

PHYSICO-CHEMICAL AND ELECTROCHEMICAL DELIGNIFICATION AS A PRETREATMENT OF LIGNOCELLULOSIC BIOMASS FOR DIFFERENT APPLICATIONS: A MINI-REVIEW

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In recent years, the applications of lignocellulosic biomass (LCB) have substantially increased due to its versatility in different areas of study and interest. Therefore, it is evident that the delignification pretreatment of LCB is fundamental to assure the viability and commercial quality of the final product for different industrial uses. The efficiency of delignification, the obtainment of the desired products, and the required quality depend mainly on the type of pretreatment and the method used. This paper presents a state-of-the-art overview of physical, chemical, organic, biological, hybrid (combination of two or more pretreatments), and other novel pretreatments for the delignification of different lignocellulosic biomass. Additionally, the conditions necessary for the application of the pretreatments, the effect of the variables involved, and the advantages and disadvantages of each method are discussed. Finally, advances in the development of sustainable methods are discussed.

Keywords: delignification, lignocellulosic biomass, lignin applications, pretreatment, soluble sugars

INTRODUCTION

In recent decades, the applications of lignocellulosic biomass (LCB) have substantially increased due to its versatility in different areas of study and interest. In the biofuels industry, biochemicals, bioethanol, and bioproducts are produced from LCB to reduce the use of fossil fuels,¹⁻³ while the paper industry produces cardboard, paper, pulp, and other cellulose-based products.⁴⁻⁵ Likewise, the use of natural cellulose fibers (NCFs) has gained importance due to their unique hierarchical microstructures, which greatly improve the tensile strength, flexural strength, and toughness of composites. In the textile industry, their traditional applications are in products such as ropes, mats, mattresses, *etc.*,⁶⁻⁸ while in the construction industry they are used for reinforcement in the polymeric matrix of concrete, which increases the mechanical properties, improves thermal insulation, and lightens the weight of the concrete.⁹⁻¹¹

Lignocellulosic biomass is composed of three

dominant constituents, namely cellulose, hemicelluloses, and lignin, each of which has a function in the plant wall, providing support, hardness, and durability to the plant, as shown in Figure 1. Hemicelluloses and lignin coat cellulose by chemical and physical bonds. However, they are highly recalcitrant to biochemical deconstruction.¹² Therefore, pretreatment is an essential step in each of the aforementioned applications. This causes the elimination or reduction of recalcitrant constituents, such as hemicelluloses and lignin, to obtain a cellulose-rich solid residue. In the case of biofuels, delignification improves the yield and efficiency of the LCB bioconversion process by using cellulose as a starting material for saccharification and fermentation during biofuel production.¹³ In the paper industry, delignification is a crucial process for obtaining the pulp or cellulose paste necessary for the manufacture of paper. The cellulose undergoes pretreatment to remove residual lignin, and bleaching to increase the brightness of the final

product.^{14,15} In the textile industry, delignification creates compressible pores and exposes a greater amount of active functional groups in NCFs, which improve their mechanical properties and increase their tenacity for use in textile products.¹⁶ Additionally, in the construction industry, by reducing the recalcitrant constituents in the NCFs, the absorption properties are altered, requiring less

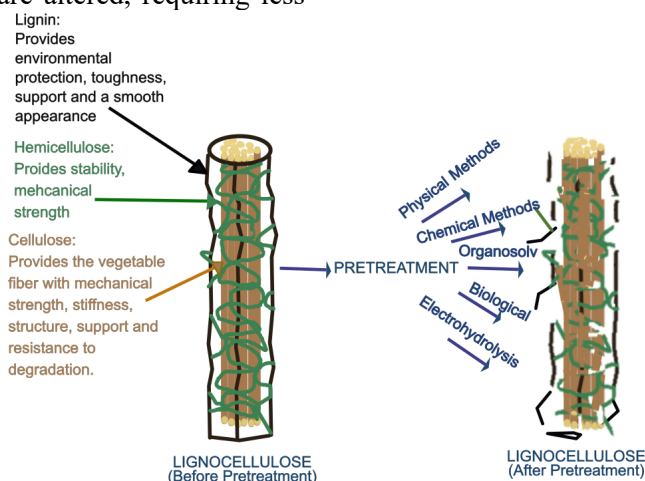


Figure 1: Chemical components of LCB and their functions in the plant wall

On the other hand, homogeneous and heterogeneous catalytic reactions on LCB substrates have been extensively studied in various alkaline aqueous solutions, organic acids, and biological and physical solvent processes. Delignification pretreatments were often performed using high solvent concentrations, elevated temperatures, and long exposure times. However, delignification methods continue to be studied to reduce the use of toxic chemicals, reaction times, energy expenditure, and negative environmental impacts associated with the pretreatment process.

This paper presents the research trends of delignification methods, with a focus on conventional and more novel pretreatments, with their advantages and limitations. In particular, this review focuses on the sustainability of different approaches, the major objective being to decrease energy consumption, and the generation of toxic wastes, without affecting the effectiveness of delignification.

DELIGNIFICATION PRETREATMENT METHODS

There are a wide variety of pretreatment methods to carry out the delignification of NCFs. They can be classified as physical, chemical, biological, or hybrid in nature and most of these treatments are characterized by the intensive use of chemicals

water to maintain the desired water/cement (w/c) ratio in the concrete mix. Similarly, the surface of the NCFs is affected by removing the lignin, becoming less smooth, which increases the adhesion between the fibers and the interfaces in composite materials, such as concrete. Therefore, the final mechanical properties are improved.¹⁷⁻²⁰

and/or energy. Some of them are described below.

Physical methods

Mechanical comminution (reduction)

Currently, a variety of mechanical methods for coarse size reduction are applied to improve the digestibility of LCB, including crushing, grinding, milling, and chopping, involving balls, rollers, rods, vibration, hammer, or wet and colloidal pressing media. After crushing or chopping, the size of the materials decreases from 30 to approximately 10 mm, while grinding reduces the size from 2 to 0.2 mm. Mechanical pretreatment techniques for delignification increase the specific surface area and decrease the degree of crystallinity and polymerization of the cellulose. However, the most prominent disadvantage of physical delignification pretreatments, which negatively impact the environment, is the high energy consumption. Studies have shown that the characteristics of the biomass and the required final particle size are factors that determine the amount of energy needed for mechanical crushing or grinding.²¹ Several studies have evaluated the size reduction of corn stover, switchgrass, and malleable woods, concluding that they require an energy consumption between 11.0 and 27.6 kWh/metric ton. In comparison, rigid woods, such as poplar and pine chips, require between 85.4 and 118.5 kWh/metric

ton.²² Therefore, these rigid woods require much higher energy consumption, and thus their processing is more harmful to the environment.

Milling

The post-grinding LCB particle size can be as small as 0.2 mm. Several studies show that LCB particles < 0.4 mm do not have a significant impact on the hydrolysis yield and rate.²³ However, by using another type of milling method, such as rod milling, planetary ball milling, or hammer milling, the particle size and degree of crystallinity are further reduced. This results in a high surface contact and pore volume of the LCB, favoring a higher yield in hydrolysis or pyrolysis as a second delignification pretreatment. Nonetheless, the significant drawback of this milling method is the high energy consumption and cost of mechanical equipment required for this process.²⁴

Pyrolysis

Pyrolysis is a physical method used as a delignification pretreatment for LCB. It consists of placing the vegetable fiber in a muffle at temperatures above 300 °C. The cellulose is decomposed into residual carbon and gaseous products.²⁵ Recent studies show the efficiency of the conjugate pyrolysis method using rod milling (hybrid pretreatment) – as rod milling involves a lower thermal degradation temperature than hammer milling, it increases the efficiency of pyrolysis. When the pyrolysis method is used as a first pretreatment at lower temperatures, the rate of decomposition is very low. This generates products, which, when a second pretreatment of mild acid hydrolysis delignification (NH₂SO₄ at 97 °C for 2.5 h) is performed, can convert between 80% and 85% of the cellulose into reducing sugars and more than 50% into glucose.²⁶ However, greenhouse gas emissions generated by pyrolysis are estimated to be 9 times higher than those emitted by mechanical pretreatments.

Microwave irradiation

Microwave irradiation pretreatment is a heating method that uses non-ionizing electromagnetic radiation with wavelengths in the range of 300–300,000 MHz. Thus, microwave radiation selectively transfers energy to various substances, *e.g.*, lignocellulosic material. Several studies have demonstrated the shortcomings of microwave irradiation pretreatment when used alone for delignification. However, when used in conjunction

with a variety of pretreatments (hybrid pretreatment), its efficiency is greatly increased. One example is microwave-assisted solvolysis at temperatures below 200 °C, to obtain basic chemical products.²⁷ In addition, microwave treatments assisted by pyrolysis (under high temperature conditions) above 400 °C can transform biomass into biofuels.²⁸ Following microwave irradiation, enzymatic hydrolysis of vegetable fibers is considered an effective pretreatment technique that increases the content of hydrolyzed glucose.²⁹ Likewise, it is possible to perform more than two delignification pretreatments on a vegetable fiber, depending on the final application.³⁰ In that study, the authors applied a first pretreatment of thermal hydrolysis (70 °C for 30 min) to black tea residues to eliminate polyphenols and other impurities. Subsequently, they used a hybrid pretreatment of acid and alkaline hydrolysis containing 4.5 M hydrogen peroxide (H₂O₂) and sodium hydroxide (NaOH) 5% w/v, in a ratio of acid/alkaline to black tea residue of 1:20 (g/mL). Finally, a third pretreatment of microwave radiation was applied to bleach the substance under microwave heating for 30 s. The results obtained were satisfactory; however, the number of pretreatments applied complicates their industrial application.

Sonication

Ultrasound delignification pretreatment consists in applying high-energy mechanical acoustic waves at different frequency and intensity,^{31–33} which produces mechano-acoustic and sono-chemical effects. This mechanism is attributed to the cavitation generated when the acoustic wave passes through a liquid and applying a shear force/velocity/pressure on the lignocellulosic biomass, causes the formation and violent collapse of bubbles in a liquid medium, simultaneously generating high pressure conditions (10³ bar) and temperature (10⁴ K), which can induce physical and chemical changes.^{33,34} The mechanisms of action of ultrasound are mainly classified as physical and chemical, for example, the main physical effects are the circulation of liquids, together with the associated turbulence.³⁵ Furthermore, pyrolysis can occur in the organic compound trapped in the cavitating bubble, considered as a chemical effect.³⁶ Ultrasonic extraction is effective in separating different types of polysaccharides, such as cellulose and hemicelluloses, by applying various procedures, such as the removal of co-extracted phenolics from isolated hemicelluloses and the separation of starch from pectic polysaccharides or hemicelluloses from

lignocellulosic biomass.³⁷ This treatment was applied to wood, resulting in the weakening of the chemical bonds between lignin and polysaccharides, increasing the hemicelluloses removal capacity.³⁸⁻⁴⁰ However, several authors⁴¹⁻⁴³ report better results with hybrid ultrasonic pretreatment using an alkaline/acid/organosolv solvent, obtaining the dissolution of 43.9–49.1% lignin, and 27.1–28.1% hemicelluloses, of 43.3–46.2% lignin and 32.2–41.4% hemicelluloses, and of 61.0–78.5% lignin, respectively. The main limitation of ultrasound pretreatment is that, when a solvent with high viscosity is used, it prevents the formation and growth of cavitation bubbles, hindering the effectiveness of the pretreatment.⁴⁴

Chemical pretreatments

Acid hydrolysis

For acid pretreatment, several studies have been carried out using inorganic acids, such as hydrochloric, sulfuric, nitric, and phosphoric acids, as well as organic acids, such as oxalic, maleic, and formic acids.⁴⁵ Acid hydrolysis pretreatment is effective due to the susceptibility of the glycosidic bonds of cellulose and hemicelluloses to the acid. The decomposition of the long chains of hemicelluloses and cellulose is caused by the hydronium ions originating from the acid catalyst, resulting in monosaccharides, which enhance the hydrolysis of the amorphous portion of cellulose and hemicelluloses. Therefore, it increases the recovery of digestible cellulose in the solid fraction and hemicelluloses as monomers in the liquid fraction.⁴⁶ Although concentrated acids, *e.g.*, hydrochloric and sulfuric acid, can achieve a sugar conversion rate over 90% in delignification, they are generally avoided because concentrated acids are corrosive, toxic, dangerous, require high maintenance operating costs, and cause undesired degradation of the cellulose. This can result in the generation of inhibitory compounds, such as aldehyde, phenolic, and 5-hydroxymethylfurfural acids.⁴⁷ Biological and chemical detoxification methods exist to overcome the effect of these inhibitors; however, environmentally friendly, faster, more effective, and less expensive pretreatments are still being studied.⁴⁸ Dilute acid pretreatments in ranging from 0.5% to 5% and at temperatures above 160 °C appear to be the favored method for industrial applications due to the higher yield of sugar derived from hemicelluloses. Studies reveal that the most used acid is dilute sulfuric acid (H₂SO₄) for LCB delignification.⁴⁹ In 2005, Saha *et al.* subjected wheat straw LCB to an acid hydrolysis

pretreatment using 0.75% v/v diluted H₂SO₄ at 121 °C for 1 h, resulting in a saccharification yield of 74%.⁵⁰ Similarly, Dionísio *et al.* used diluted H₂SO₄ as a pretreatment for the delignification of sugarcane bagasse, obtaining 89.5% solubilization of hemicelluloses and recovering 82% of monosaccharides (*e.g.*, arabinose and xylose).⁵¹ However, better results can be obtained by using a hybrid pretreatment, such as acid and alkaline hydrolysis,^{52,53} microwave-assisted acid hydrolysis,⁵² and acid hydrolysis and pyrolysis.⁵³

Alkali hydrolysis

Delignification by alkaline hydrolysis is a chemical pretreatment method based on the solubilization of lignin in an alkaline solution. The reagents commonly used for alkaline hydrolysis are calcium, sodium, ammonia, and potassium hydroxide. The alkaline hydrolysis process consists of a saponification reaction that causes the breaking of intermolecular ester bonds between lignin and hemicelluloses, resulting in the solubilization of fragments corresponding to hemicelluloses and lignin. This is because the alkaline solution causes enzymes to interact with the cellulose, which causes swelling and results in a reduction of the degree of polymerization and crystallinity. Therefore, the internal surface area increases. Likewise, by eliminating acetyl groups and uronic acid substitutions in hemicelluloses, the susceptibility of carbohydrates to enzymatic hydrolysis is increased.

Several studies have shown the advantages of the acid hydrolysis method as pretreatment. Sodium hydroxide with a concentration ranging from 0.5% to 10% has been used with a reaction duration of 5–60 min, resulting in 50% hemicelluloses dissolution and between 60% and 80% delignification.⁵⁴ On the other hand, when using a concentration of 1%–30% Na₂CO₃ with a temperature between 60 °C and 180 °C, lower results between 20% and 40% of hemicelluloses dissolution and between 40% and 60% delignification were obtained.⁵⁵ When using an ammonia hydroxide solution with a concentration between 5% and 30% at a temperature between 30 and 210 °C, the authors obtained hemicelluloses solubilization ranging from 10% to 50% and delignification of 0%–80%, a result of deep swelling of the lignin.⁵⁶ To reduce costs, an additional step was included: a Ca(OH)₂ solution of 0.05–0.15 g for 1–8 h. The results showed a reduction of both hemicelluloses dissolution and delignification of 20%–40% and 60%–80%, respectively.⁵⁷ An alkaline pretreatment does not improve the susceptibility of cellulose to enzymes

because it does not reduce its crystallinity during the saccharification process. However, by intensive lignin removal, the enzymatic hydrolysis of cellulose can be improved.

Oxidative pretreatment

Oxidative pretreatments increase the efficiency of preferential cellulose digestibility by delignification through deconstructing the cell wall structure of the lignocellulose and exposing the cellulose surface. Commonly used oxidants are organic peracids, chlorites, ozone, and hydrogen peroxide (H_2O_2). Oxidative delignification is carried out mainly by electrophilic attack of electron-rich sites, causing fragmentation and depolymerization of the lignin macromolecule. In the pulping and bleaching industries, H_2O_2 pretreatment is widely used. In general, H_2O_2 is brought to basic conditions (pH 11.6), which causes the generation of superoxides and O_2^- and OH radicals, which play important roles during the oxidative delignification of LCB. In 2022, Huang *et al.* reported the elimination of 70% of lignin using a H_2O_2 based pretreatment.⁵⁸ In 2023, using the same pretreatment, Wang *et al.* reported an increase in hemicelluloses and lignin removal by 92.2% and 98%, respectively.⁵⁹ One of the advantages of this type of treatment is that the contact time with the LCB is relatively short. However, for large-scale pretreatment applications, the cost of oxidizing reagents may increase.

Ionic liquids

Ionic liquids are salts in a liquid state and are formed by both types of ions (cations/anions) with a low melting point below 100 °C.^{60,61} The characteristics of these ionic liquids are strong thermal stability, high ionic conductivity, negligible vapor pressure, low volatility, flammability and ionic acidity. They could be called “green solvents” due to their recyclability in various chemical reactions in industrial processes.^{62,63}

Typically, an ionic liquid is used in a concentration of 5 to 10% to solid loading, applying a temperature of 120 °C (considering that the melting point of the ionic liquid should be less than 100 °C) in a range of time of 1 to 5 h, with occasional shaking.⁶⁴ The ionic liquid can dissolve cellulose, hemicelluloses and lignin, it competes with the lignocellulose material by breaking the hydrogen bonds between polysaccharide chains and the ether/ester bonds between lignin-carbohydrate, allowing for greater energy conversion capacity and leads to a more easily degradable biomass.^{65,66} Gao

*et al.*⁶¹ tested the effect of ionic liquid pretreatment on fir, mango leaves, rice straw, and water hyacinth to improve anaerobic digestion. The results showed a reduction in cellulose crystallinity from 21.0 to 15.2%, increased surface area and lignin removal from 23.7 to 64.8%. Furthermore, the biogas yield increased from 64 to 140% after anaerobic digestion.^{66,67} However, hybrid pretreatments showed better results, for example, ultrasonic-ionic liquid⁶⁸ average yields of biomass recovered from pretreated wheat straw and bagasse subjected to different frequencies (20–50 kHz) were 91.89% and 85.96%, respectively. With basic pretreatment with ionic liquid,^{69,70} the lignin removal rate was 81.73%. In 2020, Lin *et al.*⁷¹ developed a method for pretreatment of furfural waste to remove lignin by combining ionic liquid and alkaline peroxide. The treatment showed a lignin removal efficiency of 75.09%. Also, using ionic liquids for wheat straw pretreatment, Asim *et al.*⁷² reported a high delignification of 79% and a lignin recovery of 77%. Similarly, Ziaei-Rad *et al.*⁷³ obtained a hemicelluloses removal rate of 64.45% and a delignification rate of 80% of wheat straw biomass. With their promising chemical properties and high delignification efficiency, ionic liquids require carefully recycling, which may generate additional costs.

Biological pretreatments

Biological pretreatments have attracted the interest of researchers, mainly considering their low cost and environmental friendliness. Due to the low consumption of energy and chemical reagents, a biological pretreatment does not generate any inhibitors during the delignification process of LCB. The pretreatment uses bacteria or fungi that cause degradation of lignin or complex cells in the LCB by enzymes.⁷⁴ The enzymes commonly used for lignin removal are versatile peroxidase, peroxidase, manganese peroxidase, and laccases. There are two extracellular enzyme systems in the microorganisms involved; the ligninolytic system depolymerizes lignin and the hydrolytic system is responsible for degrading hemicelluloses and cellulose.⁷⁵ In this regard, fungi have the ability to degrade lignin and hemicelluloses. Commonly used fungi are brown, soft, and white rot fungi. In 2018, Guan *et al.* studied the effectiveness of chemical and biological pretreatment conditions on LCB, where it was found that the most efficient delignification of LCB was obtained with a biochemical hybrid pretreatment.⁷⁶ It was also found that the LCB pretreated with a liquid digestate fraction containing microbes and

CaO had 20.73% higher lignin removal compared to the reference and 57.56% higher methane production. In addition, the lignin reduction rate was 101.51% and 36.89% higher compared to biological and chemical pretreatments, respectively. However, the disadvantages of biological pretreatments lie in the slow rate of delignification and high rate of cellulose consumption, as most white rot fungi can degrade polysaccharides and lignin simultaneously, resulting in a loss of carbohydrates.⁷⁷

Organosolv pretreatment

The delignification of LCB using a pretreatment with organic solvents, which attain a high solubility of lignin, causes the internal breakdown of the bonds between hemicelluloses and lignin, resulting in a relatively pure cellulose residue. During the delignification process, the volume of pores on the cellulose surface increases, improving accessibility for saccharification and enzymatic hydrolysis.⁷⁸ A wide range of organic solvents, such as acetone, acetic acid, tetrahydrofuran (THF), methanol, organic acid, and ethylene glycol have been studied.^{77,78} Catalysts are commonly used to improve the delignification rate or decrease the reaction temperature; the catalysts used are acids (phosphoric, hydrochloric, and sulfuric acid), alkalis (sodium hydroxide, ammonia, and lime) and some salts.⁷⁸ The advantages of this type of pretreatment lie in the recycling of the solvents used by distillation and the high-quality lignin obtained, which has an added value as it is used in industrial applications. Pretreatment with organic solvents is often carried out at temperatures above 150 °C for a period of 1–3 h. The results show a delignification between 60% and 90%, while the glucose yield during the LCB saccharification process varies from 46% to 99%.⁷⁹ However, this pretreatment has some disadvantages as well, *e.g.*, the high cost of organic solvents. Therefore, it is essential to try to recover them, which is an energy intensive process. In addition, this pretreatment must be carried out under controlled conditions because of the volatility and high flammability of organic solvents.

Electrohydrolysis

Electrohydrolysis is a relatively new and less studied delignification pretreatment. The principle of the electrohydrolysis reaction mechanism is based on Ohmic heating, electrophoresis, and electroosmosis. These break the bonds between molecules, resulting in the alteration of the complex structure of the LCB material into conductive

water.⁸⁰

In 2019, Kainthola *et al.* adopted a new electrohydrolysis method for delignification of LCB by using graphite electrodes, varying the potential from 10 to 30 V and the time from 15 to 80 min, using a DC power supply. They obtained a maximum solubilization of 55% at 25 V for 60 min.⁸¹ Contrastingly, Veluchamy *et al.* modified the variables of the electrohydrolysis pretreatment, and with a potential of 15 V for a time of 45 min, and obtained an increase of methane production from 274 to 301 mL CH₄/gVS.⁸² However, delignification pretreatment by electrohydrolysis is considered a highly novel method, which is not yet fully studied and understood. Therefore, this process requires more research for deeper understanding.

Efficiency of the delignification process using hybrid methods

As efficiency is currently sought by combining different pretreatments, a review of some hybrid methods was carried out, where the conditions and percentage of sugar removal were observed. The results are shown in Table 1.

Figure 2 shows the efficiency percentage obtained by different methods of delignification, as reported by some authors.^{22,24,26,38,39,44,46,47,52,55,58} According to the information in Table 1 and Figure 2, higher efficiencies are reported in the use of hybrid methods for delignification treatment of different natural fibers. However, in the most efficient processes, the use of strong oxidizing agents and high energy consumption still predominate, conditions that have a strong impact on the environment. In this sense, research on fiber delignification has great opportunities to continue exploring alternatives that reduce toxic wastes, lower energy consumption and preferably be sustainable.

RESEARCH NEEDS AND FUTURE PERSPECTIVES

Existing pretreatment methods are effective in reducing or eliminating the non-cellulosic components from a variety of LCB. However, there are methods that use toxic reagents that prevent further use of the lignin obtained as a by-product of delignification, or increase costs by requiring treatment to recover the reagents, such as organosolv, oxidative with H₂O₂, electrohydrolysis, to mention just a few of these methods. Moreover, some approaches to obtaining a higher percentage of pure cellulose, a higher degree of crystallinity and delignification rate may have a negative impact

on the environment by requiring high energy consumption, or be economically challenging by demanding expensive equipment and materials. Additionally, the results of removing recalcitrant elements vary not only depending on the method and conditions used, but also on the LCB in question. Still, these limitations are thresholds for the scientific community to overcome by developing new approaches, modifying the existing ones or seeking to combine several methods with

the aim of making the delignification treatment friendly to the environment, producing less toxic waste, requiring lower energy consumption, reducing delignification times and material costs, allowing easy recovery of the by-products – recalcitrant elements that can be further turned into value-added products, in order to achieve sustainable processing.

Table 1
Some hybrid delignification pretreatments and their results

Feedstock	Pretreatment	Parameters	Removal (%)	Refs
Dry sugar cane leaves	Mechanical comminution	Ball mill of 0.02196 m diameter, 1 hp motor 1440 rpm	15.92 lignin	[83]
Poplar wood	Hydrothermal-ball milling-acid	Power of 3.54 kW for 1 h, 180 °C	93.93 hemicelluloses	[84]
Corn stover	Microwave irradiation-organosolv	Deep eutectic solvents, 160 °C and 30 min	89.75 lignin	[85]
Wheat straw (variety Riband)	Ultrasound-organosolv	100 W, 20 kHz, 0-35 min at 60 °C, 0.5 M NaOH methanol: H ₂ O (60/40 v/v)	67.4–78.5 lignin	[86]
Wheat straw	Thermal-acid hydrolysis	100–175 °C, 0.5–2% H ₂ SO ₄ v/v	90 lignin	[87]
Wheat straw	Thermal-alkali hydrolysis	125 °C, 7% NaOH	45 lignin	[88]
Wheat straw	Ionic liquid-acid hydrolysis	[TEA][HSO ₄], 130 °C, 3 h, 20 wt%	80 lignin	[72]
Xylose residue	Organosolv-alkali	Methanol/water (40 mL, 65/35 v/v) containing 0.25–2.0 wt% NaOH	86.7 lignin	[89]
<i>Pinus massoniana</i>	Biological-DES	Fungal culture-deep eutectic solvent (DES), 80 °C at 120 °C	84 lignin	[90]
Rice straw	Electro-hydrolysis	25 V, 60 min	55 lignin	[91]
Cotton stalk	Biological-EnZolv	2% EnZolv at 121 °C for 1 h at 15 psi	78.68 lignin	[92]
Poplar and cellic CTec2 (Novozymes A/S)	Thermal-acid	Hydrogen peroxide and acetic acid (30% w/w), 80 °C for 2 h	92.1 lignin	[93]

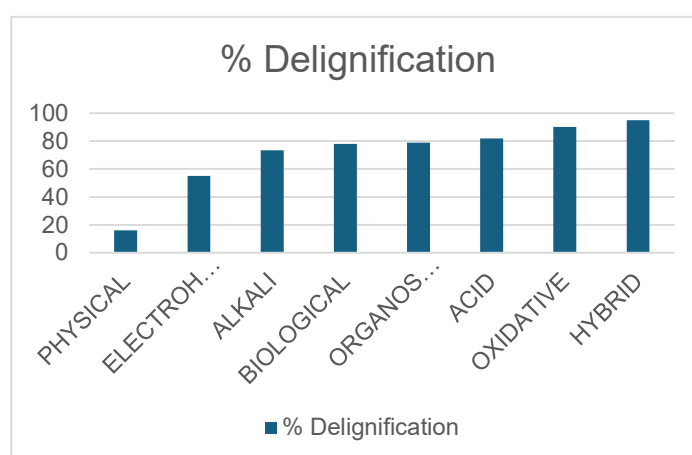


Figure 2: Comparison of delignification percentage obtained by different treatments^{22,24,26,38,39,44,46,47,52,55,58}

CONCLUSION

In this mini-review, different pretreatments for the delignification of natural fibers have been overviewed. Considering the existing scientific advances and trends that have shown some remarkable results, as well as the advantages and disadvantages of each approach pointed out in this paper, the conclusions that can be drawn are listed below.

Conventional physical and chemical pretreatments have proven to be efficient in the removal of soluble sugars. However, most of these pretreatments have considerable disadvantages, such as excessive energy consumption, the use of reagents that can generate hazardous wastes, and the use of expensive equipment. Also, conventional physical and chemical pretreatments sometimes make it difficult to handle the by-products derived from the delignification of natural fibers. However, the chemical and oxidant delignification pretreatments are more efficient, presenting a higher percentage of delignification, with a soluble sugar removal above 90%. Additionally, the hybrid pretreatments (chemical-oxidant) showed soluble sugar removals close to 95%.

Finally, more sustainable and environmentally friendly pretreatments, *e.g.*, hydrogen peroxide pretreatment or electrohydrolysis present great advantages. This is because they do not use excessive energy, nor do they use complex chemical reagents that are difficult to handle or remove from valuable by-products. However, these are relatively novel approaches and in-depth research studies are required to provide a thorough understanding of the delignification mechanisms and the products generated.

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REFERENCES

- ¹ A. E. Plesu Popescu, J. L. Pellin, J. Bonet and J. Llorens, *J. Clean Prod.*, **320**, 1 (2021), <https://doi.org/10.1016/j.jclepro.2021.128810>
- ² A. Azarpour, O. Mohammadzadeh, N. Rezaei and S. Zendejboudi, *Energ. Convers. Manag.*, **269**, 1 (2022), <https://doi.org/10.1016/j.enconman.2022.115945>
- ³ M. Antar, D. Lyu, M. Nazari, A. Shah, X. Zhou *et al.*, *Renew. Sustain. Energ. Rev.*, **139**, 1 (2021), <https://doi.org/10.1016/j.rser.2020.110691>
- ⁴ B. Soares, A. M. da Costa Lopes, A. J. D. Silvestre, P. C. Rodrigues Pinto, C. S. R. Freire *et al.*, *Ind. Crop. Prod.*, **160**, 1 (2021), <https://doi.org/10.1016/j.indcrop.2020.113128>
- ⁵ H. Shekhar, G. Kant and S. Srivastava, *Mater. Today Proc.*, **78**, A1 (2023), <https://doi.org/10.1016/j.matpr.2023.03.570>
- ⁶ C. Chen, J. Tan and X. Wang, *Carbohydr. Polym.*, **297**, 1 (2022), <https://doi.org/10.1016/j.carbpol.2022.119996>
- ⁷ Z. Zhang, K. Fu and Y. Li, *Compos. Commun.*, **27**, 1 (2021), <https://doi.org/10.1016/j.coco.2021.100898>
- ⁸ M. R. M. Asyraf, M. Rafidah, S. Ebadi, A. Azrina and M. R. Razman, *Cellulose*, **29**, 6493 (2022), <https://doi.org/10.1007/s10570-022-04695-3>
- ⁹ S. Niyasom and N. Tangboriboon, *Constr. Build. Mater.*, **283**, 1 (2021), <https://doi.org/10.1016/j.conbuildmat.2021.122627>
- ¹⁰ R. G. Romero, E. Onofre and A. C. Espíndola, *J. Phys. Conf. Ser.*, **2699**, 1 (2024), <https://doi.org/10.1088/1742-6596/2699/1/012002>
- ¹¹ R. Sánchez-Torres, E. Onofre-Bustamante, A. C. Espíndola-Flores, A. B. Morales-Cepeda and F. J. Rodríguez-Gómez, *Civil Eng. Res. J.*, **12**, 1 (2021), <https://doi.org/10.19080/cerj.2021.12.555841>
- ¹² B. Soares, A. M. da Costa Lopes, A. J. D. Silvestre, P. C. Rodrigues Pinto, C. S. R. Freire *et al.*, *Ind. Crop. Prod.*, **160**, 1 (2021), <https://doi.org/10.1016/j.indcrop.2020.113128>
- ¹³ Z. M. Madadi, M. Nazar, S. W. Ali Shah, N. Li *et al.*, *Ind. Crop. Prod.*, **200**, 1 (2023), <https://doi.org/10.1016/j.indcrop.2023.116815>
- ¹⁴ D. Shang, H. Lu, C. Liu, D. Wang and G. Diao, *J. Clean Prod.*, **380**, 1 (2022), <https://doi.org/10.1016/j.jclepro.2022.135108>
- ¹⁵ M. Dai, M. Sun, B. Chen, H. Xie, D. Zhang *et al.*, *Resour. Conserv. Recycl.*, **198**, 1 (2023), <https://doi.org/10.1016/j.resconrec.2023.107162>
- ¹⁶ C. Chen, P. Xu and X. Wang, *J. Bioresour. Bioprod.*, **9**, 102 (2023), <https://doi.org/10.1016/j.jobab.2023.12.001>
- ¹⁷ A. Sellami, M. Merzoud and S. Amziane, *Constr. Build. Mater.*, **47**, 1117 (2013), <https://doi.org/10.1016/j.conbuildmat.2013.05.073>
- ¹⁸ M. S. Islam and S. J. Ahmed, *Constr. Build. Mater.*, **189**, 768 (2018), <https://doi.org/10.1016/j.conbuildmat.2018.09.048>
- ¹⁹ A. Sellami, M. Merzoud and S. Amziane, *Constr. Build. Mater.*, **47**, 1117 (2013), <https://doi.org/10.1016/j.conbuildmat.2013.05.073>
- ²⁰ G. D. O. Okwadha and D. M. Makomele, *J. Build. Eng.*, **16**, 129 (2018), <https://doi.org/10.1016/j.jobe.2018.01.002>
- ²¹ H. Z. Chen and Z. H. Liu, *Biotechnol. J.*, **10**, 866 (2015), <https://doi.org/10.1002/biot.201400705>
- ²² K. Rajendran, E. Drielak, V. Sudarshan Varma, S. Muthusamy and G. Kumar, *Biomass Convers. Biorefin.*, **8**, 471 (2018), <https://doi.org/10.1007/s13399-017-0269-3>
- ²³ X. Bai, G. Wang, Y. Yu, D. Wang and Z. Wang, *Bioresour. Technol.*, **250**, 770 (2018), <https://doi.org/10.1016/j.biortech.2017.11.085>
- ²⁴ B. J. Gu, J. Wang, M. P. Wolcott and G. M. Ganjyal, *Bioresour. Technol.*, **251**, 93 (2018), <https://doi.org/10.1016/j.biortech.2017.11.103>
- ²⁵ N. A. Karim, M. M. Ramli, C. M. R. Ghazali and M.

- N. Mohtar, *Mater. Today: Procs.*, **16**, 2088 (2019), <https://doi.org/10.1016/j.matpr.2019.06.096>
- ²⁶ M. B. Folgueras, F. J. Fernández, C. R. Ardila, M. Alonso and S. Lage, *Energ. Proc.*, **1**, 60 (2017), <https://doi.org/10.1016/j.egypro.2017.10.283>
- ²⁷ K. Kohli, S. Katuwal, A. Biswas and B. K. Sharma, *Bioresour. Technol.*, **303**, 1 (2020), <https://doi.org/10.1016/j.biortech.2020.122897>
- ²⁸ M. Ishfaq Bhat, N. C. Shahi, U. C. Lohani, S. Singh, Q. Sidique *et al.*, *Bioresour. Technol.*, **351**, 1 (2022), <https://doi.org/10.1016/j.biortech.2022.127029>
- ²⁹ P. J. Jacqueline and G. Velvizhi, *Sustain. Chem. Pharm.*, **37**, 21 (2024), <https://doi.org/10.1016/j.scp.2023.101347>
- ³⁰ B. Debnath, P. Duarah and M. K. Purkait, *Int. J. Biol. Macromol.*, **244**, 1 (2023), <https://doi.org/10.1016/j.ijbiomac.2023.125354>
- ³¹ Y. Liu, Y. Ding, Y. Li, X. Wang, Y. Sun *et al.*, *J. Text. Inst.*, **1**, 1 (2024), <https://doi.org/10.1080/00405000.2023.2296691>
- ³² J. Jun Poon, M. Ching Tan and P. Loo Kiew, *Cellulose Chem. Technol.*, **54**, 725 (2020), <https://doi.org/10.35812/CelluloseChemTechnol.2020.54.72>
- ³³ H. Rabemanolontsoa and S. Saka, *Bioresour. Technol.*, **199**, 83 (2016), <https://doi.org/10.1016/j.biortech.2015.08.029>
- ³⁴ M. R. Sanjay, S. Siengchin, J. Parameswaranpillai, M. Jawaid, C. I. Pruncu *et al.*, *Carbohydr. Polym.*, **207**, 108 (2019), <https://doi.org/10.1016/j.carbpol.2018.11.083>
- ³⁵ A. Ebringerová and Z. Hromádková, *Open Chem.*, **8**, 243 (2010), <https://doi.org/10.2478/s11532-010-0006-2>
- ³⁶ E. M. Sul'man, M. G. Sul'man and E. A. Prutenskaya, *Catal. Ind.*, **3**, 28 (2011), <https://doi.org/10.1134/S2070050411010120>
- ³⁷ J. B. Gadhe, R. B. Gupta and T. Elder, *Cellulose*, **13**, 9 (2006), <https://doi.org/10.1007/s10570-005-9018-z>
- ³⁸ B. B. Pranav and B. P. Aniruddha, *Bioresour. Technol.*, **110**, 697 (2012), <https://doi.org/10.1016/j.biortech.2012.01.042>
- ³⁹ J. X. Sun, R. C. Sun, X. F. Sun and Y. Q. Su, *Carbohydr. Res.*, **339**, 291 (2004), <https://doi.org/10.1016/j.carres.2003.10.027>
- ⁴⁰ R. C. Sun and J. Tomkinson, *Eur. Polym. J.*, **39**, 751 (2003), [https://doi.org/10.1016/S0014-3057\(02\)00274-4](https://doi.org/10.1016/S0014-3057(02)00274-4)
- ⁴¹ R. C. Sun and J. Tomkinson, *Ultrason. Sonochem.*, **9**, 85 (2002), [https://doi.org/10.1016/S1350-4177\(01\)00106-7](https://doi.org/10.1016/S1350-4177(01)00106-7)
- ⁴² R. C. Sun, X. F. Sun and X. H. Ma, *Ultrason. Sonochem.*, **9**, 95 (2002), [https://doi.org/10.1016/S1350-4177\(01\)00102-X](https://doi.org/10.1016/S1350-4177(01)00102-X)
- ⁴³ V. Zhenquan Ong, T. Yeong Wu, C. B. Tien Loong Lee, N. W. Ren Cheong and K. P. Yee Shak, *Ultrason. Sonochem.*, **58**, 104598 (2019), <https://doi.org/10.1016/j.ultsonch.2019.05.015>
- ⁴⁴ W. X. Li, W. Z. Xiao, Y. Q. Yang, Q. Wang, X. Chen *et al.*, *Ind. Crop. Prod.*, **170**, 1 (2021), <https://doi.org/10.1016/j.indcrop.2021.113692>
- ⁴⁵ Z. Shao, Y. Fu, P. Wang, Y. Zhang, M. Qin *et al.*, *Int. J. Biol. Macromol.*, **165**, 1727 (2020), <https://doi.org/10.1016/j.ijbiomac.2020.10.026>
- ⁴⁶ M. K. Gill, G. S. Kocher and A. S. Panesar, *Carbohydr. Polym. Technol. Appl.*, **2**, 1 (2021), <https://doi.org/10.1016/j.carpta.2020.100029>
- ⁴⁷ X. Sun, Z. Zhou, D. Tian, J. Zhao, J. Zhang *et al.*, *Int. J. Biol. Macromol.*, **234**, 1 (2023), <https://doi.org/10.1016/j.ijbiomac.2023.123593>
- ⁴⁸ Q. Ma, W. Zhou, X. Du, H. Huang and Z. Gong, *Bioresour. Technol.*, **382**, 04 (2023), <https://doi.org/10.1016/j.biortech.2023.129218>
- ⁴⁹ B. C. Saha, L. B. Iten, M. A. Cotta and Y. V. Wu, *Process Biochem.*, **40**, 3693 (2005), <https://doi.org/10.1016/j.procbio.2005.04.006>
- ⁵⁰ S. R. Dionísio, D. C. J. Santoro, C. I. D. G. Bonan, L. B. Soares, L. E. Biazzi *et al.*, *Fuel*, **304**, 1 (2021), <https://doi.org/10.1016/j.fuel.2021.121290>
- ⁵¹ S. Tian, L. Guo, S. Ju, W. Li, L. Xu *et al.*, *Sep. Purif. Technol.*, **318**, 1 (2023), <https://doi.org/10.1016/j.seppur.2023.123930>
- ⁵² H. Liao, J. You, P. Wen, W. Ying, Q. Yang *et al.*, *Ind. Crop. Prod.*, **170**, 1 (2021), <https://doi.org/10.1016/j.indcrop.2021.113820>
- ⁵³ Y. Liu, W. Wang, Y. Wang, L. Liu, G. Li *et al.*, *J. Anal. Appl. Pyrol.*, **166**, 1 (2022), <https://doi.org/10.1016/j.jaap.2022.105588>
- ⁵⁴ M. Tajkarimi, H. P. Riemann, M. N. Hajmeer, E. L. Gomez, V. Razavilar *et al.*, *Int. J. Food Microbiol.*, **122**, 23 (2008), <https://doi.org/10.1016/j.ijfoodmicro.2007.11.040>
- ⁵⁵ C. E. Wyman, B. E. Dale, R. T. Elander, M. Holtzapple, M. R. Ladisch *et al.*, *Bioresour. Technol.*, **96**, 1959 (2005), <https://doi.org/10.1016/j.biortech.2005.01.010>
- ⁵⁶ X. Li and T. H. Kim, *Bioresour. Technol.*, **102**, 4779 (2011), <https://doi.org/10.1016/j.biortech.2011.01.008>
- ⁵⁷ L. Yang, J. Cao, Y. Jin, H. Chang, H. Jameel *et al.*, *Bioresour. Technol.*, **124**, 283 (2012), <https://doi.org/10.1016/j.biortech.2012.08.041>
- ⁵⁸ Ch. Huang, Y. Zhan, J. Cheng, J. Wang, X. Meng *et al.*, *Bioresour. Technol.*, **359**, 1 (2022), <https://doi.org/10.1016/j.biortech.2022.127462>
- ⁵⁹ A. Shrotri, H. Kobayash and A. Fukuoka, *Chem. Eng. J.*, **476**, 1 (2023), <https://doi.org/10.1016/j.cej.2023.146657>
- ⁶⁰ L. Neubert, J. Sunthornvarabhas, M. Sakulsombat and K. Sriroth, *Cellulose Chem. Technol.*, **54**, 301 (2020), <https://doi.org/10.35812/CelluloseChemTechnol.2020.54.32>
- ⁶¹ J. Gao, L. Chen, K. Yuan, H. Huang and Z. Yan, *Bioresour. Technol.*, **150**, 352 (2013), <https://doi.org/10.1016/j.biortech.2013.10.026>
- ⁶² A. James, M. Sekomeng Johannes, M. Faks Fanyana, F. Ojo and J. Bamidele, *Cellulose Chem. Technol.*, **57**, 935 (2023), <https://doi.org/10.35812/cellulosechemtechnol.2023.57.82>
- ⁶³ S. Behera, R. Arora, N. Nandhagopal and S. Kumar, *Renew. Sustain. Energ. Rev.*, **36**, 91 (2014), <https://doi.org/10.1016/j.rser.2014.04.047>

- ⁶⁴ D. Fu, G. Mazza and Y. Tamaki, *J. Agric. Food Chem.*, **58**, 1 (2010), <https://doi.org/10.1021/jf903616y>
- ⁶⁵ N. Lorenz, S. Jackapon, S. Morakot and S. Klanarong, *Cellulose Chem. Technol.*, **54**, 301 (2020), <https://doi.org/10.35812/CelluloseChemTechnol.2020.54.32>
- ⁶⁶ J. C. Stevens, L. Das, J. K. Mobley, S. O. Asare, B. C. Lynn *et al.*, *ACS Sustain. Chem. Eng.*, **7**, 15928 (2019), <https://doi.org/10.1021/acssuschemeng.9b02151>
- ⁶⁷ G. P. Naik, A. K. Poonia and P. K. Chaudhari, *J. Indian Chem. Soc.*, **98**, 100147 (2021), <https://doi.org/10.1016/j.jics.2021.100147>
- ⁶⁸ X. Yu, X. Bao, C. Zhou, L. Zhang, A. El-Gasim *et al.*, *Ultrason. Sonochem.*, **41**, 410 (2018), <https://doi.org/10.1016/j.ultsonch.2017.09.003>
- ⁶⁹ Y. Liu, Z. Yan, Q. He, W. Deng, M. Zhou *et al.*, *Process Biochem.*, **111**, 95 (2021), <https://doi.org/10.1016/j.procbio.2021.08.026>
- ⁷⁰ R. O. Almeida, A. Moreira, D. Moreira, M. E. Pina, M. G. V. S. Carvalho *et al.*, *RSC Adv.*, **12**, 3979 (2022), <https://doi.org/10.1039/d1ra08410k>
- ⁷¹ K. Lin, L. Feng, K. Niu, W. Liu, H. Zhan *et al.*, *Waste Biomass Valor.*, **11**, 1301 (2020), <https://doi.org/10.1007/s12649-018-0515-3>
- ⁷² A. M. Asim, M. Uroos, S. Naz and N. Muhammad, *J. Mol. Liquids*, **325**, 1 (2021), <https://doi.org/10.1016/j.molliq.2020.115013>
- ⁷³ Z. Z. Rad, J. Fooladi, M. Pazouki and S. N. Gummedi, *Biomass Bioenerg.*, **151**, 1 (2021), <https://doi.org/10.1016/j.biombioe.2021.106140>
- ⁷⁴ F. Chen, C. Martín, T. A. Lestander, A. Grimm and S. Xiong, *Bioresour. Technol.*, **344**, 1 (2022), <https://doi.org/10.1016/j.biortech.2021.126256>
- ⁷⁵ Y. Liu, Z. Yan, Q. He, W. Deng, M. Zhou *et al.*, *Process Biochem.*, **111**, 95 (2021), <https://doi.org/10.1016/j.procbio.2021.08.026>
- ⁷⁶ R. Guan, A. C. Wachemo, H. Yuan, Y. Liu, D. Zou *et al.*, *Sci. Total Environ.*, **637–638**, 9 (2018), <https://doi.org/10.1016/j.scitotenv.2018.04.366>
- ⁷⁷ P. Xue, M. Liu, H. Yang, H. Zhang, Y. Chen *et al.*, *Fuel*, **338**, 1 (2023), <https://doi.org/10.1016/j.fuel.2022.127276>
- ⁷⁸ G. Song, M. Madadi, X. Meng, Ch. Sun, M. Aghbashlo *et al.*, *Chem. Eng. J.*, **481**, 148713 (2024), <https://doi.org/10.1016/j.cej.2024.148713>
- ⁷⁹ D. Cardoza, M. del Mar Contreras, M. Lara-Serrano, S. Morales-de la Rosa, J. M. Campos-Martín *et al.*, *Process Saf. Environ. Prot.*, **183**, 1059 (2024), <https://doi.org/10.1016/j.psep.2024.01.063>
- ⁸⁰ B. J. Poddar, S. P. Nakhate, R. K. Gupta, A. R. Chavan, A. K. Singh *et al.*, *Int. J. Environ. Sci. Technol.*, **19**, 3429 (2022), <https://doi.org/10.1007/s13762-021-03248-8>
- ⁸¹ C. Veluchamy, V. W. Raju and A. S. Kalamdhad, *Bioresour. Technol.*, **235**, 274 (2017), <https://doi.org/10.1016/j.biortech.2017.03.137>
- ⁸² J. Kainthola, M. Shariq, A. S. Kalamdhad and V. V. Goud, *Renew Energ.*, **142**, 1 (2019), <https://doi.org/10.1016/j.renene.2019.04.083>
- ⁸³ C. Veluchamy, V. W. Raju and A. S. Kalamdhad, *Bioresour. Technol.*, **252**, 52 (2018), <https://doi.org/10.1016/j.biortech.2017.12.093>
- ⁸⁴ R. A. Patil and U. B. Deshannavar, *Mater. Today: Procs.*, **5**, 18135 (2018), <https://doi.org/10.1016/j.matpr.2018.06.149>
- ⁸⁵ L. H. Xu, C. Y. Ma, C. Zhang, Y. Xu, J. L. Wen *et al.*, *Renew Energ.*, **201**, 691 (2022), <https://doi.org/10.1016/j.renene.2022.10.083>
- ⁸⁶ N. Wang, A. Xu, K. Liu, Z. Zhao, H. Li *et al.*, *Chem. Eng. J.*, **482**, 1 (2024), <https://doi.org/10.1016/j.cej.2024.148786>
- ⁸⁷ M. M. Kininge and P. R. Gogate, *Ultrason. Sonochem.*, **82**, 1 (2022), <https://doi.org/10.1016/j.ultsonch.2021.105870>
- ⁸⁸ A. M. Rahmani, V. K. Tyagi, A. A. Kazmi and C. S. P. Ojha, *Energy*, **283**, 1 (2023), <https://doi.org/10.1016/j.energy.2023.129083>
- ⁸⁹ A. M. Rahmani, V. K. Tyagi, N. Gunjyal, A. A. Kazmi, C. S. P. Ojha *et al.*, *Environ. Res.*, **216**, 1 (2023), <https://doi.org/10.1016/j.envres.2022.114436>
- ⁹⁰ L. Zhong, C. Wang, M. Xu, X. Ji, G. Yang *et al.*, *Energ. Fuels*, **35**, 5039 (2021), <https://doi.org/10.1021/acs.energyfuels.1c00320>
- ⁹¹ F. Li, Y. Liu, J. Jia and H. Yu, *Bioresour. Technol.*, **380**, 1 (2023), <https://doi.org/10.1016/j.biortech.2023.129110>
- ⁹² S. Subramaniam, K. Karunanandham and S. Uthandi, *Bioresour. Technol.*, **387**, 1 (2023), <https://doi.org/10.1016/j.biortech.2023.129655>
- ⁹³ P. Wen, J. Chu, J. Zhu, Y. Xu and J. Zhang, *Renew Energ.*, **188**, 1022 (2022), <https://doi.org/10.1016/j.renene.2022.02.094>