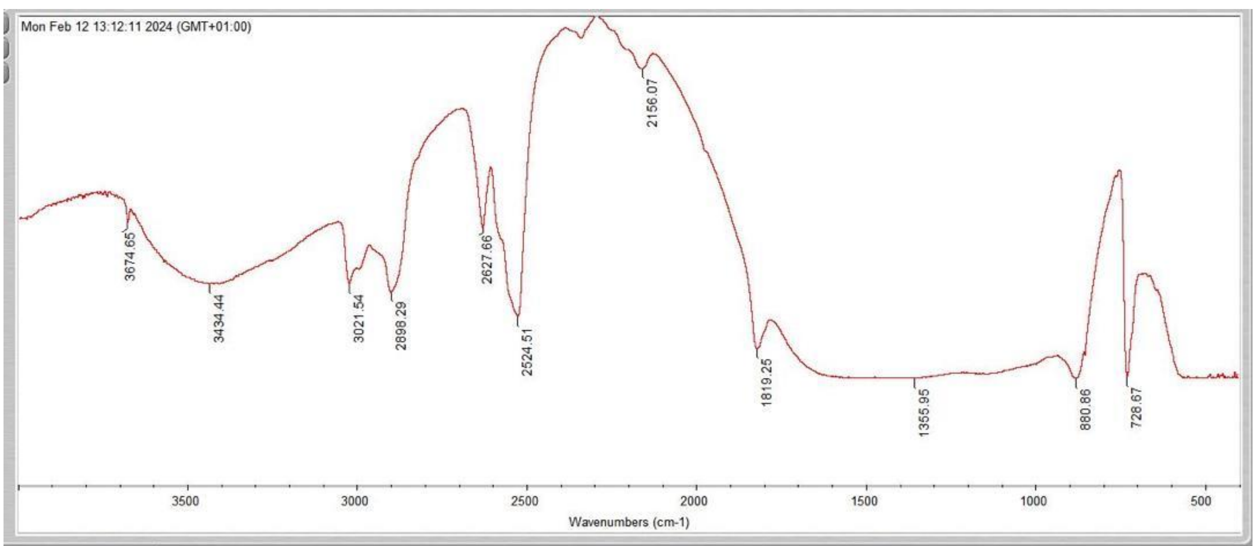

Figure 5. FTIR spectra of 50g of carbon nanomaterial

Conclusion

The research study involves carbonization and synthesis of CNT using the microwave method from rice husk waste materials. The carbon nanotube (CNT) synthesized was characterized using XRD (X-ray diffraction), SEM (Scanning Electron Magnifier), EDX (Energy-dispersive X-ray) and FTIR (Fourier Transform Infrared Spectroscopy. The Energy-dispersive X-ray (EDX) analysis reveals the presence of carbon, oxygen and sulphur is (65.60, 20.10 and 14.30) %, respectively. The results confirm the high purity of carbon nanomaterial at an atomic ratio of (6.7: 1.8: 1.3). The SEM results reveal a well-developed agglomeration with a significant reduction in grain size and the particle size distribution fell in the range of 20 µm to 100 µm, with a mean particle size of 385 nm. The XRD pattern shows broad diffraction peaks that lies between 26.5º to 30.5º values of 2θ indicates pristine carbon (111), with little diffraction at 32.5º indicating (220). The presence of carbon demonstrated by the peak near to 2θ of 45º to 49.5º and peak near to 54° to 58.5º of 2θ value correspond to interlayer spacing of about 0.75nm (311) and indicate presence hydroxyl group in carbon powder. The FTIR results show that the peaks in the sample are analogous, C–H with medium stretching peaks was observed around 2898.29 cm^{-1} in the sample. Similarly, C≡C stretching was also found in rice husk carbon nanomaterial at 2156.07 cm^{-1} which suggests the presence of alkynes. Peak at 1580.4 cm^{-1}in the sample represent the possibility of C=C stretch which may be due to functional groups alkene for aromatic and the band at 728.67 cm^{-1}, corresponds to =C-H out of plane bending vibrations As established from the results, the carbon nanotube from rice husk waste material has excellent prospective potential for producing high valuable adsorbent product for reducing environmental pollution as well as other nano-materials based application.

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