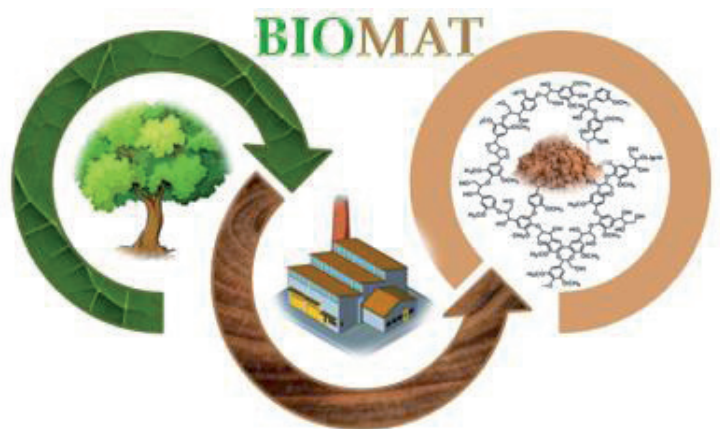


MARIA CURIE-SKŁODOWSKA UNIVERSITY, POLAND
SS. CYRIL AND METHODIUS UNIVERSITY, MACEDONIA
KTH ROYAL INSTITUTE OF TECHNOLOGY, SWEDEN



*From biomass to functional materials: advances in
lignin isolation, characterization and applications*

by

MONIKA WAWRZKIEWICZ, BEATA PODKOŚCIELNA, ANNA WOŁOWICZ
MARTA GOLISZEK-CHABROS, JADRANKA BLAZHEVSKA GILEV,
OLENA SEVASTYANOVA, MARIJA PROSHEVA

Lublin 2025

Reviewer: ELŻBIETA GRZĄDKA, UMCS, Lublin, Poland

Technical editing, typesetting and proofreading: ANNA WOŁOWICZ

© by Maria Curie-Skłodowska University Press, Lublin 2025

ISBN 978-83-227-9904-8

Maria Curie-Skłodowska University Press
ul. Idziego Radziszewskiego 11, 20-031 Lublin, Poland
tel. +48 81 537 53 04
www.wydawnictwo.umcs.eu
e-mail: wydawnictwo_sekretariat@mail.umcs.pl

Sales Department
tel./fax +48 81 537 53 02
Online bookstore: www.wydawnictwo.umcs.eu
e-mail: wydawnictwo@umcs.eu

This glossary has been created as part of the project entitled
*“Improving teaching competencies in design of new generation
biomaterials from wood waste”*

Project reference: 2024-1-PL01-KA220-HED-000246133
from the Erasmus+ programme:

KA220-HED - Cooperation partnerships in higher education.



**Co-funded by
the European Union**

Co-funded by the European Union. The views and opinions expressed are solely those of the author or authors and do not necessarily reflect the views and opinions of the European Union or the Foundation for the Development of the Education System. Neither the European Union nor the Foundation for the Development of the Education System can be held responsible for them.



Dear Readers,

In the face of growing environmental challenges, increasing fossil fuel consumption and the urgent need for sustainable solutions, both science and industry are increasingly turning to renewable raw materials. One of the most promising components of plant biomass is lignin - an organic compound found alongside cellulose and hemicellulose in the cell walls of vascular plants. Although lignin was long regarded primarily as a low-cost by-product of the paper industry, modern research highlights its enormous potential as a raw material for the development of functional materials. In an era of industrial transformation, the transition to green technologies and the reduction of CO₂ emissions, lignin is emerging as a key element in the future of materials science. Its widespread availability, renewability, and potential for chemical modification make it a highly attractive raw material.

This compendium presents recent advances in lignin research, focusing on its extraction from lignin-containing waste biomass, structural characterization, and the development of functional materials based on lignin. The content is organized into four main chapters, each exploring different aspects of lignin science and its potential applications. The first chapter is devoted to the characteristics of lignin - its definition, sources, chemical structure, and isolation methods. The reader will also find an overview of the global markets and extraction technologies for this raw material. The second chapter presents the practical applications of lignin, including its use in the development of adsorbents for the removal of dyes and heavy metals, as well as in environmentally friendly polymer composites. More advanced applications are also discussed, such as the production of vanillin, carbon fibers, and the use of lignin in cosmetics and construction materials. The third chapter examines methods for evaluating the properties of lignin-containing composites and adsorbents. Several analytical techniques are presented, such as Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and thermal and mechanical property analysis. The compendium concludes with a brief summary (chapter four) of the progress made to date, along with reflections on future research directions in the field of lignin-based materials.

This publication was developed within the framework of international project entitled "Improving teaching competencies in design of new generation biomaterials from wood waste" (BIOMAT), funded by the European Union under the Erasmus+ programme "Cooperation partnerships in higher education (KA220-HED)".

We invite you to explore this compendium, which we hope will inspire students, researchers, and practitioners in their pursuit of sustainable, bio-based solutions for the industries of the future.

Authors

CONTENTS

1	LIGNIN CHARACTERIZATION	7
1.1	LIGNIN - DEFINITION, SOURCES, STRUCTURE	7
1.2	LIGNIN ISOLATION AND CLASSIFICATIONS	10
1.2.1	ISOLATION OF NATIVE LIGNIN	10
1.2.2	INDUSTRIAL PULPING PROCESSES AND CORRESPONDING TECHNICAL LIGNINS	12
1.2.3	COMPARATIVE PROPERTIES OF TECHNICAL LIGNINS	20
1.3	GLOBAL MARKET AND FORECASTS	24
1.3.1	LIGNIN EXTRACTION TECHNOLOGIES AND COMMERCIAL PRODUCTS	24
1.3.2	THE WORLDWIDE LIGNIN MARKET AND FORECAST	26
1.4	SELECTED METHODS OF LIGNIN CHARACTERIZATION	28
1.4.1	GEL PERMEATION CHROMATOGRAPHY	28
1.4.2	NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY	29
1.5	LIGNIN UPGRADE	31
1.5.1	FRACTIONATION OF TECHNICAL LIGNINS: PATHWAYS TO TAILORED PROPERTIES	31
1.5.2	CHEMICAL MODIFICATION OF LIGNIN	35
2	LIGNIN APPLICATION	40
2.1	ADSORBENTS WITH LIGNIN ADDITION FOR DYES REMOVAL	45
2.2	ADSORBENTS WITH LIGNIN ADDITION FOR REMOVAL OF METAL IONS	52
2.3	GREEN COMPOSITES WITH LIGNIN	66
2.3.1	APPLICATION OF LIGNIN AS FILLER IN GREEN POLYMER COMPOSITES	69
2.3.2	POLY(VINYL ALCOHOL)/LIGNIN COMPOSITES	71
2.3.3	POLY(LACTIC ACID)/LIGNIN COMPOSITES	76
2.3.4	USE OF DIFFERENT POLYMERS FOR PREPARATION OF POLYMER/LIGNIN COMPOSITES	80
2.4	ANOTHER APPLICATION OF LIGNIN	82
2.4.1	BENZENE, TOLUENE AND XYLENE	82
2.4.2	VANILLIN	83
2.4.3	CARBON FIBRE	84
2.4.4	COSMETIC FORMULATIONS	85
2.4.5	CONSTRUCTION	86
3	EVALUATION OF PROPERTIES OF POLYMERIC ADSORBENTS AND COMPOSITES WITH LIGNIN ADDITION	102
3.1	SELECTED METHODS FOR EVALUATING THE PROPERTIES OF POLYMERIC ADSORBENTS AND COMPOSITES CONTAINING LIGNIN	102
3.1.1	FOURIER TRANSFORM INFRARED SPECTROSCOPY	103

3.1.2	THERMAL PROPERTIES	105
3.1.3	MECHANICAL PROPERTIES	111
3.1.4	SCANNING ELECTRON MICROSCOPY AND TRANSMISSION ELECTRON MICROSCOPY	114
3.1.5	QUARTZ CRYSTAL MICROBALANCE	117
3.1.6	LASER ABLATION	119
4	SUMMARY	126

CHAPTER 1

LIGNIN CHARACTERIZATION

1.1 Lignin - definition, sources, structure

Lignin is one of the most abundant biopolymers on Earth and the primary natural source of aromatic carbon in biomass. Lignin, together with cellulose and hemicellulose, is a main structural component of lignocellulosic biomass, including trees, grasses, and other vascular plants. In addition to these three major biopolymers, lignocellulosic biomass also contains minor components such as extractives, proteins, ash (minerals), and small amounts of organic acids and sugars (Figure 1.1). It provides mechanical strength to the plant cell wall, facilitates water transport through vascular tissues, and protects against microbial attack and enzymatic degradation (Sjöström and Alén, 1998).

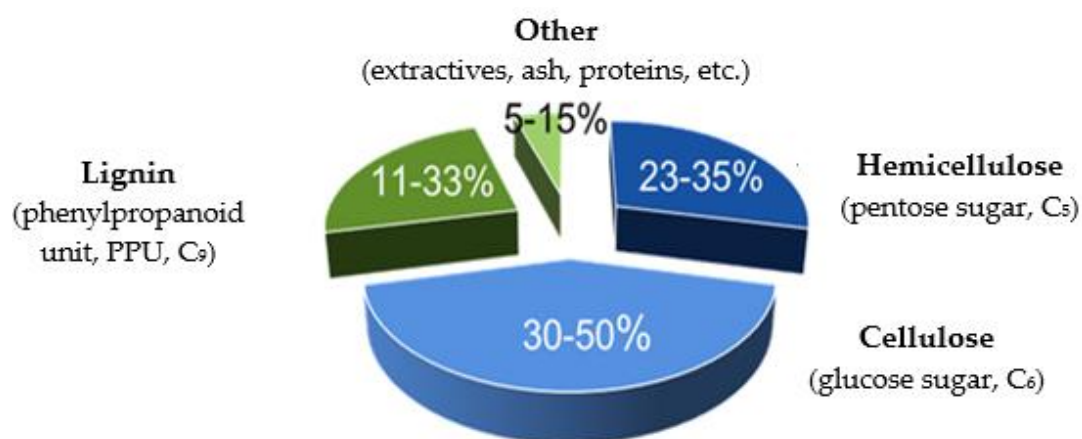


Figure 1.1. Typical composition of the lignocellulosic biomass (Sjöström and Alén, 1998).

The lignin content in lignocellulosic biomass varies depending on the plant source. In wood, lignin typically makes up 20–30% of the dry weight, with softwoods generally containing more lignin than hardwoods. In contrast, grasses and agricultural residues (such as wheat straw or sugarcane bagasse) usually contain 15–25% lignin. These differences reflect both

botanical origin and plant function, influencing the chemical structure and reactivity of the extracted lignin.

Chemically, lignin is a complex, highly branched polyphenolic macromolecule built from three primary phenylpropanoid monomers: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. These monomers polymerize through radical coupling reactions, resulting in a heterogeneous structure with various interunit linkages.

The phenylpropanoid units in lignin are referred to as (Figure 1.2):

- H unit (p-hydroxyphenyl): derived from p-coumaryl alcohol,
- G unit (guaiacyl): derived from coniferyl alcohol,
- S unit (syringyl): derived from sinapyl alcohol.

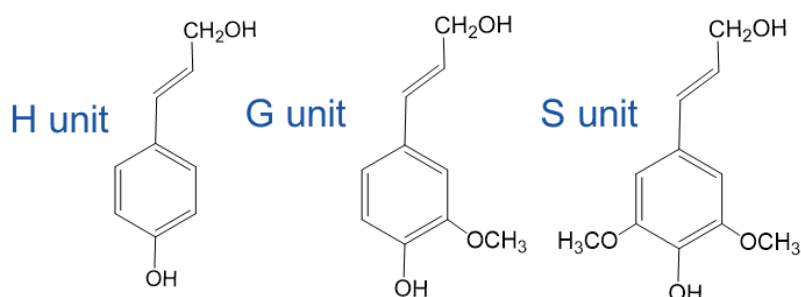


Figure 1.2. Structural units in lignin (Sjöström, 1981).

The relative abundance of these monomeric units differs among plant species, which determines the type and properties of lignin, as shown in Table 1.1 (Lin and Dence, 1992).

Table 1.1. Content and chemical composition of lignin in various types of lignocellulosic biomass.

Plant type		Content in biomass	p-Coumaryl alcohol (H)	Coniferyl Alcohol (G)	Sinapyl Alcohol (S)
		%			
	Softwoods/gymnosperms	24-33	< 5	>95	0
	Hardwoods/angiosperms	19-28	0-8	25-50	45-75
	Grasses (cereal straws, bamboo, bagasse, sisal)/ Monocotyledonous	11-27	5-35	35-80	20-55

The most common linkage in native lignin is the β -O-4 ether bond, which accounts for about 49–65% of all connections. This bond is relatively easy to break during chemical processing, making it important for lignin depolymerization. Other types of linkages include β -5 (phenylcoumaran), β - β (resinol), 5-5' (biphenyl), β -1, and 4-O-5, each occurring to a lesser extent and contributing to the overall complexity and rigidity of the polymer. The composition and frequency of these linkages differ slightly between softwood and hardwood lignins. Quantitative data on the occurrence of these interunit bonds were reported by Erickson et al. (1973) for softwood lignin and Nimz (1974) for hardwood lignin (beech wood). These values are based on analyses of isolated native lignins, typically obtained in around 50% yield from plant biomass. A schematic summary of these interunit connections, along with their relative abundance, is shown in Figure 1.3, which illustrates the intricate architecture of lignin and its highly branched nature.

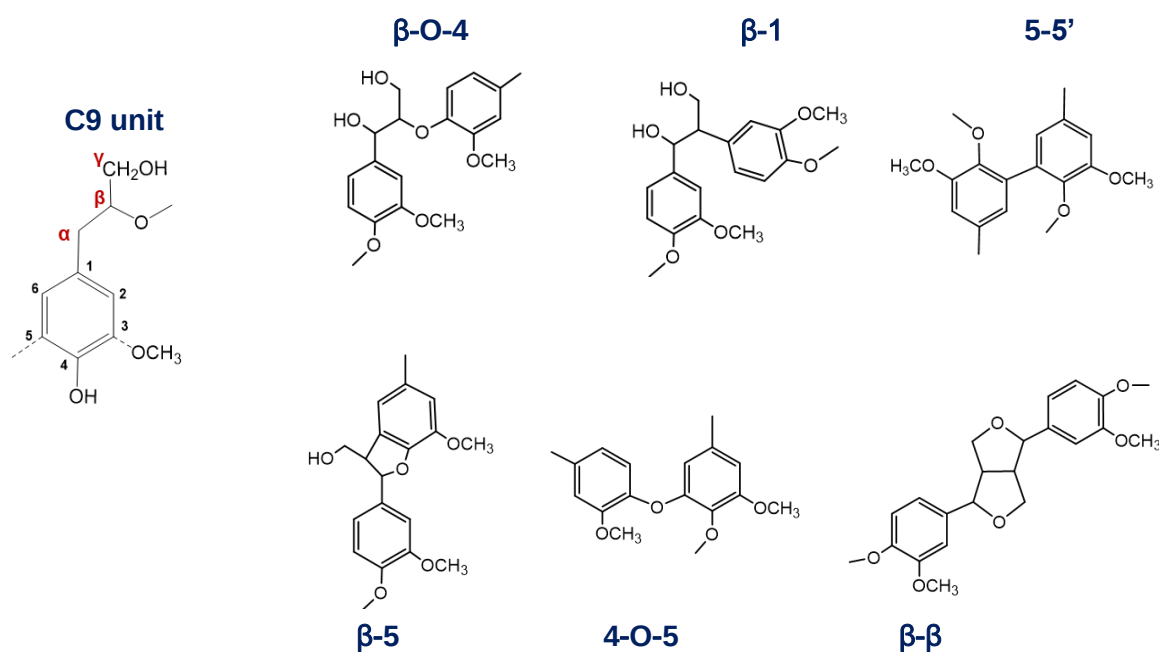


Figure 1.3. Types of interunit linkages in native lignin (Erickson et al., 1973; Nimz, 1974).

The schematic structures of native lignin differ significantly between softwoods and hardwoods, primarily due to their monomeric composition and interunit linkages (Brunow 2001; Ralph et al., 2004). Softwood lignin is predominantly composed of guaiacyl (G) units derived from coniferyl alcohol, which leads to a more condensed and highly crosslinked structure due to the availability of the free C5 position on the aromatic ring. This structural characteristic allows the formation of additional C-C bonds such as 5-5' and β -5 linkages, making softwood lignin more resistant to chemical degradation and thermally more stable. In contrast, hardwood lignin contains a mixture of guaiacyl (G) and syringyl (S) units, the latter derived from sinapyl alcohol. The S units have two methoxyl groups on the

aromatic ring, blocking the C5 position and thereby limiting crosslinking. As a result, hardwood lignin is less condensed and more linear in structure, which often makes it more reactive and easier to process chemically. The representative model structures are shown in Figure 1.4, illustrating the molecular architecture of lignin from different botanical origins.

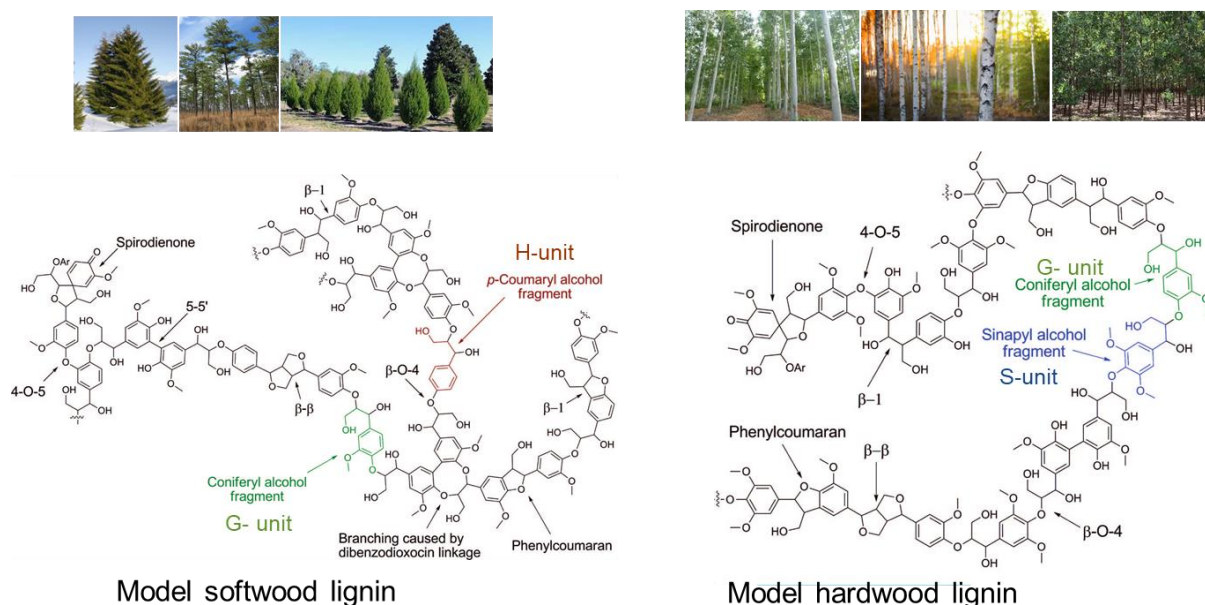


Figure 1.4. Native lignin structure (adopted from Zakzeski et al., 2010; Ralph et al., 2004).

In summary, lignin is a complex aromatic biopolymer that varies in structure depending on its botanical origin. The monomeric composition and degree of crosslinking determine the physical and chemical properties of lignin, affecting its potential for valorization. Understanding these structures is essential for developing biobased materials, including thermoplastics, resins, and bio-based polymers.

1.2 Lignin isolation and classifications

1.2.1 Isolation of native lignin

The structural study of lignin in its native, unaltered form has been a longstanding challenge in plant biochemistry. Essentially, the procedures to isolate lignin are classified according to whether the lignin is selectively removed from other plant constituents and subsequently recovered from the resulting solution or, conversely, the non-lignin constituents are removed, leaving the lignin as an insoluble residue.

Early attempts to isolate lignin included solvent extractions using neutral solvents such as ethanol or ethanol–benzene mixtures, as demonstrated by Braun in the 1930s and 1940s

(Braun, 1940). He showed that a small fraction of lignin could be extracted from wood using such methods. However, these techniques yielded only a small percentage of the total lignin and left most of it bound tightly within the plant cell wall. To achieve higher extraction yields, harsher chemical treatments such as acidolysis were often employed—though at the cost of significantly modifying the lignin structure.

To overcome these limitations, Anders Björkman developed a novel method in 1956 that laid the foundation for modern structural studies of lignin. His approach, now known as the Björkman method, involved extensive milling of wood in a ball mill to disrupt the cell wall structure, followed by extraction with a neutral organic solvent—typically 1,4-dioxane–water. The resulting milled wood lignin (MWL) represents the most native-like lignin fraction accessible in sufficient purity for detailed chemical characterization.

The key innovation of this method lies in its mechanical pre-treatment. Ball milling breaks down the physical integrity of the plant cell wall, liberating lignin that is otherwise retained through physical entrapment and non-covalent interactions. According to Björkman, this method can extract up to two-thirds of the total lignin from wood at room temperature under optimal conditions. The extracted lignin typically appears as a light-colored powder and, most importantly, retains much of the native polymer's original structure, making it well-suited for structural elucidation (Bjorkman, 1954; Björkman, 1956).

A schematic representation of the extraction process can be used to summarize the key steps:

- ball milling of wood particles in the presence of a dispersing medium,
- solvent extraction with dioxane–water or Methyl Cellosolve,
- precipitation, filtration, and purification of the extracted lignin,
- structural analysis of the isolated MWL.

Despite its advantages, the isolation of native lignin—even using the Björkman method—presents several challenges:

- low yield: typically only 20–35% of total lignin is recovered, limiting its use in material applications,
- time-consuming: high-purity MWL often requires extraction over several weeks to achieve maximal yield,
- structural bias: although considered minimally altered, MWL may be enriched in more soluble, low-molecular-weight lignin fractions and underrepresent the highly crosslinked domains,
- limited scalability: the labor- and equipment-intensive nature of ball milling and prolonged extraction make this method impractical for large-scale applications,
- subtle modifications: even mild conditions can sometimes result in partial depolymerization or oxidation of sensitive lignin linkages.

These limitations are important to consider when interpreting the structural data of isolated lignins. Nevertheless, MWL remains the gold standard for native lignin research

and continues to serve as a reference material for comparison with technical lignins, which are produced by industrial delignification processes and discussed in the following section.

1.2.2 Industrial pulping processes and corresponding technical lignins

Large-scale extraction of lignin is primarily driven by the pulp and paper industry and, more recently, biorefinery initiatives. Unlike native lignin isolated under mild laboratory conditions, technical lignins are obtained through various industrial delignification processes that aim to liberate cellulose for further processing. These methods significantly alter the structure of lignin, resulting in materials that are chemically and physically distinct from their native counterparts. Despite this, technical lignins represent a vast and underutilized renewable resource with promising potential for material and chemical applications (Vishtal and Kraslawski, 2011).

Depending on the pulping conditions—such as the use of sulfur compounds, organic solvents, or alkali—different types of technical lignins are produced, each with distinct characteristics. The most prominent classes include kraft lignin, lignosulfonates, soda lignin, and organosolv lignin, among others. Each of these carries a structural fingerprint based on the source material (softwood, hardwood, non-woody biomass) and the severity of the treatment.

To illustrate the industrial context of lignin extraction and utilization, Figure 1.5 provides a schematic overview of the main industrial delignification processes illustrating lignin's journey from biomass to application. It begins with the separation of lignin from lignocellulosic biomass using different chemical processes (e.g., kraft, soda, organosolv (Laurichesse and Avérous, 2014)). These processes are typically categorized based on the presence or absence of sulfur-containing chemicals, and they strongly influence the structure and chemical properties of the resulting technical lignins.

1. Sulfur-Containing Processes

These processes dominate the global pulp and paper industry and are characterized by the use of sulfur-based chemicals, which introduce structural changes to the lignin and often leave sulfur residues in the final product.

Kraft (Sulfate) Process

The kraft process is the most widely used chemical pulping method, responsible for approximately 85% of all industrial lignin production. It involves cooking wood chips under alkaline conditions using a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na₂S) at temperatures of 155–175 °C and pressures of 0.7–1.0 MPa. During this process, 90–95% of the lignin originally present in the biomass is degraded and solubilized in the black liquor, which also contains spent cooking chemicals (Sjöström, 1981).

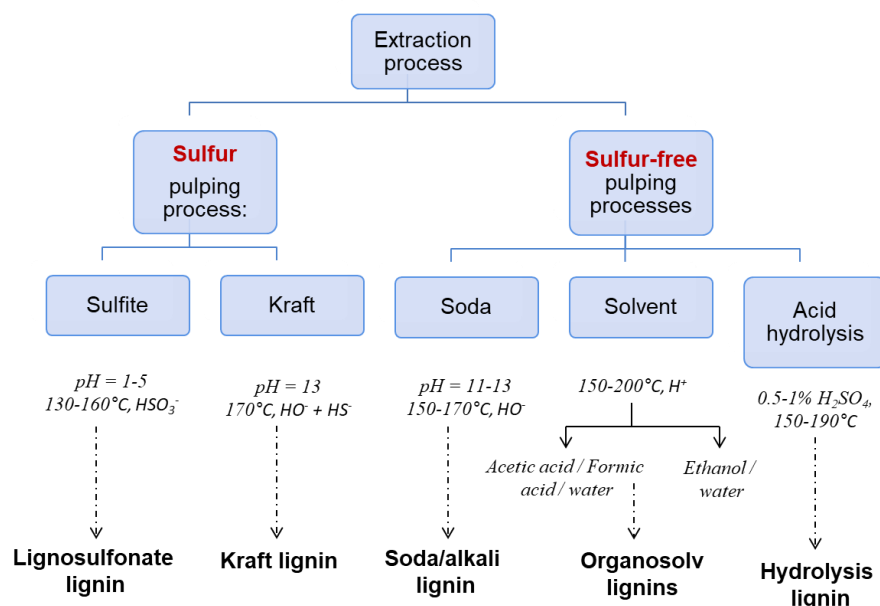


Figure 1.5. Pulping processes and corresponding lignins.

In conventional kraft pulp mills, this dissolved lignin is predominantly burned in the recovery boiler to regenerate the inorganic pulping chemicals and to produce steam and electricity for the mill's internal energy needs. As such, lignin plays a critical role in closing the chemical loop and maintaining the energy balance within the mill. However, when the mill produces excess energy or when boiler capacity becomes a limiting factor, a portion of this surplus kraft lignin can be selectively recovered for value-added applications.

The lignin obtained from this process is referred to as kraft lignin. It is characterized by a relatively high content of phenolic hydroxyl groups, extensive C–C condensed structures, and ash impurities, especially sulfur, introduced during the cooking process. Due to the cleavage of ether bonds and repolymerization under harsh conditions, kraft lignin is chemically distinct from native lignin.

Extraction of kraft lignin from black liquor is commonly achieved through acid precipitation, using carbon dioxide (CO₂) to lower the pH to ~9–10 (partial precipitation), followed by sulfuric acid (H₂SO₄) to reach pH <3 (full precipitation). Alternatively, membrane ultrafiltration can be applied to separate lignin without altering the liquor pH. Both methods yield a solid lignin fraction that can be used in the development of resins, carbon fibers, dispersants, and composite materials.

Globally, kraft pulp production is dominated by a few key regions and corporations with access to large, sustainable forest resources. The largest producers of softwood kraft pulp are primarily located in North America and Northern Europe, where coniferous forests are abundant. Leading companies include West Fraser, International Paper, and Domtar in Canada and the United States, and Södra, Stora Enso, and Metsä Fibre in Sweden.

and Finland. These companies operate modern mills that produce high-strength softwood kraft pulp used extensively in packaging, hygiene products, and specialty papers.

In contrast, hardwood kraft pulp production is concentrated in regions with fast-growing plantation species, particularly eucalyptus. Major producers include Suzano and Klabin in Brazil, APRIL and Asia Pulp & Paper (APP) in Indonesia and China, and Ence in Spain. Portugal is also a significant European producer, where The Navigator Company leads with large-scale, efficient mills based on eucalyptus globulus. These operations supply high-quality bleached hardwood kraft pulp (BEKP) to the global market and are actively involved in energy self-sufficiency and biorefinery development.

Together, these global players not only supply the majority of the world's kraft pulp but also generate vast quantities of black liquor, making them key stakeholders in the development of kraft lignin valorization strategies.

Importantly, only a portion of the lignin can be sustainably extracted from the kraft process. The major share must remain in the system to support chemical recovery and energy generation. Therefore, effective lignin valorization strategies must be integrated with mill operation constraints to avoid disrupting the recovery cycle.

Sulfite Process

In contrast to the strongly alkaline kraft process, the sulfite pulping process is conducted under acidic to neutral conditions, using sulfurous acid (H_2SO_3) in combination with bisulfite salts of various cations, such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), or ammonium (NH_4^+) (Sjöström 1981; Vishtal and Kraslawski, 2011). This cooking process is typically performed at temperatures of 130–160 °C over a period of 4–8 hours. During this time, the lignin undergoes extensive sulfonation reactions, leading to the introduction of sulfonic acid ($-\text{SO}_3\text{H}$) groups predominantly at the α -carbon of the side chains. As a result, the lignin becomes highly water-soluble and exhibits polyelectrolyte behavior, forming what is known as lignosulfonates.

Lignosulfonates are the primary lignin fraction obtained from the sulfite process. They are recovered directly from the spent sulfite liquor (SSL), which is the by-product of pulping. Due to their solubility, lignosulfonates do not precipitate easily, and separation usually involves ultrafiltration, precipitation by alcohols or acidification, and subsequent drying. The recovery of pulping chemicals from the sulfite process is more complex and less efficient than in the kraft process. However, some mills combust the organic material in the spent liquor to recover energy and partially regenerate chemicals like SO_2 and base via wet scrubbing of flue gases, often using lime-based processes.

While most kraft lignin is still used internally as an energy source, a significant portion of lignosulfonates is commercialized. Lignosulfonates are produced in millions of tons annually and used in a wide range of applications owing to their surface-active properties,

moderate molecular weights, and abundant functional groups (carboxylic, hydroxyl, sulfonic).

In addition to their widespread use as dispersants, binders, emulsifiers, and dust suppressants, lignosulfonates are also used as feedstock for the production of vanillin. This is one of the few examples of a successful commercial-scale conversion of technical lignin into a fine chemical. Vanillin is traditionally synthesized via oxidative depolymerization of lignosulfonates using oxygen or other oxidants under alkaline conditions.

Although the production of vanillin from lignin has declined in favor of petroleum-based or biosynthetic routes in recent years, Borregaard (Norway) continues to operate a commercial process that produces vanillin from softwood lignosulfonates, offering it as a bio-based alternative to synthetic vanillin. This pathway highlights the potential of sulfonated lignins not only as functional additives but also as precursors to aromatic fine chemicals.

Despite their broad utility, lignosulfonates have some limitations. Their relatively high sulfur content and structural heterogeneity can hinder their incorporation into high-performance polymer systems. Still, ongoing research explores their chemical modification to enhance compatibility with synthetic polymers, enable their use in adhesives, and improve their reactivity for conversion into value-added products.

Additionally, the combustion of lignosulfonate-containing residues remains a viable energy recovery route, contributing to on-site energy demands in integrated pulp mills. This dual role—energy and material—makes lignosulfonates a critical intermediate in the biorefinery model aiming for the full valorization of lignocellulosic biomass.

Sulfite pulping is a less common chemical pulping method today, but it remains important for the production of lignosulfonates (LS), widely used in industrial applications. The leading global producer of lignosulfonates is Borregaard AS (Norway), which operates an integrated biorefinery in Sarpsborg, producing sulfite pulp and a wide range of specialty lignosulfonate products marketed under the "Borresperse" and "Vanillex" brands. Other notable producers include Sappi (South Africa and Germany), Lignotech USA (a joint venture between Borregaard and Georgia-Pacific), Rayonier Advanced Materials (RYAM) in Canada, and Domsjö Fabriker in Sweden (part of Aditya Birla Group).

Although softwood (especially spruce) has historically been the dominant raw material in sulfite pulping—resulting in lignosulfonates rich in guaiacyl (G) units—the process can also be applied to hardwoods and non-wood biomass. The choice of feedstock influences the structure and molecular weight distribution of the resulting LS, and some producers use mixed hardwood-softwood blends to tailor product properties. However, softwood remains preferred for high-performance applications due to the favorable characteristics of its lignin in sulfonation and downstream functionality.

2. Sulfur-Free Processes

In recent years, sulfur-free processes have gained attention, particularly for applications where low sulfur content or chemical reactivity is important. These methods produce lignins with fewer structural modifications compared to sulfur-rich processes.

Soda Process

The soda pulping process is a sulfur-free chemical method for delignification that uses only sodium hydroxide (NaOH) under strongly alkaline conditions ($\text{pH} > 12$). Delignification is typically carried out at temperatures ranging from 150 to 170 °C and pressures of 0.5–1.0 MPa, depending on the feedstock and target pulp quality. The absence of sulfur in the cooking liquor differentiates this method from kraft and sulfite pulping and makes it especially attractive for applications that are sensitive to sulfur contamination, such as in polymer synthesis or catalytic reactions (Vishtal and Kraslawski, 2011).

The soda process is particularly suited for non-wood biomass, including agricultural residues (e.g., wheat and rice straw, sugarcane bagasse), flax, kenaf, jute, and other annual plants. These raw materials are abundant and renewable but often contain high levels of silica (in grasses) and nitrogenous compounds (in leaves and some husks), which present challenges for conventional chemical recovery systems. As a result, soda pulping is more common in small-scale or semi-integrated mills, especially in regions with limited access to softwood or hardwood forests.

The lignin obtained from this process is known as soda lignin. It is sulfur-free, which is a significant advantage over kraft and lignosulfonate lignins for downstream applications requiring high purity or compatibility with sensitive catalysts. Structurally, soda lignin is considered closer to native lignin than kraft lignin, as it undergoes fewer condensation reactions due to milder cooking conditions. However, it may still be chemically modified to some extent and often contains impurities such as:

- silica, derived from the plant matrix of grasses and cereals,
- nitrogen-containing residues, especially from non-wood feedstocks,
- ash, depending on the cleaning and filtration steps.

Soda lignin generally has a moderate molecular weight (1,000–3,000 Da) and lower polydispersity compared to kraft or hydrolysis lignins. Its low sulfur content, good reactivity (due to the presence of phenolic hydroxyls), and relatively clean composition make it suitable for use in phenolic resins, polyurethane foams, thermoset plastics, and even animal nutrition products, where biocompatibility and low toxicity are essential.

In terms of industrial production, soda pulping is operated by several companies worldwide. Examples include:

- GreenValue Enterprises LLC – a U.S.-based company offering Green Value lignins derived from soda processes, targeting applications in polymers and coatings,
- GranBio (Brazil) – known for its work on non-wood biomass valorization, including lignin extraction technologies,

- UPM (Finland) and Stora Enso have also explored soda lignin in the context of biorefinery integration for straw and agricultural by-products, though primarily at the pilot scale,
- wheat straw pulp mills in China and India, use soda pulping and sometimes recover lignin for local value chains, though often without formal branding.

Despite its advantages, commercial recovery of soda lignin is still limited due to underdeveloped recovery infrastructure, especially in small mills. Nevertheless, as biorefinery concepts advance, soda lignin is gaining attention as a valuable co-product that can be recovered, purified, and upgraded into higher-value materials—especially in sulfur-sensitive or green chemistry applications.

Organosolv Process

The organosolv pulping process is a sulfur-free delignification method that uses organic solvents—typically ethanol, methanol, acetic acid, or formic acid—mixed with water (and sometimes acid or alkaline catalysts) to extract lignin from lignocellulosic biomass. This process is carried out at temperatures of 140–200 °C, with pressures depending on the solvent volatility. Organosolv pulping allows for the selective solubilization of lignin while leaving behind a cellulose-rich pulp. Due to the absence of sulfur and the relatively mild chemical conditions, the lignin recovered—known as organosolv lignin—is considered one of the most "native-like" technical lignins available at scale (Sannigrahi et al., 2009; Hage et al., 2009).

Organosolv lignin typically has:

- low ash and sulfur content (usually <0.1%),
- low to moderate molecular weight (500–5,000 Da),
- high chemical purity,
- a relatively high proportion of β -O-4 linkages, depending on the process severity,
- good solubility in organic solvents but poor solubility in water.

These properties make organosolv lignin attractive for use in high-performance materials, thermosetting resins, bio-based adhesives, and carbon fibers. However, large-scale commercialization has faced technical and economic challenges.

Several companies and initiatives have attempted to commercialize organosolv processes and lignin:

- Alcell Process (Canada): One of the most well-known organosolv processes, developed by Repap Enterprises Inc. in the 1980s–1990s. It used aqueous ethanol under acidic conditions to extract lignin from hardwoods (mainly poplar and birch). The process reached the pilot and demonstration scale, and the lignin—called Alcell lignin—was noted for its high purity and reactivity. However, the project was discontinued due to economic constraints, particularly the high costs associated with solvent recovery and scaling up the pulping system.

- Lignol Innovations (Canada): A spin-off from the Alcell concept, Lignol aimed to produce ethanol and organosolv lignin from hardwood biomass. It operated a pilot plant in British Columbia and explored markets for functionalized lignins in polyurethanes and phenolic resins. Despite promising results, Lignol suspended operations in the 2010s due to funding and scale-up issues.
- Chempolis (Finland): Developed a proprietary formic acid-based organosolv process called Formico. Their biorefinery concept allows for the co-production of clean cellulose, hemicellulose-derived sugars, and organosolv lignin. Chempolis has partnered with industries in India and China to implement pilot-scale and semi-commercial plants.
- AVAP® Process (American Process Inc., USA): Uses a mixture of ethanol and sulfur dioxide in a unique organosolv-sulfite hybrid process to fractionate biomass. The lignin produced is of high purity and suitable for thermoplastic blends and carbon applications. Pilot-scale demonstrations have been conducted in the U.S. and Europe.

Despite its appealing properties, organosolv lignin has not yet achieved widespread industrial use. The main challenges include:

- high capital and operating costs associated with solvent handling, recovery, and recycling,
- corrosion and material compatibility issues due to organic acids and elevated temperatures,
- process integration difficulties with existing pulp mills or ethanol biorefineries,
- low yield and energy efficiency compared to kraft or sulfite pulping,
- market uncertainty around large-scale applications for high-purity lignin,
- limited experience and technical readiness level (TRL) for large-scale continuous operation.

In addition to lignin-related hurdles, another major limitation lies in the quality and marketability of the cellulose fibers produced by organosolv pulping. Unlike kraft pulp, organosolv pulp generally exhibits lower fiber strength, making it less suitable for conventional paper-making. To improve the economics of the process, there is growing interest in diversifying cellulose applications—for example, using it to produce nanocellulose, cellulose esters, or fermentable sugars. Likewise, hemicellulose-derived sugars can be converted into platform chemicals like furfural or xylitol.

Ultimately, to make organosolv biorefineries economically feasible, it is essential to valorize all three biomass fractions—lignin, cellulose, and hemicellulose—in an integrated manner.

Acid hydrolysis processes

Acid hydrolysis is one of the oldest and most established chemical methods for converting lignocellulosic biomass into fermentable sugars, which can be further processed into

bioethanol and other sugar-based platform chemicals. In this process, dilute mineral acids, most commonly sulfuric acid (H_2SO_4) or occasionally hydrochloric acid (HCl), are used to hydrolyze cellulose and hemicellulose at elevated temperatures (typically 100–200 °C) and moderate pressure. The residual solid material, acid hydrolysis lignin (AHL), is separated from the hydrolysate and considered a by-product of limited reactivity (Rabinovich, 2014; Rabinovich et al., 2016).

The process proceeds in either batch or percolation mode, with hydrolysis times ranging from minutes to several hours. Acid hydrolysis is highly efficient in depolymerizing hemicellulose and crystalline cellulose into C5 and C6 sugars, which can then be fermented to ethanol, xylitol, furfural, or other bio-based chemicals. In modern biorefinery concepts, these sugars serve as intermediates for a variety of renewable products.

While widely practiced in the past, acid hydrolysis has not yet been commercialized at a large scale in today's second-generation biorefineries. The main reasons are its corrosive nature, energy intensity, and the formation of inhibitory compounds (e.g., furfural, HMF, organic acids) that limit microbial fermentation. However, research and pilot-scale activities continue, particularly in efforts to optimize sugar yields, reduce degradation products, and integrate downstream detoxification and valorization strategies.

Current efforts focus on:

- integrated hydrolysis–fermentation systems with improved acid recovery,
- use of continuous reactors with short residence times to reduce by-product formation,
- exploring acid hydrolysis as a pretreatment before enzymatic hydrolysis to improve sugar accessibility,
- investigating catalytic or two-stage hydrolysis schemes to separate hemicellulose and cellulose fractions more selectively.

Notable ongoing projects include academic and industrial collaborations in Europe, China, and Brazil, where acid-catalyzed pretreatments are combined with enzymatic saccharification or fermentation to ethanol, isobutanol, or organic acids. Companies such as GranBio (Brazil) and Beta Renewables (Italy, formerly) have evaluated dilute acid systems as part of hybrid process chains, though not exclusively relying on them.

The lignin fraction that remains after acid hydrolysis is known as acid hydrolysis lignin (AHL). This lignin is often highly condensed, with extensive C–C crosslinking, low solubility, and reduced reactivity due to harsh reaction conditions. While challenging to valorize chemically, AHL has shown potential as a carbon-rich precursor for sorbents and carbon materials, thermoset composites and fillers, low-grade fuels or fuel briquettes, soil conditioners, and compost additives.

However, the commercialization of AHL applications remains limited, and in most pilot-scale hydrolysis setups, the focus is still primarily on maximizing sugar yield, while lignin handling remains a secondary concern.

In summary, while acid hydrolysis offers a powerful route to unlock fermentable sugars from biomass, it still faces significant economic and technical barriers for full-scale deployment. The future viability of this method may depend on integrated strategies that can simultaneously extract high yields of sugars while also upgrading or valorizing the lignin by-product sustainably and profitably.

Ionic Liquid-Based Extraction

Still largely experimental, this approach uses ionic liquids (e.g., imidazolium-based salts) to dissolve lignocellulose and fractionate lignin. Extraction can occur at 60–120 °C, depending on the ionic liquid. The ionic liquid lignin recovered is structurally similar to organosolv lignin but may contain ionic contaminants or require neutralization. Its reactivity and functional group availability make it a promising option for advanced applications, although not yet used at scale.

1.2.3 Comparative properties of technical lignins

Technical lignins (kraft, soda, organosolv, and lignosulfonate), generated through different pulping or biomass fractionation methods, have distinct chemical structures, molecular weights, solubility behaviors, and thermal characteristics (Table 1.2, adapted from Vishtal and Kraslawski, 2011). These differences strongly influence their suitability for materials applications.

Table 1.2. Properties of technical lignins.

Lignin type	Sulfur-lignins		Sulfur-free lignins	
Raw materials	 Softwood/ Hardwood	 Softwood/ Hardwood	 Annual plants	 Softwood/ Hardwood Annual plants
Solubility	Alkali	Organic solvents	Alkali	Wide range of organic solvents
Number-average molar mass (M_n , g/mol)	1000-3000	15,000-50,000	800-3000	500-5000
Polydispersity	2.5-3.5	6-8	2.5-3.5	1.5-2.5
T_g , °C	140-150	130	140	90-110

Kraft Lignin

Kraft lignin is one of the most widely available technical lignins, generated as a by-product during the kraft pulping of softwood biomass. In this process, sodium hydroxide and sodium sulfide break down the lignocellulosic structure, liberating lignin into the black

liquor phase. This process results in a lignin that is chemically modified compared to native lignin, featuring a high content of phenolic hydroxyl groups, condensed structures, and residual sulfur compounds. Although not the primary product, kraft lignin can be precipitated and recovered from black liquor - typically via acidification or carbonation - when valorization is desired.

Visually, kraft lignin appears dark brown, indicative of its high aromaticity and presence of chromophores resulting from condensation reactions. Despite being produced in a sulfur-based process, the residual sulfur content is relatively low, especially after washing and purification, which is beneficial for many materials applications.

In terms of solubility, kraft lignin is partially soluble in polar organic solvents like acetone and dimethyl sulfoxide, and more readily soluble in alkaline aqueous solutions due to the ionization of phenolic groups. However, its solubility is highly dependent on molecular weight and the degree of purification or fractionation.

The molecular weight of kraft lignin varies considerably depending on the source, isolation, and fractionation method. Reported number-average molecular weights (M_n) typically range from ~1.0 to 3.0 kDa, with polydispersity indices (PDI) from 2.5 to 3.5, indicating a broad molecular size distribution. This heterogeneity is a hallmark of technical lignins and can be addressed through solvent fractionation or ultrafiltration, yielding fractions with more defined sizes and properties.

Thermally, kraft lignin shows a high glass transition temperature (T_g) in the range of 140 °C to over 150 °C, due to crosslinked structure. The thermal degradation temperature (T_d) is typically between 300–400 °C, which reflects its excellent thermal stability and makes it well-suited for use in high-temperature processes.

Because of its abundant availability, low cost, structural rigidity, and thermal resistance, kraft lignin has attracted significant interest as a renewable feedstock for materials development. It is widely explored for use in:

- carbon fiber precursors, where high aromatic content and char yield are advantageous,
- thermosetting resins, replacing phenol in phenol-formaldehyde formulations,
- polyurethane foams, where it can act as a polyol substitute,
- polymer composites, as a reinforcing or reactive filler,
- binders for electrodes or coatings, when functionalized or blended.

Despite these promising applications, unfractionated kraft lignin's heterogeneity and limited solubility remain challenging. However, advances in fractionation, purification, and chemical modification continue to expand its utility in high-value applications.

Lignosulfonate

Lignosulfonates are sulfonated technical lignins generated as by-products of the sulfite pulping process, most commonly applied to softwood feedstocks. In this process, lignin

is solubilized through the action of sulfur dioxide and base (e.g., calcium, sodium, or magnesium), which introduces sulfonic acid groups onto the lignin backbone, dramatically enhancing its hydrophilicity.

These sulfonic groups make lignosulfonates the only technical lignin type that is readily soluble in water across a wide pH range. This solubility, combined with their dark brown appearance and high molecular heterogeneity, reflects their chemically modified and partially degraded structure. Lignosulfonates often contain residual carbohydrates and ash, and exhibit high sulfur content, which can be both a functional benefit (e.g., in dispersants) and a limitation for thermal or electronic applications.

In terms of molecular properties, lignosulfonates are among the highest-molecular-weight technical lignins, with M_n values ranging from 15 to over 50 kDa and PDI between 4.0 and 8.0, indicating a very broad molecular weight distribution. Their glass transition temperature (T_g) typically lies in the range of 130–160 °C, which is fairly high, but their thermal degradation temperature (T_d) is relatively low, ranging from 200 to 250 °C. This reduced thermal stability is largely attributed to the presence of ionic functional groups and non-lignin impurities, which start decomposing at lower temperatures.

Thanks to their water solubility, anionic character, and low cost, lignosulfonates are widely applied in:

- dispersants and deflocculants, especially in cement, gypsum, and dye formulations,
- concrete plasticizers, which improve workability and reduce the water content,
- binders and adhesives for pellets, feedstock, or bricks,
- emulsifiers in agrochemical and industrial formulations,
- dust suppression agents in mining and construction,
- precursors for vanillin production, through oxidative cleavage of the aromatic side chains.

Despite these versatile uses, lignosulfonates are less suitable for thermoset or hydrophobic polymer applications due to their high polarity, low thermal stability, and complex composition. Their strong affinity for water and the presence of sulfur groups can also interfere with some catalytic or electronic processes. However, chemical modification, purification, or depolymerization can unlock new possibilities, including lignin-based hydrogels, superplasticizers, or even functional coatings.

As one of the earliest forms of commercialized lignin, lignosulfonates remain a cornerstone in bulk applications, particularly in water-based systems. Their use in value-added products such as vanillin also demonstrates their potential in bio-aromatic platform chemicals, aligning with the goals of a circular and fossil-free chemical industry.

Soda Lignin

Soda lignin is a sulfur-free technical lignin generated during the alkaline pulping of non-wood biomass, such as grasses, wheat straw, sugarcane bagasse, or annual plants. In contrast

to kraft pulping, the soda process uses sodium hydroxide alone, without sulfur-based reagents, to break the bonds between lignin and carbohydrates. As a result, soda lignin tends to retain a less condensed structure and contains no sulfur, making it chemically cleaner and often more reactive in subsequent functionalization steps.

Visually, soda lignin appears reddish-brown, which reflects its moderate level of chromophores and lower extent of oxidative or condensative modifications compared to kraft lignin. Like other technical lignins, it is partially soluble in polar solvents, with solubility depending on its molecular weight and the degree of purification. In alkaline solutions, solubility improves due to the ionization of phenolic and carboxylic groups.

The number-average molecular weight (M_n) of soda lignin typically falls between 1.5 and 3.0 kDa, with a polydispersity index (PDI) ranging from 2.0 to 4.0, indicating a moderately broad distribution of molecular sizes. The glass transition temperature (T_g) ranges from 120 to 150 °C, which reflects a balance between molecular mobility and chain rigidity. Its thermal degradation temperature (T_d) spans from 280 to 380 °C, suggesting reasonable thermal stability—slightly lower than kraft lignin but still sufficient for many thermoset and thermoplastic applications.

Thanks to its sulfur-free nature, moderate molecular weight, and relatively low environmental impact, soda lignin is increasingly explored as a bio-based raw material in:

- adhesives and binders, which contribute to cohesion and mechanical strength,
- polyurethane foams, acting as a renewable polyol substitute,
- biodegradable packaging materials, due to their rigidity and antioxidant activity,
- lignin-based thermoplastics or films, particularly when blended with other bio-based polymers.

One important advantage of soda lignin is its origin from non-wood agricultural residues, making it particularly attractive from a circular bioeconomy perspective. However, its availability is more limited than kraft lignin on the global scale, and variability in source biomass can affect consistency in performance.

Organosolv Lignin

Organosolv lignin is a sulfur-free technical lignin obtained through organosolv pulping, a solvent-based biomass fractionation process that uses organic solvents (e.g., ethanol, methanol, acetone) and often acid catalysts (e.g., HCl or oxalic acid) to selectively extract lignin from hardwood or non-wood feedstocks. This mild, non-sulfur method disrupts the lignin–carbohydrate complex while minimizing condensation reactions, resulting in a lignin that is chemically closer to its native structure than kraft or soda lignins.

Organosolv lignins are typically light brown in color, which reflects their lower degree of chemical modification, minimal chromophore formation, and reduced impurity content. They are sulfur-free, making them ideal for applications sensitive to sulfur contamination. These lignins are soluble in polar organic solvents, such as acetone, ethanol, and dimethyl

sulfoxide, and exhibit good compatibility with hydrophobic polymer matrices—especially when properly functionalized.

Organosolv lignins have low to moderate molecular weights, with M_n typically ranging from 0.5 to 3.0 kDa and PDI between 1.5 and 3.0, reflecting relatively narrow molecular distributions compared to kraft or lignosulfonate lignins. Their glass transition temperatures (T_g) span 90–110 °C, while thermal degradation temperatures (T_d) typically range from 250 to 370 °C. These values indicate moderate thermal stability, suitable for most thermoplastic processing environments, especially after chemical modification.

Due to their high purity, low ash and carbohydrate content, and native-like aromatic structure, organosolv lignins are widely regarded as premium-grade lignins for advanced materials development. They are increasingly investigated and applied in:

- reactive building blocks for bio-aromatic chemicals and resins,
- bio-based coatings and barrier films, thanks to their purity and functionalizability,
- thermoplastics and biocomposites, where they serve as blendable fillers or compatibilizers,
- antioxidant additives, due to their phenolic hydroxyl groups,
- UV-blocking agents, for incorporation into transparent or flexible films,
- lignin nanoparticles, where narrow M_w distribution and purity enhance control over morphology and stability.

Organosolv lignin's main advantages lie in its chemical uniformity, structural regularity, and high functional group accessibility, making it highly suitable for downstream processing, chemical modification, and performance-critical applications. However, its limited commercial availability—due to relatively high processing costs and lower scale of organosolv pulping—currently restricts widespread industrial use.

Nonetheless, with increasing interest in biorefinery integration and green solvent systems, organosolv lignins are expected to play a growing role in next-generation bio-based materials, offering a versatile and cleaner alternative to traditional technical lignins.

1.3 Global market and forecasts

1.3.1 Lignin extraction technologies and commercial products

Black liquor, the by-product of the kraft pulping process, contains a significant portion of the original lignin in dissolved form, along with hemicellulose and spent cooking chemicals. Traditionally, this liquor is combusted in recovery boilers to generate energy and regenerate chemicals. However, increasing interest in lignin valorization has led to the development of technologies that selectively extract lignin from black liquor for use in high-value applications.

Several patented and commercialized extraction technologies have been developed to recover lignin in solid form:

LignoBoost®

Originally developed by Chalmers University of Technology and Innventia (Sweden), and now commercialized by Valmet. The process involves acidifying black liquor with carbon dioxide to precipitate lignin, followed by sulfuric acid treatment, filtration, washing, and drying. LignoBoost produces high-purity lignin and has been proven at a commercial scale, notably by Stora Enso at the Sunila Mill in Finland (Tomani, 2010).

LignoForce™

Developed by FPInnovations and NORAM (Canada) and commercialized by Domtar in the USA. This process includes a pre-oxidation step with oxygen to reduce sulfur emissions and improve filterability. It is used to produce BioChoice® lignin (Kouisni et al., 2016).

SILVA™ Process

Developed at Oregon State University, this process uses acidification and membrane filtration. It is still in the pilot stage and has not yet been commercialized.

Membrane Separation Technologies

These methods use ultrafiltration or nanofiltration membranes to isolate lignin without acidification. They offer continuous processing but face challenges like membrane fouling and high operational costs (Giummarella et al., 2016).

Several types of kraft lignins are now available on the market, mostly produced from softwood black liquor and extracted using the technologies described above. These lignins vary in molecular weight, ash and sulfur content, and solubility (Table 1.3). These lignins are increasingly used in phenolic resins, polyurethanes, dispersants, binders, battery materials, and as carbon precursors. Their appeal lies in their renewable origin, high phenolic content, and potential to replace petroleum-derived phenols in industrial applications.

Table 1.3. Commercial kraft lignins and their producers.

Brand Name	Company	Origin	Technology	Notes
Lineo®	Stora Enso (Finland)	Softwood (Sunila)	LignoBoost®	High-purity, low sulfur; used in resins, adhesives, carbon materials
BioChoice®	Domtar (USA/Canada)	Softwood (Plymouth)	LignoForce™	First commercial kraft lignin in North America
Indulin® AT	WestRock (USA)	Softwood	Proprietary	Benchmark kraft lignin; widely used in research

Wayagamack Lignin	Kruger Inc. (Canada)	Softwood	In-house (pilot)	High-purity; limited availability
Protobind®	Granbio (Brazil)	Eucalyptus (Hardwood)	Organosolv-related	Not kraft but marketed for similar uses

In addition to kraft lignins, several commercial lignins are produced through alternative delignification processes. These include lignosulfonates from the sulfite pulping process and soda and organosolv lignins, typically derived from non-wood biomass or specialized biorefinery operations. Although produced in smaller volumes than kraft lignins, these lignins are important for certain applications due to their distinct chemical and physical characteristics (Table 1.4).

Table 1.4. Selected commercial non-kraft lignins and their producers.

Brand Name	Company	Lignin Type	Feedstock	Applications
Borresperse®	Borregaard (Norway)	Lignosulfonate	Softwood	Dispersants, binders, vanillin production
Protobind®	GranBio (Brazil)	Organosolv	Hardwood (Eucalyptus)	Resins, coatings, carbon materials
Green Value Lignin™	GreenValue Enterprises (USA)	Soda	Agricultural residues	Polymers, composites
Hydrolysis lignin (generic)	Various (Russia, Belarus)	Acid hydrolysis	Wood/agro-residues	Fuel, soil improvers, carbon precursors

1.3.2 The worldwide lignin market and forecast

The global availability of technical lignin exceeds 100 million tonnes annually, yet only around 1.65 million tonnes are currently utilized in commercial markets. The largest share (~80%) is lignosulfonates derived from sulfite pulping, used primarily in construction, dispersants, animal feed, and chemical intermediates. Kraft lignin accounts for ~16% of the commercial lignin market and has experienced significant growth—production increased by 150% between 2014 and 2018, from 75,000 to 265,000 tonnes annually. Leading producers include Domtar, Stora Enso, and West Fraser, using technologies such as LignoBoost and LignoForce to extract lignin from black liquor (Dessbesell et al., 2020). The technical lignin market is projected to grow at a compound annual growth rate (CAGR) of around 7% through 2028. Lignosulfonates are expected to increase from 1.1 to 2.0 million tonnes, and kraft lignin could reach 2.5 million tonnes by 2025 under optimistic conditions (Dessbesell et al., 2020; Li and Takkellapati, 2018).

Emerging applications—particularly in intermediate-volume, intermediate-value markets—are considered the most feasible commercial entry points (Figure 1.6). These include phenol-formaldehyde (PF) resins, polyols for polyurethane foams, dispersants, and thermoplastics.

Lignin modification (e.g., depolymerization, oxypropylation) is often required to improve solubility, reactivity, and processability for these higher-value uses. In PF resin production, up to 50–75% substitution of petroleum-based phenol with lignin-derived alternatives has been demonstrated with no loss in performance (Dessbesell et al., 2020).

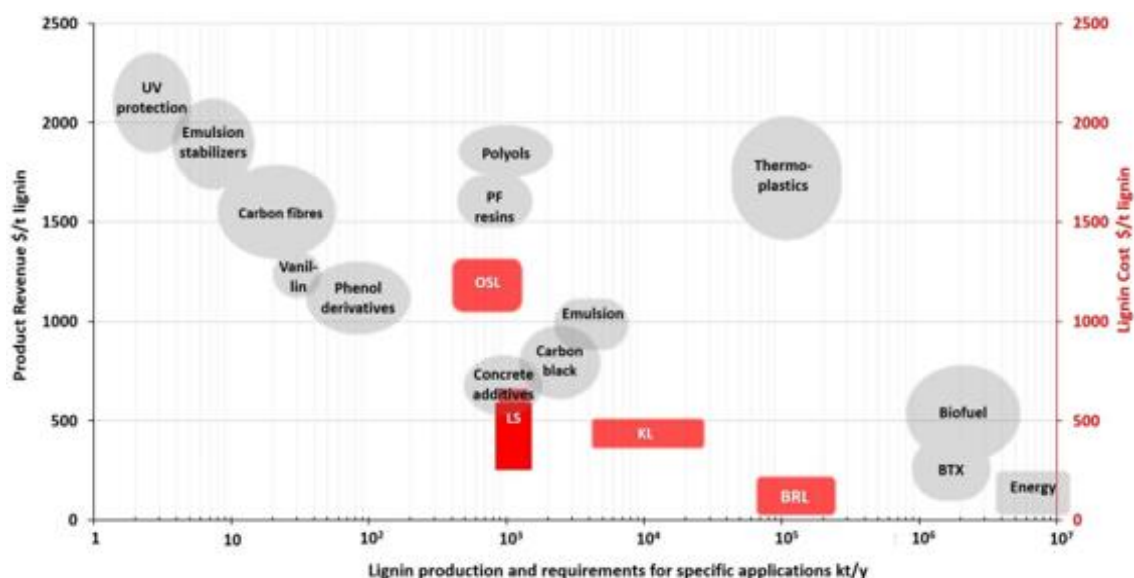


Figure 1.6. Evaluation of lignin market potentials based on publicly available information. Abbreviations: OSL – organosolv lignins, LS – liginosulfonates, KL – Kraft lignins, BRL – (crude) biorefinery lignins (adapted from Balakshin et al., 2021).

Lifecycle assessments (LCAs) have shown that lignin-based products frequently outperform fossil-based alternatives in terms of climate impact. Depending on methodological assumptions, greenhouse gas savings range from 5% to over 90%. For example, lignin-derived adipic acid can reduce emissions by 62–78% compared to fossil-based counterparts (Moretti et al., 2021).

Despite technological maturity in lignin extraction and upgrading, barriers remain in standardization, consistent quality, and downstream integration. A successful path forward is expected to involve phased commercialization, strategic partnerships, and alignment with high-demand sectors such as construction and bio-based chemicals. Short- and medium-term focus remains on phenols and polyols, while high-value applications like carbon fibers and aromatic compounds may play a larger role in the long term (Li and Takkellapati, 2018; Dessbesell et al., 2020).

1.4 Selected methods of lignin characterization

Lignin's suitability for use in polymer materials and composite systems is strongly dependent on its chemical and physical characteristics. Being an amorphous, heterogeneous macromolecule, lignin exhibits a wide variation in molecular weight, functional group content, and thermal behavior depending on its botanical origin and isolation method (Lin and Dence, 1992). Understanding and quantifying these properties is essential for designing lignin-based materials with predictable performance in composites, adhesives, coatings, foams, and films.

Key properties of lignin that affect its functionality in polymeric systems include:

- molecular weight and distribution: affects flow, processability, and mechanical strength,
- chemical structure and functional groups: determine reactivity and compatibility with other polymers; key groups include phenolic, aliphatic hydroxyl, methoxyl, and carboxylic acids,
- composition and purity: impurities such as carbohydrates, ash, and sulfur can hinder performance,
- thermal stability: critical for melt processing or high-temperature applications,
- glass transition temperature: affects mechanical behavior and phase compatibility,
- mechanical properties: moduli (Young's, storage/loss), elasticity, and strength dictate end-use performance,
- morphology and crystallinity: affect interfacial adhesion and dispersion in composites,
- physical properties: solubility, surface energy, and viscosity influence processability and formulation,
- decomposition behavior: rate and products determine suitability for thermal applications,
- special properties: antioxidant, antimicrobial, electrical, or magnetic properties offer functional opportunities.

1.4.1 Gel Permeation Chromatography

Gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC), is a widely used analytical technique for determining the molecular weight distribution of lignin. It provides key parameters such as number-average molecular weight (M_n), weight-average molecular weight (M_w), and the polydispersity index ($PDI=M_w/M_n$). These parameters are essential for evaluating the processability, compatibility, and mechanical performance of lignin-based materials in polymeric systems.

GPC separates molecules based on their hydrodynamic volume (related to size in solution). As the lignin sample passes through a column packed with porous gel, larger molecules elute first because they are excluded from entering the pores, while smaller molecules penetrate deeper and elute later. The retention time is then correlated with molecular weight using calibration standards—typically polystyrene standards, though they may not perfectly match lignin's structure and conformation.

Due to its heterogeneous and highly polar structure, lignin is often only partially soluble in common organic solvents, which complicates accurate GPC analysis. Therefore, chemical derivatization is commonly used to improve solubility and minimize intermolecular interactions (e.g., hydrogen bonding) that can skew results (Baumberger et al., 2007; Schlee et al., 2009).

Acetylation is the most common method, particularly for kraft and organosolv lignins. Acetylation masks free hydroxyl groups (aliphatic and phenolic) by converting them into acetate esters, increasing solubility in solvents such as tetrahydrofuran (THF) or dimethylformamide (DMF). Methylation is another route, often using diazomethane or iodomethane to convert hydroxyls into methyl ethers. This method is effective for retaining molecular structure, but may not fully suppress hydrogen bonding. Acetobromination is a powerful derivatization method primarily used for hydrophobic lignins such as kraft or organosolv types. It introduces bromoacetyl groups to block hydroxyls, improving solubility in organic solvents and facilitating GPC analysis.

The choice of solvent system depends on the lignin type and derivatization: acetylated or methylated lignins are typically analyzed in organic solvents like THF or DMF, whereas water-soluble lignosulfonates are analyzed in aqueous GPC systems, often using buffered solutions such as 0.1 M NaNO₃ or NaOH. In the case of lignosulfonates, derivatization is usually not required, but their polyelectrolyte nature demands careful control of ionic strength and pH to minimize column interactions and improve reproducibility. Since calibration with polystyrene standards may not accurately reflect lignin's structure, particularly for lignosulfonates, advanced detection methods such as multi-angle light scattering (MALS) are often used for more accurate molecular weight determination.

1.4.2 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is one of the most powerful and quantitative techniques for characterizing the functional group content in lignin, particularly various hydroxyl groups and carboxylic acids. The distribution and abundance of hydroxyl groups influence lignin's reactivity in chemical modifications such as esterification, etherification, and crosslinking. High phenolic OH content enhances antioxidant activity and reactivity toward formaldehyde or isocyanates (e.g., in phenolic resins or polyurethane foams). Aliphatic OHs are more suitable for polyol substitution.

The method is based on derivatization of lignin with a phosphorus-containing reagent, most commonly 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP), which reacts selectively with free hydroxyl and carboxyl groups. The phosphorus-tagged groups are then analyzed using nuclear magnetic resonance spectroscopy, where each type of functional group appears in a distinct chemical shift region of the ^{31}P spectrum. This allows for accurate quantification (typically in mmol/g lignin) of aliphatic OH, syringyl (S) and guaiacyl (G) phenolic OHs, p-hydroxyphenyl (p-H) OHs, condensed phenolic structures, and carboxylic acid groups (Granata and Argyropoulos, 1995).

In the spectra shown in Figure 1.7, which compare spruce (SL) and eucalyptus (HL) kraft lignins, clear differences in hydroxyl group distributions are observed. Aliphatic-OH signals appear around 150.5–145.5 ppm, with SL showing a higher intensity than HL, reflecting its higher aliphatic content. Syringyl OHs (S-OH) are typically observed around 143.5–142.0 ppm, while guaiacyl OHs (G-OH) span two regions: G-condensed OH between 141.5–140 ppm and G-non-condensed OH between 140–138 ppm. The p-H-type phenolic OHs show signals near 138–137 ppm, and carboxylic acid groups appear further downfield in the 135–133 ppm range. As expected, the HL spectrum (from eucalyptus) shows more intense signals for S-OH, characteristic of hardwood lignins, while SL (from spruce) is richer in G-OH and aliphatic OH, consistent with softwood lignin structures.

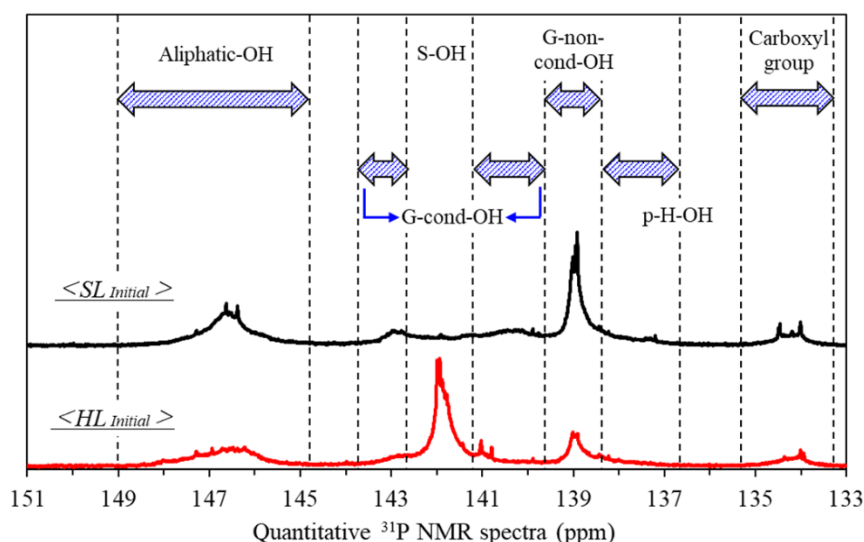


Figure 1.7. Example of ^{31}P NMR spectra for spruce (SL) and eucalyptus (HL) kraft lignin (adapted from Tagami, 2018).

Despite its high sensitivity and functional specificity, ^{31}P NMR also presents several important limitations that must be addressed to ensure accurate and reproducible results. The method requires careful sample preparation, including thorough drying under vacuum to remove residual moisture, and derivatization under strictly anhydrous

conditions to prevent side reactions with water, which can interfere with the phosphorus reagent—typically 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP). Accurate quantification further depends on the use of a reliable internal standard (e.g., cyclohexanol) and precisely weighed lignin samples. It is also critical to recognize that impurities in lignin, such as residual carbohydrates (e.g., hemicellulose, cellulose fragments) or polymeric degradation products, can contribute additional aliphatic hydroxyl signals, artificially inflating the measured OH content. Therefore, prior purification of the lignin (e.g., via solvent extraction or enzymatic hydrolysis) is strongly recommended before analysis. Additionally, since the functional group content is calculated relative to sample weight, the presence of non-organic residues such as ash or inorganic salts can distort the results by diluting the lignin content. As such, determining and correcting for ash content is advisable, particularly when analyzing technical lignins from kraft processes.

Despite these considerations, ^{31}P NMR remains the gold standard for quantitative hydroxyl group profiling in lignin, offering unmatched resolution between aliphatic, phenolic, and carboxylic functionalities. It is especially valuable for monitoring chemical modifications, comparing lignins from different botanical origins, or assessing structural changes after fractionation or processing.

Additionally, 2D-HSQC NMR is often used to identify interunit linkages (β -O-4, β -5, β - β) and residual carbohydrate impurities, aiding in structural elucidation.

1.5 Lignin upgrade

1.5.1 Fractionation of technical lignins: pathways to tailored properties

For many lignin-based applications, especially in polymer systems, it is crucial to work with lignin fractions that exhibit narrower molecular weight distributions and more consistent chemical properties. High polydispersity, variability in functional group content, and the presence of impurities often limit the performance and reproducibility of technical lignins. Fractionation techniques are therefore essential to isolate lignin fractions with targeted molecular weights (M_w) and tailored properties such as thermal stability, reactivity, solubility, and processability.

Solvent Fractionation

Solvent fractionation relies on the principle of differential solubility of lignin fragments in organic solvents with varying polarity, hydrogen-bonding capacity, and dispersion interactions. When lignin is exposed to a solvent, only fractions with compatible solubility parameters dissolve, allowing for sequential extraction of lignin populations with different molecular weights and chemical compositions. The method typically involves suspending lignin in a given solvent under mild conditions (room temperature

or slightly elevated, e.g., 40 °C), separating the soluble and insoluble fractions by filtration, and then recovering the solubilized lignin by evaporating the solvent and freeze-drying. The insoluble residue can be re-treated with another solvent, continuing the fractionation sequence.

A broad range of solvents has been tested historically, but for industrial relevance, solvent selection is limited by toxicity, boiling point, recyclability, and compliance with green chemistry principles. In the work by Duval et al. (2016), solvents like ethyl acetate, ethanol, methanol, acetone, and various short-chain alcohols were screened. The selected sequence, as shown in Figure 1.8 —EtOAc, EtOH, MeOH, and acetone—provided an efficient, reproducible protocol for fractionating kraft lignin into five fractions with low polydispersity ($PDI < 2$) and M_n values ranging from ~350 to ~6500 g/mol.

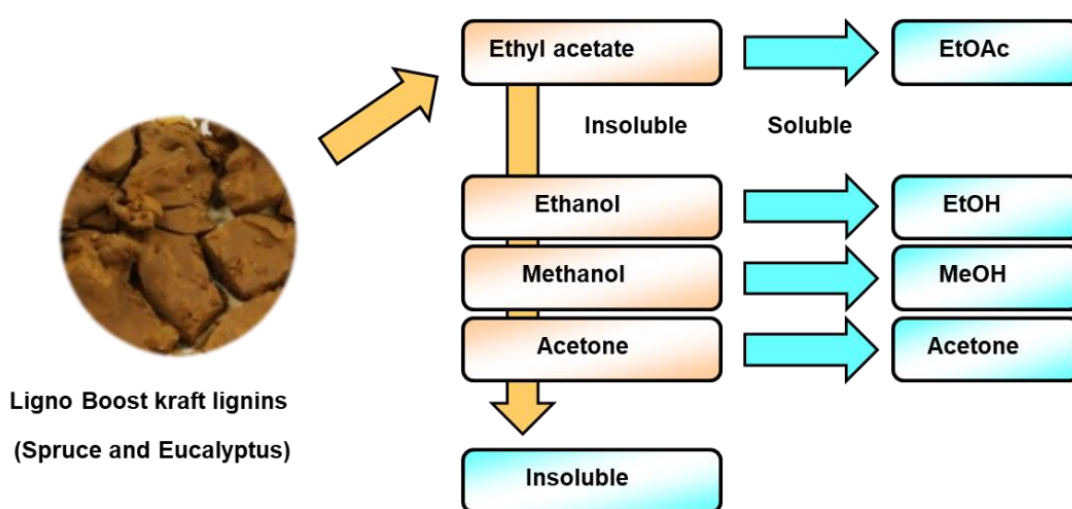


Figure 1.8. Solvent fractionation of lignin: based on differential solubility (adapted from Tagami, 2018).

The extraction power of the solvents correlated with their Hansen solubility parameters (HSPs), particularly the polarity parameter (δ_P), although HSP theory was not fully predictive. HSPs describe the solubility behavior of a substance based on dispersion, polar, and hydrogen bonding components. Low- M_w fractions were primarily recovered with EtOAc and EtOH, while higher- M_w lignin required MeOH and acetone. Each solvent selected a distinct M_w population, enabling tuning of properties such as thermal stability, reactivity, and purity. For example, the EtOAc-soluble fraction contained oligomeric phenolic compounds free of carbohydrate contamination, making it suitable for thermoset synthesis or antioxidant applications.

Solvent fractionation is thus a flexible, scalable approach that allows tailored separation of technical lignin into fractions with defined M_w , functionality, and purity—important parameters for downstream chemical modification or integration into polymer systems.

Ionic Liquid Fractionation

Ionic liquid (IL) fractionation uses designer solvents—salts in a liquid state at or near room temperature—to selectively dissolve lignin based on its molecular structure, polarity, and hydrogen-bonding ability. ILs can disrupt lignin's supramolecular interactions and selectively solubilize fractions with specific structural or molecular weight characteristics, enabling precise tuning of lignin properties. The method involves dissolving lignin in a chosen IL or IL mixture under a controlled temperature (typically 60–120 °C), followed by selective precipitation of fractions through the addition of antisolvents (e.g., water or ethanol) or sequential extraction with different ILs. The solubilized lignin fractions are then isolated by filtration or centrifugation, followed by washing and drying.

Different ILs offer unique solvation profiles depending on their cation-anion combinations. Common cations include imidazolium-based structures (e.g., [Bmim]⁺), and anions such as chloride, acetate, dimethylphosphate, or tosylate are often used. The choice of IL controls the selectivity of the extraction and the degree of lignin dissolution or swelling. For example, in the study by Lauberts et al. (2016), alder soda lignin was fractionated using [Bmim]Cl, [Bmim]Me₂PO₄, [Bmim]OAc, and [Bmim]OTs. The obtained fractions had reduced polydispersity and distinct structural profiles compared to those obtained with traditional solvents (e.g., dichloromethane, methanol, n-propanol). IL-derived fractions showed improved purity, lower M_w dispersity, and enhanced reactivity.

IL fractionation provides precise molecular-level control but requires careful consideration of IL cost, recyclability, and purification. While not yet widely adopted industrially, IL systems hold significant potential for high-value lignin valorization where narrow M_w distribution and structural uniformity are required.

Ultrafiltration

Ultrafiltration (UF) is a membrane-based separation technique that enables the fractionation of lignin according to molecular size. The principle is based on the selective retention of macromolecules above a defined molecular weight cut-off (MWCO), while smaller fragments pass through the membrane as permeate. In cross-flow UF systems, the feed solution flows tangentially to the membrane surface, minimizing fouling and allowing continuous operation (Figure 1.9).

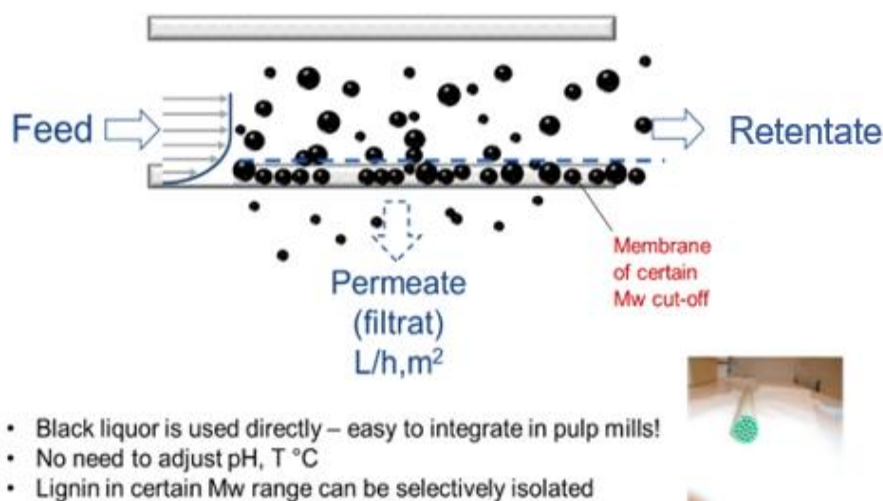


Figure 1.9. Membrane filtration: fractionation of lignin-based on molecular size.

Membrane pore sizes typically range from 1 to 100 kDa, making UF particularly suitable for separating low- and high-M_w lignin components from black liquor or other lignin-containing streams.

Materials used in lignin ultrafiltration include ceramic membranes (e.g., TiO₂ or ZrO₂-based) and polymeric membranes (e.g., regenerated cellulose), chosen for their chemical resistance and mechanical stability under alkaline and high-temperature conditions. Operating parameters such as temperature (typically 40–65 °C), transmembrane pressure (1–4 bar), and flow rate are optimized to balance flux, selectivity, and membrane longevity. UF can be implemented at lab, pilot, or industrial scale and does not require lignin precipitation or pH adjustment, making it compatible with kraft mill conditions.

In the study by Sevastyanova et al. (2014), UF was applied to kraft black liquor using a stepwise setup with 1, 5, and 10 kDa MWCO membranes. This allowed the isolation of seven lignin fractions with distinct Mw and properties. The process yielded fractions with reduced polydispersity, tunable T_g (70–170 °C), and differentiated rheological and thermal behavior—demonstrating the suitability of UF for producing application-specific lignins.

Fractionation of lignin by solvent systems, ionic liquids, or ultrafiltration enables control over key material parameters such as M_w, PDI, hydroxyl content, and thermal behavior. These parameters directly affect the suitability of lignin for various applications—ranging from thermoplastics and carbon fibers to antioxidants and adhesives. Among the methods reviewed, ultrafiltration stands out as a robust, scalable approach for obtaining defined fractions with tunable thermal and chemical properties, critical for performance in lignin-based polymer systems.

1.5.2 Chemical modification of lignin

As illustrated in Figure 1.10 (Laurichesse and Avérous, 2014), unmodified technical lignins—such as Kraft, Lignosulfonate, Organosolv, and Soda—can be directly used as fillers, additives, antioxidants, UV stabilizers, surfactants, or components in composites and polymer blends, either as crude lignins or after fractionation.

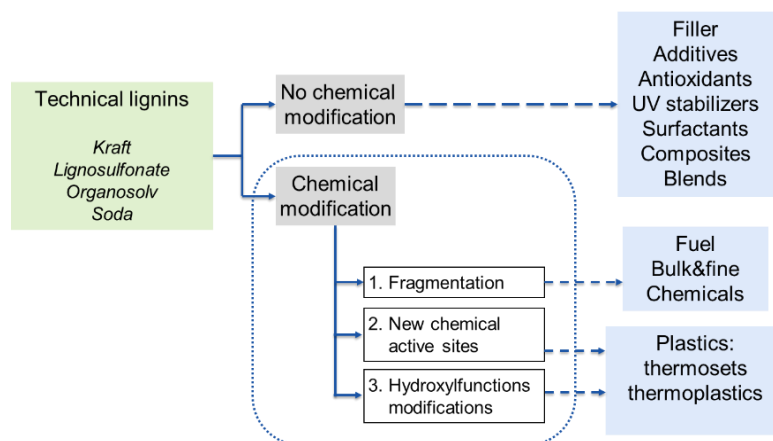


Figure 1.10. Uses of lignin with or without chemical modification (adapted from Laurichesse et al., 2014).

These applications leverage lignin’s intrinsic properties such as aromaticity, thermal stability, and antioxidant activity, often without the need for extensive processing.

However, the full valorization of lignin typically requires chemical modification to tailor its structure, reactivity, or compatibility with other materials. Through targeted chemical transformations, lignin can be converted into fuels, bulk, and fine chemicals, or serve as a reactive component in thermoset and thermoplastic formulations. Such modifications significantly broaden its application scope, enabling the development of value-added and performance-specific products.

In the following sections of this chapter, we will explore the main chemical modification strategies used to unlock lignin’s potential in advanced material and chemical applications.

Lignin is a highly functional, complex aromatic polymer that offers significant potential for the production of bio-based chemicals and materials. To enhance its reactivity and widen its industrial applicability, lignin is frequently subjected to chemical modification. According to Laurichesse and Avérous (2014) two primary strategies have been developed to modify lignin chemically: (1) the creation of new chemical active sites, and (2) the functionalization of existing hydroxyl groups. These approaches are summarized in Figure 1.10 and are explored in detail below.

Creation of New Chemical Active Sites

This strategy focuses on introducing new reactive functionalities into the lignin structure, thereby expanding its chemical reactivity and allowing the development of tailored lignin-based macromolecules and materials (Figure 1.11).

Several types of reactions are used for this purpose:

- amination: involves introducing amino groups ($-\text{NH}_2$) via reactions such as the Mannich reaction, often in the presence of formaldehyde and amines; this enhances the cationic character of lignin and its reactivity with other polymers,
- sulfonation and sulfomethylation: these introduce sulfonic acid groups, improving lignin's solubility and surface activity, and are particularly useful in dispersants and surfactants,
- halogenation (e.g., Br, Cl, I): introduces halogens to increase reactivity or impart flame-retardant properties,
- nitration: addition of nitro groups ($-\text{NO}_2$), enhancing electron-withdrawing capacity and reactivity,
- alkylation/dealkylation: grafting of alkyl chains or removal of methoxyl groups can improve compatibility with hydrophobic polymers or generate active phenol sites,
- hydroxyalkylation: often involves reaction with formaldehyde or glyoxal to introduce hydroxymethyl groups, increasing the number of sites for condensation reactions in resin synthesis.

These modifications target specific positions on the aromatic rings or side chains, creating a more reactive and versatile lignin structure suited for subsequent chemical reactions or direct incorporation into polymers.

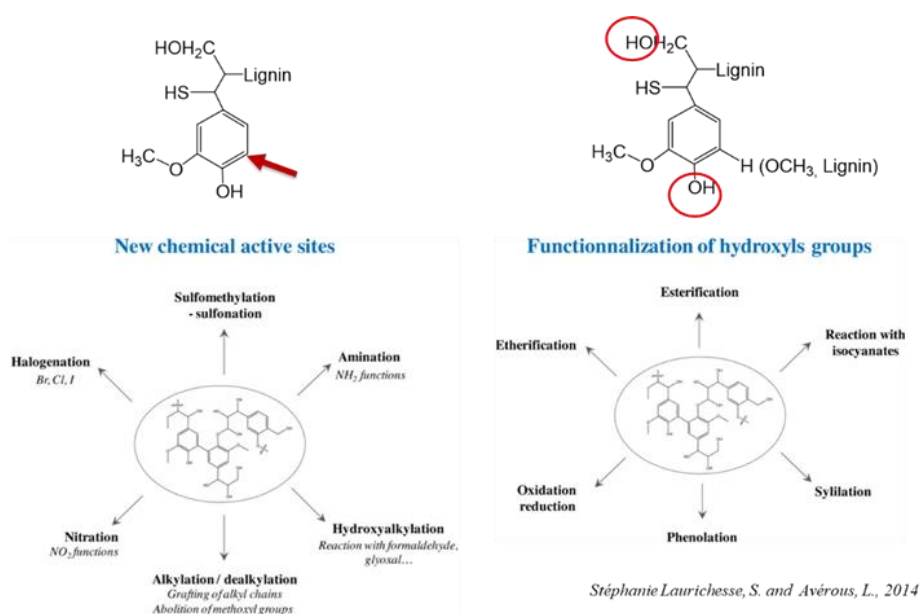


Figure 1.11. Illustration of two main approaches in the chemical modification of lignin macromolecule: through the functionalization of hydroxyl groups and the introduction of new chemical sites into aromatic ring of phenylpropanoid unit (PPU).

Functionalization of Hydroxyl Groups

Lignin is naturally rich in both aliphatic and phenolic hydroxyl groups. Functionalization of these sites enhances lignin's solubility, processability, and compatibility with other polymers, particularly in the synthesis of thermosets and thermoplastics. Common approaches include:

- **esterification:** converts hydroxyls into esters, often improving hydrophobicity and compatibility with synthetic polymers,
- **etherification:** formation of ether linkages through reaction with epoxides or alkyl halides, reducing polarity and improving thermal processability,
- **phenolation:** introduction of additional phenol groups, increasing reactivity towards formaldehyde and enhancing bonding in phenolic resins,
- **urethanization** (reaction with isocyanates): this forms urethane linkages, enabling lignin use in polyurethanes and foams,
- **oxidation/reduction:** modifies the oxidation state of hydroxyls to aldehydes or ketones (and vice versa), enabling further derivatization,
- **silylation:** replacement of hydroxyl hydrogens with silyl groups, improving thermal stability and solubility in organic solvents.

These functionalizations not only increase lignin's chemical versatility but also allow for controlled integration into polymer matrices, enabling the development of high-performance bio-based materials. The chemical modification of lignin through the formation of new active sites or the functionalization of hydroxyl groups is critical to unlocking its potential in advanced applications. Each method offers unique benefits depending on the desired end use, whether for surfactants, adhesives, resins, or bioplastic

Acknowledgement:

We gratefully acknowledge Dr. Alina Nikolaichuk for her valuable assistance with the literature collection and review for chapter 1.

References:

- Balakshin, M.Y., Capanema, E.A., Sulaeva, I., Schlee, P., Huang, Z., Feng, M., Borghei, M., Rojas, O.J., Potthast, A., Rosenau, T. (2021). New opportunities in the valorization of technical lignins. *ChemSusChem*. 14, 1016–1036. <https://doi.org/10.1002/cssc.202002553>.
- Baumberger, S., Abaecherli, A., Fasching, M., Gellerstedt, G., Gosselink, R., Hortling, B., Li, J., Saake, B., de Jong, E. (2007). Molar mass determination of lignins by size-exclusion chromatography: towards standardisation of the method. *Holzforschung*. 61, 459–468. <https://doi.org/10.1515/HF.2007.067>.
- Baumberger, S., Dole, P., Lapierre, C. (2007). Using size exclusion chromatography to probe the molecular characteristics of lignins. *Holzforschung*. 61, 286–289. <https://doi.org/10.1515/HF.2007.064>.

- Björkman, A. (1954). Isolation of lignin from finely divided wood with neutral solvents. *Nature*. 174, 1057–1058.
- Björkman, A. (1956). Studies on finely divided wood. Part 1. Extraction of lignin with neutral solvents. *Svensk Papperstidn.* 59, 477–485.
- Braun, K. (1947). Lignin and its chemical structure. *JACS*. 69, 546–553.
- Brunow, G. (2001). Methods to reveal the structure of lignin. In: Hon, D. N.-S., Shiraishi, N. (Eds.), *Wood and Cellulosic Chemistry* (2nd ed., pp. 89–196). Marcel Dekker, New York.
- Dessbesell, L., Paleologou, M., Leitch, M., Pulkki, R., Xu, C. (2020). Global lignin supply overview and kraft lignin potential as an alternative for petroleum-based polymers. *Renew. Sustain Energy Rev.* 123, 109768. <https://doi.org/10.1016/j.rser.2020.109768>.
- Duval, A., Vilaplana, F., Crestini, C., Lawoko, M. (2016). Solvent screening for the fractionation of industrial kraft lignin. *Holzforschung*. 70, 11–20. <https://doi.org/10.1515/hf-2014-0346>.
- El Hage, R., Brosse, N., Chrusciel, L., Sanchez, C., Sannigrahi, P., Ragauskas, A. (2009). Characterization of milled wood lignin and ethanol organosolv lignin from miscanthus. *Polym. Degrad. Stabil.* 94, 1632–1638.
- Erickson, M., Larsson, S., Miksche, G.E. (1973). Gas-chromatographische analyse von ligninoxidationsprodukten. VII. Zur zstruktur des lignins der fichte. *Acta Chem. Scand.* 27, 903–904.
- Giummarella, N., Lindgren, C., Lindström, M.E., Henriksson, G. (2016). Lignin prepared by ultrafiltration of black liquor: Investigation of solubility, viscosity, and ash content. *Biores.* 11, 3494–3510.
- Granata, A., Argyropoulos, D. S. (1995). 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a reagent for the accurate determination of the uncondensed and condensed phenolic moieties in lignins. *J. Agric Food Chem.* 43, 1538–1544. <https://doi.org/10.1021/jf00054a023>.
- Kouisni, L., Gagné, A., Maki, K., Holt-Hindle, P., Paleologou, M. (2016). LignoForce system for the recovery of lignin from black liquor: feedstock options, odor profile, and product Characterization. *ACS Sustain. Chem. Eng.* 4, 5152–5159. <https://doi.org/10.1021/acssuschemeng.6b00907>.
- Lauberts, M., Viksna, A., Dobeles, G., Sevastyanova, O., Andersone, A. (2016). Fractionation of technical lignin with ionic liquids as a method for improving purity and antioxidant activity. *Ind. Crops Prod.* 92, 220–225. <https://doi.org/10.1016/j.indcrop.2016.08.034>.
- Laurichesse, S., Avérous, L. (2014). Chemical modification of lignins: Towards biobased polymers. *Prog. Polym. Sci.* 39, 1266–1290. <https://doi.org/10.1016/j.progpolymsci.2013.11.004>.
- Li, T., Takkellapati, S. (2018). The current and emerging sources of technical lignins and their applications. *Biofpr.* 12, 756–787. <https://doi.org/10.1002/bbb.1913>.
- Lin, S.Y., Dence, C. W. (Eds.). (1992). *Methods in Lignin Chemistry*. Springer-Verlag, Berlin, Heidelberg. <https://doi.org/10.1007/978-3-642-74065-7>.

- Moretti, C., Corona, B., Hoefnagels, R., Vural-Gürsel, I., Gosselink, R., Junginger, M. (2021). Review of life cycle assessments of lignin and derived products: lessons learned. *Sci. Total Environ.* 770, 144656. <https://doi.org/10.1016/j.scitotenv.2020.144656>.
- Nimz, H.H. (1974). Beech lignin—proposal of a constitutional scheme. *Angew. Chem., Int. Ed.* 13, 313–321. <https://doi.org/10.1002/anie.197403131>.
- Rabinovich, M.L. (2014). Lignin by-products of soviet hydrolysis industry: resources, characteristics, and utilization as a fuel. *Cellul. Chem. Technol.* 48, 613–631.
- Rabinovich, M.L., Fedoryak, O., Dobeles, G., Andersone, A., Gawdzik, B., Lindström, M.E., Sevastyanova, O. (2016). Carbon adsorbents from industrial hydrolysis lignin: The USSR/Eastern European experience and its importance for modern biorefineries. *Renew. Sustain. Energy Rev.* 57, 1008–1024. <https://doi.org/10.1016/j.rser.2015.12.195>.
- Ralph, J., Lundquist, K., Brunow, G., Lu, F., Kim, H., Schatz, P.F., Marita, J.M., Hatfield, R.D., Ralph, S.A., Christensen, J.H. Boerjan, W. (2004). Lignins: Natural polymers from oxidative coupling of 4-hydroxyphenylpropanoids. *Phytochem. Rev.* 3, 29–60. <https://doi.org/10.1023/B:PHYT.0000047809.65444.a4>.
- Sannigrahi, P., Ragauskas, A J., Miller, S.J. (2009). Lignin structural modifications resulting from ethanol organosolv treatment of loblolly pine. *Energy Fuels.* 24, 683–689.
- Schlee, P., Sulaeva, I., Potthast, A., Rosenau, T. (2009). Size-exclusion chromatography of technical lignins in dimethyl sulfoxide/water and dimethylacetamide. *Holzforschung.* 63, 433–440. <https://doi.org/10.1515/HF.2009.092>.
- Sevastyanova, O., Helander, M., Chowdhury, S., Lange, H., Wedin, H., Zhang, L., Ek, M., Kadla, J.F., Crestini, C., Lindström, M.E. (2014). Tailoring the molecular and thermo-mechanical properties of kraft lignin by ultrafiltration. *J. Appl. Polym. Sci.* 131, 40799. <https://doi.org/10.1002/app.40799>.
- Sjöström, E. (1981). *Wood Chemistry: Fundamentals and Applications*. Academic Press, New York.
- Sjöström, E., Alén, R. (1998). Analytical methods in lignin chemistry, In: R. Alén (Ed.), *Analytical Methods in Wood Chemistry, Pulp, and Papermaking*. Springer, Berlin, Heidelberg, pp. 87–124. https://doi.org/10.1007/978-3-662-03698-2_4.
- Tagami, A. (2018). *Towards Molecular Weight-Dependent Uses of Kraft Lignin*. Licentiate thesis, KTH Royal Institute of Technology, Stockholm, Sweden.
- Tomani, P. (2010). The LignoBoost process. *Cellul. Chem. Technol.* 44, 53–58.
- Vishtal, A., Kraslawski, A. (2011). Challenges in industrial applications of technical lignins. *Biores.* 6, 3547–3568.
- Zakzeski, J., Bruijninx, P.C.A., Jongerius, A.L., Weckhuysen, B.M. (2010). The catalytic valorization of lignin for the production of renewable chemicals. *Chem. Rev.* 110, 3552–3599. <https://doi.org/10.1021/cr900354u>.

CHAPTER 2

LIGNIN APPLICATION

At present, the majority of lignin produced as a by-product in the pulp and paper industry (Bajwa et al., 2019) is combusted on-site to provide energy and enable chemical recovery in the kraft process; however, a portion of it can be extracted and utilized in value-added applications (Luo and Abu-Omar, 2017). Only a small fraction of industrial lignin—primarily lignosulfonates, representing less than 2% of the total lignin produced—is currently used for the production of specialty chemicals and other value-added products (Aro and Fatehi, 2017). In recent years, there has been a notable surge in interest regarding the potential value-added applications of industrial lignin, particularly as a sustainable and renewable source of feedstock for the production of valuable chemicals, materials, and fuels (Dessbesell et al., 2020; Norgren and Edlund, 2014). The growing interest can be attributed to several factors, including the limited availability of fossil resources, the search for alternative and renewable energy sources, growing concerns about the global impact of greenhouse gas emissions, the increasing quantities of lignin generated in various biorefineries that are not utilized for energy recovery, along with policy initiatives promoting a higher share of biomass-based content in commercial products (Bajwa et al., 2019).

The physical and chemical properties of lignin which are decisive for their potential application depend largely on its type (lignosulfonates, kraft lignin, and organosolv), source and its isolation procedure (Ariyanta et al., 2023). One of the unique advantages of lignin is that it can be used directly as an “additive” or it can be further processed to obtain renewable fuels, chemicals, and novel materials (Ariyanta et al., 2023; Ravi et al., 2023). Lignin is characterized by specific structural (poly-aromatic) and chemical properties, which can be targeted for specific applications (Ariyanta et al., 2023). For instance, the material noteworthy characteristics, including its capacity for UV-light absorption, antioxidant properties, biodegradability, and biocompatibility, render it a promising candidate for utilization as a carrier for various active materials. Furthermore, its hydrophobic properties, antioxidant activities, antimicrobial properties, high glass transition temperature, and large thermal stability, when compared to the chemically synthesized polymeric materials, suggest

its potential for application in coating materials (Ariyanta et al., 2023). Lignin and its derivatives have been investigated for a wide range of applications across various industries, including fuel and chemical production, as additives in specialty materials, in pulp and paper industry (Haq et al., 2020; Norgren and Edlund, 2014; Rana et al., 2018; Ravi et al., 2023), agroindustry (Ariyanta et al., 2023), medicine (Nan et al., 2022), pharmaceuticals (Nan et al., 2022), and environmental applications etc. (Fattahi et al., 2024; Rana et al., 2018; Roa et al., 2021; Zhang et al., 2023). The principal lignin application sectors are summarized in Figure 2.1.

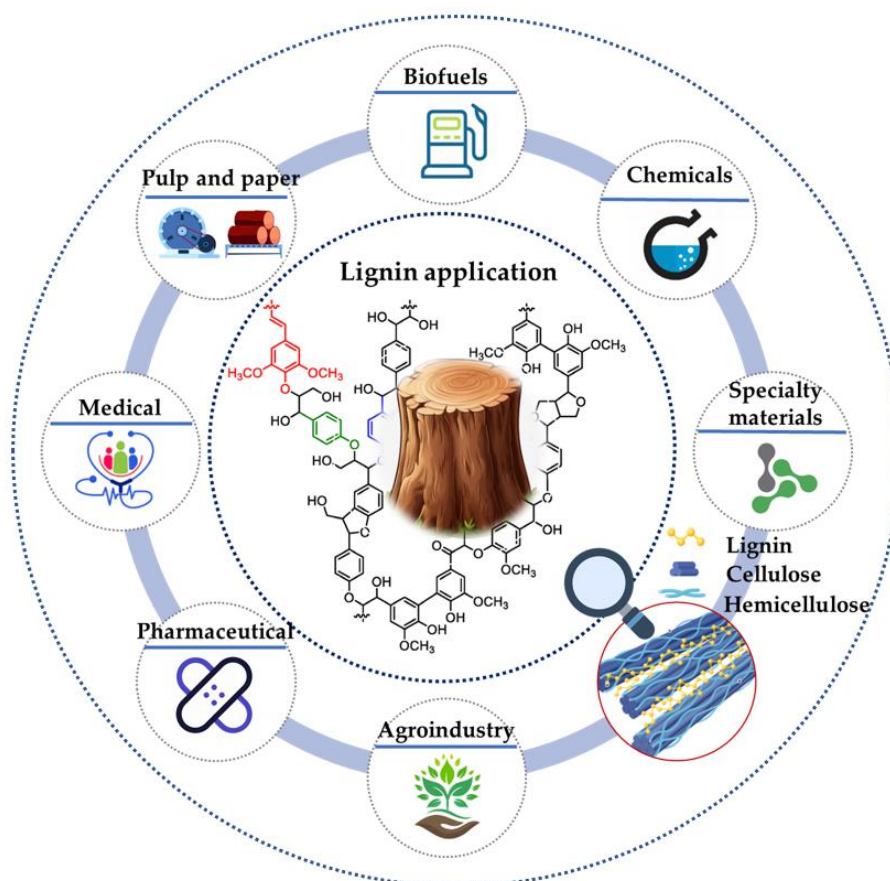


Figure 2.1. Main lignin application sectors.

Non-modified lignin has been considered for use as additive, filler, antioxidant, stabilizer, and UV-surfactants, whereas the chemically modified lignin has potential for valorization in bio-based polymers, biofuels, and chemical reagents development (Patel et al., 2023). Despite numerous potential applications of lignin (Table 2.1) and the extensive research carried out to isolate high-value lignin-derived products, lignin has not been yet used on the wide industrial scale. The main difficulties associated with the use of lignin on an industrial scale include, among others: (i) unique chemical reactivity of lignin, (ii)

presence of various inorganic and organic pollutants, or (iii) non-uniform structure (Bajwa et al., 2019; Vishtal and Kraslawski, 2011).

Table 2.1. Potential applications of lignin in various industrial sectors.

Sector	Application	References
Biofuels	Bio-oil from pyrolysis and liquefaction, production of bioethanol and biodiesel, green diesel via Fischer-Tropsch process, syngas from gasification, heat energy from combustion	(Ali et al., 2024; Haq et al., 2020; Rana et al., 2018)
Chemicals	Phenolic compounds, benzene, xylene, toluene, vanillin, vanillin acid, fuels, catechol, aldehydes, dimethyl sulfoxide (DMSO), flocculants, paints, adhesives	(Ali et al., 2024; Haq et al., 2020; Rana et al., 2018; Sethupathy et al., 2022)
Special materials	Biomedical, biocomposites, bioplastics, adsorbents, thermoplastics (filter, copolymer), thermosets (epoxy, phenolic, urethane resins), carbons (activated carbon, carbon fibers, biochar, carbon foam, carbon black, graphite, graphene, catalyst support, carbon electrodes, filters, lubricants), board binders, foams, densification of biomass pellets, battery components, energy storage, fire retardant, cement additives	(Ali et al., 2024; Haq et al., 2020; Rana et al., 2018; Sethupathy et al., 2022)
Pulp and paper	High tensile strength, packaging and lamination, sizing agent	(Haq et al., 2020; Rana et al., 2018; Tayeb et al., 2023)
Medical Pharmaceutical	Antimicrobial agents, antioxidants, cosmetics, probiotics, lignin-based porous biomaterials: drug delivery system, 3D printing composites, nanocapsule and nanosphere, powder and tablet, pharmaceutical excipients, creams, tissue engineering: bone, skin and cartilage tissue, prosthetics, wound dressing: healing, medical and implantable devices, biosensors	(Haq et al., 2020; Nan et al., 2022; Rana et al., 2018; Sethupathy et al., 2022)
Environmental	Dust controlling agent, soil stabilization, herbicide, pesticide, water retention agent, wastewaters treatment: dyes, heavy metal ions and other emerging pollutants removal	(Haq et al., 2020; Fattahi et al., 2024; Santander et al., 2021; Rana et al., 2018; Roa et al., 2021; Zhang et al., 2023)
Agroindustry	Active substance in coating (packaging material in the food industry: antioxidant and antimicrobial agent, UV barrier); soil enrichment (prevents the nutrients from leaching by the immobilization of microbial biomass, facilitate soil aggregation); plant growth stimulator; carrier for various active materials such as pesticides, insecticides, herbicides, fungicides; weed killing; lignin-based hydrogel for agriculture (heavy metals adsorption and as agricultural sustained release agents)	(Ariyanta et al., 2023)

Lignin may also be used as biosorbent of toxic substances from the environment (Goliszek et al., 2021). It can be subjected to chemical modification that increases the number of functional groups. Despite its relatively poor porous structure properties, including low BET specific surface area (1-5 m²/g), it has become the subject of many studies due to the various functional groups present on its surface, including: hydroxyl, carboxyl, phenolic, ether, carbonyl and ketone (Goliszek et al., 2019). Among different lignin-containing materials dedicated for sorption processes polymeric microspheres (Figure 2.2) are considered as one of the most effective as they can be simply functionalized and also can be readily used in packed columns for continuous flow operation.

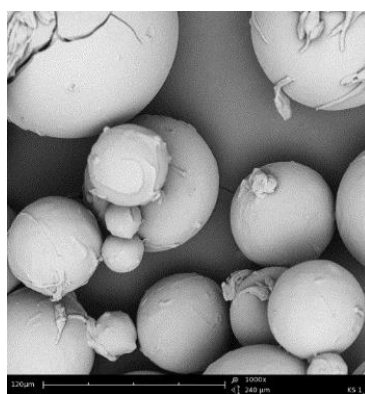


Figure 2.2. Lignin-containing polymer microspheres for sorption processes.

Lignin-based sorbents are gaining attention as sustainable, high-performance materials for various environmental applications and they are going to play a key role in addressing global water pollution challenges due to their sustainability, cost-effectiveness as well as versatile functionalization (Guo et al., 2008; Goliszek et al., 2018). At present, the synthesis of lignin-based polymers mainly concentrated on the following four strategies: (1) direct blending between lignin and other functional polymers or nanoparticles, the corresponding materials are constructed by non-covalent bond interaction, here, lignin would play the role of enhancer, stabilizer, binder, and dispersant; (2) chemical modification by active groups of lignin; (3) graft copolymerization of lignin by combing two or multiple monomers based on the free radical polymerization, and then obtain good compatibility adsorptive materials; (4) the polymerization of lignin derived small molecular monomers from its selective depolymerization, such as alkenes, aldehydes, and phenolic compounds (Shao et al., 2023). The mechanism of adsorption of environmentally harmful substances on the lignin surface is based on the reaction of these functional groups. These groups can bind them by donating an electron pair and thus form complexes in solution or new chemical bonds with the adsorbate. Lignin interacts with cationic and anionic dyes due to its charged functional groups.

Among various methods of toxic species removal from water and wastewater the adsorption, chemical methods, membrane, electric-, and photocatalytic ones are applied. All of them possess their advantages and disadvantages which are decisive for their potential application (Figure 2.3).

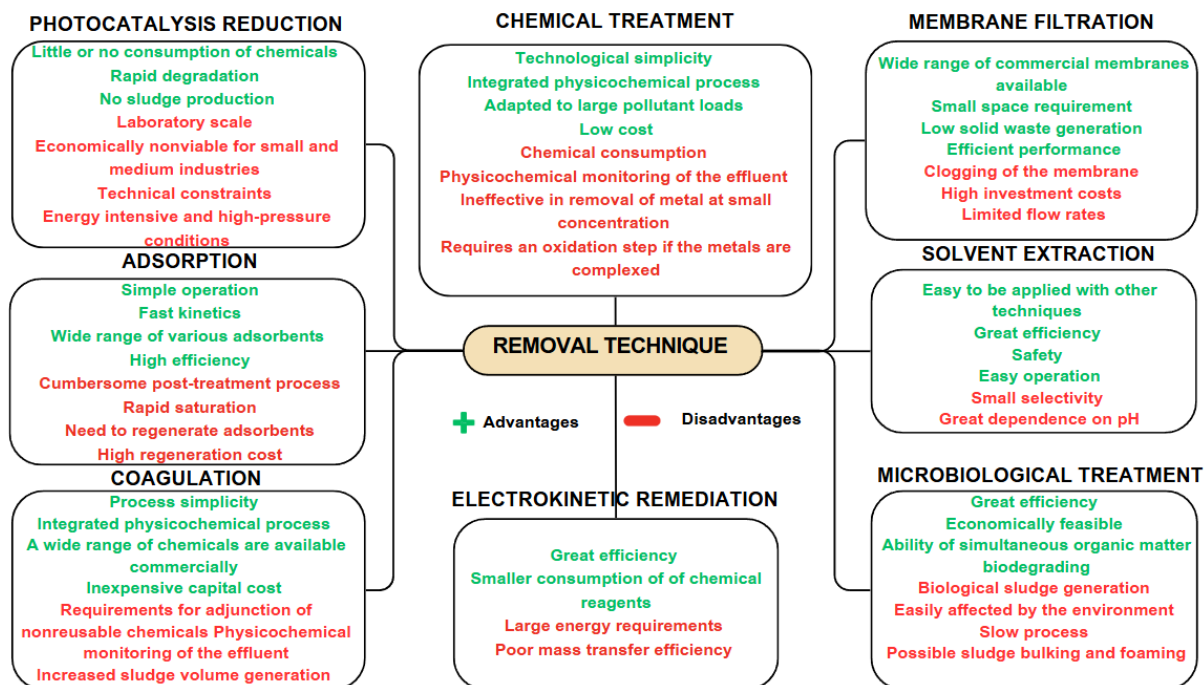


Figure 2.3. Comparison of the industrial wastewater treatment technologies containing metals.

Most existing wastewater treatment technologies face challenges concerning complex technology, high cost and the risk of secondary pollution. The applied methods should ensure proper treatment efficiency to meet the established Maximum Contaminant Level (MCL) standards in the wastewater discharged into the environment; however some of these methods are not fully effective (Qasem et al., 2021). Therefore, research on the implementation and development of better wastewater treatment systems is important to improve water quality and protect the environment. The effectiveness of pollutant removal technologies depends on several factors such as solution pH, initial concentration of metal, temperature, phase contact time, and amount of adsorbent (Oladimeji et al., 2024). The adsorption method is one of those widely used for elimination of them due to its advantageous (simple apparatus, easy operation, low cost, large efficiency, possibility of using different types of sorbents, fast kinetics, wide range of applications compared to the other treatment technologies) (Wang et al., 2022). However, adsorption still faces the challenge of reducing the cost of applied sorption materials with the possibility of increasing the removal efficiency of metal ions. In recent years to solve these problems biomass was applied for the preparation of new hybrid materials, composites or polymeric microspheres

applied for the removal of metal included in wastewater treatment. Application of lignin due to its widespread availability, biodegradability, environmental friendliness, biocompatibility results in decreasing the total cost of the adsorption method and the opportunities of its easy modification cause an increase of its reactivity and ensure large removal efficiency (Santander et al., 2021; Wang et al., 2022). However, there is a problem with poor solubility and dispersion of unmodified lignin, therefore the inactivated structure and functional groups cannot provide sufficient adsorption efficiency for metal pollutants (Ge and Li, 2018). In order to impart excellent adsorbent properties to lignin and expand its range of applications, some of chemical modifications such as oxidation, sulfonation, carboxylation, alkylation, and amination reactions are made. Modification of lignin improves its reactivity, enhances its affinity for harmful substances included in wastewater resulting in enhanced adsorption properties (Li et al., 2019; Santander et al., 2021; Wang et al., 2022).

2.1 Adsorbents with lignin addition for dyes removal

One of the pollutants of the environment, especially water, is dyes. They appear as a consequence of the coloring of different types of products, e.g. textiles, plastics, paints, varnishes, paper or pharmaceuticals (Figure 2.4).

The largest use of dyes is recorded in Asia, particularly in China. The yearly world production of dyes is 700 000-1000 000 tonnes which corresponds to over 100 000 commercial products whereby azo dyes constitute 70% (Gupta and Suhas, 2009).

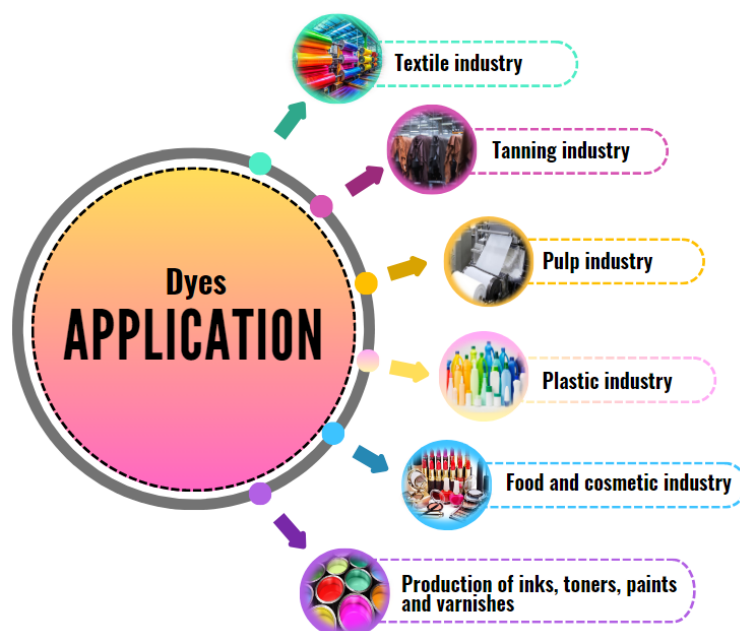


Figure 2.4. The use of dyes in different industries.

At the same time, they appear as a component of post-production wastewater (Figure 2.5) and can contaminate receiving water bodies. Typically, after dyeing fabrics, 80% of the dye is adsorbed by the material, and the remaining 20% of the dye is discharged into the water (Ghosh and Pramanik, 2024).

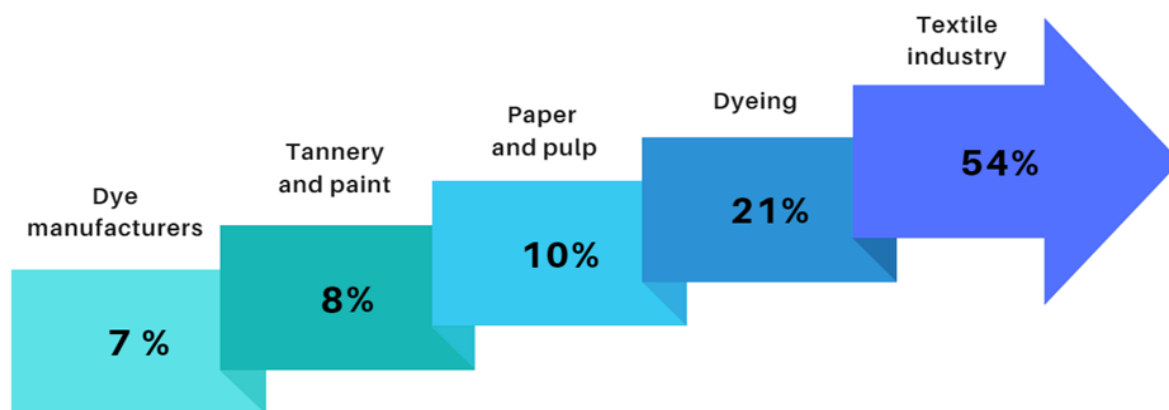


Figure 2.5. Main industries responsible for the dye presence in the effluent in the environment.

Dyes are considered an objectionable type of pollutant, they can be toxic, mutagenic, and carcinogenic to fauna, flora, and humans. The toxic effects of synthetic dyes may be because most of these compounds are xenobiotics, i.e. chemical compounds foreign to the organism and not found in natural waters, while at the same time exhibiting biological activity. Azo-type dyes are particularly hazardous to the environment as they can degrade to toxic aromatic amines under certain conditions. Dyes can cause human contact allergic reactions such as dermatitis, rhinitis, or occupational asthma. They can also cause damage to the nervous (e.g. inhibition of intracellular enzyme of the central nervous system), reproductive (e.g. cytotoxic effect on spermatozoa cells, decline in ovarian protein and glucose), immune and enzymatic (e.g. inactivation of enzymatic activities, block of enzymes such as glutathione reductase) systems and dysfunction of the kidneys (e.g. sarcoma and cancer), liver (e.g. hepatocarcinoma, an increase of serum alkaline phosphates and γ -glutamyl transferase) or genetic material (e.g. intercalate with the helical structure of DNA and RNA, increased frequency of micronuclei) (Al-Tohamy et al., 2022; Wawrzkievicz et al., 2025).

The content of dyes in the effluent varies very widely from 2 to 50%, depending on the dyeing method used and the type of product being dyed as presented in Figure 2.6 (Hessel et al., 2007). In addition to dyes, wastewater from this industry may contain heavy metal ions, electrolytes, sizing agents, detergents, acids, and alkalis as well as oxidants and reducing agents which can enter wastewater in significant quantities (Hessel et al., 2007, Figure 2.6). The parameters of textile industry effluents are following: pH 6.2–11.5, biochemical oxygen demand 80–6000 mg/L, chemical oxygen demand 150–12000 mg/L, total suspended solids

15–8000 mg/L, total dissolved solids 2900–3100 mg/L, surfactants 1–134 mg/L, chloride 1000–1600 mg/L, total Kjeldahl nitrogen 70–80 mg/L, and total chromium 1–5 mg/L (Turhan & Turgut, 2009).

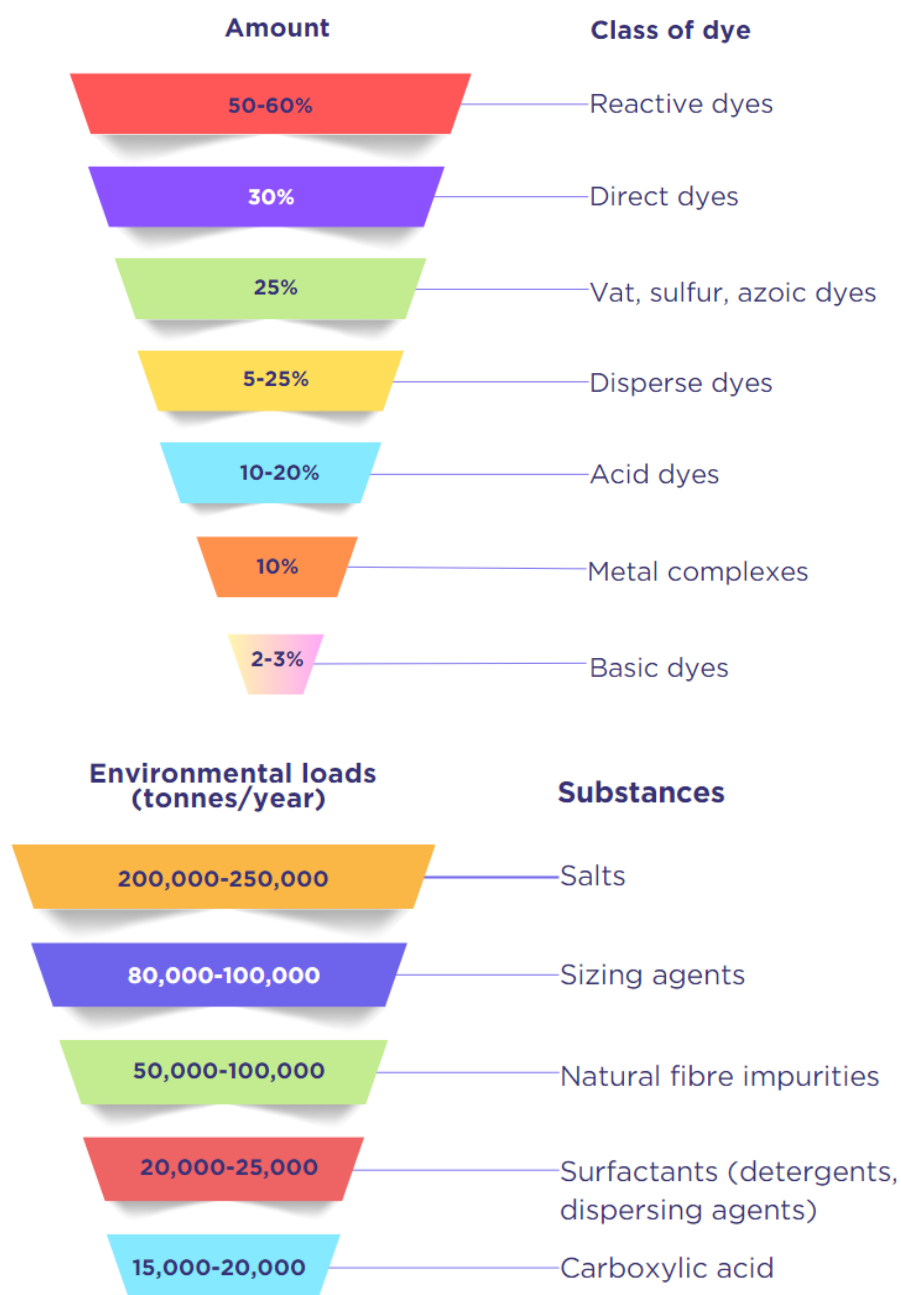


Figure 2.6. Main charging of dyes and auxiliaries from the textile industry in Europe.

The diverse composition of dye-containing effluents and their varied origins make it necessary to search for simple and effective methods of treating them. The adsorption technique as one of the physical methods of 86.8–99% yield for dye removal from industrial effluents meets the above criteria (Katheresan et al., 2018). It has been estimated that the average cost of wastewater treatment by adsorption is US\$ 5–200/m³, while other

technologies are in the range of US\$ 10-450/m³ (Dotto et al., 2015). It is therefore particularly important to obtain new adsorptive polymeric materials known as adsorbents, especially those containing biocomponents in their composition. It makes them more biodegradable and low-cost as stated above. In recent years, adsorbents containing such biodegradable additives as lignin (Jiang et al., 2023), cellulose (Ali Aslam et al., 2023), or starch (Fang et al., 2022) have attracted great interest in wastewater treatment technologies. More than a dozen examples are described below on the preparation of lignin-enhanced adsorbents and polymeric materials for the removal of toxic dyes of various types from model solutions and wastewater. Kraft lignin (KL), produced from the kraft pulping of softwood chips was aminated using 2-chloroethylamine hydrochloride (CEH) to obtain amine-crosslinked lignin (ACL). Three adsorbents ACL-1, ACL-2 and ACL-3 were prepared, differing in the content of the CEH dosage from 0.041 to 0.111 mol (Figure 2.7).

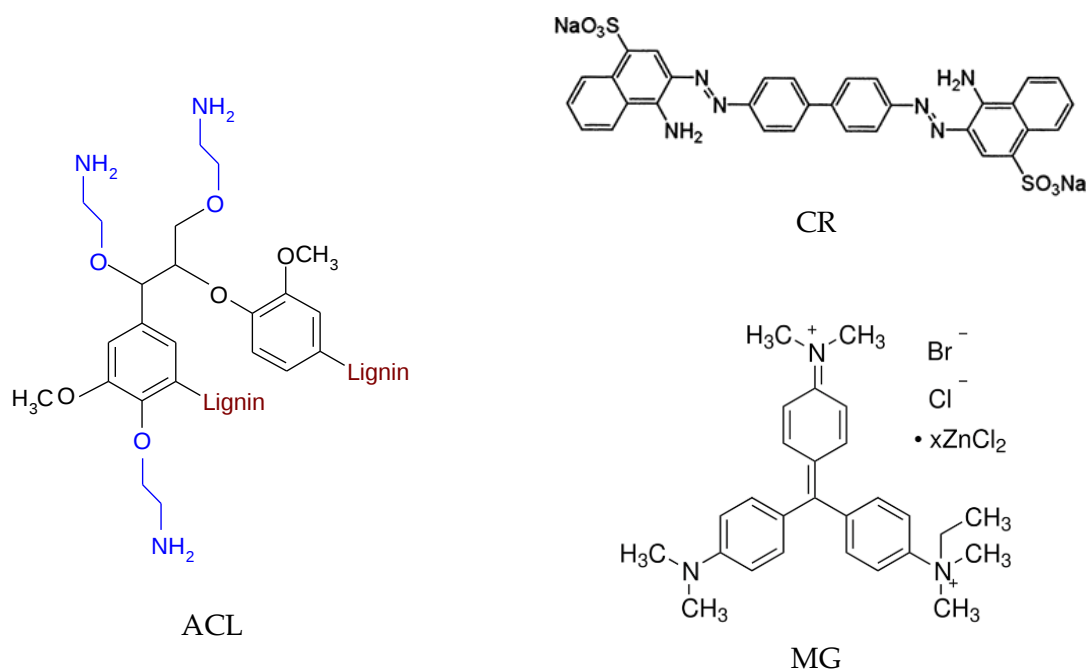


Figure 2.7. Structures of ACL and dyes (CR – Congo Red, MeG – Methylene Green).

Elemental contents of adsorbents were found to be 58.20-63.46% C, 2.30-6.10% N and 0.76-1.54% S. KL consists of 66.32% C, 0.40% N, and 1.89% S. The surface area of KL was 24.40 m²/g, whereas the surface area of ACL-2 significantly increases to 101.21 m²/g. Pore size analysis confirms mesoporous characteristics in the pore size range of 17–30 nm for all adsorbents. The pore volumes for KL and ACL-2 were found to be 0.18 and 0.68 cm³/g, respectively. The point of zero charge (pH_{pzc}) of ACL-2 was determined as 6.58. The adsorption efficiency of the amine-crosslinked lignin was investigated for both anionic (Congo Red, CR) and cationic (Methylene Green, MeG) dyes. The adsorption capacity of ACL-2 increases with decreasing pH, reaching 518.59 mg/g at pH 3 for CR. By contrast, the positively charged MEG was retained in the amount of 472.57 mg/g at the alkaline condition

of pH 9. Adsorption efficiency decreases by approximately 18% from the second cycle onward, displaying a gradual decline with an increasing number of cycles. By contrast, for MeG, the adsorption efficiency remains relatively stable. After five cycles, the CR adsorption efficiency remains above 78%, and that of MeG consistently exceeds 93%. Adsorption of the dyes includes hydrogen bonding (between hydroxyl or amino groups on the lignin and azo groups of CR), NH- π interactions and π - π stacking interactions (aromatic rings of dyes and π -electrons from the lignin structure), and electrostatic interactions depending on dyes solution pH (under acidic conditions due to the positive charge of the protonated amine groups of the lignin and the negative charge of the anionic CR and under alkaline conditions, lignin molecules acquire a negative charge, which increases their electrostatic attraction with the cationic MeG) (Oh et al., 2024).

Three lignin-derivatized mono-aldehydes, including 4-hydroxy benzaldehyde (H), vanillin (G), and syringaldehyde (S) were used by Jin et al. (2022) to react with melamine through a one-step polycondensation reaction, which enabled obtaining lignin-derivatized porous polymer networks (LPPNs). The studies confirmed the spherical morphology of three LPPNs, with the average particle diameters between 50 and 100 nm and a surface area of 511.9 – 739.4 m²/g. The presence of hydroxyl and amine groups in LPPNs structure facilitated the removal of organic dyes such as Malachite Green (MG), Methyl Orange (MO), Acid Orange 7 (AO7), and Methylene Blue (MB). Under experimental conditions (i.e. 25 mL/10 mg - adsorbent dosage, 200 mg/L - dye concentration, contact time - 120 min, temperature - 298 K), the high removal efficiency for MG, MB, MO, and AO7 was determined to be 91.1–96.6%, 90.3–92.3%, 89.4–91.5%, and 80.9–83.2%, respectively. In particular, LPPN-H showed a higher adsorption capacity for MG removal (1449.8 mg/g) over LPPN-G (1320.8 mg/g) and LPPN-S (1279.4 mg/g) which indicates their potential use in industrial wastewater treatment plants.

Li et al. (2016) obtained lignin hollow microspheres from esterified organosolv lignin with maleic anhydride via self-assembly in the mixed tetrahydrofuran-Fe₃O₄ nanoparticles medium. The extraction of lignin fractions was based on an organosolv method from wood powder. Fe₃O₄ nanoparticles were embedded strongly in the lignin-based materials via electrostatic interactions, which are expected to interact with electron-rich oxygen atoms of hydroxyl groups of lignin. The magnetic lignin adsorbents were applied for methylene blue removal and the adsorption capacity was found to be 31.23 mg/g. The desorption and regeneration processes were studied in three cycles using 0.4 M NaCl + 0.002 M NaOH (pH < 12) as an eluting solution with 98% removal efficiency.

Wang et al. (2024) prepared similar adsorbents, i.e. magnetic micrometer-sized particles AL-CTS@MNPs from alkaline lignin (AL), chitosan (CTS) and Fe₃O₄ nanoparticles (MNPs) by “one-pot method”. The synthesis involves cross-linking of AL and CTS via glutaraldehyde (GA) and modification with polyethyleneimine (PEI) as well as the incorporation of magnetic particles. The value of p*H*_{pzc} was 6.22. To establish the adsorptive properties of the ALCTS@MNPs toward different types of dyes, the anionic

dyes: Methyl Orange (MO), Congo Red (CR), Acid Blue 113 (AB113), Reactive Black 5 (RB5), the amphoteric dye: Rhodamine B (RhB), and the cationic dyes: Methyl Green (MeG), Methylene Blue (MB), and Neutral Red (NR) were selected in the experiments. The maximum adsorption capacities of AL-CTS@MNPs increased from 143.50 mg/g to 329.50 mg/g for MO and from 15.10 mg/g to 20.00 mg/g for RhB with increasing temperature from 298 K to 318 K. MO and RhB removal decreased with the increasing amounts of NaCl, CaCl₂ and Na₂SO₄ from 0.025 mol/L to 0.100 mol/L in the solutions containing 50 mg/L dye and electrolytes. The sorption – desorption cyclic stability of AL-CTS@MNPs was relatively good, and the removal rate was maintained at >95 % after 5 cycles using 0.1 M NaOH + 20% ethanol.

Meng et al. (2020) used a cosolvent-enhanced lignocellulosic fractionation (CELf) method as a highly effective lignin-first pretreatment approach that is capable of extracting highly pure technical-grade lignin from corn stover. CELf applies an aqueous mixture of tetrahydrofuran (THF) and dilute acid to greatly enhance the fractionation of lignin, hemicellulose, and cellulose fractions in biomass while promoting lignin fragmentation by limiting certain lignin condensation reactions typically suffered at high reaction severities. The obtained CELf lignin was depolymerized, containing lower aryl ether linkages and higher phenolic hydroxyl groups than the typical native milled wood lignin, or kraft lignin, which favors the subsequent amination process by diethylenetriamine (DETA) in the presence of formaldehyde under acid conditions. BET specific surface area (S_{BET}) values were 4.2 and 5.9 m²/g for the CELf lignin and aminated lignin, respectively. The mesoporosity of adsorbents was confirmed. The maximum adsorption capacity of the aminated CELf lignin was 502.7 mg/g towards anionic azo dye Direct Blue 1 (DB1). The electrostatic force is a major interaction for DB1 dye adsorption at lower pH. The dye-removal efficiency decreased to 65% for the fourth use, probably because of the saturation of the adsorbent surface, however aminated CELf lignin can remain as an efficient adsorbent even after multiple reuses.

Lignin produced as waste from the bioethanol production of corn stover was added to copper ferrite magnetic material (LCF) to produce low cost adsorbent for the removal of Crystal Violet (CV) dye (Ali et al., 2022). LCF's point of zero charges was in the neutral pH range (6.1). This novel material, lignin copper ferrite exhibited a maximum adsorption capacity of 34.129 mg/g. Thermodynamic results showed the physical nature of interactions between CV and LCF adsorbent. It was found that the 97% removal was achieved in equilibrium time 5 min, LCF amount 0.025 g at an initial concentration of CV at 10 mg/L, at room temperature, and pH 8. Furthermore, it was found that this adsorption was deleteriously affected by a pH decrease from 8 to 2. LCF can be reused for five cycles with a removal efficiency 86%, and this reaches 60% after 10 cycles.

Bio-based sodium alginate/lignin (SA/L) hydrogel beads were fabricated by a facile cross-linking with calcium ion and used for the removal of Methylene Blue (MB) by Chen

et al. (2022). The maximum adsorption capacity (254.3 mg/g) was obtained for the beads containing 20% lignin, with a removal efficiency of 84.8%. The optimal conditions of sorption was pH 12, and the 45°C temperature. The adsorption process for MB was endothermic, and the rate-limiting step was chemical adsorption. The removal efficiency was higher than 90% after five cycles, revealing that the prepared adsorbent showed good regeneration ability.

Su et al. (2023) used lignin as a renewable resource abundant in nature, to completely replace phenol and develop a lignin-based phenolic resin (LPF) adsorbent for the removal of Congo Red (CR) dye. The adsorbent demonstrated great potential in the field of anionic dye adsorption with a maximum adsorption capacity of 406.35 mg/g (i.e. 92.1% removal rate) at optimal adsorption conditions such as initial pH 6, temperature of 30°C, the reaction time of 1 h, and adsorbent dosage of 1 g/L. The adsorption capacity was essentially the same at the 1st and 2nd reuses, and the adsorption rate decreased from 92.1% to 79.2% after five cycles.

A lignin-based fibrous adsorbent was developed by Kim et al. (2022) using bio-aldehyde cellulose as a crosslinking agent and polyvinyl alcohol (PVA) as an additional polymer (L/PVA). The solvent used in the electrospinning process was dimethyl sulfoxide of the flow rate and acceleration voltage maintained at 2 ml/h and 2 kV, respectively. With the adsorptive capacity of 16.64 mg/g for anionic dye Methyl Orange and 354.61 mg/g for cationic dye Methylene Blue, the L/PVA fiber served as an effective nanomaterial for their removal. Owing to the deprotonated hydroxyl and carboxyl groups of lignin, strong electrostatic interactions, hydrogen bonding, and π - π stacking occurred between the adsorbent and cationic dye, which resulted in an exceptional ability to remove the dye.

The layered double hydroxide of nickel and aluminium modified with lignin (NiAl-L) was prepared by the co-precipitation synthesis method and used for adsorption of Malachite Green (MG), Methylene Blue (MB) and Rhodamine B (RB) by Ahmad et al. (2025). The surface areas of NiAl, L, and NiAl-L were following: 16.206, 5.073, and 55.878 m²/g, respectively. Confirming mesoporosity, the pore size of the materials ranged from 2 to 13 nm, with L > NiAl > NiAl-L having the smallest pores. The NiAl, L, and NiAl-L had respective pore volumes of 0.039, 0.001, and 0.003 cm³/g. The interaction between functional groups of MG and adsorption sites of NiAl-L surface is stronger and more specific, leading to higher selectivity than MB and RB. The maximum malachite green's adsorption capacities by NiAl, L, and NiAl-L were 156.250, 142.857, and 175.439 mg/g, respectively. The percentage of MG adsorbed in the first cycle was 94.27%. Even as the cycles progressed, the efficiency reduction remained below 10% until the fourth cycle (pH 4, time 2 h, temperature 303 K, MG concentration 30 mg/L). NiAl-L demonstrated potential as a candidate adsorbent for selective adsorption of malachite green from wastewater.

New spherical sulfonic lignin adsorbent (SSLA) was synthesized to remove and recover the cationic dyes from aqueous solutions, e.g., Cationic Red GTL (GTL), Cationic Turquoise GB (GB), and Cationic Yellow X-5GL (X-5GL) (Liu and Huang, 2006). SSLA beads were prepared using sodium lignosulfonate as raw material, which was provided by

a bamboo pulp mill in Sichuan in China. Some physicochemical properties of SSLA are as follows: specific surface area 106.5 m²/g, particle diameter 200-600 µm, pore volume 0.958 mL/g, mean pore diameter 35.83 nm, and specific density 1.036 g/mL. It was observed that with an increase in solution pH ranging from 3.0 to 11.0, the equilibrium adsorption capacities for GTL, GB, and X-5GL increase from 77.6 to 199.8 mg/g for the solutions of the initial concentration 200 mg/L. The adsorption capacities of SSLA for the uptake of cationic dyes increase with the temperature increasing from 26 to 45° C indicating the process to be endothermic. The adsorption capacities towards GTL, GB, and X-5GL were calculated to be 536.0, 550.0, and 582.0 mg/g, respectively. These values were significantly higher than for the adsorption of these dyes on commercial powdered activated carbon and cation exchange resin type R732.

The cited literature examples indicate that adsorbents containing lignin in their composition can be considered effective in removing toxic dyes from water and industrial effluents.

2.2 Adsorbents with lignin addition for removal of metal ions

Among all metals, a certain group is made up of metals referred to as “heavy metals”. This term has been and is now widely used in the literature and legislation although it has not been precisely defined so far. A review of the current use of this term indicates that metal density (specific gravity), mass and atomic number, chemical properties, and toxicity are the most commonly used criteria decisive for including a metal in the heavy metals group (Duffus, 2002). Taking these criteria into account, it can be concluded that an element that is considered a heavy metal in one classification is not such one according to another, so despite the belief that it is known which indicates it does not always mean the same thing for different people (Hodson, 2004). According to Duffus (2002) this group includes metals and metalloids such as arsenic. The term “heavy metal” defined by Ali and Khan (Ali and Khan, 2018) generally relates to any naturally occurring metallic chemical elements of relatively large density (>5.0 g/cm³) and large atomic weight (>20). This group includes 51 elements qualified as “heavy metals” (Ali and Khan, 2018). The inconsistent use of the term “heavy metals” reflects the inconsistency in the scientific literature, so in this review, the authors will use the term metals (Ali and Khan, 2018, Duffus, 2002).

Environmental metal pollution is becoming an increasingly serious problem not only locally but also globally (Chmielewski et al., 2020). Metals are ubiquitous in the environment and can be found in the atmosphere, lithosphere, hydrosphere, or biosphere (Briffa et al., 2020; Qasem et al., 2021). The main sources of metals in the environment are natural and anthropogenic sources but anthropogenic activities introduce from 3 to 10 times more pollutants into the atmosphere than natural ones (Nordberg et al., 2015; Santander et al., 2021) (Figure 2.8).

The amount of metals released into the environment in this way varies thus spreading such pollutants into the environment occurs through industrial effluent discharge, improper waste management, combustion of fossil fuels, gas and dust emissions, fertilization, use of pesticides, and transport (Briffa et al., 2020; Chmielewski et al., 2020; Masindi et al., 2021).

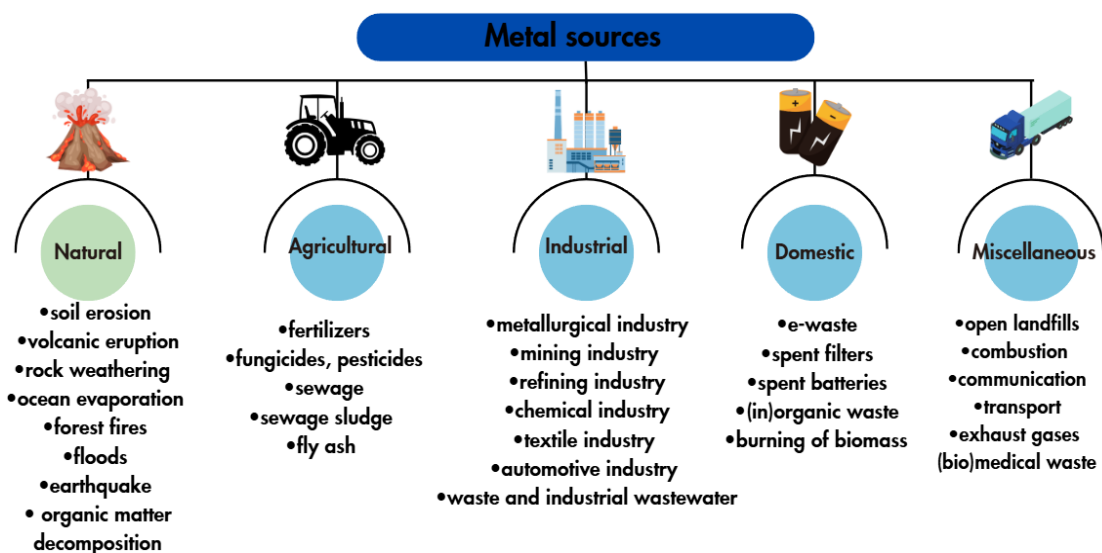


Figure 2.8. Natural and anthropogenic sources of metals in the environment (Briffa et al., 2020; Chmielewski et al., 2020; Masindi et al., 2021; Tonk et al., 2022).

Metal dispersion depends on many factors such as air circulation, temperature, surface water movement, and wind speed as well as direction (Masindi et al., 2021). Both accidentally and intentionally introduced metals into the environment from these sources cause soil, water, and air pollution (Briffa et al., 2020). Therefore they remain in constant circulation in the environment and are incorporated into individual links of the food chain (soil - plant - animal - human), resulting in their bioaccumulation and biomagnification (Abdelmonem et al., 2025; Chmielewski et al., 2020; Masindi et al., 2021). Moreover, due to their large durability (the time of residence in the soil can be even >1000 years) and long half-life mutagenic, carcinogenic, and teratogenic properties they are extremely dangerous for the environment and living organisms (Dasharathy et al., 2022). Table 2.2 presents the sources of selected metals in an environment with their effects on human beings.

Table 2.2. Characterization of selected metals - sources, effects on human beings and permitted limit (Briffa et al., 2020; Costa et al., 2023; Femina et al., 2023; Genchi et al., 2020; Kiouri et al., 2025; Staszak and Regel-Rosocka, 2024; Qasem et al., 2021; Wołowicz et al., 2022; Wołowicz and Hubicki, 2020; Wołowicz, 2019).

Metals/ Pa (μg)	Main sources/application	Effects on human beings: main organ/system affected
Cu/ 2000	Plumbing systems, electronics, cables industry, building construction market, energy and renewables, agriculture and farming, art, interior design, transportation, electroplating processes, metal finishing, textile dyeing, pigments for ceramics, glass and plastics, production of polymers, healthcare, pharmaceuticals, food	Liver, kidneys, brain, thymus, cornea/ hematological, gastrointestinal, immunological, respiratory, reproductive system; Excess: endemic tyrolean infantile cirrhosis, indian childhood cirrhosis, DNA damage, cancer, Wilson's disease (WD), Non-Wilsonian disorders, Alzheimer's disease, diabetes, idiopathic copper toxicosis; Deficiency: fatigue, frequently getting sick, feeling cold, unexplained weight loss, a stunt in growth, arthritis, Menkes disease, cardiovascular diseases, anemia, ATP7A-related isolated distal motor, neuropathy, zinc-induced myeloneuropathy, aceruloplasminemia, skin inflammation and sores, bruising paleness, hair thinning or balding, osteoporosis, brittle bones, joint pain, muscle soreness
Zn/ 3000	Brass coating, rubber products, die-casting alloy, bronze and brass, galvanizing, chemicals, cosmetic ingredients, spray deodorants	Brain, sensory, thymus, skin/ reproductive, gastrointestinal, respiratory system; Excess: lethargy, focal neuronal deficits, nausea and vomiting, stomach pain and diarrhea, respiratory disorder after inhalation of zinc smoke, mental fume fever, elevated risk of prostate cancer, changes of taste, frequent infections; Deficiency: decreased nerve conduction, depression, loss of taste and smell, neurosensory and neuropsychiatric disorders, thymus atrophy, skin lesions, worse wound healing, acrodermatitis enteropathica Danbolt-Closs syndrome, infertility, retarded genital development, hypogonadism, impairment of physical growth and development, immune dysfunction, frequent infections
Ni/70	Stainless steel, nickel plating, nickel alloy production, aerospace equipment production, paints, ceramics, medical applications, electronics, food and beverage production, batteries, chemicals	Bone, lung, kidney, liver, brain and endocrine glands/gastrointestinal system, respiratory system, reproductive system; pulmonary fibrosis, allergic contact dermatitis, carcinogenicity (lung cancer; nasal cancer), reproductive toxicity, cardiovascular and kidney diseases, non-cancer respiratory effects, acute health effects: nausea, vomiting, abdominal discomfort, diarrhea, visual disturbance, headache, giddiness, and cough
Pb/10	Lead-based batteries, alloys, cable sheathing, solder,	Liver, kidneys, brain, lungs, spleen, bones/ hematological, cardiovascular, immunological,

	pigments, rust inhibitors, glazes, plastic stabilizers, ammunition	reproductive systems
As/10	Electronics, semiconductor production, detectors, lasers, mobile phones, CD players, GPS systems, lead ammunition production, bearing alloy additive, warfare agents (Lewisites), wood impregnation, glass industry, clarifying and decolorizing agent, tanning, pigment production, plant protection products, poultry and pig feed additives, medical applications, anemia treatment, anticancer therapy	Kidneys, brain, lungs, liver, spleen, bones, skin, hair, nails/ hematological, cardiovascular, immunological, reproductive, endocrine, metabolic systems; disrupts the Krebs cycle, gastroenteritis, water and electrolyte disorders, collapse, pale gray skin, irritation and damage to blood vessels, anemia, leukopenia, nervous system disorders, damage to the mucous membranes, skin, membrane lesions, keratosis of the epidermis of the feet and hands, ulceration, transverse white lines on the nail plates, so-called Mees lines, skin cancer, liver, kidney, leukemia
Cr/50	Steel mills: production of ferrochrome, stainless steel for bathroom equipment, car parts, military vehicles, weapons, galvanization processes, anti-corrosion protection, production of pigments and paints, preservatives for printing, photography, tanning industry, fabric dyeing, fungicides, wood preservation, medical applications - prostheses and implants	Lung, liver, brain, kidney, heart, skin/ respiratory, circulatory, hematopoietic, gastrointestinal, reproductive systems; circulatory system and heart disease, DNA strand break, genotoxicity, lung and bronchial cancer, respiratory system damage (mucosal ulceration, nasal septum perforation, bronchial asthma), skin damage, eyelid edema, diarrhea, hemorrhagic diathesis, hemorrhage, liver necrosis, renal tubular necrosis, hematopoietic system poisoning
Cd/3	Steel industry, plastic industries, metal refineries, coating, plating, batteries, paints, pigments, stabilizer	Liver, kidneys, lungs, brain, bones, testes/immunological, cardiovascular systems
Hg/6	Production of batteries, measuring devices, electric switches and relays, dental amalgam for filling, skin-lightening products, cosmetics, pharmaceuticals, electrolytic production of chlorine and caustic soda	Lungs, kidneys, liver, brain/immunological, cardiovascular, reproductive, endocrine systems

Pa - permitted amounts

In this section, the obtained lignin-based adsorbents for metal ions removal are reviewed. The as-obtained lignin-based adsorbent as well as the modified lignin-based adsorbents were considered.

The first group of lignin materials called **non-modified lignin** isolated from the black liquor obtained from paper industry residues was applied for metals removal from wastewater. **The alkaline lignin** is obtained during the pulping process (separating lignin from lignocellulose) at high pH and temperature (423–453 K) using large doses of NaOH

and Na₂S by breaking the linkages holding the phenyl-propane units together. This process increases the solubility of lignin in the water/alkaline solutions due to generations of free phenolic and hydroxyl groups resulting in a black liquor formation. Then the lignin is isolated through acidification and precipitation (Ge and Li, 2018). The lignin from black liquor was applied for Pb(II), Cu(II), Cd(II), Zn(II), and Ni(II) removal from aqueous solutions. The surface of isolated lignin contains the carboxylic and phenolic groups, with the twofold carboxylic groups advantage. In their deprotonated form, these groups interact with the metal ions. The obtained series of affinity of divalent metal ions for the carboxylic acid functional groups are following: Pb(II) > Cu(II) > Zn(II) > Cd(II) > Ni(II), whereas for the phenolic groups, it is Pb(II) > Cu(II) > Cd(II) > Zn(II) > Ni(II). Metal ion adsorption was largely dependent on pH and ionic strength and increased with the increasing pH. The sorbent was characterized by good kinetics - the adsorption equilibrium was reached after 20 min of phase contact time and the initial adsorption rate values decreased in the following sequence: Pb(II) > Cu(II) > Cd(II) $\approx$ Zn(II) $\approx$ Ni(II). The adsorption capacities were 0.432 mmol/g, 0.360 mmol/g, 0.226 mmol/g, 0.172 mmol/g and 0.102 mmol/g for Pb(II), Cu(II), Cd(II), Zn(II) and Ni(II), respectively. The kinetic data were well described by the pseudo-second order kinetic model (PSO) whereas the isotherm data by the Langmuir isotherm model (Guo et al., 2008). Lignin extracted from the black liquor was also applied for Pb(II) and Zn(II) (Srivastava et al., 1994) and Cr(III) (Wu et al., 2008) removal from the aqueous solution. These studies show that the source of lignin determines its adsorption properties. The lead adsorption on lignin is found to be greater than that of the zinc (the adsorption capacities were 1587 mg/g for Pb(II) and 73 mg/g for Zn(II)) and the adsorption capacity increases with the increasing pH (Srivastava et al., 1994) whereas the adsorption capacity for Cr(III) was 17.97 mg/g (Wu et al., 2008) being much higher compared to that for the commercial lignin (Lalvani et al., 2000). Adsorption of Pb(II) and Zn(II) on lignin follows both Freundlich and Langmuir isotherm models indicating that no single but complex mechanism is involved in the adsorption process (Srivastava et al., 1994). The Cr(III) adsorption proceeds through the inner-sphere complexation between Cr(III) and lignin. The presence of other metals causes competitive adsorption between Cr(III) and Pb(II), Cu(II), Zn(II), Cd(II) ions in the order Pb(II) > Cu(II) > Zn(II) and Cd(II) (Wu et al., 2008). The other examples of alkaline lignin application for metal removal are presented in Table 2.3.

Table 2.3. Comparison of adsorption capacities of alkaline lignin for metal removal.

Adsorbent	Metal	Adsorption capacity	pH; T(K)	Other	Ref.
alkaline commercial lignin (Sigma–Aldrich), low sulfonate content	Cr(VI) in water	31.6 mg/g (Dubinin–Radushkevich)	2	ion-exchange mechanism; PSO, %D=70% (0.1 M NaOH)	Albadarin et al., 2011

alkaline lignin (beech, poplar woods) by alkali glycerol delignification	Pb(II) Cd(II)	9.0 mg/g 7.5 mg/g	5; T=290, 310, 330K	ion-exchange mechanism; Langmuir model, Pb(II): %R=95.8 %, 4 h, 330 K, Cd(II): %R=95.0 %, 10 h, 290 K, endothermic adsorption	Demirbas, 2004
alkaline lignin (wheat straw)	Cu(II)	26.0 ± 1.3 mg/g (Langmuir), 24.9 ± 2.1 mg/g (Sips)	6; T=293±0.5K	%R=95% (t=90 min, 5g/L); PSO	Todorciuc et al., 2015
Kraft lignin derived from Eucalyptus black liquor	Cu(II)** Cd(II)	87.05 mg/g (T=298K) 137.14 mg/g (T=298K)	T=287, 298, 313K	PSO; Langmuir model, Cu(II): 68.63 mg/g, 287K, 94.68 mg/g, 313K Cd(II): 59.58 mg/g, 287K, 175.36 mg/g, 313K	Mohan et al., 2006
Kraft lignin	Cu(II)* Cd(II) Zn(II) Cr(VI)	-	4, T=297K 6, T=297K 6, T=297K 2; T=297K	110 rpm, 3 h, Cu(II), Zn(II), Cd(II): Freundlich isotherm, Cr(VI): Langmuir isotherm, adsorption series: Cr(VI) > Cd(II) > Cu(II) > Zn(II)	Šćiban et al., 2011
Kraft lignin (pine lignin)	Cu(II) Cd(II) Pb(II) Zn(II) Ca(II)	Cu(II): 2.0 µmol/20 mg, pH 4.5, 6.0 µmol/20 mg at pH 5.5, Pb(II): 1.5->10 µmol/20 mg for pH 4.0-5.5	4-6	ion-exchange mechanism; adsorption series: Pb(II) > Cu(II) > Zn(II) > Cd(II) > Ca(II)	Crist et al., 2002
Kraft lignin SWKL (softwood lignin), HWKL (hardwood lignin)	Cu(II) Cd(II)	Cu(II)/Cd(II): 5.12/3.23 mg/g (softwood), 4.24/2.85 mg/g (hardwood)	Cu(II): 5.3±0.1, T=297K Cd(II): 6.5±0.1, T=297K	Cu(II): %R=90%, Cd(II): %R=85%, t=30 min	Harmita et al., 2009

PSO - pseudo second order rate kinetics, T – temperature, %D – desorption yield, t – time, * - single, binary systems, ** - single, binary and multi-component systems

Lignosulfonate obtained from the sulfite pulping process in the presence of sulfur dioxide and sodium, magnesium, ammonium or calcium hydroxide containing approximately 6.5% elemental sulfur in the form of sulfonate groups on the lignin macromolecules due to its solubility in water, is not frequently applied for metal removal. The lignosulfonate spheres prepared by crosslinking with sodium alginate and epichlorohydrin could be applied for Pb(II) removal in the batch and column procedures. The adsorption capacity of lignosulfonate spheres for Pb(II) was 27.1 mg/g (pH 5.0, 303K, the batch studies). The intraparticle diffusion plays an important role in the Pb(II) adsorption and the adsorption of

metal could be well described by the Langmuir isotherm model indicating monolayer adsorption (Li et al., 2015a).

Organosolv lignin separated from the biomass with various organic chemicals e.g., methanol, ethanol, acetic acid, and formic acid in the presence of a catalyst is obtained by the ecofriendly method without the application of toxic sulfides, extreme pressures and temperature. This type of lignin contains a small amount of sulfur, is soluble in organic solvents, and possesses limited solubility in water which makes this material attractive in metals adsorption from wastewater. The adsorption ability of organosolv lignins (OrgL) (softwood (SW) organosolv lignin, SWOrgL and hardwood (HW) organosolv lignin, HWOrgL) towards Cu(II) and Cd(II) was examined. It was found that the sorption of metals increased with the decreasing ionic strength and the increasing pH. The adsorption capacities were 1.37 mg/g (SWOrgL) and 2.54 mg/g (HWOrgL) for Cu(II) and 0.92 mg/g (SWOrgL) and 2.06 mg/g (HWOrgL) for Cd(II). The adsorption capacities were smaller compared to those of the kraft lignin (KL) (SWKL > HWKL > HWOrgL > SWOrgL) therefore the additional pretreatment or/and modification might be necessary to improve the adsorption capacities. The time required to reach the system equilibrium was 80 min. The kinetic data were fitted well by the pseudo second order kinetic equation while the adsorption isotherm cannot be described well by both the Langmuir or Freundlich model. The adsorption of metal(II) involved weak ion exchange interactions between the functional groups (phenolic, carboxylic groups) and metallic ions being limited by the existence of competitive effects of H⁺ and Na⁺ ions of adsorption sites (Harmita et al., 2009). The other studies show that the adsorption of Cu(II) ions from the aqueous solution on the ethanol-based organosolv lignin was dependent on the initial concentration ($C_0=3\times10^{-4}$ - 6×10^{-4} mol/L) and pH (3.5-5.5) (amount of Cu(II) ions adsorbed onto the lignin (q_t) increased with the increasing C_0 and pH) and temperature (293-323K) (q_t values decreased with an increase in temperature). The maximum percentage removal was 40.74% within 10 min at $C_0=3\times10^{-4}$ mol/L and $T=20^\circ\text{C}$) and the adsorption capacities were also quite small being 1.68 mg/g. The desorption yield was 40% using 0.1 mol/L HCl and the adsorption process was fitted well by the Freundlich isotherm (Acemioğlu et al., 2003).

The hydrolysis lignin obtained during lignin separation from plants by the acid hydrolysis process and condensation reactions causing the CO bonds to be replaced by CC is rarely applied for metal removal from wastewaters due to being not cost effective, low yield of lignin, application of toxic and corrosive acids and anticorrosive vessels requirements (Esteghlalian et al., 1997; Selig et al., 2007). As it was pointed out by Merdy et al. (2002) a small adsorption capacity (4 mg/g, pH 6) of hydrolysis lignin from wheat straw was obtained for Cu(II) at 297K and the existence of Ca(II) did not influence the adsorption yield. The carboxylic and phenolic groups are involved in copper(II) adsorption with relatively stable surface complex formation.

The second group of lignin materials is **modified lignin based adsorbents**. As it was mentioned above in most cases the non-modified lignin materials do not possess large adsorption ability for metal removal from aqueous solutions (commonly less than 10 mg/g) therefore in their inactivated form, they possess limited applicability which is consistent with few available literature data (Ge et al., 2014a). From the practical point of view, the modification/activation procedures ensure the material desirable features (hydrophobicity, hydrophilicity, adsorption capability, stability, selectivity) which makes these materials more attractive from the application point of view (Li et al., 2019; Santander et al., 2021; Wang et al., 2022). Lignin could be modified by hybridization, crosslinking, condensation, hydrogen bond network formation, copolymerization, or grafting of functional groups. The reactivity of the phenol hydroxyl groups, the active hydrogen atom (para and ortho sites), and the alcohol hydroxyl groups as well as the side chains makes the lignin modification easy. By grafting, special functional groups could be introduced into the lignin structure which is classified into three categories: sulfur-containing, oxygen-containing and nitrogen-containing groups. These groups have free valence electrons therefore they interact with metals resulting in their more efficient removal (Ge and Li, 2018; Santander et al., 2021; Wang et al., 2022).

Modified lignin with the sulfur-containing functional groups

Sulfur according to the hard and soft acids and bases theory (HSAB) is a soft base that has a strong affinity for soft acids such as metal ions e.g. Cd(II), Cu(II), Hg(II), Pb(II) etc. Moreover, sulfur is characterized by small affinity for light metal ions such as Na(I), K(I), Mg(II). The functional groups containing sulfur e.g. mercaptan (thiol), xanthate, dithiocarbamate, sulfonate groups are widely used for designing and preparation of advanced adsorbents containing lignin for metals removal from water and wastewaters (Supanchaiyamat et al., 2019). Sulfomethylation and sulfonation are the most widely used methods for lignin modification which allow for incorporation of methylene sulfonate (CH_2SO_3) and sulfonate (SO_3) into lignin macromolecules providing good hydrophilicity (Ge et al., 2014b). The bi-functionalized aminated and sulfomethylated lignin (ASL) was synthesized by the Mannich reaction and sulfomethylation and applied for Cu(II) and Pb(II) removal. ASL exhibited the adsorption capacity values being 45.4 mg/g for Cu(II) and 53.8 mg/g for Pb(II) (pH 6.0, $T=298\text{K}$). The kinetic studies were well described by the PSO model, ASL is characterized by fast kinetics (the time required to reach the system equilibrium was 60 min at the initial concentration, $C_0=50\text{ mg/L}$, ASL dosage: 0.5 g/150 mL and $T=298\text{K}$ whereas the isotherm data followed the Dubinin-Radushkevich model. The amino and sulfonic groups take part in Cu(II) and Pb(II) binding by the complex formation (amine groups) and electrostatic interactions (sulfonic groups) (Ge et al., 2014a).

The sulfonic functional groups were incorporated into the lignin structure by the sulfur trioxide (SO_3) micro-thermal-explosion process in order to form the mesoporous lignin

based biosorbent (MLBB) from rice straw which further was applied for Pb(II) removal. As it was pointed out by the authors, the large surface area of MLBB (186 m²/g), its mesoporous structure (mean pore size distribution=5.50 nm, mean pore value=0.35 cm³/g) and the abundance of sulfonic functional groups (S: 2.51 ± 0.01%) are responsible for the excellent adsorption capacity of Pb(II) (adsorption capacity was equal to 952 ± 31 mg/g at 293 K). 5 hr was sufficient to reach the system equilibrium. The PSO and Langmuir models fit the experimental data properly suggesting that the chemical sorption takes place and the adsorption occurred on a homogeneous surface (Xu et al., 2017).

Another kind of sulfur-containing groups that can form largely stable complexes with metals is xanthate prepared with the participation of an organic compound containing the hydroxyl groups and carbon disulfide. The lignin xanthate resin (LXR) was prepared by a two-step reaction using alkaline lignin and carbon disulfide and after its characterization, it was applied for Pb(II) removal (Figure 2.9a). LXR is characterized by a 4.8 times larger adsorption capacity than alkaline lignin at 303K. Such enhanced removal ability of LXR is attributed to the xanthate groups and porous structure with the pore diameter below 100 nm of synthesized material. Pb(II) adsorption was spontaneous (ΔG° possesses negative values) and endothermic in nature (ΔH° possesses positive values) (Li et al., 2015b). The adsorption capacity was 64.9 mg/g at pH 5.0 and 303K based on the Langmuir model and the adsorption kinetics followed the pseudo-first order kinetic model (PFO).

Lignin could be also modified by the dithiocarbamate groups (DTC) due to their good sorption capacity for metals compared to the alkaline and alkaline earth metals and this moiety introduced into lignin is the best explored (Ge and Li, 2018). This large metal adsorption ability was proved in a few studies (Ge et al., 2014c; Ge et al., 2016a; Li et al., 2015c). For example, lignin dithiocarbamate (LDTC), obtained by anchoring the dithiocarbamate to the ortho sites of phenol hydroxyl groups in the alkaline lignin matrix, shows large adsorption ability for Cu(II) (adsorption capacity, q_e =175.9 mg/g) and for Pb(II) (q_e =103.4 mg/g) at pH 6.0 and 298 K. The elemental analysis indicated that the LDTC material contains a larger amount of S and N atoms and smaller of C atoms (39.86% of C, 17.18% of N, 5.93% of H and 20.90% of S) compared with alkaline lignin. 1 g of LDTC contained 3.26 mmol of dithiocarbamate groups which confirmed their successful introduction of into alkaline lignin. Moreover, the adsorption of metals on LDTC from the multi-component solutions confirmed large biosorbent ability for Pb(II) adsorption which was confirmed by the selectivity series Pb(II) > Cu(II) > Cd(II) > Zn(II). Adsorption on LDTC follows the PSO and Dubinin–Radushkevich models (Ge et al., 2014c).

Another example was the surface functionalized porous lignin (SFPL) (Figure 2.9b) synthesized by a two-step process containing a porous structure with a large number of mesopores (41.3 nm) and 12 times larger specific surface area (22.3 m²/g) compared to the original lignin as well as a larger amount of dithiocarbamate groups (2.8 mmol/g). The SFPL shows 13 larger higher adsorption capacity being 188 mg/g for Pb(II) (pH 5.0,

298 K) than that of the original whereas the percentage removal of Pb(II) was 99% ($C_0=20$ mg/L, volume of the solution, $V=50$ mL $t=30$ min, $m=0.01$ g of SFPL). SFPL is characterized by the fast kinetics (equilibrium time, $t_{eq}=30$ min). Kinetics is well described by the PSO model and the adsorption is endothermic and spontaneous whereas the isotherm data followed the Langmuir isotherm model (Li et al., 2015c). Organosolv lignin functionalized with the dithiocarbamate groups (OLDTC) prepared by a microwave-assisted method was evaluated for the Hg(II) adsorption ability. The maximum adsorption capacity equal to 210 mg/g for Hg(II) and being 2.8 fold higher than that of original lignin. The time required to reach the system equilibrium was 40 min and the adsorption kinetics was fitted well by the PSO model while the adsorption isotherm was described by the Freundlich isotherm model indicating a heterogeneous surface of the prepared lignin material (Ge et al., 2016a).

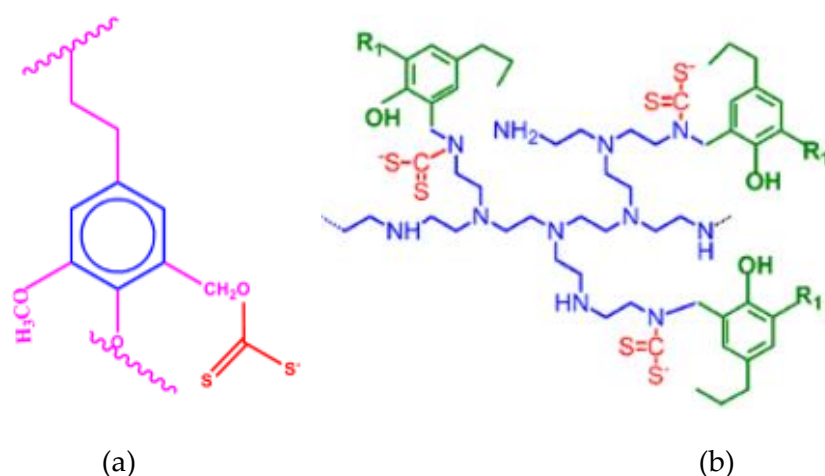


Figure 2.9. Structures of the lignin xanthate resin (a) and surface-functionalized porous lignin with dithiocarbamate groups (b) (from Ge et al., 2014c; Li et al., 2015c).

Functionalization of lignin by the thiol groups increases the adsorbent selectivity for metals, decreases the water solubility of lignin and improves the adsorbent separation. For example, the 1,2,4-triazole-3-thiol modified lignin-based adsorbent obtained by the UV-initiated thiol-yne click reaction could be useful for Cd(II) removal with a large adsorption capacity of 72.4 mg/g (pH 6.0, 298 K) and an improved selectivity, which was 8.6-fold higher than that of the original lignin (kinetics: PSO model, isotherm: Langmuir model) (Jin et al., 2017).

Modified lignin with the oxygen-containing functional groups

Lignin possesses the oxygen-containing groups e.g. carboxylic and hydroxyl functional ones. The increase number of oxygen-containing groups (hydroxyl, ethers) can improve the metals adsorption due to the presence of N donor atoms and their free electron pairs results in metal ions chelation or their reduction (Supanchaiyamat et al., 2019). Additionally, the increasing number of oxygen-containing groups can improve not only the adsorption ability but also lignin dispersion (Ge and Li, 2018). On the other hand, the

oxygen-rich macromolecules are sensitive to inter- and intramolecular hydrogen bonding, which can lead to flocculation and reduce adsorbent/metal ion interactions (Supanchaiyamat et al., 2019). Metal adsorption on the materials with oxygen-containing functional groups could proceed by the ion exchange mechanism, metal complexation, or redox mechanism due to the presence of electron donating groups such as ether or hydroxyl ones (Liang et al., 2013b).

The micron-sized lignin based ion exchanger particles (LBP) containing the carboxyl, lactones and phenolic groups was prepared by condensation polymerization of sodium lignosulfonate with the glucose derivatives (functionalized with 5-hydroxymethylfurfural and levulinic acid) under the acidic conditions (in diluted H_2SO_4) and used in the removal of metals such as Cu(II), Cd(II), Cr(III), Ni(II), Pb(II) (Liang et al., 2013a) and Cr(VI) (Liang et al., 2013b) (surface area 13-20 m^2/g , pore diameter $<10 \text{ \AA}$). The LBP shows an enhanced affinity for Pb(II). The adsorption capacity decreased in the order: Pb (II) (194.6 mg/g) $\gg$ Cu(II) (60.0 mg/g) $>$ Cd(II) (48.8 mg/g) $>$ Ni(II) (42.5 mg/g) $>$ Cr(III) (41.8 mg/g). The uptake capacity of LBP decreased slightly in four sorption-desorption cycles and the largest reduction of adsorption capacity was observed for Cr(III) for which the smallest equal to 13.35% desorption yield was achieved in the first cycle. The desorption yields by using 0.5 mol/L hydrochloric acid as an eluting agent calculated based on all cycles were 98.23%, 90.28%, 80.03%, and 71.75% for Cu(II), Ni(II), Cd(II), and Pb(II). Desorption proceeds via the ion exchange between the hydrogen ions from HCl and the retained metal ions onto LBP (Liang et al., 2013a). Moreover, the maximum Cr(VI) adsorption capacity was found to be 74.29 mg/g and the optimal pH was 2. The adsorption process was endothermic and spontaneous. The proposed mechanism involved the electrostatic attractions between the chromate ions and protonated LBP, then the reduction of Cr(VI) to Cr(III) and the bonding of Cr(III) with the oxygen-containing functional groups (Liang et al., 2013b). A metal reduction was also observed during Au(III) adsorption on the gel adsorbents of crosslinked with lignocatechol, lignophenol and lignopyrogallol. The adsorption capacity was 1.9-2.4 mol Au(III)/kg of dry gel. The main advantages of new gel adsorbents are not only high selectivity towards Au(III) but also large adsorption ability regardless of the pH. The highest selectivity for Au(III) shows gel crosslinked with lignophenol. The ether and hydroxyl functional groups of the gels are responsible for Au(III) reduction to metallic gold, Au(0) (Parajuli et al., 2006a). The breakthrough test carried out to separate Au(III) from Pd(II) and Pt(IV) from low-concentration metals solution by crosslinking with lignophenol shows a small selectivity for Pd(II) and Pt(IV) - these metals appear immediately in the eluate whereas the breakthrough point for Au(III) was observed after 20 h. The adsorption capacity of the gel crosslinked with lignophenol was much smaller than 0.05 mol/kg (feed rate=6 mL/h, weight of adsorbent packed into column= 0.2 g, C_0 =100 mg/L for Pt(IV), Pd(II), C_0 =100 mg/L for Au(III), HCl=1 mol/L, T =5-20°C) in the column test compared to the batch one (Parajuli et al., 2006a).

The lignin functionalization by the catechol (polyphenolic ligand) increases the number of phenol hydroxyl groups largely compared to the natural lignin which has about 10% of hydroxyl groups and causes branching of the molecule. The lignin based gel obtained using catechol shows a large adsorption capacity for Pb(II) ($q_e=370.8$ mg/g), smaller for Cd(II) ($q_e=129.3$ mg/g) and much smaller for Co(II) ($q_e=43.6$ mg/g) at pH 5.2 and 313K. More than 50% of Pb(II) was adsorbed after 30 min of phases contact time whereas the complete removal was obtained after 24 h shaking. The examination of pH effects on metals adsorption shows that the selectivity order with respect to the pH width range among the tested metal ions is as follows: Pb(II) > La(III) > Fe(III) > Al(III) > Ni(II) > Zn(II) > Cd(II) > Co(II) indicating the possibility of their separation at specifying pH values ($m=20$ mg, $V=15$ ml, $C_0=0.2$ mmol/L, pH 5, $T=303$ K). The separation test of Pb(II) and Zn(II) shows that the crosslinked lignocatechol gel could be reused and applied in 10 cycles of sorption-desorption for Pb(II) ion (pH 3, feed rate of 10 ml/h, C_0 Pb(II)=10 mg/L, eluting agent 1 mol/L HCl) with the high efficiency (in all cases adsorption and elution were almost quantitative). The authors pointed out that adsorption of metals proceeds mainly by the cation exchange interactions between the metal(II) ions and phenol hydroxyl groups (Parajuli et al., 2005).

The oxidative modification of lignin obtained during the wheat straw organosolv process by a polyoxometalate was conducted to increase the oxygen-containing adsorption sites using O_2 or H_2O_2 as co-oxidants. The condensation degree of lignin and oxygen-containing group contents (COOH and aliphatic OH) increased significantly without the polymer structure changes. Under the optimal experimental conditions (pH 5, $T=293$ K) the adsorption capacity of modified lignin increased twofold ($q_e=155.4$ mg/g) and threefold ($q_e=35.9$ mg/g) for Pb(II) and Cd(II) compared to the parent lignin, respectively (Dizhbite et al., 2013). The oxidized lignin solubility decreased due to the condensation reactions and the sorption ability was the best applying the polyoxometalate/ H_2O_2 system as a result of the largest primary COOH groups content which increases the sites for metal binding by coordinative linkages (Dizhbite et al., 2013). The slight increase of the adsorption capability of Cd(II) ions by oxidized lignins (373K, 2h, H_2O_2) comes from different sources: cane bagasse pretreated by sulfuric acid, soda pulping bagasse, eucalypt Kraft lignin, and commercial Kraft lignin compared with those of the original lignin which was also observed by the other authors and explained by the presence of a greater amount of carboxyl groups in the modified lignin (Quintana et al., 2008).

The carboxymethylated formic lignin shows large adsorption capability for Pb(II) ions which increased with the pH increase and decreased with the ionic strength increase. The adsorption was 107.5 mg/g for Pb(II) at pH 6.0 being higher than for Cd(II) 67.7 mg/g at pH=5.0 (Ge and Li, 2018).

The lignin from the wheat straw was modified to obtain dimethyl-acetoxy-(2-carboxymethyl ether)-lignin ammonium chloride (DALAC). The result of lignin modification was the introduction of quaternary amine (3.66%) and carboxyl (1.37%) functional groups

which showed large adsorption ability of Cu(II) ions at pH 5.5 and 298K. The obtained adsorption capacity was $q_e=399.0$ mg/g under the optimal experimental conditions: 0.1 g/L, pH 5.5, $t=6$ h (Tian et al., 2014).

Lignin modified with nitrogen-containing functional groups

The amination processes of lignin introduce the amine $-NH_2$ groups into its structure which makes the formation of new useful materials for metal removal possible.

Lignin was isolated from an industrial black liquor by acid precipitation and then modified by the Mannich reaction to obtain the aminated epoxy lignin. The pH of a solution affects the adsorption capacity for Cu(II) and Pb(II) and the optimum pH was chosen to be 6-7 to avoid metal precipitation. The adsorption capacity was 72.48 mg/g and 55.35 mg/g for Cu(II) and Pb(II), respectively. The values of thermodynamic parameters indicated that the adsorption process was spontaneous and endothermic in nature (Liu et al., 2013).

The lignin-PEI was obtained by subjecting lignin to enzymatic hydrolysis, and then crosslinking it with polyethyleneimine in order to introduce amine functional groups. The lignin-PEI adsorbent was characterized by a nitrogen content of 9.02% and a specific surface area of 20.32 m²/g. The Cr(VI) adsorption process occurs via ion exchange, electrostatic attraction, complexation, and Cr(VI) reduction. The batch method was employed to determine the maximum adsorption capacity, which was found to be 898.2 mg/g at pH 2, 48 h, 318 K. Chromium regeneration by the 0.2 mol/L HNO₃ after 4 cycles ensured 35.1% adsorption efficiency (Shi et al., 2020).

Lignin microspheres (LMS), prepared by the inverse suspension copolymerization method, were used for the removal of Pb(II) from aqueous solutions (diameter 348 μ m, surface area 9.6 m²/g). The total amount of amine functional groups was 7.5 mmol/g. LMS showed a much larger adsorption capacity for Pb(II) (33.9 mg/g) than alkaline lignin and poplar lignin. LMS could be reused and easily regenerated, although a slight decrease in adsorption capacity of 12.5% was observed after five adsorption-desorption cycles (Ge et al., 2016b).

Lignin-poly(N-methylaniline) nanocomposites synthesized by the chemical oxidative polymerization (particle diameter of 68.3 nm) exhibited large adsorption ability for Ag(I). The adsorption capacity was 1556.8 mg/g at 303 K. The sorption mechanism involved ion exchange (the H⁺ ions on the poly(N-methylaniline) chains were replaced by Ag(I) ions), reduction of Ag(I) to Ag(0) leads to the formation of silver nanoparticles and their subsequent growth to larger sizes. Although the desorption of silver from the lignin-poly(N-methylaniline)-Ag complex is not possible, these nanomaterials could be used directly as antimicrobial agents (Lü et al., 2014).

The lignin gels (PA-lignin, EN-lignin) containing the primary amine (PA) and ethylenediamine (EN) functional groups were effective in the adsorption of noble metal ions such as Au(III), Pd(II), and Pt(IV) from acid solutions whereas the base metals such as

Cu(II), Fe(III), Ni(II), and Zn(II) were almost not adsorbed on these gels. The largest adsorption capacity was obtained for Au(III) ions and the selectivity order was Au(III) > Pt(IV) > Pd(II) for EN-lignin and Au(III) > Pt(IV) > Pd(II) for PA-lignin. The main adsorption mechanism was the formation of the ion pairs between negative charge metal chloro-complexes and protonated functional groups of gels in the acidic media and also reduction of Au(III) was confirmed. The PA-lignin was also used to separate traces of Pd(II) from a large excess of Cu(II) using the column method, demonstrating the possibility of metal separation and preconcentration of traces of Pd(II). The adsorption capacity for Pd(II) was 0.18 mol/kg gel (Parajuli et al., 2006b).

Incorporation of the soft N and S donors (EHL-NS) into enzymatic hydrolysis lignin (EHL) contributed to the chemical complexation of Hg(II) with EHL-NS resulting in its enhanced adsorption of Hg(II) from aqueous solutions. The adsorption capacity was 180 mg/g at 298K (Huang et al., 2017).

Adsorptive composite materials

The adsorptive composite materials had also good retention properties towards metal ions. Graphene oxide (GO) and polyaniline (PANI) contain many functional groups e.g. imines in PANI which are able to interact with metal ions (Zhang et al., 2023).

The in-situ polymerization was used for the preparation of lignosulfonate (LS)-graphene oxide(GO)-polyaniline (PANI) nanocomposite (LS-GO-PANI). Two GO surface sheets in LS-GO-PANI were uniformly surrounded by nanofibers of 50 nm. The composite was used for Pb(II) removal and the maximum adsorption capacity was 216.4 mg/g at pH 5 and T=303 K (Yang et al., 2014). The free radical polymerization was applied for the lignin/chitosan adsorbent (LS/CS) preparation (lignosulfonate+chitosan) as well as for Pb(II) removal from aqueous solutions. The porous properties of adsorbent were proved and the pore diameter was 1 μ m. The maximum adsorption capacity for Pb(II) was 345 mg/g at pH 7 and T=293 K. The adsorption of Pb(II) proceeds via electrostatic attractions and metal chelation mechanism. The adsorption process was spontaneous and endothermic (Pan et al., 2021). Preparation of the chitosan/lignosulfonate adsorbent (CSLS) involved the utilization of free radical polymerization, yielding a porous structure with a diameter of 1 μ m. This material was employed for Pb(II) removal. The maximum adsorption capacity for Pb(II) was larger compared to that of LS/CS material being equal to 525 mg/g at pH 4 and T=293 K. CSLS demonstrated a recycling capacity of >92% after five adsorption-desorption cycles, with desorption step being executed by 0.1 mol/L HCl (Zhang et al., 2021).

The Cr(VI) removal ability was examined by the lignin/polyaniline composite (Seo et al., 2019), MoS₂/lignin-derived carbon (MoS₂@LDC) nanocomposites (the pore size distribution: 35-45 nm) (Chen et al., 2021), the lignin/graphene oxide composite nanospheres (LGNs) (Yan et al., 2021) and the graphene hydrogels (LGH) (Sun et al., 2021). The lignin/polyaniline composite was obtained in the polymerization reaction of polyaniline

and lignin (N-containing functional groups were introduced into the lignin structure). The adsorption efficiency was close to quantitative being 99% (Seo et al., 2019). The removal efficiency of Cr(VI) on MoS₂/lignin-derived carbon was >95%. The maximum adsorption capacity was 198.7 mg/g at pH 2±0.1, T=298.15 K and C₀=20 mg/L whereas the selectivity series was Cr(VI)>Cu(II)>Zn(II)>Ni(II)>Cd(II). The Cr(VI) adsorption mechanism was the surface complexation and reduction (Chen et al., 2021). The lignin/graphene oxide composite nanospheres being spherical in shape, possess a smooth surface and due to the presence of GO improved stability and enhanced amount of oxygen-containing functional groups. The adsorption capacity for Cr(VI) was determined to be 368.78 mg/g at pH 2. The adsorption process on LGNs is believed to occur via the following mechanisms: ion exchange, surface complexation, electrostatic attraction, and reduction. The lignin/graphene oxide composite nanospheres could be regenerated with 0.1 mol/L NaOH, and a slight reduction in adsorption efficiency of 9.7% was observed after five sorption-desorption cycles (Yan et al., 2021). The maximum adsorption capacity of LGH for Cr(VI) was 1743.9 mg/g at pH 2, 18 h. This adsorbent was regenerated by the 0.1 mol/L NaOH with the removal efficiency >88% after 5 sorption-desorption cycles (Sun et al., 2021).

Many other examples of lignin based adsorbents such as hybrids, nanocapsules, polymers, etc. application for metals removal could be found in the review paper (Zhang et al., 2023).

At present, lignin plays an important role in the preparation of adsorbents for metal removal and separation. As demonstrated by the results described above, native lignin usually shows smaller metal capacity compared to functionalized lignin. By introducing sulfur-containing, nitrogen-containing and oxygen-containing functional groups, lignin adsorbents achieved improved adsorption for metal ions. In the preparation of lignin-based materials, the selection of a suitable raw material as well as appropriate preparation steps are crucial. The development of a lignin-based materials preparation method of less complexity of the preparation process together with avoiding toxic materials used to modify the lignin without secondary pollution to the environment is still a great challenge.

2.3 Green composites with lignin

Polymers and polymer composites play an essential role in the development of new technologies and modern living due to their exceptional combination of different characteristics such as versatility, flexible design, and durability. Their strength and durability, in addition to the lightweight without compromising their performance, make them an important prerequisite for the development of new technologies in the aviation and automotive industries. Their design flexibility due to which polymer-based products can be produced in various complex shapes and structures, relatively cost-effective raw material and processing, combined with the possibility to change the polymer properties by incorporation of different fillers leads to the application of the polymers in almost every

industry, starting from electronics to medicine and healthcare, customer goods, construction, packaging and textile (Cabrera, 2021; La Mantia and Morreale, 2011; Shekar and Ramachandra, 2018; Thakur et al., 2010; Thakur et al., 2014).

Traditional synthetic polymers and polymer-based composites are a well-established class of materials that are mainly prepared from petroleum-based resources. Common examples of the most used polymers include polyethylene, polypropylene, polyvinyl chloride, and polystyrene. Despite their widespread application, petroleum-based polymers possess several significant disadvantages, specifically regarding their environmental impact and sustainability. A leading issue regarding synthetic polymer materials is their non-biodegradability, so they remain in nature for a very long time, thus contributing to the rapidly growing pollution. Moreover, there are issues with the disposal, reclaim, reuse, and recycling of polymers since the existing recycling methods are often inefficient or underdeveloped resulting in a rapid increase in plastic waste. Another problem related to plastic waste is the migration of harmful chemicals into water and soil, as well as the release of micro and nanoplastics. All of this represents a serious problem that has a significant negative impact on both the health and quality of life of people and the entire living world. The problems related to the sustainability of this type of plastic are related to the raw material for their production, which is based on petroleum resources, given that the fossil fuel reserves are decreasing. Given these shortcomings of traditional plastics, it is of utmost importance to transition to the more sustainable production of polymers and polymer composites that are biodegradable to overcome the environmental problems posed by the excessive use of plastics from petroleum-based resources (Balart et al., 2020; Cabrera, 2021; La Mantia and Morreale, 2011; Shekar and Ramachandra, 2018; Thakur et al., 2010; Thakur et al., 2014). Green polymers and green polymer composites are emerging as a response to the limitations of traditional plastics. Green polymers and green polymer composites are types of polymers that are synthesized from renewable natural resources or polymers that are biodegradable and have little impact on the environment. The use of this kind of resource promotes sustainability and environmental friendliness. Green polymer composites combine biodegradable and polymers from renewable resources with fillers from renewable resources like natural fibres, lignin, cellulose etc. whose role is to enhance the performance of the polymer matrix (Shekar and Ramachandra, 2018; Thakur et al., 2010; Thakur et al., 2014). Green polymers and green polymer composites possess a range of advantages that make them a key step towards a more sustainable future. These materials are mostly synthesized from monomers that are derived from renewable natural raw materials, such as various plants, thus eliminating dependence on petroleum-based resources, as well as reducing the carbon footprint. Green polymers are biodegradable, meaning they break down naturally after being disposed of in landfills, thus reducing the amount of plastic waste. Additionally, green polymers and green polymer composites tend to be safer and present fewer health risks to the environment. This has been a significant problem with traditional plastics. The sustainability of green polymer composites is also seen in the fact that natural fibers, such as flax, hemp, or jute, are used as

fillers, as well as cellulose or lignin, which occur as by-products from the wood industry, agriculture, the tobacco industry, etc. Through the valorization of agricultural by-products and waste materials, not only is a step forward towards greater sustainability but a significant contribution is made to the circular economy. Green polymers and green polymer composites often exhibit competitive mechanical properties and durability compared to traditional polymers and polymer composites (Balart et al., 2020; Shekar and Ramachandra, 2018; Thakur et al., 2010; Thakur et al., 2014). Thanks to the listed advantages, green polymers and green polymer composites are becoming more widely accepted by multiple industries. Thus, in the food industry, polylactic acid is increasingly used for food containers, bags, and wraps, in response to the growing demand for eco-friendly packaging solutions. In the automotive industry, green polymers are used to make interior panels, seat frames, and dashboard covers, where their lightweight properties help improve fuel efficiency and reduce emissions. In construction, where low emissions of harmful chemicals into the living space are of utmost importance, green polymers and green polymer composites are used for insulation or coatings. These materials also find application in the consumer goods sector, i.e., they are used to produce furniture, utensils, etc., helping to reduce dependence on fossil fuel-based plastics (La Mantia and Morreale, 2011). These applications demonstrate the versatility and environmental potential of green composites in shaping a more sustainable future across a range of industries.

Green polymer composites are prepared using different methods. Some of the most common methods include solution casting and melt mixing (La Mantia and Morreale, 2011; Ridho et al., 2022; Thakur et al., 2010; Thakur et al., 2014; Wang et al., 2021). These methods will be explained in the text that follows.

Solution casting is a widely used method for the preparation of polymer-based composites. This method involves dissolution of a polymer and filler in a suitable solvent to create a homogeneous solution (Figure 2.10a). Afterwards, this solution is casted or spread onto an appropriate mold or substrate, where the gradual evaporation of the solvent leads to the formation of a solid film. The evaporation of the solvent might occur at ambient conditions or in controlled conditions in chambers with controlled temperature and humidity. This is a highly versatile method that allows the selection of polymers and solvents based on the desired characteristics of the final product. The controlled evaporation of solvent has a significant influence on the film's structural characteristics, uniformity, and stability. By dispersion of the filler within the polymer solution, even distribution and formation of a strong interface between the two phases (polymer matrix and filler) is ensured (Borbolla-Jiménez et al., 2023; Tang et al., 2016; Thakur et al., 2014; Wang et al., 2021). The main advantage of the solvent casting method is the precise control over the evaporation process. The slow evaporation of the solvent leads to uniform distribution of filler which has a positive influence over the materials properties. Furthermore, by adjusting the conditions of the solvent evaporation, greater control over the properties of the final film is ensured. This is also a cost-effective and quite simple method that requires minimal equipment and

fewer steps. The main drawback of this process is related to the scaling up. Namely, the considerable amounts of solvent which this method requires, not only will increase the costs of the process but also may raise concerns related to environmental and safety regulations (Borbolla-Jiménez et al., 2023; Tang et al., 2016).



Figure 2.10. Schemes of (a) the solvent casting method and of melt mixing method (b).

The mentioned drawback of the solution casting can be overcome by melt mixing. This method is very effective and often is used to prepare polymer composites in which the filler is in nanodimensions. Compared to the solution casting, melt mixing does not require usage of solvents, which makes it more eco-friendly process. The method involves heating the polymer and applying shear forces to it, causing the polymer to soften and the filler to be uniformly dispersed within the polymer matrix. This is most often done using extruders (Figure 2.10b). The polymer and the filler are fed into the barrel of the extruder in which they are both heated using different heaters to melt the polymer and thoroughly mixed using a turning screw to promote uniform dispersion of the filler. The composite exits the extruder through a die.

The melt mixing method is very practical and straightforward as the need for hazardous solvents and the associated disposal issues are avoided. Additionally, this method is quite adaptable and has great potential to be scaled up, as it can be integrated with existing manufacturing equipment such as extruders and injection molding machines. The limitations of the melt mixing are related to the processing parameters and the properties of the fillers. Specifically, many polymers degrade under higher temperatures which inevitably compromises the properties of the final product. Achieving uniform dispersion of the filler can be an important challenge as some fillers tend to aggregate or have low compatibility with the matrix. These issues also can lead to compromised properties of the composite. To avoid these problems careful control of the process is of great importance (Albdiry, 2024; Pötschke et al., 2005).

2.3.1 Application of lignin as filler in green polymer composites

Lignin is among the most used fillers for the synthesis of green polymers. This natural biopolymer has an important role in advancing the sustainability of polymer

composites. The incorporation of lignin into polymer matrices not only enhances material properties but also contributes to environmental conservation by improving biodegradability (Low et al., 2021; Thakur et al., 2014). The introduction of lignin into polymer matrices has several benefits, some of which are improving the thermal stability of the polymer matrices, as well as improving the mechanical properties. Additionally, its antioxidant and antimicrobial properties have the potential to further enhance the properties of polymer matrices, thereby expanding the use of green polymer composites in the food industry (food packaging) or in healthcare applications. Lignin-derived flame retardants represent a promising sustainable alternative to traditional halogenated flame retardants. The performance of lignin-based flame retardants can be further improved by chemical modification while maintaining environmental safety (Bass and Epps, 2021; Komisarz et al., 2023; Low et al., 2021; Morena and Tzanov, 2022; Ridho et al., 2022; Thakur et al., 2014; Wang et al., 2021; Yang et al., 2020).

Undoubtedly, lignin's role as a filler enhances various polymer properties, significantly increasing its value. Beyond its functional benefits, lignin also holds economic importance. As a low-cost by-product, its use as a filler reduces the production costs of green composites without compromising their performance, making it a highly viable and sustainable option. Lignin nanoparticles further expand the application of lignin in the preparation of polymer composites, thereby increasing its value. Due to the large specific surface area, and thus reactivity, the introduction of these nanoparticles into a polymer matrix causes a significant improvement in a number of their properties, such as antibacterial activity, antioxidative properties and mechanical properties (Low et al., 2021).

In addition to the benefits of using lignin as a filler in polymer matrices, which are seen in enhanced composite properties and increased eco-friendliness and sustainability, several disadvantages and challenges arise during the synthesis of lignin-based polymer composites. These challenges have a significant impact on the processing, performance and commercialization of the lignin-based polymer composites. Therefore, developing effective solutions to overcome these challenges is of great importance.

One of the problems associated with lignin is that its quality, chemical composition, molecular weight and consequently, its properties depend largely on the source from which the lignin is isolated, as well as the method used to isolate it. Because of this, standardization of the synthesis procedure for lignin-based polymer composites is difficult, and the reproducibility of the properties of these composites is also compromised. The incompatibility of lignin with most matrices is also a serious problem that must be addressed. Incompatibility with the matrix leads to poor dispersion and aggregation of lignin, as well as poor adhesion of lignin and matrix, which compromises the structural integrity of the composite and thus its properties. Lignin competes with well-established nanomaterials and synthetic fillers which offer superior properties and easier processing. For example, despite its flame-retardant properties, lignin does not meet the industrial standards

for this type of material, so additional modification of lignin is needed, this can increase the production complexity and costs (Kim and Chung, 2024; Low et al., 2021; Ridho et al., 2022; Yang et al., 2020).

While lignin offers significant potential as a filler in polymer composites, its widespread application is hindered by regulatory and production challenges. These issues can be overcome by further research and testing which should develop strategies for reproducible lignin processing and composite synthesis which will result in obtaining lignin-based composites with properties competitive with those of already commercial products. Promoting the use of lignin in materials science aligns with global sustainability goals by reducing waste biomass, enhancing material properties, and minimizing environmental impact.

The incorporation of lignin into polymer matrices is a focus of numerous scientists, especially due to the excellent properties of the obtained composites.

2.3.2 Poly(vinyl alcohol)/lignin composites

Poly(vinyl alcohol) (PVA) is one of the most widely used matrices for the synthesis of lignin composites due to several favourable properties such as biodegradability, mechanical strength, and ease of processing. PVA is synthesized through a two-step process that begins with the polymerization of vinyl acetate to form poly(vinyl acetate) (PVAc), followed by hydrolysis to produce PVA (Gaaz et al., 2015; Nagarkar and Patel, 2019; Türkoğlu et al., 2024). PVA is highly soluble in water which is of great importance for its industrial application. Its strong hydrophilicity and non-toxicity make PVA ideal for use in packaging, and in addition of its biocompatible, it is particularly valuable in medicine and pharmaceuticals, including drug delivery systems and wound dressings. Biodegradability and recyclability are also crucial for waste management, as they enable PVA to break down under environmental conditions, thereby reducing long-term plastic waste. The structure of PVA contains hydroxyl groups that are highly susceptible to enzymatic activity, enabling the degradation of the polymer in the presence of microorganisms. PVA has high solubility in water, a property that promotes hydrolysis and further accelerates its degradation. Owing to its water solubility, PVA can be recycled through solvent-based recovery processes, helping to reduce waste and support sustainability. In light of the application of PVA as a polymer matrix for the synthesis of green composites, PVA is known for its compatibility with a wide range of natural and synthetic fillers. This compatibility originates from its hydrophilic nature that enables strong interactions with polar fillers (Gaaz et al., 2015; Nagarkar and Patel, 2019; Türkoğlu et al., 2024; Adithyamol et al., 2024; Cao et al., 2024; El-Nemr et al., 2020; Parvathy et al., 2021; Han et al., 2025; Haque et al., 2021; Hararak et al., 2021; Huang et al., 2021; Liu et al., 2024; Odili et al., 2025; Pham et al., 2024).

Despite its advantages, PVA faces several challenges related to its water solubility which can lead to degradation in moist environments. Compared to other synthetic polymers, the production costs for PVA are higher, while its low thermal stability is low limits its use in high-temperature applications (Gaaz et al., 2015; Türkoğlu et al., 2024).

The introduction of lignin into PVA results in a significant improvement in a range of PVA properties. For instance, the incorporation of lignin significantly enhances tensile strength and elasticity. Additionally, when combined with lignin, PVA exhibits good thermal stability, moisture retention and ultraviolet resistance (Adithyamol et al., 2024; Cao et al., 2024; El-Nemr et al., 2020; Parvathy et al., 2021; Han et al., 2025; Haque et al., 2021; Hararak et al., 2021; Huang et al., 2021; Liu et al., 2024; Odili et al., 2025; Pham et al., 2024).

The incorporation of lignin into a PVA matrix presents several challenges that must be addressed to fully harness lignin's potential in enhancing the properties of PVA. One of the primary issues is the compatibility between lignin and PVA. Lignin has an amphiphilic nature, meaning it contains both hydrophilic and hydrophobic regions, which complicates its dispersion in the hydrophilic PVA matrix. To improve compatibility, lignin must undergo modification, enabling better integration with PVA. Due to the formation of hydrogen and π - π interactions between lignin particles, this filler tends to agglomerate when introduced into the polymer matrix which results in reduced mechanical properties of the composite. This behaviour diminishes the effectiveness of lignin as a reinforcing agent (Parvathy et al., 2021; Hararak et al., 2021; Pham et al., 2024).

Processing challenges related to the viscosity, solvent selection and mixing techniques further hinder the preparation of polymer/lignin composites, as the inadequate mixing can result in poor dispersion of lignin and reduced properties of the composites (Odili et al., 2025). Therefore, it is of utmost importance to develop methods for improving the dispersion of lignin throughout the PVA matrix, which will inevitably have a positive impact on the properties of the composite.

Strategies to overcome these issues include optimizing synthesis processes, modifying lignin and reducing the size of lignin to nano dimensions, which would not only enhance the dispersion of lignin through the polymer matrix but also improve its compatibility with PVA (Parvathy et al., 2021; Hararak et al., 2021; Pham et al., 2024).

The following section focuses on specific examples from the literature on the incorporation of lignin into a PVA matrix and its impact on the properties of the final product.

Cao et al. (2024) synthesized lignin nanoparticle/PVA composites by phenolation of bagasse lignin (BL) using a ternary deep eutectic solvent (DES). According to the study, the phenolation of lignin results in an increased number of phenolic hydroxyl groups on the surface of lignin. Through phenolation, the interaction between the lignin and the PVA matrix was improved. The preparation of this composite was through several steps as shown in Figure 2.11.

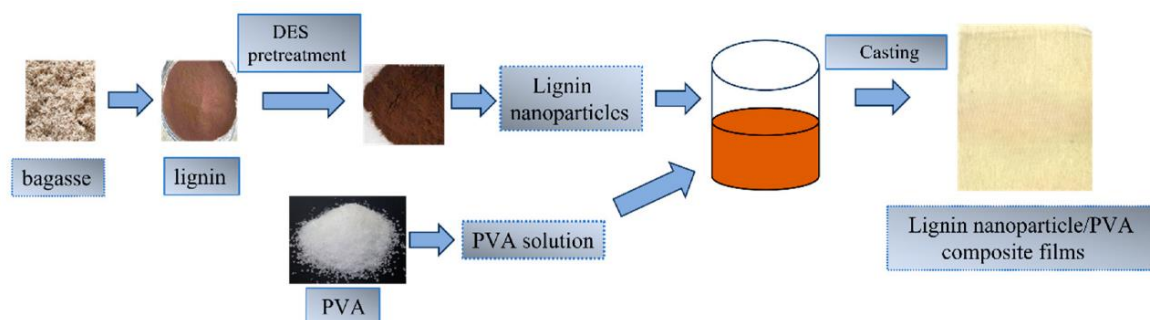


Figure 2.11. Schematic illustration of the fabrication process of lignin nanoparticle/PVA composite films (Cao et al., 2024).

Shortly, the bagasse lignin was subjected to phenolation using DES which consisted of choline chloride, formic acid and oxalic acid. Afterwards, this lignin was dissolved in sodium hydroxide solution, followed by dialysis to purify the lignin and precipitate the lignin nanoparticles. The nanoparticles from non-treated lignin were labelled as BLNPs, and the nanoparticles from the phenolated lignin were labelled as DLNPs. For preparation of composites, the PVA was dissolved in water and the DLNPs in concentrations of 1, 3, 5 and 10 wt% were added to the PVA solution. The mixture was sonicated to ensure good dispersion of DLNPs and cast into Petri dishes, after drying free-standing films were obtained (Cao et al., 2024).

Various properties of the DLNPs/PVA films were investigated, among them, the antioxidative potential was determined by monitoring the radical scavenging activity of the different composites towards 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical. The results are shown in Figure 2.12.

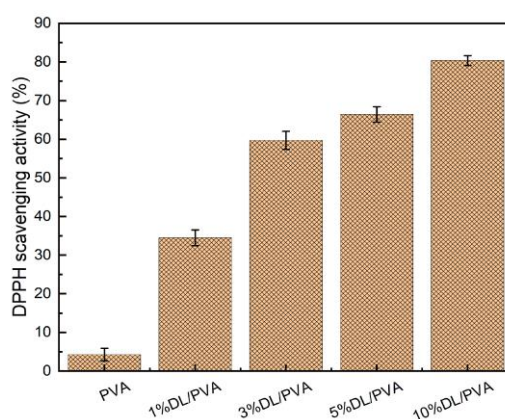
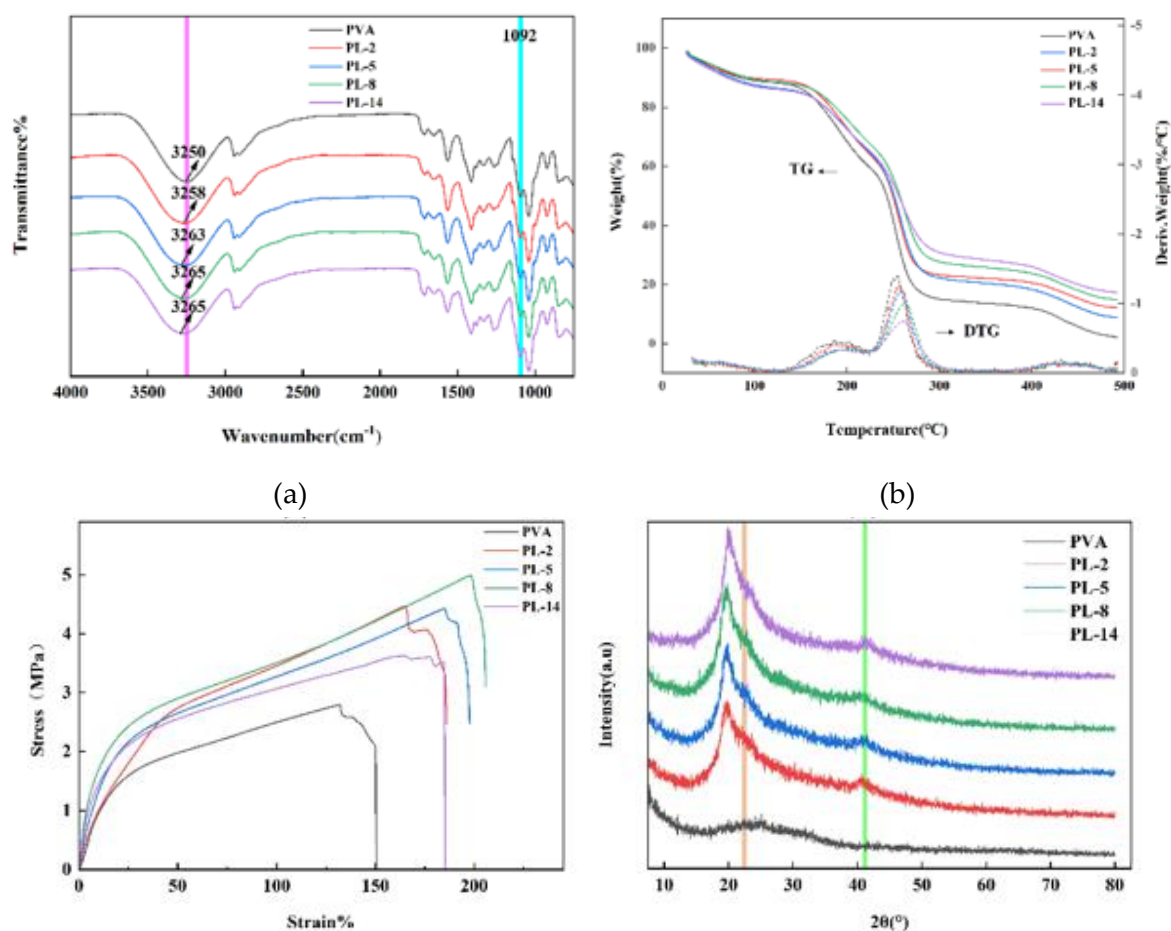


Figure 2.12. DPPH radical scavenging activity of PVA and DL/PVA composite films with different concentrations of DLNP (Cao et al., 2024).

From the results presented in Figure 2.12, the PVA has very low radical scavenging activity. The incorporation of even 1 wt% of DLNPs results in a significant increase in the activity.

Depending on the concentration of DLNPs, the radical scavenging activity varies from 34.5% (for 1 wt%) to 80.3% (for 10 wt%). The extraordinary radical scavenging activity of the composites was attributed to the phenolic compounds in DLNPs, which successfully capture free radicals by donating phenolic hydrogen atoms. In addition to these properties, the prepared DLNPs/PVA composites possessed improved mechanical properties and thermal stability, as well as significant UV-shielding performance (Cao et al., 2024).

Liu et al. (2024) developed a novel PVA/lignin slow-release envelope material that has essential nitrogen and sulphur elements for plants. To enhance the compatibility between lignin (L) and PVA, lignin was aminated (AL) under alkaline conditions using the Mannich reaction. PVA/AL composites were then prepared via solution casting. Specifically, 5 wt% PVA solution was prepared by dissolving PVA in deionized water. Separately, AL solution was prepared by dissolving a specific amount of AL and dipotassium hydrogen phosphate in deionized water. Afterwards, the two solutions were mixed with the addition of 2 wt% of glycerol as a plasticizer. The concentration of AL was 2, 5, 8 and 14 wt%, the samples were named PL-2, PL-5, PL-8 and PL-14, respectively. PVA/AL solutions were coated on urea particles by alternating cycles of high-pressure spraying and hot air drying to avoid dissolution of the urea. Lie et al. (2024) investigated various properties of the prepared composites, and some of the results are shown in Figure 2.13.



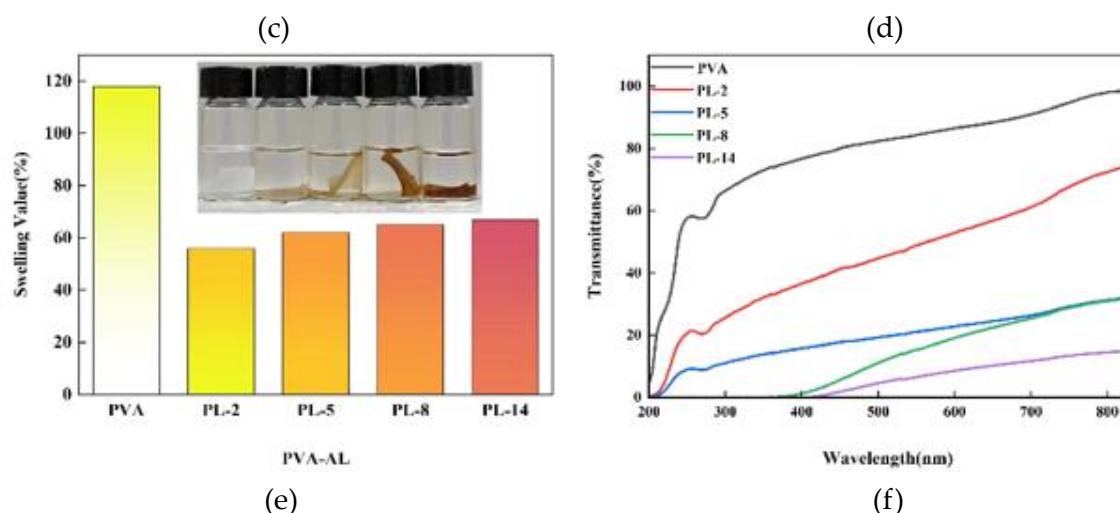


Figure 2.13. Infrared spectra (a), thermogravimetric (b), stress–strain (c), XRD (d), solubility (e), and UV optical resistance (f) of PVA, PL-2, PL-5, PL-8, and PL-14 (Liu et al., 2024).

Specifically, Figure 2.13a shows the infrared spectra of the PVA/AL composites, while Figure 2.13b shows the results of the thermogravimetric analysis. The stress–strain behaviour is shown in Figure 2.13c, and the X-ray diffraction (XRD), solubility test results and UV (ultra-violet) optical resistance are shown in order. From the infrared spectra, a shift in the O–H stretching vibration peak from 3250 cm^{-1} in pure PVA to 3265 cm^{-1} in the composite film was noticed, suggesting strong hydrogen bonding between PVA and AL, which should enhance the structural stability of the composites. The composite films exhibited higher thermal degradation temperatures compared to PVA, with the maximum decomposition rate increasing from $249.8\text{ }^{\circ}\text{C}$ to $261.7\text{ }^{\circ}\text{C}$, which results from the hydrogen bonding between PVA's hydroxyl groups and lignin's functional groups. These results were further confirmed by XRD. The incorporation of AL into PVA results in an increase in tensile strength and elongation at break up to a certain lignin concentration. Specifically, at 14 wt% lignin, the decrease in these properties can be attributed to the saturation of hydrogen bonding between PVA and AL. The excess unreacted aminated lignin may cause uneven dispersion within the PVA matrix, leading to the formation of weak points in the film. Since water swelling is one of the major drawbacks of biopolymers, its reduction is of great importance. Hydrogen bonding between AL and PVA resulted in the formation of a dense network that reduced the swelling behaviour and hydration properties of the composite. The results from the UV optical resistance measurements suggested that the incorporation of lignin leads to improved UV shielding properties of the composites. This behaviour originates from the structure of lignin which contains a large number of phenolic hydroxyl groups, methoxy groups and benzene rings (Liu et al., 2024). In addition to these studies, there are other researches that confirm the assumption that the incorporation of lignin leads to a significant improvement in a range of different characteristics of PVA (Parvathy et al., 2021; Han et al., 2025; Haque et al., 2021; Huang et al., 2021). For instance, Hararak et al.

(2021) produced lignin/PVA composites by solution casting with significantly improved mechanical and thermal properties as well as enhanced UV-shielding properties with the incorporation of 0.2 wt% spherical lignin particles. The modulus of the composite with 0.2 wt% lignin increases from 1.7 ± 0.1 to 2.0 ± 0.2 GPa (Hararak et al., 2021). Improvement of the tensile strength of PVA (0.7 to 2.7 MPa) by the addition of 0.75 wt.% lignin was reported by Odil et al. (2025). Adithyamol et al. (2024) reported that lignin/PVA composites presented strong antimicrobial activity, with effective antibacterial efficacy against *Escherichia coli* and *Staphylococcus aureus*, accompanied with significant antifungal properties.

Due to their biodegradability, antimicrobial properties, antioxidant activity and mechanical strength, the PVA/Lignin composites have a great potential for industrial application in various fields. Namely, their antimicrobial properties are quite beneficial in biomedical applications for producing wound dressings or drug delivery systems. The biodegradability, antimicrobial properties and antioxidant activity are important characteristics for the development of active packaging and biodegradable films in the food industry.

2.3.3 Poly(lactic acid)/lignin composites

Poly(lactic acid) (PLA) is a polyester obtained from renewable resources. Similar to PVA, its eco-friendly and biodegradable properties make it a highly appealing material for replacing traditional plastics in a variety of industries, such as food and biomedicine. PLA can be synthesized through several different methods including direct condensation polymerization, azeotropic dehydration condensation or lactide ring-opening polymerization. The latter method is the most used approach since it produces PLA with high molecular weight and enhanced properties (Bikiaris et al., 2023; Boey et al., 2021; Li et al., 2020; Vayshbeyn et al., 2023). It is biodegradable, and its degradation mainly through hydrolysis. The hydrolysis involves the penetration of water into the polymer which leads to cleavage of the ester linkages to non-toxic products such as lactic acid. The biodegradation of PLA occurs under certain conditions, which may pose a problem when decomposing PLA in natural environments since it can be a relatively slow process (Bikiaris et al., 2023; Boey et al., 2021; Li et al., 2020; Vayshbeyn et al., 2023). PLA is a biocompatible polymer that degrades in the human body without releasing harmful substances, so it is often used in the production of drug delivery systems, scaffolds or surgical sutures (Vayshbeyn et al., 2023). PLA has certain drawbacks that limit its widespread industrial application. Some of these shortcomings are the low impact strength and brittleness, as well as its hydrophobic nature and low thermal stability (Vayshbeyn et al., 2023).

The mentioned disadvantages can be mitigated by introducing different fillers within PLA matrix. By meticulous selection of fillers and processing methods, the properties of PLA composites can be modulated to meet specific industrial requirements (Bikiaris et al., 2023; Boey et al., 2021; Li et al., 2020; Vayshbeyn et al., 2023). Lignin is a suitable filler for

overcoming the issues associated with the brittleness of PLA, as its incorporation can lead to improved toughness and flexibility. Lignin, due to its high thermal stability, can enhance the stability of PLA at higher temperatures, as well as provide improved stability against UV irradiation (Shi et al., 2023).

The following text will provide specific examples of PLA/lignin composite synthesis, along with a presentation of their key characteristics.

Makri et al. (2022) prepared PLA composites by incorporation micro- and nano- lignin in concentrations between 0.5 wt% and 5 wt%. The PLA/lignin composites were prepared by solvent casting followed by melt mixing. First, the PLA was dissolved in chloroform, whether, the lignin was dissolved in acetone. The two solutions were mixed and let to dry. Afterwards, PLA/Lignin (PLA/L) and PLA/Nanolignin (PLA/NL) composites were prepared by melt mixing in melt mixer at 190 °C. Thin films of the composites were prepared by compression molding. The combination of two preparation methods ensured improved dispersion of lignin. The dispersion was investigated by transmission electron microscopy, and the micrographs are shown in Figure 2.14.

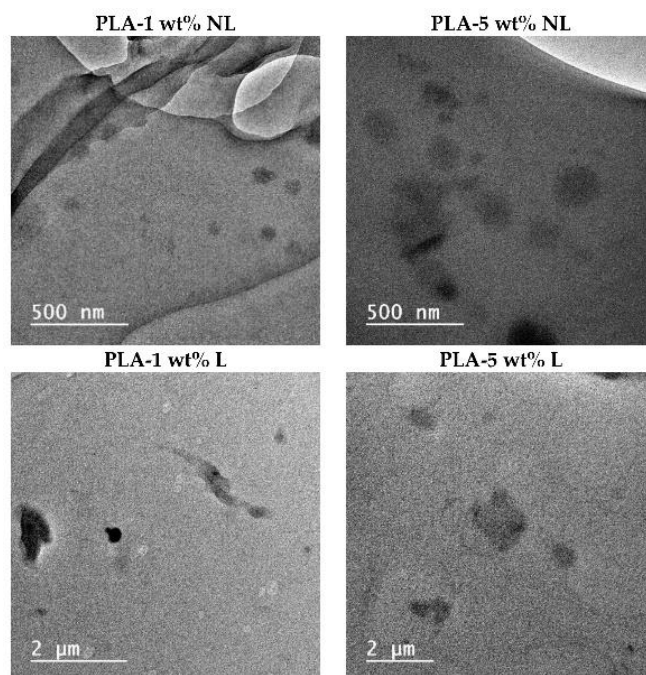


Figure 2.14. TEM micrographs of PLA–L and PLA/NL composites containing 1 and 5 wt% filler (Makri et al., 2022).

This analysis demonstrated that the nanolignin had better dispersion compared to microlignin, even though in both cases aggregation at higher concentrations was observed. Namely, the particle size of NL was between 30–120 nm at 1 wt% and increased to 50–200 nm at 5 wt%, suggesting that the NL stayed in nanodimensions during the melt mixing. On the other hand, the particle size of microlignin was between 300–1300 nm at 1 wt% and increased to 300–1800 nm at 5 wt%. Makri et al. concluded that nanolignin

remained well dispersed at nanoscale, but the microlignin formed larger aggregates (Makri et al., 2022).

In Figure 2.15, the mechanical properties of the different samples are shown.

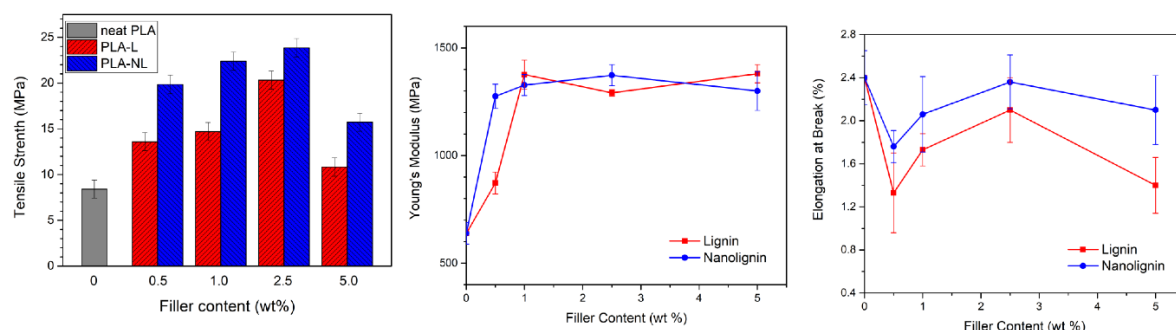


Figure 2.15. Mechanical properties of PLA/L and PLA/NL (Makri et al., 2022).

Regarding the mechanical properties of their samples, Makri et. al (2022) concluded that the tensile strength significantly increases by addition of lignin, specifically at concentration of 2.5 wt%, at which the PLA/NL had tensile strength of 23.86 MPa, but with further addition of lignin this property starts to decrease. Regarding the Young's modulus, the samples with 5 wt% L and 2.5 wt% NL showed highest values of 1380 MPa and 1373 MPa, respectively, demonstrating improved rigidity of the films. With the addition of both fillers, the elongation of break decreased as a result of increased rigidity and reduced flexibility caused with the incorporation of lignin. It was noted that the better dispersion of NL and the enhanced interactions between PLA and NL contributed to significant improvement of the mechanical properties even at concentrations of 2.5 wt% nanolignin.

Hong et al. (2021) prepared PLA biocomposites with different concentrations (5 – 20 wt%) chemically modified lignin. In this study, the lignin was modified through esterification with maleic acid introducing carboxyl groups on the surface of lignin. The modification of lignin improves the interaction with the PLA matrix during the melt mixing process, since the surface polarity of lignin was increased.

The facilitated hydrogen bonding between PLA and the modified lignin resulted in improved mechanical properties of the composite, Figure 2.16. Specifically, composites with modified lignin exhibited significantly increased tensile strength compared to the composites with unmodified lignin. Similar effect was observed in the case of the tensile modulus, the composite with 20 wt% of modified lignin had modulus of about 5 GPa.

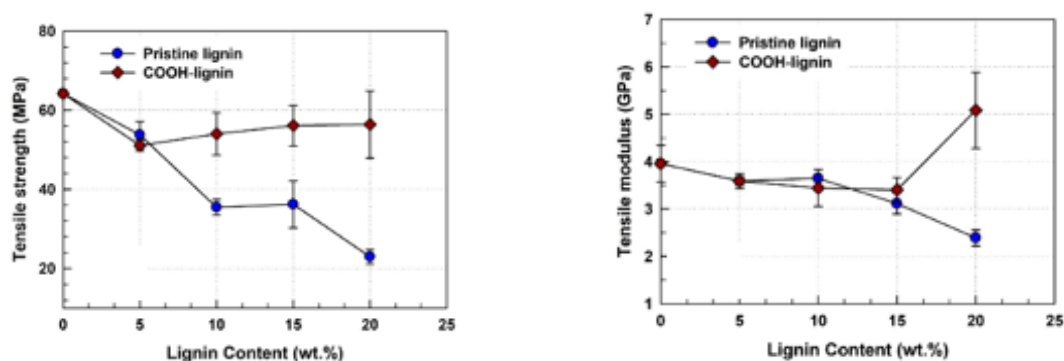


Figure 2.16. Tensile strength and tensile modulus of PLA composites with modified and unmodified lignin (Hong et al., 2021).

The PLA composite with modified lignin were used to produce 3D printed objects with single-screw filament extruder. The objects and the scanning electron microscopy (SEM) of them are shown in Figure 2.17.

SEM micrographs revealed that by increasing the content of lignin the surface of the 3D printed filaments became rougher and darker due to the lower melt strength of the PLA/lignin composite, as well as due to the dark colour of lignin. The surface roughness of the samples with more than 15 wt% lignin was significantly increased, which prevented layer-by-layer binding of the 3D printed filaments and wide gaps between the filaments were observed. The authors attributed this behaviour to the decreased melt flow from the nozzle of the extruder and the resulting inadequate adhesion between layers (Hong et al., 2021).

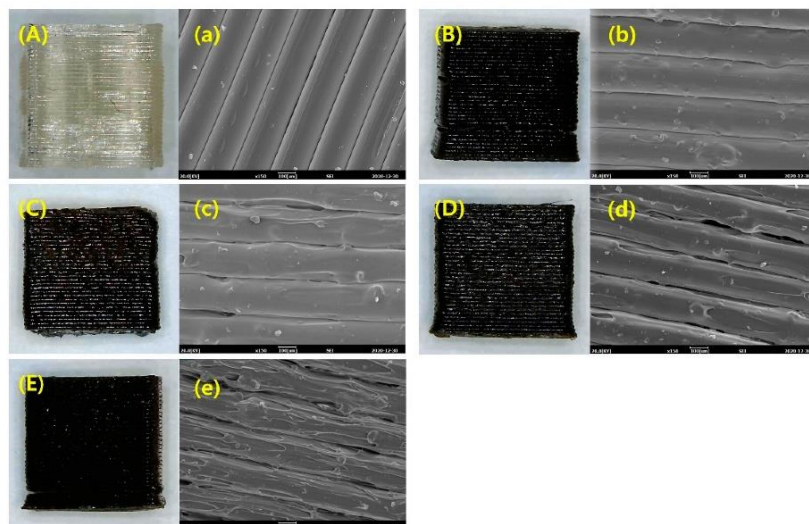


Figure 2.17. Optical image and SEM micrographs of 3D printed objects from PLA (A, a) and PLA-modified lignin with contents of 5 wt.% (B, b), 10 wt.% (C, c), 15 wt.% (D, d), and 20 wt.% (E, e) (Hong et al., 2021).

The positive impact of lignin on PLA has been reported by a number of other authors (Shi et al., 2023; Zhai et al., 2021). For instance, Terzopoulou et al. (2022) reported that the incorporation of 0.5 – 2.5 wt% lignin results in significantly improved antioxidative properties. Shar et al. (2023) reported that oxygen barrier performance of the PLA matrix was significantly enhanced up to 58.3% by the incorporation of lignin. The incorporation of lignin lead to improve antimicrobial behaviour of PLA as demonstrated from Buzarovska et al. (2021). Several different studies have demonstrated that the incorporation of lignin within PLA matrix enhances its mechanical strength, thermal stability, and other beneficial properties (Abdelwahab et al., 2021; Johansson et al., 2023; Liang et al., 2022; Zaidi et al., 2023).

Without a doubt, the improved properties of PLA with the addition of lignin increase the utility value of this polymer. The use of a relatively inexpensive filler such as lignin, which is derived from natural raw materials and is biodegradable, will not only reduce the production costs of PLA composites, but will also make a significant contribution to waste management and sustainability. PLA/lignin composites could find widespread application in the food industry for sustainable food packaging, in the biomedical industry for medical packaging or production of scaffolds.

2.3.4 Use of different polymers for preparation of polymer/lignin composites

In addition to the presented examples of the synthesis of composites based on PVA and PLA and lignin as a filler, there are numerous studies that present the benefits of using lignin in various polymer matrices.

For instance, poly(caprolactone) (PCL) is also used as a matrix for the synthesis of composites with lignin as a filler (Bergamasco et al., 2024; Kayan and Kayan, 2023; Tarrés et al., 2022). Bergamasco et al. (2024) reported that the application of lignin coating on PCL membranes had several benefits. One of them is the improved wettability towards polar and apolar liquids, i.e the amphiphilic behaviour of the lignin was translated to the PCL. In addition, lignin introduced antibacterial functionalities to the PCL which were effective towards *Staphylococcus aureus* and *Escherichia coli*. The antibacterial activity was different for different types of lignin with eucalyptus lignin (AL-EU) showing superior antibacterial activity compared to oak lignin (AL-OA), Figure 2.18. (Bergamasco et al., 2024).

Beside green polymer, other polymer matrices (Andrade-Guel et al., 2022; Kargarzadeh et al., 2020; Roy et al., 2020; Wang et al., 2020; Younesi-Kordkheiliand Pizzi, 2020) which are not derived from natural resources or are not biodegradable also take advantages of the lignin as a green filler that not only enhances the performance of the polymer matrices but also contributes to the sustainability and the circular economy by promoting the use of natural by products.

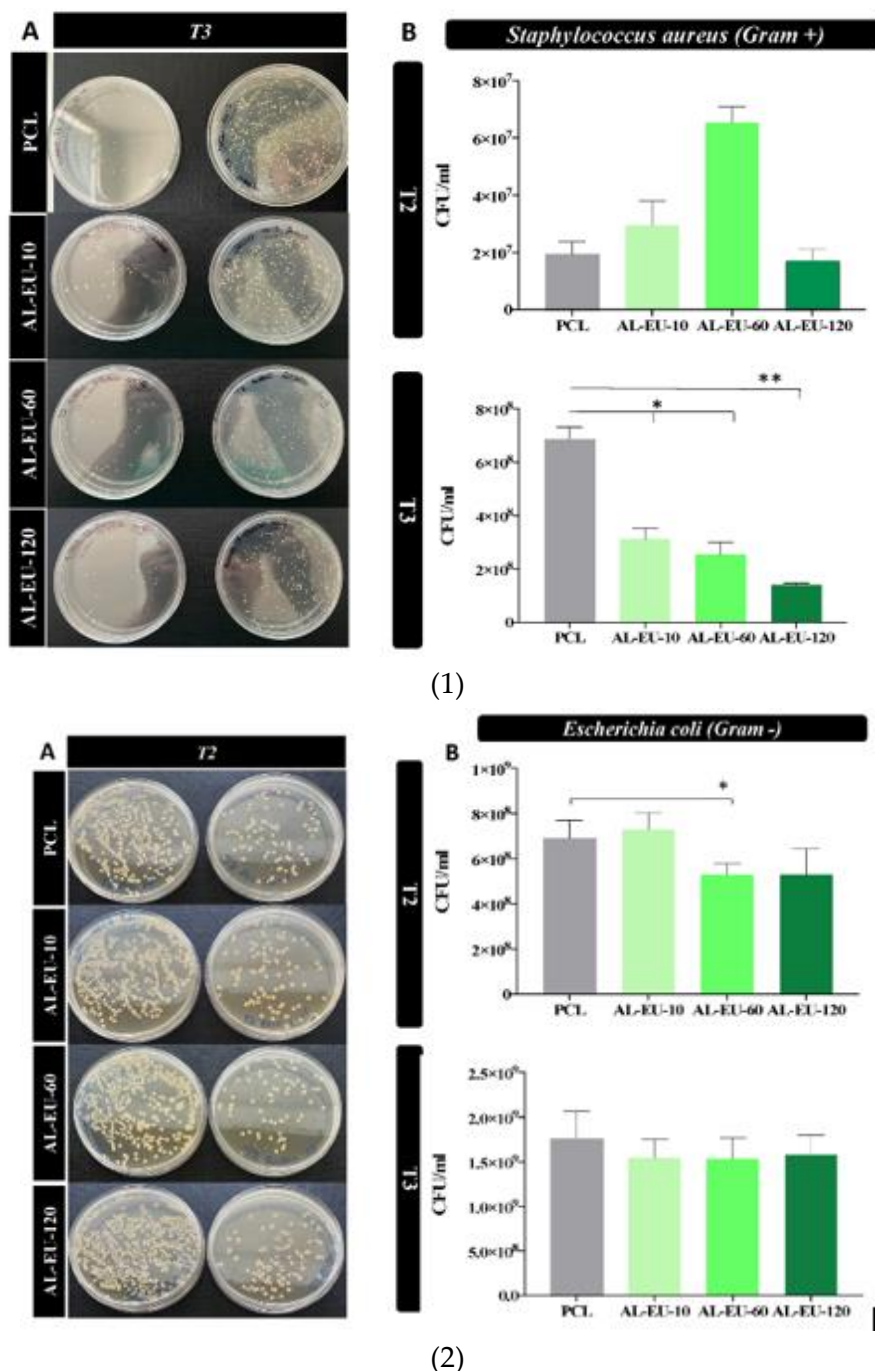


Figure 2.18. (1–A) Petri dishes obtained from *S. aureus* cultures with blank PCL and PCL-Lignin, (1-B) *S. aureus* bacterial population (CFU/mL). (2–A) Petri dishes obtained from *E. coli* cultures with blank PCL and PCL-Lignin, (2-B) *E. coli* bacterial population (CFU/mL) (Bergamasco et al., 2024).

Poly(urethane) PU is one of those matrices (Hu et al., 2024; Wang et al., 2023; Zhang et al., 2022; Zhao et al., 2021). PU has favourable mechanical properties and good thermal stability that contribute to its widespread application. But since it is produced by petrol-based resources its sustainability and eco-friendliness are the main concern regarding its use. The

use of lignin filler might be the solution for increasing the environmental sustainability of the PU based composites in addition to improving their properties. Zhang et al (2022) prepared eco-friendly and durable tent fabrics using waterborne polyurethane and lignin. The fabric demonstrated significantly improved age-resistance. PU/lignin fabrics exhibited improved waterproof-breathable characteristics, with a significant enhancement at lignin concentration of 2%. As a result, the fabric had favourable water vapor transmission rates and hydrostatic pressure capabilities, making the materials suitable for outdoor applications.

Due to their diverse properties, cost-effective production, and ability to be molded into various shapes, polymers will continue to be widely used across numerous industries in the future. Since their use is inevitable, enhancing their sustainability and environmental compatibility by adopting circular economy principles will be crucial. In this context, the incorporation of natural fillers into polymer matrices plays a vital role in expanding the application of biodegradable polymers such as PLA and PVA across multiple industries. Lignin, in particular, has the potential to enhance the sustainability of polymers derived from petroleum-based raw materials. Owing to its complex structure, lignin exhibits several characteristics that make it an attractive filler. Numerous studies have demonstrated that incorporating lignin improves the mechanical and thermal stability of polymer matrices. Additionally, polymer/lignin composites have shown significant antimicrobial activity, as well as excellent antioxidant properties and enhanced barrier performance. These attributes highlight the potential for expanding the use of polymer/lignin composites across various industries. Solution casting and melt mixing remain the most commonly used methods for synthesizing lignin-based composites. However, to fully exploit lignin's potential, improving its dispersion and compatibility with polymer matrices is essential. One promising approach to overcoming these challenges involves modifying lignin by introducing functional groups that enhance its compatibility with polymer matrices.

2.4 Another application of lignin

2.4.1 Benzene, toluene and xylene

Benzene, toluene and xylene (BTX) are isolated from the aromatic fraction of petroleum and have a wide range of industrial applications. Their chemical structures are presented in Figure 2.19. Aromatic compounds are valuable chemical raw materials that are further converted into other organic compounds used in industry. Aromatic hydrocarbons are used to produce, among other, terephthalic acid which is a key raw material for the production of PET (polyethylene terephthalate), used in the production of plastic bottles. Benzene and toluene are added to fuels as octane-boosting ingredients. This makes the fuels more resistant to detonation, which increases engine efficiency, especially in the aviation

industry. Xylene is mainly used as a solvent and thinner for paints and varnishes. The annual demand for BTX is approximately 108 million metric tonnes (Gong, 2023).

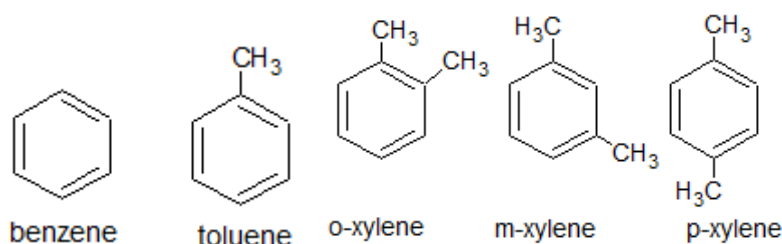


Figure 2.19. Structural diagrams of the BTX hydrocarbons.

Unfortunately, aromatics are still yielded from fossil resources like naphtha, coal, and natural gas. Therefore, the creation of bio-based aromatics is a crucial step in advancing the chemical industry's transition to sustainability.

Lignin is a sustainable, renewable raw material substitute for petroleum-based chemicals, especially for the BTX production of commodities and the sequential secondary, tertiary, and manufactured products in the petrochemical industry. Lignin possesses a phenolic polymer structure that is made up of p-hydroxy-phenyl, guaiacol, and syringyl groups, and hence has great potential to provide renewable aromatic compounds for future use as feedstocks to the chemical manufacturing industry. In order to obtain BTX from lignin, lignin has to be depolymerized to aromatic constituents which are mainly phenolics, and these oxygenated aromatic monomers in the next step are catalytically hydrodeoxygenated/ upgraded to bio-oil that can be refined to bio-BTX (Gong, 2023). Currently, the main sources used to produce BTX are wood, kraft lignin, and lignosulfonate.

BTX production from lignin would allow for independence from depleting fossil fuel deposits and constantly rising oil prices.

2.4.2 Vanillin

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is the main flavor constituent of vanilla. Its chemical structure is presented in Figure 2.20. It has a very wide range of applications in perfumery, food, and pharmaceuticals. Synthetic vanillin obtained from guaiacol is fully dependent on petroleum-derived compounds.

Synthesis of vanillin from renewable sources should result in a more sustainable and greener process. Currently vanillin is one of the only molecular phenolic compounds that are produced on an industrial scale from biomass, manufactured by Borregaard AS, a company from Norway, which produces and sells vanillin obtained from lignosulfonate (Arrigo et al., 2024; Fache et al., 2016). One possible path to produce vanillin based on

biomass is through controlled oxidation of lignin through the use of oxidizing agents, such as oxygen, hydrogen peroxide, or ozone (Araújo et al., 2010).

The challenges related to the efficient conversion of lignin to vanillin are connected to its complex and heterogeneous nature which results in the limited selectivity of conversion and the very low yields of the conversion processes.

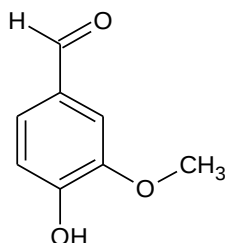


Figure 2.20. Chemical structure of vanillin.

2.4.3 Carbon fibre

Carbon fiber is the highest-strength fiber for manufacturing lightweight materials. Currently, it is mainly obtained from PAN (polyacrylonitrile), which is derived from fossil resources. It is widely used in the automotive industry for lighter cars, to reduce fuel consumption; also in aerospace and wind energy. The graphical representation of carbon fibers is presented in Figure 2.21.

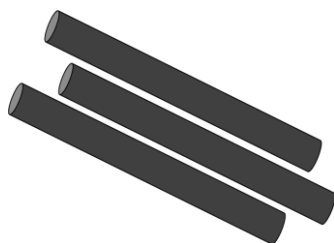


Figure 2.21. Carbon fibers – graphical representation.

Lignin is considered a promising precursor for carbon fiber production because of its high carbon content and relatively low cost. There are different methods of preparation of carbon fibers from lignin such as: melt spinning, dry and wet spinning, dry jet wet spinning, and electrospinning. It can be processed into carbon fibers through multiple stages, including (1) extraction, (2) purification, (3) spinning, (4) stabilization, and (5) carbonization. The main difficulties are related to the wide molecular weight distribution of lignin as well as its nonlinear molecular structure which results in uneven fiber diameter and poor quality of precursor fibers (Liu et al., 2022).

Lignin-based carbon fiber holds great promise for making high-performance composites more sustainable and affordable. Researchers and companies worldwide are working to scale up its production for commercial use.

2.4.4 Cosmetic formulations

It is also reported in the literature that lignin has multifunctional barrier properties, protecting against harmful UV radiation, and antibacterial properties. It was found that lignin applied to linen fabric can be successfully used as an additive in the production of clothing that protects against the harmful effects of strong solar radiation. An additional advantage of the developed product is the fact that lignin, as a natural polymer, does not deteriorate the hygienic properties of clothing (Zimniewska et al., 2008).

UV-protectable properties of lignin increase its application areas for cosmetic formulations. Currently, the most frequently used ingredient of sunscreen preparations is nano-sized titanium dioxide. However, there are concerns that the substance may have potential toxicity and the ability to cause allergies in some people, prompting work on the development of alternative ingredients. New, natural compounds are being sought to replace toxic or allergenic ingredients in tanning cosmetics, with an emphasis on their effectiveness and safety.

Lignin has a remarkable ability to act as a blocker of ultraviolet radiation due to the large number of phenolic units, ketones, and other chromophores present in its structure, which combined with the aromatic rings, are capable of forming large conjugated π systems, which are capable of absorbing UV radiation (Lee et al., 2019).

Lignin's multifunctional properties make it a promising ingredient for sustainable and high-performance cosmetics (Figure 2.22). As the industry shifts toward natural and eco-friendly alternatives, lignin could play a key role in the future of skincare, haircare, and personal care products (Sadeghifar and Ragauskas, 2020).



Figure 2.22. Eco-friendly sunscreen with lignin.

2.4.5 Construction

Lignin has binder properties that are responsible for the compactness of the structure of wood cells. It acts as a cementing medium to bind together the fibers of cellulose in a rigid-woody structure. It gives wood compressive strength and maintains its stiffness. Therefore it can be used as an adhesive that fills the gaps between concrete particles. As a result, new concrete may be created that is more resistant to stress than the original one.

What is more, lignin is the alternative to bitumen, a crude oil product, which is used in traditional asphalt as a binder of gravel in the asphalt mixture and gives strength (Moretti et al., 2022). The graphical representation of “green” roads with lignin is presented in Figure 2.23. The use of lignin in road construction is also related to its limited biodegradability and the formation of humus, which is formed from organic remains as a result of the activity of decomposer microorganisms. Therefore it is assumed to obtain the durable surface that is not subject to cracks and losses.

Lignin-modified construction materials hold great promise for reducing environmental impact, enhancing durability, and improving workability. With ongoing research, it could play a key role in next-generation eco-friendly buildings and infrastructure.



Figure 2.23. “Green” roads with lignin – graphical representation.

Following numerous hypotheses put forward by scientists directly involved in lignin research, it is assumed that the development of work on lignin will be intensified soon, which will certainly contribute to valuable and innovative solutions in the field of modern and low- and/or waste-free technologies.

References:

- Abdelmonem, B.H., Kamal, L.T., Elbaz, R.M., Khalifa, M.R., Abdelnaser, A. (2025). From contamination to detection: The growing threat of heavy metals. *Heliyon*. 11, e41713. <https://doi.org/10.1016/j.heliyon.2025.e41713>.
- Abdelwahab, M.A., Jacob, S., Misra, M., Mohanty, A.K. (2021). Super-tough sustainable biobased composites from polylactide bioplastic and lignin for bio-elastomer application. *Polymer*. 212, 123153. <https://doi.org/10.1016/j.polymer.2020.123153>.

- Acemioğlu, B., Samil, A., Alma, M.H., Gundogan R. (2003). Copper(II) removal from aqueous solution by organosolv lignin and its recovery. *J. Appl. Polym. Sci.* 89, 1453-1725. <https://doi.org/10.1002/app.12251>.
- Adithyamol, V. V., Varma, P., Kandasubramanian, B. (2025). Developing lignin/Pva- tea tree oil composites for enhanced antibacterial and antifungal properties. *Biomedical Materials and Devices*. 3, 682-687. <https://doi.org/10.1007/s44174-024-00242-9>.
- Ahmad, N., Arsyad, F.S., Royani, I., Hanifah Y., Lesbani, A. (2025). Lignin-NiAl layered double hydroxide composite adsorbent for selective removal of Malachite Green from aqueous solutions of cationic dyes. *Chem. Afr.* <https://doi.org/10.1007/s42250-025-01241-z>.
- Albadarin, A.B., Al-Muhtaseb, A.a.H., Al-laqtah, N.A., Walker, G.M., Allen, S.J., Ahmad, M.N.M. (2011). Biosorption of toxic chromium from aqueous phase by lignin: mechanism, effect of other metal ions and salts. *Chem. Eng. J.* 169, 20-30. <https://doi.org/10.1016/j.cej.2011.02.044>.
- Albdiry, M. (2024). Effect of melt blending processing on mechanical properties of polymer nanocomposites: a review. *Polym. Bull.* 81, 5793–5821. <https://doi.org/10.1007/s00289-023-05012-z>.
- Ali Aslam A., Ul Hassan, S., Haris Saeed, M., Kokab, O., Ali, Z., Shahid Nazir, M., Siddiqi, W. (2023). Cellulose-based adsorbent materials for water remediation: harnessing their potential in heavy metals and dyes removal. *J. Clean. Prod.* 421, e138555. <https://doi.org/10.1016/j.jclepro.2023.138555>.
- Ali, H., Khan, E. (2018). What are heavy metals? long-standing controversy over the scientific use of the term ‘heavy metals’—proposal of a comprehensive definition. *Toxicol. Environ. Chem.* 100, 6e19. <https://doi.org/10.1080/02772248.2017.1413652>.
- Ali, R., Elsagan, Z., AbdElhafez, S. (2022). Lignin from agro-industrial waste to an efficient magnetic adsorbent for hazardous Crystal Violet removal. *Molecules*. 27, 1831. <https://doi.org/10.3390/molecules27061831>.
- Ali, S., Rani, A., Dar, M.A., Qaisrani, M.M., Noman, M., Yoganathan, K., Asad, M., Berhanu, A., Barwant, M., Zhu, D. (2024). Recent advances in characterization and valorization of lignin and its value-added products: Challenges and future perspectives. *Biomass*. 4, 947–977. <https://doi.org/10.3390/biomass4030053>.
- Al-Tohamy, R., Ali, S. S., Li, F., Okasha, K. M., Mahmoud, Y. A.-G., Elsamahy, T., Jiao, H., Fu, Y., Sun, J. (2022). A critical review on the treatment of dye-containing wastewater: ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety. *Ecotoxicol. Environ. Saf.*, 231, e113160. <https://doi.org/10.1016/j.ecoenv.2021.113160>.
- Andrade-Guel, M., Cabello-Alvarado, C., Avila-Orta, C. A., Pérez-Alvarez, M., Cadenas-Pliego, G., Reyes-Rodríguez, P. Y., Rios-González, L. (2022). Green flame-retardant composites based on PP/TiO₂/lignin obtained by melt-mixing extrusion. *Polymers*. 14, 1300. <https://doi.org/10.3390/polym14071300>.

- Araújo, J.D.P., Grande, C.A., Rodrigues, A.E. (2010). Vanillin production from lignin oxidation in a batch reactor. *Chem. Eng. Res. Des.* 88, 1024-1032.
<https://doi.org/10.1016/j.cherd.2010.01.021>.
- Ariyanta, H.A., Sari, F.P., Sohail, A., Restu, W.K., Septiyanti, M., Aryana N., Fatriasari, W., Kumar A. (2023). Current roles of lignin for the agroindustry: applications, challenges, and opportunities. *Int. J. Biol. Macromol.* 240, 124523.
<https://doi.org/10.1016/j.ijbiomac.2023.124523>.
- Aro, T., Fatehi, P. (2017). Production and application of lignosulfonates and sulfonated lignin. *ChemSusChem*. 10, 1858-2106. <https://doi.org/10.1002/cssc.201700082>.
- Bajwa, D.S., Pourhashem, G., Ullah, A.H., Bajwa, S.G. (2019). A concise review of current lignin production, applications, products and their environmental impact. *Ind. Crops. Prod.* 139, 111526. <https://doi.org/10.1016/j.indcrop.2019.111526>.
- Balart, R., Montanes, N., Dominici, F., Boronat, T., Torres-Giner, S. (2020). Environmentally friendly polymers and polymer composites. *Materials*. 13, 1–6.
<https://doi.org/10.3390/ma13214892>.
- Bass, G.F., Epps, T.H. (2021). Recent developments towards performance-enhancing lignin-based polymers. *Polym. Chem.* 12, 4130–4158. <https://doi.org/10.1039/d1py00694k>.
- Bergamasco, S., Fiaschini, N., Hein, L. A., Brecciaroli, M., Vitali, R., Romagnoli, M., Rinaldi, A. (2024). Electrospun PCL filtration membranes enhanced with an electrosprayed lignin coating to control wettability and anti-bacterial properties. *Polymers*. 16, 674.
<https://doi.org/10.3390/polym16050674>.
- Bikiaris, N.D., Koumentakou, I., Samiotaki, C., Meimaroglou, D., Varytimidou, D., Karatza, A., Kalantzis, Z., Roussou, M., Bikiaris, R.D., Papageorgiou, G.Z. (2023). Recent Advances in the Investigation of Poly(lactic acid) (PLA) Nanocomposites: Incorporation of Various Nanofillers and their Properties and Applications. *Polymers*. 15, 1196.
<https://doi.org/10.3390/polym15051196>.
- Boey, J.Y., Mohamad, L., Khok, Y. Sen, Tay, G.S., Baidurah, S. (2021). A review of the applications and biodegradation of polyhydroxyalkanoates and poly(lactic acid) and its composites. *Polymers*. 13, 1544. <https://doi.org/10.3390/polym13101544>.
- Borbolla-Jiménez, F.V., Peña-Corona, S.I., Farah, S.J., Jiménez-Valdés, M. T., Pineda-Pérez, E., Romero-Montero, A., Del Prado-Audelo, M.L., Bernal-Chávez, S.A., Magaña, J.J., Leyva-Gómez, G. (2023). Films for wound healing fabricated using a solvent casting technique. *Pharmaceutics*. 15, 1917. <https://doi.org/10.3390/pharmaceutics15071914>.
- Briffa, J., Sinagra E., Blundell, R. (2020). Heavy metal pollution in the environment and their toxicological effects on humans. *Heliyon*. 6, 2020.
<https://doi.org/10.1016/j.heliyon.2020.e04691>.
- Bužarovska, A., Blazevska-Gilev, J., Pérez-Martnez, B.T., Balahura, L.R., Pircalabioru, G.G., Dinescu, S., Costache, M. (2021). Poly(l-lactic acid)/alkali lignin composites: properties,

- biocompatibility, cytotoxicity and antimicrobial behavior. *J. Mater. Sci.* 56, 13785–13800. <https://doi.org/10.1007/s10853-021-06185-6>.
- Cabrera, F.C. (2021). Eco-friendly polymer composites: a review of suitable methods for waste management. *Polym. Compos.* 42, 2653–2677. <https://doi.org/10.1002/pc.26033>.
- Cao, X., Li, X., Wu, R., Liu, B., Lin, W. (2024). Enhancing the performance of biodegradable lignin nanoparticle/PVA composite films via phenolation pretreatment of lignin using a novel ternary deep eutectic solvent. *Coatings.* 14, 1544. <https://doi.org/10.3390/coatings14121544>.
- Chen, H., Zhang, Z., Zhong, X., Zhuo, Z., Tian, S., Fu, S., Chen, Y., Liu, Y. (2021). Constructing MoS₂/lignin-derived carbon nanocomposites for highly efficient removal of Cr(VI) from aqueous environment. *J. Hazard. Mater.* 408, 124847–124857. <https://doi.org/10.1016/j.jhazmat.2020.124847>.
- Chen, T., Liu, H., Gao, J., Hu, G., Zhao, Y., Tang, X., Han, X. (2024). Efficient removal of Methylene Blue by bio-based sodium alginate/lignin composite hydrogel beads. *Polymers.* 14, 2917. <https://doi.org/10.3390/polym14142917>.
- Chen, W.H., Dai, C., Xiang, K., Kou, H., Guo, J., Ying H., Chen, X., Wu, J. (2024). Selective adsorption of anionic dyes by a macropore magnetic lignin-chitosan adsorbent. *Int. J. Biol. Macromol.* 269, e131955. <https://doi.org/10.1016/j.ijbiomac.2024.131955>.
- Chmielewski, J., Gworek, B., Florek-Łuszczki, M., Nowak-Starz, G., Wójtowicz, B., Wójcik, T., Żeber-Dzikowska, I., Strzelecka, I., Szpringer, M. (2020). Heavy metals in the environment and their impact on human health. *Chem. Industry.* 99/1, 50-56. <https://doi.org/10.15199/62.2020.1.3>.
- Costa, M.I., Sarmiento-Ribeiro, A.B., Gonçalves, A.C. (2023). Zinc: From biological functions to therapeutic potential. *Int. J. Mol. Sci.* 24, 4822. <https://doi.org/10.3390/ijms24054822>.
- Crist, R.H., Martin, J.R., Crist, D.R. (2002). Heavy metal uptake by lignin: Comparison of biotic ligand models with an ion-exchange process. *Environ. Sci. Technol.* 36, 1485. <https://doi.org/10.1021/es011136f>.
- D'Arrigo, P., Rossato, L.A.M., Strini, A., Serra, S. (2024). From waste to value: Recent insights into producing vanillin from lignin. *Molecules.* 29, 442. <https://doi.org/10.3390/molecules29020442>.
- Dasharathy, S., Arjunan, S., Maliyur Basavaraju, A., Murugasen, V., Ramachandran, S., Keshav, R., Murugan, R. (2022). Mutagenic, carcinogenic, and teratogenic effect of heavy metals. *Evid. - Based Complement. Altern. Med.* 8011953. <https://doi.org/10.1155/2022/8011953>.
- Demirbas, A. (2004). Adsorption of lead and cadmium ions in aqueous solutions onto modified lignin from alkali glycerol delignification, *J. Hazard. Mater.* B109, 221–226. <https://doi.org/10.1016/j.jhazmat.2004.04.002>.

- Dessbesell, L., Paleologou, M., Leitch, M., Pulkki, R., Xu, Ch. (2020). Global lignin supply overview and kraft lignin potential as an alternative for petroleum-based polymers. *Renewable Sustainable Energy Rev.* 123, 109768. <https://doi.org/10.1016/j.rser.2020.109768>.
- Dizhbite, T., Jashina, L., Dobeles, G., Andersone, A., Evtuguin, D., Bikovens, O., Telysheva, G. (2013). Polyoxometalate (POM)-aided modification of lignin from wheat straw biorefinery. *Holzforschung.* 67, 539–547. <https://doi.org/10.1515/hf-2012-0193>.
- Dotto, G. L., Santos, J. M. N., Rodrigues, I. L., Rosa, R., Pavan, F. A., Lima, E. C. (2015). Adsorption of Methylene Blue by ultrasonic surface modified chitin. *J. Colloid Interface Sci.* 446, 133-140. <https://doi.org/10.1016/j.jcis.2015.01.046>.
- Duda-Chodak, A., Błaszczak, U. (2008). The impact of nickel on human health. *J. Elementol.* 13, 685-696.
- Duffus, J.H. (2002). „Heavy metals” – a meaningless term? (IUPAC Technical Report), *Pure Appl. Chem.* 74, 793-807. <https://doi.org/10.1351/pac200274050793>.
- El-Nemr, K.F., Mohamed, H.R., Ali, M.A., Fathy, R.M., Dhmees, A.S. (2020). Polyvinyl alcohol/gelatin irradiated blends filled by lignin as green filler for antimicrobial packaging materials. *IJEAC.* 100, 1578–1602. <https://doi.org/10.1080/03067319.2019.1657108>.
- Esteghlalian, A., Hashimoto, A.G., Fenske, J.J., Penner, M.H. (1997). Modeling and optimization of the dilute-sulfuric-acid pretreatment of corn stover, poplar and switchgrass. *Biores. Technol.* 59, 129-136. [https://doi.org/10.1016/S0960-8524\(97\)81606-9](https://doi.org/10.1016/S0960-8524(97)81606-9).
- Fache, M. Boutevin, B., Caillol, S. (2016). Vanillin production from lignin and its use as a renewable chemical. *ACS Sustainable Chem. Eng.* 4, 35–46. <https://doi.org/10.1021/acssuschemeng.5b01344>
- Fang, K., Deng, L., Yin, J., Yang, T., Li, J., He, W. (2022). Recent advances in starch-based magnetic adsorbents for the removal of contaminants from wastewater: a review. *Int. J. Biol. Macromol.* 218, 909-929. <https://doi.org/10.1016/j.ijbiomac.2022.07.175>.
- Fattahi, N., Fattahi, T., Kashif, M., Ramazani, Ali, Jung, W.-K. (2024). Lignin: a valuable and promising bio-based absorbent for dye removal applications. *Int. J. Biol. Macromol.* 276, Part 1, 133763. <https://doi.org/10.1016/j.ijbiomac.2024.133763>.
- Femina, C.C, Kamalesh, T., Senthil Kumar, P., Rangasamy G. (2020). A critical review on the sustainable approaches for the removal of toxic heavy metals from water systems. *Ind. Eng. Chem. Res.* 62, 8575-8601. <https://doi.org/10.1021/acs.iecr.3c00709>.
- Gaaz, T.S., Sulong, A.B., Akhtar, M.N., Kadhum, A.A.H., Mohamad, A.B., Al-Amiery, A.A., McPhee, D.J. (2015). Properties and applications of polyvinyl alcohol, halloysite nanotubes and their nanocomposites. *Molecules.* 20, 22833–22847. <https://doi.org/10.3390/molecules201219884>.
- Ge, Y., Li, Z. (2018). Application of Lignin and its derivatives in adsorption of heavy metal ions in water: a review. *ACS Sustain. Chem. Eng.* 6, 7181–7192. <https://doi.org/10.1021/acssuschemeng.8b01345>.

- Ge, Y., Li, Z., Kong, Y., Song, Q., Wang, K. (2014a). Heavy metal ions retention by bi-functionalized lignin: Synthesis, applications, and adsorption mechanisms. *J. Ind. Eng. Chem.* 20, 4429–4436. <https://doi.org/10.1016/j.jiec.2014.02.011>.
- Ge, Y., Wu, S., Qin, L., Li, Z. (2016a). Conversion of organosolv lignin into an efficient mercury ion adsorbent by a microwave-assisted method. *J. Taiwan Inst. Chem. Eng.* 63, 500–505. <https://doi.org/10.1016/j.jtice.2016.03.017>.
- Ge, Y., Xiao, D., Li, Z., Cui, X. (2014b). Dithiocarbamate functionalized lignin for efficient removal of metallic ions and the usage of the metal-loaded bio-sorbents as potential free radical scavengers. *J. Mater. Chem. A* 2, 2136–2145. <https://doi.org/10.1039/C3TA14333C>.
- Ge, Y., Xiao, D., Li, Z., Cui, X. (2014c). Dithiocarbamate functionalized lignin for efficient removal of metallic ions and the usage of the metal-loaded bio-sorbents as potential free radical scavengers. *J. Mater. Chem. A* 2, 2136–2145. <https://doi.org/10.1039/C3TA14333C>.
- Ge, Y.Y., Qin, L., Li, Z.L. (2016b). Lignin microspheres: An effective and recyclable natural polymer-based adsorbent for lead ion removal. *Mater. Design*. 95, 141–147. <https://doi.org/10.1016/j.matdes.2016.01.102>.
- Genchi, G., Carocci, A., Lauria, G. et al. (2020). Nickel: Human health and environmental toxicology. *Int. J. Environ. Res. Public Health*. 17, 679. <https://doi.org/10.3390/ijerph17030679>.
- Ghosh, S., Pramanik, K. (2024). A comprehensive review on lignin based electrospun nanomaterials as suitable adsorbents for remediation of detrimental water and air pollutants. *Water Air Soil Pollut.* 235, 485. <https://doi.org/10.1007/s11270-024-07280-5>.
- Goliszek, M., Kołodźńska, D., Pylypchuk, I.V., Sevastyanova, O., Podkościelna, B. (2021). Synthesis of lignin-containing polymer hydrogels with tunable properties and their application in sorption of nickel(II) ions. *Ind. Crops Prod.* 164, 113354. <https://doi.org/10.1016/j.indcrop.2021.113354>.
- Goliszek, M., Podkościelna, B., Fila, K., Riazanova, A.V., Aminzadeh, S., Sevastyanova, O., Gunko, V.M. (2018). Synthesis and structure characterization of polymeric nanoporous microspheres with lignin. *Cellulose*. 25, 5843–5862. <https://doi.org/10.1007/s10570-018-2009-7>.
- Goliszek, M., Sobiesiak, M., Fila, K., Podkościelna, B. (2019). Evaluation of sorption capabilities of biopolymeric microspheres by the solid-phase extraction. *Adsorption*. 25, 289–300. <https://doi.org/10.1007/s10450-019-00008-6>.
- Gong, W.H. (2023). BTX from lignin. In: *Industrial Arene Chemistry: Markets, Technologies, Sustainable Processes and Cases Studies of Aromatic Commodities*. Mortier, J. (Ed) <https://doi.org/10.1002/9783527827992.ch60>.
- Guo, X., Zhang, S., Shan, X. (2008). Adsorption of metal ions on lignin. *J. Hazard. Mater.* 151, 134–142. <https://doi.org/10.1016/j.jhazmat.2007.05.065>.
- Gupta V.K., Suhas. (2009). Application of low-cost adsorbents for dye removal – a review. *J. Environ. Manage.* 90, 2313–2342. <https://doi.org/10.1016/j.jenvman.2008.11.017>.

- Han, Z.-W., Wang, H.-M., Chen, X., Wu, Y.-C., Hou, Q.-X. (2025). Lignin reinforced eco-friendly and functional materials with tailored interfacial barrier performance. *JCIS*. 684, 735-757, <https://doi.org/10.1016/j.jcis.2025.01.033>.
- Haq, I., Mazumder, P., Kalamdhad, A.S. (2020). Recent advances in removal of lignin from paper industry wastewater and its industrial applications – a review. *Bioresour. Technol.* 312, 123636. <https://doi.org/10.1016/j.biortech.2020.123636>.
- Haque, A.N.M.A., Zhang, Y., Naebe, M. (2021). A review on lignocellulose/poly (vinyl alcohol) composites: cleaner approaches for greener materials. *Cellulose*. 28, 10741–10764. <https://doi.org/10.1007/s10570-021-04234-6>.
- Hararak, B., Winotapun, C., Inyai, J., Wannid, P., Prahsarn, C. (2021). Production of UV-shielded spherical lignin particles as multifunctional bio-additives for polyvinyl alcohol composite films. *J. Nanoparticle Res.* 23, 193. <https://doi.org/10.1007/s11051-021-05308-z>.
- Harmita, H., Karthikeyan, K.G., Pan, X. (2009). Copper and cadmium sorption onto kraft and organosolv lignins. *Biores. Technol.* 100, 6183-6191. <https://doi.org/10.1016/j.biortech.2009.06.093>.
- Hessel, C., Allegre, C., Maisseu, M., Charbit, F., Moulin, P. (2007). Guidelines and legislation for dye house effluents. *J. Environ. Manage.* 83, 171-180. <https://doi.org/10.1016/j.jenvman.2006.02.012>.
- Hodson, M.E. (2004). Heavy metals geochemical bogey men? *Environ. Poll.* 129, 341-343. <https://doi.org/10.1016/j.envpol.2003.11.003>.
- Hong, S.H., Park, J.H., Kim, O.Y., Hwang, S.H. (2021). Preparation of chemically modified lignin-reinforced PLA biocomposites and their 3D printing performance. *Polymers*. 13, 667. <https://doi.org/10.3390/polym13040667>.
- Hu, J., Huang, M., Zhou, X., Luo, R., Li, L., Li, X. (2024). Research status of lignin-based polyurethane and its application in flexible electronics. *Polymers*. 16, 2340. <https://doi.org/10.3390/polym16162340>.
- Huang, J., Guo, Q., Zhu, R., Liu, Y., Xu, F., Zhang, X. (2021). Facile fabrication of transparent lignin sphere/PVA nanocomposite films with excellent UV-shielding and high strength performance. *Int. J. Biol. Macromol.* 189, 635–640. <https://doi.org/10.1016/j.ijbiomac.2021.08.167>.
- Huang, W.-X., Zhang, Y.-H., Ge, Y.-Y., Qin, L., Li, Z.-L. (2017). Soft nitrogen and sulfur incorporated into enzymatic hydrolysis lignin as an environmentally friendly antioxidant and mercury adsorbent. *Biores.* 12, 7341-7348. <https://doi.org/10.15376/biores.12.4.7341-7348>.
- Jiang, M., Ma, Y., Wang, T., Niu, N., Chen, L. (2023). Hybrid lignin particles via ion-crosslinked for selective removal of anionic dyes from water. *Int. J. Biol. Macromol.* 238, e124080. <https://doi.org/10.1016/j.ijbiomac.2023.124080>.
- Jin, C., Liu, Y., Fan, J., Liu, T., Liu, G., Chu, F., Kong, Z. (2022). Lignin-inspired porous polymer networks as high-performance adsorbents for the efficient removal of malachite green dye. *Colloids Surf. A: Physicochem. Eng. Asp.* 643, e128760.

<https://doi.org/10.1016/j.colsurfa.2022.128760>.

Jin, C., Zhang, X., Xin, J., Liu, G., Wu, G., Kong, Z., Zhang, J. (2017). Clickable synthesis of 1,2,4-Triazole modified lignin-based adsorbent for the selective removal of Cd(II). *ACS Sustainable Chem. Eng.* 5, 4086–4093. <https://doi.org/10.1021/acssuschemeng.7b00072>.

Johansson, M., Skrifvars, M., Kadi, N., Dhakal, H.N. (2023). Effect of lignin acetylation on the mechanical properties of lignin-poly-lactic acid biocomposites for advanced applications. *Ind. Crops Prod.* 202, 117049. <https://doi.org/10.1016/j.indcrop.2023.117049>.

Kargarzadeh, H., Galeski, A., Pawlak, A. (2020). PBAT green composites: effects of kraft lignin particles on the morphological, thermal, crystalline, macro and micromechanical properties. *Polymer.* 203, 122748. <https://doi.org/10.1016/j.polymer.2020.122748>.

Katheresan, V., Kansedo, J., Lau S.Y. (2018). Efficiency of various recent wastewater dye removal methods: a review, *J. Environ. Chem. Eng.* 6, 4676–4697.

<https://doi.org/10.1016/j.jece.2018.06.060>.

Kayan, G.Ö., and Kayan, A. (2023). Polycaprolactone composites/blends and their applications especially in water treatment. *ChemEng.* 7, 104.

<https://doi.org/10.3390/chemengineering7060104>.

Kim, S., Chung, H. (2024). Biodegradable polymers: from synthesis methods to applications of lignin-graft-polyester. *Green Chem.* 26, 10774–10803.

<https://doi.org/10.1039/d4gc03558e>.

Kim, Y., Park, J., Bang, J., Kim, J., Kim, J.H., Hwang, S.W., Kwak, H.W. (2022). Highly persistent lignocellulosic fibers for effective cationic dye pollutant removal. *ACS App. Polym. Mater.* 4, 6006–6020. <https://doi.org/10.1021/acsapm.2c00837>.

Kiouri, D.P., Chasapis, C.T., Mavromoustakos, T. et al. (2025). Zinc and its binding proteins: essential roles and therapeutic potential. *Arch. Toxicol.* 99, 23–41.

<https://doi.org/10.1007/s00204-024-03891-3>.

Komisarz, K., Majka, T.M., Pielichowski, K. (2023). Chemical and physical modification of lignin for green polymeric composite materials. *Materials.* 16, 16.

<https://doi.org/10.3390/ma16010016>.

La Mantia, F.P., Morreale, M. (2011). Green composites: a brief review. *COMPOS.* 42, 579–588. <https://doi.org/10.1016/j.compositesa.2011.01.017>.

Lalvani, S.B., Hübner, A., Wiltowski, T.S. (2000). Chromium adsorption by lignin. *Energy Sources.* 22, 45–56. <https://doi.org/10.1080/00908310050014207>.

Lee, S.C., Tran, T.M.T., Choi J.W., Won, K. (2019). Lignin for white natural sunscreens. *Int. J. Biol. Macromol.* 122, 549–554. <https://doi.org/10.1016/j.ijbiomac.2018.10.184>.

Li, G., Zhao, M., Xu, F., Yang, B., Li, X., Meng, X., Teng, L., Sun, F., Li, Y. (2020). Synthesis and biological application of polylactic acid. *Molecules.* 25, 5023.

<https://doi.org/10.3390/molecules25215023>.



- Li, Y., Wu, M., Wang, B., Wu, Y., Ma, M., Zhang, X. (2016). Synthesis of magnetic lignin-based hollow microspheres: a highly adsorptive and reusable adsorbent derived from renewable resources. *ACS Sustain. Chem. Eng.* 4, 5523-5532.
<https://doi.org/10.1021/acssuschemeng.6b01244>.
- Li, Z., Ge, Y., Wan, L. (2015a). Fabrication of a green porous lignin-based sphere for the removal of lead ions from aqueous media. *J. Hazard. Mater.* 285, 77-83.
<https://doi.org/10.1016/j.jhazmat.2014.11.033>.
- Li, Z., Ge, Y., Zhang, J., Xiao, D., Wu, Z. (2019). Chemical modification of lignin and its environmental application, In: Inamuddin, T.S., Kumar Mishra, R., Asiri, A. (Eds.), *Sustainable Polymer Composites and Nanocomposites*, Springer, Cham, pp. 1345-1364.
https://doi.org/10.1007/978-3-030-05399-4_45.
- Li, Z., Kong, Y., Ge, Y. (2015b). Synthesis of porous lignin xanthate resin for Pb²⁺ removal from aqueous solution. *Chem. Eng. J.* 270, 229-234. <https://doi.org/10.1016/j.cej.2015.01.123>.
- Li, Z., Xiao, D., Ge, Y., Koehler, S. (2015c). Surface-functionalized porous lignin for fast and efficient lead removal from aqueous solution. *ACS Appl. Mater. Interfaces.* 7, 15000-15009. <https://doi.org/10.1021/acsami.5b03994>.
- Liang, F.B., Song, Y.L., Huang, C.P., Li, Y.X., Chen, B.H., (2013a). Synthesis of novel lignin based ion-exchange resin and its utilization in heavy metals removal. *Ind. Eng. Chem. Res.* 52, 1267-1274. <https://doi.org/10.1021/ie301863e>.
- Liang, F.B., Song, Y.L., Huang, C.P., Zhang, J., Chen, B.H. (2013b). Adsorption of hexavalent chromium on a lignin-based resin: equilibrium, thermodynamics, and kinetics. *J. Environ. Chem. Eng.* 1, 1301-1308. <https://doi.org/10.1016/j.jece.2013.09.025>.
- Liang, R., Yang, X., Yew, P.Y.M., Sugiarto, S., Zhu, Q., Zhao, J., Loh, X.J., Zheng, L., Kai, D. (2022). PLA-lignin nanofibers as antioxidant biomaterials for cartilage regeneration and osteoarthritis treatment. *J. Nanobiotechnol.* 20, 327.
<https://doi.org/10.1186/s12951-022-01534-2>.
- Liu, F., Wang, Q., Zhai, G., Xiang, H., Zhou, J., Jia, C., Zhu, L., Wu, Q., Zhu, M. (2022). Continuously processing waste lignin into high-value carbon nanotube fibers. *Nat. Commun.* 13, 5755. <https://doi.org/10.1038/s41467-022-33496-2>.
- Liu, M.-H., Huang, J.-H. (2006). Removal and recovery of cationic dyes from aqueous solutions using spherical sulfonic lignin adsorbent. *J. Appl. Polym. Sci.*, 101, 2284-2291.
<https://doi.org/10.1002/app.23671>.
- Liu, X.L., Zhu, H.X., Qin, C.R., Zhou, J.H., Zhao, J. R., Wang, S.F. (2013). Adsorption of heavy metal ion from aqueous single metal solution by aminated epoxy-lignin. *Biores.* 8, 2257-2269.
- Liu, Y., Cao, L., Wang, L., Qi, Y., Zhao, Y., Lu, H., Lu, L., Zhang, D., Wang, Z., Zhang, H. (2024). Preparation and application of degradable lignin/poly (vinyl alcohol) polymers as urea slow-Release coating materials. *Molecules.* 29, 1699.
<https://doi.org/10.3390/molecules29081699>.

- Low, L.E., Teh, K.C., Siva, S.P., Chew, I.M.L., Mwangi, W.W., Chew, C.L., Goh, B.H., Chan, E.S., Tey, B.T. (2021). Lignin nanoparticles: the next green nanoreinforcer with wide opportunity. *ENMM*. 15, 100398. <https://doi.org/10.1016/j.enmm.2020.100398>.
- Lü, Q.-F., Luo, J.-J., Lin, T.-T., Zhang, Y.-Z. (2014). Novel lignin–poly(N-methylaniline) composite sorbent for silver ion removal and recovery. *ACS Sustainable Chem. Eng.* 2, 465–471. <https://doi.org/10.1021/sc400475r>.
- Luo, H., Abu-Omar, M.M. (2017). Chemicals From Lignin, In: Martin A. Abraham (Ed.), *Encyclopedia of Sustainable Technologies*. Elsevier, pp. 573-585. <https://doi.org/10.1016/B978-0-12-409548-9.10235-0>.
- Makri, S.P., Xanthopoulou, E., Klonos, P.A., Grigoropoulos, A., Kyritsis, A., Tsachouridis, K., Anastasiou, A., Deligkiozi, I., Nikolaidis, N., Bikiaris, D.N. (2022). Effect of Micro- and Nano-Lignin on the Thermal, Mechanical, and Antioxidant Properties of Biobased PLA–Lignin Composite Films. *Polymers*. 14, 5274. <https://doi.org/10.3390/polym14235274>.
- Masindi, V., Mkhonza, P., Tekere, M. (2021). Sources of Heavy Metals Pollution, In: Inamuddin, Ahamed, M.I., Lichtfouse, E., Altalhi, T. (Eds.), *Remediation of Heavy Metals. Environmental Chemistry for a Sustainable World*, 70, Springer Nature, Berlin/Heidelberg, Germany, pp. 419–454. https://doi.org/10.1007/978-3-030-80334-6_17.
- Meng, X., Scheidemantle, B., Li, M., Wang, Y., Zhao, X., Toro-González, M., Singh, P., Pu, Y., Wyman, C.E., Ozcan, S., Cai, C.M., Ragauskas A.J. (2020). *ACS Omega*. 5, 2865-2877. <https://doi.org/10.1021/acsomega.9b03717>.
- Merdy, P., Guillon, E., Aplincourt, M., Dumonceau, J., Vezin, H. (2002). Copper sorption on a straw lignin: Experiments and EPR characterization. *J. Colloid Interface Sci.* 245, 24-31. <https://doi.org/10.1006/jcis.2001.7972>.
- Mohan, D., Pittman, C. U., Steele, P. H. (2006). Single, binary and multi-component adsorption of copper and cadmium from aqueous solutions on kraft lignin - a biosorbent. *J. Colloid Interface Sci.* 297, 489-504. <https://doi.org/10.1016/j.jcis.2005.11.023>.
- Morena, A. G., Tzanov, T. (2022). Antibacterial lignin-based nanoparticles and their use in composite materials. *Nanoscale Adv.* 4, 4447–4469. <https://doi.org/10.1039/d2na00423b>.
- Moretti, Ch., Corona, B., Hoefnagels, R., van Veen, M., Vural-Gürsel, I., Strating, T., Gosselink, R., Junginger, M. (2022). Kraft lignin as a bio-based ingredient for Dutch asphalts: an attributional LCA, *Sci. Total Environ.* 806, 150316. <https://doi.org/10.1016/j.scitotenv.2021.150316>.
- Nagarkar, R., and Patel, J. (2019). Polyvinyl alcohol: a comprehensive study. *Acta Sci. Pharm. Sci.* 3,34-44.
- Nan, N., Hu, W., Wang, J. (2022). Lignin-based porous biomaterials for medical and pharmaceutical applications. *Biomedicines*. 10, 747. <https://doi.org/10.3390/biomedicines10040747>.

- Nordberg, M., Nordberg, G.F., Fowler, B.A. Friberg, L. (Eds.). Handbook on the toxicology of metals. Academic Press, 2015. <https://doi.org/10.1016/C2011-0-07884-5>.
- Norgren, M., Edlund, H. (2014). Lignin: Recent advances and emerging applications, *Curr. Opin. Colloid Interface Sci.* 19, 409-416. <https://doi.org/10.1016/j.cocis.2014.08.004>.
- Odili, C.C., Gbenebour, O.P., Olanrewaju, O.A., Badaru, T.O., Adeosun, S.O. (2025). Physiochemical performance of electrospun PLA-lignin and PVA-lignin. *J. Mater. Sci: Mater. Eng.* 20, 10. <https://doi.org/10.1186/s40712-025-00218-7>.
- Oh, D.H., Heo, J.W., Xia, Q., Kim, M.S., Kim, Y.S. (2024). Amine-crosslinked lignin for water pollution attributable to organic dye remediation: versatile adsorbent for selective dye removal and reusability. *Heliyon*, 10, e37497. <https://doi.org/10.1016/j.heliyon.2024.e37497>.
- Oladimeji, T.E., Oyedemi, M., Emetere, M.E., Agboola, O., Adeoye, J.B., Odunlami, O.A. (2024). Review on the impact of heavy metals from industrial wastewater effluent and removal technologies. *Heliyon*. 10, e40370. <https://doi.org/10.1016/j.heliyon.2024.e40370>.
- Pan, J., Zhu, J., Cheng, F. (2021). Preparation of sodium lignosulfonate/chitosan adsorbent and application of Pb²⁺ treatment in water. *Sustainability*. 13, 2997-3010. <https://doi.org/10.3390/su13052997>.
- Parajuli, D., Adhikari, C.R., Kuriyama, M., Kawakita, H., Ohto, K., Inoue, K., Funaoka, M., (2006a). Selective recovery of gold by novel lignin-based adsorption gels. *Ind. Eng. Chem. Res.* 45, 8–14. <https://doi.org/10.1021/ie050532u>.
- Parajuli, D., Inoue, K., Ohto, K., Oshima, T., Murota, A., Funaoka, M., Makino, K. (2005). Adsorption of heavy metals on crosslinked lignocatechol: a modified lignin gel. *React. Funct. Polym.* 62, 129-139. <https://doi.org/10.1016/j.reactfunctpolym.2004.11.003>.
- Parajuli, D., Kawakita, H., Inoue, K., Funaoka, M. (2006b). Recovery of gold(III), palladium(II), and platinum(IV) by aminated lignin derivatives. *Ind. Eng. Chem. Res.* 45, 6405–6412. <https://doi.org/10.1021/ie0603518>.
- Parvathy, G., Sethulekshmi, AS, Jayan, J.S., Raman, A., Saritha, A. (2021). Lignin based nano-composites: Synthesis and applications. *PSEP*. 145, 395–410. <https://doi.org/10.1016/j.psep.2020.11.017>.
- Patel, R., Dhar, P., Babaei-Ghazvini, A., Dafchahi, M.N., Acharya, B. (2023). Transforming lignin into renewable fuels, chemicals, and materials: A review. *Bioresour. Technol. Rep.* 22, 101463. <https://doi.org/10.1016/j.biteb.2023.101463>.
- Pham, D.H., Kumar, B., Kim, J. (2024). Environment-friendly, high-performance lignin-derived and polyvinyl alcohol blended resin for all-green natural fiber-reinforced composite. *IJPEM*. 12, 607-619. <https://doi.org/10.1007/s40684-024-00650-8>.
- Pötschke, P., Bhattacharyya, A.R., Janke, A., Pegel, S., Leonhardt, A., Täschner, C., Ritschel, M., Roth, S., Hornbostel, B., Cech, J. (2005). Melt mixing as method to disperse carbon nanotubes into thermoplastic polymers. *Fuller. Nanotub. Carbon Nanostructures*. 13, 211–224. <https://doi.org/10.1081/FST-200039267>.

- Qasem, N.A.A., Mohammed, R.H., Lawal, D.U. (2021). Removal of heavy metal ions from wastewater: a comprehensive and critical review. *npj Clean Water*. 4, 36.
<https://doi.org/10.1038/s41545-021-00127-0>.
- Quintana, G.C., Rocha, G.J.M., Goncalves, A.R., Velasquez, J.A. (2008). Evaluation of heavy metal removal by oxidised lignins in acid media from various sources. *Biores*. 3, 1092-1102.
- Rana, R., Nanda, S., Meda, V., Dalai, A.K., Kozinski, J.A. (2018). A review of lignin chemistry and its biorefining conversion technologies. *J. Biochem. Eng. Bioprocess. Technol.* 1, 1000105.
- Ridho, M.R., Agustiany, E.A., Rahmi Dn, M., Madyaratri, E.W., Ghozali, M., Restu, W.K., Falah, F., Rahandi Lubis, M. A., Syamani, F. A., Nurhamiyah, Y., Hidayati, S., Sohail, A., Karungamye, P., Nawawi, D.S., Iswanto, A.H., Othman, N., Mohamad Aini, N.A., Hussin, M.H., Sahakaro, K., et al., Fatriasari, W. (2022). Lignin as green filler in polymer composites: development methods, characteristics, and potential applications. *Advances in Materials Science and Engineering*. 2022, 1363481. <https://doi.org/10.1155/2022/1363481>.
- Roa, K., Oyarce, E., Boulett, A., ALSamman, M., Oyarzún, D., Pizarro, G.D.C., Sánchez, J. (2021). Lignocellulose-based materials and their application in the removal of dyes from water: A review. *Sustain. Mater. Technol.* 29, e00320.
<https://doi.org/10.1016/j.susmat.2021.e00320>.
- Roy, K., Debnath, S. C., Potiyaraj, P. (2020). A Review on recent trends and future prospects of lignin based green rubber composites. *J. Polym. Environ.* 28, 367–387.
<https://doi.org/10.1007/s10924-019-01626-5>.
- Sadeghifar, H., Ragauskas, A. (2020). Lignin as a UV light blocker-a review. *Polymers*. 12, 1134. <https://doi.org/10.3390/polym12051134>.
- Santander, P., Butter, B., Oyarce, E., Yáñez, M., Xiao, L.-P., Sánchez, J. (2021). Lignin-based adsorbent materials for metal ion removal from wastewater: A review. *Ind. Crops Prod.* 167, 113510. <https://doi.org/10.1016/j.indcrop.2021.113510>.
- Santander, P., Butter, B., Oyarce, E., Yáñez, M., Xiao, L.-P., Sánchez, J. (2021). Lignin-based adsorbent materials for metal ion removal from wastewater: A review. *Ind. Crops Prod.* 167, 113510. <https://doi.org/10.1016/j.indcrop.2021.113510>.
- Šćiban, M.B., Klasnja, M.T., Antov, M.G. (2011). Study of the biosorption of different heavy metal ions onto Kraft lignin. *Ecol. Eng.* 37, 2092-2095.
<https://doi.org/10.1016/j.ecoleng.2011.08.006>.
- Selig, M.J., Viamajala, S., Decker, S.R., Tucker, M.P., Himmel, M.E., Vinzant, T.B. (2007). Deposition of lignin droplets produced during dilute acid pretreatment of maize stems retards enzymatic hydrolysis of cellulose. *Biores. Technol.* 23, 1333–1339.
<https://doi.org/10.1021/bp0702018>.
- Sethupathy, S., Morales, G.M., Gao, L., Wang, H., Yang, B., Jiang, J., Sun, J., Zhu, D. (2022). Lignin valorization: Status, challenges and opportunities. *Biores. Technol.* 347, 126696.
<https://doi.org/10.1016/j.biortech.2022.126696>.

- Shakoor Shar, A., Wang, N., Chen, T., Zhao, X., Weng, Y. (2023). Development of PLA/ligninbio-composites compatibilized by ethylene glycol diglycidyl ether and poly (ethylene glycol) diglycidyl ether. *Polymers*. 15, 4049. <https://doi.org/10.3390/polym15204049>.
- Shao, L., Liu, N., Wang, Z., Zhan, P., Zhang, L., Wu, Z. (2023). Functional lignin-based polymers: isolation, synthetic methods and high-valued applications. *ChemistrySelect*. 8, e202301633. doi.org/10.1002/slct.202301633.
- Shekar, H. S. S., Ramachandra, M. (2018). Green composites: a review. *Mat. Today: Proc.* 5, 2518–2526. <https://doi.org/10.1016/j.matpr.2017.11.034>.
- Shi, K., Liu, G., Sun, H., Weng, Y. (2023). Polylactic acid/lignin composites: A review. *Polymers*. 15, 2807. <https://doi.org/10.3390/polym15132807>.
- Shi, X., Qiao, Y., An, X., Tian, Y., Zhou, H. (2020). High-capacity adsorption of Cr(VI) by lignin-based composite: Characterization, performance and mechanism. *Int. J. Biol. Macromol.* 159, 839–849. <https://doi.org/10.1016/j.ijbiomac.2020.05.130>.
- Srivastava, S.K., Singh, A.K., Sharma, Ashutosh (1994). Studies on the uptake of lead and zinc by lignin obtained from black liquor – a paper industry waste material. *Environ. Technol.* 15, 353–361. <https://doi.org/10.1080/09593339409385438>.
- Staszak, K., Regel-Rosocka, M. (2024). Removing Heavy metals: cutting-edge strategies and advancements in biosorption technology. *Materials*. 17, 1155. <https://doi.org/10.3390/ma17051155>.
- Su, W., Li, P., Wang, M., Yi, D., Jiang, B., Wu, W. (2023). Simple preparation of lignin-based phenolic resin carbon and its efficient adsorption of Congo Red. *Water*. 15, 2777. <https://doi.org/10.3390/w15152777>.
- Sun, Y., Liu, X., Lv, X., Wang, T., Xue, B. (2021). Synthesis of novel lignosulfonate-modified graphene hydrogel for ultrahigh adsorption capacity of Cr(VI) from wastewater. *J. Clean. Prod.* 295, 126406–126419. <https://doi.org/10.1016/j.jclepro.2021.126406>.
- Supanchaiyamat, N., Jetsrisuparb, K., Knijnenburg, J.T.N., Tsang, D.C.W. Andrew, Hunt, J. (2019). Lignin materials for adsorption: Current trend, perspectives and opportunities. *Biores. Technol.* 272, 570–581. <https://doi.org/10.1016/j.biortech.2018.09.139>.
- Tang, Q., Tang, J., Müller, M. (2016). Process-directed self-assembly of multiblock copolymers: solvent casting vs spray coating. *Eur. Phys. J. Spec. Top.* 225, 1785–1803. <https://doi.org/10.1140/epjst/e2016-60121-6>.
- Tarrés, Q., Aguado, R., Domínguez-Robles, J., Larrañeta, E., Delgado-Aguilar, M. (2022). Valorization of kraft lignin from black liquor in the production of composite materials with poly(caprolactone) and natural stone groundwood fibers. *Polymers*. 14, 5178. <https://doi.org/10.3390/polym14235178>.
- Tayeb, A., Tajvidi, M., Bousfield, D. (2023). Paper-based oil barrier packaging using lignin-containing cellulose nanofibrils. *Molecules*. 25, 1344. <https://doi.org/10.3390/molecules25061344>.

- Terzopoulou, Z., Xanthopoulou, E., Pardalis, N., Pappa, C.P., Torofias, S., Triantafyllidis, K.S., Bikiaris, D.N. (2022). Synthesis and characterization of poly(lactic acid) composites with organosolv lignin. *Molecules*. 27, 8143. <https://doi.org/10.3390/molecules27238143>.
- Thakur, V.K., Singha, A.S., Mehta, I.K. (2010). Renewable resource-based green polymer composites: analysis and characterization. *IJPAC*. 15, 137–146. <https://doi.org/10.1080/10236660903582233>.
- Thakur, V.K., Thakur, M.K., Raghavan, P., Kessler, M.R. (2014). Progress in green polymer composites from lignin for multifunctional applications: a review. *ACS Sustain. Chem. Eng.* 2, 1072–1092. <https://doi.org/10.1021/sc500087z>.
- Tian, J.L., Ren, S.X., Fang, G.Z., Ma, Y.L., Ai, Q. (2014). Preparation and performance of dimethyl-acetoxy-(2-carboxymethyl ether)-lignin ammonium chloride amphoteric surfactant. *Biores.* 9, 6290-6303.
- Todorciuc, T., Bulgariu, L., Popa, V.I. (2015). Adsorption of Cu(II) from aqueous solution on wheat straw lignin: equilibrium and kinetic studies. *Cellul. Chem. Technol.* 49, 439–447.
- Turhan, K., Turgut, Z. (2009). Decolorization of direct dye in textile wastewater by ozonization in a semi-batch bubble column reactor. *Desalination*. 242, 256-263. <https://doi.org/10.1016/j.desal.2008.05.005>.
- Türkoğlu, G.C., Khomarloo, N., Mohsenzadeh, E., Gospodinova, D.N., Neznakomova, M., Salaün, F. (2024). PVA-based electrospun materials—a promising route to designing nanofiber mats with desired morphological shape—a review. *IJMS*. 25, 1668. <https://doi.org/10.3390/ijms25031668>.
- Vayshbeyn, L.I., Mastalygina, E.E., Olkhov, A.A., Podzorova, M.V. (2023). Poly(lactic acid)-based blends: a comprehensive review. *App. Sci.* 13, 5148. <https://doi.org/10.3390/app13085148>.
- Vishtal, A., Kraslawski, A. (2011). Challenges in industrial applications of technical lignins. *BioRes.* 6, 3547-3568. <https://doi.org/10.15376/biores.6.3.3547-3568>.
- Wang, F., Jiang, M., Pan, Y., Lu, Y., Xu, W., Zhou, Y. (2023). 3D printing photo-induced lignin nanotubes/polyurethane shape memory composite. *Polym. Test.* 119, 107934. <https://doi.org/10.1016/j.polymertesting.2023.107934>.
- Wang, H.M., Wang, B., Yuan, T.Q., Zheng, L., Shi, Q., Wang, S.F., Song, G.Y., Sun, R.C. (2020). Tunable, UV-shielding and biodegradable composites based on well-characterized lignins and poly(butylene adipate-co-terephthalate). *Green Chem.* 22, 8623–8632. <https://doi.org/10.1039/d0gc03284k>.
- Wang, H.M., Yuan, T.Q., Song, G.Y., Sun, R.C. (2021). Advanced and versatile lignin-derived biodegradable composite film materials toward a sustainable world. *Green Chem.* 23, 3790–3817. <https://doi.org/10.1039/d1gc00790d>.
- Wang, T., Jiang, M., Yu, Niu, X.N., Chen, L. (2022). Application of lignin adsorbent in wastewater treatment: a review. *Sep. Purif. Technol.* 302, 122116. <https://doi.org/10.1016/j.seppur.2022.122116>.

- Wawrzkievicz, M., Podkościelna, B., Tarasiuk B. (2025). Modified starch as a component of environmentally friendly polymer adsorbents – from synthesis and characterization to potential application in the removal of toxic C.I. Basic Yellow 2 dye. *Measurement*. 240, 115556. <https://doi.org/10.1016/j.measurement.2024.115556>.
- Wołowicz, A. (2019). Zinc(II) removal from model chloride and chloride–nitrate(V) solutions using various sorbents. *Physicochem. Probl. Miner. Process.* 55, 1517–1534. <https://doi.org/10.5277/ppmp19080>.
- Wołowicz, A., Hubicki, Z. (2020). Enhanced removal of copper(II) from acidic streams using functional resins: batch and column studies. *J. Mater. Sci.* 55, 13687–13715. <https://doi.org/10.1007/s10853-020-04982-z>.
- Wołowicz, A., Staszak, K., Hubicki, Z. (2022). Removal of copper(II) in the presence of sodium dodecylbenzene sulfonate from acidic effluents using adsorption on ion exchangers and micellar-enhanced ultrafiltration methods. *Molecules*. 27, 2430. <https://doi.org/10.3390/molecules27082430>.
- Xu, F., Zhu, T.-T. Qing-Quan Rao, Shui, S.-W., Li, W.-W., He, H.-B., Yao, R.S. (2017). Fabrication of mesoporous lignin-based biosorbent from rice straw and its application for heavy-metal-ion removal. *J. Environ. Sci.* 53, 132–140. <https://doi.org/10.1016/j.jes.2016.03.026>.
- Yan, Z., Wu, T., Fang, G., Ran, M., Shen, K., Liao, G. (2021). Self-assembly preparation of lignin–graphene oxide composite nanospheres for highly efficient Cr(VI) removal. *RSC Adv.* 11, 4713–4722. <https://doi.org/10.1039/d0ra09190a>.
- Yang, H., Yu, B., Xu, X., Bourbigot, S., Wang, H., Song, P. (2020). Lignin-derived bio-based flame retardants toward high-performance sustainable polymeric materials. *Green Chem.* 22, 2129–2161. <https://doi.org/10.1039/d0gc00449a>.
- Yang, J., Wu, J.-X., Lü, Q.-F., Lin, T.-T. (2014). Facile preparation of lignosulfonate–graphene oxide–polyaniline ternary nanocomposite as an effective adsorbent for Pb(II) ions. *ACS Sustain. Chem. Eng.* 2, 1203–1211. <https://doi.org/10.1021/sc500030v>.
- Younesi-Kordkheili, H., Pizzi, A. (2020). Ionic liquid- modified lignin as a bio- coupling agent for natural fiber- recycled polypropylene composites. *Compos. B: Eng.* 181, 107587. <https://doi.org/10.1016/j.compositesb.2019.107587>.
- Zaidi, S.A.S., Kwan, C.E., Mohan, D., Harun, S., Luthfi, A.A.I., Sajab, M.S. (2023). Evaluating the stability of PLA-lignin filament produced by bench-top extruder for sustainable 3D printing. *Materials*. 16, 1793. <https://doi.org/10.3390/ma16051793>.
- Zhai, S., Liu, Q., Zhao, Y., Sun, H., Yang, B., Weng, Y. (2021). A review: Research progress in modification of poly (lactic acid) by lignin and cellulose. *Polymers*. 13, 1–15. <https://doi.org/10.3390/polym13050776>.
- Zhang, X., Can, J., Jiang, Y., Liu, G., Wu, G., Kong, Z., 2017. A novel gallic acid-grafted-lignin biosorbent for the selective removal of lead ions from aqueous solutions. *Biores.* 12, 5343–5357.

Zhang, Y., Li, T.T., Lou, C.W., Lin, J.H. (2022). Facile method for tent fabrics with eco-friendly/durable properties using waterborne polyurethane/lignin: preparation and evaluation. *J. Ind. Text.* 51, 4149S-4166S.

<https://doi.org/10.1177/1528083720931884>.

Zhang, Z., Chen, Y., Wang, D., Yu, D., Wu, Ch. (2023). Lignin-based adsorbents for heavy metals. *Ind. Crops. Prod.* 193, 116119. <https://doi.org/10.1016/j.indcrop.2022.116119>.

Zhao, W., Liang, Z., Feng, Z., Xue, B., Xiong, C., Duan, C., Ni, Y. (2021). New kind of lignin/polyhydroxyurethane composite: green synthesis, smart properties, promising applications, and good reprocessability and recyclability. *ACS Appl. Mater. Interfaces.* 13, 28938–28948. <https://doi.org/10.1021/acsami.1c06822>.

Zimniewska, Kozłowski, R., M., Batog, J. (2008). Nanolignin modified linen fabric as a multifunctional product. *Mol. Cryst. Liq. Cryst.* 484, 43/[409]-50/[416].

<https://doi.org/10.1080/15421400801903395>.



CHAPTER 3

EVALUATION OF PROPERTIES OF POLYMERIC ADSORBENTS AND COMPOSITES WITH LIGNIN ADDITION

3.1 Selected methods for evaluating the properties of polymeric adsorbents and composites containing lignin

Evaluation of the properties of polymeric materials obtained based on lignin or with the addition of lignin requires the use of a variety of testing methods that enable the analysis of their structure, mechanical, thermal, chemical properties, or adsorption capacities. The applied testing methods and techniques depend on the potential application of the obtained materials.

The most commonly applied methods for the determination of properties and structure of materials include spectroscopic (e.g. Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR), Ultraviolet-Visible Spectroscopy (UV-Vis)), thermal (Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA)), mechanical (strength tests) ones, as well as adsorbent-specific analyses such as specific surface area measurement (Brunauer, Emmett, and Teller adsorption theory, BET) or adsorption kinetics studies. Owing to these methods, it is possible not only to characterize precisely the properties of materials but also to optimize their applications, e.g. in removing toxic pollutants from wastewater, and the production of biocomposites or biomaterials for innovative applications.

Different testing methods depending on the type, nature, and form of the obtained material (co/polymer, polymeric blend, composite, or polymer nano/microspheres) are used. This approach enables a comprehensive assessment of the material properties, to ensure their suitability for the intended applications and specific functional requirements.

3.1.1 Fourier Transform Infrared Spectroscopy

Infrared spectroscopy is one of the most important research methods in the analysis of lignin-containing polymeric materials, owing to its ability to provide detailed information on the chemical structure and interactions between components. This allows, among others for identification and confirmation of the presence of lignin functional groups, assessment of interactions of lignin with the polymer matrix, analysis of chemical modifications of lignin, and quantification of lignin in the polymer. In combination with the thermogravimetric analysis, this makes thermal and chemical characterization of lignin degradation possible.

Infrared spectroscopy belongs to a family of vibrational spectroscopy techniques used to study samples in the gaseous, liquid, and solid states. One of the most frequently used techniques in this field is attenuated total reflectance/Fourier transform infrared spectroscopy (ATR/FTIR), which exploits the phenomenon of total internal reflection of infrared radiation and has become a routine analytical tool in many laboratories due to its simplicity and rapid acquisition of results. The spectra obtained with this method enable the identification of groups of atoms in a molecule and their mutual orientation in the structure of the chemical compound under study (Lancefield et al., 2019).

The spectrometers used for the ATR/FTIR analysis are equipped with a special ATR attachment that allows measurements to be made. Infrared radiation is directed at a crystal with a high refractive index, causing multiple reflections within the crystal. Some of the radiation energy is absorbed by the test substance, resulting in a change in the intensity of the beam reaching the detector (Figure 3.1).

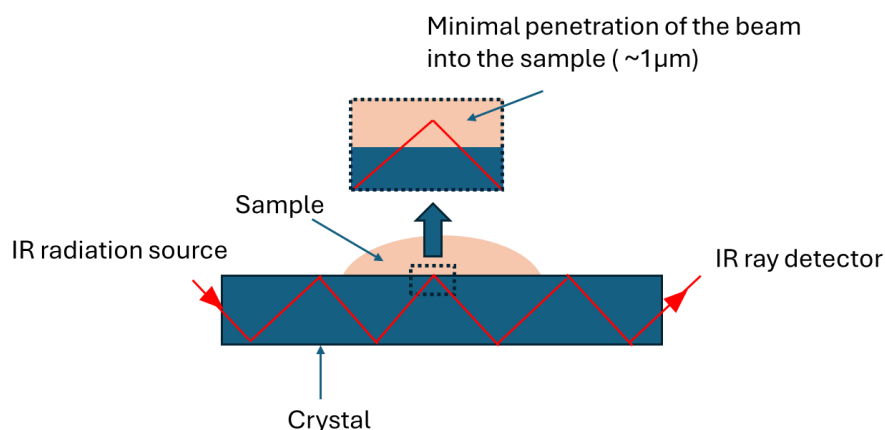


Figure 3.1. The phenomenon of total internal reflection inside the ATR attachment crystal.

Liquid samples are poured directly onto the surface of the crystal, while semi-solid substances (e.g. pastes or creams) are spread evenly over the entire surface of the attachment window. For powder, chips, or granules samples, the material is pressed against the surface of the crystal using a special holder that ensures direct contact between the sample and the crystal. The crystals most commonly used in ATR technology are germanium, zinc selenide, and diamond. Despite its high cost, diamond is the most desirable material due to its exceptional mechanical durability and chemical resistance. Crystals from germanium or zinc selenide are more susceptible to mechanical damage such as scratches. ATR/FTIR is a very convenient analytical technique because it combines most of the advantages of vibrational spectroscopy, such as presented in Figure 3.2.



Figure 3.2. Advantages of ATR/FTIR spectroscopy.

In conclusion, infrared spectroscopy, especially the ATR/FTIR technique, is an indispensable tool in the study of lignin-containing polymeric materials. This enables not only the analysis of the chemical structure but also the evaluation of its modifications and interactions with other components, making it a versatile and efficient technique (Goliszek et al., 2019; Sammons et al., 2013)

3.1.2 Thermal properties

Assessing the thermal stability of polymer-based materials is very important as these materials are very common and occur in the immediate environment of people. Polymers and composites can be exposed to high temperatures not only during processing (injection molding or forming), but also during use (e.g. in electrical equipment or automotive applications), and even under extreme conditions such as fire. Therefore it is of significant importance to test the thermal resistance of materials. Not only from the point of view of determining the maximum temperature at which the material retains its mechanical, chemical, and structural properties but above all from the point of view of human and environmental safety. The main methods analyzing the thermal properties of polymeric materials include differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), or coupled methods: thermogravimetric analysis-Fourier transform infrared spectroscopy (TGA-FTIR) or thermogravimetric analysis-mass spectrometry (TGA-MS), dynamic mechanical analysis (DMA) (Figure 3.3), and for the flammability analysis, Cone Calorimetry is used, among others. A selection of the most frequently used techniques will be discussed below.

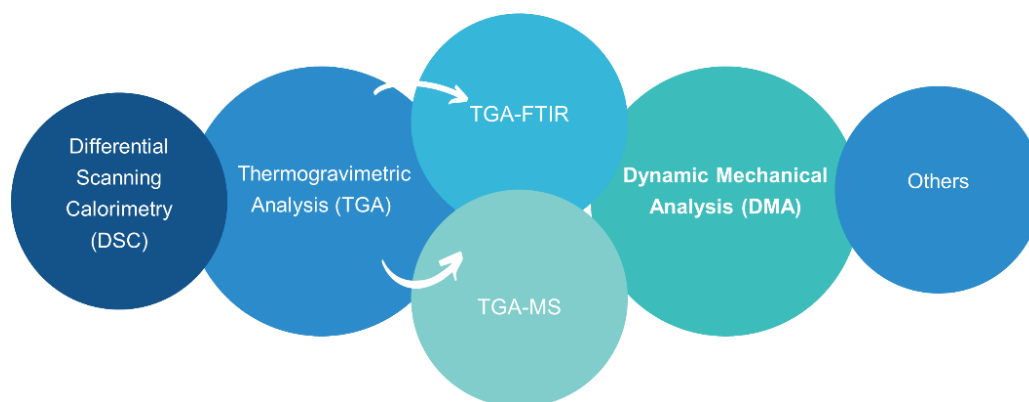


Figure 3.3. Selected methods of thermal analysis.

Differential Scanning Calorimetry (DSC)

DSC is a thermo-analytical method for quantitatively studying thermal processes occurring in the sample during analysis. The technique is an essential tool in studying the thermal properties of solids, particularly polymers. The key assumption of the method

is a controlled time dependence of the temperature change, which should be at least approximately linear.

During exothermic or endothermic transformations, the test sample is temporarily at a different temperature from that of the reference sample. These differences are recorded as peaks on a graph (known as a thermogram), which allows precise identification and analysis of the processes under study (Aguilar-Méndez et al., 2010).

DSC is widely used in polymer research, allowing the determination of such parameters as:

- crystallization temperature (the point at which a polymer changes from a liquid phase to an ordered solid phase),
- melting point (the temperature at which the crystalline structure disappears and the polymer changes to a liquid phase),
- melting point (the temperature at which the crystalline structure disappears and the material becomes liquid),
- glass transition temperature (the temperature at which the transition from a liquid or plastic to a glassy state takes place),
- thermal decomposition temperature (the limiting temperature at which a material begins to decompose).

Moreover, modified calorimeters allow real-time studies of, for example, photopolymerization reactions or the cross-linking of, for example, polyester resins at elevated temperatures.

DSC is also used in other fields such as pharmaceutical research, the food industry, and materials engineering. The technique also plays an important role in the design of new materials and process optimization (Gill et al., 2010).

The glass transition temperature (T_g) of lignin marks the temperature range over which lignin changes from a hard, glassy material to a softer, more rubber-like state (Lin and Dence, 1992). For technical lignins, T_g values can vary widely, typically ranging from about 80 °C to over 180 °C, depending on factors such as molecular weight, degree of structural condensation, functional group composition, and moisture content. Lower T_g values are generally associated with more flexible or less condensed lignin structures, whereas higher T_g indicates higher thermal resistance and stiffness. DSC is well suited to measure T_g in lignin, as lignin typically does not show sharp melting points but exhibits broad transitions. The presence of water significantly affects T_g , acting as a plasticizer and lowering the observed T_g value, so careful drying is often necessary for accurate characterization.

The DSC thermograms in Figure 3.4 of the four lignin samples (OE, KE, OS, and KS) illustrate how both botanical origin and extraction method influence lignin structure and, consequently, its glass transition temperature (T_g).

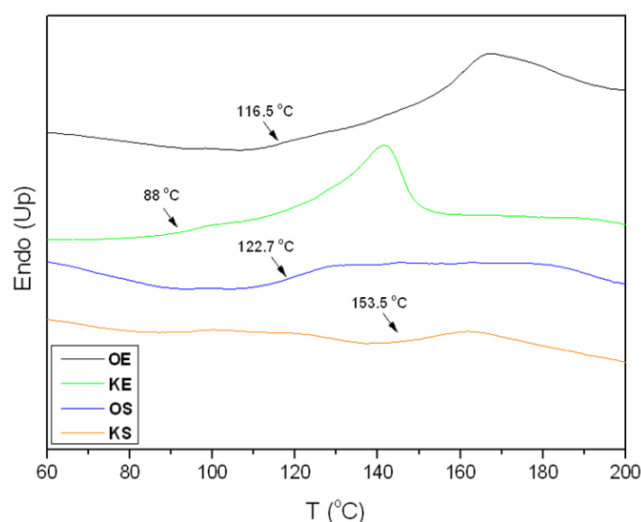


Figure 3.4. T_g 's values for technical lignins: organosolv eucalyptus (OE) and spruce (OS), and kraft eucalyptus (KE) and spruce (KS) (adapted from Gordobil, et al. 2016).

Thermogravimetric Analysis (TGA)

The analysis of the temperature distribution of a given polymer is extremely important in several respects: technological, application, and recycling. The results of thermal analysis help to optimize the manufacturing process of a given polymer and provide information on physical and chemical phenomena (e.g. phase transitions, absorption, adsorption, chemisorption, oxidation, etc.) (Jędrzejczak et al., 2021).

Thermogravimetric analysis is a technique for measuring the thermal stability of materials, including polymers. TGA is performed using a thermogravimeter, the key component which is a highly sensitive microbalance equipped with a thermocouple which is placed in an oven that is raised above it for controlled heating of the samples. The microbalance is thermally isolated from the environment. Depending on the requirements, the analysis can be made under different atmospheric conditions: most commonly, measurements are performed in an oxidizing atmosphere, an inert atmosphere (e.g. using helium as an inert gas), or under reduced pressure. During the measurement, changes in the mass of the sample are recorded as a function of time or temperature. The aforementioned changes in the sample mass during TGA can be caused by several phenomena and transformations presented in Figure 3.5.

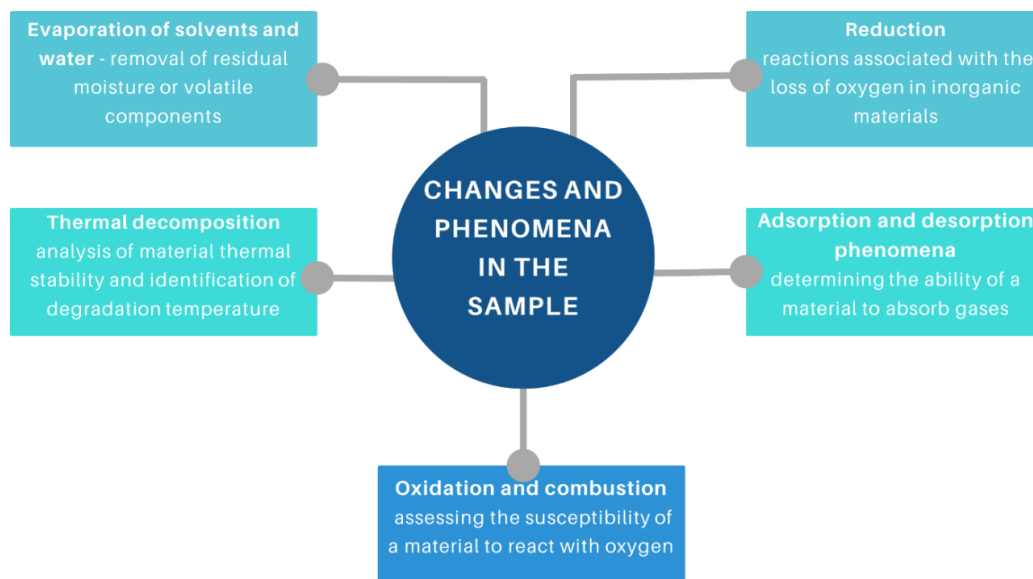


Figure 3.5. Possible variations in the sample during TGA analysis.

Moreover, it is also possible to record such parameters:

- initial decomposition temperature (T_{IDT}),
- maximum rate of thermal degradation (V_{max}),
- temperature attributed to the largest mass loss (T_{max}),
- individual stages of decomposition (T_1 , T_2 , T_3 , etc.),
- final decomposition temperature (T_f),
- residual mass (RM) (Menczel and Prime, 2009).

The TG analysis provides key information about thermal decomposition mechanisms and the presence of different material fractions such as volatile components, organic matter, and decomposition end products.

The TG analysis is a key tool in the study of polymeric materials, including lignin or other biopolymers. It can be used to determine thermal stability, degradation mechanisms, and component compatibility. The addition of lignin-containing aromatic rings can improve the thermal resistance of materials but it also affects their degradation mechanisms and the amount of carbon residues. Thermogravimetry can be used to fine-tune the composition of biopolymer blends for specific applications (Watkins et al., 2015).

Lignin generally begins to decompose around 200–250 °C, with the main weight loss occurring between 300–500 °C due to the cleavage of alkyl-aryl ether bonds (such as β -O-4 linkages) and the degradation of side chains and aromatic rings. Beyond this range, the formation of a stable carbonaceous char occurs, which is further oxidized in an oxygen atmosphere to determine the amount of fixed carbon and inorganic ash.

Figure 3.6 illustrates a typical two-stage TGA protocol in which lignin is first pyrolyzed in nitrogen (25–950 °C) and then combusted in oxygen (450–800 °C).

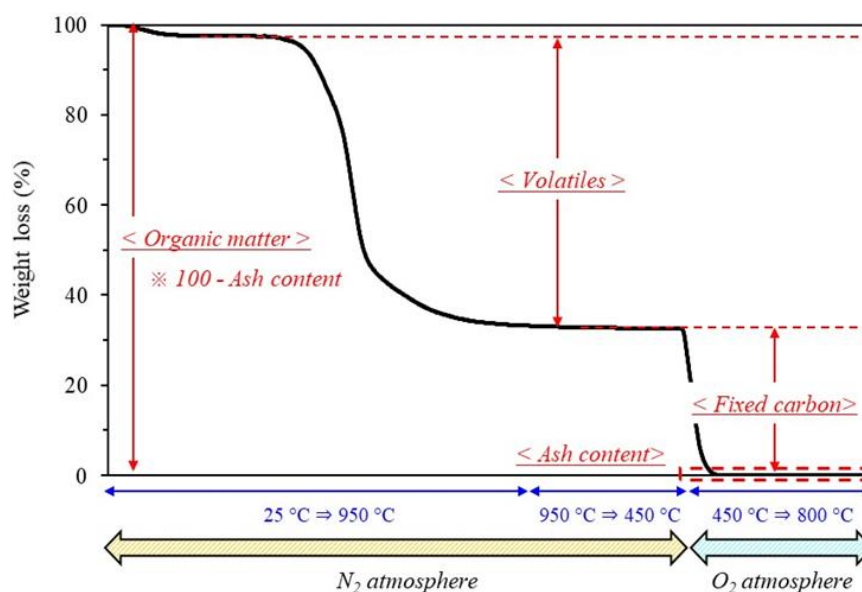


Figure 3.6. Thermogravimetric analysis of lignin (adapted from Tagami, 2018).

In the nitrogen phase, the initial weight loss corresponds to the release of moisture and light volatiles, followed by the major decomposition of organic matter (volatiles), which represents the thermal degradation of lignin's polymeric structure. The residual material at the end of this stage is largely fixed carbon. In the subsequent oxidative stage, the fixed carbon is combusted, leaving only the inorganic ash. By analyzing the weight loss in each stage, it is possible to quantify the organic matter (100% - ash), volatile content, fixed carbon, and final ash content.

This comprehensive approach enables detailed characterization of lignin's thermal behavior, which is crucial for its application in carbon materials, biochar production, and flame-retardant systems. The TGA analysis in both nitrogen and oxygen atmospheres also enables the estimation of the higher heating value (HHV) of lignin. HHV reflects the total energy released upon complete combustion, including the latent heat of vaporization of water in the combustion products. This parameter is crucial for evaluating lignin's potential as a bioenergy feedstock.

Together, DSC and TGA define the safe processing window and degradation behavior of lignin in high-temperature environments.

Porous structure

Porosity is one of the most important structural characteristics of solids, defined as the presence of voids, called pores, in their internal structure. These pores can vary in size, shape, and distribution and their presence affects physical, mechanical, and chemical properties of the material. In practice, porosity plays an important role in many technological and scientific applications.

Classification of pores by size (according to IUPAC):

- micropores - smallest pores with the diameters of less than 2 nm (20 Å),
- mesopores - diameters ranging from 2 nm to 50 nm (20-500 Å),
- macropores - these are pores with the diameters larger than 50 nm (500 Å).

For complete description of porous materials, there must be determined the following parameters (Lowell et al., 2004):

- specific surface area (SSA) - this is usually expressed in (m²/g) and is determined from the formula:

$$SSA = \frac{S_c}{m_c} \quad (1)$$

where: the specific surface area SSA is the ratio of the total surface area S_c divided by the total mass of the substance m_c ,

- the total pore volume V - expressed in (cm³/g), the volume occupied by the pores in 1 g of sorbent,
- the average pore radius (Å):

$$r = \frac{V}{SSA} 10^3 \quad (2)$$

- the distribution of pore volumes concerning their radii - the proportion of pores of different diameters in the total pore volume of a given material.

The specific surface area is one of the basic parameters for the evaluation and characterization of porous polymers. The specific surface area of the pore volume and the average pore radius are calculated using the BET method (Brunauer, Emmett, and Teller adsorption theory) (Brunauer et al., 1938). According to this method, the tests are carried out at the boiling point of liquid nitrogen (-195 °C) using nitrogen as the adsorbate and assuming a surface area of 0.162 nm² (16.2 Å²) for the nitrogen molecule N₂.

Porous polymer microspheres (Figure 3.7) have many advantages, the most important of which is that they are insensitive to changes in the pH of the mobile phase. Unfortunately, there is also an imperfection, namely the micropores present in the internal structure of such fillers. According to Stuurman et al. (1987) and Nevejans and Verzele (1987), the microporosity of styrene-divinylbenzene (ST-DVB) fillers is a consequence of the spatial structure of the monomers themselves. The presence of pores with diameters smaller than 20 Å in the internal structure of ST-DVB fillers allows solvent molecules to penetrate the copolymer network, regardless of the porosity of the material itself. This phenomenon has been confirmed by the tests using the exclusion chromatography (SEC) method. This involves determining the pore volume distribution function by applying polystyrene standards of different molecular weights as pore indicators and tetrahydrofuran as the eluent. The BET equation should not be applied for microporous adsorbents because the polymer is tested in the dry state and under these conditions, the polymer micropores are

not accessible to nitrogen molecules. Nevertheless, it allows a comparison of the porous structure of polymeric packings.

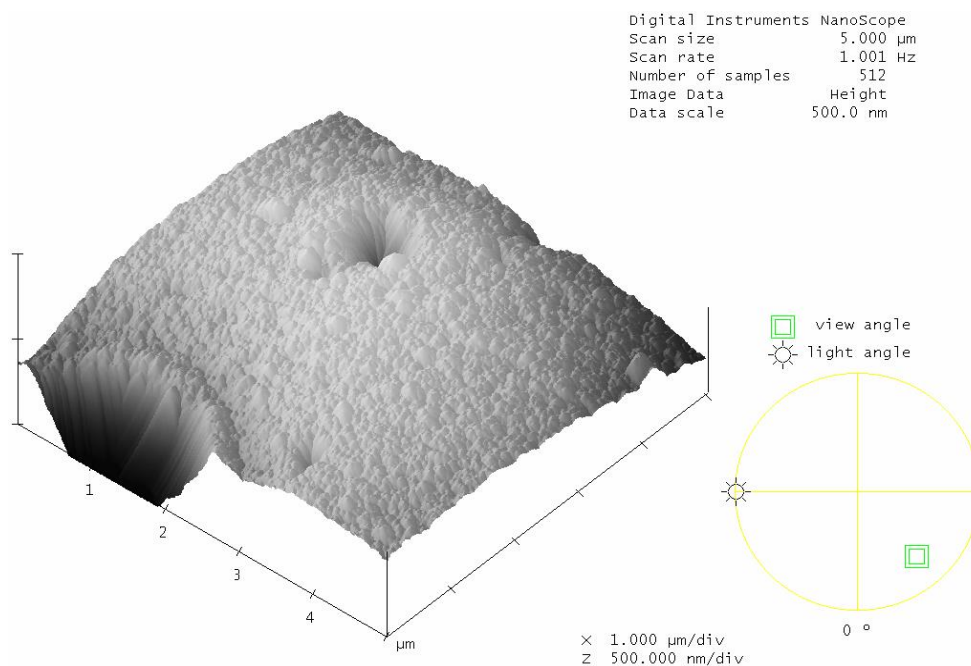


Figure 3.7. Fragment of a DVB copolymer microsphere made with an atomic force microscope (AFM) - magnification x27,000.

The porous structure of microspheres is important because porous microspheres have a much larger surface area accessible to interactions with other substances. This is critical in applications such as catalysis, adsorption, or drug delivery, where a larger surface area means a better performance. In medicine and pharmaceuticals, the porosity of microspheres affects the release time of drugs. The pores can regulate the rate of drug release, allowing a much longer and more controlled effect.

3.1.3 Mechanical properties

The application of polymer composites is primarily determined by their mechanical properties, as these define the material's performance and stability under specific conditions and loads. Mechanical properties encompass both resistance to deformation (such as strength and elasticity) and the ability of a material to undergo deformation (plasticity). When a force is applied to a material, it induces a certain type of deformation, if the force is sufficiently large, it may result in material fracture. Therefore, understanding the relationship between applied force and the resulting deformation is crucial. Additionally, for future material applications, it is essential to determine the maximum stress that the material

can withstand without undergoing permanent (plastic) deformation (Brown, 2002; Pelleg, 2012).

Depending on the applied force, mechanical testing can be divided into tensile, compression, shear, torsion, or bending. Among the various tests, the tensile test is one of the most used methods for the determination of the mechanical properties of polymers and polymer composites. In this test, the sample is deformed until it breaks by gradually increasing the stress along the axis of the sample (Brown, 2002; Pelleg, 2012). In Figure 3.8 shows the instrument for tensile test measurements.

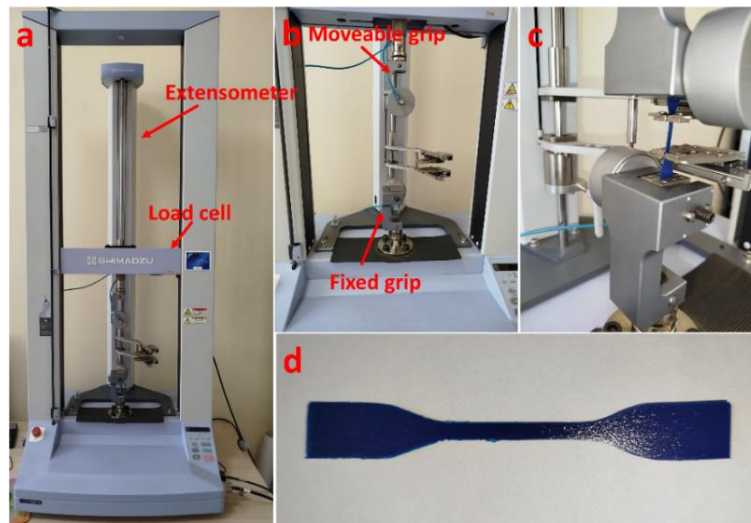


Figure 3.8. Tensile test instrument (a), grips and extensometer (b), mounting of a specimen (c) and specimen for tensile test measurements (d).

This instrument is designed to elongate the specimen at a constant rate of elongation and to continuously and simultaneously measure the stress (applied force) and elongation using an extensometer. The specimen is mounted on the ends of the instrument holders (grips). Usually, one of the grips is fixated on the test frame, and the other one is attached to the moveable part of the test frame.

In order to follow the extension rate and time, an extensometer is attached to the instrument. The results of this measurement are presented as stress (force) versus strain, where the strain is usually a dimensionless value. A standard specimen (test piece) for this test is shown in Figure 3.8d. The most common cross-sectional geometry of the specimen is rectangular or round (Mitchell, 2004).

The stress (σ) of the material is defined using formula 3, while the strain (ϵ) is defined using formula 4 (Brown, 2002; Liu, 2005).

$$\sigma(\text{MPa}) = \frac{F \text{ (N)}}{A \text{ (mm}^2\text{)}} \quad (3)$$

$$\varepsilon = \frac{(l_f - l_0) (mm)}{l_0 (mm)} \quad (4)$$

where, F is force, A is the cross-sectional area, l_0 is the original length and l_f is the length at applied force.

The stress that is usually measured in a tensile test is based on the dimensions of the sample before the application of force, and this stress is known as engineering stress. During the application of tensile force, the original dimensions of the sample are changed, as the cross-sectional area contracts and gets thinner. Due to this change of dimensions, the actual stress in the material is higher than the engineering stress, and this stress is known as true stress.

In Figure 3.9 a general stress-strain curve is shown.

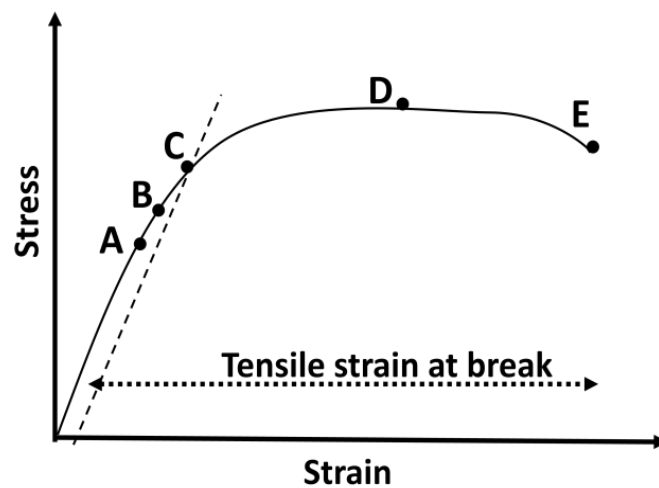


Figure 3.9. Stress-strain curve.

Using the stress-strain curve, several parameters can be determined through which the behaviour of a polymer composite when exposed to stress can be quantitatively described. Some of these parameters will be explained in the text that follows.

The modulus of elasticity (Young's modulus) – E , is a mechanical property that measures the material's resistance to elastic deformation when stress is applied. In Figure 3.9, point A represents the proportional limit, while, point B represents the elastic limit. In the region of the proportional limit, the material will return to its original form after unloading. The elastic limit is the maximum stress that a material can sustain without permanent deformation. The slope of the linear part of the stress-strain curve represents the modulus of elasticity (Liu, 2005). This parameter gives a quantitative description of the stiffness of the material and is defined using formula 5:

$$E \text{ (MPa)} = \frac{\sigma}{\varepsilon} \quad (5)$$

The maximum amount of stress that a material can withstand before breaking is called tensile strength (ultimate strength) ($\sigma_{\max}$). The tensile strength is the highest point on the stress-strain curve (Figure 3.8, point D) (Liu, 2005). This parameter can be defined using formula 6:

$$\sigma_{\max} \text{ (MPa)} = \frac{F_{\max}}{A} \quad (6)$$

where $F_{\max}$ is the maximum applied force and A is the original cross-sectional area.

Yield strength (σ_y) quantifies the stress at which the material starts to deform plastically. This means that after reaching this point the material will not return to its original state after the stress is removed. For materials that do not have yield points on their stress-strain curve, the yield strength is determined using the 0.2% offset method (the offset can vary depending on the material), which is why it is often referred to as offset yield strength. This method involves drawing a line parallel to the linear part of the stress-strain curve (Figure 3.9) starting from the x-axis at a strain of 0.2%. The intersection of this line with the stress-strain curve defines the yield strength (point C in Figure 3.9) (Pelleg, 2012; Liu, 2005). Using formula 7, the yield strength can be determined:

$$\sigma_y \text{ (MPa)} = \frac{F_y}{A} \quad (7)$$

where F_y is the stress at the yield point and A is the original cross-sectional area.

Failure Stress (σ_f) point E in Figure 3.9 is the tensile strength of the material at failure it is measured in MPa. The tensile strain at break (ε_f) defines the strain of the material at failure stress, it can be calculated using formula 4 (Brown, 2002).

The examination of mechanical properties is of great importance in polymer science and engineering, as they provide information about how materials would behave under certain conditions in real-world applications. Understanding these properties enables the optimization of polymer and polymer composite processing to meet specific requirements effectively.

3.1.4 Scanning Electron Microscopy and Transmission Electron Microscopy

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are important and powerful techniques that allow us to study the morphology, microstructure and interfacial properties of the lignin/polymer composites.

Besides the different working principles which will be discussed later, SEM and TEM differ in several fundamental aspects. Some of the being the different information that can be obtained from them. SEM provides 3D topographical information about the sample surface, whereas, TEM provides 2D information about the structure, defects, and crystallography

of the materials. SEM offers a resolution that ranges from ten nanometers. On the other hand, TEM offers higher resolution, sometimes below one nanometer (Inkson, 2016).

The working principle of SEM is based on directing a focused beam of high-energy electrons onto the surface of a sample. The electrons interact with atoms in the sample, and due to this interaction two types of electrons are produced, secondary electrons and backscattered electrons. The secondary electrons that are ejected from the surface of the specimen provide details about topography and surface features. The backscattered electrons are reflected from the specimen and they offer contrast based on atomic number differences in the material. These signals are detected and processed into images that display the sample's morphology (Inkson, 2016; Mohammed and Abdullah, 2018.; Zhou et al., 2007).

In Figure 3.10 the schematic illustration of SEM is shown.

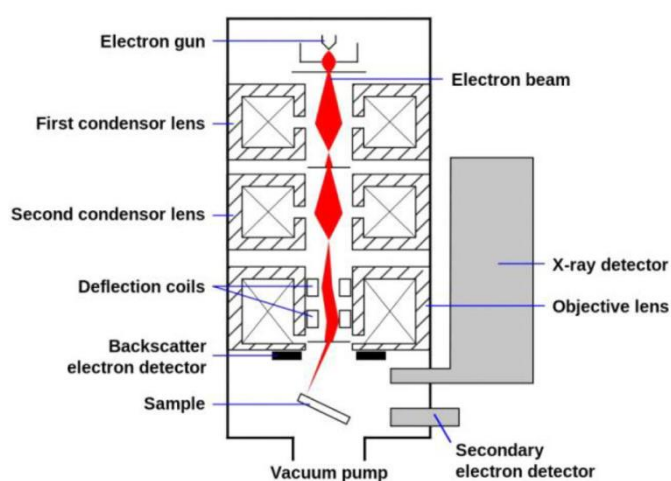


Figure 3.10. Schematic illustration of SEM (Alqaheem and Alomair, 2020).

Shortly, the sample subjected to analysis is placed in a vacuum chamber to prevent electron scattering. Shortly, the sample undergoing analysis is placed in a vacuum chamber to prevent electron scattering, thus ensuring precise imaging. From an electron gun, an electron beam of high-energy electrons is generated, and the beam is focused on the sample. Secondary and backscattered electrons are released and collected by the detector, afterwards, they are analyzed using appropriate software (Alqaheem and Alomair, 2020; Mohammed and Abdullah, 2018). The magnification in this microscopy can reach up to 1 million (Alqaheem and Alomair, 2020).

The sample preparation in SEM depends on the conductivity of the materials. For instance, graphene, carbon nanotubes, and other electrically conductive nanomaterials can be analyzed without any preparation, they are only fixed on carbon tape (Zhou et al., 2007). The non-conductive materials must be coated with metal, such as gold or palladium, to electrical conductivity. The coating is usually applied by sputtering and its thickness is around 10 nm. Before coating the sample should be inserted in liquid nitrogen and then

cut by a sharp blade to eliminate the surface bend (Alqaheem and Alomair, 2020; Zhou et al., 2007).

There are several types of SEMs depending on the conditions and characteristics under which they operate. The choice of appropriate SEM is based on the sample's properties, as well as, the imaging needs. Some of these techniques will be discussed further in the text. The conventional SEM is appropriate for detailed surface morphology analysis, but it requires dry samples and the application of metal coating if non-conductive samples are investigated. The low vacuum SEM operates at higher pressures and nonconductive or wet samples can be analyzed without extensive preparation. The limitation of this technique is the lower resolution due to electron scattering. Environmental SEM offers the possibility for the samples to be analyzed in their natural state. This technique is mostly used for the investigation of biological and soft materials. The shortcoming of this technique is the reduced resolution and the operational complexity (Mohammed and Abdullah, 2018; Zhou et al., 2007).

SEM is a widely used method for studying the morphology of samples of different nature, such as polymers, metals, ceramic, and biological samples, due to the possibility of achieving resolutions down to a few nanometers. Owing to this, a highly detailed observation of the sample's surface can be done. Using SEM, 3D representations of samples can be obtained due to its significant depth of field, which enhances image clarity and structural detail (Inkson, 2016). In addition to these advantages, SEM also has certain disadvantages that limit its use. One of its drawbacks is the need for a vacuum environment which limits its application only to solid samples since gases and liquids tend to evaporate under such conditions. The application of coating from conductive material over the nonconductive samples so they can be investigated with SEM, can lead to modifications of the surface characteristics and possibly affect the measurement accuracy (Alqaheem and Alomair, 2020).

The working principle of TEM involves the generation of the electron beam from an electron gun, where the beam is focused on the sample using electromagnetic lenses. The electrons that have considerably higher energies compared to the electrons from SEM, pass through a very thin sample. The transmitted electrons are collected by a parallel detector to form images with high resolution. The schematic illustration of TEM is shown in Figure 3.11. The analysis is aided by the appropriate software. The magnification in TEM can reach up to 50 million times (Alqaheem and Alomair, 2020; Inkson, 2016).

The samples that are examined with SEM could be bulkier. However, this is not the case with TEM. Samples examined with TEM need to be very thin, with a diameter that does not exceed 2.5 mm, so the sample can fit into the holder, and a thickness that do not exceed 150 μm so that electrons can pass through the material. Since most of the polymers are soft, before cutting them they should be immersed in liquid nitrogen. To improve the image contrast, in some cases, the samples are stained using sodium oxide and uranyl acetate,

afterwards, the samples are washed. Before analysis, the samples are mounted on a metallic mesh. According to this, the sample preparation for TEM analysis is much more complicated compared to that of SEM (Alqaheem and Alomair, 2020; Inkson, 2016).

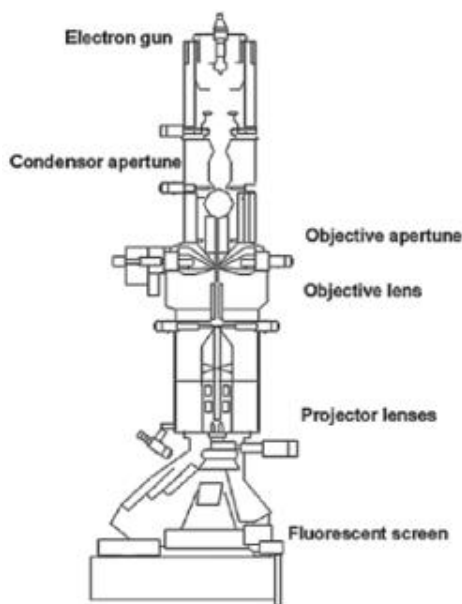


Figure 3.11. Schematic illustration of TEM (Alqaheem and Alomair, 2020).

TEM possesses many advantages that make it a very valuable tool for the analysis of nanomaterials and materials. The main advantage is the ability to observe structures at the atomic level, due to this, TEM is a powerful technique for investigation of material defects or crystallography. The complex preparation of samples might be the main challenge regarding TEM, the thickness of the samples can result in reduced image quality. Another drawback is that the operation of TEM and the interpretation of the results require a high level of expertise (Inkson, 2016).

Due to their ability to provide high-resolution imaging and detailed structural information at the micro and nanoscale, SEM and TEM are valuable techniques in polymer science and engineering. These methods allow observation and analysis of the morphology and structure of materials with exceptional precision, providing important insights that drive progress in polymer engineering.

3.1.5 Quartz Crystal Microbalance

Quartz crystal microbalance (QCM) is a versatile technique, used to monitor mass variations on a surface, by detecting the changes in the resonance frequency of a quartz crystal substrate (Prosheva et al., 2021). The simplicity of the operation of this method, as well as the possibility to work in room temperature conditions, low costs, good sensitivity,

and reproducibility (Pohanka, 2021; Trajcheva et al., 2021), makes it an attractive monitoring candidate for a growing number of areas, such as adsorption, supervision, biosensing, gas and vapor sensing, electrochemistry, thin film deposition etc. Another advantage is the possibility of being combined with other methods for analyses (optical reflectometry, scanning force microscopy) (Johannsmann et al., 2021).

The core of this methodology is the AT-cut quartz crystal piezoelectric substrate, Figure 3.12. Conducting metal films (eg. gold) can be found on each side of the disk substrate, which serves as electrodes, enabling the crystal to oscillate once an altering voltage is applied.

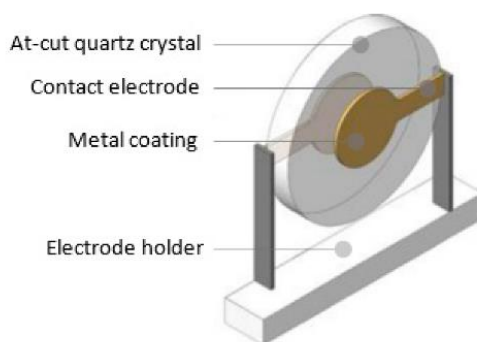


Figure 3.12. Schematic representation of AT-cut quartz crystal, with gold electrodes on both sides of the substrate (Migoń et al., 2020).

The resonance frequency is highly dependent on the mass (removal/addition of mass) and therefore thickness of the crystal (Chen et al., 2016). The variations in the frequency can be monitored in real-time, thus obtaining useful information regarding the interactions or reactions that take place on the surface of the substrate. From a historical point of view, this technique was invented in 1959 by Sauerbrey (1959), who turned basic physics principles into this useful technique. He was the one to make a statement about the straightforward relationship between mass and frequency shift when the resonator oscillates in shear-thickness mode and the analyte is a thin film. Since the majority of resonators were working in that particular mode in the time of the discovery of the QCM, with thin films serving as coatings of the electrodes, his discovery led to the development of film-thickness monitors for various surface phenomena and dynamics (Sauerbrey, 1959; Vogt et al., 2004).

Sauerbrey (1959) explained that the decrease of the frequency can be explained with the help of formula (8) (Johannsmann et al., 2021):

$$\omega_0 \approx \left(\frac{k_R}{m_R} \right)^{\frac{1}{2}} \quad (8)$$

where, k_R stands for effective stiffness and m_R is the effective mass. By analyzing the mathematical notation that this technique revolves around, one can conclude that increasing the crystal's weight means slowing down the resonant vibration.

One of the most exploited Sauerbrey's formula (9) (Trajcheva et al., 2021; Vogt et al., 2004), is showing the relationship between the sensitivity and the changes in mass and frequency:

$$\Delta m = -C\Delta f \quad (9)$$

as expected, the mass change is presented by Δm , Δf is the frequency change and C is the sensitivity constant, which is dependent on the intrinsic properties of the quartz. The sensitivity constant for the most commonly used, 5-MHz, crystal substrate is around 17.7 ng/cm²Hz. The change in frequency is the correspondence between the frequency of a clean quartz substrate and the one of a coated substrate ($\Delta f = f_{clean} - f_{coated}$).

One of the many possible uses of this resourceful technique is the investigation of adsorption-desorption phenomena of lignin-containing films in real time (Cui et al., 2020). In this case, the mathematical equations would convert to more appropriate ones (formulae 5 and 6), giving the changes in frequency and dissipation as a function of the adsorption-desorption processes.

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}}\Delta m \quad (10)$$

where Δm is once again the deviation in the value of the resonating surface mass, Δf remains the frequency change, and f_0 is the crystal's resonance frequency (5 MHz). The density of the substrate is $\rho_q=2.648$ g/cm³ and its shear modulus is $\mu_q=29.47$ GPa. Symbol A stands for surface area (aprox. 1.539 cm²).

On the other hand, the dissipation factor (ΔD) is directly connected to the dissipated energy (E_{diss}) and the total stored energy (E_{stor}), like shown in formula 11. E_{stor} is actually the maximal energy that is stored in the oscillator in the course of one oscillation cycle.

$$\Delta D = \frac{E_{diss}}{2\pi E_{stor}} \quad (11).$$

3.1.6 Laser ablation

Laser ablation/deposition is quite versatile technique that offers the possibility of modification of surfaces, to induce accelerated aging or for synthesis of nanoparticles from various precursors (Gebauer et al., 2020; Ghavipanjeh and Sadeghzadeh, 2024; Hu et al., 2019; Kawasaki et al., 2022; Kolar et al., 2000; Lei et al., 2020; Lin et al., 2021; Ye et al., 2017). The laser ablation technique was first used in 1965 to obtain thin semiconductors and dielectric films. It is a process in which material is removed from a solid surface using an intense laser beam, subsequently, the ablated material is deposited on a substrate, therefore this method can be referred to laser ablation or laser deposition. The laser beam can be either continuous or pulsed, so the laser ablation can be named pulsed laser ablation. Continuous wave lasers generate constant laser beams and the energy that is delivered is uniform. On the other hand, the laser beam in a pulsed laser is generated in short bursts (pulse), and each pulse can last a different time depending on the type of laser. The thermal damage in

a pulsed laser is minimized, which makes it suitable for fine material processing. The laser ablation technique offers a wide range of possibilities, given that the laser source is located outside the deposition reactor. This means that the deposition can be performed under different conditions, i.e. vacuum, in the presence of an inert gas or a reaction gas. Depending on the characteristics of the laser used, deposition of materials of different nature can be performed, for example: noble metals, polymer films, carbon nanomaterials, etc. With PLD, laser-ablated particles have high kinetic energy up to several keV, which allows the deposition of thin films at relatively low temperatures compared to other techniques (Bleu et al., 2018; Stafe et al., 2013).

Figure 3.13 shows a schematic illustration of the reactor for PLA. The basic components of a PLA reactor are holders for substrates and a target (the material to be ablated), a laser beam aperture closed by a NaCl lens, a lens for laser beam focusing (the type of lens can vary from the target and laser beam), openings for vacuum pump and inlet for gas injection.

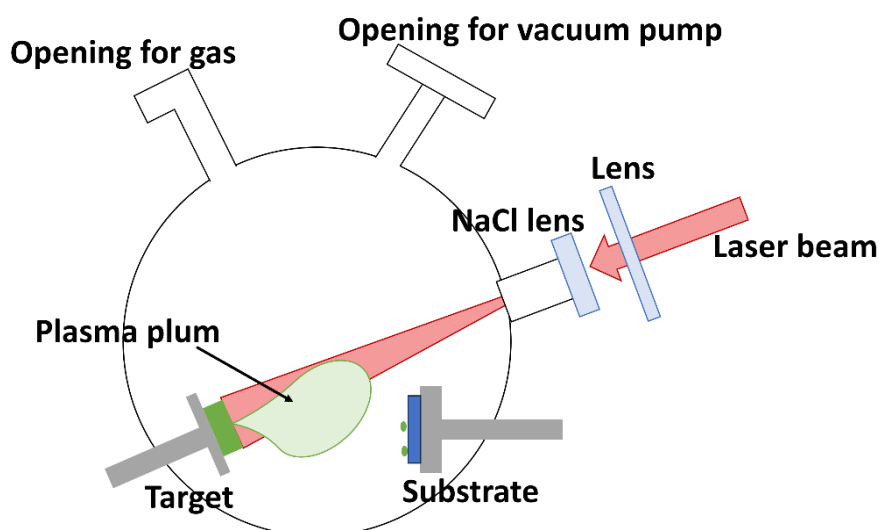


Figure 3.13. Schematic illustration of the reactor for PLA.

During the laser ablation process, the laser beam is generated by a laser source, which is focused using the lens. The laser beam can be continuous or pulsed and is directed toward the target, which is the compound that needs to be ablated. The target absorbs the laser energy, and as a result, the thermal motion of the atoms in the target increases. Once the absorbed energy exceeds the evaporation or sublimation energy of the target, atoms or molecules are removed from the surface, forming a plasma plume that expands rapidly into the reactor. The species from the plasma then start to deposit on the surface of the substrate. To facilitate better adhesion, the type of substrate should be carefully selected, as well in some cases it can be heated to enhance the film formation (Bleu et al., 2018; Zhang and Guan, 2014).

Depending on the wavelength of the laser beam and mode of operation, there are different types of lasers (Stafe et al., 2013):

- Nd-YAG laser – this laser has beam with wavelength of approximately 1064 nm (infrared) and pulse duration in nanoseconds,
- Ti-Sapphire laser – this laser can generate very short pulses (usually in femtoseconds) and the wavelength is tuneable, usually between 700 nm to 1000 nm (near-infrared),
- excimer laser – this laser operates in the ultraviolet range (190 nm to 350 nm) and produces short and powerful pulses typically in nanoseconds,
- CO₂ laser – this laser operates in the far infrared region and has wavelength of approximately 10.6 μm . This laser can have continuous wave or pulsed, but the pulses are typically longer, about a second.

In Figure 3.14a is shown a CO₂ laser which operates in pulsed mode and its control board, while in Figure 3.14b is shown the glass reactor in which a pulsed laser deposition is performed.



Figure 3.14. CO₂ laser and its control board (a) and glass reactor (b).

Pulsed laser ablation technique offers different advantages when it comes to synthesis of materials. This is highly versatile process which allows great precision over the composition of deposited material and deposition of high-quality thin films at relatively low substrate temperatures. By adjustment of the laser parameters and the deposition conditions it is possible excellent control over the morphology of the deposited film. Another advantage is that this is fast method which is significant in large scale production (Bleu et al., 2018).

In polymer science, laser ablation is beneficial method for studying the aging of polymers at irradiation with different wavelength, for modification of polymer surfaces or nanostructuring.

References:

- Aguilar-Méndez, M.A., Martin-Martínez, E.S., Ortega-Arroyo, L., Cruz-Orea, A. (2010). Application of differential scanning calorimetry to evaluate thermal properties and study of microstructure of biodegradable films. *Int. J. Thermophys.* 31, 595–600. <https://doi.org/10.1007/s10765-010-0735-7>.
- Alqaheem, Y., Alomair, A. A. (2020). Microscopy and spectroscopy techniques for characterization of polymeric membranes. *Membranes*. 10, 33. <https://doi.org/10.3390/MEMBRANES10020033>.
- Bleu, Y., Bourquard, F., Tite, T., Loir, A. S., Maddi, C., Donnet, C., Garrelie, F. (2018). Review of graphene growth from a solid carbon source by pulsed laser deposition (PLD). *Front. in Chem.* 6, 572. <https://doi.org/10.3389/fchem.2018.00572>.
- Brown, R. (2002). *Handbook of polymer testing*. Rapra Technology Limited, Shawbury.
- Brunauer, S., Emmett, P.H., Teller, E. (1938). Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* 60, 309–319. <https://doi.org/10.1021/ja01269a023>.
- Chen, Q., Xu, S., Liu, Q., Masliyah, J., and Xu, Z. (2016). QCM-D study of nanoparticle interactions. *Adv. Coll. Int. Sci.* 233, 94-114. <https://doi.org/10.1016/j.cis.2015.10.004>.
- Cui, M., Duan, Y., Ma, Y., Al-Shwafy, K. W. A., Liu, Y., Zhao, X., Huang, R., Qi, W., He, Z., Su, R. (2020). Real-time QCM-D monitoring of the adsorption-desorption of expansion on lignin. *Langmuir*. 36, 4503–4510. <https://doi.org/10.1021/acs.langmuir.0c00104>.
- Gebauer, J., Burkhardt, M., Franke, V., Lasagni, A.F. (2020). On the ablation behavior of carbon fiber-reinforced plastics during laser surface treatment using pulsed lasers. *Materials*. 13, 1–17. <https://doi.org/10.3390/ma13245682>.
- Ghavipanjeh, A., Sadeghzadeh, S. (2024). Simulation and experimental evaluation of laser-induced graphene on the cellulose and lignin substrates. *Sci. Rep.* 14, 4475. <https://doi.org/10.1038/s41598-024-54982-1>.
- Gill, P., Moghadam, T. T., Ranjbar, B. (2010). Differential scanning calorimetry techniques: applications in biology and nanoscience. *J. Biomol. Tech.* 21, 167-193.
- Goliszek, M., Podkościelna, B. (2019). Synthesis and characterization of polymer biocomposites with lignin. *Physicochem. Probl. Miner. Process.* 55, 45–56. <https://doi.org/10.5277/ppmp19055>.
- Gordobil, O., Moriana, R., Zhang, L., Labidi, J., & Sevastyanova, O. (2016). Assessment of technical lignins for uses in biofuels and biomaterials: Structure-related properties, proximate analysis, and chemical modification. *Ind. Crops. Prod.* 83, 155–165. <https://doi.org/10.1016/j.indcrop.2016.01.034>.
- Hu, D., Ren, C., Kong, F., Zhang, C., Shao, T., and Yan, P. (2019). Aging characteristics of polymeric materials by repeated surface flashovers in vacuum under microsecond pulse. *IEEE TDEI.* 26, 171–178. <https://doi.org/10.1109/TDEI.2018.007472>.
- Inkson, B.J. (2016). Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) for materials characterization, In: Hübschen, G., Altpeter, I., Tschuncky,

- R., Herrmann H.-G. (Eds.), *Materials Characterization Using Nondestructive Evaluation (NDE) Methods*. Woodhead Publishing, pp. 17-43
- Jędrzejczak, P., Puszka, A., Kubiak, A., Podkościelna, B., Klapiszewski, Ł. (2021). New lignin-based hybrid materials as functional additives for polymer biocomposites: From design to application. *Int. J. Biol. Macromol.* 190, 624-635.
<https://doi.org/10.1016/j.ijbiomac.2021.09.025>.
- Johannsmann, D., Langhoff, A., and Leppin, C. (2021). Studying soft interfaces with shear waves: principles and applications of the quartz crystal microbalance (QCM). *Sensors*. 21, 3490. <https://doi.org/10.3390/s21103490>
- Kawasaki, T., Zen, H., Sakai, T., Sumitomo, Y., Nogami, K., Hayakawa, K., Yaji, T., Ohta, T., Nagata, T., and Hayakawa, Y. (2022). Degradation of lignin by infrared free electron laser. *Polymers*. 14, 2401. <https://doi.org/10.3390/polym14122401>.
- Kolar, J., Strlic, M., Pentzien, S., Kautek, W. (2000). Near-UV, visible and IR pulsed laser light interaction with cellulose. *Appl. Phys. A*. 71, 87–90. <https://doi.org/10.1007/s003390000491>.
- Lancefield, C.S., Constant, S., de Peinder, P. (2019). Abundance and molecular weight characteristics of technical lignins by attenuated total reflection-FTIR spectroscopy combined with multivariate analysis. *ChemSusChem*. 12, 2037–2046.
<https://doi.org/10.1002/cssc.201802809>.
- Lei, Y., Alshareef, A. H., Zhao, W., Inal, S. (2020). Laser-scribed graphene electrodes derived from lignin for biochemical sensing. *ACS Appl. Nano Mater.* 3, 1166–1174.
<https://doi.org/10.1021/acsanm.9b01795>.
- Lin, Y., Zhang, Q., Deng, Y., Wu, Q., Ye, X.P., Wang, S., Fang, G. (2021). Fabricating graphene and nanodiamonds from lignin by femtosecond laser irradiation. *ACS Omega*, 6, 33995–34002. <https://doi.org/10.1021/acsomega.1c05328>.
- Lin, S.Y., Dence, C.W. (Eds.). (1992). *Methods in lignin chemistry*. Springer-Verlag, Berlin, Heidelberg. <https://doi.org/10.1007/978-3-642-74065-7>.
<https://dl.asminternational.org/technical-books/monograph/135/Mechanics-and-Mechanisms-of-FractureAn>
- Lowell, S., Shields, J.E., Thomas, M.A., Thommes, M. (2004). *Characterization of porous solids and powders: surface area, pore size and density*, Kluwer Academic Publishers, The Netherlands.
- Menczel, D.J., Prime, B.R. (Eds.) (2009). *Thermal Analysis of Polymers: Fundamentals and Applications*, John Wiley & Sons, Inc. Hoboken, New Jersey.
- Migoń, D., Wasilewski, T., Suchy, D. (2020). Application of QCM in peptide and protein-based drug product development. *Molecules*. 25, 3950.
<https://doi.org/10.3390/molecules25173950>
- Mitchell, B. S. (2004). *An introduction to materials engineering and science for chemical and materials engineers*. (online). John Wiley & Sons, Inc., Hoboken, New Jersey.

- Mohammed, A., Abdullah, A. (2018). Scanning electron microscopy (SEM): a review. Proceedings of 2018 International Conference on Hydraulics and Pneumatics – HERVEX.
- Nevejans F., Verzele M. (1987). On the structure and chromatographic behaviour of polystyrene phases. *J. Chromatogr. A.* 406, 325-342. [https://doi.org/10.1016/S0021-9673\(00\)94040-8](https://doi.org/10.1016/S0021-9673(00)94040-8).
- oldbook.iupac.org/terms/view/M03853 (accessed 11 February 2025).
- Pelleg, J. (2012). Mechanical properties of materials, first ed. Springer, Dordrecht.
- Pohanka, M. (2021). Quartz Crystal Microbalance (QCM) sensing materials in biosensors development. *Intern. J. Electrochemical Sci.* 16, 211220. <https://doi.org/10.20964/2021.12.15>.
- Prosheva, M., Ehsani, M., Pérez-Martínez, B. T., Gilev, J. B., Joseph, Y., Tomovska, R. (2021). Dry sonication process for preparation of hybrid structures based on graphene and carbon nanotubes usable for chemical sensors. *Nanotechnology.* 32, 215601. <https://doi.org/10.1088/1361-6528/abe6c9>.
- Sammons, R.J., Harper, D.P., Labbé, N. (2013). Characterization of organosolv lignins using thermal and FT-IR spectroscopic analysis. *Biores.* 8, 2752–2767.
- Sauerbrey, G. (1959). The use of quartz oscillators for weighing thin layers and for microweighing, *Phys.* 155, 206–222. <https://doi.org/10.1007/BF01337937>.
- Stafe, M., Aurelian, M., Puscas, N.N. (2013). Pulsed laser ablation of solids: basics, theory and applications. Springer, Berlin Heidelberg.
- Stuurman H.W., Kohler J., Jansson S.O., Lizen A. (1987). Characterization of some commercial poly (styrene-divinylbenzene) copolymers for reversed-phase HPLC. *Chromatographia.* 23, 341-349.
- Tagami, A. (2018). Towards molecular weight-dependent uses of kraft lignin. Licentiate thesis, KTH Royal Institute of Technology, Stockholm, Sweden.
- Tonk, S., Aradi, L.E., Kovács, G., Turza, A., Rápó, E. (2022). Effectiveness and characterization of novel mineral clay in Cd²⁺ adsorption process: linear and non-linear isotherm regression analysis. *Water.* 14, 279. <https://doi.org/10.3390/w14030279>.
- Trajcheva, A., Politakos, N., Pérez, B.T., Joseph, Y., Blazevska Gilev, J., Tomovska, R. (2021). QCM nanocomposite gas sensors – expanding the application of waterborne polymer composites based on graphene nanoribbon. *Polymer.* 213, 123335. <https://doi.org/10.1016/j.polymer.2020.123335>.
- Vogt, B. D., Lin, E.K., Wu, W.I., White, C.C. (2004). Effect of film thickness on the validity of the sauerbrey equation for hydrated polyelectrolyte films. *J. Phys. Chem. B.* 108, 12685–12690. <https://doi.org/10.1021/jp0481005>.
- Watkins, D., Nuruddin, M., Hosur, M., Tcherbi-Narteh, A., Jeelani, S. (2015). Extraction and characterization of lignin from different biomass resources. *J. Mater. Res. Technol.* 4, 26-32.
- Ye, R., Chyan, Y., Zhang, J., Li, Y., Han, X., Kittrell, C., Tour, J.M. (2017). Laser-induced graphene formation on wood. *Adv. Mater.* 29, 1702211. <https://doi.org/10.1002/adma.201702211>.

Zhang, D., Guan, L. (2014). Laser Ablation, In: Hashmi, S., Ferreira Batalha, G., Van Tyne, C. J., Yilbas, B., Comprehensive Materials Processing. Elsevier, pp. 125-169.

Zhou, W., Apkarian, R.P., Lin Wang, Z., Joy, D. (2007). Fundamentals of scanning electron microscopy, In: Zhou, W., Lin Wang, Z., Scanning microscopy for nanotechnology: techniques and applications. Springer Science & Business Media, pp. 1-40.



CHAPTER 4

SUMMARY

Lignin, a major component of biomass, holds great promise as a renewable raw material for the production of polymer-based materials. While its structural complexity poses a significant challenge for utilization, its unique chemical features – such as its aromatic structure, functional groups, and natural abundance – make it an attractive candidate for value-added applications. As a complex aromatic biopolymer, lignin's structure varies depending on its botanical source, with differences in monomeric composition and degree of crosslinking influencing its physical and chemical properties. Understanding these structural characteristics is crucial for the development of biobased materials, including thermoplastics, resins, and bio-based polymers.

Ongoing intensive research on lignin focuses on its isolation, functionalization, and characterization, as well as exploring innovative applications for this versatile biopolymer.

The procedures for isolating native lignin are designed either to selectively remove it from other plant constituents and recover it from solution or, to remove non-lignin constituents, leaving lignin as an insoluble residue. In addition to native lignin, there are also technical lignins, which are by-products of industrial delignification processes aimed at liberating cellulose for further processing. The nature of technical lignin depends on the specific pulping method used—such as treatments with sulfur compounds, organic solvents, or alkalis—resulting in various types of technical lignins, including kraft lignin, lignosulfonates, soda lignin, and organosolv lignin.

The Kraft (sulfate) process is characterized by the production of (kraft) lignin with a relatively high content of phenolic hydroxyl groups, extensive C-C condensed structures, and ash impurities, especially sulfur, introduced during the cooking process. Due to the cleavage of ether bonds and repolymerization under harsh conditions, kraft lignin is chemically different from natural lignin.

The sulfite pulping process is carried out under acidic to neutral conditions, using sulfuric acid in combination with bisulfite salts of various cations, which leads to the introduction

of sulfonic acid groups predominantly at the α -carbon of the side chains. As a result, the lignin becomes highly soluble in water and exhibits polyelectrolyte behavior, forming lignosulfonates.

The soda pulping process is a sulfur-free process that uses only sodium hydroxide under strongly alkaline conditions. This process produces soda lignin, which has a moderate molecular weight and lower polydispersity compared to kraft or hydrolyzed lignins. Its low sulfur content, good reactivity (due to the presence of phenolic hydroxyls), and relatively pure composition make it suitable for use in phenolic resins, polyurethane foams, thermosetting plastics, and even animal feed products, where biocompatibility and low toxicity are essential.

The organosolv pulping process is a sulfur-free delignification method that uses organic solvents to extract lignin from lignocellulosic biomass. The organosolv lignin obtained by this process has low ash and sulfur content, low to moderate molecular weight, high chemical purity, good solubility in organic solvents, and poor solubility in water, making it attractive for use in high-performance materials, thermosetting resins, bio-based adhesives, and carbon fibers.

Life cycle assessments indicate that lignin-based products often outperform their fossil-based counterparts in terms of climate impact. Depending on the methodological assumptions, greenhouse gas (GHG) emissions reductions can range from 5% to over 90%.

Although the technologies for lignin extraction and upgrading are relatively mature, significant challenges remain in areas such as standardization, consistent product quality, and integration into downstream processes. A successful path forward is likely to involve phased commercialization, strategic partnerships, and alignment with high-demand sectors—including construction and bio-based chemicals.

In the short to medium term, efforts are primarily focused on the production of phenols and polyols. However, high-value applications such as carbon fibers and aromatics are expected to play an increasingly important role over the longer term.

Lignin characterization is crucial for the design of lignin-based materials with predictable performance in applications such as composites, adhesives, coatings, foams, and films. The most commonly used techniques for lignin characterization include: gel permeation chromatography: an analytical method used to determine the molecular weight distribution of lignin, and nuclear magnetic resonance spectroscopy: a quantitative technique employed to analyze the content and types of functional groups in lignin, particularly various hydroxyl groups and carboxylic acids.

It is also important to note that, for many lignin-based applications, especially in polymer systems, it is crucial to work with lignin fractions that exhibit a narrower molecular weight distribution and more consistent chemical properties. High polydispersity, variability in functional group content, and the presence of impurities often limit the performance and reproducibility of technical lignins. Therefore, fractionation techniques are essential

to isolate lignin fractions with target molecular weights and tailored properties such as thermal stability, reactivity, solubility, and processability.

In addition to fractionation, full valorization of lignin usually requires chemical modification, to adjust its structure, reactivity or compatibility with other materials. Through targeted chemical transformations, lignin can be converted into fuels, bulk and fine chemicals, or serve as a reactive component in thermoset and thermoplastic formulations. Such modifications significantly expand its range of applications, enabling the development of value-added products with specific performance.

Lignin and its derivatives have shown potential for application in various fields, including biofuels and chemicals, additives in specialty materials, agroindustry, medicine, pharmaceuticals and environmental technologies .

While large-scale industrial use remains limited, ongoing research continues to explore and develop new value-added applications for this abundant biopolymer. One particularly promising area is the use of lignin as a biosorbent for removing toxic substances from the environment. To enhance its adsorption properties and expand its application range, lignin is often subjected to chemical modifications, such as oxidation, sulfonation, carboxylation, alkylation, and amination. These modifications improve the reactivity of lignin and its affinity for harmful contaminants in wastewater, thereby enhancing its performance as an adsorbent.

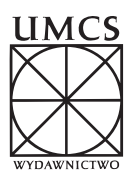
Lignin plays a valuable role as a functional filler in the synthesis of green polymers, contributing to environmental sustainability by enhancing biodegradability and improving material performance . It enhances the thermal stability of polymer matrices and strengthens their mechanical properties. Furthermore, lignin's inherent antioxidant and antimicrobial properties offer further benefits, potentially enhancing the functionality of polymer composites for applications in sectors such as food packaging and healthcare. Lignin-derived flame retardants also represent a promising sustainable alternative to conventional halogenated flame retardants. Their performance can be further optimized through chemical modifications, all while maintaining environmental safety.

Lignin is a valuable feedstock for producing aromatic compounds such as benzene, toluene, and xylene, offering a renewable alternative to fossil-derived chemicals and helping reduce dependence on oil. It is also a promising precursor for carbon fiber production due to its high carbon content and low cost. Various spinning techniques—melt, dry/wet, dry-jet wet, and electrospinning—have been developed to produce lignin-based carbon fibers, which are being explored for use in sustainable high-performance composites.

Beyond structural applications, lignin shows potential in cosmetics due to its antioxidant and antimicrobial properties, offering a sustainable ingredient for personal care products. Its natural binding ability, crucial in wood cell walls, also makes it suitable as a bio-based adhesive—for example, in enhancing the strength and durability of concrete.

To characterize lignin-based materials, key analytical techniques include FTIR, DSC, TGA, SEM, and TEM, along with methods for evaluating mechanical strength, porosity, sensor performance (QCM), and laser ablation synthesis.

Continued research on lignin is anticipated to contribute significantly to the development of sustainable technologies aimed at reducing environmental impact and industrial waste.



ISBN 978-83-227-9904-8