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Physicochemical Characterization of Millet Stalk-Derived Activated Carbon from Agricultural Waste

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Abstract

Activated carbon (AC) possess several desirable properties that enable their use in adsorption and these properties can be established through various techniques. The physicochemical characterization of millet stalk-derived activated carbon from agricultural waste using Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) analysis was analysed. Agricultural waste of millet stalks was collected from local farmers within Kaduna state, Nigeria. The FTIR analysis was then performed by scanning the potassium bromide (KBr) pellet in the FTIR spectrometer within the wavelength range of 400 – 4000 cm^{-1}. For SEM, the AC prepared in optimal conditions and analyzed using a Philips XL30 microscope. XRD used an Empyrean Pan Analytical XRD diffractometer from Worcestershire and scans were conducted over a range of angles (2θ) from 5° to 60°. The result revealed that the FTIR peak in the region around 3200 cm^{-1} indicates the presence of hydroxyl groups (-OH) from carboxylic acids while the peak at 1200 and 1500 cm^{-1} which are absent in the raw millet stalk suggest C-O and C=O bonds respectively from alcohols or esters. Also, rough, uneven surface seen in the SEM micrograph of millet stalk activated carbon is a typical characteristic of activated carbon produced from lignocellulosic materials. The broad peak observed in the activated carbon sample in the 2θ region around 25–30° can be attributed to the (002) plane of disordered carbon from the XRD analysis. Therefore, the physicochemical characterization using SEM, FTIR and XRD techniques, confirming that millet stalk exhibits the characteristic properties of an effective activated carbon.

Keywords: Activated Carbon, Agricultural By-product, FTIR, SEM, XRD, Millet

Introduction

Using agricultural wastes as a source of activated carbon is an eco-friendly and long-lasting solution to the issues of managing agricultural waste and environmental contamination (Gupta et al., 2022). Agricultural activities generate a lot of leftovers and waste, which, if improperly managed, could be harmful to the environment (Matsagar & Wu, 2022; Nath et al., 2023). The waste from agricultural operations, such as bagasse, wheat straw, and fruit peels, as well as crop left overs like rice husks, coconut shells, and maize cobs, are some examples of these by-products. Additionally, they may include lingering plant parts including stems, leaves, and roots (Abdel-Shafy & Mansour, 2018; Gupta et al., 2022). There are two advantages to investigating these agricultural by-products as possible sources of activated carbon (Blachnio et al., 2020; Matsagar & Wu, 2022). In the first place, it helps with the effective management and valorisation of agricultural waste, reducing the environmental costs of their disposal or incineration (Sadh et al., 2018). Second, it offers an economical and sustainable resource for the production of activated carbon, which is important in the purification of water (Blachnio et al., 2020; Sadh et al., 2018). This strategy offers a win-win solution for both agriculture and environmental management and is consistent with the ideas of the circular economy and resource sustainability (Matsagar & Wu, 2022).

The main component of plant materials is cellulose, which can absorb organic compounds and heavy metal cations in water (Mandal et al., 2016). It is possible to find many waste biomass sources in nature whose adsorption characteristics have been described, such as rice husk, sawdust, tea and coffee grounds, peanut shells, orange peel, activated carbon, and dry tree leaves and bark. Heavy metal ion adsorption is a result of physicochemical inter exchange, specifically ion exchange or complex formation between metal ions and functional groups on the cell surface (Ofon et al., 2022; Vasilachi et al., 2021). The primary factors influencing the adsorption equilibrium and rate qualities, which are necessary for plant design, are pore structures and surface features of adsorbents (De Gisi et al., 2016). The development of new adsorbents leads to the introduction of new adsorption technology applications. The first consideration when planning an adsorption operation is adsorption equilibrium (Albatrni et al., 2022; De Gisi et al., 2016).

Activated carbons possess several desirable properties that enable their use in adsorption. Properties, such as large surface area and porosity, together with surface chemistry react with molecules with specific functional groups. Activated carbon has a porous and crystalline structure. With this, it also has a chemical structure. The adsorption capacity of activated carbon is determined by its porous structure. But it is strongly influenced by a relatively small amount of chemically bonded heteroatom, mainly oxygen and hydrogen (Wang & Huang, 2008). The variation in the arrangement of electron clouds in the carbon skeleton results in the creation of unpaired electrons and incompletely saturated valences which influence the adsorption properties of active carbons, mainly for polar compounds. Agricultural waste and by-products can be used for the production of AC with a high adsorption capacity, considerable mechanical strength, and low ash content (Savova *et al*., 2001).

Materials and Method

Raw Materials Collection and Preparation

Agricultural waste of millet stalks was collected from local farmers within Kaduna state, Nigeria. The samples were washed, sun-dried and pulverized in a blender then sieved using a 150 μm sieve to remove larger particles and increase the surface area for activated carbon production. The resulting powder was oven-dried for 24 hours at 105˚C and subsequently stored in Ziplock bags until when needed for the experiments.

Fourier-Transform Infrared Spectroscopy (FTIR) Analysis

The functional groups of millet stalk and millet stalk activated carbon were analyzed using a Shimadzu-8400S Fourier Transform Infrared Spectrometer (FTIR) (Kyoto, Japan). A potassium bromide KBr pellet was prepared by mixing 10g of activated carbon with potassium bromide (KBr) powder, which was then compressed using a pellet press to form the pellet. The FTIR analysis was then performed by scanning the KBr pellet in the FTIR spectrometer within the wavelength range of 400 – 4000 cm^{-1}. The FTIR spectra was interpreted to identify the functional groups present in the samples (Ali et al., 2020).

Scanning Electron Microscopy (SEM)

In order insight into the morphology of activated carbon, scanning electron microscopy (SEM) analysis was conducted. Pore structure and structural changes happening after chemical activation were also observed. In the present work, the raw millet stalk powder and the activated carbon prepared in optimal conditions were analyzed by this technique using a Philips XL30 microscope.

The agricultural waste (millet stalk) and activated carbon samples were placed on the aluminum holder stub using a double sticky carbon tape. Then, the samples were completely dried in the drying oven at 60°C for about 3 hours and then left overnight in the drying oven. The samples were loaded in the SEM holder switched on and then placed in a relatively high-pressure chamber where the working distance is short and the electron optical column is differentially pumped to keep the vacuum adequately low at the electron gun. The agricultural waste (millet stalk) and activated carbon samples were placed on the aluminium holder stub using a double sticky carbon tape. Then, the samples were completely dried in the drying oven at 60°C for about 3 hours and then left overnight in the drying oven. The samples were loaded in the SEM holder switched on and then placed in a relatively high-pressure chamber where the working distance is short and the electron optical column is differentially pumped to keep the vacuum adequately low at the electron gun.

X-ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) analysis was performed on both millet stalk and millet stalk activated carbon to assess their crystallinity. This analysis used an Empyrean Pan Analytical XRD diffractometer from Worcestershire, United Kingdom. The device features a proportional counter (20 x 24 mm) and a scintillation detector (30 mm diameter), with a maximum output of 4 kW (60 kV and 100 mA). For the measurements, .5 grams of each powdered sample were compressed into pellets using a hydraulic press with a force of 25 kN. The XRD scans were conducted over a range of angles (2θ) from 5° to were conducted over a range of angles (2θ) from 5° to 60°. We conducted X-ray diffraction (XRD) tests on millet stalk and its activated carbon to check how crystalline these materials are. The tests were done using a specialized machine from Worcestershire, UK, which has advanced features for detecting X-rays. To prepare the samples, we took .5 grams of each and pressed them into small pellets using a hydraulic press. The XRD measurements were taken at angles between 5° and 60°.

Result and Discussion

Fourier-Transform Infrared Spectroscopy (FTIR)

The FTIR analysis of millet stalk and millet stalk activated carbon in Table 1 and Figure 1. The peaks observed in the FTIR spectrum reveal critical information about these functional groups and their roles in the adsorption process. It can be seen that the peak present in the millet stalk activated carbon is significantly different from the raw millet stalk. For instance, the peak in the region around 3200 cm^{-1} indicates the presence of hydroxyl groups (-OH) from carboxylic acids. This contributes to the hydrophilicity of the adsorbent which enhance adsorption of polar compounds (Nkoh et al., 2022). The presence of peaks at 1200 and 1500 cm^{-1} which are absent in the raw millet stalk suggest C-O and C=O bonds respectively from alcohols or esters, adding to the hydrophilic nature of the material, which helps in the interaction with organic contaminants. The peaks around 1800, 2200 cm^{-1} corresponds to the presence of carbonyl groups, such as carboxylic acids or ketones (Batista et al., 2018). These groups can interact with polar organic molecules through dipole-dipole interactions, further enhancing adsorption efficiency. Additionally, the more prominent peak at 600 cm^{-1} in the activated carbon infers to an out-of-plane C–H bending, indicating the presence of aromatic rings. This suggests the formation of a more graphitic, stable carbon structure, which enhances the mechanical strength and adsorptive surface area of the millet stalk activated carbon. All the peaks are more prominent with higher intensities in the millet stalk activated Carbon when compared with the raw millet. This suggests the successful development of a material with improved surface functionality. These findings align with other studies by Yu et al. (2022) and Ghorbani et al. (2020) that have examined agricultural waste-derived activated carbons.

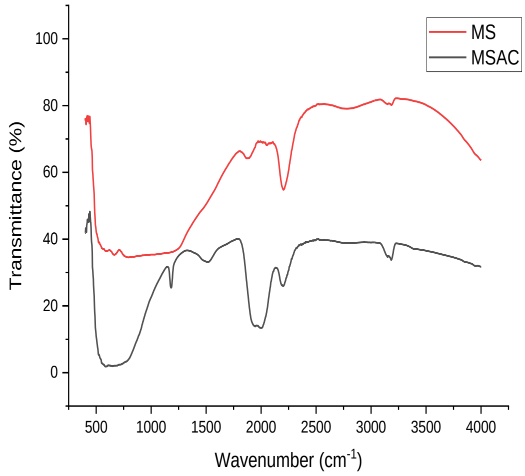

Figure 1: FTIR spectra of millet stalk (MS) and millet stalk-derived activated carbon (MSAC)

Table 4.2: FTIR peak assignment of millet stalk and millet stalk activated carbon

Peak	Assignment	MS	MSAC
600 cm^{-1}	C-H bond of aromatic ring	B	S
1200 cm^{-1}	C–O carbonyl groups	✕	✓
1600 cm^{-1}	C=O carbonyl groups	✕	✓
2000 cm^{-1}	C≡C vibration of alkyne	✓	✓
2200 cm^{-1}	C≡C vibration of alkyne	✓	✓
3200 cm^{-1}	O-H stretching of hydroxyl groups	✓	✓

Key: ✓ = present, ✕ = absent, B= Broad, S= Symmetric

Scanning Electron Microscopy (SEM)

The SEM micrograph of millet stalk and millet stalk-derived activated carbon is shown in Plate 1. From the plate, it can be seen that the visible pores in the activated carbon vary in size and shape, suggesting an effective activation process due to the chemical activation treatment with H_3PO_4. The rough, uneven surface seen in the SEM micrograph of millet stalk activated carbon is a typical characteristic of activated carbon produced from lignocellulosic materials. This result shows strong correlation with similar works on agricultural waste activated carbons (Ghorbani et al., 2020; Ratan et al., 2018). The surface roughness is a result of the decomposition of organic components, which creates cavities and channels suitable for adsorption.

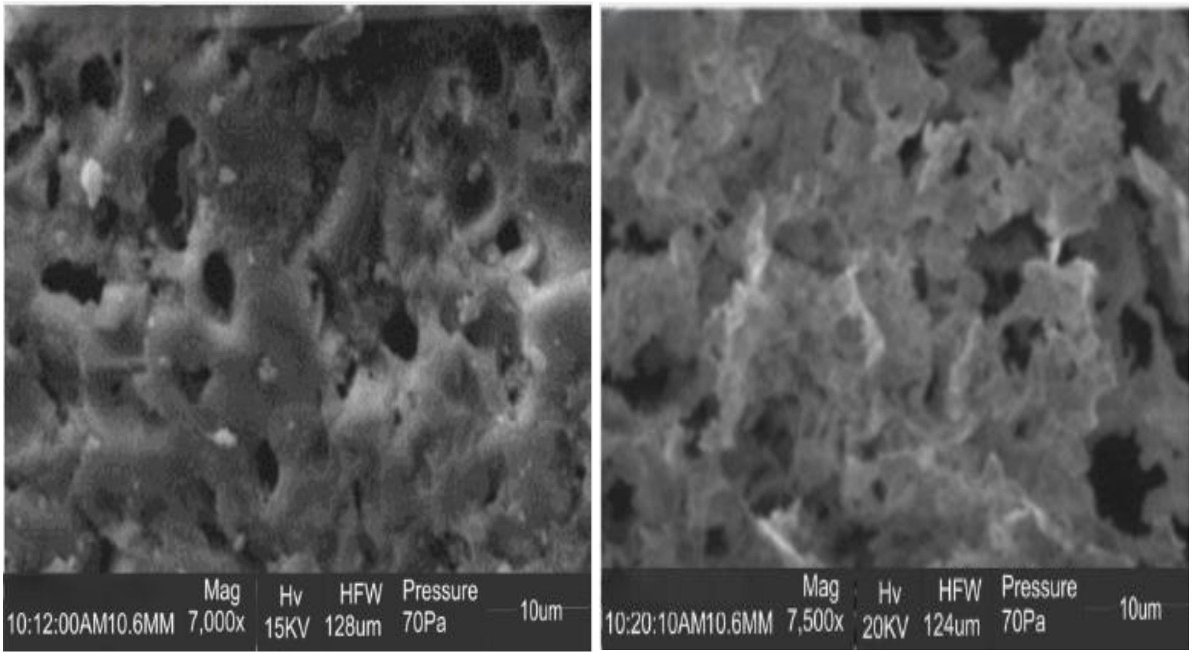

Plate 1: SEM micrograph of (a) millet stalk activated carbon and (b) millet stalk

X-ray Diffraction (XRD) Analysis

The XRD analysis of the millet stalk and millet stalk activated carbon from the result is shown in Figure 2. It is clear from the result that the preparation of the activated carbon by acid activation resulted in the structural transformation of millet stalk, by breaking the crystalline structure which led to the formation of an amorphous material with enhanced surface area and adsorption capacity. The broad peak observed in the activated carbon sample in the 2θ region around 25–30° can be attributed to the (002) plane of disordered carbon, which is consistent with findings reported by Shrestha et al. (2019). This broad peak is characteristic of amorphous carbon and indicates the successful activation of the raw material into a highly porous structure. Similarly, the sharp peaks seen in the raw sample are indicative of the presence of crystalline phases, which may be attributed to mineral impurities or other inorganic compounds naturally found in millet stalk. Similar studies such as those reported by Ogbodo et al. (2021) and Shrestha et al(2019) have also reported that raw plantain peels and Shorea robusta lose their crystalline minerals after thermal or chemical activation processes.

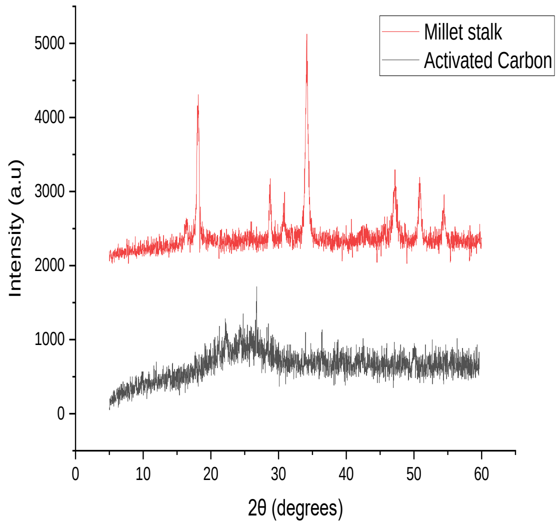

Figure 2: XRD diffractogram of millet stalk and millet stalk-derived activated carbon

Conclusion

Producing activated carbon from agricultural residues can be more economical compared to conventional activated carbon production methods, which often rely on non-renewable resources. This has the potential to lower water treatment costs for municipalities and industries. The activated carbon with optimal phenol adsorption properties was thoroughly characterized using SEM, FTIR and XRD techniques, confirming that millet stalk exhibits the characteristic properties of an effective activated carbon.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Credit Authorship Contribution Statement

Sanni, D.A: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Data curation, Visualization, Project administration, Writing - original draft. **Woke, G.N.** and **Gbarakoro, T.N.**: Supervision, Methodology, Validation, Formal analysis, Data curation, Visualization, Review & Editing.

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