Sustainable Mechanochemical Engineering of Biochar for Advanced Hydrophobic Coatings

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Abstract. This study presents an innovative and sustainable approach for the functionalization of biochar through mechanochemical amidation in the presence of octadecylamine. The proposed methodology represents an attractive alternative to conventional solution-based processes, as it reduces solvent consumption, operational costs, and environmental impact while offering excellent scalability. The obtained material was extensively characterized by spectroscopic and morphological techniques, which confirmed the successful formation of amide functional groups on the biochar surface and excluded the simple adsorption of amine molecules onto the carbon matrix. The introduction of long alkyl chains significantly enhanced the hydrophobicity of the biochar, owing to both the exposure of hydrophobic moieties and the increased surface roughness. These features make the modified material particularly suitable for the development of water-repellent coatings for hemp fibers. Through a dip-coating process, the treated hemp fibers exhibited remarkable hydrophobic behavior, reaching a water contact angle of 126° after only one deposition layer. Furthermore, the biochar-coated hemp fibers demonstrated excellent oil absorption performance from emulsion systems,

1. Introduction

Hydrophobic materials are of growing interest in materials science due to their wide range of applications, including self-cleaning surfaces, anti-stain textiles, separation systems, and functional coatings.[1]
Hydrophobicity can be achieved either through chemical modification of surfaces [2] or by applying hydrophobic coatings.[3] Surface functionalization provides strong and stable binding but often requires complex procedures and may have environmental drawbacks. In contrast, coatings are more versatile, cost-effective, and applicable to different substrates, although their long-term stability can be limited by possible leaching. Among coating techniques, dip-coating is widely used due to its simplicity and scalability.
Carbon-based materials, such as graphene derivatives, are commonly employed because of their tunable surface chemistry and suitability for hydrophobic applications in textiles, corrosion-resistant coatings, and glass surfaces.[4]
Functionalization of carbon materials typically requires the introduction of oxygen-containing groups, often via graphite oxidation (e.g., Hummers method), which is effective but environmentally demanding. More sustainable approaches may reduce functionalization efficiency.
Biochar, a biomass-derived carbon material, represents a sustainable alternative with high porosity and tunable properties. It is widely used in environmental applications and can be chemically modified to enhance its functionality. [5] Compared to graphite, biochar can be oxidized under milder conditions, enabling further chemical transformations such as esterification or amidation to tune surface polarity.
However, most functionalization strategies rely on solvent-based processes that require large reagent consumption and long reaction times.[6] To address these limitations, this work proposes a solvent-free mechanochemical approach using planetary ball milling to functionalize biochar with octadecylamine, aiming to produce hydrophobic materials in a more sustainable and efficient way.
The modified biochar is further evaluated as a coating for hemp fibers, a renewable material with good mechanical and thermal properties but intrinsic hydrophilicity. Surface modification is expected to enhance their hydrophobic and oleophilic behavior, enabling efficient oil uptake from aqueous systems.

2. Results and discussion

2.1. Biochar selection

Octadecylamine (ODA) was selected as a long-chain alkyl amine suitable for imparting hydrophobic properties to the coatings. [6]

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To determine the functional groups present in pristine biochar (BC), oxidized biochars (oBC), and the milled one (oBC_{BM}) a comprehensive characterization was performed using elemental analysis (EA), Fourier-transform infrared spectroscopy (FTIR), Brunauer–Emmett–Teller (BET) surface area measurements, and pH analysis. The corresponding results are reported in Table 1 and Figure 1.

Table 1. Elemental analysis, surface area, and pH of the biochar and its derivatives

Sample	C (%)	H (%)	O (%)	N (%)	O/C	SA (m^2/g)[a]	pH[b]
BC	78.9	2.7	18.0	0.4	0.23	81	7.97
oBC	**72.7**	2.8	24.0	0.5	0.33	<1	4.30
oBC_{BM}	**69.7**	1.3	28.9	0.1	0.41	103	4.00

The FTIR spectrum reported in Figure 1 shows a distinct absorption band at around 1700 cm^{-1}, attributed to the C=O stretching vibrations of carbonyl groups. This band becomes more intense and broadened with increasing oxidation degree. The marked decrease in pH further confirms the carboxylic nature of the carbonyl functionalities, which are essential for the subsequent amidation step. It has to be noted that the additional milling step perfomed on the oxidized powder , reducing the particle size of the carbon material, increases the surface area and exposes a greater number of functional groups, thereby improving their availability for subsequent reactions.

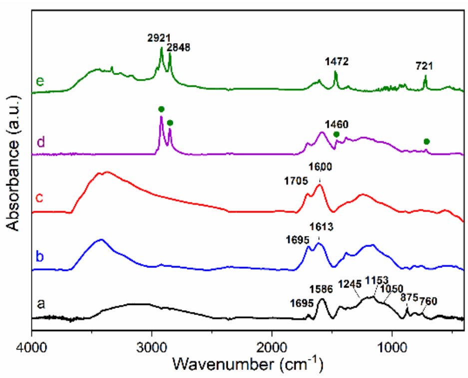

Figure 1. FTIR of a) Biochar (BC), b) Oxidized biochar (oBC), c) milled oxidized Biochar (oBC_{BM}), f) oBC_{BM}/ODA, g) ODA. Solid dots showing the wavenumbers related to ODA.

2.2. Mechanochemical functionalization and characterization of oBC_{BM} with ODA

The reaction was performed in the same conditions lately reported. [7] In a silicon nitride jar, oBC_{BM} and ODA in a ratio of 1 to 1 were added and milled for 2h at 300 rpm in a planetary ball milling. The resulting powder, oBC_{BM}/ODA, was recovered without any solvent and washed three times with 30 ml of ethanol to remove the excess amine residue. After drying at 60°C for 12h, the powder was characterized first by WAXD and TGA.

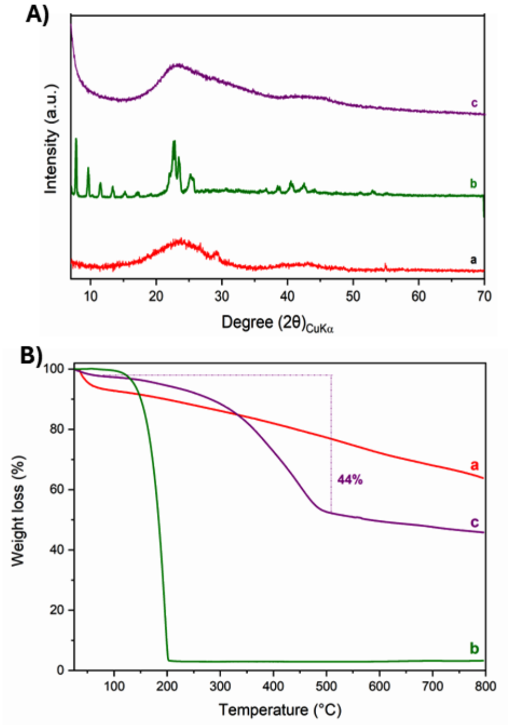

Figure 2. A) WAXD and B) TGA of a) oBC_{BM}, b) ODA and c) oBC_{BM}/ODA

Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) were conducted on the obtained powder. As illustrated in Figure 1d, the spectrum exhibits characteristic absorption bands attributable to octadecylamine (ODA) at 2916, 2845, and 717 cm^{-1}, corresponding to the $–CH_2$ stretching vibrations of the alkyl chain. Furthermore, a noticeable shift is observed from 1472 cm^{-1} in the pristine amine to 1463 cm^{-1} in the functionalized powder, which can be ascribed to modifications induced by the grafting process.

TGA analysis (Figure 2B) confirms a high degree of functionalization, with a weight loss of up to 44%. This result is supported by elemental analysis, which shows a significant increase in nitrogen content from 0.1% in the starting oBC_{BM} to 2.4% in the oBC_{BM}/ODA material after reaction.

Furthermore, the WAXD analysis (Figure 2A) shows the absence of crystalline peaks and the appearance of a broad amorphous halo.

XPS analysis was performed on oBC_{BM}/ODA as the best sample to rule out a simple sorption mechanism and ensure the formation of a new covalent bond. For the sake of comparison, further analyses were also carried out for BC/ODA, to verify the different nature of the covalent bond formed.

From the fit outcomes (Figure 3), it was observed that nitrogen reacted differently depending on whether the biochar had undergone prior oxidation. Specifically, when the ODA treatment was performed on pristine BC, pyridinic groups constituted the predominant fraction among all nitrogen-containing groups. Conversely, when biochar was oxidized and milled before functionalization, the nitrogen distribution shifted toward pyridone/amine groups, suggesting distinct reaction pathways and thus confirming the amide formation.

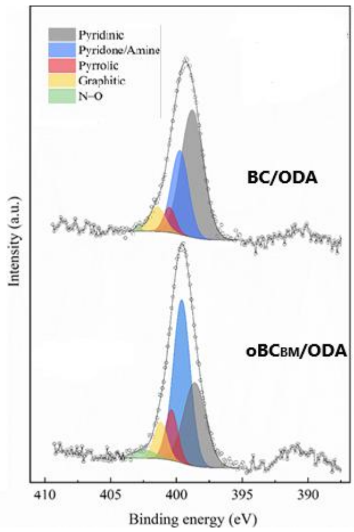

Figure 3. N1s spectra peaks fit of the two ODA-modified carbons

2.3 Application of oBC_{BM}/ODA as hydrophobic coating

A dip coating of the oBC_{BM}/ODA was performed on hemp fiber to evaluate a possible application in removing oil from the emulsion. The dip coating was chosen as the coating technique because it is a quick, easy, affordable, and high-quality method that, being economical and well-managed, represents a useful approach to providing a sustainable water-repellent coated fiber. Limonene was chosen as green solvent. (Figure 4)

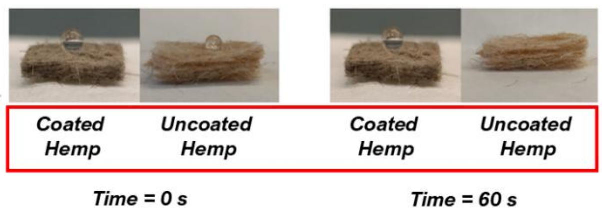

Figure 4. Contact angles of hemp fibers before and after dip-coating in limonene dispersions

Contact angle measurements provide insight into the polarity changes induced by the coating. As shown in Figure 4, uncoated hemp exhibits an initial contact angle of 123°, which decreases to zero within 60 s due to water penetration into the inherently hydrophilic fiber structure. In contrast, hemp fibers coated with oBC_{BM}/ODA using a limonene-based dispersion display a comparable initial contact angle of 126°, but only decrease to 117° after 60 s, indicating a transition to hydrophobic behavior.

The notably reduced affinity for water suggests the possibility of removing apolar molecules in a water emulsion. Therefore, to demonstrate the absorption capacity of the oBC_{BM}/ODA composite, an oil/water separation experiment was performed

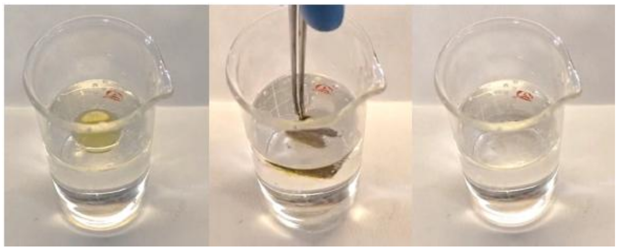

Figure 5. Oil adsorption by hydrophic coated hemp.

As evidenced by Figure 5, the coated fibers demonstrated a remarkable oil absorption capacity (up to 1400%), outperforming previously reported approaches, highlighting their potential for environmental cleanup applications, especially in oil-water separation systems

3. Conclusions

This work presents an innovative, low-cost, scalable, and fully sustainable strategy for biochar functionalization via a solvent-free mechanochemical amidation process using octadecylamine (ODA). The approach replaces conventional solvent-based methods, operating at room temperature with minimal reagent use and leveraging renewable carbon feedstocks, thereby significantly reducing environmental impact.
Successful covalent grafting of ODA was confirmed through spectroscopic and morphological analyses. The mechanochemical treatment increases the degree of functionalization and yields a hydrophobic carbon-based material suitable as a filler for water-repellent coatings When applied to hemp fibers via dip-coating, the modified biochar imparts strong hydrophobicity, reaching a contact angle of up to 126°. The treated fibers also exhibit excellent oil absorption capacity (up to 1400%), outperforming previously reported systems and highlighting their potential for oil–water separation and environmental remediation applications. Overall, the renewable nature of the material, the green synthesis route, and the achieved multifunctional properties make this system promising for anti-wetting, anti-icing, and antifouling coatings in marine and outdoor environments.

Acknowledgement
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