A MORPHOLOGICAL COMPARISON OF HYDRO-CHAR MADE FROM AGRICULTURAL WASTE AND HYDROTHERMAL CARBONIZATION AND MICROWAVE-ASSISTED TECHNIQUES

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Abstract:
This study investigates the adsorption capacities of hydro-chars derived from rice straw, wheat straw, and bagasse synthesized via hydrothermal carbonization (HTC) and microwave-assisted methods. SEM analysis reveals that Wheat Straw Hydro-Char synthesized via the microwave-assisted method exhibits a highly porous, well-preserved fibrous and vascular structure, contributing to a high surface area. In comparison, Rice Straw Hydro-Char also demonstrates notable adsorption capabilities, characterized by high porosity and a fibrous structure, though its structural complexity is somewhat less than that of Wheat Straw Hydro-Char. Bagasse Hydro-Char, while still showing considerable porosity and surface area, has a smoother surface and a less intricate network of pores compared to the other hydro-chars. Overall, Wheat Straw Hydro-Char is identified as the superior adsorbent due to its complex porous network, extensive surface area, and well-preserved structures, which provide numerous active sites for adsorption. The presence of micro and nano-sized pores further enhances its adsorption capacity. The findings suggest that Wheat Straw Hydro-Char (m-HWS) is the most effective material among the three for applications requiring high adsorption potential, followed by Rice Straw Hydro-Char and then Bagasse Hydro-Char.

Keywords: Hydro-Char, Bagasse, SEM, and adsorption
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Introduction

Saving water is essential for the planet's health and humanity's future. As society and technology progress, the environmental cost is becoming increasingly steep. Rapid growth has led to significant pollution and environmental disruption. Water demand has surged across agricultural, industrial, and domestic sectors, consuming 70%, 22%, and 8% of available fresh water, respectively. This increased usage has resulted in large quantities of wastewater, which contains numerous pollutants, including heavy metals (1-3).

Heavy metals pose serious environmental threats as they enter aquatic systems through industrial activities such as mining, ore refining, fertilizer production, tanneries, battery manufacturing, paper industries, and pesticide use. Water pollution negatively impacts human health, ecosystems, and aquatic life. Heavy metals such as chromium (Cr), iron (Fe), selenium (Se), vanadium (V), copper (Cu), cobalt (Co), nickel (Ni), cadmium (Cd), mercury (Hg), arsenic (As), lead (Pb), and zinc (Zn) are particularly hazardous to humans and other life forms(4). Removing these heavy metals from wastewater is crucial not only to mitigate their toxic effects but also to recover valuable materials (5-9).

Conventional methods for removing pollutants from wastewater include chemical

precipitation, ion exchangers, chemical oxidation/reduction, reverse osmosis, electrodialysis, and ultrafiltration. However, these techniques have limitations such as low efficiency, sensitive operating conditions, and the production of secondary sludge, which increases costs. Adsorption with activated carbon is a powerful technology for treating domestic and industrial wastewater due to its straightforward operating requirements and low cost. However, the high cost of activated carbon remains a significant limitation (10, 11).

The adsorption of heavy metals using low-cost biomass from agricultural waste materials has attracted considerable attention as an alternative. Agricultural waste materials or bio adsorption materials offer several advantages over conventional treatment methods. These benefits include low cost, regeneration ability, high adsorption efficiency, reduced chemical or biological sludge production, and the potential for metal recovery. Agricultural materials, particularly cellulosic ones, have a high potential for bio adsorption due to their structures, which include hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, and starch. The high adsorption efficiency of agricultural waste biomass is attributed to the presence of functional groups such as acetamido, alcoholic, carbonyl, phenolic, amido, amino, and sulfhydryl groups (12-17).

Various agricultural waste biomasses effectively adsorb heavy metals and pollutants from wastewater. Sugarcane bagasse treated with citric acid and Fe_3O_4 adsorbs Cd (II) and Pb(II) at 1183 mg/g and 34.5 mg/g, respectively(18). Rice bran with SnO_2/Fe_3O_4 adsorbs Reactive Blue 4 and Crystal Violet at 218.82 mg/g and 159.24 mg/g (19). Teff straw with H_3PO_4 and KOH removes 92.5% of Cr (VI) (20). Moringa oleifera husk with cetyl trimethyl ammonium bromide improves Pb(II) adsorption efficiency to 98.89%(21). Pine bark treated with acids enhances Pb(II) adsorption(22). Sugarcane bagasse with NaOH increases Cr (III) adsorption from 20.34 mg/g to 58.00 mg/g (23). Activated sawdust treated with H_2SO_4 outperforms untreated sawdust for Chrysoidine removal (24). Fly ash with calcium oxide shows a sorption capacity of 38.57 mg/g for Crystal Violet. Coffee leaves with poly ethyleneimine increase removal percentages of Reactive Black 5 and Methyl Orange to 76% and 80%. Onion skin with thioglycolic acid raises Pb (II) adsorption from 4.878 mg/g to 6.173 mg/g (17, 25).

Sugarcane (Saccharum officinarum), wheat straw, and rice straw are significant agricultural byproducts with notable potential for various applications. Sugarcane bagasse, a byproduct from global sugarcane production, contains 44% cellulose, 28% hemicellulose, 21% lignin, 5% ash, and 2% extractives. It is widely used for biofuel production and water treatment, demonstrating effectiveness in removing heavy metals like Cu (II), Cd (II), and Pb (II), and achieving 90% efficiency in nitrite removal. Wheat straw, produced after harvesting wheat, consists of 35–40% cellulose, 20–35% hemicellulose, and around 20% lignin. Its low lignin content makes it suitable for bio ethanol production, and when activated, it serves as an efficient material for removing pollutants, including heavy metals and dyes, from water. Rice straw, with 28–48% cellulose, 12–16% lignin, 15–20% ash, and 9–14% silica, is another abundant resource. It is used in producing bio fuels, bio composites, and adsorbents for wastewater treatment. Activated rice straw effectively adsorbs heavy metals and dyes, making it a cost-effective material for environmental management (26-29).

This work focuses on the use of three commonly available types of biomasses—rice straw, wheat straw, and bagasse—for preparing carbon adsorbents (as agriculture waste adsorbents). Rice straw, a by product from rice cultivation, and wheat straw, which is used as household fuel after harvest are both abundant agricultural residues. Bagasse, generated as waste from sugar cane processing, constitutes about 30% of the crushed cane. These agricultural wastes are freely available and abundant, making them promising candidates for producing activated carbons. The article explores the feasibility of using these biomass-derived activated carbons as low-cost adsorbents for treating

wastewater, specifically highlighting their effectiveness in removing heavy metals from aqueous solutions. Additionally, the study will compare the morphology of rice straw, wheat straw, and sugarcane bagasse using SEM images to assess their suitability and performance as adsorbents. SEM images will be used to investigate the surface topography, porosity, shape, structural integrity, and effects of any surface modifications of the adsorbents.

Materials and method

To conduct hydrothermal carbonization using a conventional oven, agricultural residues such as rice straw, wheat straw, and bagasse were sourced locally from fields and farms in India. Approximately 60 grams of naturally dried agricultural waste were individually combined with 400 ml of deionized water. This mixture was loaded into a 500 ml stainless steel autoclave. The autoclave was heated to 300 °C and maintained at this temperature for 5 hours, with pressure monitored using a pressure gauge to maintain around 1000 psi. After controlled thermal treatment, the autoclave was cooled to room temperature, allowing collection of the solid hydrochar product derived from the agricultural waste. The agricultural waste hydrochar was rinsed with DI water and dried at 80 °C in an oven. Once dry, the sample underwent grinding and sieving to achieve a uniform particle size ranging from 0.5 to 1.0 mm (fig 1). To remove any remaining impurities like ash, the hydrochar was rinsed again with DI water and dried at 80 °C. The resulting purified hydrochar samples were stored for future experimental use. For the production of modified hydrochar, approximately 3 grams of the prepared hydrochar samples were immersed in a solution containing 20 ml of 10% hydrogen peroxide (H2O2) for 2 hours at room temperature (22 °C ± 0.5 °C). After the reaction, the modified hydrochar was thoroughly rinsed with DI water and dried at 80 °C. The resulting modified hydrochar samples were carefully stored for future experimentation and applications.

For the microwave hydrothermal carbonization (MHTC), approximately 1 gram of agricultural waste was placed into a glass vial, and 5 mL of distilled water was added to achieve a consistent water-to-biomass ratio used in previous studies. Optimal reaction conditions were tailored to the specific type of biomass employed; for instance, seaweed rich in cellulose required adjustments to maximize cellulose conversion to hydrochar. Cellulose, being a complex carbohydrate resistant to degradation, necessitates elevated temperatures, pressures, and extended reaction times for thorough conversion. The sealed glass vial was placed in a microwave reactor, where stirring commenced, and the temperature was ramped up to 200 °C, aligning with prior research findings in approximately 20 minutes. Subsequently, the HTC process was maintained at this temperature for a designated reaction period. Throughout the procedure, pressure was monitored and recorded automatically. Following reaction completion, the reactor was cooled to 60 °C, and liquid and solid products were separated via vacuum filtration using F1001 grade filter paper (125 mm size). Liquid products were refrigerated at 4 °C for subsequent analysis, while solid char was dried in a conventional oven at 105 °C for 3 hours and stored at room temperature. Hydrochar produced through microwave hydrothermal treatment was denoted as MHC, whereas hydro-char from conventional heating (with a 4-hour reaction time) was labelled as HC (30).

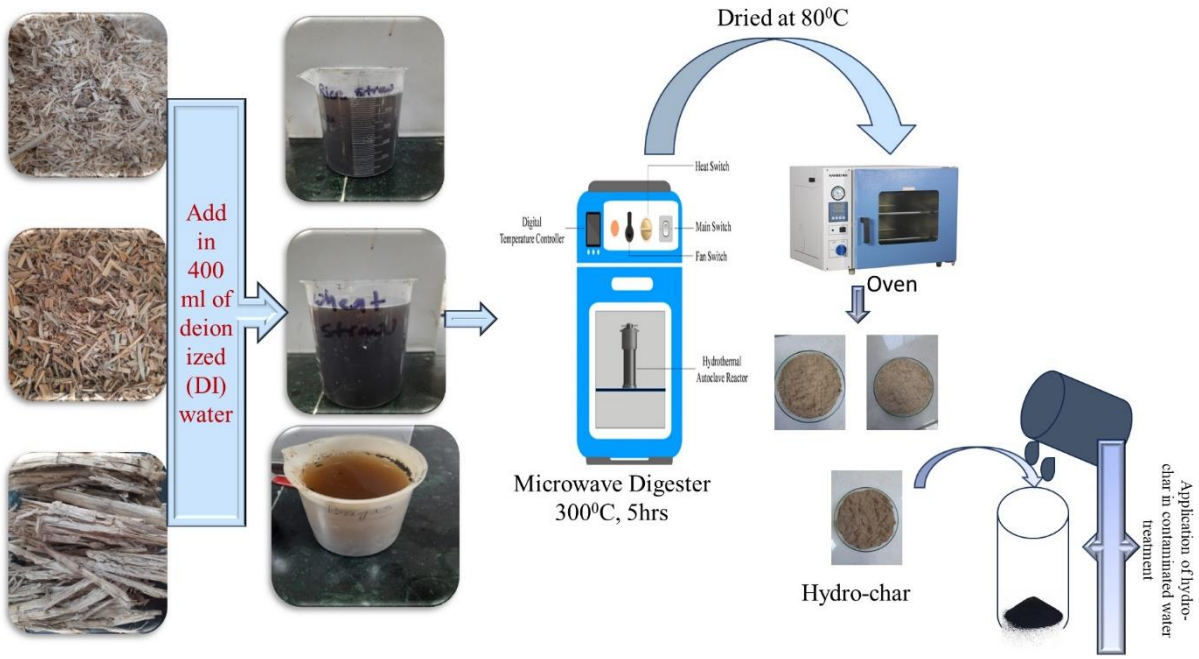

Figure 1. Schematic diagram of hygro-char formation methodology

Result and Discussion

Comparative Analysis of Hydro-Char Derived from Rice Straw, Bagasse, and Wheat Straw Based on SEM Imaging

SEM (Scanning Electron Microscope) images of hydro-chars derived from rice straw, wheat straw, and bagasse can reveal important morphological characteristics that can influence their adsorption capacities for heavy metals. The SEM images of hydro-chars derived from wheat straw, rice straw, and bagasse using hydrothermal carbonization (HTC) and microwave-assisted method illustrate significant structural differences.

Based on the SEM images, the Wheat Straw Hydro-Char synthesized via microwave-assisted method exhibits the most promising characteristics as an adsorbent due to its complex porous network, high surface area, and structural integrity. In low magnification the HTC hydro-char of wheat straw Fig. 2. (images a) shows a dense, layered morphology with smaller and irregular pores it shows a layered structure with visible fibrous elements while medium magnification Fig 2. (images b and c) reveals clear pore structures with regions of high porosity, highlighted by arrows. While the microwave assisted method hydro-char of wheat straw in Fig 2. (images d, e, f) exhibits a fragmented structure with larger, well-defined, tubular pores, indicating a higher surface area, marked by arrows and circles. These features contribute to its high porosity and surface area, making it a robust network for adsorption.

Comparatively, the Rice Straw Hydro-Char synthesized via microwave-assisted and hydrothermal carbonization (HTC) method also has high porosity and surface area, with a rough, fibrous structure at low magnification Fig 3. (image a) a detailed porous surface at medium magnification Fig 3. (images b and c), and micropores, ridges, and valleys at high magnification in Fig 3. (images d, e, and f) all highlighted with arrows and circles. Although it demonstrates significant adsorption potential, its structural complexity is slightly less than that of wheat straw hydro-char.

The Bagasse Hydro-Char, synthesized via both method with its relatively smooth surface at low magnification in Fig 4. (image a) intricate network of pores at medium magnification in Fig 4. (images b and c), and detailed micropores at high magnification Fig in 4. (images d, e, and f) shows significant porosity and surface area but is less complex than the other two, as highlighted by arrows and circles. Overall, Wheat Straw Hydro-Char, synthesized via microwave-assisted method stands out as the superior adsorbent due to its hierarchical porosity and preserved

structures, followed closely by Rice Straw Hydro-Char, and then Bagasse Hydro-Char. The hierarchical porosity and preserved structures in wheat straw hydro-char make it a superior candidate for applications requiring high adsorption capacity.

Based on the SEM results, Wheat Straw Hydro-Char synthesized via microwave-assisted method appears to have a slight edge over Rice Straw and Bagasse Hydro-Chars in terms of adsorption potential due to the following reasons:

1) Complex Porous Network: Wheat straw hydro-char shows a highly porous and well-preserved fibrous and vascular structure, contributing to a high surface area.

2) Surface Area: The detailed porous network and preserved structures indicate a larger surface area.

3) Structural Integrity: The preserved vascular structures suggest a robust material that can offer more adsorption sites.

4) Micro and Nano Pores: The presence of micro and nano-sized pores in Wheat straw hydro-char indicates a larger number of active sites for adsorption.

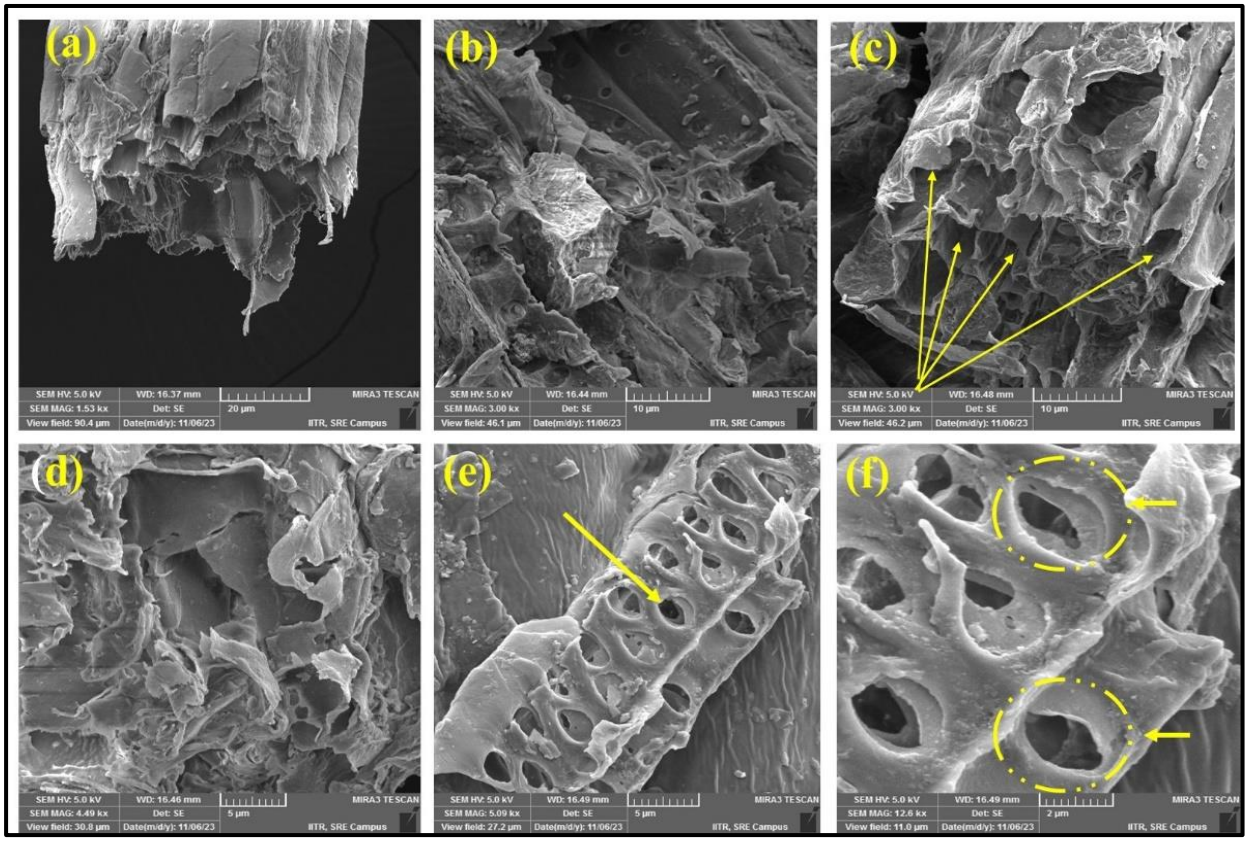

Figure 2. Sem images of wheat straw hydro-char HWS (a, b, c) and m-HWS (b,c,d) at different magnification.

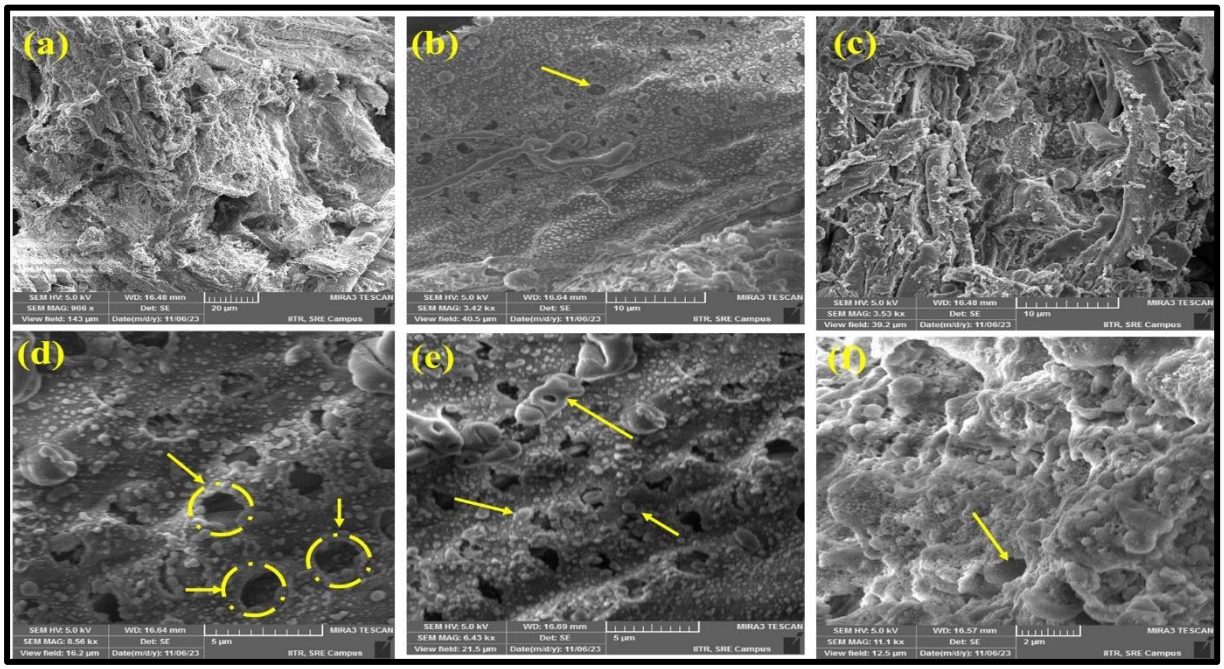

Figure 3. Sem images of wheat straw hydro-char HRS (a, b, c) and m-HRS (b,c,d) at different magnification.

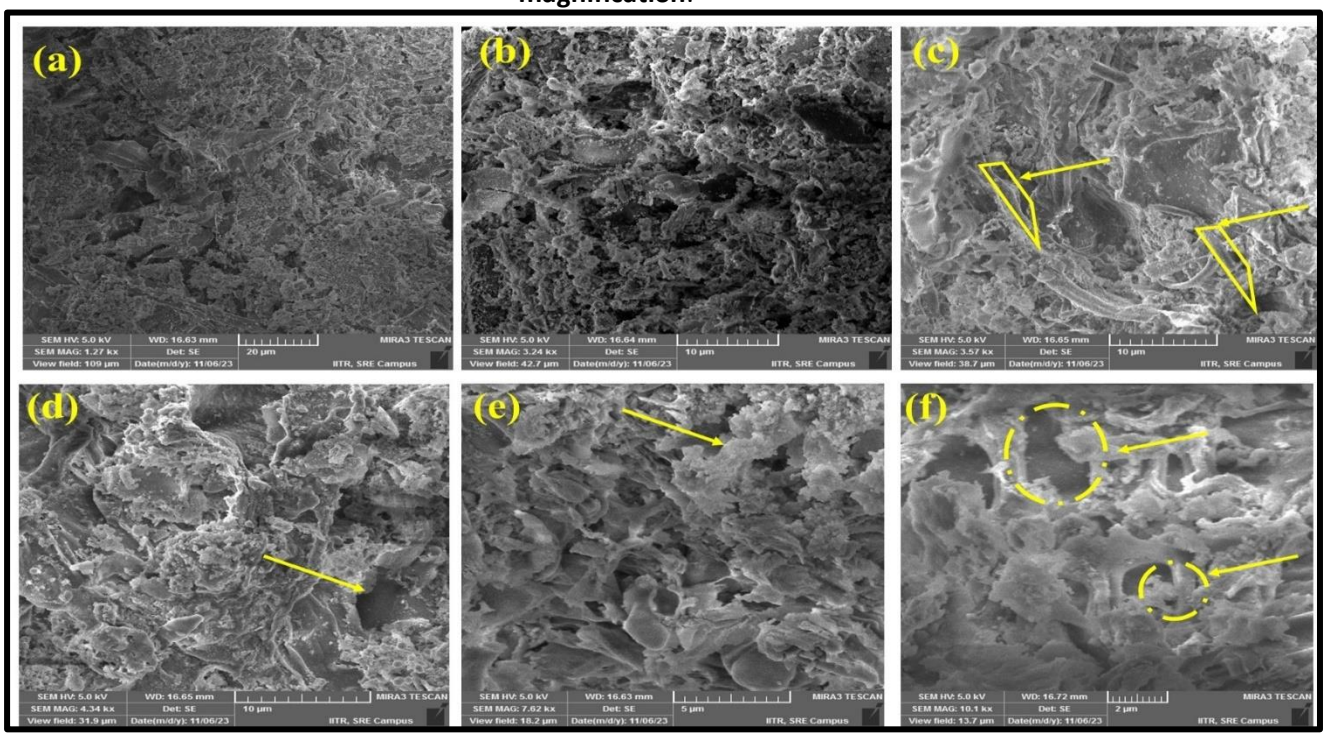

Figure 4. Sem images of wheat straw hydro-char HBG (a, b, c) and m-HBG (b,c,d) at different magnification.

Supporting Characterization Techniques

The SEM data is further supported by FTIR, TGA, and BET analyses:

Fourier Transform Infrared Spectroscopy (FTIR): The FTIR analysis reveals the presence of functional groups that are critical for adsorption processes. For instance, the decrease in aliphatic –OH and C–H stretching peaks and the weakening of carboxyl or carbonyl C=O and C–O peaks in microwave-assisted hydrochars (m-HWS, m-HRS, m-HBG) indicate the transformation and possible enhancement of surface chemistry for adsorption [Reference]. This supports the SEM findings of enhanced porous structures

in Wheat Straw Hydro-Char, which facilitate better adsorption (30).

Thermo-gravimetric Analysis (TGA): TGA provides insights into the thermal stability and decomposition behaviour of the hydro-chars. The significant weight loss during the second stage of decomposition, primarily due to the volatilization of free and non-structural water and functional groups, correlates with the SEM-observed porous structures. The higher thermal stability of Wheat Straw Hydro-Char, as indicated by TGA, supports its structural integrity, which is crucial for adsorption (30).

Brunauer-Emmett-Teller (BET) Surface Area Analysis: The BET analysis shows that microwave-assisted hydro-chars have higher specific surface areas compared to conventional hydro-chars. specifically, the higher BET surface area of Wheat Straw Hydro-Char (m-HWS) corroborates the SEM observations of a complex porous network and high surface area, making it an excellent adsorbent. The specific surface area and pore volume directly influence the adsorption capacity, supporting the SEM results. In summary, the FTIR, TGA, and BET analyses collectively validate the SEM findings that Wheat Straw Hydro-Char (m-HWR) exhibits the most promising characteristics as an adsorbent due to its complex porous network, high surface area, and structural integrity. This makes it superior to Rice Straw and Bagasse Hydro-Chars in adsorption applications (30).

Conclusion

The SEM analysis of hydro-chars derived from rice straw, wheat straw, and bagasse, produced through the Hydrothermal Carbonization (HTC) and microwave-assisted process, reveals significant insights into their potential as adsorbents for heavy metals. Among the three hydro-chars, m-HWS exhibits the most promising characteristics, including a complex porous network, high surface area, and well-preserved structural integrity. At various magnifications, m-HWS shows a layered structure with visible fibrous elements and regions of high porosity, including detailed micropores and preserved vascular structures. These features contribute to its superior adsorption capacity by providing an extensive network of active sites for heavy metal capture. Comparatively, Rice Straw Hydro-Char also demonstrates a high degree of porosity and structural complexity, although slightly less than that of Wheat Straw Hydro-Char. Bagasse Hydro-Char, while possessing significant porosity and surface area, is structurally simpler and therefore exhibits lower adsorption potential. Supporting characterization techniques, including FTIR, TGA, and BET analyses, further validate these SEM findings. FTIR confirmed the presence of functional groups essential for adsorption, TGA demonstrated the thermal stability and robust structure of the hydro-chars, and BET analysis highlighted the superior specific surface area of Wheat Straw Hydro-Char. In summary, the hierarchical porosity, high surface area, and structural integrity of Wheat Straw Hydro-Char make it the most effective adsorbent among the hydro-chars studied, with significant potential for applications in environmental remediation and heavy metal adsorption.

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