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TÍTULO DO TRABALHO:

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

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Resumo

O objetivo desta revisão é identificar lacunas de conhecimento e necessidades de pesquisa relacionadas à utilização de biochar e nano-biochar para remediação ambiental sustentável. Os nanocompósitos Biochar oferecem uma alternativa promissora para lidar com a poluição de águas residuais, esgotos e efluentes industriais, imobilizando ou removendo poluentes e patógenos. Além disso, o biochar serve como material de eletrodo em baterias de íons de lítio devido à sua alta área superficial e condutividade elétrica. A biorremediação usando aplicações de biochar pode fornecer soluções inovadoras para solos contaminados resultantes de resíduos de petróleo, derramamentos de óleo de hidrocarbonetos e outros compostos perigosos. Biochar aumenta a retenção de água no solo, a disponibilidade de nutrientes, a capacidade de troca catiônica e o pH do solo, criando condições favoráveis para o crescimento das culturas. Pode até absorver o metano produzido nas entranhas dos animais. O biocarvão derivado do bagaço de cana-de-açúcar, tratado com grupos funcionais ativados, é particularmente eficaz na remediação de poluentes ambientais, especialmente no Brasil. Além da sua utilização como combustível alternativo, o biochar e o nanobiochar do bagaço contribuem para um ambiente mais limpo, promovendo o sequestro de carbono, melhorando a fertilidade do solo, apoiando a biorremediação e permitindo a reciclagem de resíduos agrícolas. O biochar é obtido como substrato sólido rico em carbono através da pirólise do bagaço de cana-de-açúcar em temperaturas acima de 300 °C em ambiente livre de oxigênio. Nano-biochar, um composto inovador de tamanho nanométrico, é preparado a partir de biochar a granel usando abordagens de cima para baixo, como moagem de bolas, centrifugação, sonicação e síntese hidrotérmica. Comparado ao biochar a granel normal, o Nano-biochar apresenta vantagens significativas em termos de área de superfície, tamanho de poro, volume total de poro e funcionalidades de superfície. No geral, as funções e propriedades biocatalíticas do nanobiochar têm amplas aplicações em sensores, imobilização de enzimas e produção de polímeros.

Palavras-chave:
Bagaço de Cana; Nano-biocatalisador; Biorremediação de resíduos de petróleo; Economia circular

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, 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 nanobiochar 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 (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 (Iwuozor 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

The 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 characteristics and their effective material properties. These following properties make Nano-biocatalysts promising candidates for various applications (Ouyang et al., 2023). They include 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 and Eco-friendly: Minimizing environmental impact.

Review and Analysis
Oil Spill Cleanup Methods

When dealing with oil spills on sea surfaces, three primary methods (Ouyang et al., 2023), are commonly employed in onsite oil spill removal and include the following as shown in Figure 1. Mechanical Methods: involve physical techniques and equipment (including booms, skimmers, and sorbents. 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. Biological Methods: These utilize specific microorganisms to interact with or react to oil contamination. 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).

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

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: Biological Processes: These biological treatments 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. Chemical Processes: The Chemical methods include gasification, pyrolysis, hydrothermal carbonization, flash carbonization, torrefaction and Pyrolysis is commonly used to generate biochar from sugarcane bagasse biomass, while hydrothermal carbonization produces hydrochar (Figure 2). 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.

Material Characterization for Nano-Biocatalyst from Sugarcane Bagasse Fly Ash

The previous literature reported the efficiency of nanobiocatalysts, 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 analysis, Field emission scanning electron microscopy, and focused ion beam imaging with energy-dispersive X-ray spectrometry and Fourier transform infrared spectroscopy. This characterization provides 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 using 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 take more time for large-scale cleanup and sometimes 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 (Ivshina, 2015). Notably, using oil sorbents to treat oil spills in water is a smart approach. It allows for complete oil collection and recovery directly from water surfaces, making it eco-friendly, cost-effective, and recyclable. Researchers have increasingly emphasized the development of effective and eco-friendly oil sorbents for oil spill cleanup (Ouyang et al., 2023). The various Nano-catalyst synthesis methods have been widely used to modify bulk biochar and nano-biochar to enhance their properties (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), and ultrasonic modification (Li et al., 2017b) and Liu et al., (2020) modified wood chip Nano biochar using 3-mercaptopropyltrimethoxysilane.

The chemical method involves the significant mechanism of amine-modified adsorbents of surface and functional group modifications which play a very vital role in material characterization for the removal of carbon-dioxide gas, via two ways, (i) the Amine impregnation method and (ii) the Amine grafting (bonding) method. 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. 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. This modified Nano biochar exhibited significantly higher specific surface area 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 nanobiochars (Vishnu et al., 2022). 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 to support material environments (Visser et al., 2023). This is because biochar has many of the traits that a catalyst support needs, such as high surface area, tunable pore structure, and high stability in acidic and basic environments. 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.

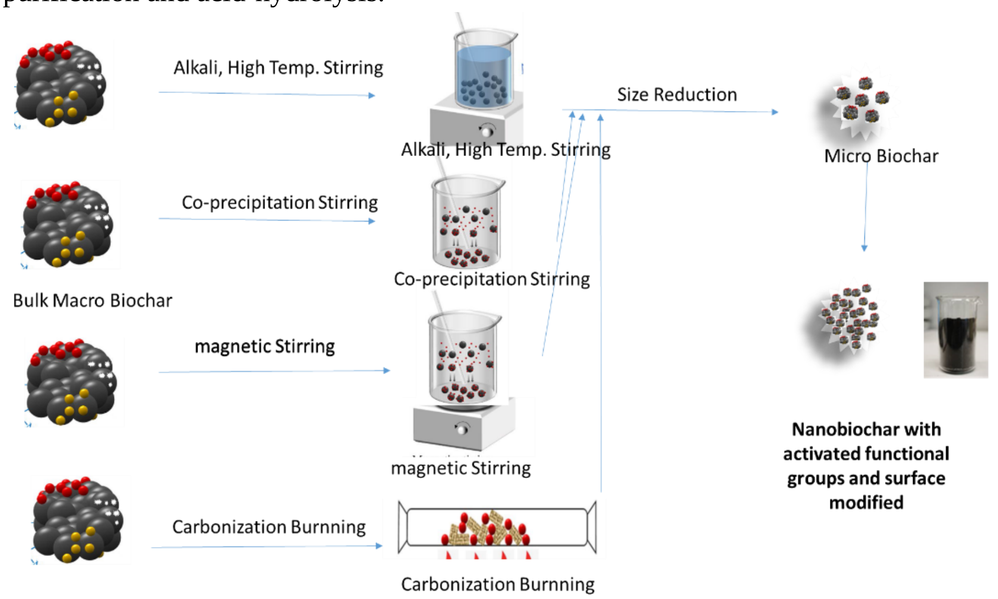

Figure 2. Methods for preparation of Nanobiochar

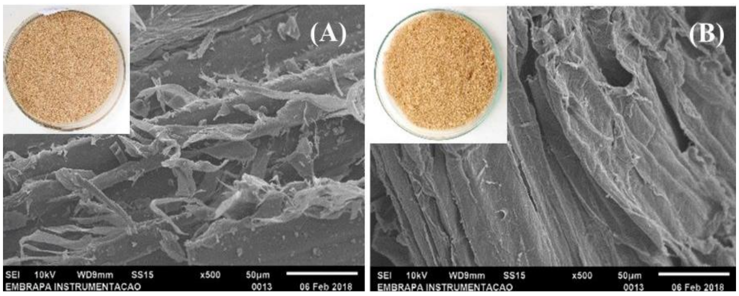

Figure 3. Scanning electron microscopy micrographs and images of (A) Raw sugarcane bagasse, (B) Alkali treated sugarcane bagasse

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, transmission electron microscopy, and atomic force microscopy analyses were performed (Figure 3). Elemental analysis may be denoted by the presence of sulfur impurities in CNCs, along with other main components. Structural changes were assessed using Fourier-transform infrared spectroscopy and X-ray diffraction, while thermal analysis may reveal that CNCs exhibited lower thermal stability and higher crystallinity compared to native cellulose. These characterization studies play a significant role in confirming the functionality, stability, and potentiality of fabricated nanobiochar.

Conclusions

Overall, this chemical methodology holds promise as a resourceful process for carbon nanocrystals (CNC) research using sugarcane bagasse (SCB). The reformation of sugarcane bagasse into carbon nanocrystals develops their adsorption and absorption competencies for liquid and solid waste removal. During the gasification of biomass, the CO_2 is trapped and put in storage in the biochar. Also, the biochar treatment in the carbon-assisted water electrolysis process includes a carbon-based electrode that is recycled in the manufacture of hydrogen gas. This sequesters carbon (for greater than 1,000 years), and is reprocessed in numerous applications including soil improvement, construction materials, biofuel, etc. Moreover, this helps indirectly for climate resilience and circular economy which leads to enforcing the sustainable development of waste management and reuse of sugarcane waste byproducts

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