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Biochar and Nanobiochar: A Biobased Engineered Nanobiocatalyst from Sugarcane Bagasse in Petrochemical Waste Management

Abstract

The objective of this review is to identify knowledge gaps and research needs related to the utilization of biochar and Nano-biochar for sustainable environmental remediation. Biochar nanocomposites offer a promising alternative for handling wastewater pollution, sewage, and industrial effluents by immobilizing or removing pollutants and pathogens. Additionally, biochar serves as an electrode material in lithium-ion batteries due to its high surface area and electrical conductivity. Bioremediation using biochar applications can provide innovative solutions for contaminated soil resulting from petroleum waste products, hydrocarbon oil spills, and other hazardous compounds. Biochar enhances soil-water retention, nutrient availability, cation exchange capacity, and soil pH, creating favorable conditions for crop growth. It can even absorb methane produced in animals' guts. Sugarcane bagasse-derived biochar, treated with activated functional groups, is particularly effective for remediating environmental pollutants, especially in Brazil. Beyond its use as an alternative fuel, biochar and Nano-biochar from bagasse contribute to a cleaner environment by promoting carbon sequestration, enhancing soil fertility, supporting bioremediation, and enabling agro-waste recycling. Biochar is obtained as a solid carbon-rich substrate through the pyrolysis of sugarcane bagasse at temperatures above 300 °C in an oxygen-free environment. Nano-biochar, an innovative Nano sized composite, is prepared from bulk biochar using top-down approaches such as ball-milling, centrifugation, sonication, and hydrothermal synthesis. Compared to normal bulk biochar's, Nano-biochar exhibits significant advantages in terms of surface area, pore size, total pore volume, and surface functionalities. Overall, the biocatalytic functions and properties of biochar have wide-ranging applications in sensors, enzyme immobilization, and polymer production.

Keywords:

Sugarcane Bagasse; Nano-biocatalyst; Petroleum waste Bioremediation; Circular economy

Introduction

Sugarcane's Role, its Production and Biochar from sugarcane Bagasse

Sugarcane plays a crucial role in Brazil's commercial development, contributing to the production of sugar, alcohol, food, and beverages. Brazil is projected to achieve a record sugar production of 43.1 million tons in the 2024/2025 fiscal year. Globally, sugarcane production exceeded 1.8 billion tons in 2021, with 51.7% coming from the Americas (mainly Brazil), 41.4% from Asia, and 5.1% from Africa (FAO, UN 2024). Brazil's average productivity is estimated at 72 tons per hectare, with the southeast region contributing approximately 60% of the national harvest (CONAB, 2023). Sugarcane biomass accounts for 16.4% of Brazil's internal energy supply (MMW2022). After extracting sugarcane juice, fibrous residue (bagasse) remains, rich in cellulose and hemicellulose. Sugarcane bagasse constitutes 30% of the harvested plant mass and has an annual worldwide production of 700 million tons (Iwuzor

et al., 2022). Biochar, prepared from sugarcane bagasse, has various applications and plays a significant role in environmental pollutant cleanup. Biochar can enhance soil-water retention, nutrient availability, cation exchange capacity, and soil pH, promoting crop growth. It can also absorb methane produced in animals' guts. In Brazil, biochar from sugarcane bagasse, with its activated functional groups, is a strong candidate for environmental pollutant remediation (Hiranobe et al., 2024).

Research Goals and its Applications

Research aims to explore sugarcane by-products (such as cellulose, biochar, carbon dots, and polymer nanocomposites) for sustainable energy generation, feedstock production, and environmental remediation. Biochar nanocomposites show promise for handling wastewater pollution, immobilizing pollutants, and serving as electrode material in lithium-ion batteries due to their large surface area and electrical conductivity. In summary, sugarcane and its residues offer diverse prospects for industrial use and environmental solutions, making them valuable resources in Brazil and beyond for sustainable waste recycling and management.

Methodologies used in the production of Biochar's

Nano-Biochar Production and its Prerequisite Properties

Biochar is obtained as a solid carbon-rich substrate through the pyrolysis of sugarcane bagasse. This process occurs at temperatures above 300 °C in an oxygen-free environment. The resulting biochar serves as a valuable material due to its carbon content and stability. The Nano-biochar is an innovative Nano sized composite derived from bulk biochar. The preparation of Nano-biochar involves top-down approaches, including the following major physical and chemical methods, they are **Ball-milling** (Mechanical treatment to reduce particle size), **Centrifugation** (Separation based on density), **Sonication** (Ultrasonic waves to disperse and homogenize particles), **Hydrothermal synthesis** (Controlled reaction in a water-based environment), etc. The Nano-biochar exhibits several advantages over normal bulk biochars and they possess the following characters and its effective material properties.

- ❖ Increased **surface area**
- ❖ Smaller **pore size**
- ❖ Greater **total pore volume**
- ❖ Enhanced **surface functionalities**
- ❖ **High Porosity**: Providing ample space for reactions and adsorption.
- ❖ **High Surface Area**: Maximizing interaction with target molecules.
- ❖ **Reusability**: Enabling multiple cycles of use.
- ❖ **Antifouling**: Resisting fouling or clogging.
- ❖ **High Selectivity**: Targeting specific reactions.
- ❖ **Tolerability**: Maintaining stability under various conditions.
- ❖ **Mechanical Capacity**: Withstanding mechanical stress.
- ❖ **Eco-friendly**: Minimizing environmental impact.

These properties make Nano-biocatalysts promising candidates for various applications (Ouyang et al., 2023).

Review and Analysis

Biochar Production Techniques from Sugarcane Bagasse

Researchers have explored various techniques for producing biochar from sugarcane bagasse (Ouyang et al., 2023). These methods fall into three main categories:

1. **Biological Processes:** These biological treatment involve the use of specific microorganisms (such as bacteria, algae, and fungi) to transform biomass into biochar, biofuels, and syngas. Thermochemical techniques are particularly notable in this context.
2. **Chemical Processes:** The Chemical methods include gasification, pyrolysis, hydrothermal carbonization, flash carbonization, and torrefaction. The Pyrolysis is commonly used to generate biochar from sugarcane bagasse biomass, while hydrothermal carbonization produces hydro char.
3. **Thermochemical Processes:** These encompass a range of techniques and paired processes for biomass conversion, resulting in valuable products such as biochar, bio-oil, and syngas.

Oil Spill Cleanup Methods

When dealing with oil spills on sea surfaces, three primary methods (Ouyang et al., 2023), they are commonly employed in onsite oil spill removal, and it includes the following as shown in Figure.1.

Oil Spill Treatment Techniques	Method	Technology
	Natural Method	Natural Attenuation Booming and Skimming Wiping with Absorbent Mechanical Removal
	Physical Method	Low pressure flushing Washing Cutting vegetation Stripping
	Chemical Method	Dispersants Demulsifiers Gelling agents Surface film chemicals In-situ burning
	Biological Method	Bioremediation Phytoremediation Microbialremediation

Figure.1. Oil Spill Treatment Techniques

1. **Mechanical Methods:** These natural methods involve physical techniques and equipment. Examples include booms, skimmers, and sorbents. Mechanical methods are considered less harmful to the environment compared to chemical and biological approaches (Fingas, 2012; Ivshina, 2015).
2. **Chemical Methods:** Chemical approaches include in-situ burning, dispersants, and solidification using solidifiers. In-situ burning can quickly eliminate oil spills but releases toxic compounds (carbon dioxide, aromatic hydrocarbons, and nitrogen oxides) into the atmosphere.

3. **Biological Methods:** These utilize specific microorganisms to interact with or react to oil contamination. However, biological methods may introduce secondary pollution due to exotic species (Azubuike et al., 2016).

Depending on the specific conditions of an oil spill, these methods can be used individually or in combination. Chemical methods involve surfactants or solidifiers, which can be toxic and unsustainable (Ouyang et al., 2023).

Material Characterization for Nano-Biocatalyst from Sugarcane Bagasse Fly Ash

The previous literature reported the efficiency of Nanobiocatalyst, the research conducted material characterization techniques for a synthesized Nano-biocatalyst derived from sugarcane bagasse fly ash observed assessing specific properties such as surface area, pore volumes, pore sizes, surface structures, chemical elements, and chemical functional groups. Their characterization methods employed were **Brunauer–Emmett–Teller (BET) analysis, Field emission scanning electron microscopy and focused ion beam (FESEM-FIB) imaging with energy-dispersive X-ray spectrometry (EDX) and Fourier transform infrared spectroscopy (FT-IR)**. These characterizations provide valuable insights into the properties of the Nano-biocatalyst (Praipipat et al., 2024).

Although the **biological method** for oil spill cleanup is ecologically safe and involves the use of specific microorganisms (such as bacteria, algae, and fungi) to biodegrade oil into simple and non-toxic molecules (Azubuike et al., 2016). However, this method may be more time period for large scale cleanup and sometime unintentionally introduce secondary pollution to marine environments due to the introduction of exotic species. In contrast, the **mechanical method** focuses on recovering oil spills using specialized equipment, including booms, skimmers, and sorbents. This method is considered the least harmful to the environment compared to chemical and biological approaches (Fingas, 2012; Ivshina, 2015). Notably, using **oil sorbents** to treat oil spills in water is a smart approach. It allows for complete collection and recovery of oil directly from water surfaces, making it eco-friendly, cost-effective, and recyclable. Researchers have increasingly emphasized the development of effective and environmentally friendly oil sorbents for oil spill cleanup (Ouyang et al., 2023) (see Figure 2 and 3).

The various Nano-catalyst synthesis methods have been widely used to modify bulk biochar and Nano-biochar to enhance their properties (Ndirangu et al., 2019; Wang et al., 2021). These modifications predominantly include acid-base modification (Mahmoud et al., 2020a), thiol modification (Lyu et al., 2020), metal modification (Jenie et al., 2020; Nath et al., 2019; Qiao et al., 2019), and ultrasonic modification (Li et al., 2017b). Lyu et al., (2020) modified wood chip Nano biochar using 3-mercaptopropyltrimethoxysilane (3-MPTS).

The chemical method involves the significant mechanism of Amine modified adsorbents of surface and functional group modifications play a very significant role in this material characterization for the removal of carbon-dioxide gas, it includes two ways, (i) the Amine impregnation method and (ii) the Amine grafting (bonding) method. The Amine impregnation involves simple modifications of mixing and fixed amine on a solid support and immobilization of amine in porous solid support to modify the materials termed amine impregnation. These amine-modified adsorbents are efficient in capturing carbon-dioxide from the source. There are (1) Branched polyethylenimine (BPEI), in which the primary, secondary amines are more affinity and involved in removing carbon dioxide gas while compared to

tertiary amines (less affinity); (2) Linear polyethylamine (LPEI), in this the secondary amines are more affinity and involved in removing carbon-dioxide gas while comparing to primary and tertiary amine (less affinity) and (3) Poly(allyl)amine (PALL or PAA), in these the primary amines are more affinity and involved in removing carbon-dioxide gas while comparing to tertiary amine (less affinity).

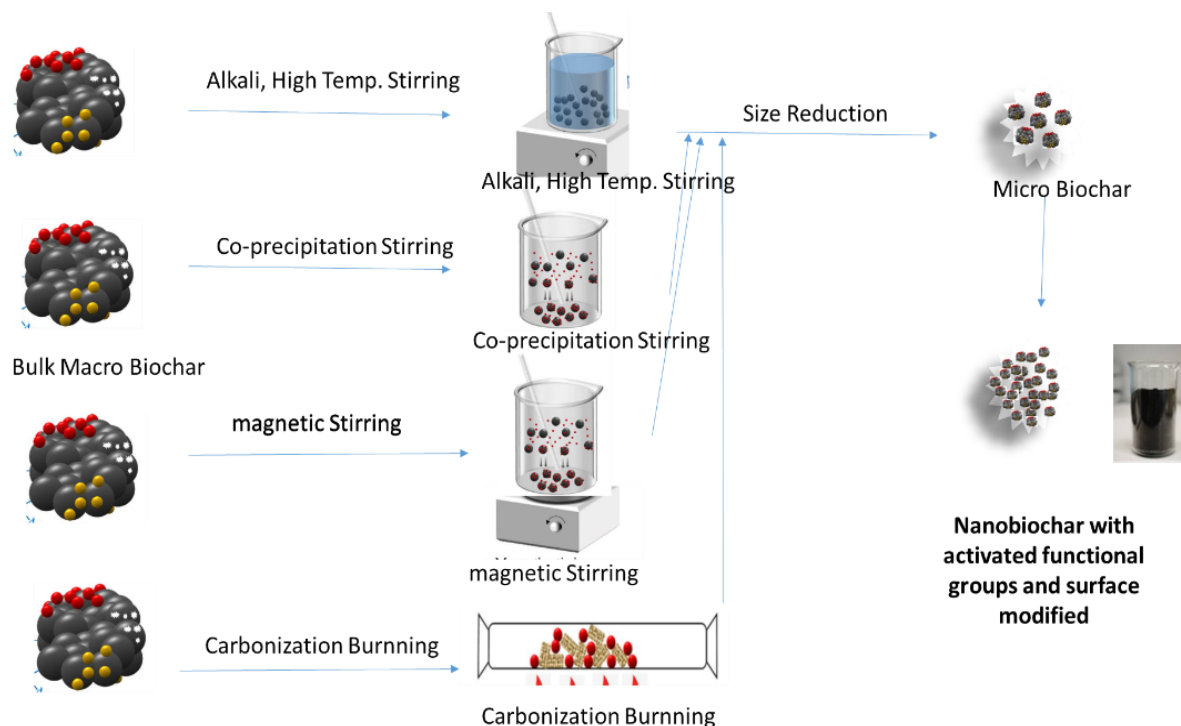


Figure.2. Methods for preparation of Nanobiochar

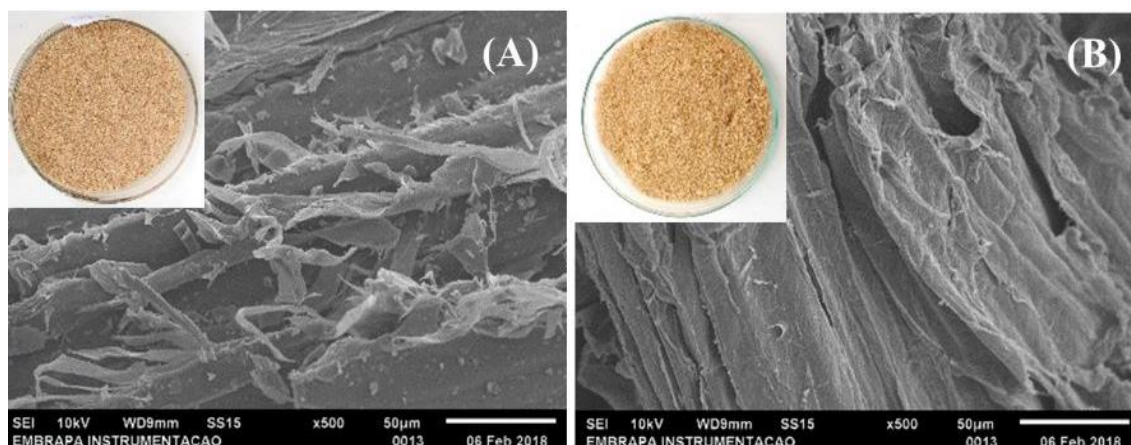


Figure.3. Scanning electron microscopy micrographs and images of (A) Raw sugarcane bagasse, (B) Alkali treated sugarcane bagasse

The amine grafting (bonding), allows silica to react with three hydroxyl groups from amino silanes having covalent bonds and the primary and secondary amines are more affinity towards the removal of carbon-dioxide from the source. These modified Nano biochar exhibited significantly higher specific

surface area (SSA) compared to the original biochar. Additionally, its zeta potential became more negative, and it had additional surface functional groups. Xu et al., (2019) reported that ball-milled N-doped biochar showed improved SSA and pore volume after adding ammonium hydroxide. Nath et al., (2019) modified Nano biochar with iron oxides, enhancing its surface properties and adsorption capacity. Modified Nanobiochars demonstrate stronger pollutant removal capabilities than non-modified Nanobiochar (Vishnu et al., 2022; Wang and Wang, 2018).

The Biochar recently found an application in carbon-assisted water electrolysis (CAWE), which is a process where a carbon-based electrode is used as a sacrificial anodic electrode in the production of hydrogen gas (Evan et al., 2024). The use of biochar, known for producing polycyclic aromatic carbons during its synthesis that is then retained in the biochar, is well suited for use in carbon-assisted water electrolysis (Ying et al., 2022). The focus of biochar's application in hydrogen production is as a catalyst support material environments (Visser et al., 2023). This is because biochar has many of the traits which a catalyst support needs, such as high surface area, tunable pore structure, and high stability in acidic and basic environments.

Conclusions

The modification of sugarcane bagasse (SCB) into carbon nanocrystals (CNCs) enhances their adsorption and absorption capabilities for liquid and solid waste. These Nano biocatalytic materials find wide applications in sensors, enzyme immobilization, and polymer production. The process of creating CNCs from SCB involves two chemical treatment stages: chemical purification and acid-hydrolysis. During chemical purification, SCB undergoes treatment with acidic sodium chlorite and alkali, resulting in chemically purified cellulose. Subsequent acid-hydrolysis removes CNCs from the purified cellulose. To characterize the morphology and topography of these nanocrystals, FE-SEM (field-emission scanning electron microscopy), TEM (transmission electron microscopy), and AFM (atomic force microscopy) analyses were performed. FE-SEM and AFM confirmed the TEM analysis, revealing rod-like nanocrystals with typical dimensions of 250-480 nm in length and 20-60 nm in diameter. Elemental analysis (EDX) indicated the presence of sulfur impurities in CNCs, along with other main components. Structural changes were assessed using FTIR (Fourier-transform infrared spectroscopy) and XRD (X-ray diffraction), while thermal analysis (TG-DTG-DTA) revealed that CNCs exhibited lower thermal stability and higher crystallinity compared to native cellulose. Overall, this chemical methodology holds promise as a resourceful process for CNC research using SCB. In the course of gasification of biomass, the CO₂ is trapped and put in storage in the biochar. The biochar application in carbon-assisted water electrolysis (CAWE) process where a carbon-based electrode is recycled in the manufacture of hydrogen gas. These biochar, which sequesters carbon (for greater than 1,000 years), and reprocessed in numerous applications including soil improvement, construction materials, biofuel etc. Moreover this helps indirectly for climate resilience and circular economy which leads to enforce the sustainable development of waste management and reuse of sugarcane waste byproducts

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