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Hydrophobic and Robust Sugarcane Bagasse-Based Biosorbents for Oil Spill Cleanup: Synergy of Hydrothermal Treatment and Cellulose Nanofibril Reinforcement

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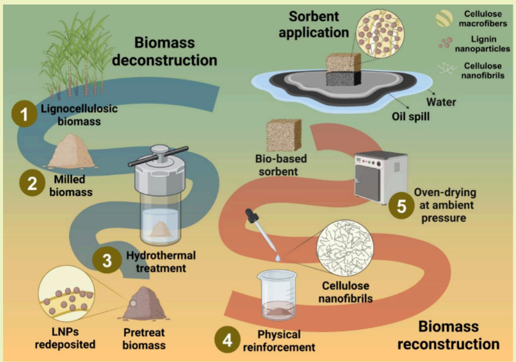

ABSTRACT: Lignocellulosic fibers, particularly those derived from agro-industrial residues, offer a promising alternative for sustainable oil sorbents. However, their practical application in oil spill remediation is often limited by insufficient mechanical resistance, poor hydrophobicity, and challenges in cost-effective processing. To address these limitations, this study proposes a novel approach aligned with Green Chemistry principles, developing an oil sorbent entirely from sugarcane bagasse (SCB) through a sustainable two-step process. First, the biomass was deconstructed via physical milling and hydrothermal treatment with water at 200 °C. Then, the fiber network was reconstructed by incorporating 0.1 wt % cellulose nanofibrils (CNFs) derived from SCB, followed by oven-drying. This is the first report to explore the synergistic effect of redeposited lignin nanoparticles (LNPs) and CNF reinforcement to produce a robust and hydrophobic sorbent from SCB. The resulting sorbent exhibited enhanced mechanical resistance, supporting loads greater than its own weight without structural failure. It also showed inherent hydrophobicity and high oleophilicity with absorption capacities of 4.1 g/g for corn oil, 3.5 g/g for light crude oil, and 5.1 g/g for medium crude oil. Microscopy analyses confirmed the presence of LNPs on the fiber surfaces after hydrothermal treatment, contributing to hydrophobicity alongside micro- and nanoscale surface roughness from fiber packing and LNPs. This work demonstrates how hydrothermal treatment combined with CNF reinforcement can effectively convert sugarcane bagasse into a high-performance, cost-effective, and eco-friendly sorbent for oil spill remediation.

KEYWORDS: *Lignocellulosic fiber, lignin nanoparticles, nanocellulose, hydrophobicity, lightweight material*

INTRODUCTION

Oil spill remediation remains a critical environmental challenge, with millions of gallons of oil entering water bodies annually due to incidents, such as ship ruptures, extraction mishaps, and natural seepage.[1,2] Conventional cleanup methods, including *in situ* burning and the application of chemical dispersants, often exacerbate environmental damage by introducing secondary pollution.[3−5] In contrast, sorbent materials have received attention for their potential to remove oil from water efficiently with minimal secondary impact.[6−8] These materials are typically reusable and can be incinerated for energy recovery at the end of their service life.[5]

Research has explored diverse oil sorbent materials, including inorganic compounds,[9−11] synthetic polymers,[12−14] and lignocellulosic biomass-based alternatives.[15−18] Among these, lignocellulosic biomasses derived from sources such as wood,[19−21] agricultural residues (e.g., sugarcane and corn residues),[18,22,23] and energy crops (e.g., switchgrass and elephant grass)[24] offer a cost-effective and biodegradable approach.[8,25] Common strategies involve purifying the biomass to produce cellulose-enriched solids, followed by conversion into micro- or nanoparticles. These particles are then dried under specific conditions, such as supercritical or freeze-drying, to create aerogels or cryogels, respectively.[18,24] While effective, these methods often require high energy inputs for temperature and pressure control.[26]

A more economical alternative is oven-drying at ambient pressure, which is suitable for large-scale applications. Moreover, using lignocellulosic fibers as the primary component rather than cellulose solutions or nanoparticles reduces production costs and enhances sustainability. Ferreira and Rezende developed an oven-drying method to prepare lightweight materials from eucalyptus pulp without energy-intensive drying steps, cellulose solubilization, or conversion into nanoparticles.[27] This method was later applied to sugarcane bagasse, demonstrating its versatility.[16] In both

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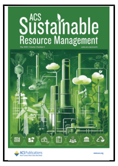

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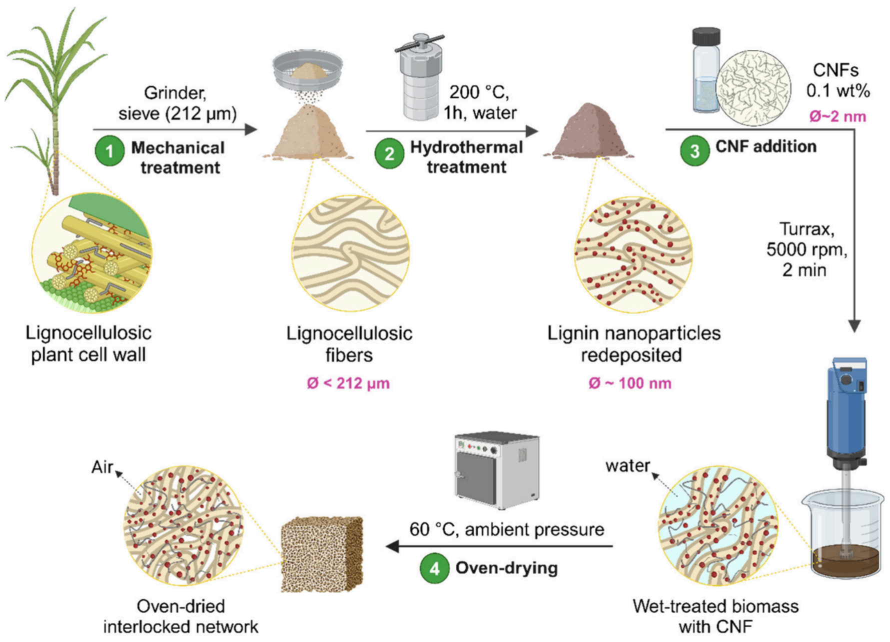

Figure 1. Schematic illustration of the lignocellulosic fiber sorbent preparation process. The method involves: (1) milling SCB, (2) performing hydrothermal treatment to enable lignin redeposition onto fiber surfaces, (3) combining the treated substrate with CNFs at a final concentration of 0.1 wt %, and (4) oven-drying at 60 °C under ambient pressure to produce the mechanically reinforced hydrophobic sorbent. The resulting sorbent is labeled HS-CNF (Table 1).

cases, pretreatment ensured mechanical interlocking, preventing structural collapse during drying.

Chemical modifications to enhance the hydrophobicity and oleophilicity of natural fibers are commonly used to reduce water uptake and improve oil retention in spill remediation. For instance, cellulose modified with octadecylamine achieved a water contact angle (WCA) of 135° and an oil adsorption capacity of 14 g of silicon oil per gram of material.[24] Similarly, a poplar wood sponge modified with polydimethylsiloxane attained a WCA of up to 138° and an oil adsorption capacity of 25 g/g.[19] However, modifications involving long-chain amines and organosilicons pose environmental and health concerns,[28] highlighting the need for greener alternatives.

Lignin, a major component of lignocellulosic biomass, has emerged as a promising alternative due to its inherent hydrophobic properties.[29] By incorporating or retaining lignin, additional functionalities such as thermal stability,[30] UV shielding,[31] and antimicrobial activity[32] can be achieved, alongside improved oil selectivity.[16] Hydrothermal treatment, also known as autohydrolysis, offers a sustainable, chemical-free method to deconstruct lignocellulosic biomass, while preserving most of its lignin content. This treatment involves hydrolyzing the hemicellulose fraction at controlled temperatures (130−220 °C)[33−35] and can also promote the condensation and redeposition of lignin onto the fiber surfaces,[36] potentially creating hydrophobic layers for various applications.[37]

The mechanical limitation of lignocellulosic sorbents can pose a significant challenge for their practical use. Loose-form sorbents or discrete particles are prone to detachment and dispersion in marine environments, which reduces their effectiveness in oil spill remediation and creates a new pollution problem.[38] To address this, reinforcing lignocellulosic-based sorbents through physical or chemical crosslinking is paramount. Cellulose nanofibrils (CNFs) are a promising additive, enhancing both mechanical performance and structural resistance.[39] CNFs are nanoscale fibrillar structures derived from cellulose, featuring diameters in the nanometer range and lengths in the micrometer range.[40] They combine high tensile strength and flexibility, enhancing mechanical properties through physical interactions even at very low concentrations.[41]

In this study, we propose a novel and sustainable strategy for producing oil sorbents entirely from sugarcane bagasse by combining hydrothermal treatment (with no added catalyst) and CNFs. To the best of our knowledge, this is the first study to explore the synergistic use of redeposited lignin nanoparticles (LNPs) and CNF reinforcement to develop a robust and hydrophobic sorbent solely from sugarcane bagasse (SCB). The hydrothermal treatment, performed at 200 °C for 1 h, preserved the lignin in the substrate, facilitating its redeposition onto the fiber surface and enhancing hydrophobicity. The controlled pretreatment conditions were key to optimizing the sorbent performance. The incorporation of CNFs provided essential mechanical stability. The resulting sorbent demonstrated excellent oil removal efficiency across various types of oils, presenting a sustainable and cost-effective solution for oil spill remediation.

■ EXPERIMENTAL SECTION

Materials. Sugarcane bagasse was kindly donated by Raízen (Piracicaba, Brazil) and dried overnight in a convection oven (Tecnal TE-394/3) at 60 °C. The crude oil samples used for sorption analysis, classified by the American Petroleum Institute (API) as light petroleum (API > 40) and medium petroleum (API 28.8), were sourced from sedimentary basins along the Brazilian coast and generously supplied by the Laboratory of Research and Development of Methodologies for Analysis of Oils (LabPetro). Corn oil (ρ_{oil} = 0.92 g/cm^3) and citric acid (≥99.5% purity) were purchased from Sigma-Aldrich.

CNFs were prepared from SCB using an organosolv treatment followed by TEMPO-mediated oxidation, following a methodology previously developed by this group with minor modifications.[42] The organosolv treatment was performed using a 40:60 (v/v) ethanol/water solution at a solid-to-liquid ratio of 1:10 (w/v) in a sealed reactor at 200 °C for 1 h. This step partially removed lignin and hemicellulose, improving cellulose accessibility and facilitating fiber disintegration. The resulting pulp was then subjected to TEMPO-mediated oxidation with a NaClO concentration of 25 mmol/g to introduce surface carboxylate (COO^-) groups, enhancing further fibrillation.[42] To promote mechanical fibrillation and obtain individualized CNFs, the oxidized material was ultrasonicated for 15 min using a probe-type sonicator operating at 60% amplitude (330 W power and 20 kHz frequency) in an ice bath. The resulting CNFs exhibited an average diameter of approximately 2 nm and a length of about 660 nm. The surface charge, determined by zeta potential measurements, was −49 ± 1 mV. The morphology of the CNFs is presented in Figure S1.

Preparation of Hydrophobic CNF-Reinforced Lignocellulosic Sorbents. Figure 1 illustrates the process used to produce lignocellulosic sorbents with an interlocked fiber network. The process includes SCB milling, hydrothermal treatment, CNF incorporation, and sorbent preparation via oven-drying. Each step is described in detail in the following sections.

Mechanical and Hydrothermal Treatment. SCB was ground using a grinder (SL-31, SOLAB) and sieved through a 212 μm mesh (BERTEL) (Step 1, Figure 1). The milled, *in natura* SCB fibers (labeled as INFs) were then subjected to hydrothermal treatment at an INF-to-water ratio of 1:10 (wt %) (Step 2, Figure 1). The mixture of INFs and water was placed in a stainless-steel reactor, which was heated in a silicon oil bath at 200 °C for 1 h. After the reaction, the reactor was cooled to room temperature. The fibers were separated from the liquid using a 75 μm mesh sieve, rinsed with 100 mL of water, and stored wet at 4 °C to prevent fiber coalescence until sorbent preparation. These hydrothermally treated fibers were labeled HFs (Table 1).

Table 1. Abbreviations and Descriptions of the Sorbents and Fibers Used in This Study[a]

Abbreviation	Description
HS	Hydrothermally treated sorbent
HS-CNF	Hydrothermally treated sorbent reinforced with CNFs
INS-CNF	*In natura* sorbent reinforced with CNFs
AS	Alkaline treated sorbent
AS-CA	Alkaline treated sorbent crosslinked with citric acid
HS-CA	Hydrothermally treated sorbent crosslinked with citric acid
INFs	*In natura* fibers
HFs	Hydrothermally treated fibers
AFs	Alkaline treated fibers
BFs	Bleached fibers

[a] Hydrothermal, alkaline, and bleaching treatments were applied to modify the lignocellulosic structure, while citric acid and CNFs were used for chemical and physical crosslinking, respectively.

CNF Incorporation and Oven Drying. The sorbent was prepared by incorporating CNFs into a dispersion of HFs. CNFs were tested at concentrations of 0.01, 0.1, and 1 wt % relative to the fiber weight. At 0.01 wt %, the material lacked sufficient mechanical strength and collapsed under pressure. At 1 wt %, the material became excessively compacted during the drying process, significantly reducing the surface area of the sorbent. The optimal concentration was determined to be 0.1 wt %, as it improved the mechanical strength without excessive compression during oven-drying. CNFs were added to HFs at this concentration, and the mixture was homogenized using an Ultra Turrax (IKA T25, Staufen, Germany) at 5000 rpm for 2 min (Step 3, Figure 1). The homogenized mixture was then transferred into cylindrical stainless-steel molds and dried in a convection oven at 60 °C under ambient pressure until a constant mass was achieved (Step 4, Figure 1).

Control Experiments: CNF-Reinforced Untreated SCB and Hydrothermally Treated Sorbents Cross-Linked with Citric Acid. Control experiments were conducted to verify the effectiveness of our proposed system. To evaluate the need for hydrothermal treatment, sorbents were prepared using *in natura* SCB fibers combined with CNFs, following the same protocol used for sorbents made from hydrothermally treated fibers. These sorbents were labeled INS-CNF.

To assess the role of CNFs as a reinforcement agent, we tested citric acid (CA) as a crosslinker, based on a methodology previously used by our research group for crosslinking alkaline-treated fibers.[16] For CA crosslinking, fibers were dispersed at 40 g/L in a CA solution (1.4 g of citric acid per 1 g of fiber). The dispersion was stirred with a glass rod, transferred to cylindrical stainless-steel molds, and dried at 60 °C in a convection oven until a constant mass was achieved. The temperature was then increased to 150 °C for 5 min to induce CA crosslinking.[43,44] These samples were labeled as HS-CA.

To verify the effect of hydrothermal treatment on fiber hydrophobicity and the role of lignin, SCB underwent two distinct treatments: one for partial lignin removal and another for nearly complete lignin removal. In the first treatment, SCB was subjected to alkaline treatment with 2% (w/v) NaOH at a 1:10 wt % ratio, based on a method developed by our research group.[16] The alkaline-treated fibers were labeled AFs. In the second treatment, 40 g of SCB was immersed in 800 mL of a 5% (w/w) NaOH solution and heated to 70 °C. Hydrogen peroxide (24% w/w in water) was gradually added, and the mixture was stirred at 500 rpm for 40 min. The resulting bleached pulp was filtered, rinsed with water, and neutralized.[42] The bleached fibers were labeled BFs.

Characterization. *Composition Analysis.* The biomass composition was analyzed following the National Renewable Energy Laboratory (NREL) protocols to determine sugars, soluble and insoluble lignin, and ash content.[45] Briefly, SCB samples were hydrolyzed with 72 wt % H_2SO_4. The solid fraction was separated from the liquor using porcelain crucibles, dried at 105 °C to a constant mass, and then calcined at 800 °C in a muffle furnace (EDG10P-S, EDG). Soluble sugars were analyzed by high-performance liquid chromatography (HPLC) on an Agilent series 1200 chromatograph equipped with a refractive index detector (model G1322A) and an Aminex HPX-87H column (Bio-Rad). The mobile phase consisted of diluted H_2SO_4 (5.10^{-3} mol/L). Soluble lignin was quantified by absorbance measurements at 280 nm by using a UV-vis spectrophotometer (Cary 50 Probe, Varian, Agilent, Santa Clara, CA, USA).

Results are presented as means and standard deviations of replicates. Statistical analyses were performed by analysis of variance (ANOVA one-way). Significant differences between means were verified through the F-test, and Tukey's test at a 95% confidence level was used to compare the mean values. All of the statistical analyses were conducted using Statistica software (Dell). All assays were performed at least in duplicate.

Surface Morphology Analyses. The surface morphology of fibers and sorbents was examined by field-emission scanning electron microscopy (FESEM, Quanta 250, FEI) at 5 kV using a secondary electron detector. Samples were coated with an iridium MCS 010 coater (Bal-Tec) with a current of 11.3 mA for 120 s before analysis. Lignin nanoparticles that redeposited on hydrothermally treated fibers were analyzed using ImageJ by counting 1,805 particles from six regions, and a histogram was generated for size distribution.

SCB fibers were also characterized by using a Leica TCS SP5 confocal laser scanning microscope (CLSM). Hydrothermally treated fibers were placed on glass slides, covered with coverslips, and excited with an argon laser at 488 nm. The emitted fluorescence was detected within the 500−700 nm range. Observations were made using an HCX PL APO 20×/0.7 objective lens.

Fiber Wettability. The wettability of INFs, HFs, AFs, and BFs was assessed by depositing a 2 μL Milli-Q water droplet onto an individual fiber and observing absorption for up to 60 s using an optical microscope (Nikon Eclipse 80i) equipped with a Nikon Plan Fluor 4×/0.13 WD lens.

Water Contact Angle Measurements. Static WCA was measured using a drop shape analyzer (DSA100, Krüss). Water droplets (2 μL) were deposited on the sorbent surface, and contact angles were recorded every second for 5 s. Standard deviations were calculated using Krüss ADVANCE software.

Mechanical Testing. Compression tests were performed on HS-CNF and INS-CNF (0.1 wt % CNF reinforcement) following the ASTM D695 standard. Samples were cut into cubes, conditioned at 23 ± 2 °C and 50 ± 5% relative humidity for 48 h, and tested in a universal testing machine (Instron model 3366) at 1.3 mm/min. Young's modulus was determined from the linear region of the stress−strain curves (<5% strain).

Fourier-Transform Infrared Spectroscopy (FTIR). Lignocellulosic sorbents were characterized by FTIR (Agilent, model CARY 630) in the 4000 to 400 cm^{-1} range using the attenuated total reflectance (ATR) mode.

Apparent Density Determination. The apparent density (ρ_{app}) of the sorbent samples was determined by cutting the samples into cubes, measuring their dimensions with a caliper, and calculating the volume. The apparent density (eq 1) is defined as the ratio of the mass (m) to the total volume (V) of the sorbent.

$$\rho_{\text{app}} = \frac{m}{V} \tag{1}$$

Oil Adsorption Capacity. The oil adsorption capacity of HS-CNF was evaluated according to ASTM-F726-17, with minor adaptations to measure adsorption in the absence of water for the three oil types. Sorbents (0.5 g) were cut into 1.5 cm cubes and conditioned before testing. Adsorption capacity (S) (g of sorbate/g of adsorbent) was calculated using eq 2, where S_{O} (g) is the initial dry weight of the sorbent, S_{ST} (g) is the final weight after adsorption, and S_{S} is the net oil adsorbed ($S_{\text{S}} = S_{\text{ST}} - S_{\text{O}}$), as defined in ASTM-F726-17.

$$S = \frac{S_{\text{S}}}{S_{\text{O}}} = \frac{S_{\text{ST}} - S_{\text{O}}}{S_{\text{O}}} \tag{2}$$

An alternative sorption test was conducted to evaluate the influence of water on oil removal. In this test, 200 μL of oil was added to a container filled with distilled water, and then, the HS-CNF sorbent was introduced to collect the oil.

■ RESULTS AND DISCUSSION

Effect of Hydrothermal Treatment on Substrate Chemical Composition and Morphology. Hydrothermal treatment was applied to SCB to modify its chemical composition and impart hydrophobicity without chemical additives. As shown in Figure 2, the treatment significantly reduced hemicellulose content from 25 to 2 wt %, leading to an increase in cellulose from 38 to 56 wt %. Although the absolute lignin content decreased, the removal of hemicellulose led to an increase in the relative lignin concentration (28 to 37 wt %, Table S1). This reduction aligns with the known effect of hydrothermal treatment at temperatures above 185 °C, where hemicellulose hydrolyzes into monomers even without acid addition, and smaller lignin fractions may also be solubilized.[46,47]

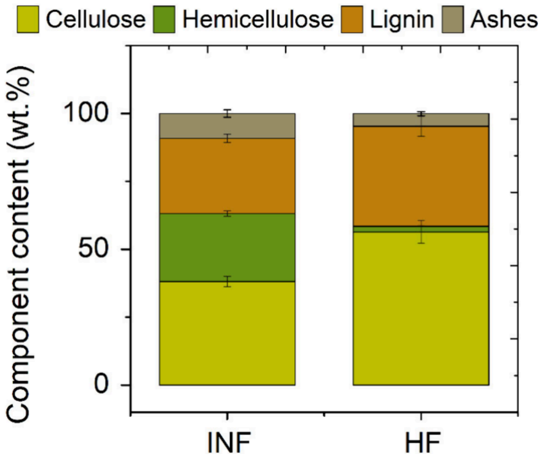

Figure 2. Chemical composition of *in natura* sugarcane bagasse fibers (INFs) and hydrothermally treated fibers (HFs). Tukey's test ($p < 0.05$) confirms significant differences in all mean values before and after treatment. Error bars represent the standard deviation of triplicates.

The impact of hydrothermal treatment on fiber morphology was further analyzed using FESEM. Images of *in natura* (Figure 3a) and hydrothermally treated (Figure 3b) fibers revealed notable surface modifications. LNPs, ranging from approximately 100 to 300 nm in diameter (Figure S2), were observed on hydrothermally treated fibers (Figure 3b) but were absent in *in natura* fibers (Figure 3a). Additional FESEM images are shown in Figure S3.

In addition to LNPs, FESEM analysis revealed larger lignin clusters exceeding 1 μm in diameter on fiber surfaces (yellow arrow, Figure 3b). These clusters, significantly larger than surrounding LNPs, were further analyzed using CLSM imaging (Figure 3c), where their autofluorescence under laser excitation confirmed the presence of lignin.[48−50]

Hydrothermal treatment appears to play a key role in restructuring surface components, leading to lignin redistribution into nanoparticles and clusters. This morphological alteration may enhance the fiber hydrophobicity and entanglement. Similar lignin redeposition effects have been reported in studies using scanning electron microscopy, both with and without diluted acid.[37,51−54]

Due to the presence of lignin nanoparticles and clusters on hydrothermally treated fibers, their hydrophobic nature was evaluated through wettability tests on individual fibers of untreated and hydrothermally treated SCB (Figure 4). Small water droplets (2 μL) were deposited on the fiber surface, and the droplet shape was observed by optical microscopy. For comparison, alkaline-treated and bleached fibers, with lignin contents of 14 and 5 wt %, respectively, were also tested. Hydrothermally treated fibers exhibited a pronounced hydrophobicity, consistent with the residual and redeposited lignin (Figure 4). Untreated SCB fibers also showed hydrophobicity due to their inherent lignin content and possibly some residual waxes. In contrast, alkaline-treated fibers (AFs) demonstrated partial wetting, indicative of increased hydrophilicity, likely due to the lower lignin content (14 wt %) and the absence of redeposited lignin nanoparticles (Figure S4). Bleached fibers (5 wt % lignin) wetted instantly, reinforcing the strong correlation between lignin presence and fiber hydrophobicity (Figure 4). Notably, while lignin is hydrophobic, its properties can be altered by extraction methods, sometimes making it more hydrophilic.[55]

In summary, hydrothermal treatment induced significant morphological and compositional changes in the SCB (Figure 5). Hemicellulose, which dissolves in water during treatment, was removed during washing, while lignin underwent condensation at high temperatures.[56−58] This process led to the formation of spherical lignin structures that redeposited onto fiber surfaces (Figure 3b), imparting a characteristic darker brown color to the treated biomass (Figure S5).[46] These LNPs covered large portions of the fiber surface. The observed color and structural changes reflect the chemical and

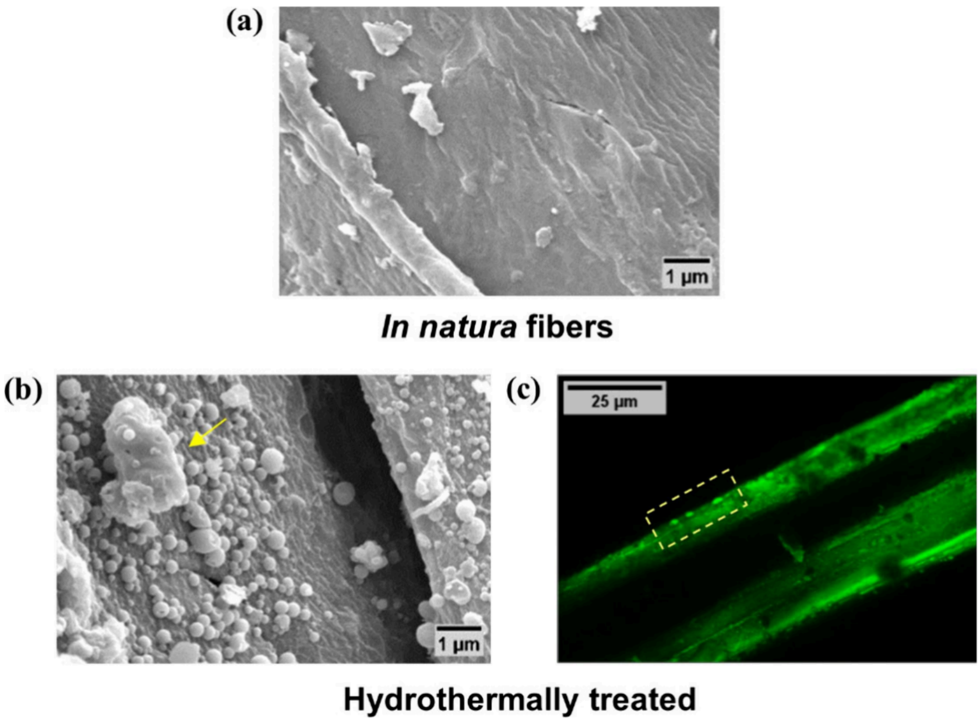

Figure 3. FESEM images of (a) *in natura* and (b) hydrothermally treated SCB fibers (yellow arrow indicates lignin cluster) and (c) CLSM image showing lignin nanoparticle clusters (bigger than 1 μm), indicated by a yellow dashed rectangle.

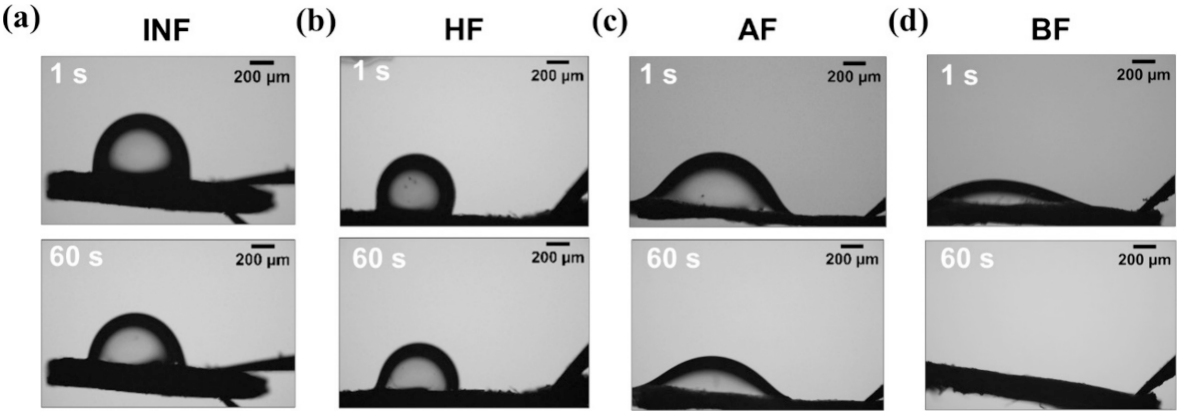

Figure 4. Wettability tests were performed using (a) sugarcane bagasse *in natura* fibers (INFs), (b) hydrothermally treated fibers (HFs) treated with water at 200 °C for 1 h, (c) alkaline fibers (AFs) treated with a 2% w/v NaOH solution at 120 °C for 1 h, and (d) bleached fibers (BFs) with a 5% w/w NaOH solution and hydrogen peroxide (24% w/w in water). The results indicate higher contact angles in INFs and HFs, reflecting lower wettability compared to that of AFs, which was partially wetted. In contrast, BFs, with the lowest lignin content, wetted instantly. Water droplets on the INFs and HFs remained on the surface for at least 60 s before the video was stopped. The lignin content for each fiber type was as follows: INFs, 28 wt %; HFs, 37 wt %; AFs, 14 wt %; and BFs, 5 wt %.

morphological transformations of lignin during hydrothermal treatment, suggesting that the hydrophobicity of native lignin, recondensed on the surface, was largely preserved, enhancing the water-repellent properties of the sorbent.

Sorbent Prepared with Hydrothermally Treated Fibers Mechanically Reinforced with CNFs. The hydrothermally treated sorbent (HS) maintained its integrity after demolding and manual handling, despite lacking reinforcement or crosslinking (Figure S6a). This suggests fiber cohesion, likely due to intermolecular interactions. However, it exhibited low mechanical strength and collapsed under light pressure (Figure S6b), highlighting the need for structural reinforcement, especially for marine applications. Despite this limitation, the hydrophobic nature of the fibers allowed HS to withstand magnetic stirring in water without collapsing (Figure S6c,d).

To enhance mechanical properties, CNFs were incorporated into hydrothermally treated fibers at 0.1 wt %. The resulting HS-CNF sorbent (1 cm^3 and 0.5 g) withstood a 1000 g load without failure (Figure 6a), demonstrating the reinforcing potential of the CNFs. Their high strength and surface area likely facilitated physical crosslinking, forming an interconnected fiber network without chemical agents, offering a sustainable reinforcement strategy. Compression tests further confirmed this effect, with HS-CNF exhibiting a Young's modulus of 3.81 ± 0.22 MPa and resistance up to 70% strain (Figure 6b,c), ensuring robustness under mechanical stress.

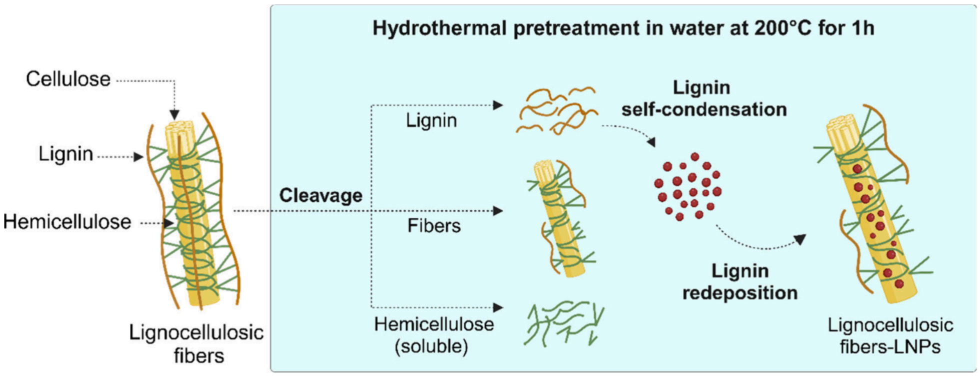

Figure 5. Schematic illustration of the lignin removal process during hydrothermal treatment followed by condensation and redeposition onto the fiber surface.

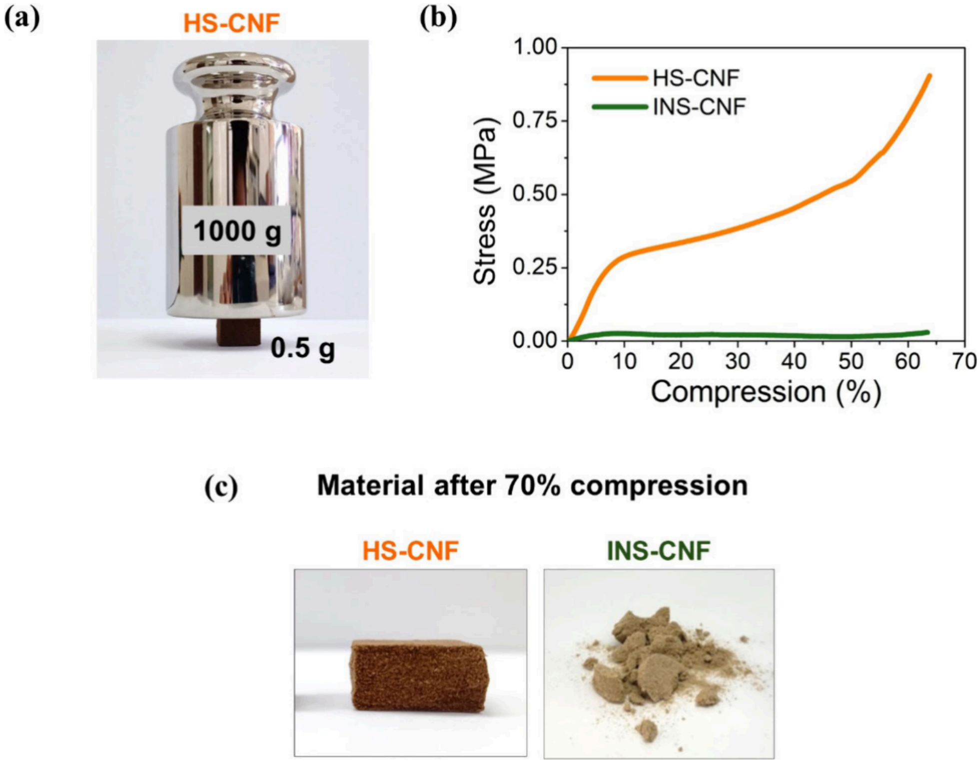

Figure 6. (a) Image of HS-CNF sorbent (0.5 g), reinforced with 0.1 wt % CNF, supporting a 1000 g weight without collapsing; (b) compressive mechanical testing of HS-CNF and INS-CNF; (c) visual comparison of HS-CNF and INS-CNF sorbents immediately after release of a 70% compression.

HS-CNF also demonstrated excellent durability in water, maintaining structural integrity under agitation (Figure S7 and Video S1). This resilience is important for oil spill remediation. Additionally, its low apparent density (0.170 ± 0.003 g/cm^3) is comparable to lightweight materials such as coir-polyurethane composites (0.26 g/cm^3)[59] and sugarcane foams (0.09 g/cm^3 and 0.116 g/cm^3),[16,60] ensuring buoyancy for efficient oil sorption.

The role of hydrothermal treatment was further evidenced by comparing HS-CNF to a sorbent prepared with *in natura* sugarcane bagasse fibers (INS-CNF). INS-CNF exhibited a significantly lower Young's modulus (0.46 ± 0.03 MPa) and collapsed under compression (Figure 6b,c), indicating the importance of hydrothermal treatment in improving fiber interactions. The treatment likely increased functional groups on the fiber surface, promoting hydrogen bonding between the fibers and CNFs, resulting in a cohesive structure. Without these modifications, *in natura* fibers remained more recalcitrant, limiting CNF integration and mechanical reinforcement.

To evaluate CNFs as reinforcing agents, an alternative crosslinking approach using citric acid (HS-CA) was tested. This strategy had previously been shown to effectively crosslink alkaline-treated SCB fibers.[16] CA is a good comparison since it is a green crosslinking agent, based on a chemical mechanism. Despite its effectiveness with alkaline-treated fibers, citric acid failed to crosslink hydrothermally treated fibers, as HS-CA (1 cm^3 and 0.5 g) collapsed under a 1000 g load (Figure 7a).[26]

FTIR analysis (Figure 7b) suggested that increased lignin exposure after hydrothermal treatment hindered ester bond formation, preventing effective crosslinking. In contrast, alkaline-treated fibers exhibited partial lignin removal, enabling

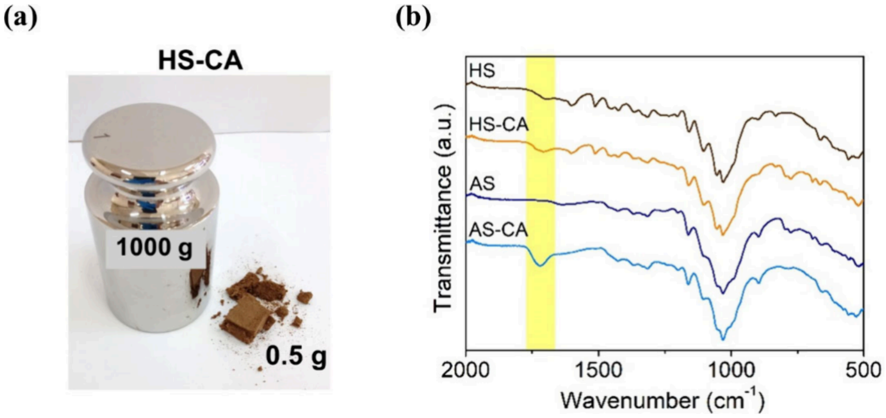

Figure 7. (a) Image of HS-CA, which collapsed under 1000 g weight; (b) ATR-FTIR spectra of lignocellulosic sorbent evidencing the carbonyl region at 1740 cm^{-1} for different sorbents: hydrothermal treated sorbent (HS), hydrothermal treatment followed by citric acid crosslinking sorbent (HS-CA), alkaline treated sorbent (AS), and alkaline treatment followed by citric acid crosslinking sorbent (AS-CA).

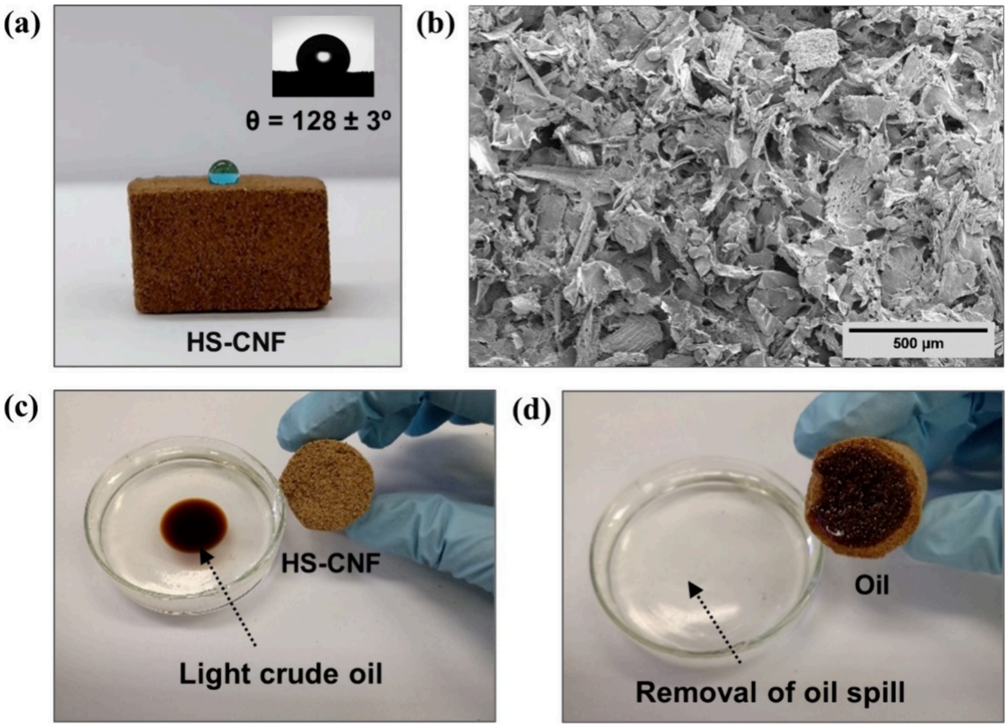

Figure 8. (a) HS-CNF with a blue water droplet and its corresponding water contact angle; (b) FESEM image showing microroughness on the sorbent surface; (c) removal of light petroleum from the surface of distilled water; (d) water surface after oil absorption, showing the sorbent with sorbed oil.

successful citric acid crosslinking, as indicated by a pronounced ester band at 1740 cm^{-1}. These findings align with studies showing that lignin-rich surfaces restrict chemical cross-linking,[16,61] emphasizing the need for tailored treatment strategies.

CNFs successfully reinforced hydrothermally treated fibers through physical crosslinking, while citric acid crosslinking was ineffective due to lignin interference. Alkaline-treated sorbents with CNFs demonstrated high mechanical strength but were highly hydrophilic, becoming wet upon contact with water. This behavior resulted from the low lignin content, which could not enhance the surface hydrophobicity, along with the inherent hydrophilicity of CNFs. On the other hand, hydrothermally treated fibers retained their hydrophobic properties, with CNFs having minimal effect on wettability. These results underscore the impact of biomass composition and treatment methods on optimizing lignocellulosic sorbents for practical uses.

Hydrophobicity and Oleophilicity of the Sorbent. The HS-CNF not only demonstrated improved mechanical properties but also exhibited enhanced hydrophobic characteristics, with a water contact angle of 128 ± 3° (Figure 8a and Video S2). The hydrophobicity of the HS-CNF was influenced by the retention of the native hydrophobicity of lignin in hydrothermally treated fibers, surface roughness from fiber packing (Figure 8b), and nanoscale redeposition of LNPs (Figure 3b). Additionally, porosity further enhanced water repellency.[16] These factors work synergistically to create a hydrophobic material with lignin forming a hydrophobic barrier and the hierarchical surface roughness amplifying water repellency.

Table 2. Comparison of the Oil Sorption Capacity of the Prepared HS-CNF Sorbent with Other Lignocellulosic Biomass Sorbents Reported in the Literature[a]

Biomass	Sorbent	Modification Methods	Type of Oil	Adsorption Capacity	Ref.
Sugarcane bagasse	HS-CNF	Hydrothermal treatment/Physical reinforcement (CNF)	Corn oil, light and medium crude oil	4.1 g/g, 3.5 g/g, and 5.1 g/g	Present work
Sugarcane bagasse	Foam	Alkaline treatment/Chemical crosslinking (CA)	Corn oil	9 g/g	16
Sugarcane bagasse	Cryogel*	Alkali treatment/Crosslinking (PVA)/Freeze-drying/MTMS coating	Crude oil	25 g/g	18
Populus fiber	Loose fibers	Hydrothermal treatment/Acetylation	Corn oil	21.57 g/g	21
Coconut fibers	Loose fibers	Protic ionic liquid	Crude oil	1.40 g/g	17
Cotton fiber	Loose fiber	C18 fatty acid-modification	Crude oil	35.58 g/g	22
Rice husks	Loose fiber	Alkali treatment	Marine diesel	20 g/g	23
Balsa wood	Sponge	$NaClO_2$ solution/Alkali treatment/Freeze-drying/Silylation (MTCS)	Oil and organic solvent	2.44 to 17.3 g/g	20
Poplar wood	Sponge	Mixed solution of $NaClO_2$ and CH_3COOH/Alkali treatment/Freeze-drying/Crosslinking (PVA)/PDMS	Silicone oil	25 g/g	19
Water hyacinth	Membrane	$NaClO_2$ solution/Alkali treatment/Additional bleaching (H_2O_2)/Freeze-drying/Periodate oxidation and ultrasound-assisted defibrillation/ODA	Silicone oil	14 g/g	24

[a] The table includes details on the sorbent, modification methods, types of oil used, and adsorption capacities. For entries marked with an asterisk (*), we use the term "cryogel" to describe materials that were freeze-dried and "aerogel" for those that were supercritically dried, as defined by Buchtová et al.[65]

This behavior aligns with wettability models like Wenzel and Cassie-Baxter,[62,63] where multi-scale roughness helps trap air at the solid-liquid interface, reducing water penetration. The LNPs contribute to this effect by increasing surface roughness at both the microscale and nanoscale.

After the hydrophobicity of the material was confirmed, oil adsorption capacity tests were performed using three oils: corn vegetable oil, light crude oil (API > 40), and medium crude oil (API 28.8). While vegetable oils and simpler solvents are often used in similar studies, crude oils offer a more realistic evaluation of sorbent performance under practical conditions. Table 2 provides a detailed comparison of the oil sorption capacities of the HS-CNF material, alongside values reported in the literature for other biobased sorbents.

The HS-CNF sorbent exhibited oil adsorption capacities ranging from 3.5 to 5.1 g of oil per gram of sorbent, depending on the type of oil. The highest performance was observed for medium crude oil, followed by corn vegetable oil, with the lowest uptake recorded for light crude oil. These differences can be attributed to the viscosity and chemical composition of each oil. Medium crude oil, being more viscous and containing a higher proportion of heavy fractions, tends to adhere more strongly to the sorbent surface, facilitating greater retention. Given the complex composition of petroleum, which includes a wide variety of hydrocarbons and compounds, the development of sorbents tailored to specific oil types is essential.

Table 2 also presents a comparison between HS-CNF and other lignocellulosic-based sorbents reported in the literature. The HS-CNF material demonstrated adsorption capacities within the typical range for natural sorbents (1−35 g/g), confirming its practical performance. Notably, materials with higher capacities, such as cotton fibers (35.58g/g)[22] and poplar wood sponges (25g/g),[19] often involve complex or multi-step chemical modifications, including fatty acid grafting, acetylation, or the use of synthetic crosslinkers. Although these approaches are effective and useful for target applications, they often rely on hazardous reagents or energy-intensive drying techniques, such as freeze-drying or supercritical drying,[18−20,24] which may hinder scalability and environmental compatibility. In contrast, the HS-CNF produced herein applied a greener approach, relying solely on biomass and water, without the need for chemical crosslinking or hazardous substances and presenting oil adsorption capacity in the same range of the materials presented in literature. It also capitalizes on the intrinsic hydrophobicity of lignin, eliminating the need for additional surface functionalization.

While the sorption capacity of the HS-CNF may not be the highest, it provides a more environmentally friendly alternative to other biobased sorbents and a sustainable foundation for future improvements. The preparation process follows Green Chemistry principles,[64] using renewable raw materials (sugarcane bagasse fibers), minimizing hazardous substances, and reducing waste. Importantly, the process avoids the use of toxic chemicals and eliminates energy-intensive steps such as high-temperature drying or chemical activation, thereby supporting sustainability and reducing the overall environmental impact.

Furthermore, the production of HS-CNF is economically viable, as it uses sugarcane bagasse, an abundant and low-cost agro-industrial residue, as the main component. Although CNFs are generally considered costly, their use in this study was limited to only 0.1 wt %, significantly reducing the overall material cost when compared to sorbents based primarily on nanocellulose. Combined with the green hydrothermal pretreatment (using only water under moderate conditions) and the absence of additional modification steps, the resulting sorbent offers a low-cost and scalable solution for oil removal.

In oil spill scenarios, a high sorption capacity alone is not enough; fast absorption is also required to capture the oil before it spreads further. The HS-CNF sorbent demonstrated high oleophilicity and rapid absorption, immediately soaking up a drop of light crude oil upon contact (Video S3). Furthermore, it effectively retained the absorbed oil, preventing release and dripping, which is essential for collection and removal. Tests in distilled water showed the HS-CNF sorbent's high selectivity for oil removal and retention (Figure 8c,d and Video S4). After light crude oil was removed from water, the sorbent retained the oil without losing integrity (Video S4).

The combination of oil sorption capacity, rapid absorption, and strong oil retention suggests that the HS-CNF sorbent has great potential for addressing oil spills under real-world conditions. These results emphasize the value of lignocellulosic biomass as a sustainable and eco-friendly solution for mitigating oil pollution in aquatic ecosystems and highlight the importance of exploring natural materials for environmental remediation.

In this study, oil recovery from the sorbent could potentially be achieved through solvent extraction. While this method is generally effective, it typically requires substantial amounts of organic solvents, which may pose environmental and economic concerns.[66] Other recovery strategies have been reported in the literature, including mechanical squeezing,[67] which is especially suitable for flexible sorbents, and distillation,[68] a solvent-free method that allows oil recovery and reuse. Furthermore, incineration of oil-saturated sorbents has been widely considered a viable end-of-life strategy,[69] enabling energy recovery from both the sorbent matrix and the absorbed oil. Among the reported methods, mechanical squeezing stands out as the most environmentally friendly, as it enables oil recovery and sorbent reuse without the need for solvents or high energy input.[67] However, its effectiveness is dependent on the flexibility of the sorbent material. Therefore, further research is needed to develop sorbents with suitable mechanical flexibility through sustainable and eco-friendly fabrication strategies.

CONCLUSION

This study presents a sustainable approach to developing a renewable oil sorbent from sugarcane bagasse by combining hydrothermal treatment and cellulose nanofibril reinforcement. Hydrothermal treatment, using only water, preserves lignin and promotes lignin nanoparticle redeposition, naturally enhancing fiber hydrophobicity without synthetic hydrophobizing agents. This modification also introduces nanoscale roughness, further improving water repellency and oil sorption selectivity. The incorporation of 0.1 wt % CNF strengthens the fiber network without chemical cross-linkers, maintaining the sorbent lightweight structure. The material exhibited oil adsorption capacities of 3.1−5.1 g oil/g, comparable to other biobased sorbents, but was achieved through a scalable, low-cost, and environmentally friendly process. By integrating biobased modifications with minimal chemical input, this work contributes to the development of sustainable sorbents for oil spill remediation, aligning with Green Chemistry principles.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssusresmgt.5c00110.

AFM image of cellulose nanofibrils; composition analysis of sugarcane bagasse samples; histogram of lignin nanoparticle diameter size distribution; morphological characterization of lignin nanoparticles by FESEM; comparative FESEM images of hydrothermally and alkaline-treated fibers; photographs of biomass color before and after treatment; photographs of the performance of HS and HS-CNF sorbents during water resistance tests (PDF)

Video showcasing the integrity of HS-CNF under magnetic stirring in water (AVI)

Video showcasing HS-CNF's water repellency (AVI)

Video showcasing HS-CNF's oleophilicity (AVI)

Video showcasing HS-CNF's efficiency in recovering light crude oil from distilled water (AVI)

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P.S.F. is the main author of this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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REFERENCES

(1) Naz, S.; Iqbal, M. F.; Mahmood, I.; Allam, M. Marine Oil Spill Detection Using Synthetic Aperture Radar over Indian Ocean. *Mar Pollut Bull.* **2021**, *162*, 111921.

(2) Dong, Y.; Liu, Y.; Hu, C.; MacDonald, I. R.; Lu, Y. Chronic Oiling in Global Oceans. *Science* **2022**, *376*, 1300−1304.

(3) Kleindienst, S.; Paul, J. H.; Joye, S. B. Using Dispersants After Oil Spills: Impacts on the Composition and Activity of Microbial Communities. *Nat. Rev. Microbiol* **2015**, *13* (6), 388−396.

(4) Jørgensen, K. S.; Kreutzer, A.; Lehtonen, K. K.; Kankaanpää, H.; Rytkönen, J.; Wegeberg, S.; Gustavson, K.; Fritt-Rasmussen, J.; Truu, J.; Kõuts, T.; Lilover, M. J.; Seiler, T. B.; Hollert, H.; Johann, S.; Marigómez, I.; Soto, M.; Lekube, X.; Jenssen, B. M.; Ciesielski, T. M.; Wilms, L. B.; Högström, R.; Pirneskoski, M.; Virtanen, S.; Forsman, B.; Petrich, C.; Phuong-Dang, N.; Wang, F. The EU Horizon 2020 Project GRACE: Integrated Oil Spill Response Actions and Environmental Effects. *Environ. Sci. Eur.* **2019**, *31* (1), 44.

(5) Ouyang, D.; Lei, X.; Zheng, H. Recent Advances in Biomass-Based Materials for Oil Spill Cleanup. *Nanomaterials* **2023**, *13* (3), 620.

(6) Liu, H.; Geng, B.; Chen, Y.; Wang, H. Review on the Aerogel-Type Oil Sorbents Derived from Nanocellulose. *ACS Sustain Chem. Eng.* **2017**, *5* (1), 49−66.

(7) Dong, T.; Li, Q.; Nie, K.; Jiang, W.; Li, S.; Hu, X.; Han, G. Facile Fabrication of Marine Algae-Based Robust Superhydrophobic Sponges for Efficient Oil Removal from Water. *ACS Omega* **2020**, *5* (34), 21745−21752.

(8) Zamparas, M.; Tzivras, D.; Dracopoulos, V.; Ioannides, T. Application of Sorbents for Oil Spill Cleanup Focusing on Natural-Based Modified Materials: A Review. *Molecules* **2020**, *25* (19), 4522.

(9) Okiel, K.; El-Sayed, M.; El-Kady, M. Y. Treatment of Oil-Water Emulsions by Adsorption Onto Activated Carbon, Bentonite and Deposited Carbon. *Egyptian Journal of Petroleum* **2011**, *20* (2), 9−15.

(10) Thakkar, S. V.; Pinna, A.; Carbonaro, C. M.; Malfatti, L.; Guardia, P.; Cabot, A.; Casula, M. F. Performance of Oil Sorbents Based on Reduced Graphene Oxide-Silica Composite Aerogels. *J. Environ. Chem. Eng.* **2020**, *8* (1), 103632.

(11) Aivalioti, M.; Vamvasakis, I.; Gidarakos, E. BTEX and MTBE Adsorption onto Raw and Thermally Modified Diatomite. *J. Hazard Mater.* **2010**, *178* (1-3), 136−143.

(12) Alassod, A.; Gibril, M.; Islam, S. R.; Huang, W.; Xu, G. Polypropylene/Lignin Blend Monoliths Used as Sorbent in Oil Spill Cleanup. *Heliyon* **2020**, *6* (9), e04591.

(13) d'Auris, A. de F.; Rubertelli, F.; Taini, A.; Vocciante, M. A Novel Polyurethane-Based Sorbent Material for Oil Spills Management. *J. Environ. Chem. Eng.* **2023**, *11* (6), 111386.

(14) Bhardwaj, N.; Bhaskarwar, A. N. A Review on Sorbent Devices for Oil-Spill Control. *Environmental Pollution* **2018**, *243*, 1758−1771.

(15) Doshi, B.; Sillanpää, M.; Kalliola, S. A Review of Bio-Based Materials for Oil Spill Treatment. *Water Res.* **2018**, *135*, 262−277.

(16) Ferreira, E. S.; Cranston, E. D.; Rezende, C. A. Naturally Hydrophobic Foams from Lignocellulosic Fibers Prepared by Oven-Drying. *ACS Sustain Chem. Eng.* **2020**, *8* (22), 8267−8278.

(17) Cardoso, C. K. M.; Mattedi, S.; Lobato, A. K. de C. L.; Andrade Moreira, Í. T. Remediation of Petroleum Contaminated Saline Water Using Value-Added Adsorbents Derived from Waste Coconut Fibres. *Chemosphere* **2021**, *279*, 130562.

(18) Thai, Q. B.; Nguyen, S. T.; Ho, D. K.; Tran, T. Du; Huynh, D. M.; Do, N. H. N.; Luu, T. P.; Le, P. K.; Le, D. K.; Phan-Thien, N.; Duong, H. M. Cellulose-Based Aerogels from Sugarcane Bagasse for Oil Spill-Cleaning and Heat Insulation Applications. *Carbohydr. Polym.* **2020**, *228*, 115365.

(19) Cai, Y.; Wu, Y.; Yang, F.; Gan, J.; Wang, Y.; Zhang, J. Wood Sponge Reinforced with Polyvinyl Alcohol for Sustainable Oil-Water Separation. *ACS Omega* **2021**, *6* (19), 12866−12876.

(20) Wang, Z.; Lin, S.; Li, X.; Zou, H.; Zhuo, B.; Ti, P.; Yuan, Q. Optimization and Absorption Performance of Wood Sponge. *J. Mater. Sci.* **2021**, *56* (14), 8479−8496.

(21) Zhang, Y.; Yang, S.; Wu, J. Q.; Yuan, T. Q.; Sun, R. C. Preparation and Characterization of Lignocellulosic Oil Sorbent by Hydrothermal Treatment of Populus Fiber. *Materials* **2014**, *6* (9), 6733−6747.

(22) Shin, Y.; Han, K. S.; Arey, B. W.; Bonheyo, G. T.; Bonheyo, G. T. Cotton Fiber-Based Sorbents for Treating Crude Oil Spills. *ACS Omega* **2020**, *5* (23), 13894−13901.

(23) Bazargan, A.; Tan, J.; Hui, C. W.; McKay, G. Utilization of Rice Husks for the Production of Oil Sorbent Materials. *Cellulose* **2014**, *21* (3), 1679−1688.

(24) Bajpai, S.; Nemade, P. R. Silane and Fluorine Free Facile Hydrophobicization of Water Hyacinth Biomass for Oil-Water Separations. *Chemosphere* **2024**, *358*, 142164.

(25) Najar, I. N.; Sharma, P.; Das, R.; Tamang, S.; Mondal, K.; Thakur, N.; Gandhi, S. G.; Kumar, V. From Waste Management to Circular Economy: Leveraging Thermophiles for Sustainable Growth and Global Resource Optimization. *J. Environ. Manage* **2024**, *360*, 121136.

(26) Ferreira, E. S.; Rezende, C. A.; Cranston, E. D. Fundamentals of Cellulose Lightweight Materials: Bio-Based Assemblies with Tailored Properties. *Green Chem.* **2021**, *23* (10), 3542−3568.

(27) Ferreira, E. S.; Rezende, C. A. Simple Preparation of Cellulosic Lightweight Materials from Eucalyptus Pulp. *ACS Sustain Chem. Eng.* **2018**, *6* (11), 14365−14373.

(28) Ye, J.; Cai, P.; Huang, Z.; Pan, Y. Highly Hydrophobic All-Biomass Aerogels with Advanced Oil Absorption and Recyclability. *ACS Appl. Polym. Mater.* **2023**, *5* (5), 3632−3642.

(29) Herrera, R.; Poohphajai, F.; Sandak, A.; Gordobil, O. Simultaneous Improvement of Surface Wettability and UV Resistance of Wood with Lignin-Based Treatments. *Polymers (Basel)* **2023**, *15* (16), 3409.

(30) Zhang, Y.; Zhang, Y.; Cao, Q.; Wang, C.; Yang, C.; Li, Y.; Zhou, J. Novel Porous Oil-Water Separation Material with Super-Hydrophobicity and Super-Oleophilicity Prepared from Beeswax, Lignin, and Cotton. *Science of the Total Environment* **2020**, *706*, 135807.

(31) Zhang, Y.; Naebe, M. Lignin: A Review on Structure, Properties, and Applications as a Light-Colored UV Absorber. *ACS Sustain Chem. Eng.* **2021**, *9* (4), 1427−1442.

(32) Tanganini, I. C.; Camargos, C. H. M.; Jackson, J. C.; Rezende, C. A.; Ceccato-Antonini, S. R.; Faria, A. F. Self-Assembled Lignin Nanoparticles Produced from Elephant Grass Leaves Enable Selective Inactivation of Gram-Positive Microorganisms. *RSC Sustainability* **2024**, *2* (2), 459−474.

(33) Lourencon, T. V.; Greca, L. G.; Tarasov, D.; Borrega, M.; Tamminen, T.; Rojas, O. J.; Balakshin, M. Y. Lignin-First Integrated Hydrothermal Treatment (HTT) and Synthesis of Low-Cost Biorefinery Particles. *ACS Sustain Chem. Eng.* **2020**, *8* (2), 1230−1239.

(34) Zhang, B.; Biswal, B. K.; Zhang, J.; Balasubramanian, R. Hydrothermal Treatment of Biomass Feedstocks for Sustainable Production of Chemicals, Fuels, and Materials: Progress and Perspectives. *Chem. Rev.* **2023**, *123* (11), 7193−7294.

(35) Ruiz, H. A.; Thomsen, M. H.; Trajano, H. L. *Hydrothermal Processing in Biorefineries: Production of Bioethanol and High Added-Value Compounds of Second and Third Generation Biomass*; Springer International Publishing, 2017; DOI: 10.1007/978-3-319-56457-9.

(36) Bajpai, P. *Pretreatment of Lignocellulosic Biomass for Biofuel Production*; Sharma, S. K., Ed.; Jaipur, 2016; DOI: 10.1007/978-981-10-0687-6.

(37) Donohoe, B. S.; Decker, S. R.; Tucker, M. P.; Himmel, M. E.; Vinzant, T. B. Visualizing Lignin Coalescence and Migration Through Maize Cell Walls Following Thermochemical Pretreatment. *Biotechnol Bioeng* **2008**, *101* (5), 913−925.

(38) U.S. Environmental Protection Agency. *Understanding Oil Spills And Oil Spill Response*; 1999; https://www.epa.gov/emergency-response-research/oil-spill-research (accessed 2025-01-13).

(39) Yildirim, N.; Shaler, S. M.; Gardner, D. J.; Rice, R.; Bousfield, D. W. Cellulose Nanofibril (CNF) Reinforced Starch Insulating Foams. *Cellulose* **2014**, *21* (6), 4337−4347.

(40) Kargarzadeh, H.; Mariano, M.; Gopakumar, D.; Ahmad, I.; Thomas, S.; Dufresne, A.; Huang, J.; Lin, N. Advances in Cellulose Nanomaterials. *Cellulose* **2018**, *25*, 2151−2189.

(41) Missio, A. L.; Otoni, C. G.; Zhao, B.; Beaumont, M.; Khakalo, A.; Kämäräinen, T.; Silva, S. H. F.; Mattos, B. D.; Rojas, O. J. Nanocellulose Removes the Need for Chemical Crosslinking in Tannin-Based Rigid Foams and Enhances Their Strength and Fire Retardancy. *ACS Sustain Chem. Eng.* **2022**, *10* (31), 10303−10310.

(42) Pinto, L. O.; Bernardes, J. S.; Rezende, C. A. Low-Energy Preparation of Cellulose Nanofibers from Sugarcane Bagasse by Modulating the Surface Charge Density. *Carbohydr. Polym.* **2019**, *218*, 145−153.

(43) Meftahi, A.; Khajavi, R.; Rashidi, A.; Rahimi, M. K.; Bahador, A. Preventing the Collapse of 3D Bacterial Cellulose Network via Citric Acid. *J. Nanostructure Chem.* **2018**, *8* (3), 311−320.

(44) Ottenhall, A.; Seppänen, T.; Ek, M. Water-Stable Cellulose Fiber Foam with Antimicrobial Properties for Bio Based Low-Density Materials. *Cellulose* **2018**, *25* (4), 2599−2613.

(45) Sluiter, J.; Sluiter, A. *Summative Mass Closure: Laboratory Analytical Procedure (LAP) Review and Integration*; NREL/TP-510-48087; 2011; https://www.nrel.gov/docs/gen/fy11/48087.pdf.

(46) Martín, C.; Dixit, P.; Momayez, F.; Jönsson, L. J. Hydrothermal Pretreatment of Lignocellulosic Feedstocks to Facilitate Biochemical Conversion. *Front. Bioeng. Biotechnol.* **2022**, *10*, 1.

(47) Ibbett, R.; Gaddipati, S.; Davies, S.; Hill, S.; Tucker, G. The Mechanisms of Hydrothermal Deconstruction of Lignocellulose: New Insights from Thermal-Analytical and Complementary Studies. *Bioresour Technol.* **2011**, *102* (19), 9272−9278.

(48) Chimenez, T. A.; Gehlen, M. H.; Marabezi, K.; Curvelo, A. A. S. Characterization of Sugarcane Bagasse by Autofluorescence Microscopy. *Cellulose* **2014**, *21* (1), 653−664.

(49) Maceda, A.; Terrazas, T. Fluorescence Microscopy Methods for the Analysis and Characterization of Lignin. *Polymers (Basel)* **2022**, *14* (5), 961.

(50) Coletta, V. C.; Rezende, C. A.; Rodrigues Da Conceição, F.; Polikarpov, I.; Gontijo Guimarães, F. E. Mapping the Lignin Distribution in Pretreated Sugarcane Bagasse by Confocal and Fluorescence Lifetime Imaging Microscopy. *Biotechnol Biofuels* **2013**, *6*, 43.

(51) Li, H.; Pu, Y.; Kumar, R.; Ragauskas, A. J.; Wyman, C. E. Investigation of Lignin Deposition on Cellulose During Hydrothermal Pretreatment, Its Effect on Cellulose Hydrolysis, and Underlying Mechanisms. *Biotechnol. Bioeng* **2014**, *111*, 485−492.

(52) Xiao, L.-P.; Sun, Z.-J.; Shi, Z.-J.; Xu, F.; Sun, R.-C. Impact of Hot Compressed Water Pretreatment on the Structural Changes of Woody Biomass for Bioethanol Production. *Bioresources* **2011**, *6* (2), 1576−1598.

(53) Selig, M. J.; Viamajala, S.; Decker, S. R.; Tucker, M. P.; Himmel, M. E.; Vinzant, T. B. Deposition of Lignin Droplets Produced During Dilute Acid Pretreatment of Maize Stems Retards Enzymatic Hydrolysis of Cellulose. *Biotechnol Prog.* **2007**, *23* (6), 1333−1339.

(54) Kristensen, J. B.; Thygesen, L. G.; Felby, C.; Jørgensen, H.; Elder, T. Cell-Wall Structural Changes in Wheat Straw Pretreated for Bioethanol Production. *Biotechnol Biofuels* **2008**, *1*, 5.

(55) Ruwoldt, J.; Blindheim, F. H.; Chinga-Carrasco, G. Functional Surfaces, Films, and Coatings with Lignin - A Critical Review. *RSC Adv.* **2023**, *13* (18), 12529−12553.

(56) Wang, H.; Xiong, F.; Tan, Y.; Yang, J.; Qing, Y.; Chu, F.; Wu, Y. Preparation and Formation Mechanism of Covalent-Noncovalent Forces Stabilizing Lignin Nanospheres and Their Application in Superhydrophobic and Carbon Materials. *ACS Sustain Chem. Eng.* **2021**, *9* (10), 3811−3820.

(57) Cheng, M. H.; Maitra, S.; Clennon, A. N. C.; Appell, M.; Dien, B. S.; Singh, V. The Effects of Sequential Hydrothermal-Mechanical Refining Pretreatment on Cellulose Structure Changes and Sugar Recoveries. *Biomass Convers Biorefin* **2024**, *14*, 27149.

(58) Trajano, H. L.; Engle, N. L.; Foston, M.; Ragauskas, A. J.; Tschaplinski, T. J.; Wyman, C. E. The Fate of Lignin during Hydrothermal Pretreatment. *Biotechnol Biofuels* **2013**, *6* (1), 110.

(59) Hoang, P. H.; Dat, H. T.; Cuong, T. D.; Dien, L. Q. Pretreatment of Coir Lignocellulose for Preparation of a Porous Coir-Polyurethane Composite with High Oil Adsorption Capacity. *RSC Adv.* **2022**, *12* (24), 14976−14985.

(60) Halysh, V.; Sevastyanova, O.; Pikus, S.; Dobele, G.; Pasalskiy, B.; Gun'ko, V. M.; Kartel, M. Sugarcane Bagasse and Straw as Low-Cost Lignocellulosic Sorbents for the Removal of Dyes and Metal Ions from Water. *Cellulose* **2020**, *27* (14), 8181−8197.

(61) Ma, Y.; You, X.; Rissanen, M.; Schlapp-Hackl, I.; Sixta, H. Sustainable Cross-Linking of Man-Made Cellulosic Fibers with Poly(Carboxylic Acids) for Fibrillation Control. *ACS Sustain Chem. Eng.* **2021**, *9* (49), 16749−16756.

(62) Wenzel, R. N. Resistance of Solid Surfaces to Wetting by Water. *Ind. Eng. Chem.* **1936**, *28* (8), 988−994.

(63) Cassie, A. B. D.; Baxter, S. Wettability of Porous Surfaces. *Trans. Faraday Soc.* **1944**, *40*, 546−551.

(64) Warner, J. C.; Cannon, A. S.; Dye, K. M. Green Chemistry. *Environ. Impact Assess Rev.* **2004**, *24* (7-8), 775−799.

(65) Buchtová, N.; Pradille, C.; Bouvard, J. L.; Budtova, T. Mechanical Properties of Cellulose Aerogels and Cryogels. *Soft Matter* **2019**, *15* (39), 7901−7908.

(66) Zamparas, M.; Tzivras, D.; Dracopoulos, V.; Ioannides, T. Application of Sorbents for Oil Spill Cleanup Focusing on Natural-Based Modified Materials: A Review. *Molecules* **2020**, *25*, 4522.

(67) Wang, S.; Peng, X.; Zhong, L.; Tan, J.; Jing, S.; Cao, X.; Chen, W.; Liu, C.; Sun, R. An Ultralight, Elastic, Cost-Effective, and Highly Recyclable Superabsorbent from Microfibrillated Cellulose Fibers for Oil Spillage Cleanup. *J. Mater. Chem. A Mater.* **2015**, *3* (16), 8772−8781.

(68) Cheng, H.; Gu, B.; Pennefather, M. P.; Nguyen, T. X.; Phan-Thien, N.; Duong, H. M. Cotton Aerogels and Cotton-Cellulose Aerogels from Environmental Waste for Oil Spillage Cleanup. *Mater. Des* **2017**, *130*, 452−458.

(69) Tan, J. Y.; Low, S. Y.; Ban, Z. H.; Siwayanan, P. A Review on Oil Spill Clean-up Using Bio-Sorbent Materials with Special Emphasis on Utilization of Kenaf Core Fibers. *BioResources* **2021**, *16* (4), 8394−8416.