Switchable Biomaterials for Wastewater Treatment

by

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ABSTRACT

The development of novel switchable biomaterials has gained significant attention due to their potential in wastewater treatment, offering sustainable and cost-effective solutions for contaminant removal. This thesis presents a comprehensive review of the diverse applications of switchable biomaterials, including chitosan, polylactic acid (PLA), cellulose, biochar, rubber, resin, and crude fibers. These materials exhibit stimulus-responsive functionalities that facilitate recyclability and pollutant recovery, making them promising candidates for environmental remediation. Despite substantial advancements, challenges such as stability, recyclability, and performance optimization remain. Future research should focus on improving these aspects while exploring novel hybrid materials to enhance their applicability in real-world scenarios.

Based on the research gaps identified by the literature review, the thesis work further focuses on the development and optimization of a spiropyran-assisted cellulose aerogel (CNF-SP) aerogel with UV-induced switchable wettability, and the evaluation of its performance as an effective sorbent for oil spill cleanup. Beyond oil spill remediation, the switchable properties of the aerogel hold great potential for broader wastewater treatment applications, particularly in selectively adsorbing hydrophobic and hydrophilic contaminants. The aerogel initially exhibited strong hydrophobicity (124°) and showed UV-induced switchable wettability due to the photo-response structure of spiropyran. Upon UV irradiation, the hydrophobicity of the aerogel could

be switched to hydrophilicity (31°), while visible light irradiation could restore its hydrophobicity. The three-dimensional (3D) porous structure of the CNF-SP aerogel combined with the hydrophobic properties of spiropyranol led to its great oil adsorption performance (27-30 g/g of oil adsorption ratio). To systematically optimize the material, the central composite design (CCD) was applied, as it allows for efficient exploration of the interaction effects among multiple factors. The raw materials, including carboxymethyl cellulose, carboxyethyl spiropyran, polyvinyl alcohol, and nano zinc oxide, were specifically chosen due to their roles in enhancing mechanical stability, responsiveness, and adsorption capacity. The optimized CNF-SP aerogel demonstrated a high oil sorption efficiency, particularly in acid and cold environments. Moreover, the switchable function indicated that the aerogel exhibited reusability and renewability, with the added benefit of UV-induced oil recovery. However, potential limitations, such as the scalability of the synthesis process and real-world deployment challenges, remain key concerns that require further investigation. Through the development of the CNF-SP aerogel, this thesis directly addresses challenges in oil spill remediation by offering a material capable of adapting to diverse environmental conditions while ensuring high oil adsorption efficiency and sustainability. The study underscores the transformative potential of switchable biomaterials in mitigating the environmental impact of water pollution, reaffirming their role as a critical advancement in the field of wastewater treatment.

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CHAPTER 1

INTRODUCTION

1.1 Background

Water contamination is an increasingly urgent global issue, exacerbated by rapid industrialization, intensive agricultural practices, and widespread urbanization. These activities contribute to the pervasive release of pollutants, including heavy metals, organic compounds, pharmaceuticals, and oils, into natural water bodies. These contaminants not only disrupt aquatic ecosystems but also pose significant risks to public health, potentially leading to severe consequences such as bioaccumulation in the food chain, toxic exposure, and the proliferation of antibiotic-resistant bacteria. Additionally, regulatory policies and economic constraints often limit the implementation of advanced water treatment technologies, necessitating the development of cost-effective and adaptable solutions.

Traditional wastewater treatment methods, such as chemical precipitation, adsorption, coagulation, flocculation, and membrane filtration, have long been employed to mitigate these environmental threats. While effective to a certain extent, these conventional approaches often suffer from several drawbacks. High operational costs, energy-intensive processes, the generation of secondary pollutants, and limited efficacy in treating complex, multi-component mixtures of contaminants are among the key challenges (Hoang et al., 2021; Zhang et al., 2019). For instance, adsorption processes may require frequent regeneration of adsorbent materials, which can be economically unfeasible on a large scale. Membrane filtration systems, though

efficient, are prone to fouling and require regular maintenance, further increasing the operational burden.

Given these limitations, there is a pressing need for more sustainable, efficient, and adaptable solutions in wastewater treatment. This has driven the exploration of innovative materials that can not only address the shortcomings of traditional methods but also offer enhanced performance in diverse and challenging environmental conditions. One of the most promising areas of research in this context is the development of switchable biomaterials.

Switchable biomaterials are advanced materials that can dynamically alter their physical and chemical properties in response to external stimuli such as changes in pH, temperature, magnetic fields, or light. This tunable nature allows for greater control over the adsorption and release of contaminants, potentially leading to more precise and effective water treatment solutions. Materials such as cellulose, biochar, chitosan, and natural rubber are at the forefront of this research, offering a range of environmental benefits, including biodegradability, low toxicity, and the ability to be sourced from renewable resources (Lin et al., 2023).

Moreover, the incorporation of switchable functionalities into these biomaterials can significantly enhance their selectivity for specific contaminants, improve their recyclability, and extend their lifespan in treatment systems. For example, cellulose-based materials can be chemically modified to introduce functional groups that selectively bind to heavy metals or organic pollutants, while biochar can be

engineered to respond to changes in environmental conditions, thereby optimizing its adsorption capacity. Existing research has explored diverse strategies for oil/water separation, employing experimental and modeling techniques, sustainable technologies, and feasibility studies. Several studies have highlighted the importance of integrating multi-functional approaches to optimize separation efficiency and recyclability, which directly aligns with the objectives of this research (Usman et al., 2023).

The development of such materials also opens up opportunities for the integration of multi-functional systems that can simultaneously address different types of contaminants, reducing the need for separate treatment stages and minimizing energy consumption. Spiropyran (SP), a typical photoresponsive compound, exhibits rapid and reversible wettability transitions under UV light due to its molecular structural changes (Klajn, 2014). Recent studies have explored SP-doped membranes for oil/water separation, demonstrating UV-triggered hydrophobic-hydrophilic transitions (Dehkordi et al., 2021). However, its application in controlling the wettability of cellulose aerogels remains unexplored. As a result, switchable biomaterials are emerging as a key focus of current material science research, with the potential to revolutionize wastewater treatment by offering more efficient, cost-effective, and environmentally friendly alternatives to traditional methods (Madhav et al., 2019).

In summary, the shift towards the use of switchable biomaterials in wastewater treatment represents a significant step forward in addressing the complex challenges

posed by modern water contamination. While the existing limitations of conventional materials have been extensively discussed, there is still a lack of knowledge regarding the feasibility of applying switchable biomaterials at a large scale and their long-term stability in real-world conditions. These materials not only promise to overcome the limitations of existing treatment technologies but also contribute to the broader goal of achieving sustainable water management in an increasingly polluted world.

1.2 Statement of Problems

(1) Lack of a comprehensive literature review

Despite considerable advancements in the development of switchable biomaterials for water pollutant treatment, there is still a lack of a comprehensive review of the functionalities of different types of innovative switchable biomaterials and an in-depth analysis of the underlying mechanisms of pollutant removal during their applications. The literature review serves as a foundation for identifying gaps in material selection, optimization techniques, and potential multi-functional applications. Research gaps are to be identified in terms of the progress of their specific development and specialized applications. Future research prospects need to be discussed regarding the generation of promising switchable biomaterials, thereby contributing to more effective and sustainable wastewater treatment solutions that are both innovative and environmentally friendly.

(2) Lack of improved cellulose aerogels with switchable wettability for oily wastewater treatment

Hydrophobic cellulose aerogels have been widely used for oil spill cleanup due to their high adsorption rate, rapid process, and recyclability. To enhance their reuse and regeneration, researchers have introduced switchable wettability into these aerogels, with UV-induced switchable wettability gaining interest for its simplicity, efficiency, and fast transition. For instance, a nanofibrillated cellulose aerogel grafted with melamine and cetyltrihexylsilane showed excellent oil/water separation and 95% recovery after repeated washing and UV treatment. Spiropyran (SP), a compound that undergoes molecular changes under UV, has been used in some studies to control wettability, as seen in a porous membrane that alternated between hydrophobic and hydrophilic properties for oil/water separation. However, SP has yet to be used to control the wettability of cellulose aerogels.

1.3 Objectives

To fill the above-stated research gaps, this thesis thus aims to systematically review current research on switchable biomaterials and their applications in water contaminant removal and to develop a switchable cellulose-based material as a sorbent for handling oil spills. By integrating the literature review and experimentation, the thesis work would help advance the understanding and development of switchable biomaterials, thereby contributing to more effective and sustainable wastewater treatment. Specifically, the objectives of this thesis are:

(1) to review current research studies on various categories of switchable biomaterials, including cellulose, biomass-containing heteroatoms, biochar, and other advanced biomaterials, detailing the progress of their specific development and specialized applications and underlying mechanisms of pollutant removal; and

(2) to develop a spiropyran-assisted cellulose aerogel (CNF-SP aerogel) with UV-induced switchable wettability as an oil sorbent in oil spill cleanup by synthesizing the switchable biomaterial and optimizing the synthesis process, identifying the effects of main raw materials of the aerogel and their interactions on oil adsorption, characterizing the developed CNF-SP aerogel, investigating the influences of water environmental conditions on its performance, and utilizing the developed CNF-SP aerogel for crude oil adsorption efficiency and evaluating the material recovery. Furthermore, the study aims to explore the potential applications of the developed aerogel in broader wastewater treatment scenarios beyond oil spill remediation.

1.4 Thesis Structure

The literature review serves as the theoretical foundation for the experimental work by identifying key knowledge gaps and guiding material selection and process optimization. This thesis is structured with four main chapters. Chapter 1 is the Introduction. It provides the background of the research, the statement of problems, and outlines the objectives and structure of the thesis. Chapter 2 is the Literature Review. It offers a comprehensive review of existing research on switchable

biomaterials, discussing various materials such as cellulose, biochar, chitosan, and rubber, their applications in contaminant removal, and the challenges associated with their use. Chapter 3 is Experiment Research. It describes a new development of switchable cellulose-based areogel, including the methods used for the synthesis and characterization of the new biomaterials. Futhermore, it presents the findings from the synthesis and performance and discusses the implications for wastewater treatment. Chapter 4 is the Conclusion and Recommendations. It summarizes the key findings, discusses the limitations of the study, and provides recommendations for future research.

In general, this thesis seeks to contribute to the development of sustainable and efficient solutions for water contamination by advancing the understanding and application of switchable biomaterials. The exploration of these materials promises to bridge existing gaps in current wastewater treatment technologies, offering new pathways to achieving cleaner and safer water systems. This highlights the potential of switchable biomaterials as a cornerstone of next-generation water treatment technologies.

CHAPTER 2

A REVIEW ON SWITCHABLE BIOMATERIALS FOR WASTEWATER TREATMENT: FROM MATERIAL INNOVATIONS TO TECHNOLOGICAL ADVANCEMENTS

Chapters 2 are generated based on the following publication:

Wang, H., Chen, X., Chen, B., Yang, M., & Zhang, B. (2025). Switchable biomaterials for wastewater treatment: From material innovations to technological advancements. Chemical Engineering Journal, 160928. https://doi.org/10.1016/j.cej.2025.160928

*Hongjie Wang and Dr. Baiyu Zhang conceived of the presented idea. Hongjie Wang carried out the researches documents collection, discussed the results and contributed to the final version of the manuscript. Min Yang helped with figures illustration. Xiujuan Chen contributed to the text revision. Dr. Baiyu Zhang and Dr. Bing Chen encouraged and supervised the findings of this work.

2.1 Background

Wastewater treatment is critical for protecting both environmental and human health, involving the effective removal of contaminants from wastewater before it is released into water bodies. It has been imperative due to the increasing contamination of water sources caused by industrial, agricultural, and domestic activities (Madhav et al., 2019). Traditional technologies of wastewater treatment, such as chemical precipitation, adsorption, and membrane filtration, although effective, often come with drawbacks such as high operational costs and secondary pollution (Saravanan et al., 2021). To enhance the cost-effectiveness and sustainability of wastewater treatment technologies, a number of innovative materials have been developed. Among various materials, biomaterials have garnered significant attention since they are generally low-cost and environmentally friendly (Madhav et al., 2019). Biomaterials derived from natural sources offer a renewable and biodegradable alternative to synthetic materials, thus minimizing environmental impact. Within this context, switchable biomaterials have shown considerable promise in recent years (Fumasi et al., 2020).

Switchable biomaterials are advanced biomaterials capable of altering their properties in response to specific external stimuli, such as temperature, pH, light, or electric fields (Guo & Guo, 2016). This responsiveness enables dynamic control over their behavior, making them particularly valuable in applications like wastewater treatment, where conditions can vary significantly. Fig. 1 briefly illustrates switching mechanism.

Several types of switchable biomaterials have been explored, each exhibiting unique properties that give them many advantages and make them suitable for various applications (Esmaeilzadeh & Groth, 2019). One of the most significant advantages of switchable biomaterials has been their recyclability, which is crucial for sustainable wastewater treatment as it helps reduce the need for constant replenishment of materials and minimize waste generation. For instance, pH-responsive biomaterials could change their hydrophilicity or hydrophobicity depending on the pH level of the environment (Li et al., 2022b). Temperature-responsive biomaterials, on the other hand, could undergo phase transitions at certain temperatures. Both switchable biomaterials could be leveraged for wastewater treatment with controlled release or adsorption of contaminants (Esmaeilzadeh & Groth, 2019), making them recyclable and reusable.

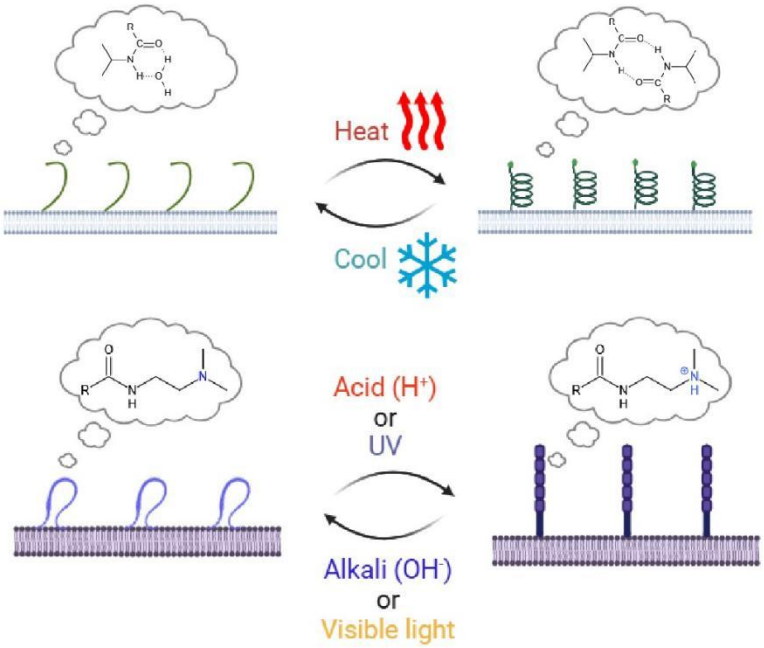

Figure 1 Schematic diagram of switching mechanism of switching biomaterials

Furthermore, switchable biomaterials often exhibited high specificity and efficiency in pollutant removal, which could be tailored by modifying their functional groups or structures (Fumasi et al., 2020). The ability to fine-tune these materials for specific contaminants enhances their practical applications in diverse wastewater treatment scenarios. Thus, they can be utilized in screening processes or tertiary treatment to selectively capture and remove target contaminants. For instance, pH-responsive cellulose hydrogels can swell or shrink in response to pH changes, allowing for the adsorption of specific pollutants and their subsequent release upon pH adjustment (Cheng et al., 2019). Light-responsive biomaterials can undergo conformational changes upon exposure to specific wavelengths, allowing for the degradation or release of bound pollutants (Wang et al., 2024). In addition, combining different types of switchable biomaterials could optimize the treatment process by leveraging the unique advantages of each type of material. For example, integrating pH-responsive materials with magnetic-responsive materials could enhance pollutant removal efficiency while simplifying the separation process (Fu et al., 2022). This synergy highlighted the importance of defining the relationship between material characteristics and their applications to maximize treatment effectiveness.

Due to the promising potential of switchable biomaterials, they have been extensively studied and applied in wastewater treatment processes and technologies to remove various contaminants as emerging materials. For the first time, the review of current research studies was conducted to provide a comprehensive and in-depth analysis of the underlying mechanisms of pollutant removal associated with different types of

innovative switchable biomaterials. By meticulously examining current studies, the development and cutting-edge applications of switchable biomaterials were identified, and valuable insights into addressing existing and emerging challenges were offered. This review was structured to cover various categories of switchable biomaterials, including cellulose, biomass-containing heteroatoms, biochar, and other advanced biomaterials, detailing the progress of their specific development and specialized applications in dye removal, oil-water separation, heavy metal adsorption, etc. By carefully collating and systematically summarizing this extensive information, this review was expected to advance the understanding and development of switchable biomaterials, thereby contributing to more effective and sustainable wastewater treatment solutions that are both innovative and environmentally friendly.

2.2 Switchable Cellulose-Based Materials

Cellulose-based materials have garnered significant attention in recent years as versatile substrates for wastewater treatment. These materials, derived from renewable sources like wood and plants, are abundant, sustainable, and biodegradable (Wang et al., 2021), as shown in Fig. 2. Cellulose in its native form typically exhibits a linear chain structure with an abundance of hydroxyl groups, allowing it to form robust hydrogen bonds. This structure configuration contributes to its high tensile strength and crystallinity, making it a promising candidate for various applications, particularly in contaminant removal (Mohamed et al., 2017). Due to these inherent properties, cellulose has been widely used to create switchable materials for wastewater

treatment through surface modification, unlocking a spectrum of enhanced functionalities.

Two primary methods are employed for cellulose surface modification: chemical elongation of the carbon chain and polymerization with compounds under the influence of crosslinking agents (Zhou et al., 2021). The former enhances cellulose reactivity by extending the carbon chain, providing access to effective functional groups. The involvement of functional groups in these modifications influences cellulose's affinity for specific substances (Hokkanen et al., 2016). For example, hydrophobic groups, including aliphatic compounds and alkane chains, are extensively utilized for modification, along with other functional groups like carboxyl groups that facilitate chemical structure changes (Cao et al., 2024). The latter introduces polymers modified by specific functional groups, such as cellulose-polymer crosslinker-small molecule organic matter, cellulose-hydrogen bond-small molecule organic matter, and cellulose-high molecular polymer, offering diverse avenues for tailored modifications (Roy et al., 2009). Cross-linking during modification leads to the formation of porous structures and reactive sites, enabling cellulose to effectively remove target pollutants. These approaches enhance the applicability of cellulose-based materials. The obtained switchable cellulose materials have been widely used to make many products, such as aerogels and separation membranes, and applied in various wastewater treatment processes (Zhao et al., 2021; Roy et al., 2009). However, potential drawbacks of these modification methods should be considered. Chemical stability and degradation over time may pose

challenges, particularly under harsh environmental conditions (Zhou et al., 2021).

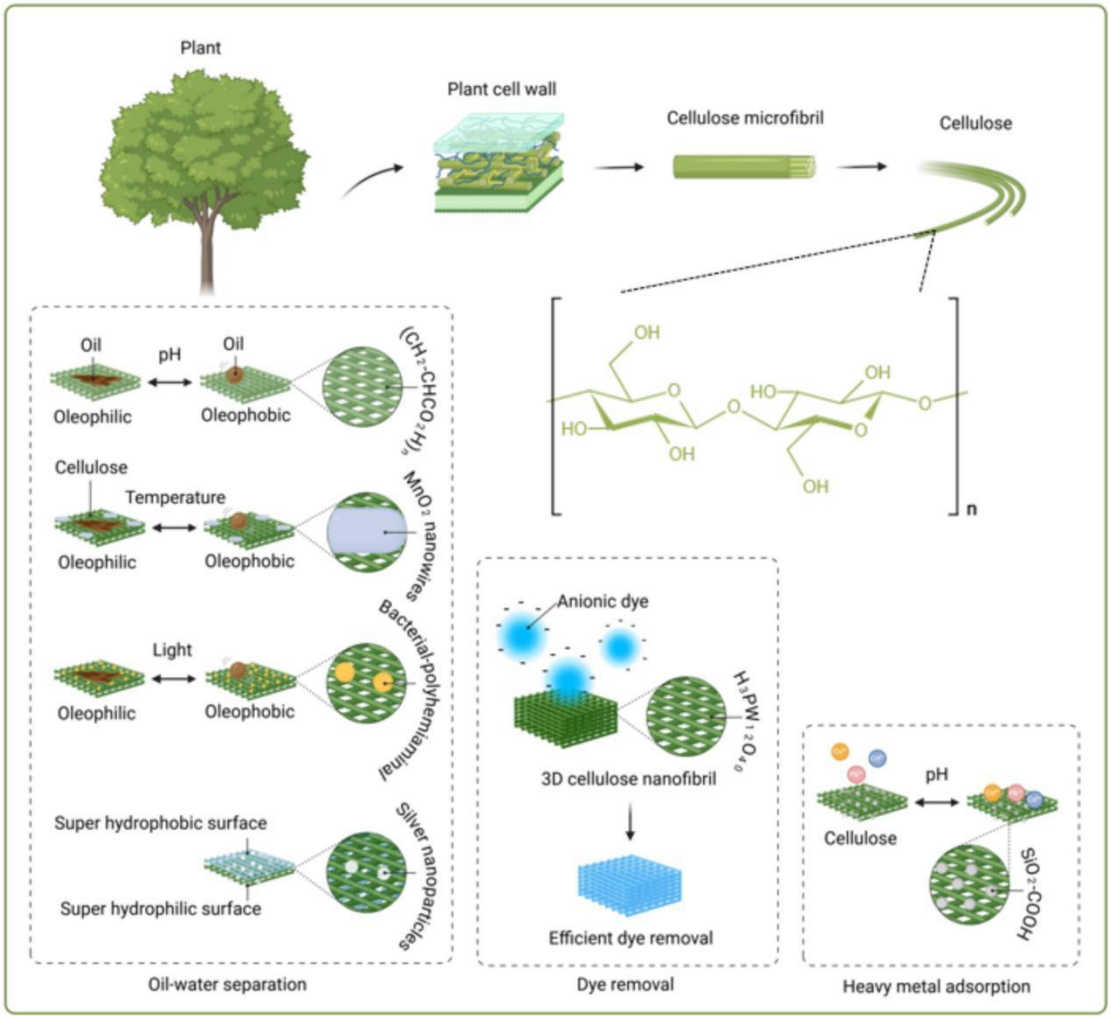

Figure 2 Brief diagram of the production process and properties of switchable cellulose

2.2.1 Oil-water Separation

Oil-water separation is a critical process in addressing environmental challenges related to oil spill accidents and oily wastewater treatment. In recent years, switchable cellulose-based materials modified with specific functional groups have emerged as promising solutions for efficient and eco-friendly oil-water separation. They offer a unique combination of properties, including tunable surface wettability, high porosity, and biodegradability, making them ideal candidates for addressing the pressing need to protect aquatic ecosystems from oil contamination. The main types of switchable cellulose-based materials for oil-water separation are summarized in Table 1, which are categorized based on their product form, specifically gels, membranes, and emulsifiers. This classification highlights differences in material structures and functions. Research has focused on the development and application of responsive properties like temperature response, pH response, and light response to enhance oil recovery from cellulose-based materials. Switchable surface wettability under specific conditions allows cellulose-based materials to handle different kinds of oils and improve the efficiency of various oily wastewater treatments (Zhao et al., 2021; Fan, Q. et al., 2022).

Table 1 Summary of switchable cellulose-based material for oil-water separation

Material	Preparation Method	Switchable Property	Performance	Recyclability	Ref.
Cellulose nanocrystal switchable gel	Introduced imidazole as a pH-sensitive salt into cellulose nanocrystals	CO_2-humidity triggers: flowing solution to solid gels	Separation efficiency ~70%	High (>10 cycles)	Ali et al., 2020
Blanket aerogels	Surface modification by tributylpentanamidine (TBPA)	CO_2-responsive: hydrophobic to hydrophilic	WCA 140° to 0°	High (>10 cycles)	Karatum et al., 2023
Bacterial cellulose/polyhemiaminal nanofiber aerogels	In situ polymerization of paraformaldehyde and 4,4′-diaminodiphenyl ether	Thermo-responsive: hydrophobic-oleophilic to underwater superoleophobic	Separation efficiency >99.4% WCA 148.4° to 30°	High (>10 cycles)	Chen et al., 2023a
BC/PHA nanofiber aerogels	a facile in situ polymerization of paraformaldehyde and 4,4’-diaminodiphenyl ether	pH-responsive: hydrophobic to hydrophilic	Separation efficiency 99.95% WCA 143° to 0°	High (>10 cycles)	Li et al., 2018
Thermo- and pH-responsive cellulose-based aerogels	Grafting poly(N,Ndimethylamino-2ethyl methacrylate) (PDMAEMA) via surface-initiated atom transfer radical polymerization	Thermo- and pH-responsive: superhydrophilic to underwater superoleophobic	Absorption rate 12 g/g WCA 120° to 0°	High (>10 cycles)	Zhao et al., 2017
Cellulose-based material (cellulose-g-PNIPAAm)	Grafting N-isopropylacrylamide (NIPAAm) onto bagasse pulp cellulose via Ce (IV)-initiated free radical polymerization	Thermo-responsive hydrophobic-oleophilic to underwater superoleophobic	Absorption rate 9.74 g/g WCA 134.2° to 0°	Moderate (>5 cycles)	Chen et al., 2018
UV induced spiropyrans-assisted aerogels	Surface modification with carboxymethyl cellulose	UV-responsive: hydrophobic to hydrophilic	Absorption rate 11.85-29.41 g/g WCA 124° to 31°	Moderate (>5 cycles)	Wang et al., 2024

pH-responsive cellulose-based material	Grafting acrylic acid and acrylamide, respectively, onto eucalyptus pulp cellulose	pH-responsive: hydrophilic to hydrophobic Acid wash after repeated use for contaminant clearance	Separation efficiency 97.6% Absorption rate >10 g/g WCA 127.8° to 36.8°	High (>10 cycles)	Cheng et al., 2019
CNFs (Cellulose nanofibers) aerogels	Grafting poly(N,Ndimethylamino-2ethyl methacrylate) (PDMAEMA) via surface-initiated atom transfer radical polymerization	CO_2-responsive: reversible emulsification/demulsification	Separation efficiency >99.96% O/W 5525.6 mg/L W/O 480 261.0 mg/L	High (>10 cycles)	Li et al., 2019a
Janus hybrid nanocellulose aerogel	Fabricated by freeze-drying of CNF suspension with methyltrimethoxysilane (MTMS) and another CNF suspension with 3-glycidoxypropyltrimethoxysilane (GPTMS) into one	Double-sided material: One side is hydrophilic and another side is hydrophobic	WCA 156° to 0° Absorption rate 52-57 g/g	High (>10 cycles)	Agaba et al., 2021
Janus cellulose membrane (JCM)	Single side hydrophobic modification Grafting Ag and stearic acid	Double-sided material: One side is hydrophilic and another side is hydrophobic	WCA 150° to 0° Separation efficiency >96%	High (>10 cycles)	Lv et al., 2019
Cellulose-based membrane	Grafting ZnO and polydopamine	UV/visible light-responsive: hydrophilic to hydrophobic	Separation efficiency >95% W/O emulsions 99.9%	High (>10 cycles)	Li et al., 2022a
Cellulose-based Mecoprop (MCPP) membrane	Incorporating natural microfibril cellulose and MnO_2 nanowires	Temperature-sensitive wettability switch: from hydrophilic to hydrophobic	Separation efficiency >99.4% O/W emulsion 99.5% W/O emulsion	High (>10 cycles)	Chen et al., 2023b

			98.9%		
CNCs (Cellulose nanocrystals) pickering emulsifiers	Grafting poly(N-3-(dimethylamino) propyl methacrylamide) (PDMAPMAm) and PDEAEMA to the CNC surface using nitroxide-mediated polymerisation	CO_2-responsive: hydrophobic to hydrophilic	O/W emulsion >99 % Shelf life: 1 month	High (>10 cycles)	Glasing et al., 2018
Cellulose-based materials	Grafted with acrylic acid (PAA) and acrylamide (PAM)	pH-responsive: hydrophilic to hydrophobic (and vice versa)	Absorption rate 68 g/g WCA 149° to 0°	High (>10 cycles)	Gao et al., 2022

Notable examples of switchable cellulose-based materials designed for oil-water separation are aerogels. For instance, Cheng et al. (2019) prepared cellulose-g-PAA and cellulose-g-PAM aerogels by grafting poly (acrylic acid) (PAA) and polyacrylamide (PAM) onto cellulose, respectively. They exhibited reversible wettability between hydrophilicity (WCA 127.8°) and hydrophobicity (WCA 36.8°), as well as oleophilicity and oleophobicity, in response to changes in pH from 1 to 9. Even after five switches, both aerogels maintained their pH-responsive surface wettability. This study also systematically investigated the pH-responsive mechanism and demonstrated that protonation-deprotonation of carboxyl and amide groups in response to pH led to reversible wettability transitions. Moreover, they displayed excellent pH-responsive adsorption-desorption properties, achieving oil/water separation efficiency of 97.6% or more. A recent study further advanced this field by exploring CO_2-switchable aerogel surfaces for enhanced oil recovery. Ali et al. (2020) successfully synthesized and characterized a CO_2-responsive switchable chemical, tributylpentanamidine (TBPA), and used it to coat aerogel composite blankets. Various coating techniques, including drop-casting, dip-coating, and physical vapor deposition (PVD), were evaluated to develop functional surfaces that could switch states from liquid phase to solid-like gel upon exposure to CO_2 and revert upon introduction of N_2. It enabled the selective blocking and unblocking of high-permeability pathways in porous aerogel, thereby redirecting injected fluids to previously unswept, oil-rich areas. This dynamic control of fluid flow improved sweep efficiency and allowed a more thorough recovery of trapped oil (35%),

effectively enhancing oil production while also facilitating better gas storage.

The transformable wetting surface of switchable cellulose aerogel can also be achieved using smart materials such as Janus and gas-responsive materials. Janus materials with asymmetric wettability on both sides can absorb different types of oil/water emulsions by selecting suitable contact surfaces. For instance, Agaba et al. (2021) synthesized a Janus hybrid nanocellulose aerogel (NA) with asymmetric wettability and strong mechanical properties, enabling unidirectional gravity-assisted separation for selective water or oil collection. In comparison, gas-triggered responses (e.g., CO_2 and N_2) do not lead to chemical accumulation on the aerogel skeletons. Li et al. (2019) prepared NAs with controllable surface wettability by grafting poly (N, N-dimethylamino-2-ethyl methacrylate) (PDMAEMA) polymer brushes via surface-initiated atom-transfer radical polymerization (ATRP). The surfaces of the aerogels transitioned from hydrophobic (WCA 156°) to hydrophilic (WCA 0°) in the presence of CO_2 and reverted with N_2, Argon, or air. Both NAs demonstrated excellent mechanical properties, compressibility, and elastic recovery (100%), making them highly reusable through multiple absorption-extrusion cycles.

Another noteworthy advancement in switchable cellulose-based materials for oil-water separation involved filtration membranes. Yu et al. (2022) developed Mecoprop (MCPP) membranes using cellulose aerogels coated with MnO_2 nanowires. The membranes exhibited smart temperature-sensitive wettability through the incorporation of poly (N-isopropylacrylamide) (PNIPAM). The membrane maintained

a hydrophilic state (WCA 0°) at temperatures below 32°C, while after the switch at temperatures above 32°C, it exhibited hydrophobic characteristics (WCA 131.2°). The MnO_2 nanowires provided excellent photothermal conversion capabilities, enabling adjustments in membrane surface wettability and reduction in oil viscosity, thereby enhancing emulsion separation performance. A high oil removal efficiency (>99.4%) was achieved and maintained under harsh acidic and alkaline conditions, making the MCPP membranes highly effective for oil-water separation applications. Li et al. (2022a) developed a PDA/SC/KFs@ZnO freestanding membrane with a similar preparation method. Compared with the MCPP membranes, this study focused on a simpler, more economical approach involving natural kapok fibers decorated with polydopamine (PDA) and ZnO nanoparticles to develop a dual-superlyophobic membrane. The kapok-based membrane achieved dual superlyophobicity and showed a broad multifunctional capacity. It was applied for rapid separation of both light and heavy oil-water mixtures, as well as emulsions containing dyes with all the removal efficiency larger than 99%.

Furthermore, switchable cellulose-based materials were also applied to realize the concept of double-sided membranes, which contained one side hydrophilic and the other hydrophobic, presenting opportunities for controlled oil-water separation processes. For example, a Janus cellulose membrane (JCM) with asymmetric wettability and potent antibacterial properties was successfully developed using a simple in situ immobilization and single-side modification approach (Lv, 2019). Initially, silver (Ag) nanoparticles were immobilized on the cellulose membrane (CM)

surface. Subsequently, one side of the CM was immersed in stearic acid ethanol solution while the other side was protected, resulting in a membrane with super hydrophobicity (WCA 0°) on one side and super hydrophilicity (WCA 150.3°) on the other. The resulting JCM displayed outstanding separation efficiency (over 96.0%) for a variety of oil-in-water and water-in-oil emulsions without requiring external energy. Moreover, the separation efficiency and flux remained stable even after 10 separation cycles, demonstrating excellent recyclability. Notably, both sides of the JCM exhibited strong antibacterial activity against Escherichia coli and Staphylococcus aureus. The antibacterial effect was attributed to the inherent antibacterial properties of Ag nanoparticles on the hydrophilic side and the non-contact antibacterial effect on the hydrophobic side.

Overall, switchable cellulose-based materials have shown significant promise in oil-water separation. They are often designed as aerogels or membranes and feature adjustable surface wettability, significant porosity, and biodegradability to enable effective separation processes. Thermo-responsive cellulose-based aerogels undergo reversible transformations between hydrophilic and hydrophobic states, which makes them particularly efficient for separating oil from water. Likewise, Janus hybrid nanocellulose aerogels, featuring asymmetric wettability, facilitate selective absorption and separation of oil-water emulsions through a unidirectional gravity-driven mechanism. These innovative strategies illustrate the potential of switchable cellulose-based materials to address complex environmental issues, such as oil spills and industrial wastewater management.

2.2.2 Dye Removal

The application of switchable cellulose-based materials in dye removal is another area of significant interest. While oil-water separation has been a primary focus of research, the adaptability of switchable cellulose-based materials extends to other wastewater treatment challenges, such as the removal of organic dyes. The ability of these materials to respond dynamically to external stimuli makes them particularly suited for tackling dye pollution, which is prevalent in industrial effluents. For example, Yang et al. (2021) introduced CO_2-responsive cellulose nanofibril aerogels (CNF/P(MAA-co-DMAEMA)) that exhibited switchable adsorption properties in response to CO_2 stimuli, making them effective for anionic dye removal through electrostatic interactions. Under CO_2-rich conditions, the protonation of tertiary amine groups significantly enhanced adsorption, enabling rapid adsorption equilibrium for dyes such as methylene blue (MB), naphthol green B (NGB), and methyl orange (MO), with maximum adsorption capacities of 598.8 mg/g, 621.1 mg/g, and 892.9 mg/g, respectively. The aerogels also demonstrated excellent recyclability, retaining over 87.7% of their efficiency after 20 cycles through efficient desorption by heating in water at 50°C.

Another example of dye removal was a kapok fiber membrane decorated with ZnO and polydopamine (PDA), which was developed by Li et al., 2022a. This membrane exhibited switchable dual-superlyophobicity, meaning it can change its wetting properties based on pre-wetting with either oil or water. The switching condition

involves pre-wetting with water, making the membrane underwater superohydrophilic (WCA 0°), or with oil, making it underoil superhydrophobic (WCA 153°). Besides over 99% separation efficiency for various oil-water mixtures and emulsions, the membrane also showed excellent adsorption properties and photocatalytic degradation capabilities for soluble dyes, such as MB. Under visible light, a dye degradation efficiency of 99.02% was achieved. This dual function of adsorption and photocatalytic degradation was attributed to the synergistic effect between ZnO and PDA, which enhanced visible light utilization and facilitated efficient photogenerated carrier transfer. The membrane maintained its high performance after 10 cycles, showing promise for practical applications in treating complex oil, water, and dye contaminant systems.

Wen et al. (2020) developed a switchable PTA/ZIF-8@CA composite material using cellulose aerogel, ZIF-8 MOF, and phosphotungstic acid (PTA) to enhance photocatalytic activity. The composite showed switchable properties depending on the pH, with optimal performance at pH 5, which facilitated efficient electron transfer and maintained the stability of ZIF-8. Under these conditions, 99.8% degradation of MB in 30 minutes and 99.7% degradation of rhodamine B in 60 minutes were obtained. When the pH was not optimal (either too acidic or too basic), the efficiency decreased due to the instability of ZIF-8 or lower photocatalytic activity. This switchability allowed the composite to adapt to different pH environments. It also showed great stability over multiple uses, retaining over 83% of its efficiency after five cycles.

2.2.3 Heavy Metal Adsorption

Switchable cellulose-based materials are highly effective in heavy metal adsorption, leveraging ligands such as amino, thiol, and carboxyl groups to efficiently chelate metal ions (Faheem et al., 2025). For example, pH-responsive silica particles functionalized with ricinoleic acid exhibit rapid switching between hydrophilic and hydrophobic states, allowing efficient adsorption of functionalized celluloses for metals like Cu^{2+}, Cd^{2+}, and Pb^{2+} (Chen et al., 2023a). The coordination of polar groups and chelating structures, as explained by the hard-soft acid-base (HSAB) theory, significantly enhances the adsorption efficiency of the modified celluloses (Zeng et al., 2023). These celluloses can be switched by pH, altering their surface properties to optimize adsorption. For example, silica particles functionalized with ricinoleic acid (SiO2-COOH) exhibit pH-responsive behavior, which led to the transition of cellulose between hydrophilic and hydrophobic states based on the pH of the solution (Ma et al. 2023). When pH ≤ 7, the carboxyl groups on the surface are protonated, resulting in a hydrophobic surface (WCA 155.5°) suitable for oil-water separation. When pH > 7, these groups deprotonate, making the surface hydrophilic (WCA 0°), which is ideal for heavy metal ion adsorption. Under alkaline conditions, the carboxyl groups were ionized, which enhanced the celluloses' ability to chelate heavy metals such as Pb^{2+}, Cd^{2+}, and Cu^{2+}. The adsorption capacity for Pb^{2+} reached up to 180 mg/g and showed less than 10% loss after five cycles. The reversible nature of the pH-responsive groups also allows for efficient desorption, aiding in material recyclability. These switchable properties make such materials highly versatile and efficient for both adsorption and

separation applications, with strong performance even under complex wastewater conditions.

Another idea is chemical treatment, which changes the electrical properties of the functional groups. Song et al. (2022) developed polyoxometalate (POM)/cellulose nanofibrils (CNFs) aerogels for oxidative desulfurization (ODS) of fuel. The switchable property of the material arises from the deposition and stabilization of phosphotungstic acid (PTA) on the surface-modified CNFs. The switching condition was facilitated by modifying the CNF surfaces with (3-Aminopropyl) trimethoxysilane (APTS), which imparted positive charges and enhanced the binding of anionic PTA clusters. The properties changed significantly after switching, as the CNF/PTA aerogel transitions from high solubility in solvents to a stable 3D network structure, enhancing interaction between PTA and the substrate. Before modification, PTA would easily dissolve, whereas, after switching, PTA became stable on the surface-modified CNFs. The specific surface area of the aerogel increased from 10.22 to 17.80 m2/g, and pore sizes decreased from 4.36 to 2.97 nm, leading to improved catalytic performance. In terms of efficiency, the optimal aerogel achieved a substrate conversion rate of 100% within 120 minutes at room temperature and retained its high catalytic efficiency (91.2%) even after five catalytic cycles.

2.2.4 Advancements and Optimization

The use of switchable cellulose-based materials in environmental remediation has been extensively explored due to their abundant, sustainable, and biodegradable

nature. The preparation of switchable cellulose-based materials typically involves chemical elongation of the carbon chain and polymerization with compounds under crosslinking agents. Functional groups such as carboxyl groups, carbonyl groups, and amino groups, are introduced to enhance the responsive switchability and versatility of cellulose. Meanwhile, functional groups such as hydrophobic aliphatic compounds and carboxyl groups are introduced to enhance the adsorption ability for contaminants. For example, chemical structure changes can be facilitated in the preparation of switchable cellulose-based materials for oil-water separation by adding hydrophobic groups, leading to the formation of porous structures and reactive sites (Telmadarreie et al., 2020). The hydrophobic groups and cellulose can be linked by metal oxides or grafted with crosslinking agents (Ingrassia et al., 2023). This is crucial for applications such as aerogels and separation membranes made from switchable cellulose-based materials, where high porosity and specific functional sites are essential for efficient pollutant removal. It should be notable that the double-sided material presents great opportunities for controlled separation processes by its simple switchable property, even though the preparation process is more complex than that of ordinary switchable materials. This type of material can be prepared by a unique approach. For example, one side of the modified material is immersed in the protective liquid to form an oil-water separation membrane with one side hydrophilic and the other hydrophobic (Kumar Gupta et al., 2015).

Comparing the various applications of switchable cellulose-based materials reveals their multifunctional capabilities and the underlying mechanisms governing their

effectiveness. In oil-water separation, the primary mechanisms involve reversible wettability transitions and selective absorption. For dye removal, electrostatic interactions and photocatalytic properties play pivotal roles, while heavy metal adsorption relies on chelation and coordination mechanisms. Despite these advancements, challenges remain, particularly in achieving uniform and reproducible switchable properties, enhancing recyclability, and scaling up for industrial applications. For example, realizing switchable properties of strongly polar groups remains difficult, which hinders the recyclability of switchable cellulose-based materials for heavy metal removal. Besides, ongoing research and a deeper understanding of the intricate mechanisms underlying switchable properties would help provide a foundation for optimizing the design and performance of switchable cellulose-modified materials.

The antibacterial properties of current switchable cellulose-based materials are predominantly driven by nano-metal particles. This underscores the potential of metallic materials like metal-organic frameworks (MOFs) that have higher specific surface areas for cellulose modification (Yang et al., 2024; Abdelhamid & Mathew, 2022). MOFs are renowned for their high surface area, tunable pore structures, and abundant active sites (Liu et al., 2018). When combined with cellulose, the obtained composites would benefit from improved mechanical stability, flexibility, and processability, facilitating their application in diverse treatment scenarios. For instance, cellulose-MOF composites have demonstrated enhanced removal efficiencies for heavy metals and organic dyes due to synergistic interactions between

the MOF's adsorption capabilities and the cellulose matrix's support (Tao et al., 2023). However, challenges persist in developing switchable cellulose-MOF composites. The inherent fragility and powdery nature of many MOFs can complicate their handling and integration into practical systems (Ren et al., 2014). Ensuring uniform dispersion of MOFs within the cellulose matrix is crucial to maintain performance consistency. Additionally, the stability of MOFs in aqueous environments, especially under varying pH conditions, remains a concern, as many MOFs may degrade or leach metal ions into the water (Wang et al., 2022). Addressing these challenges requires careful selection of MOF types and the development of robust synthesis methods to create stable, efficient, and environmentally safe switchable cellulose-MOF composites (Han et al., 2024a).

2.3 Switchable Biomass Containing Heteroatoms

Parallel to the advancements in switchable cellulose-based materials, other switchable biomass-derived materials such as chitosan, polylactic acid (PLA), and proteins are also promising candidates for wastewater treatment applications. They are also derived from renewable sources and exhibit distinctive attributes like high adsorption capacity, biocompatibility, and functionalizable characteristics. Fig. 3 illustrates the production process and properties of switchable chitosan, PLA, and proteins. The development and utilization of these switchable biomass-derived materials generally involved modification with heteroatoms such as nitrogen, sulfur, and oxygen to enhance their functional properties, which are critical for the effective removal of

contaminants. Each of them offers unique characteristics and performance advantages.

Chitosan is derived from the shells of crustaceans and is known for its high adsorption capacity, facilitated by its amino functional groups, making it highly effective in applications such as oil-water separation, dye removal, heavy metal adsorption, and antimicrobial treatments (Basem et al., 2024; Baig et al., 2022). Chitosan's ability to form gels and films further enhances its versatility. PLA, sourced from renewable materials like corn starch, sugar, and cassava, is a biodegradable polymer recognized for its high mechanical strength and ease of processing. The applications of PLA extend to oil-water separation and the creation of biodegradable membranes. Proteins sourced from various biological origins, such as animal tissues and plants, are notable for their ability to form molecular membranes and their high affinity for specific substances. This functional diversity allows proteins to be effectively used in oil-water separation and biological purification processes. Their capacity to undergo conformational changes in response to environmental conditions adds to their applicability in dynamic treatment processes (Kaltashov & Eyles, 2002).

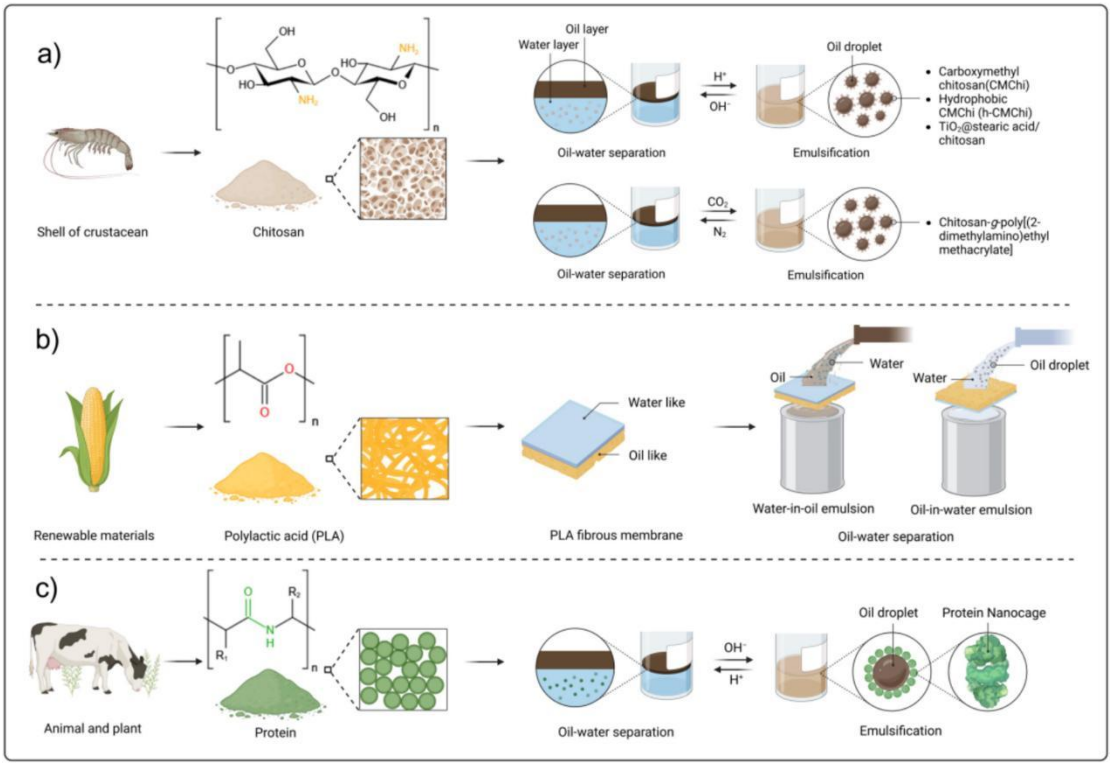

Figure 3 The production process and properties of switchable chitosan, polylactic acid and proteins

2.3.1 Oil-Water Separation

Switchable chitosan-based materials have been extensively utilized for oil-water emulsification and separation due to their tunable properties and responsiveness to environmental stimuli. Carboxymethyl chitosan (CMChi) and hydrophobically modified CMChi (h-CMChi) have been reported for oil-water emulsification (Fig. 3(a)) (Kalliola et al., 2018). CMChi formed nanoparticles at pH 6-7, and hydrophobic modifications in h-CMChi allowed it to emulsify oil at a wider pH range. CMChi exhibited phase inversion at a lower pH (pH 3-4) as oil content increased, while h-CMChi required a higher pH (pH 6-7) after hydrophobic modification. The emulsified oil reached 300 mg of oil per milligram of CMChi material used at pH 7-10, and per milligram of h-CMChi emulsified up to 1300 mg of oil. Both emulsions could be switched by altering the pH with NaOH or HCl, taking approximately 10 seconds for mixing and 2 minutes for separation. Another chitosan-based material, chitosan-g-poly[(2-dimethylamino)ethyl methacrylate] (Chi-g-PDMAEMA) was modified to exhibit CO_2-switchable properties by grafting poly[(2-dimethylamino)ethyl methacrylate] onto chitosan, enabling it to switch between hydrophilic and hydrophobic states upon exposure to CO_2 or N_2 (Ren et al., 2018). This switching allowed for efficient and reversible oil-water separation and re-emulsification. The transition occurred under ambient conditions within approximately 10 minutes, with CO_2 leading to protonation and dispersion of the polymer in water, while N_2 deprotonated and re-aggregated it at the oil-water interface. Before switching, the Chi-g-PDMAEMA stabilized emulsions by forming a gel-like

network, and upon CO_2 bubbling, the emulsions break, with a significant change in properties—interfacial tension increased from 23 mN/m to 34.1 mN/m. The Chi-g-PDMAEMA could remove up to 99% of oil in water and could be recycled at least four times without losing efficiency.

In comparison, h-CMChi achieved efficient oil-water separation by enhancing its affinity to the oil phase; Chi-g-PDMAEMA was pH responsive and switched between hydrophilic and hydrophobic states depending on the environmental pH, adapting to different separation conditions. In terms of stability, h-CMChi showed great chemical stability under neutral conditions, while it may be affected in extreme pH environments. The stability of Chi-g-PDMAEMA depended on the graft density of poly[(2-dimethylamino)ethyl methacrylate] and environmental pH, and although the structure remained intact under the right conditions, prolonged exposure to harsh environments could lead to decreased performance. With regard to recyclability, the performance of h-CMChi may decline after multiple uses due to contamination or degradation, while Chi-g-PDMAEMA showed better recycling potential due to its pH response properties, which can be regenerated through simple pH regulation. Thus, Chi-g-PDMAEMA has advantages in terms of adaptability and recyclability, but the choice of materials should be made according to the specific application needs and environmental conditions.

Hydrophobic magnetic chitosan-based aerogels were also developed to achieve CO_2-switchable properties for oil-water separation by incorporating Fe_3O_4

nanoparticles and coating with Candelilla wax (Yin et al., 2020). The CO_2-switchable aerogels responded to external magnetic fields due to the magnetic Fe_3O_4 nanoparticles and switched between hydrophilic (WCA 0°) and hydrophobic (WCA 147.9°) states under magnetic control. This enabled per gram of aerogel to absorb up to 43.8 g of oil with an absorption rate of 3.3 to 82.1 g/g·s, and to achieve a complete oil separation in just a few seconds. It could remove over 99% of oil from water and could be recycled for up to 10 cycles and still retain over 90% of their original efficiency. Additionally, carboxylated carbon nanotube/chitosan aerogels (CCNT/CA) with temperature-switchable wettability were achieved by incorporating carboxylated carbon nanotubes into a chitosan matrix (Fan, S. et al., 2022). At temperatures above 45℃, the CCNT/CA was hydrophobic (WCA 132°) and could be used to efficiently absorb oil, while at temperatures below 25℃, it became hydrophilic switching (WCA 0°) and could release the absorbed oil. Due to the enhanced thermal conductivity provided by the carbon nanotubes, this switch took approximately 15 minutes, which was significantly faster than non-modified aerogels (up to 120 minutes). Depending on the oil type, the oil absorption capacity of CCNT/CA ranged from 23.8 to 53 times its weight, with a separation efficiency of about 85%. Impressively, the CCNT/CA could be recycled for up to 15 cycles with only a 5% reduction in oil absorption capacity.

Besides chitosan-based switchable materials, a Janus PLA fibrous membrane with asymmetric wettability on each side was fabricated for efficient oil-water separation (Fig. 3(b)) (Qin et al., 2020). The asymmetric structure resulted in high flux (above

2000 L/m²·h) and excellent separation efficiency (up to 98%) for oil-water mixtures, and the membrane demonstrated a flux recovery ratio of 85% after 5 separation cycles. Sarker et al. (2017) investigated Pickering emulsions stabilized by E2 protein (part of the pyruvate dehydrogenase multienzyme complex found in thermophilic bacterium Geobacillus stearothermophilus) nanocages for potential applications in pollutant removal (Fig. 3(c)). Aspartic acid and glycine (PDB ID: 1B5S, amino acids 381 and 382) were replaced with two cysteine amino acids by site-directed mutagenesis, and this mutant was designated as E2LC2 and had pH-responsive properties. The optimal formulation, with a rosemary oil (n-butanol)/water ratio of 0.11 (v/v) and an E2LC2 mass fraction of 0.35 wt%, exhibited stability in neutral to basic pH, ionic strengths up to 250 mM, and temperatures up to 50 °C. Before switching, the emulsions were stable with a droplet size of approximately 300 nm, while switching to pH 4 led to phase separation, characterized by extensive flocculation and coalescence. Restoring pH to 8 recovered the stability of the emulsions, and the quality was maintained for 5 cycles, demonstrating the potential for these Pickering emulsions to repeatedly remove diesel and gasoline while maintaining stability.

2.3.2 Other Applications

In addition to oil-water separation, switchable biomass-derived materials containing heteroatoms have also been used in other areas of wastewater treatment in recent years. For example, a reusable thermo-responsive chitosan-based flocculant, CS-g-PNNPAM (chitosan grafted with poly(N-isopropylacrylamide)), was

investigated for the simultaneous removal of tetracycline (TC) and copper ions (Cu (II)) from wastewater (Ren et al., 2017). This flocculant demonstrated exceeding 90% of removal efficiencies for both TC and Cu (II), using a temperature-induced flocculation mechanism. The flocculation mechanism was revealed to be the interactions between the CS-g-PNNPAM, TC, and Cu (II) via hydrophobic interactions, hydrogen bonding, and metal complexation. Sequential weakening of these switchable interactions allowed for the selective recovery of TC and Cu (II) from the flocs. TC was recovered at lower temperatures (20-25°C), while Cu (II) was recovered through a chelating agent wash (e.g., EDTA solution). This enabled the flocculant to be reused, maintaining over 85% efficiency after 5 cycles.

A charge-switchable nanocomposite, DA-CMCS@Zn^{2+}@heterocycles (dopamine-modified carboxymethyl chitosan with zinc ions and heterocyclic compounds), was developed for pH-responsive infiltration into acidic biofilms, effectively targeting Gram-negative bacteria, Gram-positive bacteria, and fungi (Liang et al., 2023a). Fabricated through flash nanoprecipitation with pH-sensitive carboxymethyl chitosan, the nanocomposite exhibited a surface charge change from negative (pH 7) to positive (pH 4-5), which matched the acidic pH of biofilm environments. This charge-switching property, combined with its nano-scale size (approximately 100 nm), facilitated strong adhesion to the surface of microorganisms, enhancing its antimicrobial activity.

2.3.3 Comparative Production and Optimizing Analysis

The utilization of switchable biomass containing heteroatoms has garnered significant interest in the field of environmental remediation, particularly for wastewater treatment applications. Proteins are more likely to form molecular membranes with switchable properties, positioning them as promising candidates for applications in oil-water separation and biological purification (Vinothkumar & Henderson, 2010). Their modification does not require special processes such as electrostatic spinning to form a dense film, as cellulose does. Thus, they would have application prospects in the production of filtration membranes and microbial reactors. Chitosan and PLA, both of which are like cellulose, can be used to make switchable porous materials. Modification methods are generally used to extend their carbon chains or polymerize with other molecules (Zhou et al., 2021). It is also common to insert metals such as zinc during modification processes (Kumar et al., 2015). Though the modification methods to prepare switchable biomass containing heteroatoms and switchable celluloses are similar, leading to similar switchable principles and the corresponding applications, switchable celluloses are much cheaper due to the lower cost of pristine celluloses. According to Sigma-Aldrich, a chemical reagent company, the price for cellulose (microcrystalline, powder, 20 μm) is $CAD 0.169/g, the price for chitosan (medium molecular weight) is $CAD 1.376/g, and the price for PLA is $CAD 214/g.

The extraction processes of biomass (PLA, chitosan, and protein) and cellulose play crucial roles in determining their feasibility, cost-effectiveness, and environmental impact. PLA benefits from a relatively simple extraction process, encompassing fermentation, separation, and purification (Vaidya et al., 2005). The ease of extraction

makes PLA an attractive option for various applications in the future, though the current price of pure PLA is relatively high due to complicated purification steps after separation, resulting in low efficiency (Lim et al., 2010). In contrast, the intricate processes of chitosan extraction, such as deproteinization, decolorization, deashing, degreasing, and decalcification, contribute to a higher extraction cost (Kou et al., 2021). Despite these challenges, chitosan's properties of cationic nature allow it to neutralize negatively charged colloidal particles, promoting the formation of larger flocs that can be easily separated through sedimentation or filtration processes (Yang et al., 2016). It makes chitosan valuable in wastewater treatment applications.

The varied complexity in the extraction processes of PLA, chitosan, and cellulose underscores the importance of understanding the trade-offs between cost, feasibility, and the performance each switchable biomaterial brings to the table. When considering the extraction processes collectively, it becomes evident that the selection of a switchable biomaterial depends not only on its inherent properties but also on the feasibility and sustainability of its extraction. Switchable PLA could be a cost-effective and straightforward option if it improves production processes, such as using bacteria to produce sugar and catalyze its degradation into PLA (Djukić-Vuković et al., 2019). Switchable chitosan, despite its more complex extraction process, offers distinctive properties that justify its use in specific applications. Although switchable celluloses have a slightly lower adsorption capacity (10-52 g/g) in single pollutants compared to switchable PLA and chitosan (23.8-53 g/g), they are more suitable for large-scale applications in wastewater treatment due to

the significantly lower price at the present stage.

Heteroatom doping (e.g., nitrogen, sulfur, etc.) can significantly enhance the interaction between biological materials and pollutants, improving their adsorption capacity and removal efficiency (Miao et al., 2020). However, there are still challenges to achieving uniform chemical modification, including feedstock variability, difficulty in controlling reaction conditions, and competition for side reactions, which can lead to instability in contaminant removal performance and recyclability. Optimizing reaction parameters (e.g., temperature, pH, concentration) can help improve modification consistency (Stewart, 2012), but implementation on an industrial scale remains challenging. In addition, advanced catalytic processes such as metal-doped biochar can improve adsorption and degradation efficiency (Liu et al., 2022), but metal leaching and by-product generation need to be controlled to avoid secondary pollution. The other method is enzymatic functionalization, which has strong selectivity and mild reaction, but the stability, cost and large-scale application of the enzyme are still limiting factors (Han et al., 2024). In comparation. cellulose extraction boasts a relatively straightforward process involving pretreatment, chemical treatment, and mechanical treatment, which leads to its lowest cost and ease of achievement (Sabiha-Hanim & Asyikin Abd Halim, 2019). This accessibility positions switchable cellulose as an economical and environmentally friendly option for wastewater treatment. Therefore, future research should be combined with environmentally friendly modification strategies, such as green catalysis, nano-functionalization or biocatalizations, to improve the stability and reusability of

heteroatomic-doped materials.

2.4 Switchable Biochar

Biochar, a carbon-rich biomaterial derived from the pyrolysis of organic matter, has garnered significant attention in environmental remediation. Its porous structure, high surface area, and functional groups enable biochar to effectively absorb a wide range of contaminants from water matrices, including heavy metals, organic pollutants, and nutrients. The benefits of biochar in wastewater treatment are thus multifaceted. Firstly, its production from waste biomass offers an environmentally friendly and sustainable option for resource utilization (Gupta et al., 2022). The high surface area and porosity provide extensive sites for contaminant adsorption, enhancing its capacity to remove various pollutants (Leng et al., 2021). Biochar also exhibits excellent stability and longevity in aqueous environments, which is crucial for practical applications in wastewater treatment systems. Moreover, functionalization of biochar, such as chemical activation, metal doping, and surface grafting, significantly enhances its switchability by introducing responsive sites that interact with external stimuli (e.g., pH, redox conditions, and magnetic fields), thereby improving its selective adsorption and regeneration efficiency (Wen et al., 2023).

Due to these advantages, research on switchable biochar for contaminant removal is developing rapidly, contributing to improved water quality and environmental sustainability (Qiu et al., 2022). Compared with switchable cellulose and other biomass-based materials, switchable biochar mainly undergoes pyrolysis and

nanoparticle integration (as shown in Fig. 4), enhancing its adsorption and photocatalytic properties through thermal processes and the introduction of functional groups such as Fe-N sites. In contrast, cellulose modifications often involve chemical surface grafting and in situ polymerization to introduce functional groups such as carboxyl and amino groups (Wohlhauser et al., 2018). These differences highlight biochar's high surface area and porous structure for effective heavy metal and organic pollutant removal, while cellulose's versatility and reactivity are suited for tailored separation processes and responsive behaviors. Table 2 summarizes the existing studies on switchable biochar for wastewater treatment, including preparation methods, switchable functionalities, specific applications, and performance metrics as reported in the literature.

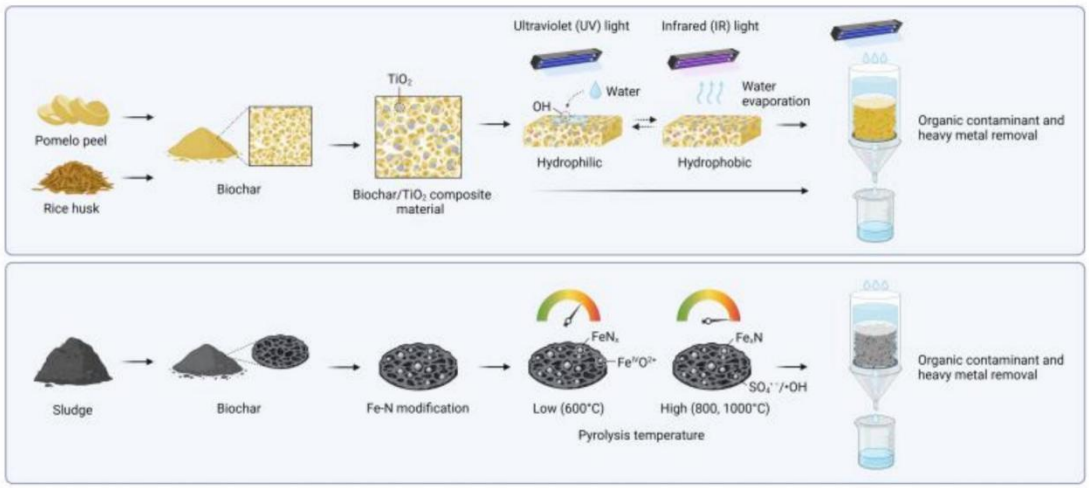

Figure 4 The production process and properties of switchable biochar

Table 2 Summary of Switchable Biochar for Water Treatment Applications

Material	Preparation Method	Switchable Functionality	Applications	Performance	Recyclability	Ref.
TiO_2/biochar composite	Integration of TiO_2 nanoparticles	Light-switchable wettability	Herbicide removal, degradation	Removal efficiency of 88% for atrazine under UV light	High (>10 cycles)	Gao et al., 2019
TiO_2/pomelo-peel-derived biochar	Dense and uniform growth of TiO_2 nanoparticles	Photocatalytic degradation	Antibiotic degradation	Degradation rate constant of 0.021 min^{-1}, 92% removal of tetracycline in 60 minutes under UV light	High (>10 cycles)	Zhang et al., 2023
		Photocatalytic properties	Heavy metal adsorption	Adsorption capacity of 95 mg/g for lead and 76 mg/g for cadmium		
Pharmaceutical sludge biochar (PSBC)	Pyrolysis with Fe-N site modification	Switchable Fe-N sites for PMS activation	Organic pollutant removal	85% removal efficiency for 4-chlorophenol within 30 minutes	High (>10 cycles)	Liang et al., 2023b
		Modulated oxidation states	Heavy metal adsorption	Adsorption capacity of 112 mg/g for lead and 89 mg/g for cadmium		

2.4.1 Organic Pollutant Removal

Switchable biochar has been extensively studied for the removal of organic contaminants, including pesticides, pharmaceuticals, and dyes. Its high surface area, porosity, and diverse functional groups—such as carboxyl, hydroxyl, and carbonyl groups—enhance its ability to bind with organic molecules, facilitating effective pollutant removal.

One notable enhancement in switchable biochar functionality involves the integration of TiO_2 nanoparticles, creating a composite material capable of alternating between adsorption and photocatalysis. For example, Gao et al. (2019) developed TiO_2/biochar composites with light-switchable wettability, serving as both herbicide safeners and foliar fertilizer adhesives. These composites exhibited hydrophobic properties under infrared (IR) light and hydrophilic properties under UV light, improving adsorption efficiency and enabling pollutant degradation. Under UV light, TiO_2 nanoparticles functioned as photocatalysts, facilitating the breakdown of adsorbed contaminants. Their study reported an atrazine removal efficiency of 88% under UV light conditions.

Further research by Zhang et al. (2023) demonstrated the benefits of biochar derived from pomelo peel, which was densely coated with TiO_2 nanoparticles to significantly enhance the photocatalytic degradation of antibiotics such as tetracycline. The switchable TiO_2/biochar composite achieved a degradation rate constant of 0.021 min^{-1} and a removal efficiency of 92% within 60 minutes of UV light exposure. This

performance surpassed that of conventional biochar, which typically removes 50-90% of antibiotics (Sen et al., 2023), highlighting the effectiveness of switchable properties in promoting photocatalytic activity.

Additionally, pyrolyzed pharmaceutical sludge biochar (PSBC) containing switchable Fe-N sites has been investigated for its ability to activate peroxymonosulfate (PMS), enabling the simultaneous removal of multiple organic pollutants (Liang et al., 2023b). The Fe-N sites in PSBC can adjust their oxidation states depending on the pyrolysis temperature (600-700 °C), optimizing pollutant degradation through oxidation. This study demonstrated an 85% removal efficiency for 4-chlorophenol within 30 minutes, with sustained efficiency over 10 regeneration cycles.

2.4.2 Heavy Metal Removal

In addition to organic pollutants, switchable biochar has shown remarkable capabilities at the same time in heavy metal removal, particularly for lead, cadmium, and arsenic. Functional groups present on biochar surfaces facilitate strong interactions with metal ions, enhancing adsorption efficiency.

TiO_2/biochar composites have also exhibited enhanced heavy metal adsorption performance due to their switchable photocatalytic properties. For instance, Zhang et al. (2023) found that TiO_2-modified biochar improved lead and cadmium ion adsorption, achieving adsorption capacities of 95 mg/g for lead and 76 mg/g for cadmium. The photocatalytic activity of TiO_2 promoted surface modifications,

increasing the affinity of biochar for metal ions and enhancing the adsorption process.

Similarly, PSBC with switchable Fe-N sites has demonstrated excellent heavy metal adsorption capabilities. Liang et al. (2023b) reported that PSBC achieved an adsorption capacity of 112 mg/g for lead and 89 mg/g for cadmium. The material's ability to regenerate through simple pH adjustment (acidic washing) ensured that its adsorption capacity remained stable over multiple reuse cycles, reinforcing its potential for long-term application in heavy metal removal.

The integration of photocatalytic and redox-active functionalities in switchable biochar materials presents a promising strategy for improving heavy metal removal efficiency. However, challenges such as metal leaching and maintaining long-term stability in various environmental conditions remain areas for further research.

2.4.3 Sustainable Opportunities

Overall, switchable biochar provides an adaptable and efficient solution for both organic contaminant and heavy metal removal in wastewater treatment. Compared to conventional biochar, switchable biochar can be regenerated and reused multiple times without significant loss of adsorption capacity. This makes it a sustainable option for long-term wastewater treatment applications. At the same time, the synthesis, modification, and application of switchable biochar present both opportunities and challenges.

First, the production of biochar involves the pyrolysis of organic matters under

controlled conditions, typically in the absence of oxygen. This process results in the biochar with high porosity and surface area. The raw materials used for biochar production, such as agricultural waste, forestry residues, or even municipal solid waste, significantly influence its properties and effectiveness in wastewater treatment (Gao et al., 2019), which can affect the consistency and predictability of treatment performance. This variability necessitates thorough characterization and standardization of biochar properties for specific applications (Amin et al., 2016).

Second, to obtain switchable biochar and enhance its adsorption capability, various functionalization and activation techniques are employed. Chemical activation involves treating biochar with activating agents such as acids, bases, or oxidizing agents, which increase its surface area and introduce additional functional groups. The prepared switchable biochar exhibits improved adsorption capacities for specific contaminants due to the increased availability of active sites and enhanced surface chemistry (Huang et al., 2021). Functionalized biochar can be tailored to target pollutants, such as heavy metals or organic compounds, making it a highly selective and effective adsorbent (Liang et al., 2023b). However, the exploration of switchable biochar to respond to external stimuli is still in its early stages. Consequently, the literature is limited, with major studies emphasizing particular modifications, such as TiO2 nanoparticle doping, to improve specific properties like photocatalytic activity (Xu et al., 2002). Future research on switchable biochar should explore alternative doping agents, such as various nanoparticles or chemical modifiers, to impart diverse responsive behaviors (Raguram & Rajni, 2022). Nevertheless, these modification

processes can be costly and complex, involving additional chemicals and steps that may increase the overall cost of switchable biochar production and application (Sajjadi et al., 2019). Additionally, the use of chemicals for activation may introduce environmental and safety concerns, necessitating careful management and disposal of by-products (Ndirangu et al., 2019).

Thus, the economic feasibility of switchable biochar must be addressed to ensure its competitiveness with conventional treatment methods. Future research may focus on optimizing production processes to enhance the yield and performance of switchable biochar while minimizing energy consumption and environmental impact. The development of cost-effective modification techniques and the exploration of novel feedstocks can further expand the applicability of switchable biochar in wastewater treatment. Investigating the underlying mechanisms that enable the switchable properties of modified biochar is also essential for optimizing their design and functionality.

The reproducibility of switchable biochar remains a challenge due to variations in feedstock composition, pyrolysis conditions, and post-treatment modifications. Differences in pyrolysis temperature, heating rate, and residence time significantly affect the biochar's porosity, surface area, and functional group availability (Sun et al., 2016), directly influencing its adsorption capacity and switchability. For instance, lower heating rates can cause micropore clogging, while higher temperatures generally enhance microporosity and adsorption efficiency (Leng et al., 2021). To

improve reproducibility, several strategies may be employed including i) standardizing feedstock composition to minimize batch-to-batch variability, ii) optimizing pyrolysis conditions to maintain a stable temperature and heating rate, and iii) employing uniform post-treatment functionalization methods such as oxidation or controlled metal ion doping to ensure consistent switchable properties (Stein et al., 2009). Further research and industrial-scale standardization efforts will be crucial for refining these approaches, ultimately enabling the large-scale application of switchable biochar in wastewater treatment.

2.5 Switchable Rubber, Resin and Crude Fiber

Crude fibers, resins, and rubber are biomaterials that have become ubiquitous industrial raw materials due to their availability and cost-effectiveness. Crude fibers, sourced from plants such as hemp, flax, or cotton, are characterized by their fibrous and porous nature, which are advantageous in the adsorption of pollutants. They contribute significantly to filtration processes in wastewater treatment by enhancing the mechanical strength and efficiency of filter media (Singh et al., 2021). Resin, often obtained from specific plant exudates or synthesized chemically, represents another category of biological materials with distinctive attributes. Found in coniferous trees like pine, resin is composed of a complex mixture of organic compounds that exhibit adhesive and hydrophobic properties, making it valuable in wastewater treatment as a natural sealant and as a material for water-resistant coatings (Dhawale et al., 2022). Rubber, primarily sourced from the latex of Hevea brasiliensis

trees, is valued for its elasticity and resilience. These properties make rubber indispensable in wastewater treatment, particularly for sealing and containment applications, as well as for creating flexible barriers and liners used in filtration systems (Chandrasekaran, 2010). The unique polymer structure of rubber molecules contributes to its flexibility and durability, which is crucial in ensuring the longevity of treatment infrastructure and preventing leaks (Zhou et al., 2024).

Fig. 5 briefly illustrates the production process, mechanism, and application of switchable crude fibers, resin, and rubber in wastewater treatment. They are grouped together in this section because all of them are easy to obtain, and there are mature, simple, and cost-efficient industrial processing methods available for their production (Yang et al., 2012). Despite their economic accessibility, the complex chemical structures of these materials pose challenges in achieving switchable properties through uniform modifications. Their intricate molecular arrangements contribute to the difficulty in implementing widespread modifications (Yang et al., 2012). This complexity underscores the need for further research and innovation to enhance their versatility and applicability in various wastewater treatment processes.

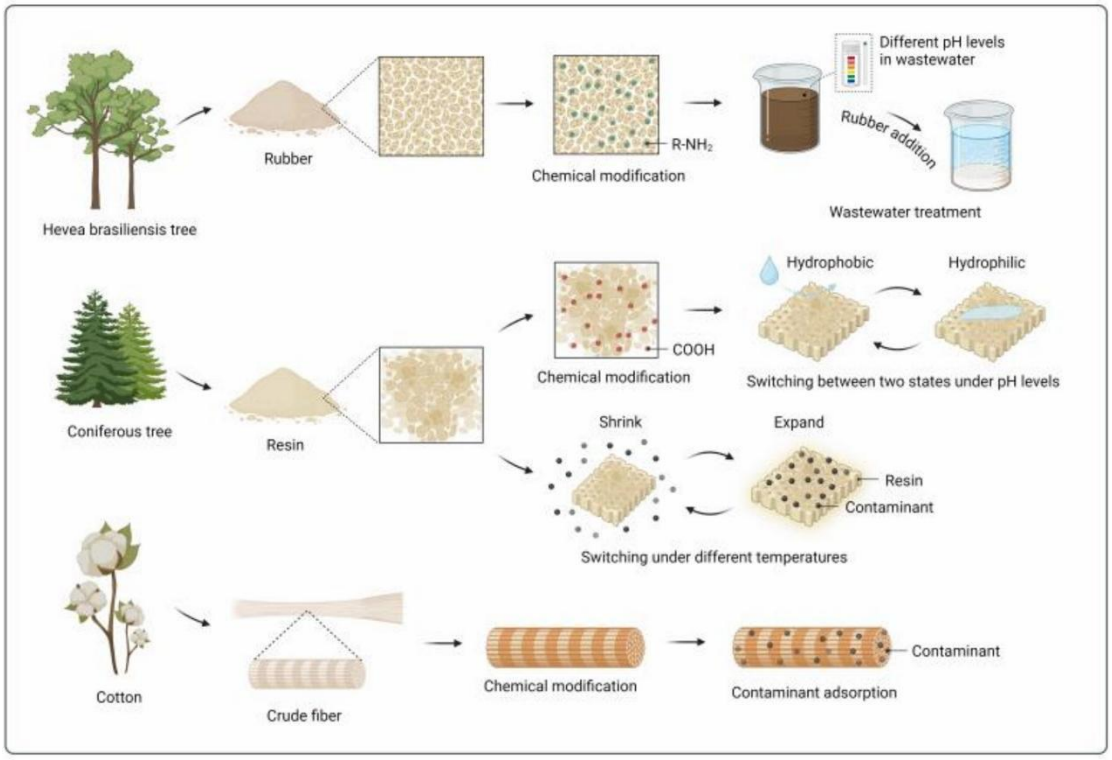

Figure 5 Brief diagram of the production process and properties of switchable rubber, resin, and crude fibers

2.5.1 Switchable Fiber

The use of switchable fibers in wastewater treatment is mainly through controlling their surface area and porosity. The production of these fibers often involves introducing functional groups that interact with contaminants through mechanisms like ion exchange, hydrogen bonding, and van der Waals forces, which can be activated or deactivated depending on the treatment requirements (Bediako et al., 2024). One common application of switchable fiber is the removal of dyes from textile wastewater. For instance, Thamer et al., (2019) prepared switchable hemp fibers by treating them with polyacrylonitrile (SC.MFF), which rendered the fibers pH-responsive properties. These fibers could switch their adsorption capacity depending on the pH of the solution, with maximum adsorption achieved at acidic conditions (pH 4-5), where the cationic groups attracted anionic dye molecules. Desorption of the dyes occurred in alkaline conditions (pH 10-11), allowing the fibers to be regenerated and reused. Experiments showed that the switchable hemp fibers could remove up to 95% of methyl blue from wastewater, and they retained over 80% of adsorption capacity after 5 regeneration cycles involving alkaline washing. Similarly, the modified flax fibers in this study exhibited high removal efficiencies for Cr(VI) ions from aqueous solutions. The semicarbazide-modified flax fiber achieved a removal efficiency of over 90% at pH 2 under optimal conditions. This was attributed to the ion-pair formation between the modified fiber and Cr(VI), which enhanced the adsorption capacity. The adsorption mechanism was primarily driven by electrostatic interactions, facilitated by the positively charged fiber surface at low pH.

The SC.MFF demonstrated significant reusability, maintaining its removal efficiency after multiple cycles of adsorption-desorption. After the regeneration process using 0.1 M K2CO3 as the desorbing agent, the fiber retained more than 80% of its initial adsorption capacity, highlighting its potential for long-term use in wastewater treatment (Akl et al., 2021).

In addition to dye and heavy metal removal, switchable fibers have been used for the adsorption of organic pollutants, including phenols, pesticides, and pharmaceuticals (Gusain et al., 2019). The hydrophobic nature of certain organic contaminants allows them to interact with the fibrous matrix of untreated fibers, thus facilitating their removal from water (Mohammed et al., 2022). The biodegradability of these crude fibers ensures they do not contribute to secondary pollution, making them an environmentally friendly option for wastewater treatment (Azanaw et al., 2022). For instance, Chen et al., (2024) modified jute fibers to achieve pH-switchable adsorption properties for heavy oil (1 to 1.48 g/cm3). The fibers were treated with carboxymethyl, which allowed them to efficiently adsorb oil under neutral pH conditions. The switching of adsorption and desorption was triggered by exposure to an ethanol-water solution (50%), which facilitated the release of adsorbed heavy oil within about 30 minutes. The pH-switchable jute fibers could remove up to 92% of heavy oil and maintain over 85% of their original adsorption capacity after 5 regeneration cycles.

2.5.2 Switchable Resin

Switchable resins are leveraged in wastewater treatment due to their properties of

adjustable surface charge, chemical affinity, and ion exchange capacity. They are thus designed to change their physicochemical characteristics, like hydrophobicity and porosity, in response to external triggers such as pH, temperature, or electrical signals (Ekeocha et al., 2021). These dynamic changes allow switchable resins to selectively adsorb and desorb pollutants, enabling efficient contaminant removal and material regeneration (Li et al., 2023).

One common type of switchable resin is the pH-responsive resin, which can modify its charge or hydrophobicity according to the pH of the surrounding environment. Dai et al., (2008) prepared pH-responsive resins by functionalizing them with carboxyl groups, which allowed the resins to switch between hydrophobic and hydrophilic states under acidic (pH 3-5) and basic (pH 8-10) conditions. These pH-responsive resins were used to selectively adsorb Bisphenol A in acidic conditions and release them in basic environments, thus facilitating reuse. Zhiheng et al. (2022) developed another pH-responsive resin capable of altering its ion exchange capacity to remove cadmium and lead from wastewater, achieving removal efficiencies of 93% and 89%, respectively, at neutral (pH 7) and slightly acidic (pH 6) conditions. The resin adsorbed heavy metals at these conditions and released them in a more acidic environment (pH 2). The resin retained over 85% of its initial adsorption capacity after 5 regeneration cycles, which involved acid washing for desorption (Zhiheng et al. 2022). Switchable solvents have gained considerable attention due to their ability to transition between hydrophobic and hydrophilic states, offering potential for environmentally friendly applications, particularly in material synthesis and extraction

processes. For example, $CyNMe_2$, a CO_2-mediated switchable hydrophilic solvent (SHS), has been utilized in the preparation of silica aerogels, where it plays a key role in extracting pore water from silica hydrogels. Under ambient pressure, the solvent undergoes a reversible phase change when exposed to CO_2, becoming hydrophilic and miscible with water, thus facilitating efficient water removal from the gel pores. This process significantly reduces the energy consumption and time required for the conventional drying methods typically used in aerogel production (Asare Bediako et al., 2019). The use of such switchable solvents is not only beneficial for enhancing material properties but also contributes to sustainable practices by reducing reliance on hazardous solvents and enabling the recovery and recycling of materials in an efficient and eco-friendly manner. Furthermore, the effectiveness of $CyNMe_2$ in the extraction of vegetable oils and as a draw solute in forward osmosis, in addition to its application in silica aerogel synthesis, demonstrates its versatility and promise in various industrial applications.

There are two types of potential switchable resins for wastewater treatment. Temperature-responsive resins exploit the temperature-dependent solubility and swelling behavior of polymers in resins. These resins can expand or contract with temperature changes, modulating their surface area and pore structure to enhance contaminant uptake. They are particularly useful in processes where temperature variations act as triggers for adsorption and desorption, thereby simplifying the regeneration process (Poplewska et al., 2014). Electro-responsive resins respond to electrical stimuli by changing their charge density or structural conformation, making

them suitable for integration into electrochemical systems where applied voltage drives the adsorption or release of contaminants (Russo et al., 2022). Their modification methods have been developed but remain application research on wastewater treatment. Despite their advantages, the use of switchable resins raises potential environmental concerns. One major issue is the possible generation of microplastics due to resin degradation over time, which could contribute to secondary pollution in water systems. Additionally, degradation byproducts from chemical modifications or prolonged exposure to wastewater conditions may introduce new contaminants, necessitating careful assessment of long-term environmental impacts (Li et al., 2023).

Temperature-responsive resins regulate the adsorption and desorption processes through temperature changes, but may require higher energy consumption to maintain a specific temperature (Poplewska et al., 2014). Electro-responsive resins respond quickly to electrical stimulation and are highly energy efficient but can be complex to integrate into existing treatment systems (Balcerak-Woźniak et al., 2024). The choice of resin should be based on specific treatment objectives, energy consumption considerations and system integration capabilities (Li et al., 2023).

2.5.3 Switchable Rubber

Switchable rubber takes advantage of its mechanical strength, flexibility, and chemical resistance to effectively remove various pollutants, while its functionalities can be adapted to meet specific treatment needs (Qi et al., 2021). For example, rubber

particles can be chemically modified with functional groups that specifically target certain pollutants, such as heavy metals and organic compounds, with the ability to activate or deactivate these groups as needed. This enhances the adsorption efficiency and selectivity of rubber, making it a promising material for treating industrial effluents (Gupta et al., 2012). In addition, the porous structure of certain rubber derivatives provides a large surface area, further boosting their adsorption capacity (Saleh & Gupta, 2014).

For instance, Lin et al., (2021) developed a pH-switchable rubber by grafting amine groups onto the rubber surface. The pH-responsive property of the resulting rubber allowed it to switch between protonated and deprotonated states, thus modifying its surface charge and adsorption behavior. In wastewater treatment applications, this pH-responsive rubber exhibited high removal efficiencies for heavy metals such as lead and cadmium, achieving removal rates of 90% and 85% when pH > 5 and pH > 6, respectively. This switchable feature enabled the rubber to adapt to fluctuating pH levels in wastewater, increasing its efficiency. The switchable rubber could be regenerated by washing with a dilute acid or base solution and retained over 80% of its adsorption capacity after five regeneration cycles.

Currently, the applications of switchable rubber remain relatively less for several reasons. First, although chemical modifications can enhance the adsorption efficiency of rubber, the overall performance of switchable rubber often falls short when compared to cellulose-based materials. Switchable cellulose derivatives tend to have

better performances due to their natural hydrophilicity, greater surface area, and ease of modification (Qiu & Hu, 2013). In addition, while switchable rubber can be regenerated and reused, its long-term performance stability may not be as robust as that of cellulose-based materials which can maintain their efficiency over extended use (Aziz et al., 2022).

2.5.4 Advancements and Optimization

Several alternative approaches and modifications have been explored to enhance the performance and applicability of switchable crude fibers, resin, and rubber in wastewater treatment. For example, resins can be functionalized with chelating agents to enhance their metal-binding properties (Wang et al., 2001). Similarly, switchable rubber can be modified with amine or carboxyl groups to target heavy metal removal (Guo et al., 2022). Composite materials, combining fibers or resin with other adsorbents like activated carbon, may offer synergistic effects and enhance overall performance (Joo et al., 2024). The ability to regenerate and reuse these switchable materials is critical for sustainable wastewater treatment by reducing operational costs and minimizing waste generation. Techniques such as chemical washing and thermal treatment have been explored for their regeneration, allowing multiple cycles of use without significant loss of efficiency (Baskar et al., 2022).

While these switchable biomaterials offer significant advantages, their development is still in its nascent stages. The selection of materials for wastewater treatment must balance performance with environmental impact and cost. Switchable biomaterials

like crude fibers offer environmental benefits due to their biodegradability and renewability. However, the complexity of synthesizing switchable functionalities, combined with the need for precise control over environmental conditions to trigger these properties, limits their applications. In addition, the costs may be high for developing and scaling up these switchable biomaterials. Thus, more research and innovation are needed to overcome these challenges and make these switchable biomaterials more accessible and practical for widespread use in wastewater treatment. For example, life cycle assessment (LCA) can be used to evaluate the overall sustainability of different materials and processes, guiding the selection of the most appropriate options for specific applications (Corominas et al., 2020). Overall, switchable crude fibers, resin, and rubber each offer unique advantages and face specific challenges in wastewater treatment. Common methods of synthesis and processing provide a foundation for their application, while research and innovation can be continued to enhance their performance and sustainability.

2.6 Challenges and Perspectives

Switchable biomaterials have offered promising advantages in wastewater treatment due to their stimulus-responsive functionalities, biocompatibility, and recyclability. However, several critical challenges hinder their large-scale adoption and long-term applicability. These challenges include mechanical stability, environmental impact, synthesis reproducibility, scalability, economic feasibility, and real-world performance validation. Table S1 reviews the performances of switchable biomaterials in

wastewater treatment in recent studies, and Table 3 summarizes their general advantages and challenges, as well as the corresponding prospective research.

Table 3: Summary of Switchable Biomaterials for Wastewater Treatment

Biomaterials	**Advantages**	**Challenges**	**Prospective research**
Cellulose	Biocompatible, biodegradable, cost-effective, pH/temperature-responsive	Lower mechanical strength and stability in harsh conditions	Improve mechanical properties, explore novel functionalities
Biomass with Heteroatoms	Abundant, simple on extraction, enhanced adsorption due to strong interactions	Complex molecular structures, uniform modification	Advanced modification techniques, synergistic effects
Biochar	Large surface area, porosity, high adsorption capacity, versatile (pH, temperature, magnetic)	Variability in raw materials and production processes	Standardize production methods, incorporate functional groups/nanoparticles
Rubber, Resin, Fiber	Flexibility, durability, ease of modification, tunable wettability	Complex synthesis processes, potential environmental impacts	Environmentally friendly synthesis, long-term stability, hybrid materials

2.6.1 Mechanical Stability and Structural Integrity

The reusability of switchable biomaterials is crucial for their practical implementation in wastewater treatment. Ensuring consistent adsorption capacity and switchability across multiple cycles requires precise material synthesis and functionalization to maintain mechanical stability and structural integrity, particularly for cellulose-based materials. While nanocellulose and chitosan-based aerogels exhibit high porosity and adsorption efficiency, they often suffer from poor structural strength, leading to degradation over multiple usage cycles. Weak intermolecular bonds, high swelling ratios, and material fragility are common issues (Ekeocha et al., 2021). Optimizing surface functional groups (e.g., hydroxyl and amino groups) plays a significant role in sustaining adsorption performance over repeated use. Hydrogels and composite materials, particularly those incorporating carbon-based materials like biochar, have demonstrated enhanced mechanical strength and resistance to deformation, contributing to their durability and extended reusability (Darmenbayeva et al., 2024; Alcalde-Garcia et al., 2023). Hydrophobic modifications or polymer integration can also mitigate water-induced degradation, improving long-term usability. Additionally, to improve recyclability, selective desorption strategies must be employed to efficiently remove pollutants while restoring the switchable properties of the materials. Controlled desorption processes would allow hydrogel-based and composite biomaterials to maintain their adsorption efficiency for multiple treatment cycles.

2.6.2 Incorporation of Nanomaterials for Enhanced Functionality

The integration of nanomaterials (e.g., TiO_2, ZnO, carbon nanotubes) into switchable biomaterials has been explored to enhance adsorption capacity, photocatalytic degradation, and antimicrobial properties (Păun et al., 2023). However, several challenges hinder large-scale implementation, particularly in terms of dispersion, stability, and environmental safety.

Dispersion challenges arise due to nanoparticle agglomeration, which can reduce surface area and reactivity, impacting overall treatment efficiency. Ensuring uniform distribution of nanomaterials within biomaterials requires advanced synthesis techniques, such as surface functionalization or in-situ incorporation methods (Shrestha et al., 2020). Stability concerns involve nanoparticle leaching during long-term use, which can lead to reduced adsorption efficiency and potential contamination (Liu et al., 2015). Optimizing nanomaterial-biomaterial interactions, such as covalent bonding or encapsulation strategies, can enhance structural integrity and prolong material lifespan. Environmental risks include nanotoxicity and bioaccumulation, as metal oxide nanoparticles and carbon-based nanomaterials may pose ecological hazards if released into water bodies. Developing biodegradable nanocomposites and eco-friendly synthesis approaches, such as biopolymer-assisted nanoparticle stabilization, will be critical for ensuring safe and sustainable integration into wastewater treatment systems (Sarkar et al., 2019). Addressing these dispersion, stability, and toxicity challenges through material innovation and process optimization is essential for realizing the full potential of nanomaterial-enhanced switchable biomaterials in real-world wastewater applications.

2.6.3 Environmental Impacts

Despite their renewable and biodegradable nature, switchable biomaterials may pose environmental risks due to secondary pollution from leaching of functionalization agents or degradation byproducts. While many of these materials degrade naturally, functionalized chitosan and cellulose may incorporate chemical groups that enhance pollutant removal but reduce biodegradability to a certain extent due to increased hydrophobicity or crosslinking density (Kanmani et al., 2017). Furthermore, concerns exist regarding the release of functionalization agents, such as nanoparticles (e.g., TiO_2, ZnO) and synthetic additives (e.g., polyethylene or polyvinyl chloride), which could accumulate in ecosystems (Jurado-Sánchez, 2022). To mitigate these risks, life cycle assessments (LCAs) and toxicity monitoring must be integrated into biomaterial research to evaluate their long-term environmental footprint.

2.6.4 Reproducibility and Performance Consistency

The effectiveness of switchable biomaterials relies on precise functionalization, yet achieving consistent modification remains a challenge due to variability in raw materials, reaction conditions, and processing techniques (Thomas et al., 2019). For instance, biochar-based materials exhibit variations in porosity and adsorption efficiency, while functionalized chitosan and cellulose can suffer from non-uniform surface modifications affecting their switchability. To enhance reproducibility, standardizing feedstock sources, optimizing pyrolysis and grafting methods, and employing enzyme-assisted modifications are essential (Becker et al., 2023). Machine

learning-driven material design offers a promising approach, enabling predictive modeling of adsorption behavior and process optimization. Additionally, real-time monitoring techniques and computational simulations can further improve synthesis control and ensure batch-to-batch consistency. Enhancing reproducibility and stability is crucial for the large-scale deployment of switchable biomaterials, ensuring reliable pollutant removal, sustained adsorption-desorption cycles, and long-term cost-effectiveness in wastewater treatment (Sharmila et al., 2024).

2.6.5 Scalability and Economic Feasibility

The scalability and sustainability of switchable biomaterials depend largely on the availability of renewable feedstocks, including cellulose, chitosan, polylactic acid (PLA), biochar, and natural fibers. These materials are selected for their low environmental footprint and minimal competition with food production (Lin et al., 2024). Cellulose, sourced from agricultural residues (e.g., straw, corn stover) and forestry by-products (e.g., wood chips, sawdust), is abundant and non-competitive with food crops (Keijsers et al., 2013). Chitosan, derived from crustacean shells, utilizes seafood industry waste, enhancing waste valorization (Hameed et al., 2022). Polylactic acid (PLA), produced via fermentation of sugars from corn or sugarcane, raises concerns about land competition. However, advances in high-yield crops and lignocellulosic biomass utilization are mitigating this issue (Spiertz & Ewert, 2009). Biochar and natural fibers are derived from agricultural by-products or grown on marginal lands, promoting carbon sequestration and soil health. The reliance on

waste-derived sources for cellulose and chitosan ensures a stable supply chain for large-scale production (Ali et al., 2024). Meanwhile, industrial integration of these biomaterials through circular economic approaches (e.g., repurposing agricultural and seafood waste) enhances sustainability. Further research into alternative feedstocks and non-food-based biomass will be key to ensuring long-term scalability without resource competition (He et al., 2015).

Scaling switchable biomaterials from laboratory research to industrial applications presents technical and economic challenges. Conventional wastewater treatment processes, such as activated carbon adsorption, membrane filtration, and chemical coagulation, benefit from established infrastructure and cost-effective operation (Ma et al., 2021). In contrast, switchable biomaterials require specialized synthesis and modification steps, which can be resource-intensive. Moreover, variability in raw material sources—such as agricultural waste for biochar or seafood byproducts for chitosan—raises concerns about supply chain stability (Xiong et al., 2019). Addressing these challenges requires integrating biomaterial-based treatment systems into existing wastewater facilities and developing cost-effective production techniques, such as low-energy drying and green chemical functionalization.

At present, the applicability of switchable biomaterials in global wastewater treatment standards is still in the exploratory stage, and no systematic research has been conducted to directly compare its removal performance with the specific requirements of international regulations (such as WHO, EPA, EU Water Framework Directive).

However, laboratory data show that most switchable biomaterials can achieve efficient removal specific contaminants. For example, switchable cellulose with adsorption capacities up to 11.6-106 g/g can maintain high performance over multiple cycles (>95%) (AJALA et al., 2023). Future studies need to further clarify its optimal usage, the number of adsorption-desorption cycles and the removal efficiency in multi-pollutant environments to assess whether it can meet or exceed the discharge standards of current sewage treatment regulations and promote its standardization in practical applications.

2.6.6 Energy Demand

The energy demands of wastewater treatment vary significantly between traditional methods (e.g., chemical coagulation, activated carbon adsorption, and membrane filtration) and switchable biomaterials. For example, membrane filtration requires 1–4 kWh/m³, while activated carbon adsorption involves thermal regeneration consuming up to 3.5 kWh/kg (Ghimire et al., 2021). Chemical coagulation also incurs energy costs for chemical production, mixing, and sludge handling (Teh et al., 2016). In contrast, switchable biomaterials, such as pH-responsive aerogels and CO_2-switchable chitosan composites, operate passively, leveraging environmental stimuli for adsorption/desorption, eliminating the need for high-pressure filtration or intensive thermal regeneration (Balogun et al., 2024). For instance, pH-responsive cellulose aerogels achieve high adsorption efficiency via simple pH adjustments, reducing mechanical energy inputs. Although synthesis and regeneration require energy,

advancements in green chemistry and low-energy fabrication methods are minimizing these costs. Additionally, mild regeneration conditions (e.g., CO_2 bubbling, pH shifts) consume far less energy than activated carbon's thermal regeneration or membrane backwashing, making switchable biomaterials a more sustainable alternative for wastewater treatment (Shi et al., 2014).

2.6.7 Performance in Complex Wastewater Matrices

The treatment of complex wastewater matrices, which generally contain multiple contaminant types such as heavy metals, dyes, pharmaceuticals, and oils, presents significant challenges for switchable biomaterials. Unlike conventional wastewater treatment methods that rely on broad-spectrum chemical coagulation, activated carbon adsorption, or membrane filtration (Pandit & Sharma, 2024), switchable biomaterials function through stimuli-responsive mechanisms that may not always accommodate the diverse physicochemical interactions occurring in mixed wastewater systems.

One of the primary challenges is competitive adsorption between contaminants. In multi-component wastewater, different pollutants may compete for active sites on the biomaterial, leading to reduced removal efficiency. For example, dyes and heavy metals often have overlapping adsorption mechanisms, and their simultaneous presence can result in selectivity loss or adsorption site saturation (Wan Ngah et al., 2011), limiting the effectiveness of a single switchable biomaterial. Additionally, the presence of surfactants, natural organic matter, or fluctuating pH levels can alter material performance by modifying the surface charge and wettability, thereby

affecting adsorption capacity and desorption efficiency (Al-Gethami et al., 2024).

Another key challenge is the lack of material adaptability to varying wastewater compositions. Many switchable biomaterials are designed for specific pollutants under controlled laboratory conditions, but real-world wastewater varies in composition, ionic strength, temperature, and competing solutes. The fine-tuning of functional groups and structural properties is crucial to maintaining high adsorption efficiency in fluctuating conditions (Belzile & Chen, 2024). Current switchable biomaterials, such as pH-responsive cellulose aerogels and CO_2-switchable chitosan composites, exhibit high efficiency in targeted pollutant removal (Ren et al., 2018; Ahmad et al., 2023), but their performance in multi-pollutant wastewater streams remains inconsistent.

To improve the performance of switchable biomaterials in complex wastewater matrices, future research may focus on: (1) Developing hybrid biomaterials that incorporate multiple functional groups or composite structures to enhance selectivity for diverse pollutants. (2) Investigating multi-contaminant interactions to better understand how co-existing pollutants impact adsorption, desorption, and material stability. (3) Optimizing environmental stimuli parameters (e.g., pH, CO_2 exposure, temperature) to ensure consistent performance across varying wastewater conditions. (4) Enhancing recyclability and reusability to prevent material degradation and loss of efficiency over multiple treatment cycles (Rando et al., 2024; Cunningham & Jessop, 2019).

2.6.8 Case Studies and Real-World Applications

Despite significant laboratory advancements, the real-world application of switchable biomaterials remains limited, primarily due to challenges in scaling, performance validation, and integration into existing treatment systems. While bioinspired cellulose membranes and functionalized biochar have demonstrated high pollutant removal efficiencies under controlled conditions, their long-term stability, reusability, and adaptability in complex wastewater matrices have yet to be fully assessed (Baig et al., 2022). Key barriers to pilot-scale implementation include material variability, regeneration efficiency, and economic feasibility (Matveeva & Bronstein, 2022). Batch-to-batch inconsistencies in biochar production, for example, can affect adsorption efficiency (La et al., 2019), while the functionalization of cellulose and chitosan-based materials may degrade over multiple cycles, reducing long-term performance (Wang & Zhuang, 2022). Additionally, the current wastewater treatment infrastructure is designed for conventional technologies, making it challenging to integrate switchable biomaterials without significant process modifications (Alayande et al., 2024). Furthermore, comprehensive pilot studies and industrial-scale evaluations are needed to assess operational feasibility, particularly in multi-contaminant wastewater environments where competitive adsorption and external factors (e.g., pH fluctuations, temperature shifts, and co-existing pollutants) may impact material performance (Al-Gethami et al., 2024). The absence of standardized testing protocols and long-term monitoring data further complicates real-world adoption. To bridge this gap, future research should prioritize large-scale

trials, focusing on material durability, regeneration cycles, and cost-effectiveness in municipal and industrial wastewater treatment plants. Collaborations between academia, industry, and regulatory bodies will be essential to establish scalability frameworks and evaluate the viability of switchable biomaterials in real-world applications.

Nevertheless, switchable biomaterials offer significant potential for industrial and municipal wastewater treatment, particularly in sectors with specific contaminant challenges. In the textile industry, where wastewater is rich in synthetic dyes and heavy metals (Premkumar et al., 2017), pH-responsive cellulose-based adsorbents provide an effective and energy-efficient alternative to conventional treatment methods (El-Khateeb et al., 2023). Similarly, in food and beverage processing, wastewater containing oils, fats, and greases (FOG) can be efficiently treated using surface-tailored switchable biomaterials (Ahmad et al., 2023), improving oil separation and reducing organic loads. Pharmaceutical manufacturing presents another key application, as these facilities discharge residual active compounds and endocrine-disrupting chemicals that are difficult to remove; functionalized biomaterials with specific binding affinities offer a promising solution for targeted pollutant capture and removal (Spiertz & Ewert, 2009). Additionally, municipal wastewater treatment plants, which manage diverse contaminants including nutrients, pathogens, and emerging pollutants (Hube & Wu, 2021), can integrate switchable biomaterials into existing treatment systems to enhance the removal of heavy metals and micropollutants without requiring extensive infrastructure modifications. By

leveraging the stimuli-responsive properties of these materials, industries can achieve higher treatment efficiencies with lower chemical and energy demands, making switchable biomaterials a promising approach for addressing both current and emerging wastewater challenges while promoting sustainable water management practices (Ghimire et al., 2021).

2.7 Summary

The development of novel biomaterials with switchable functionalities has garnered significant attention in recent years. The switchable nature of these biomaterials facilitates not only their recycling but also the recovery of pollutants, presenting sustainable and cost-effective options for wastewater treatment. This review provided a comprehensive summary on various switchable biomaterials, including cellulose, chitosan, polylactic acid (PLA), proteins, rubber, resin, crude fibers, and biochar, and their multifaceted applications in contaminant removal from wastewater according to Chapters 2.2 to 2.5. Significant advancements in the development of switchable biomaterials for wastewater treatment have been achieved, though there are still several research gaps and challenges that need to be addressed, as discussed in Chapter 2.6. Enhancing the stability, recyclability, and performance of these materials, as well as exploring novel switchable functionalities and hybrid materials, will be crucial for their successful applications in real-world scenarios. By addressing these challenges, switchable biomaterials hold great promises for providing sustainable and efficient solutions to water contamination issues and wastewater treatment.

Switchable cellulose materials offer significant advantages such as biocompatibility, biodegradability, and cost-effectiveness. They can be modified to exhibit pH-responsive or temperature-responsive behaviors, enhancing their adsorption capacities for various pollutants. It is currently the most promising for large-scale practical applications in wastewater treatment. However, the main disadvantage is their relatively lower mechanical strength and stability in harsh conditions. Future research may focus on improving the mechanical properties of switchable cellulose through cross-linking or blending with other polymers, as well as exploring novel switchable functionalities to enhance their effectiveness in diverse wastewater treatment scenarios.

CHAPTER 3

DEVELOPMENT OF A SPIROPYRAN-ASSISTED CELLULOSE AEROGEL WITH SWITCHABLE WETTABLILLITY AS OIL SORBENT FOR OIL SPILL CLEANUP

Chapters 3 are generated based on the following publication:

Wang, H., Chen, X., Chen, B., Zhao, Y., & Zhang, B. (2024). Development of a spiropyran-assisted cellulose aerogel with switchable wettability as oil sorbent for oil spill cleanup. Sci Total Environ, 923, 171451. https://doi.org/10.1016/j.scitotenv.2024.171451

*Hongjie Wang and Xiujuan Chen conceived of the presented idea. Hongjie Wang carried out the experiments and contributed to the final version of the manuscript. Dr. Yumin Zhao synthesized carboxyethyl spiropyran. Xiujuan Chen contributed to the text revision. Dr. Baiyu Zhang and Dr. Bing Chen encouraged and supervised the findings of this work.

3.1 Background

Oil spills have emerged as a global pressing environmental concern, posing severe threats to marine and terrestrial ecosystems (Zhang et al., 2019a; Zhang et al., 2019b). The release of vast quantities of petroleum into the environment has led to profound ecological disruptions, which damage ecosystem biodiversity, habitat integrity, and functionality. Corresponding to this challenge, several cleanup technologies have been developed and used for oil spill responses, such as booms, skimmers, and dispersants (Adofo et al., 2022; Doshi et al., 2018; Li et al., 2016). Among them, using oil sorbents is an effective method for removing the last traces of oil or for areas where a skimmer cannot clean. They are also the sole cleanup method for small spills (Hoang et al., 2021).

So far, many functional sorbents have been developed and applied for oil spill cleanup (Zamparas et al., 2020). Among them, hydrophobic cellulose aerogels were widely used due to their high oil adsorption rate, rapid adsorption process, and ease of recycling (Reynolds et al., 2001; Karatum et al., 2023). To further improve their reusing and regeneration abilities, researchers have tried to introduce the property of switchable wettability into cellulose aerogels (Li et al., 2018; Fan et al., 2022; Chen et al., 2022; Liu et al., 2020). Ultraviolet (UV)-induced switchable wettability attracted a wide range of interest owing to its advantages of simple operation, high efficiency, and fast wettability transition (Rajesh et al., 2021). For example, a nanofibrillated cellulose (NFC) aerogel prepared by the grafting of melamine and cetyltrihexylsilane

showed a reliable oil/water separation performance and could recover 95% of the adsorbent after repeated washing, rechlorination, and long-term UV treatment (Wang et al., 2022). In this process, the modified groups (cyanuric chloride and hexadecyltrimet-hoxysilane) connected to cellulose were excited by UV irradiation, which made the aerogel reactive. On this basis, compounds whose molecular configurations are easier to transform under UV can modify cellulose aerogels and simplify the material recovery operation.

Spiropyran (SP) is a typical compound that can change its molecular structure under UV with high transformation efficiency (Klajn, 2014). When exposed to UV light, the spirocarbon- oxygen bond of the SP molecule would break, resulting in a rearrangement of electron configuration; the two orthogonal aromatic rings would become a coplanar ring system; the adsorption wavelength would redshift; and the molecule would become a color developing body. Thus, spiropyrans have been considered to control the wettability of materials in a few studies (Zhao et al., 2021). For example, Dehkordi et al., 2021 developed a porous membrane doped with hydroxyl SP through electrospinning. The membrane showed hydrophobic and hydrophilic properties before and after UV irradiation, respectively, and was applied for oil/water separation with visible color-changing (Dehkordi et al., 2021). Spiropyran is preferred over other photoresponsive compounds due to its rapid and reversible transition between hydrophobic and hydrophilic states, making it ideal for dynamic wettability control. Unlike azobenzene, it induces a stronger polarity change, enhancing hydrophilicity shifts, and compared to diarylethene, it offers both high

efficiency and visible color change for real-time monitoring. Additionally, spiropyran derivatives can be chemically modified to enhance stability and adaptability, making them versatile for various applications (Zhao et al., 2021). However, to our knowledge, spiropyran has not been used to control the wettability of cellulose aerogels.

Therefore, this study aims to develop a spiropyran-assisted cellulose aerogel (CNF-SP aerogel) with UV-induced switchable wettability as an oil sorbent in oil spill cleanup. The CNF-SP aerogel was obtained through a simple freeze-drying method with raw materials on a 3D substrate. The raw materials mainly included carboxymethyl cellulose (CNF-COOH), carboxyethyl spiropyran (SP-COOH), polyvinyl alcohol (PVA) and zinc oxide nanoparticles (ZnO NPs). It was expected that the immobilized SP-COOH endowed the developed aerogel with the ability to switch its surface property from hydrophobic to hydrophilic through UV irradiation. In detail, (1) the CNF-SP aerogel was synthesized and optimized through central composite design (CCD), and the effects of main raw materials and their interactions on the oil adsorption performance of the aerogel were investigated; (2) the developed CNF-SP aerogel was comprehensively characterized through SEM imaging, contact-angle measurement, and synchrotron-based FTIR analyses; (3) the influences of water environmental conditions on the oil/water separation performance of the CNF-SP aerogel were analyzed; and (4) the developed CNF-SP aerogel was used as oil sorbents to separate crude oils from water, and the oil adsorption efficiency and material recovery rate were examined.

3.2 Materials and Methods

3.2.1 Materials

Piperidine, 2,3,3-trimethylindolenine, 3-iodopropionic acid, methyl ethyl ketone, 2-hydroxyl-5-nitrosalicylaldehyde, hexane, diethyl ether, methanol from Sigma-Aldrich were used for the synthesis of SP-COOH. The specific steps of SP-COOH synthesis are shown in the support information. Sodium polyacrylate (PAAS), nano iron oxide (Fe3O4, <100 nm), carboxymethyl cellulose sodium salt (CNF-COOH), ethanol, and polyvinyl alcohol (PVA) were purchased from Aldrich. Nano boron nitride (BN, < 200 nm), nano zinc oxide (ZnO, <100 nm), N, N-dimethylacetamide (DMAc), and acetone were supplied by Merck and used without purification. Crude oils, including Hibernia, Terra Nova, ANS, and Dilbit, were provided by the Newfoundland & Labrador Industrial Trade and Rural Development (IRIF).

3.2.2 Synthesis and Optimization of CNF-SP Aerogel

A diagram of CNF-SP aerogel synthesis is presented in Fig. 6. Briefly, a 3D substrate was prepared first. PAAS (810 mg) was slowly added and dissolved in 300 mL deionized water at 95 °C to obtain a PAAS solution with a 2.7 mg/mL concentration. Then, 810 mg BN and 400 mg Fe_3O_4 were evenly dispersed into 300 mL deionized water, and 100 mL PAAS solution and 10 mL ethanol were added into the dispersion and mixed through ultrasonic for 60 min. The mixture was

freeze-dried for 48 h to obtain the substrate. Next, the CNF-SP aerogel was prepared through simple freeze-drying with raw materials on the substrate. The substrate (140 mg) was immersed in 40 mL deionized water, followed by adding and mixing certain weights of CNF-COOH and PVA, then a homogeneous suspension (which was obtained through adding specific amounts of nano ZnO and SP-COOH in acetone and DMAc (Molar ratio of acetone and DMAc = 2:1) and stirring for 24 h at 40 °C) was added and further mixed into the mixture. The final mixture was then freeze-dried for 48 h to obtain the CNF-SP aerogel. Fig. 6 also illustrates the structural organization of CNF-SP aerogel, detailing how the substrate integrates with CNF nanofibers and functionalized ZnO particles. The schematic representation highlights the molecular interactions and the spatial arrangement of the components, which are crucial for achieving the desired switchable wettability and adsorption properties.

To optimize the condition of the CNF-SP synthesis, the central composite design (CCD) technique was employed. CCD is a powerful optimization method widely applied in scientific investigations to determine the optimal condition with a minimum number of experiments and reflect the interactions between multiple factors (Leili et al., 2020). CCD was chosen for its ability to model non-linear interactions and quadratic effects efficiently, offering a more comprehensive optimization framework than other methods. It also minimizes experimental workload while ensuring statistical robustness, making it ideal for complex material formulations. In this study, the CCD design method was used to investigate the effects of concentrations of PVA, CNF-COOH, SP-COOH, and ZnO in the final mixture on the

oil adsorption efficiency and the hydrophilicity of the CNF-SP aerogel. Table 4 summarizes all the factors and their levels in this study. The criteria for defining parameter ranges are provided in support information.

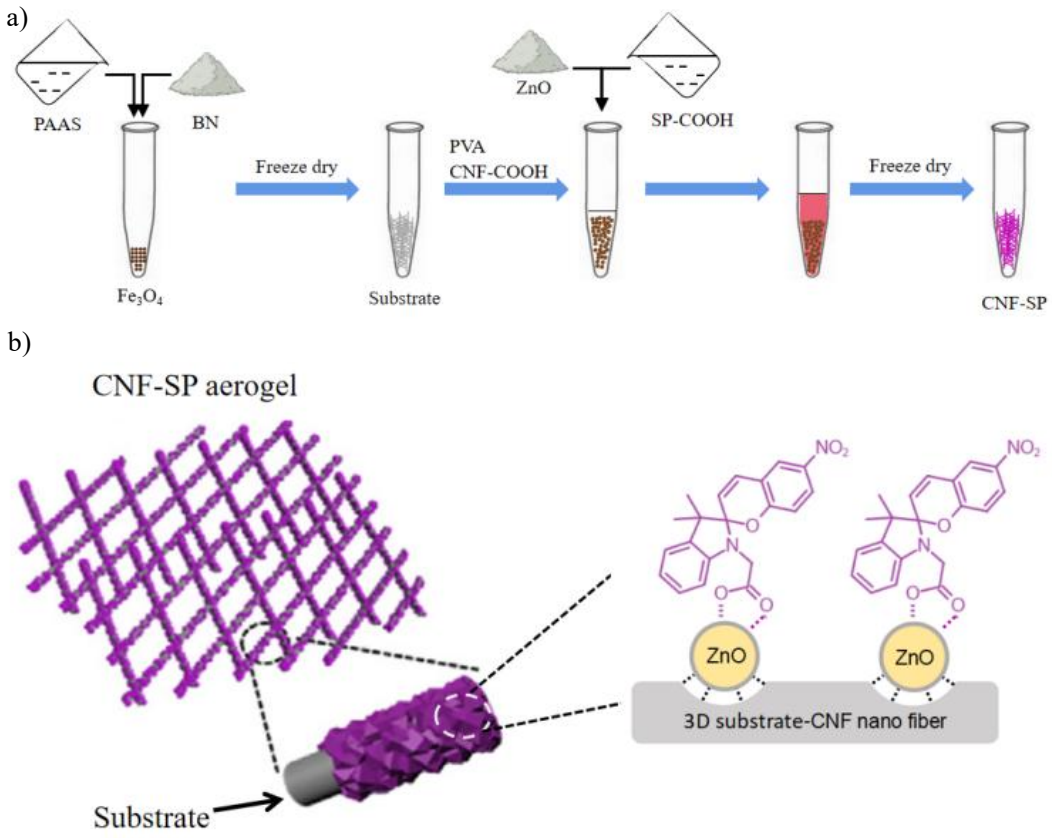

Figure 6 Diagram of CNF-SP aerogel a) synthesis and b) its structure.

The water contact angle (WCA) on the aerogel surface and the oil adsorption ratio (OAR) were used as experimental responses. Generally, a larger WCA means stronger lipophilicity and a larger OAR reflects a higher adsorption efficiency of the material. In this study, the WCA was measured using a JC2000CS contact-angle meter. For OAR measurement, the aerogel was placed in diesel oil for 10 s and weighed to determine its mass change before and after oil adsorption. Each measurement was repeated three times under the same condition to obtain an appropriate accuracy. The experiments were conducted randomly to avoid personal or subjective biases. Finally, the WCA and OAR of aerogel were further measured under the optimized experimental conditions to verify the effectiveness of the CCD method. The experimental matrix is shown in Table 4, and the result was analyzed using Design-Expert v12 (Stat-Ease Inc., Minneapolis, USA).

Table 4 Experimental factors and levels used in this study

Factors	Levels				
Coded values	-a	-1	0	1	a
A: PVA concentration (mg/L)	/	146	369.5	593	/
B: CNF-COOH concentration (g/L)	1.9	2.2	2.7	3.2	2.5
C: SP-COOH concentration (mmol/L)	4.9	7	10	13	13.5
D: Nano-ZnO concentration (mmol/L)	/	10	15	20	/

3.2.3 Aerogel Characterization

The surface morphology of CNF-SP aerogel was observed by scanning electron microscope (SEM) (FEI Quanta 400, Bruker, USA). The chemical composition of the aerogel was studied through Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectra using a Bruker Tensor 27 (Billerica, USA). The standard parameter for data collection was set at 64 scans in the wavenumber range of 400–4000 cm−1. The aerogel distributions of specific organic groups in the wavenumber range of 800–4000 cm−1 were measured and analyzed using the ATR-FTIR imaging technique at the Mid-Infrared Beamline in Canadian Light Source. The possible formation of crystals and metal oxides in the CNF-SP aerogel was tested through X-ray diffraction (XRD, Rigaku Ultima IV X-Ray diffractometer). Zeta potential was also tested to indicate the aerogel's surface charge and chemical structure stability under pH values ranging from 1 to 12 using a nanometer particle size potentiometer (ZS-90, Malvern, Canada).

3.2.4 Performance Evaluation of the CNF-SP Aerogel for Oil/water Separation

The optimized CNF-SP aerogel was used for oil/water separation and recovery. Diesel oil (0.83 kg/L) was selected as the oil representative and stained with methyl red to help intuitively demonstrate the oil adsorption performance of CNF-SP aerogel. The CNF-SP aerogel (25 mg) was put into a mixture of diesel oil and water with a volume ratio 1:1, and the mixture was slowly stirred to make it fully in contact with diesel oil and water for 15 s. Then, the used CNF-SP aerogel was taken out and the mass

adsorption rate was measured and recorded. To recover the adsorbed oil, the used aerogel was exposed under UV irradiation (365 nm, 8 W) for 40 min, and then the adsorbed liquid was gently squeezed out from the aerogel and the mass was recorded. Finally, the aerogel was dried at 35 °C and the dry weight was recorded. After drying, the sample was irradiated under visible light for 1 h to recover its hydrophobicity. These steps are considered as a usage cycle.

It should be noticed that the mass adsorption rate of the CNF-SP aerogel referred to the ratio of the absorbed liquid mass to its own mass, while the mass of oil precipitated under UV was recorded for recovered oil. Multiple usage cycles were performed to evaluate the overall performances of CNF-SP aerogel for oil/water separation and oil recovery. Each experiment was repeated three times and the average result was reported. The separation performances of various crude oils and water by the CNF-SP aerogel were measured using the same method. In addition, to analyze the influence of environmental factors on the performance of aerogel for oil/water separation, the OARs of CNF-SP aerogel at multiple water temperatures (0, 5, 15, 25, 35, and 45 °C), salinities (0, 5, 25, and 35 ‰) and pH values (4, 5, 6, 7, 8 and 10) were tested.

After applying for oil/water separation and oil recovery, the used CNF-SP aerogel was regenerated. Briefly, the used aerogel (250 mg) was immersed in 15 mL NaOH solution (10 mg/L) to dissolve cellulose and PVA, and then the mixture was centrifuged to remove the lower aqueous phase and precipitate. 15 mL HCl solution

(10 mg/L) was added to adjust the pH to about 7. Then, specific amounts of raw materials were added and mixed to adjust the concentration of each component in the sample to meet the optimized requirements. The regenerated aerogel was obtained by freeze-drying the mixture for 48 h.

Table **5** The CCD matrix for the optimization of CNF-SP aerogel

Sample #	Factors				Responses	
	A: PVA concentration	B: CNF-COOH concentration	C: SP-COOH concentration	D: Nano-ZnO concentration	Water Contact Angle (°)	Oil adsorption Ratio (g/g)
1	0	0	0	0	107	28.49
2	0	0	0	0	106	28.37
3	0	0	0	0	114	28.26
4	0	1	1	-1	95	28.29
5	-1	1	-1	1	87	25.96
6	0	0	0	1	101	27.84
7	0	-a	0	0	99	26.86
8	0	0	a	0	124	29.74
9	0	-1	1	1	112	27.32
10	0	0	0	0	105	28.13
11	0	0	0	0	104	28.55
12	-1	0	0	0	95	27.71
13	0	-1	-1	1	93	24.34
14	0	a	0	0	98	27.21
15	0	0	0	-1	102	28.05
16	0	0	-a	0	108	26.53
17	-1	-1	-1	-1	89	23.28
18	-1	1	1	1	97	28.08
19	0	0	0	0	107	28.62
20	-1	-1	1	-1	100	27.42
21	0	1	-1	-1	106	26.61

3.3 Characterization and Properties of CNF-SP Aerogel

3.3.1 Optimization of CNF-SP Aerogel through CCD

CCD is a powerful experimental design method widely used to consider the nonlinear effects among experimental factors on response (Soltani-Shahrivar et al., 2023). In this research, the water contact angle of the prepared aerogel samples was measured at room temperature (25 °C), and all the experiments of oil adsorption analysis were carried out in a dry fume hood at 25 °C. The effects of four factors (A-PVA concentration, B-CNF-COOH concentration, C-SP-COOH concentration, and D-Nano-ZnO concentration) on the hydrophilicity and oil adsorption capacity of CNF-SP aerogel were investigated, and their optimum conditions for the fabrication of CNF-SP aerogel were identified. Table 5 presents the experimental design and the corresponding results. The broad ranges of WCA (from 87° to 124°) and OAR indicated the necessity of component optimization for the CNF-SP aerogel. The detailed ANOVA results are shown in Table S2, and the factors with significant effects (p-value <0.05) on WCA and OAR are summarized in Table 6. Both WCA and OAR are repeated three times to reduce the error, which the design expert calculates to be within 0.05%. Two quadratic polynomial equations (Eqs. 1 and 2) were obtained from the experimental results expressed in coded units. They helped reflect the relationship among the four factors and responses . The p-values of both models were less than 0.05, indicating that the two models could fit the experimental results and help predict the optimum conditions for the fabrication of CNF-SP aerogel.

$$Y_{WCA} = 107.09 + 9.50A - 2.973B + 4.89C - 0.5D - 0.375AB - 1.63AC + 8.277AD - 3.88BC + 5.38BD + 3.63CD - 3.62A^2 - 3.17B^2 + 3.96C^2 - 6.62D^2 \quad (1)$$

$$Y_{OAR} = 28.53 + 0.275A + 1.041B + 1.28C - 0.105D - 0.1175AB - 0.2AC - 0.7184AD - 0.415BC + 0.0475BD - 0.09CD - 0.7238A^2 - 0.5508B^2 + 0.0338C^2 - 0.7638D^2 \quad (2)$$

Table 6 ANOVA results for the WCA and OAR of CNF-SP aerogel

		DF	Mean Square	F-value	P-Value
Water contact angle		15	95.57	31.54	0.0006
	A: Polyvinyl alcohol	1	270.40	89.24	0.0002
	B: Carboxyl cellulose sodium salt	1	4.50	1.49	0.2773
	C: SP-COOH concentration	1	302.50	99.83	0.0002
	D: Nano-ZnO concentration	2	44.75	14.77	0.0080
	AB	1	0.2250	0.074.	0.7961
	AC	1	23.23	7.66	0.0460
	AD	2	23.23	7.66	0.0300
	BC	1	120.13	39.64	0.0015
	BD	1	81.23	5.44	0.0585
	CD	2	122.88	40.55	0.0008
Oil adsorption ratio		15	35.99	23.24	0.0013
	A: PVA concentration	1	0.5617	11.60	0.0191
	B: Carboxyl cellulose sodium salt	1	53.56	34.59	0.0020
	C: SP-COOH concentration	1	19.97	412.49	<0.0001
	D: Zinc oxide	2	6.03	3.90	0.0955
	AB	1	5.29	3.42	0.1238
	AC	1	7.01	4.53	0.0866
	AD	2	0.3372	6.97	0.0358
	BC	1	1.38	28.46	0.0031
	BD	1	81.23	5.44	0.0585
	CD	2	23.00	14.85	0.0079

The model assumes that the factors interact in a manner that can be approximated by a second-degree polynomial equation. The variability in the data is assumed to be constant across different levels of the independent variables. The method assumes that the response surface can be adequately represented by a quadratic function, which may not fully capture more complex relationships. Experimental validation at additional points outside the design matrix may be necessary to confirm model accuracy.

According to the ANOVA results for WCA in Table 6 and Table S2, concentrations of PVA, SP-COOH and nano-ZnO had significant effects on the WCA of CNF-SP aerogel (with p-values <0.05). The results of the 3D response surface for WCA are shown in Fig. 7. In this study, PVA was used to bond CNF-COOH and shield hydroxyl groups during the fabrication process of CNF-SP aerogel. Thus, when the concentration of PVA was low, ZnO bonded preferentially with discrete molecules, which increased the hydrophilicity and decreased the hydrophobicity of the CNF-SP aerogel, resulting in a lower WCA, as shown in Fig. 7(a). However, when the concentration of PVA was high, nano-ZnO concentration had a positive effect on WCA. SP-COOH became hydrophobic after combining with nano-ZnO and CNF-COOH (Owais et al., 2022). When the concentration of CNF-COOH was high, some CNF-COOH molecules may not combine with nano-ZnO and SP-COOH, and thus, the concentration of SP-COOH and WCA had a positive correlation under this condition, as shown in Fig. 7(b). When the concentration of SP-COOH was high, WCA increased slightly and then decreased significantly with the gradual increase of

CNF-COOH concentration. Similarly, as shown in Fig. 7(c), when the nano-ZnO concentration was low, some SP-COOH molecules could not combine with CNF-COOH. The excessive SP-COOH might produce a small number of byproducts (e.g., the carboxyl group and the amino group form hydrogen bonds between molecules) without binding aerogel (Guan et al., 2021), which affected hydrophobicity negatively. Therefore, the interactions between the concentrations of PVA and nano-ZnO (Fig. 7(a)), CNF-COOH and SP-COOH (Fig. 7(b)), as well as SP-COOH and nano-ZnO (Fig. 7(c)) had significant effects on the hydrophobicity of CNF-SP aerogel.

It was also found that the concentrations of PVA and nano-ZnO and their interaction, as well as the interaction between the concentrations CNF-COOH and SP-COOH, showed significant effects on the oil adsorption capacity of CNF-SP aerogel. When both the concentrations of PVA and nano-ZnO were high, the oil adsorption efficiency was relatively low (Fig. 61(d)). This was because excessive PVA would also adsorb excessive nano-ZnO due to its high viscosity, forming large copolymers and occupying oil adsorption sites, thus leading to an OAR decrease. In comparison, the interaction effect between SP-COOH and CNF-COOH concentrations was more significant. As shown in Fig. 61(e), when the concentration of SP-COOH was too high, the excessive carboxyl group on SP-COOH would lead to reduced oilphilicity and decreased OAR. Similarly, when the concentration of CNF-COOH was too high, the internal hydrophilic groups (i.e., hydroxyl group) could not be effectively shielded, thus reducing the oil adsorption capacity of CNF-SP aerogel.

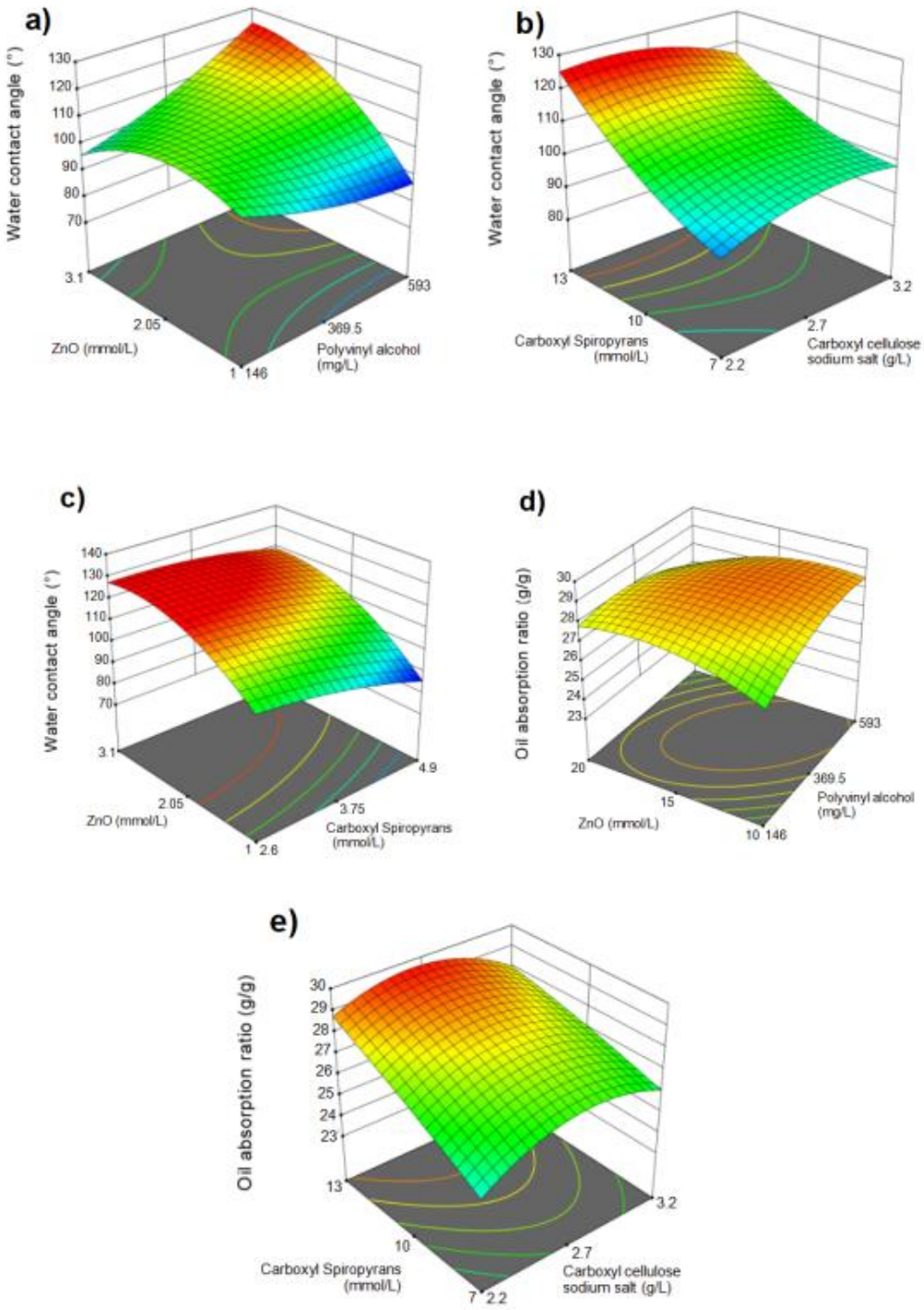

Figure 7 3D surface interaction of factors on water contact angle: a) ZnO & PVA, b) SP-COOH & CNF-COOH, and c) SP-COOH & ZnO; 3D surface interaction of factors on oil adsorption ratio: d) PVA & ZnO, and e) SP-COOH & CNF-COOH.

Therefore, all four factors were important for the fabrication of CNF-SP aerogel. The model obtained from the CCD method was used to optimize CNF-SP aerogel fabrication, with the target of achieving both maximum values of WCA and OAR. Thus, the priority was set as +5 for WCA and + 5 for OAR. Table 7 shows the predicted optimization results and actual experimental data. The WCA was expected to be 127.1°, and the actual value obtained from the experiment was 124°. The expected OAR was 29.81 g/g, and the actual value was 30.4 g/g. The experimental results and performance were consistent with predictions, indicating the obtained model's reliability. Moreover, the optimized CNF-SP aerogel was highly hydrophobic and had excellent oil adsorption capacity.

Table 7 Model prediction and the experimental results of the optimized CNF-SP preparation

	Prediction	Optimized Experimental results
Polyvinyl alcohol (mg/L)	468.33	466
Carboxyl cellulose sodium salt (g/L)	2.617	2.63
Carboxyl spiropyrans (mmol/L)	13.0	13.0
Zinc oxide (mmol/L)	14.3	14.3
Water contact angle (°)	127.1	124
Oil adsorption ratio（g/g）	29.81	30.4

3.3.2 Characteristics and Switchable Wettability of the CNF-SP Aerogel

Fig. 8 shows the SEM images of fresh CNF-SP aerogel before and after UV irradiation and used CNF-SP aerogel after UV irradiation. As shown in Figs. 3(a)-(c), the developed CNF-SP aerogel exhibited a 3D porous sponge-like structure with a grid size ranging from 50 to 100 μm. Besides, a number of small pores (about 1 μm in diameter) were observed in the skeletons and inner layers of CNF-SP aerogel. The 3D grid structure was formed due to the integration of BN with a sTable 5D structure and sodium acrylate as a crosslinking agent. With the help of PVA, CNF-COOH covered the skeletons and formed inner layers within the grid structure, leading to the formation of 3D porous sponge-like structure of the CNF-SP aerogel and uniform distributions of SP-COOH and nano-ZnO (Li et al., 2017). After UV light irradiation, the inner layers were partially broken into small pieces accompanied by filamentous connections (Figs. 3(d)-(f)). It indicated that during the preparation and freeze-drying process, some SP-COOHs are not only bonded by the carboxyl groups but also adhere to the surface of the material due to strong physical interactions among the adhesive molecules. Under UV irradiation, the structure and electron state of SP-COOH changed, and the attached side fell off, affecting the aerogel fibers' interaction (Kozlenko et al., 2021). As a result, the inner layers of the aerogel were partially damaged during the UV irradiation process.

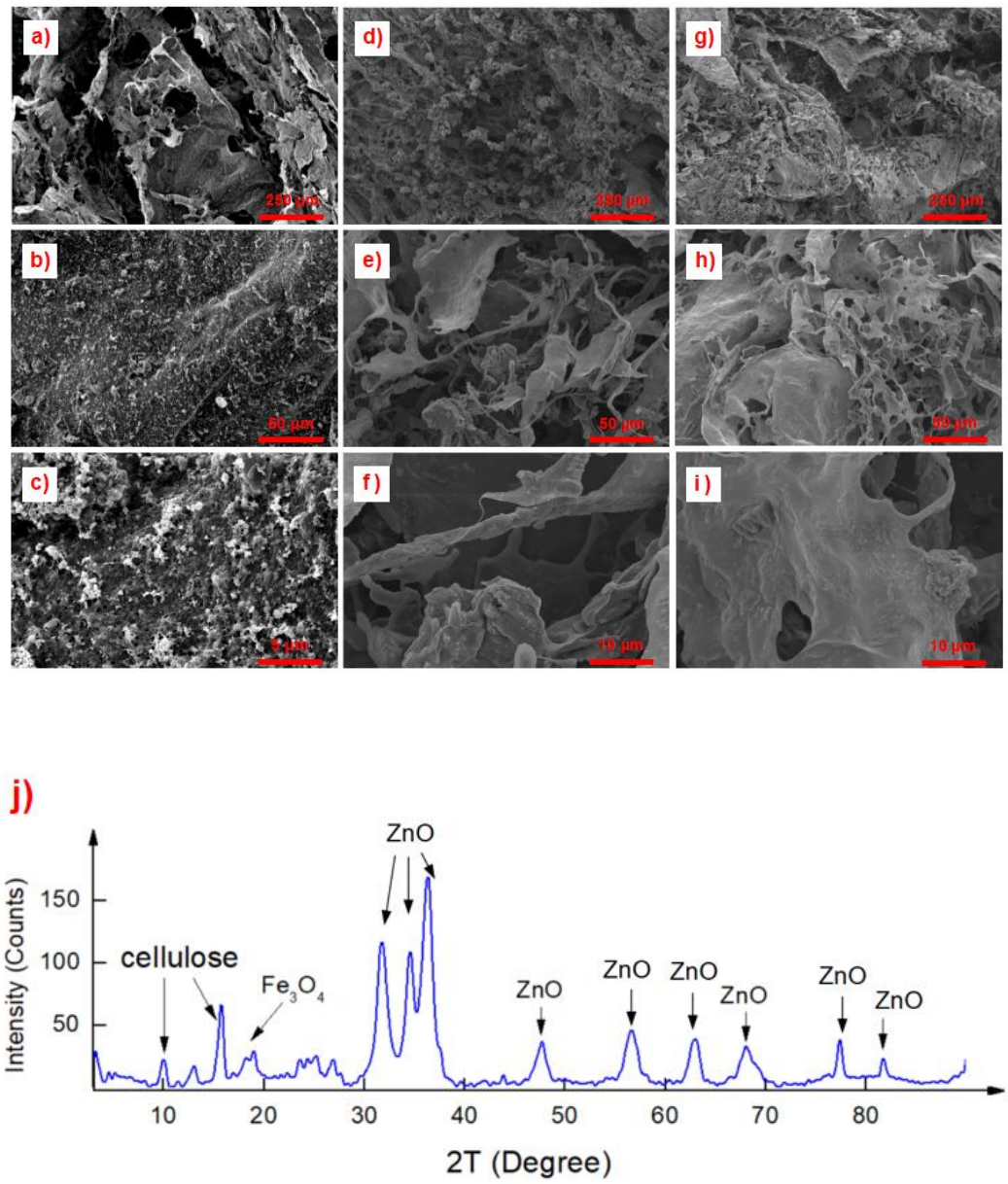

Figure 8 SEM images of CNF-SP aerogel surfaces: pristine CNF-SP aerogel ((a) to (c)), CNF-SP aerogel after UV irradiation without oil adsorption ((d) to (f)), CNF-SP aerogel after one UV cycling ((g) to (i)); and XRD pattern of CNF-SP aerogel (j).

The XRD pattern shown in Fig. 8(j) indicates that the CNF-SP aerogel has a complex crystal structure, combining the individual components. The three peaks at 2θ = 10.2, 12.4, and 16.8 were identified as cellulose (Vivian Abiaziem et al., 2019). The small peaks of Fe_3O_4 were observed at 2θ = 18 and 19 with relatively low intensity, indicating its presence and small content in the CNF-SP aerogel. The peaks at 2θ = 32.4, 34.6, 37.0 were observed, which was attributed to the crystal structure of ZnO, while the high content of ZnO led to 6 diffraction peaks when 2θ was >40 degrees (Zhang et al., 2015). Besides, the two small peaks at 2θ = 26.6 were identified as BN within the 3D substrate (Kumar et al., 2021). The peaks of cellulose and ZnO were sharp and well-defined with relatively high intensities, indicating their high crystallinity degree and large contents in the CNF-SP aerogel. This suggested that the CNF-COOH and nano-ZnO in the CNF-SP aerogel retained their structural integrity, though they were expected to form composites through strong carboxyl complexation (Hosseinaei et al., 2016). The presence of sharp and intense peaks suggests a high crystallinity index, which implies improved mechanical properties and stability of the aerogel. The retained structural integrity of CNF-COOH and nano-ZnO, despite composite formation through strong carboxyl complexation, further supports the high crystallinity of the aerogel (Hosseinaei et al., 2016).

As expected, the developed CNF-SP aerogel had the property of UV-induced switchable wettability, as shown in Fig. 9. Initially, the water contact angle (WCA) of the fresh CNF-SP aerogel was about 124°, indicating its strong hydrophobicity, which was beneficial to oil adsorption. After UV irradiation at 8 W with a wavelength of

365 nm for 40 min, the CNF-SP aerogel became hydrophilic and the WCA decreased to 31°. Subsequently, after another 40 min of exposure to visible light, the WCA returned to 124°, showing that the hydrophobicity of CNF-SP aerogel was recovered. The initial hydrophobicity of CNF-SP aerogel was due to the hydrophobic nature of SP on the surface of CNF-SP aerogel. Furthermore, the hydrophilic property of the carboxyl group on SP-COOH was eliminated after the carboxyl group bonded with nano-ZnO (Cui et al., 2022). After UV irradiation, the configuration of SP changed and hydrophilic phenolic hydroxyl groups were formed, transforming the surface property of CNF-SP aerogel from hydrophobic into hydrophilic. When exposed to visible light, spiropyran molecules form internal bonds, returning to their hydrophobic molecular structure (Wang et al., 2021a).

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In addition, the switchable wettability of the developed CNF-SP aerogel could also be induced through UV light irradiation at 285 nm and 305 nm, besides 365 nm. Previously, the UV wavelengths that could change SP conFigureuration were reported at 337 nm and 365 nm (Zhu et al., 2006; Vlassiouk et al., 2006). The broadened range of excitation bands in this research could be attributed to adding ZnO nanoparticles that could induce the excitation of conjugated organic compounds under UV irradiation (Beek et al., 2005). Also, adjacent conjugate regions were formed due to the generation of complexing among nano-ZnO, SP-COOH, and CNF-COOH during the fabrication process of CNF-SP aerogel, which resulted in a blue shift of the excitation band (Szymanski et al., 2005).

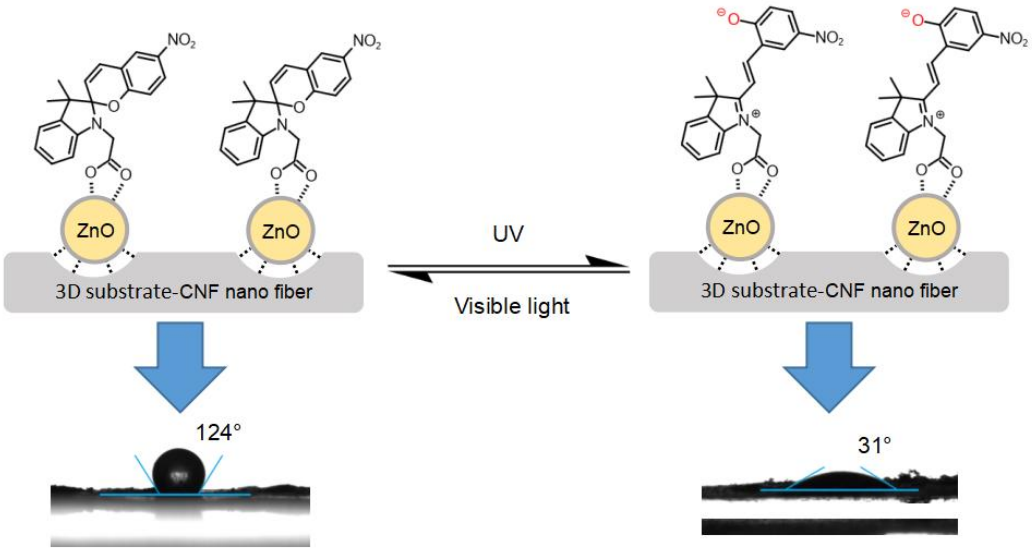


Figure 9 Nanostructure on CNF-SP aerogel surface and mechanism of the UV-induced switchable wettability.

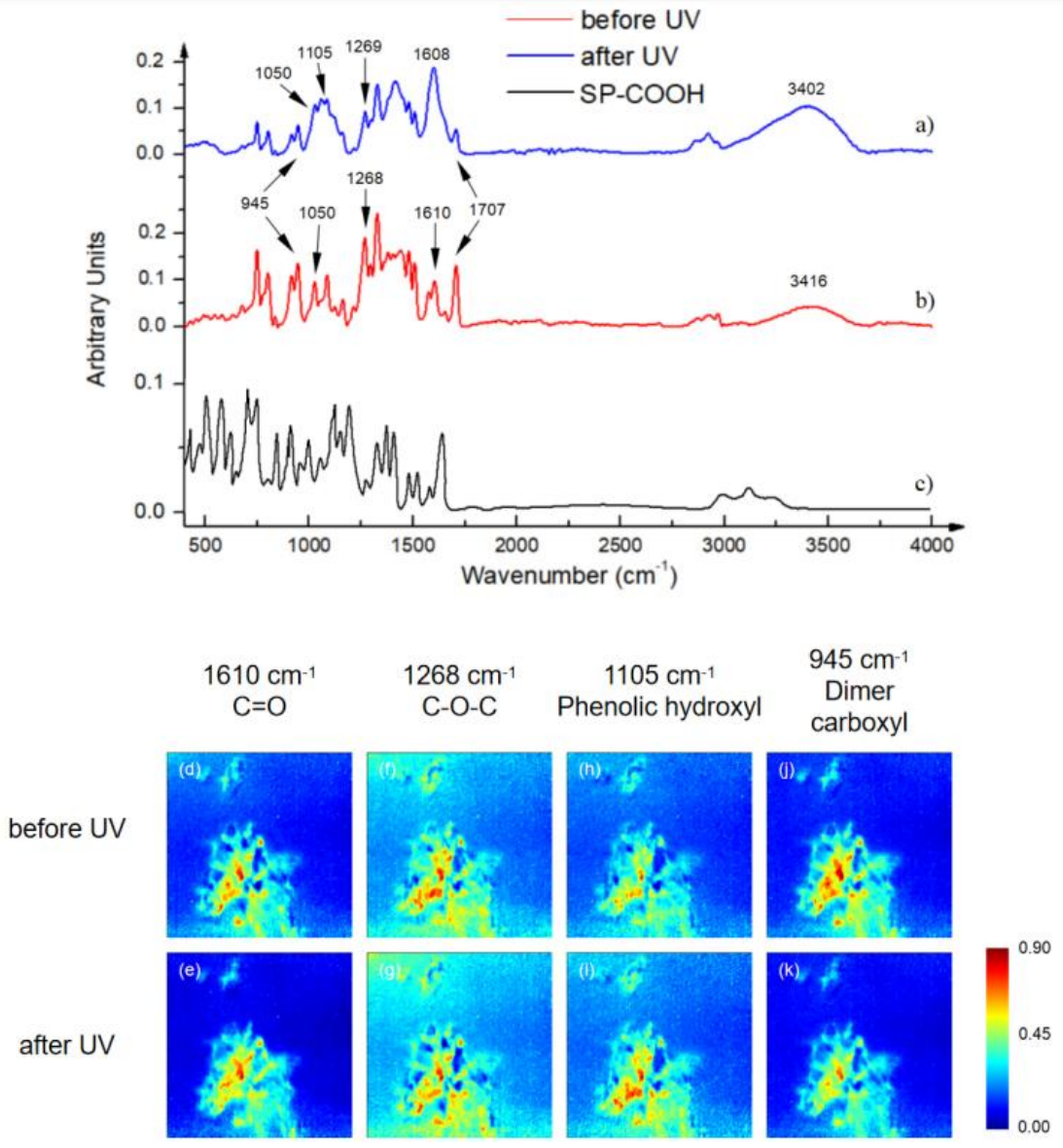


Figure 10 ATR-FTIR spectra of a) the CNF-SP aerogel before and b) after UV for 40 min, and c) SP-COOH. ATR-FTIR images of CNF-SP aerogel before and after UV irradiation at wavelength 1610 cm-1 ((d)-(e)); 1268-1269 cm-1 ((f)-(g)); 1105 cm-1 (h)-(i)); 945 cm-1 ((j)-(k)).

3.3.3 Mechanism of the UV-induced Switchable Wettability

To investigate the mechanism of the UV-induced switchable wettability further, the organic functional groups of the CNF-SP aerogels before and after UV irradiation were analyzed through ATR-FTIR spectroscopy and imaging. The spectra obtained from aerogel surfaces and SP-COOH were compared in Fig. 10. Spatial distributions of peak intensity at wavenumbers of 945 cm−1, 1105 cm−1, 1268 cm−1, and 1610 cm−1 on aerogel surfaces obtained from ATR-FTIR imaging were also summarized. Before UV irradiation, a small broad adsorption band at approximately 3400 cm−1 was observed (Fig. 10(b)), which could be attributed to the O—H stretching from carboxyl groups on the fresh CNF-SP aerogel surface. This adsorption band became much stronger after UV irradiation (Fig. 10(a)), indicating the existence of more hydroxyl groups on the UV-treated CNF-SP aerogel surface. Two peaks at 1590 and 1610 cm−1 were detected on the fresh CNF-SP aerogel surface, which corresponded to the C=O stretching of ketone and stretching vibration of benzene skeleton from SP-COOH, respectively (Wang et al., 2021b). An intensive peak replaced these two peaks at 1608 cm−1 after UV irradiation, which may be attributed to the formation of crystal water during UV irradiation (Yu et al., 2018). Besides, the peak intensity at 945 cm−1 decreased after UV irradiation due to carboxyl dimerization (Maréchal, 1987). Moreover, the C-O-C stretching of SP-COOH was identified from the peak at 1268 cm−1 (Miguez et al., 2019). After UV exposure, the peak intensity was significantly reduced and a new peak at 1105 cm−1 was found, which indicated that the C-O-C bond of SP-COOH on the

CNF-SP aerogel surface was broken during UV irradiation, leading to the formation of phenolic hydroxyl group (De Faria et al., 2021). Taken together, these results helped conclude that the formation of hydrophilic phenolic hydroxyl groups and the change of SP configuration during UV irradiation was the main mechanism to transform the surface of CNF-SP aerogel from hydrophobic into hydrophilic.

The spatial distribution changes of functional groups on CNF-SP aerogel surfaces before and after UV irradiation further supported such a conclusion. As shown in Figs. 6(e)-(f), after UV irradiation, more phenolic hydroxyl groups and fewer C-O-C bonds were detected on the aerogel surface. The comparison between Figs. 5(f)-(i) showed that the degree of color change was similar, while the transformation trend was the opposite, proving the emergence of the phenol hydroxyl group after C-O-C fracture. The dimerization of carboxyl was detected at 945 cm−1, shown in Figs. 5(j)-(k), with the decreased strength after UV exposure, suggesting the formation of acid anhydride, which was confirmed by the enhancement at 1608 cm−1 after UV irradiation. UV irradiation in a closed environment for a long time will increase the temperature and catalyze the reaction between dimer carboxylic acids to form anhydride (Pflieger et al., 2022). By comparing the FTIR spectra of SP-COOH and aerogel, the hydroxyl group stretch was observed from 3000 cm−1 to 3200 cm−1 and from 2700 cm−1 to 3000 cm−1, the molecular vibration frequency is reduced, which indicates the formation of chelating structures (Zhai et al., 2023). In addition, a sharp peak at 1707 cm−1 appeared due to the C═O stretching, indicating that the carboxyl groups bound to ZnO. At the same time, a blue shift of C—O and Zn—O tensile peaks

between 1000 cm−1 and 1150 cm−1 before and after UV irradiation was observed. These two phenomena indicated that SP-COOH, ZnO and CNF-COOH are closely bound together by forming chelating structures (Liao et al., 2013).

3.4 Performance of CNF-SP Aerogel for Oil/water Separation

3.4.1 The Effects of Water Environments

The optimized CNF-SP aerogel was then used for oil/water separation and its performance was comprehensively examined under multiple environmental conditions that may vary in different water bodies. Thus, the effects of water temperature, salinity and pH on the oil adsorption capacity of CNF-SP aerogel from immiscible oil/water mixture were investigated to provide support for its practical application. Figs. 6(a) and (b) presented the effects of water pH on the oil adsorption capacity and zeta potential of the CNF-SP aerogel, respectively. As shown in Fig. 11(a), the CNF-SP aerogel showed a satisfactory oil removal performance with 27–30 g/g of oil adsorption ratio during the pH range from 4 to 8. Especially, the oil adsorption capacity was more than 29 times its own weight under neutral and weak acidic conditions. However, when the pH value was larger than 8, the oil adsorption capacity decreased significantly. Such reduction of adsorption capacity with increasing pH value was also observed in some other cellulose aerogels (Atoufi et al., 2022), which could be attributed to the changes in structure stability and surface charge of cellulose aerogels under different pH levels. The structure of carboxyl chelates formed from CNF-COOH and nano-ZnO was reported to be stable under

neutral and acidic conditions, while it may be decomposed under alkaline conditions (Samira et al., 2021). According to Fig. 11(b), the zeta potential on the CNF-SP aerogel surface was larger than 35 mV between pH 4.0 and 6.2, while the zeta potential decreased to about 25 mV at pH 8 and less than 10 mV at pH 9, respectively. This indicated that the CNF-SP aerogel surface was stable and showed a strong positive charge under neutral and acidic conditions, although its stability was reduced under alkaline conditions.

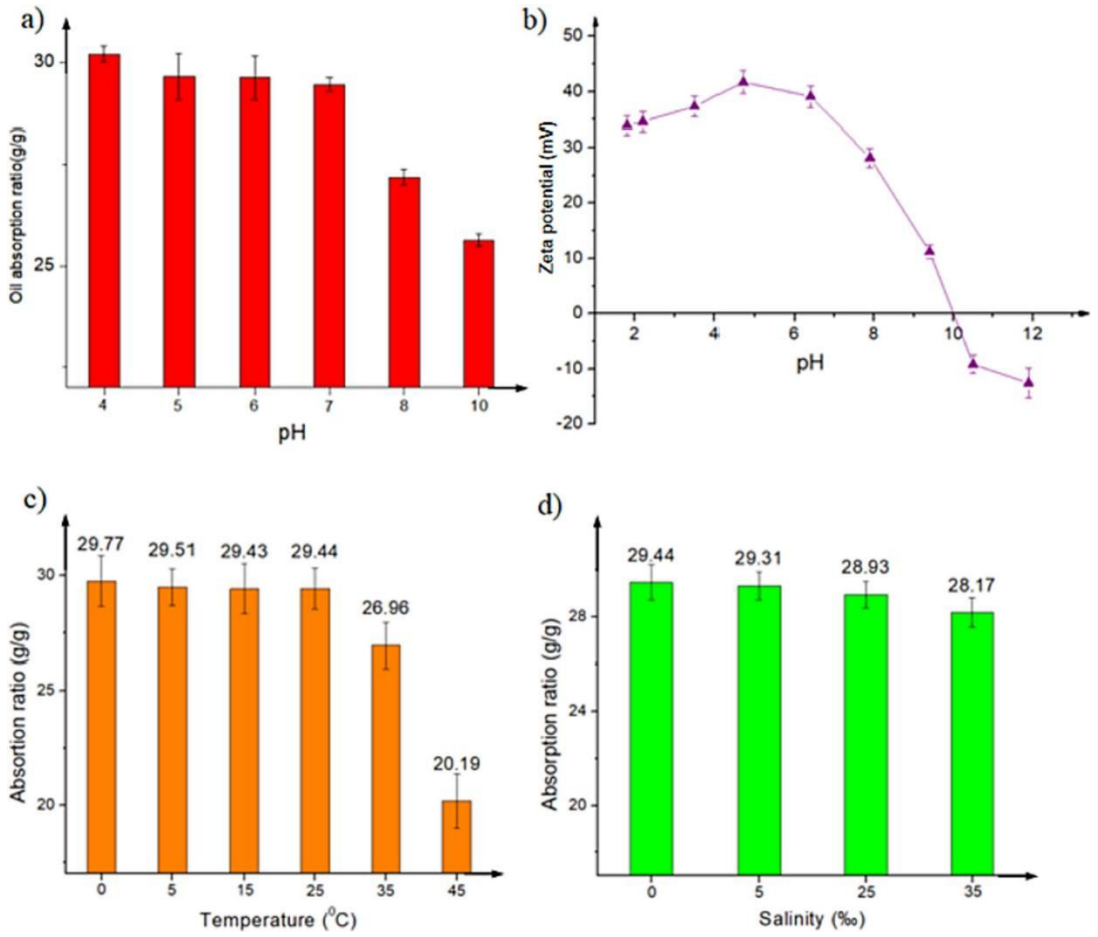


Figure 11 The effects of water pH on the oil adsorption ratio (a) and zeta potential (b) of the CNF-SP aerogel, oil adsorption ratio of the CNF-SP aerogel under different water temperature (c) and salinity (d) at pH = 7.

According to Fig. 11(c), the developed CNF-SP aerogel had an excellent oil removal performance at low or room temperature, which was reflected by the high oil adsorption ratios (29.44–29.77 g/g) under the temperature range of 0–25 °C. However, when the water temperature was increased to 35 °C and 45 °C, the oil adsorption ratio significantly declined to 26.96 and 20.19 g/g, respectively. This was because the CNF-COOH on aerogel lost its structural integrity at high temperatures (> 50 °C) (Wang et al., 2021a), negatively affecting the 3D structure of CNF-SP aerogel for oil adsorption. Hence, it may be necessary to keep the temperature lower than 45 °C during the transportation, storage, and application of CNF-SP aerogel. Fig. 11(d) shows the oil adsorption capacities of CNF-SP aerogel under the water salinity levels of 0 ‰, 5 ‰, 25 ‰, and 35 ‰. Such salinity levels were set based on the actual salinity in fresh, river estuary, offshore, and ocean water environments. It could be seen that the CNF-SP aerogel showed a stable and high oil adsorption efficiency, though the increase of salinity from 0 to 35 ‰ slightly decreased the oil adsorption ratio from 29.44 to 28.17 g/g. Such a decrease might be ascribed to the higher concentration of sodium chloride (NaCl) in higher salinity water. Chloride ions could pass through aerogel surface to form chlorine-containing complexes (e.g., ZnCl4O2) with nano-ZnO (Suzuki et al., 2010), and sodium ions could also combine with spiropyrans and CNF (Kumbhar et al., 2016, Chen et al., 2021). Thus, part of the adsorption sites for oil molecules on the CNF-SP aerogel were occupied, reducing its oil adsorption capacity (Natali et al., 2010).

Generally, the pH value is about 6–8 in freshwater (Yuan and DeGrandpre, 2008) and

7.5–8.4 in seawater (Marion et al., 2011), and the temperature in natural water environments is generally below 30 °C in all seasons (The US Geological Survey (USGS), 2018; Fondriest Environmental, Inc., 2014). Thus, the oil adsorption capacity of the developed CNF-SP aerogel could maintain at 28 ± 2 times its self-weight under most natural environmental conditions, which was at high level compared to other nanocellulose aerogels (i.e., 10–34 times higher than their self-weights) without switchable wettability (Li et al., 2020; Yang et al., 2018). Thus, the developed CNF-SP aerogel can be used for high-efficiency oil removal as an oil sorbent during oil spill response in most natural water bodies. Particularly, the excellent oil adsorption performance of the CNF-SP aerogel at low temperatures (0–5 °C) made it promising to remove light oil in winter season and cold regions.

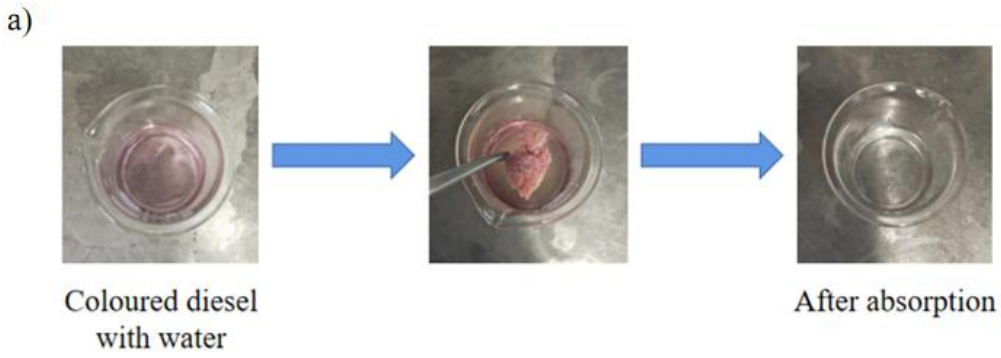
3.4.2 Oil/water Separation and Recycling Performances

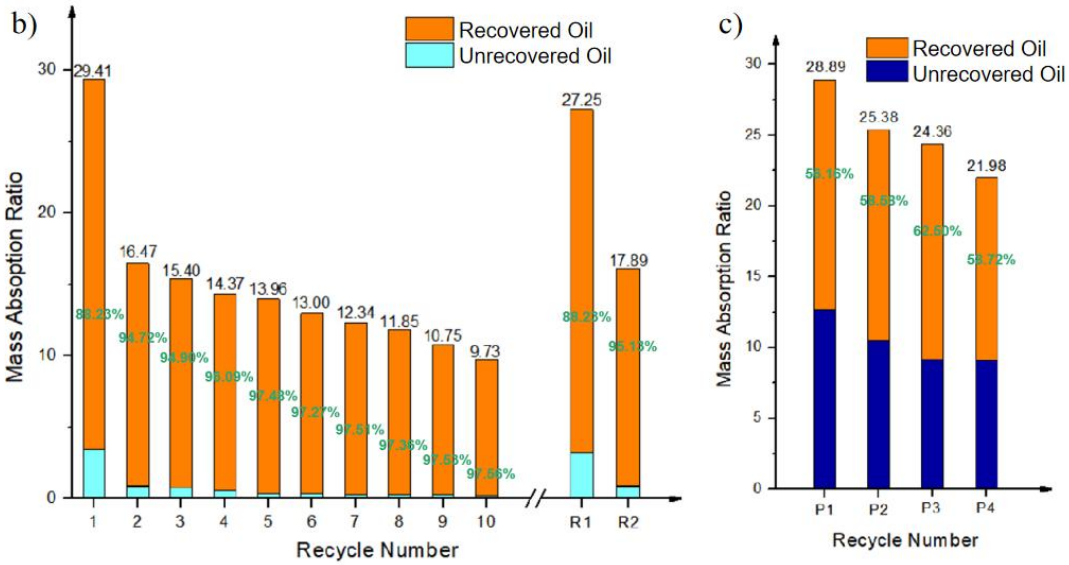
To evaluate the potential of the developed CNF-SP aerogel as oil sorbents, its performances of oil/water separation and recycling were assessed under neutral condition (pH = 7) at room temperature. As shown in Fig. 12(a), all floating diesel oil (350 mg) in the beaker could be quickly adsorbed by the CNF-SP aerogel (37 mg) within 5 s. The adsorbed liquid was collected, and its water content was tested by UV spectrophotometry. The results in Fig. S1 showed that the water content was below the detection limit. Thus, the adsorbed liquid could be considered as pure oil. Besides, the CNF-SP aerogel could be easily retrieved from water using a magnet due to the existence of ferric oxide within its substrate (Fig. S3).

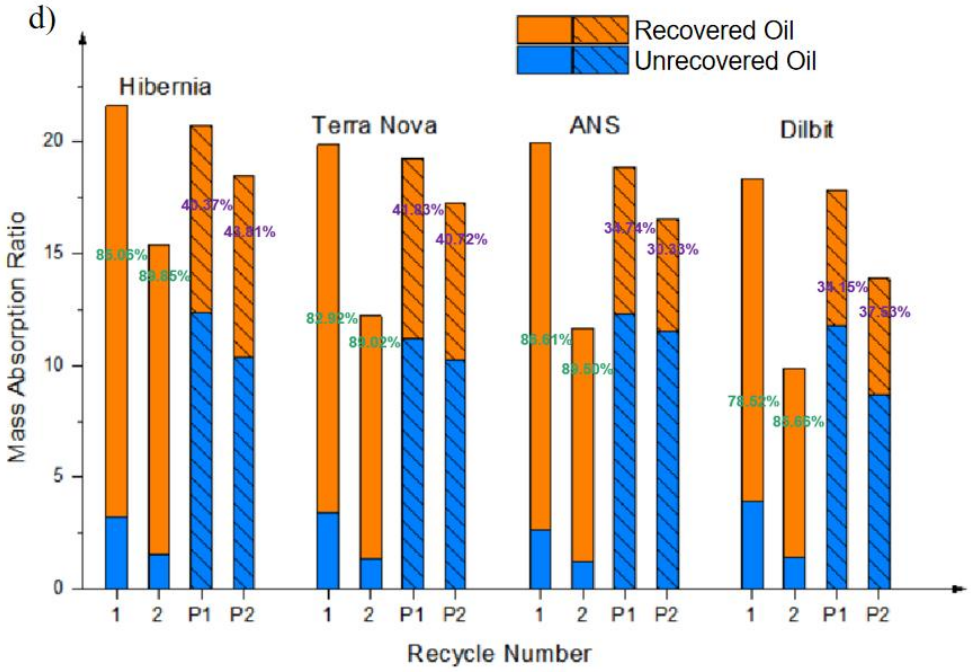
Furthermore, the adsorbed oil could be recovered, and the CNF-SP aerogel could be reused through UV irradiation. As shown in Fig. 12(b), in the first usage cycle, the OAR was 29.41 and 88.23% of the adsorbed diesel oil could be recovered after exposure to UV irradiation for 40 min. Then the CNF-SP aerogel could be reused, though the OAR decreased to 16.47 in the second cycle, while 94.72% of adsorbed oil could be recovered. The decreased OAR could be attributed to the partial damage of the microporous structure formed between cellulose and substrate under UV irradiation (Song et al., 2021), also shown in SEM images. It was found that such damage only happened in the first UV irradiation, because the OARs of CNF-SP aerogel did not decrease significantly in the subsequent cycles of usage, and the oil recovery rates were stable and high in the range of 94.9–97.5%. Compared with UV irradiation, the OAR did not decrease much by squeezing the used CNF-SP aerogel to recover oil. However, oil recovery rates were much lower than that with UV irradiation, which was only 56.16%, 58.58%, 62.50% and 58.72% in the four cycles, respectively (Fig. 12(b)). In addition, the used CNF-SP aerogel could be regenerated to mitigate waste production. After regeneration, the microporous structure of CNF-SP aerogel could be restored, thus, the oil adsorption capacity could reach the initial level.

Finally, the performances of the developed CNF-SP aerogel for the separation and recovery of crude oils were also investigated. Four crude oils (Hibernia, Terra Nova, ANS and Dilbit) were tested, and the results are shown in Fig. 12(c). Compared to diesel, the adsorption capacities of CNF-SP aerogel for crude oils were lower due to

their high viscosity, which was about 20 times its own weight. The differences in adsorption capacities among different oils were mainly caused by the difference of viscosity (Nguyen et al., 2013). The higher the viscosity, the fewer small molecules in crude oil that are conducive to adsorption and enter the aerogel, and the more unfavorable they are to adsorption and recovery (Schneider and Gerber, 2014). Thus, the viscosity of Hibernia is the lowest and the viscosity of Dilbit is the highest, leading to the largest and smallest OARs, respectively. Similar to the adsorption and recovery of diesel, the oil adsorption capacity of CNF-SP aerogel decreased after UV irradiation. Still, the high oil recovery rates for all crude oils were maintained. In contrast, the oil recovery rates through squeezing and pressing were much lower. The unrecovered oil within the used CNF-SP aerogel may make the aerogel unsuitable for regeneration. Thus, it would be more effective and sustainable to use UV irradiation for oil recovery with the developed CNF-SP aerogel.


a)
Coloured diesel with water
After absorption


b)
Recovered Oil
Unrecovered Oil
Mass Absorption Ratio
Recycle Number
29.41
16.47
15.40
14.37
13.96
13.00
12.34
11.85
10.75
9.73
27.25
17.89
c)
Recovered Oil
Unrecovered Oil
Mass Absorption Ratio
Recycle Number
28.89
25.38
24.36
21.98
P1
P2
P3
P4



*R means the aerogel has been regenerated after 10 cycles; P means the precipitated oil is obtained only by pressing and squeezing the aerogel without UV.

Figure 12 a) adsorption performance of the CNF-SP aerogel on diesel oil; recycling performance of the CNF-SP aerogel on diesel adsorption b) with UV irradiation and c) by squeezing without UV; d) adsorption and recycling performances on f the CNF-SP aerogel crude oils.

3.5 Summary

In summary, this research successfully developed and optimized a CNF-SP aerogel with UV-induced switchable wettability for oil/water separation in oil spill cleanup. Due to the UV switchable structure of spiropyranol and the effective shielding of the hydrophilic groups on cellulose, the developed CNF-SP aerogel initially showed strong hydrophobicity. Such hydrophobicity could be switched to hydrophilicity after UV irradiation, which could be restored after visible light irradiation. The CNF-SP aerogel had a 3D porous structure and initial hydrophobic properties favorable for adsorbing oil. Through material concentration optimization, the hydrophilic groups of cellulose were shielded inside the CNF-SP aerogel and chelated with zinc oxide, leading to strong hydrophobicity of the CNF-SP aerogel surface. The CNF-SP aerogel showed great oil adsorption efficiency (27–30 g/g of oil adsorption ratio) through a simple process under most natural environments, particularly at low temperatures (0–5 °C). In addition, the developed CNF-SP was reusable and renewable, and its reusability was significantly improved through UV irradiation due to its UV-induced switchable wettability. Overall, the developed CNF-SP aerogel exhibited high oil adsorption capacity and could be used to separate and recover various oils from water, demonstrating its great application as an oil sorbent in oil spill responses.

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

The research and development of switchable biomaterials represents a significant advancement in the field of environmental remediation, particularly for wastewater treatment. These materials, which include cellulose, biochar, chitosan, and other natural polymers, offer unique advantages such as responsiveness to external stimuli, recyclability, and environmental sustainability. By harnessing the intrinsic properties of these materials and optimizing them through chemical modifications and innovative processing techniques, it is possible to enhance their performance in removing various contaminants, including heavy metals, organic pollutants, and oils, from water bodies.

By delivering a comprehensive literature review, the thesis work demonstrates that switchable biomaterials are not only effective in contaminant removal but also in overcoming the limitations of traditional water treatment methods. For example, the integration of switchable functionalities into biomaterials like cellulose and biochar has led to improved adsorption capacities, enhanced selectivity, and greater stability under varying environmental conditions. Additionally, the ability to recover and reuse these materials further underscores their potential as cost-effective and sustainable solutions for large-scale water treatment applications. However, while significant progress has been made, challenges remain in the widespread application of these materials. Issues such as variability in raw material sources, the complexity of synthesis processes, and the need for standardization in production methods must be

addressed to ensure the consistent performance of switchable biomaterials. Future research should focus on developing more robust and versatile materials that can withstand harsh environmental conditions, exploring hybrid materials that combine the strengths of different biomaterials, and optimizing the synthesis processes to reduce costs and environmental impacts.

By developing a spiropyran-assisted cellulose nanofiber (CNF-SP) aerogel with UV-induced switchable wettability and evaluating its performance as an effective sorbent for oil spill cleanup, this thesis addresses the challenges of oil spill remediation and provides a promising solution for managing wastewater generated during such events. The CNF-SP aerogel, with its UV-responsive switchable wettability, exhibits remarkable versatility by transitioning between hydrophobic and hydrophilic states under UV and visible light irradiation for 40 min, respectively. This performance allows it to be recycled more than 9 times. CNF-SP areogel adapts for diverse environmental conditions, particularly in low-temperature scenarios. Additionally, the aerogel's 3D porous structure and optimized material composition ensure high oil adsorption capacity, achieving an oil adsorption ratio of 27–30 g/g. Its reusability and renewable nature, combined with efficient recovery of adsorbed oil, make it a sustainable and practical option for mitigating the environmental impact of oil spills.

4.2 Research Contributions and Recommendations

The research contributions of the thesis work include:

(1) A first thorough review of switchable biomaterials for wastewater treatment with the key findings including (i) switchable biomaterials offer sustainable and cost-effective solutions for wastewater treatment, (ii) the stimulus-responsive properties of switchable biomaterials significantly enhance material recyclability, (iii) switchable cellulose is promising for large-scale practical applications, and (iv) most of the current switchable biomaterials remain challenges in mechanical strength.

(2) The development of a new spiropyran-assisted cellulose aerogel (CNF-SP) aerogel with the key findings including (i) CNF-SP demonstrated reliable UV-induced switchable wettability, (ii) CNF-SP achieved high-performance oil adsorption recycling up to 9 times, and (iii) CNF-SP could be applied under various environmental conditions including the cold regions.

Future research should focus on optimizing the scale production of switchable biomaterials for water treatment, environmental impact assessment, technology integration, and interdisciplinary collaboration. On the production side, continuous flow processes such as roll-to-roll manufacturing can be explored for efficient, controlled large-scale synthesis, while non-chromatographic purification techniques such as high salt-out methods can be used to simplify production processes and maintain material properties. For environmental sustainability, the biodegradability of water-soluble polymers under different conditions should be systematically evaluated, and the use of bioprecursors such as agricultural waste to synthesize photocatalysts should be explored to reduce the environmental burden. In addition, combining

switchable biomaterials with nanofiltration membranes or advanced oxidation processes, such as photocatalysis, can improve contaminant removal efficiency and expand applications. To accelerate the adoption of technologies, materials scientists, environmental engineers, and industry practitioners should be encouraged to establish interdisciplinary collaboration teams and strengthen communication with policy makers to ensure that new materials comply with environmental regulations and promote the development of sustainable water treatment technologies.

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APPENDIXS

- Comparison with Conventional Wastewater Treatment Methods

Switchable biomaterials exhibit high adsorption capacities (11.6 – 106 g/g) compared to activated carbon (0.5 – 3.0 g/g) (Zhou et al., 2024) and offer selective removal of dyes, oils, and heavy metals with efficiencies often exceeding 95%. However, unlike conventional wastewater treatment technologies such as chemical coagulation, activated carbon adsorption, and membrane filtration capable of treating multiple pollutants simultaneously, switchable biomaterials are primarily optimized for specific contaminants (Ma et al., 2021). Their main advantage lies in their rapid adsorption-desorption cycles, reducing waste generation and lowering maintenance costs due to easy regeneration (Wang et al., 2021).

From an environmental perspective, conventional methods generate hazardous by-products, such as sludge containing residual heavy metals and chemicals (Yuan et al., 2011), whereas switchable biomaterials allow controlled desorption and recyclability, minimizing secondary pollution (Crini & Lichtfouse, 2018). Cost-wise, traditional systems benefit from established infrastructure but incur ongoing operational costs for chemical dosing and sludge disposal. In contrast, switchable biomaterials, despite higher initial material processing costs, offer long-term savings through repeated use and lower waste management requirements (Čuček et al., 2015).

Scaling up switchable biomaterials requires addressing raw material sourcing (e.g.,

cellulose, chitosan, biochar) and ensuring consistency in fabrication (Matveeva & Bronstein, 2022). Current limitations include variability in raw material quality and challenges in integrating these materials into existing industrial facilities designed for continuous operation. However, their versatility, such as incorporation into dedicated adsorption columns, emergency response systems or hybrid treatment setups, suggests promising industrial applications (Toivonen et al., 2015).

- Analysis of the treatment efficiencies

Switchable biomaterials have demonstrated significant potential in wastewater treatment by offering tailored adsorption capabilities for various contaminants, including dyes, oils, and heavy metals. The compiled performance summarized in Table S1 highlights the diversity of these materials in terms of their switching mechanisms, adsorption capacities, and recyclability. Among them, switchable cellulose-based materials stand out due to their extensive modification potential and cost-effectiveness (Gao et al., 2022). Their pH- and temperature-responsive properties allow for efficient oil-water separation and dye adsorption, with certain cellulose aerogels achieving removal efficiencies above 99%. However, their mechanical stability in harsh wastewater environments remains a challenge, requiring further optimization in composite material design (Gao et al., 2022).

Switchable chitosan-based materials exhibit high adsorption capacities for oils and dyes, particularly in emulsified systems, due to their inherent hydrophilicity and surface charge modifications. The addition of CO_2-switchable functionalities

enhances their usability, enabling controlled pollutant recovery and material recyclability. Magnetic chitosan aerogels, for example, have shown excellent oil absorption capacities, with retention of efficiency over multiple cycles. Despite their versatility, the relatively high cost of chitosan extraction compared to cellulose may limit large-scale applications unless production efficiencies improve (Yang et al., 2016).

Switchable biochar and resin materials offer high adsorption capacities, particularly for heavy metals and organic pollutants (Han et al., 2024b). Biochar-based composites with Fe-N functionalization or photocatalytic TiO_2 coatings have demonstrated strong potential for heavy metal removal, achieving Pb^{2+} adsorption capacities above 100 mg/g. The switchable redox-active sites in Fe-modified biochar further enable pollutant degradation through advanced oxidation processes (Liu et al., 2022). However, variability in biochar synthesis conditions can lead to inconsistencies in adsorption performance, necessitating standardization in production methods. On the other hand, switchable resins, including electro-responsive and chelating resins, provide selective heavy metal adsorption and controlled desorption capabilities. These materials are particularly advantageous in applications requiring fine-tuned contaminant selectivity, though their scalability depends on cost-effective production (Poplewskaet al., 2014).

Other biomaterials, such as rubber and crude fibers, have also shown promising performance for selective adsorption. pH-switchable modified fibers demonstrate

effective removal of heavy metals and dyes, with reusability over multiple cycles (Mohammed et al., 2022). However, their adsorption efficiencies tend to be slightly lower compared to biochar and cellulose composites, making them more suitable for niche applications or as supplementary materials in filtration systems . Similarly, rubber-based materials, while exhibiting responsive adsorption behaviors, still face challenges related to long-term stability and large-scale deployment (Ma et al., 2021).

Table S1. Performance Summary and Comparison for Contaminant Removal of Switchable Biomaterials

Biomaterial	Product	Contaminant Type	Switching Mechanism	Treatment Performance	Recyclability	Reference
Switchable Biochar	TiO_2/pomelo-peel-derived biochar	Antibiotic degradation, Heavy Metals	UV-responsive	92% removal of tetracycline, Absorption rate 95 mg/g (Pb), 76 mg/g (Cd)	High (>10 cycles)	Zhang et al., 2023
Switchable Biochar	TiO_2/biochar composite	Antibiotic degradation	UV-responsive	88% removal efficiency for 4-chlorophenol	High (>10 cycles)	Gao et al., 2019
Switchable Cellulose	Cellulose nanocrystal switchable gel	Dyes	CO_2-responsive	Absorption rate 598.8 mg/g (MB), 621.1 mg/g (NGB), 892.9 mg/g (MO)	High (>20 cycles, >87.7% retention)	Yang et al., 2021
Switchable Cellulose	Cellulose-based material (cellulose-g-PNIPAAm)	Dyes, Heavy Metals	CO_2-responsive	99.02% dye degradation	High (>10 cycles)	Li et al., 2022
Switchable Cellulose	Cellulose-based materials	Dyes, Heavy Metals	pH-sensitive Photocatalytic	99.8% MB degradation, 99.7% RhB degradation	Moderate (>5 cycles)	Wen et al., 2020
Switchable Biochar	Pharmaceutical sludge biochar (PSBC)	Heavy Metals, Organic Pollutants	Chemical activation	85% removal efficiency for 4-chlorophenol, Absorption rate 112 mg/g (Pb), 89 mg/g (Cd)	High (>10 cycles)	Liang et al., 2023
Switchable Cellulose	Cellulose-based Mecoprop (MCPP) membrane	Heavy Metals, Organic Pollutants	CO_2-responsive	Separation efficiency >99.4%	High (>10 cycles)	Li et al., 2019a
Switchable Cellulose	Cellulose-based Membrane	Heavy Metals, Organic Pollutants	Double-sided	Separation efficiency 99.4%	High (>10 cycles)	Lv et al., 2019

Switchable Cellulose	Cellulose-based membrane	Heavy Metals, Organic Pollutants	UV-responsive	Separation efficiency 95%	High (>10 cycles)	Li et al., 2022
Switchable Cellulose	Charge-switchable Chitosan Nanocomposite	Heavy Metals, Organic Pollutants	CO_2-humidity triggers: flowing solution to solid gels	Separation efficiency ~70%	High (>10 cycles)	Ali et al., 2020
Switchable Cellulose	CNCs (Cellulose nanocrystals) pickering emulsifiers	Heavy Metals, Organic Pollutants	CO_2-responsive: hydrophobic to hydrophilic	Emulsion >99%	High (>10 cycles)	Karatum et al., 2023
Switchable Cellulose	CNFs (Cellulose nanofibers) aerogels	Heavy Metals, Organic Pollutants	Thermo-responsive: hydrophobic-oleophilic to underwater superoleophobic	Separation efficiency >99.4%	High (>10 cycles)	Chen et al., 2023
Switchable Cellulose	CNFs Aerogels	Heavy Oils	pH-responsive:	Separation efficiency 99.95%	High (>10 cycles)	Li et al., 2018
Switchable Cellulose	CO_2-responsive Cellulose Nanofibril Aerogels	Oils	Thermo- and pH-responsive: superhydrophilic to underwater superoleophobic	Absorption rate 12 g/g	High (>10 cycles)	Zhao et al., 2017
Switchable Cellulose	CO_2-responsive Chitosan Aerogels	Oils	Thermo-responsive: hydrophobic-oleophilic to underwater superoleophobic	Absorption rate 9.74 g/g	Moderate (>5 cycles)	Chen et al., 2018
Switchable Cellulose	CO_2-switchable Chitosan	Oils	UV-responsive: hydrophobic to hydrophilic	Absorption rate 11.85-29.41 g/g	Moderate (>5 cycles)	Wang et al., 2024
Switchable Cellulose	Fe-N Switchable Biochar	Oils	pH-responsive: hydrophilic to hydrophobic	Separation efficiency 97.6%	High (>10 cycles)	Cheng et al., 2019
Switchable Cellulose	Janus cellulose membrane (JCM)	Oils	CO_2-responsive: reversible emulsification/demulsification	Separation efficiency >99.96%	High (>10 cycles)	Li et al., 2019a

Switchable Cellulose	Janus Hybrid Nanocellulose Aerogel	Oils	Double-sided material	Absorption rate 52-57 g/g	High (>10 cycles)	Agaba et al., 2021
Switchable Cellulose	Janus hybrid nanocellulose aerogel	Oils	Double-sided material	Separation efficiency >96%	High (>10 cycles)	Lv et al., 2019
Switchable Cellulose	Janus PLA Fibrous Membrane	Oils	UV/visible light-responsive: hydrophilic to hydrophobic	Separation efficiency >95%	High (>10 cycles)	Li et al., 2022
Switchable Cellulose	Kapok Fiber Membrane (ZnO/PDA)	Oils	Temperature-sensitive wettability switch: from hydrophilic to hydrophobic	Separation efficiency >99.4%	High (>10 cycles)	Chen et al., 2023
Switchable Cellulose	Modified Flax Fiber	Oils	CO_2-responsive: hydrophobic to hydrophilic	O/W emulsion >99%	High (>10 cycles)	Glasing et al., 2018
Switchable Cellulose	Modified Hemp Fiber	Oils	pH-responsive: hydrophilic to hydrophobic (and vice versa)	Absorption rate 68 g/g	High (>10 cycles)	Gao et al., 2022
Switchable Crude Fiber	pH-responsive Resin	Oils	pH-responsive	Separation efficiency 95% (dyes), 90% (Cr)	Moderate (>5 cycles)	Akl et al., 2021
Switchable Crude Fiber	pH-switchable Jute Fiber	Oils	pH-responsive	Separation efficiency 92% (oils)	Moderate (>5 cycles)	Akl et al., 2021
Switchable Crude Fiber	pH-switchable Rubber	Oils	Solvent-responsive	Separation efficiency 92% (Heavy Oils)	High (>5 cycles)	Akl et al., 2021
Switchable Resin	Thermo- and pH-responsive cellulose-based aerogels	Oils	pH-responsive	Separation efficiency 93% (Cd), 89% (Pb)	High (>5 cycles)	Dai et al., 2008
Switchable Resin	TiO_2/Biochar Composite	Oils	Temperature	Temperature-dependent	Moderate (5 cycles)	Dai et al., 2008
Switchable Rubber	UV induced spiropyrans-assisted	Oils	pH-responsive	Separation efficiency 90% (Pb), 85% (Cd)	Moderate (5 cycles)	Lin et al., 2021

	aerogels					
Switchable Chitosan	Carboxymethyl Chitosan (CMChi)	Oils	pH-responsive	300 mg oil/mg CMChi (pH 7-10)	Moderate (4-10 cycles)	Kalliola et al., 2018
Switchable Chitosan	Hydrophobically modified CMChi (h-CMChi)	Oils	pH-responsive	Absorption rate 1300 mg oil/mg h-CMChi (pH 7-10)	Moderate (4-10 cycles)	Kalliola et al., 2018
Switchable Chitosan	Chitosan-g-PDMAEMA (Chi-g-PDMAEMA)	Oils	CO_2/N_2-responsive	Separation efficiency 99%	High (>4 cycles)	Ren et al., 2018
Switchable Chitosan	Hydrophobic Magnetic Chitosan Aerogel	Oils	CO_2-responsive & Magnetic	Absorption rate 43.8 g oil/g aerogel	High (>10 cycles)	Yin et al., 2020
Switchable Chitosan	Carboxylated Carbon Nanotube/Chitosan Aerogel (CCNT/CA)	Oils	Temperature-responsive	Absorption rate 23.8 - 53 g/g	High (>15 cycles)	Fan et al., 2022
Switchable PLA	Janus PLA Fibrous Membrane	Oil-Water Emulsification	Asymmetric Wettability	98% separation efficiency	Moderate (>5 cycles)	Qin et al., 2020
Switchable Protein-Based Material	E_2LC_2-Stabilized Pickering Emulsions	Oil-Water Emulsification	pH-responsive	Separation efficiency >99%	Moderate (>5 cycles)	Sarker et al., 2017
Switchable Chitosan	CS-g-PNNPAM (Chitosan grafted with PNIPAAm)	Oil-Water Separation	Thermo-responsive	Absorption rate >90% TC & Cu (II) removal	Moderate(>5 cycles)	Ren et al., 2017
Switchable Chitosan	DA-CMCS@Zn^{2+}@Heterocycles	Tetracycline and Copper Removal	pH-responsive	Separation efficiency >99%	High (>10 cycles)	Liang et al., 2023

- Synthesis of biomaterials

There are a variety of methods for synthesizing switchable biomaterials, and the choice depends on the target application and the desired material properties. Cellulose aerogels, for example, can be prepared by solution-regeneration, in which cellulose is dissolved in an appropriate solvent, and a high porosity aerogel is obtained through gelation, solvent exchange, and drying steps. The self-assembly property of nanocellulose in water suspension can also be used to prepare lightweight porous cellulose aerogels by freeze-drying or supercritical drying (Long et al., 2018). The preparation of chitosan aerogel includes the solution-gelation method and the cross-linking method. The former is obtained by dissolving chitosan in an acidic solution, inducing gelation and drying. In the latter, a crosslinking agent is added to the chitosan solution to form a crosslinking network structure, and then the aerogel is prepared by drying (Rizal et al., 2021). The biochar generation can be achieved using pyrolysis or hydrothermal method. Pyrolysis is to pyrolyze biomass in an inert atmosphere to produce biochar. The hydrothermal method is to treat biomass under high temperatures and high-pressure hydrothermal conditions to produce biochar with a high oxygen-containing functional group (Liu et al., 2022). The synthesis of switching resin and fiber can be processed using copolymerization or post-functionalization methods. The copolymerization method is to copolymerize functional monomers with other monomers to form polymers with responsive functional groups (Jin et al., 2015). The principle of post-functionalization is to

synthesize the base polymer first and then introduce responsive groups into its structure through chemical reactions to give it the ability to respond to external stimuli (Long et al., 2018). These synthetic routes provide a variety of options for the preparation of switchable biomaterials, which can be optimized and adapted to specific application needs.

- Structure Optimization for Environmental Stimuli

Switchable biomaterials exhibit reversible responsiveness to external stimuli such as pH, temperature, and CO_2, making them highly valuable for wastewater treatment applications. The performance of these materials depends on precise structural optimization at both macro- and micro-levels, which determines their stability, selectivity, and switching efficiency (Li et al., 2019).

At the macrostructural level, materials can be engineered with hierarchical porosity, multilayered interfaces, and directional wettability to enhance their responsiveness. For example, Janus membranes with asymmetric wetting properties allow for controlled oil-water separation by presenting a hydrophilic surface on one side and a hydrophobic surface on the other. This structure can be achieved through surface energy tuning and selective polymer grafting, enabling an immediate switch in interfacial properties upon environmental stimuli. Similarly, aerogels and foams with tailored pore sizes facilitate efficient diffusion of environmental triggers like CO_2, improving their actuation speed and adsorption efficiency (Lv et al., 2019).

At the microchemical level, the incorporation of functional groups plays a pivotal role in enabling reversible interactions. The introduction of carboxyl (-COOH), amine ($-NH_2$), and thiol (-SH) groups increases the ionization potential of biomaterials, allowing them to change hydrophobicity or charge state under pH variation. For instance, the modification of cellulose with polyoxometalates (POMs) significantly enhances its switching properties for oxidative catalysis, as seen in PTA-modified cellulose aerogels, which transition from a soluble state to a stable porous network upon surface functionalization. Such modifications optimize adsorption kinetics and reusability, making them effective for repeated contaminant capture and release cycles (Hokkanen & Sillanpää et al, 2016).

Additionally, thermal-responsive modifications in biomaterials such as PLA- and chitosan-based aerogels involve the incorporation of thermosensitive polymers like PNIPAAm (poly-N-isopropylacrylamide), which exhibit LCST (lower critical solution temperature) behavior (Musarurwa & Tavengwa, 2022). These materials undergo a phase transition from hydrophilic to hydrophobic above a specific temperature, enabling controllable contaminant adsorption and desorption. Similarly, CO_2-responsive modifications utilizing tertiary amine-functionalized chitosan membranes allow for CO_2-induced charge switching, which enhances their efficiency in pollutant removal by dynamically altering their electrostatic interactions (Fan et al., 2022).

By integrating both macrostructural design and microchemical modification strategies,

switchable biomaterials can achieve enhanced reusability, selectivity, and operational efficiency in real-world wastewater treatment applications. Future research should focus on optimizing hierarchical structuring and expanding the range of functional group modifications to further improve the material adaptability and sustainability in diverse environmental conditions (Yang et al., 2017).

- Energy demands of these materials versus traditional wastewater treatment techniques

Traditional wastewater treatment methods, such as activated sludge processes, are known for their significant energy consumption (Crini & Lichtfouse, 2018). Specific energy consumption for these processes ranges between 0.5 and 2.0 kWh per cubic meter of treated water, with aeration equipment being the major energy consumers. Other significant contributors to energy usage include mixing and pumping operations. For instance, low-energy-footprint technologies like trickling filters and aerated lagoons require approximately 0.18–0.42 kWh/m³ and 0.09–0.29 kWh/m³, respectively (Ghimire et al., 2021).

Switchable biomaterials, such as pH-responsive cellulose-based aerogels and CO_2-switchable chitosan composites, offer a more energy-efficient alternative due to their passive operation modes (Gao et al., 2022). These materials leverage environmental stimuli to modulate their adsorption properties without the need for continuous energy input. For example, a CO_2-responsive cellulose nanofibril aerogel can achieve high dye adsorption efficiency through reversible interactions facilitated

by simple pH adjustments, eliminating the need for mechanical aeration or intensive mixing (Li et al., 2019). While the direct energy consumption of deploying switchable biomaterials is inherently low, it is essential to consider the energy requirements associated with their synthesis and regeneration. Processes such as chemical modification, drying, and thermal treatments during material preparation can contribute to the overall energy footprint. However, advancements in green chemistry and process optimization are progressively reducing these energy demands (Pereira & Vicente, 2010).

When comparing the energy demands of traditional wastewater treatment techniques to those employing switchable biomaterials, it is evident that the latter offers a more energy-efficient approach during the operational phase. Traditional methods rely heavily on mechanical and electrical energy inputs to maintain treatment efficacy, whereas switchable biomaterials utilize intrinsic material properties activated by environmental stimuli, thereby minimizing external energy requirements (Crini & Lichtfouse, 2018). Moreover, the regeneration of switchable biomaterials often involves mild conditions, such as slight pH shifts or exposure to ambient gases like CO_2, which are less energy-intensive compared to the aeration and pumping processes in conventional treatments (Gao et al., 2022).

- Characterization of Switchable Biomaterials

To analyze the structural changes and switchable features of biomaterials, various advanced characterization techniques were employed. Contact angle measurements

were used to evaluate surface wettability, quantifying hydrophilic or hydrophobic transitions under different conditions (Huhtamäki et al., 2018). Fourier Transform Infrared Spectroscopy (FTIR) enabled the identification of functional groups and chemical modifications, while Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) provided insights into surface morphology and internal microstructural changes, respectively (Inkson, 2016). X-ray Photoelectron Spectroscopy (XPS) was utilized to assess surface chemistry and confirm elemental composition (Baer & Engelhard, 2010). Additionally, Differential Scanning Calorimetry (DSC) was performed to examine the thermal properties and switching behavior of the materials (Ratner, 2013)

- Property Prediction and Optimization

Machine learning (ML) algorithms can analyze extensive datasets to predict the physicochemical properties of biomaterials (Rickert & Lieleg, 2022), which can be used to facilitate the design of materials with tailored responsiveness to environmental stimuli. For instance, in tissue engineering, ML has been utilized to predict and optimize scaffold properties (Guo et al., 2023), which is analogous to designing switchable biomaterials with specific adsorption characteristics for wastewater treatment.

Scaffold Design and 3D Printing: Advanced computational modeling assists in the design of complex biomaterial structures, enabling the creation of scaffolds with precise architectures that enhance performance (Entezari et al., 2018). Incorporating

ML into 3D printing processes may allow for the optimization of printing parameters, resulting in improved the properties and functionality of switchable biomaterials (An et al., 2015).

Data-Driven Material Discovery: By leveraging ML, researchers can identify patterns and relationships within large datasets, expediting the discovery of new switchable biomaterials with desired properties. This approach has been applied in the design of polymeric biomaterials, where ML models predicted material behavior based on compositional and structural data (Patel & Webb, 2023).

While predictive tools offer substantial advantages, challenges such as the need for high-quality, comprehensive datasets and the complexity of accurately modeling interactions persist. Additionally, the interpretability of ML models remains a critical consideration, as understanding the underlying mechanisms driving predictions is essential for the rational design of switchable biomaterials (Linardatos et al., 2020).

- Preparation of SP-COOH

2,3,3-Trimethylindolenine (1.0 g, 6.28 mmol) was dissolved in 1 mL Methyl ethyl ketone (MEK). After addition of 3-iodopropionic acid (1.3 g, 6.50 mmol), the reaction mixture was refluxed and stirred overnight. After cooling to room temperature, the precipitated material was isolated and washed with cold hexane followed by diethyl ether to obtain iodide salt 8 (2.03 g, 90%) as a light-brown salt. A dry r.b. flask was wrapped with aluminum foil and then charged with iodide salt (0.6 g, 1.67 mmol) and 3 mL MEK. Piperidine (0.174 mL, 1.75 mmol) and 5-nitrosalicylaldehyde (0.28 g,

1.68 mmol) were added in one portion. The reaction mixture was refluxed for 3 h. Then the reaction mixture was cooled to room temperature and stored overnight in a fridge (4 °C). The precipitated material was collected and washed with cold MEK followed by MeOH to obtain SP-COOH (0.37 g, 58%) as yellow-green powder (Johnson et al., 2017).

- Criteria for Defining Parameter Ranges

The four raw material concentration ranges are defined below. According to the preliminary experimental results, when the molar ratio of PVA, CNF-COOH is 1:2, the material is stable in physical properties, and according to the calculation under ideal conditions, the molar ratio of CNF-COOH, SP-COOH, Nano-ZnO is 1:1:1. Therefore, after calculation, 369.5mg/L PVA, 2.7g/L CNF-COOH, 10mmol/L SP-COOH, and 10mmol/L Nano-ZnO were defined as level 0 in the design. At the same time, the concentration limit range of the four raw materials was tested by concentration gradient experiment to ensure that the aerogel with stable structure could be prepared. For final optimization calculations, we added two additional levels to the CNF-COOH and SP-COOH concentrations, even though they were out of their concentration range. Finally, the values in the design are defined with the limit range of the respective concentrations.

Table S2. ANOVA results for the WCA and OAR of CNF-SP aerogel

		DF	Mean Square	F-value	P-Value
Water contact angle		15	95.57	31.54	0.0006
	A: Polyvinyl alcohol	1	270.40	89.24	0.0002
	B: Carboxyl cellulose sodium salt	1	4.50	1.49	0.2773
	C: SP-COOH concentration	1	302.50	99.83	0.0002
	D: Nano-ZnO concentration	2	44.75	14.77	0.0080
	AB	1	0.2250	0.074.	0.7961
	AC	1	23.23	7.66	0.0460
	AD	2	23.23	7.66	0.0300
	BC	1	120.13	39.64	0.0015
	BD	1	81.23	5.44	0.0585
	CD	2	122.88	40.55	0.0008
Oil adsorption ratio		15	35.99	23.24	0.0013
	A: PVA concentration	1	0.5617	11.60	0.0191
	B: Carboxyl cellulose sodium salt	1	53.56	34.59	0.0020
	C: SP-COOH concentration	1	19.97	412.49	<0.0001
	D: Zinc oxide	2	6.03	3.90	0.0955
	AB	1	5.29	3.42	0.1238
	AC	1	7.01	4.53	0.0866
	AD	2	0.3372	6.97	0.0358
	BC	1	1.38	28.46	0.0031
	BD	1	81.23	5.44	0.0585
	CD	2	23.00	14.85	0.0079

- FTIR Spectrum Analysis

The FTIR spectrum results also revealed the presence of multiple carbon chain structures on SP-COOH, as indicated by the multiple C-H stretching peaks at around 2900 cm-1 (Fig. 6(c)). The presence of nitro was confirmed by the peaks at 1512 cm-1 and 1328 cm-1. The bending vibration of the carboxyl group and C-H was observed in the wavenumber range of 1400 cm-1 to 1440 cm-1, and the peak changes in this range before and after UV irradiation indicated that SP-COOH underwent a change in carbon skeleton. The stretching vibration of C=C and the bending vibration of C-H were observed at 1228 cm-1 and 931 cm-1, respectively. Furthermore, flexural vibrations generated by adjacent and para substitutions on benzene were observed in the wavenumber range of 745 cm-1 to 810 cm-1.

- Analysis of Water Content in Oil

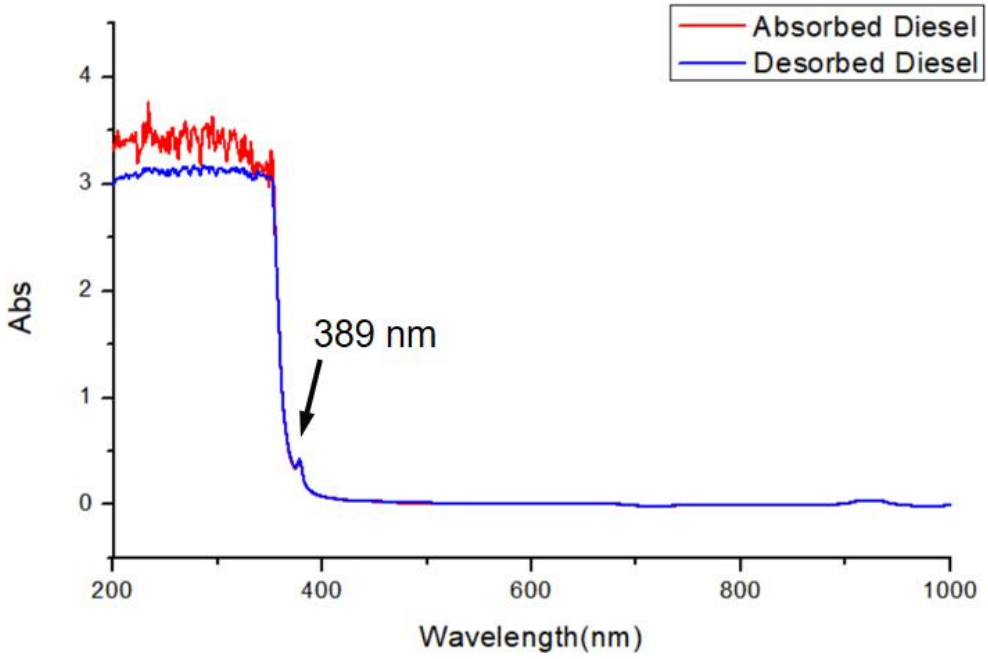

Fig. S1. UV-vis spectrophotometric comparison of absorbed and desorbed diesel oils.

Absorbed diesel was unused diesel fuel in experiments, and desorbed diesel was oil extracted from the CNF-SP aerogel after UV treatment. The peak intensity at 389 nm, which is the adsorption peak of water in diesel oil, was analyzed. The peak intensity of diesel oil desorbed from the CNF-SP aerogel was 99% of the peak intensity of the absorbed oil, while the peaks from 320 nm to 360 nm showed that desorbed diesel was above 90% of the peak intensity of absorbed oil. This meant that saturated hydrocarbon could be resolved well. Since spiropyran had a adsorption effect on unsaturated organic matter, while some of the molecules containing unsaturated hydrocarbons, such as C=O, C=C, could not be fully resolved. As a result, the peak intensity of the original diesel oil between 200 and 300 nm was greater than that of the desorbed diesel oil.

Fig. S2. The CNF-SP aerogel floated in the oil phase stained with methyl red without touching the underlying water phase after two days of resting.

- Determination of the Paramagnetic Rate of the CNF-SP Aerogel

The paramagnetic rate of the CNF-SP aerogel was determined by the Guhe method. The test results are shown in Table S3. The experiment was calibrated with Mohs salt. The calculated permeability of CNF-SP aerogel was 0.041 emu/mol which was relatively low due to the small content of ferric oxide. Nevertheless, the CNF-SP aerogel could still be easily attached by magnet, as shown in Fig. S3, in a surface dish containing water, it moved about 6 cm in 10 seconds using magnet attraction.

Table S3. The experimental result of paramagnetic rate by the Guhe method

Sample number	Sample quality (g)	Relative molecular mass (g/mol)	Δm /g I = 1 A	Height (cm)
1	0.121	284.53	54.7	14.35
2	0.098	284.53	56.5	14.3
3	0.154	284.53	56.1	14.4
Mean	0.124	284.53	55.77	14.35

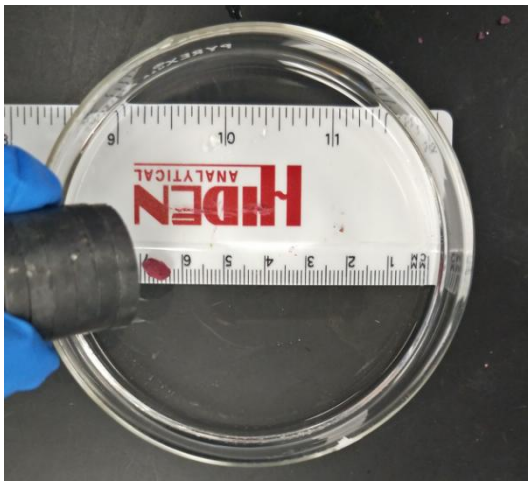

Fig S3. CNF-SP aerogel moves through the water when attracted by a magnet.

We took a 51.3mg aerogel sample for the experiment. The sample was placed in 50mL of deionized water for 15 seconds and removed. After extraction with carbon tetrachloride/methanol and Gas Chromatography/Mass Spectrometry (GC/MS) detection, the test results of pure water samples were compared. As shown in Figure S4, the aerogel sample does not precipitate after contact with water, which indicates that CNF-SP is stable in structure and will not cause secondary pollution when used.

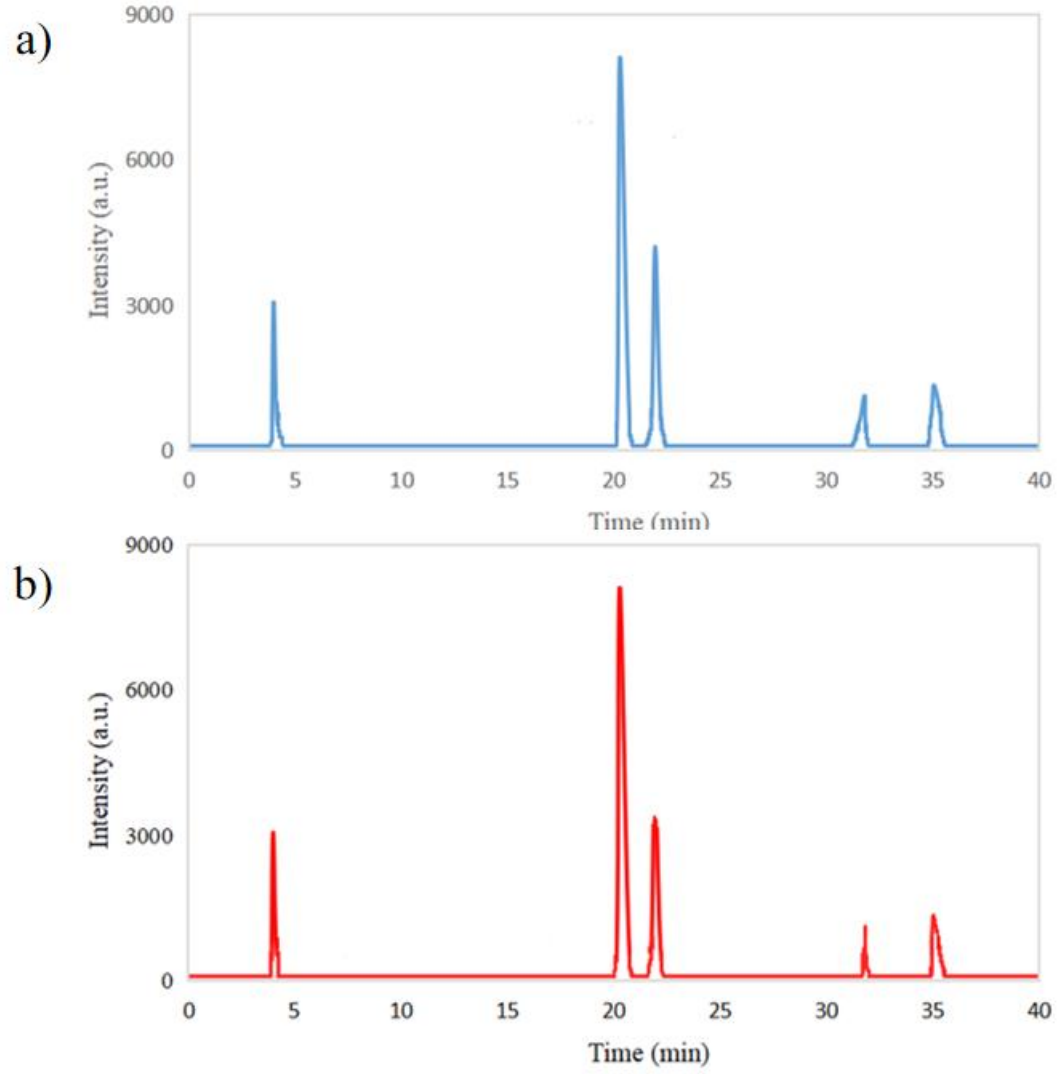

Fig S4. GC/MS identification of a) the water after dipped with CNF-SP; b) the pure deionized water

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