



The chemistry behind paper restoration: diagnostic techniques and cutting-edge innovation

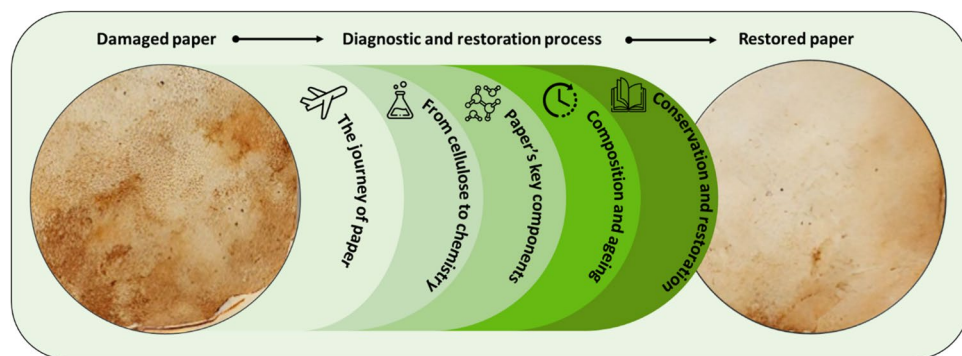
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Abstract

The conservation of ancient paper and manuscripts is a complex and evolving field that combines historical understanding, chemistry, and modern technological advancements. Paper, primarily composed of cellulose, lignin, and hemicellulose, is subject to deterioration from environmental factors such as humidity, light, and biological activity. This article reviews the key chemical processes involved in the deterioration of paper and the methodologies developed to face these effects. It explores the history and evolution of paper as a material, considering the interaction between its chemical components and environmental stressors, and discusses the implications of these interactions for the preservation of paper artefacts. The article is focused on modern conservation techniques and pioneering research in this field, such as using nanoparticles and nano-coatings to protect the paper surface. Of course, in addition to material restoration, the digital revolution has introduced a new frontier in cultural heritage preservation. Digital restoration techniques allow for virtual restoration, offering a way to present restored versions of artefacts even when the physical document is too fragile to handle. By integrating chemical science, modern conservation practices, and digital technologies, the field of paper conservation can more effectively balance preservation regarding the historical and material integrity of cultural heritage. This approach ensures that future generations will be able to continue reading and experiencing the history of humanity preserved in these invaluable artefacts.

Graphical Abstract



Keywords Papermaking · Paper restoration · Deacidification · Cellulose · Nanorestoration · Digital restoration

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Introduction: a brief history of paper

In an increasingly digital world, paper may seem like an outdated material destined to be forgotten. However, it remains one of the most influential media for communication and the transmission of knowledge in human history, with its invention fundamentally shaping the trajectory of civilisation. Over the centuries, paper has undergone significant transformations in both its production methods and the materials employed. Therefore, much of human history is preserved within its fibres, making it an invaluable historical, artistic, and cultural heritage that demands preservation. Achieving this goal requires a thorough understanding of the history of papermaking and the raw materials involved, as these directly influence the mechanical and chemical properties of paper.

The invention of paper is traditionally attributed to Ts'ai Lun, an imperial official during the Han Dynasty, who, in 105 AD, successfully produced the first documented sheet of paper [1]. Although handmade paper may have existed before his innovation, Ts'ai Lun is credited with refining and standardising the papermaking process. His contribution demonstrated its usefulness, ultimately leading to the replacement of traditional Chinese writing materials like silk [2]. Early Chinese paper was made using mulberry bark, bamboo, hemp, and other cellulose-rich fibres. The invention soon spread across Asia, eventually reaching the Arab world. By the mid-fifth century AD, paper was already known in Turkestan, and by 793 AD, the first documented paper mill had been established in Baghdad [3]. Lacking access to mulberry trees, Arab papermakers adapted the process by using hemp, cotton, and linen rags as raw materials. It remains uncertain whether Chinese papermakers had similarly used recycled materials [1]. The Arabs made significant improvements to the papermaking process, such as introducing hydraulic power for pulp preparation and refining the traditional Chinese sieve, replacing bamboo with brass to improve sheet formation [4, 5]. The journey of paper across the continents is depicted in Fig. 1, and when paper arrived in Europe, it faced initial resistance. Parchment, prized for its superior quality and durability, was the preferred medium for writing and was widely used for public records and manuscripts. Therefore, paper—a novel and relatively unfamiliar material from the East—was met with scepticism. For instance, Frederick II (1194–1250 AD) even prohibited the use of paper for official documents. However, the course of history shifted with Europe's gradual rise in literacy rates, which, although still modest compared to the Arab world, created a growing demand for writing materials. The invention of the printing press around 1450 AD marked a turning point for paper in Europe [6]. Parchment proved unsuitable for mass production because of its

high cost and limited availability, while paper excelled as a medium for printing ink. These advancements in papermaking techniques included the introduction of machinery and the use of new raw materials. However, these innovations often came at the cost of sheet quality. The advent of the chemical industry in the nineteenth century introduced new developments such as chemically processed pulp, bleaching techniques, and coated papers [4, 7].

It is clear that, throughout history, papermaking has evolved significantly, particularly in the materials added to cellulosic pulp to enhance paper properties. Two main categories of additives, sizing agents and fillers, have been employed to enhance properties such as ink absorption, opacity, brightness, and smoothness. Table 1 summarises the key materials added to cellulosic pulp throughout different historical periods, highlighting their roles in papermaking processes and their significance in the development of paper quality.

Despite these changes in additives, one constant has remained: cellulose, the primary component of paper, which defines its material characteristics and chemical-physical properties. This unique polymer has made paper one of the most revolutionary and enduring materials in human history.

This article aims to provide an overview of the fundamental concepts underlying paper composition, offering insights into its deterioration processes and the factors contributing to its alteration. Furthermore, given the cultural significance of paper, the article highlights recent advances in research and restoration methodologies, enabling the preservation of paper-based artefacts for future generations.

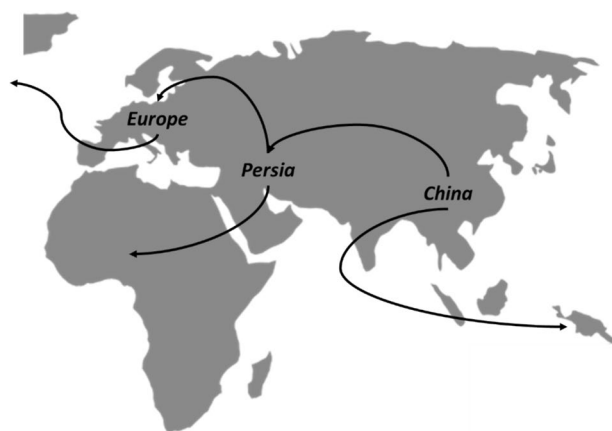


Fig. 1 A schematic representation of the historical spread of papermaking: originating in China, advancing through Arab countries, and eventually reaching Europe, where it supplanted parchment as the primary writing medium and catalysed the rise of printing

Table 1 Summary of key materials added to cellulosic pulp throughout different historical periods, highlighting their roles as sizing agents and fillers in papermaking

| Category | Material | Description | Historical period |
|----------|--|--|--|
| Sizing | Gelatine | Derived from animal hides, gelatine was used in early European papermaking as a surface sizing agent to control ink absorption and prevent feathering. It can be used internally in the sheet or externally [8, 9] | Early European papermaking (until nineteenth century) |
| | Starch | Used in both early Asian and European papermaking. In China, it was used as early as 768 A.D. for sizing, providing a smooth surface for writing [9, 10] | Ancient times (China from 768 A.D.) and Medieval Europe |
| | Alum and rosin | Introduced in the early nineteenth century, this internal sizing technique involved adding rosin and alum to pulp, which made paper more resistant to ink and water [11] | Early nineteenth century (Germany, Europe by 1835) |
| Fillers | Clay (kaolin) | A traditional filler that enhances opacity and improves print quality [12–14] | Used for centuries, particularly in the nineteenth century |
| | Calcium carbonate (CaCO ₃) | A cost-effective filler that improves paper brightness and opacity, commonly used in modern papermaking [13–17] | Gained prominence in the twentieth century |
| | Titanium dioxide (TiO ₂) | Known for its ability to increase paper opacity and brightness, but its abrasive nature can increase wear on papermaking machinery [13, 14, 18] | Twentieth century (widespread use in modern papermaking) |

From cellulose sheets to chemical paper: the evolution of papermaking and its impact on paper quality and conservation

The evolution of papermaking has significantly influenced the quality and long-term preservation of paper. As discussed in the previous paragraph, early papermaking techniques focused on using pure cellulose, providing a material with remarkable durability due to its well-ordered molecular structure and resistance to chemical deterioration. However, with the advent of chemical pulping methods, particularly in the nineteenth and twentieth centuries, the production of chemical paper introduced new challenges for paper conservation. Unlike pure cellulose, chemical paper contains additional substances such as lignin, hemicelluloses, and residual chemicals from the pulping process. As previously discussed, such compounds have different properties from cellulose and influence the final product of paper. In fact, lignin and hemicellulose contribute to the increased reactivity and susceptibility to environmental factors, leading to accelerated deterioration over time. Understanding how these changes in papermaking affect the chemical composition and stability of paper is crucial for both preserving historical documents and improving modern paper production techniques.

Cellulose for papermaking has been isolated from a variety of raw materials. Today, wood is the primary source of cellulose for most industrial applications, while alternative materials, such as cotton, are used only in specific cases [19]. In wood, cellulose is combined with other substances, including hemicelluloses,

pectins, gums, and lignin. These must be removed to isolate cellulose as an insoluble residue. The purpose of transforming plant material into pulp is to separate the fibres, which requires the application of mechanical, chemical, or thermal energy to remove lignin—the key binder holding the fibres together. Depending on the method used to achieve fibre separation, pulps are classified as mechanical, chemical, or semi-chemical [7]. Mechanical pulping involves using mechanical energy to separate the fibres, but this often results in imperfect separation, compromising the quality of the pulp. In contrast, chemical and thermal energy effectively break down and remove lignin, yielding chemical pulps with well-separated, high-quality fibres [20]. Chemical pulps are produced by cooking wood in specialised reactors with chemicals that selectively attack lignin, liberating the fibres. These pulping processes are primarily divided into two categories: alkaline (soda and sulphate) and acidic (sulphite). Alkaline cooking liquors, compared to acidic ones, penetrate wood more rapidly. They can pass through the cell walls and initiate lignin hydrolysis reactions, which also break down other chemical bonds [6]. Simultaneously, rapid hydrolysis of the polysaccharide fraction begins, starting with hemicelluloses, followed by partial degradation of cellulose. This process shortens the cellulose chain length and weakens the final product. In the soda alkaline process, soda must be continuously replenished, making the procedure costly. To address this, the process was modified by adding sodium sulphate (Na₂SO₄) to the cooking liquors, resulting in the sulphate, or Kraft, process [21, 22]. In the Kraft process, the cooking liquor for finely chopped

wood contains sodium hydroxide (NaOH) and sodium sulphide (Na₂S), which together form the "white liquor". This liquor also includes sodium carbonate (Na₂CO₃) and sodium sulphate, but these two compounds do not contribute to the delignification process [6]. The alkaline liquor must thoroughly impregnate the wood at temperatures < 120 °C to prevent the formation of lignin condensation products in the absence of alkali. During this process, the hydrolytic cleavage of lignin and hemicelluloses occurs, converting them into soluble sodium salts. The resulting by-product, called black liquor, is removed by washing the pulp. After washing, the pulp undergoes further treatments such as bleaching and drying, after which it can be referred to as cellulose.

The sulphite process involves cooking wood with an aqueous solution of sulphurous acid (H₂SO₃) in the presence of magnesium bisulphide [Mg(HSO₃)₂] or calcium. The cooking liquor in this case is acid. During this process, lignin is not completely broken down but is likely converted into soluble sulphonation products (as salts) within the reaction medium. At the end of the process, the pulp must always undergo bleaching and drying [23]. After cooking, Kraft pulp appears brownish, while sulphite pulp takes on a yellowish hue. Consequently, both types of pulp require bleaching to achieve high-quality white cellulose [22].

Bleaching can involve the removal of either the residual lignin or its discoloration. However, bleaching is a purification process that typically occurs in multiple stages:

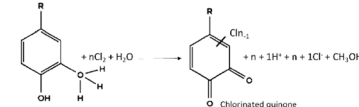
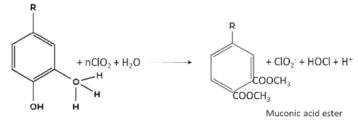
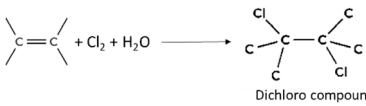
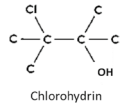
- 1) Treatment with molecular chlorine: this step targets residual lignin, forming chlorinated products through electrophilic substitution while generating hydrochloric acid as a by-product.
- 2) Treatment with oxidising agents: this stage includes the alkaline solubilisation of chlorinated derivatives, which also removes non-cellulosic carbohydrates.

Molecular chlorine and the treatments with oxidising agents, starting from ClO₂, follow two different reaction paths, as described in Table 2.

In chlorine dioxide (ClO₂), the chlorine atom has an oxidation state of +4, whereas in molecular chlorine (Cl₂), its oxidation state is +1 (reaction 1). When reduced to chloride ion (oxidation state -1), chlorine dioxide undergoes a shift of five oxidation levels, while molecular chlorine experiences a change of only two. Consequently, chlorine dioxide possesses five times the oxidation potential of molecular chlorine per chlorine atom, making it a significantly stronger oxidising agent. Beyond its role as an oxidiser, chlorine also functions as a chlorinating agent (reaction 2) [24]. In the initial phase of the bleaching process, roughly half of the chlorine applied to pulp binds with lignin, while the remaining portion oxidises lignin and is subsequently converted into chloride ions (reaction 3 and 4). After alkaline extraction, approximately 90% of the original chlorine is transformed into chloride ions, but about 10% remains in the form of chlorinated organic compounds. Chlorine also interacts with double bonds, resulting in the formation of dichlorinated products (reaction 4), which remain stable during subsequent alkali washing [24].

Chlorine dioxide, however, reacts differently with lignin. During lignin oxidation, muconic acid esters (reactions 2 and 3) are produced, while chlorine dioxide is reduced to chlorite ions and hypochlorous acid. In acidic conditions, chlorite ions break down to regenerate chlorine dioxide and chloride ions, or they may react with hypochlorous acid to produce chlorate ions. Hypochlorous acid can also interact with organic substances to create chlorinated organic compounds, either directly or by forming chlorine, which exists in equilibrium with hypochlorous acid (reactions 4–5) [24]. This equilibrium, however, is highly dependent on pH. At pH levels < 2, chlorine primarily exists as dissolved

Table 2 Comparison of the reactions in the bleaching process using molecular chlorine (Cl₂) and chlorine dioxide (ClO₂)

| | Molecular Chlorine | Chlorine dioxide (ClO ₂) |
|-----|---|---|
| (1) | $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$ | $\text{ClO}_2 + 4\text{H}^+ + 5\text{e}^- \rightarrow \text{Cl}^- + 2\text{H}_2\text{O}$ |
| (2) | $\text{RH} + \text{Cl}_2 \rightarrow \text{RCl} + \text{H}^+ + \text{Cl}^-$ | $\text{HOROCH}_3 + 2\text{ClO}_2 + \text{H}_2\text{O} \rightarrow \text{HOOROCH}_3 + \text{ClO}_2^- + \text{HOCl} + \text{H}^+$ |
| (3) |  |  |
| (4) |  |  |
| (5) | | $\text{RH} + \text{HOCl} \rightarrow \text{RCl} + \text{H}_2\text{O}$ |
| (6) | | $\text{HOCl} + \text{HCl} \leftrightarrow \text{Cl}_2 + \text{H}_2\text{O}$ |

Cl_2 . Under near-neutral conditions (pH 5), hypochlorous acid (HOCl) is the dominant species, while in alkaline environments, it dissociates into hypochlorite ions (OCl^-). By adjusting the pH during chlorine dioxide bleaching, the formation of free chlorine can be minimised, reducing the production of chlorinated compounds [24].

Compared to molecular chlorine, hypochlorous acid interacts differently with the chemical structures in lignin, leading to the formation of compounds such as chlorohydrins (reaction 4). Chlorine in these chlorohydrins is more readily removed in subsequent alkaline bleaching stages than the chlorine in dichlorinated products formed from reactions with molecular chlorine, ultimately leading to a lower accumulation of chlorinated organic compounds. Due to the combined effects of chlorine dioxide's strong oxidising power, reduced chlorination, and oxidative modifications in lignin, the substitution of Cl_2 with ClO_2 results in a five- to ten-fold decrease in the formation of organochlorine compounds [24].

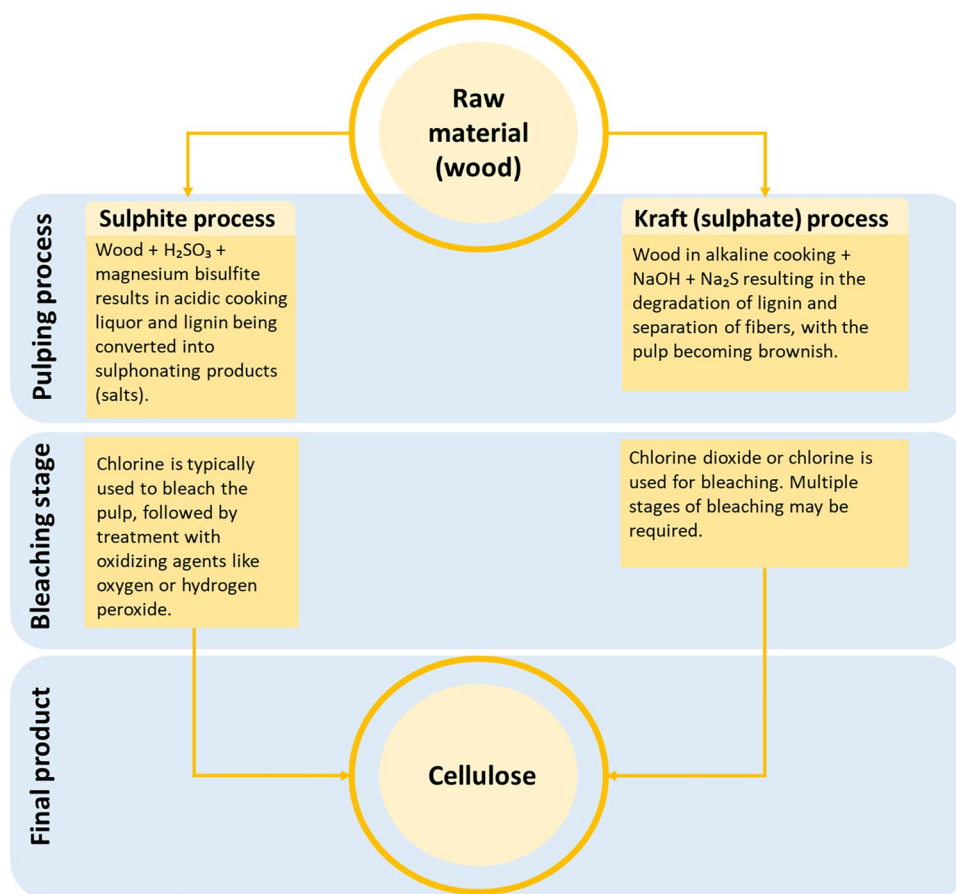
Sulphite cellulose generally requires only a single chlorine treatment, whereas sulphate cellulose often needs multiple treatments. However, these processes have a high environmental impact, prompting the adoption of alternative methods. For instance, delignification can occur during

cooking, or bleaching can be carried out with less harmful agents like chlorine dioxide or oxygen in an alkaline medium. Hydrogen peroxide (H_2O_2), a strong oxidising agent, can also be used in an alkaline environment.

Both the sulphite and sulphate processes result in lower yields due to partial cellulose degradation caused by chemical attacks. In the Kraft process, alkaline cooking at temperatures $> 150\text{ }^\circ\text{C}$ leads to partial hydrolysis of cellulose's acetal bonds. Similarly, oxidative bleaching with hypochlorite ($\text{Ca}(\text{ClO})_2$) causes hydrolytic degradation of cellulose, as oxidation of hydroxyl groups to carbonyl groups accelerates the breakdown. In contrast, bleaching with chlorine dioxide (ClO_2) primarily targets the aromatic nuclei of lignin and, to a lesser extent, its polymeric chains. Prolonged or intense oxidative bleaching can further oxidise the aromatic nuclei of lignin into quinones, resulting in the characteristic coloration associated with quinonoid structures [25, 26]. Figure 2 summarises the sulphite and the Kraft processes, leading to the final product, cellulose.

Beyond the environmental concerns related to the bleaching process, the presence of cellulose-based paper waste in wastewater treatment systems poses another significant challenge. The degradation of paper fibres in wastewater is influenced by various factors, including microbial activity and

Fig. 2 Schematic representation of the Kraft and sulphite pulping processes used to produce chemical cellulose. The Kraft process (also known as the sulphate process) involves treating wood chips with alkaline white liquor (sodium hydroxide and sodium sulphide) at high temperatures, breaking down lignin and hemicelluloses while preserving cellulose. The sulphite process uses an acidic aqueous solution of sulphurous acid and bisulphite salts to break down lignin, producing a yellowish pulp. Both processes require subsequent bleaching steps to produce high-quality white cellulose



retention time, which directly affect treatment efficiency and the persistence of organic matter in effluents. Li et al. investigated the degradation kinetics of toilet paper fibres, demonstrating that solid retention time and microbial community composition play a crucial role in determining the rate and extent of fibre breakdown in wastewater treatment plants [27]. Similarly, Kim et al. examined the aerobic degradation of cellulose in raw municipal wastewater, emphasising its kinetic variability and potential implications for treatment performance [28]. These studies highlight the need for optimised wastewater treatment strategies to enhance cellulose degradation while minimising the environmental burden of paper-derived organic pollutants. Addressing these challenges is essential for improving wastewater management and ensuring the sustainability of paper usage today.

Ingredients in a sheet of paper: cellulose, lignin, and hemicellulose.

The structure of a historical sheet of paper is the result of a delicate interplay among its primary components: cellulose, lignin, and hemicellulose. These three polysaccharides, derived from plant fibres, each contribute unique properties to paper. Cellulose, the dominant and most stable component, provides strength and flexibility, while hemicellulose enhances the sheet's cohesion. In contrast, lignin, though less desirable in paper preservation, influences discoloration and deterioration over time. Understanding the roles and interactions of these components is crucial for assessing the physical and chemical stability of historical papers as well as for developing effective conservation strategies.

Cellulose

Cellulose is the fundamental component of green plants, where it primarily serves a structural role, providing rigidity and support to cell walls. It is the most abundant organic compound in nature and a cornerstone of many biological and industrial processes. The primary sources of cellulose are wood and cotton. In cotton, cellulose exists in nearly pure form, accounting for up to 98% of its composition. In contrast, wood contains approximately 50% cellulose, combined with other compounds such as lignin, hemicelluloses, pectins, and minerals [29].

Chemically, cellulose is a polysaccharide—a macromolecule composed of a long sequence of glucose monosaccharide units. In aqueous environments, these glucose units predominantly exist in a cyclic form known as pyranose. The C(1) atom of each glucose unit, in its aldehyde oxidation state, is referred to as the anomeric carbon (Fig. 3). As with other polymers, cellulose is defined by the repetition of a fundamental structural unit, known as the repeating unit

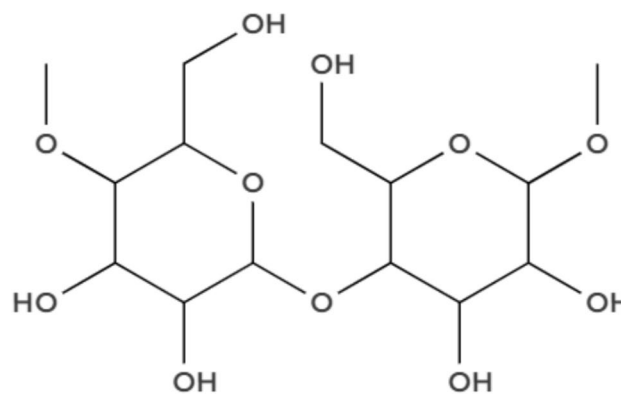


Fig. 3 Basic structure of cellulose

[30]. One of cellulose's defining characteristics is its high degree of polymerisation (DP), which refers to the number of glucose monomer units in a polymer chain. In cellulose, this number typically exceeds 5000 units, resulting in long, robust polymer chains. The glucose units are linked by $\beta(1 \rightarrow 4)$ glycosidic bonds. These bonds are formed through a condensation reaction between the hydroxyl group of one glucose molecule and the anomeric carbon of another, releasing a molecule of water in the process. Structurally, the glycosidic linkage is classified as an acetal group, which is formed by the reaction of an alcohol with a carbonyl compound [31]. The stereochemistry of the anomeric carbon plays a critical role in determining the type of glycosidic bond. If the hydroxyl group at the C(1) position of the glucose unit is oriented below the median plane of the sugar's pyranose ring, it is classified as α . Conversely, if the hydroxyl group is oriented above the plane, it is classified as β . In cellulose, the glycosidic bonds are exclusively in the β configuration, giving rise to $\beta(1 \rightarrow 4)$ linkages that contribute to cellulose's rigidity, insolubility, and resistance to enzymatic degradation. This unique structure is key to cellulose's function as a vital structural material in plants and its widespread applications in various fields.

The formation of the linear polysaccharide cellulose through $\beta(1 \rightarrow 4)$ glycosidic bonds has profound implications for its structural properties and biological functions. One notable consequence is that cellulose cannot be used as a nutrient by higher animals because of their lack of the enzyme β -glycosidase, which is required to break these bonds [32]. The $\beta(1 \rightarrow 4)$ glycosidic linkages promote the establishment of intramolecular hydrogen bonds between adjacent glucose units within the cellulose chain, significantly enhancing its stability. Additionally, individual cellulose chains associate with each other through intermolecular hydrogen bonds formed between hydroxyl groups on neighboring chains. This interaction results in the formation of tightly bound polymer bundles that are both exceptionally

strong and insoluble in water. These ordered bundles are referred to as elementary fibrils, which further aggregate to form larger structures known as microfibrils [33]. Microfibrils are integral to the structural framework of plant cell walls, as they interact with hemicelluloses, pectin, and structural proteins to form macrofibrils. Together, these macrofibrils create a robust yet flexible skeleton that supports and protects plant cells.

In its solid state, cellulose exhibits a microfibrillar organisation characterised by alternating crystalline regions and amorphous regions. The crystalline regions are highly ordered and compact, with polymer chains aligned parallel to the microfibril axis, much like the arrangement seen in some inorganic materials. In contrast, amorphous regions display less regular organisation, with chains that are misaligned and more disordered. These amorphous regions are more accessible to enzymatic degradation and absorb proportionally more water compared to the crystalline zones. Importantly, these two regions are not physically separated, as a single polymer chain can contribute to both ordered and disordered segments.

This unique organisation imparts cellulose with a degree of crystallinity, which influences many of its physical properties. For example, a higher degree of crystallinity reduces the material's accessibility to water, dyes, and chemical reagents, while also increasing its tensile strength. However, this comes at the cost of elasticity, making the fibres more

brittle as crystallinity increases [34]. Table 3 summarises the properties of crystalline and amorphous regions, considering their effect on durability of the material. In fact, the balance between crystalline and amorphous regions is therefore a key determinant of cellulose's mechanical and chemical behaviour.

Lignin and hemicellulose: their influence on properties of paper

Lignin, the second most abundant chemical compound in nature after cellulose, is an amorphous, high-molecular-weight, three-dimensional aromatic polymer whose structure cannot be universally defined. This structural variability stems from differences in its shape and size, depending on the plant species, the type of cells in which it is found, and the specific type of wood. Lignin is composed of aromatic polymers formed by phenylpropanoid units, which are interconnected by C–O–C and C–C bonds, with the latter being more resistant to chemical alteration (Fig. 4a) [30].

The lignin found in the cell walls of different tree species varies according to the precursor alcohol involved in its formation. For instance, in gymnosperms, lignin is primarily derived from coniferyl alcohol, whereas in angiosperms, sinapyl alcohol also plays a role in its synthesis.

Lignin contains several types of bonds that are difficult to hydrolyse. This, combined with its non-crystalline

Table 3 Comparison of crystalline amorphous region in cellulose: structural, chemical, and physical differences

| Feature | Crystalline regions | Amorphous regions |
|---------------------------------|--|--|
| Structure | Highly ordered parallel alignment of chains | Less regular misaligned chains |
| Hydrogen bonding | Strong intramolecular and intermolecular bonds | Weaker bonding between chains |
| Water absorption | Low, more resistant to water | High, more readily absorbs water |
| Susceptibility to deterioration | Low, resistant to enzymatic action | High, susceptible to enzymatic deterioration |
| Physical properties | High tensile strength, low elasticity | Lower tensile strength, higher elasticity |
| Accessibility to chemicals | Low, less accessible to reagents | High, more accessible to dyes/chemicals |

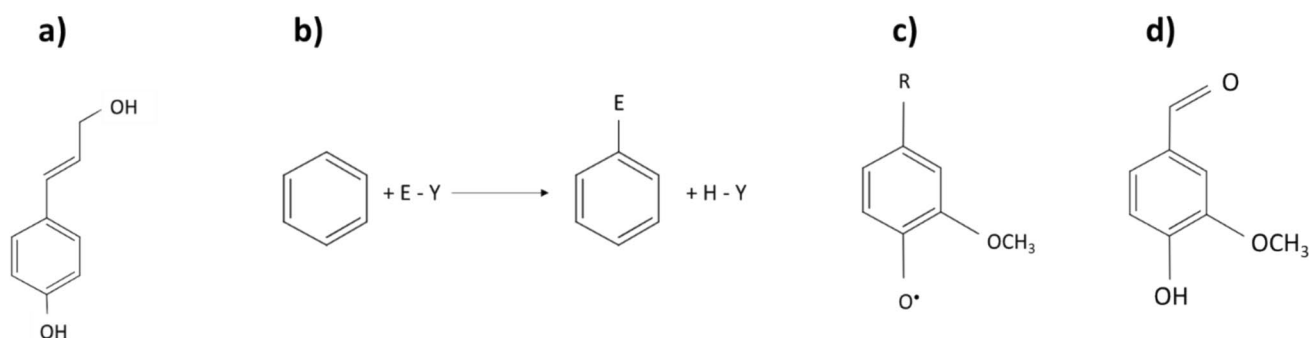


Fig. 4 **a** Example of a lignin monomer. **b** Electrophilic aromatic substitution. **c** Example of a reactive intermediate of lignin. **d** Vanillin, one of the aromatic aldehydes formed from lignin monomers

three-dimensional structure and high hydrophobicity, accounts for its mechanical strength and chemical reactivity [30, 35]. From an analytical standpoint, lignin is challenging to study because of its heterogeneous composition, variability in size and bonding, and difficulty in isolating the intact natural molecule. However, recent advancements in two- and three-dimensional solid-state nuclear magnetic resonance (NMR) spectroscopy have provided new avenues for better understanding this vital natural polymer [36–38].

As previously noted, lignin's reactivity is largely attributed to the hydroxyl, benzylic, carbonyl, and carboxylic groups present on its propanoid chains as well as its phenolic function and aromatic core. Common reactions include substitution, oxidation, and hydrolysis. The aromatic cores undergo electrophilic aromatic substitution, a characteristic reaction of benzenoid substrates (Fig. 4b). For example, during the bleaching of wood pulp with chlorine in paper production, molecular chlorine (an electrophile) attacks lignin, producing soluble chlorinated products that are substituted non-uniformly in the aromatic rings [25]. Phenolic systems, in turn, generate reactive intermediates such as radicals, quinones, and anions (Fig. 4c). Lignin's phenolic and carboxylic groups also make it vulnerable to attack by bases. Molecular oxygen, the most common oxidising agent, does not typically attack lignin unless catalysed by light and transition metal ions. This is a crucial consideration when materials with high lignin content come into contact with metal artefacts. Under other oxidising conditions, aromatic aldehydes can form from the monomers (Fig. 4d), leading to lignin degradation through the side chains of the aromatic nuclei. These methods are often used to determine the ratio of alcoholic monomers within the polymer. The ability to react hydroxyl groups along the chain, benzylic hydroxyl groups, and ether groups with sulphites (e.g., bisulphites) to form sulphonic acid salts has facilitated the extraction of cellulose from wood. This process transformed wood into

a viable source of cellulose for papermaking, although the quality of paper made from cellulose extracted in this way is significantly lower because of the chemical treatment involved [39].

Hemicelluloses, which are also found in paper, are minor components in the cell walls of plants. They are non-structural polysaccharides with low molecular weight, a degree of polymerisation lower than that of cellulose, and an amorphous structure. Hemicelluloses are closely associated with cellulose in plant cell walls, primarily through hydrogen bonds, and are covalently bonded to lignin. Their chemical composition varies between species and even within the same species during cell differentiation [40]. Hemicelluloses are made up of a limited range of sugars, including the pentoses D-xylose (which is often acetylated at positions 2 or 3), L-arabinose, and the hexoses D-mannose, D-glucose, and D-galactose. Additionally, they contain uronic acids such as D-galacturonic acid and D-glucuronic acid, which are frequently methylated at position 4 (Fig. 5). Due to their shorter chain lengths, branched structures, and non-crystalline nature, hemicelluloses are more soluble and swellable in water compared to cellulose. These characteristics also make hemicelluloses more chemically reactive, leading to faster hydrolysis and increased vulnerability to microbial degradation.

The structural differences and reactivity of hemicelluloses and lignin are key factors in explaining the enhanced durability of pure cellulose paper and their differences are summarised in Table 4. Pure cellulose consists of long, highly ordered polymer chains that form strong intermolecular hydrogen bonds, creating a stable, robust structure. In contrast, the presence of lignin and hemicelluloses introduces both structural and chemical weaknesses. Lignin is highly reactive, prone to oxidation, and generates acidic by-products that accelerate the deterioration of paper. Similarly, hemicelluloses, which are less ordered and more hydrophilic than cellulose, are particularly susceptible to hydrolysis and

Fig. 5 a D-glucose and b D-mannose

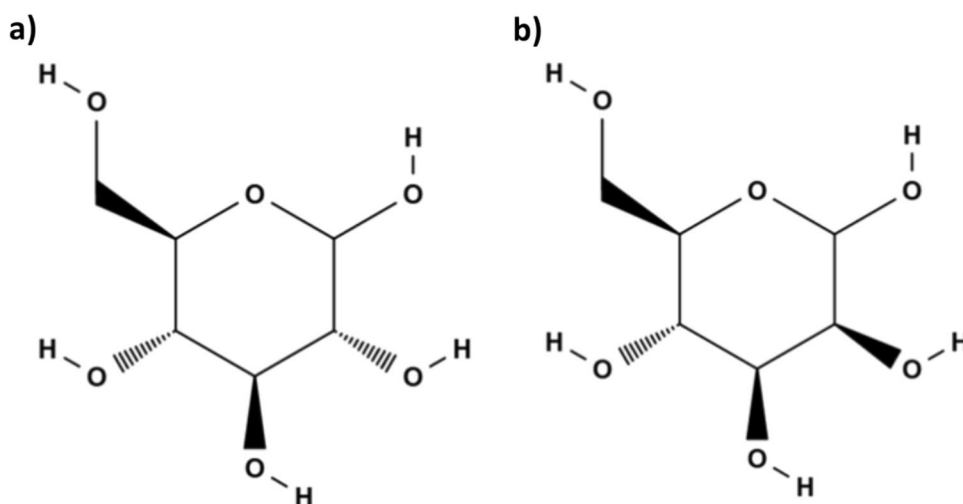


Table 4 Comparison between lignin and hemicellulose as minor components of paper sheet: the chemical and physical characteristics of these molecules influence the final product depending on the percentage of lignin and hemicellulose in the paper

| Feature | Lignin | Hemicelluloses |
|------------------------|--|--|
| Abundance | Second-most abundant organic compound in nature | Minor component of plant cell walls |
| Structure | Amorphous, high-molecular-weight, three-dimensional aromatic polymer | Non-structural polysaccharides with lower molecular weight and amorphous structure |
| Composition | Composed of phenylpropanoid units connected by C–O–C and C–C bonds | Varies by species, covalently bonded to lignin and hydrogen-bonded to cellulose |
| Bonding | Contains strong C–C and C–O–C bonds, difficult to hydrolyze | Primarily hydrogen bonds with cellulose, covalent bonds with lignin |
| Hydrophobicity | Highly hydrophobic, contributing to mechanical strength | Less hydrophobic |
| Reactivity | Reactive due to hydroxyl, benzylic, carbonyl, and carboxylic groups, phenolic functions, and aromatic core | Less reactive than lignin |
| Alteration | Susceptible to oxidation (with chlorine or molecular oxygen), produces reactive intermediates (radicals, quinones) | Less chemically reactive, but varies with species |
| Role in paper | Contributes to rigidity, chemical resistance, and water resistance | Contributes to the flexibility and water retention capacity of paper |
| Challenges in analysis | Difficult to isolate and study due to its heterogeneous structure | Easier to analyse compared to lignin, but still variable between species |
| Role in paper | Contributes to rigidity, chemical resistance, and water resistance | Contributes to the flexibility and water retention capacity of paper |

other chemical reactions that weaken the paper over time. As a result, these impurities compromise the mechanical strength and long-term stability of paper, making it more prone to ageing and damage from environmental factors.

The role of paper composition in long-term stability

At this stage, it becomes clear that paper, as a handmade product, is capable of achieving remarkable quality and durability. Table 5 gives an overview of the influence of

paper composition on deterioration and conservation. The kinetics of cellulose alteration has been widely studied across various fields, each with specific objectives and practical applications. In the context of biomass processing, it plays a crucial role in devolatilisation, influencing the efficiency of thermal conversion processes [41]. Similarly, understanding cellulose degradation is essential for improving bioresource efficiency, enabling the sustainable use of plant-derived materials [42]. In waste management and recycling, research focuses on optimising the conversion of cellulosic waste into value-added products, such as biofuels, chemicals, and biodegradable materials [43]. Additionally,

Table 5 This table summarises the effects of various components of paper, including cellulose, lignin, hemicelluloses, inks, and sizing agents, on the deterioration process and the implications for conservation efforts

| Component | Effect on deterioration | Impact on conservation |
|------------------------|--|---|
| Cellulose | Susceptible to oxidation and acid hydrolysis, which weakens its structure | Stable when pure but susceptible to external agents like humidity and light |
| Lignin | Causes increased deterioration through oxidation and acidic by-products | Increases paper's vulnerability to environmental damage |
| Hemicelluloses | More reactive, especially under acidic conditions, leading to hydrolysis | Contributes to a weaker structure, accelerating paper deterioration |
| Iron gall ink | Can accelerate deterioration, contributing to discoloration and weakening of paper | A commonly used ink, but its variability in composition complicates conservation |
| Beeswax | Promotes microorganism growth, leading to hydrolytic damage to cellulose | Enhances writability but can cause significant long-term damage due to microbial growth |
| Amino acids (gelatine) | Can cause staining and deterioration when applied as a sizing agent | Evidence of historical paper production but may require removal for preservation |

in the energy sector, particularly in power transformer operation, the study of cellulose degradation helps assess the ageing of insulating materials, ensuring equipment reliability and longevity [44] and, of course, the kinetic of cellulose degradation is fundamental in conservation purposes [45]. Then, understanding the kinetics of paper degradation is essential for predicting its long-term stability and informing both conservation efforts and industrial applications. Historical and contemporary studies have provided valuable insights into the mechanisms governing paper ageing. The work of Calvini and Gorassini is a fundamental step in the review of the kinetics to highlight which parameters are usually neglected in the experimental result interpretation [46], considering that the accelerating ageing is not diagnostic of the life expectancy of the material. Contrarily, Zou et al. [47] conducted a kinetic analysis of paper ageing through accelerated ageing experiments, developing models to predict paper permanence based on deterioration trends. These studies underscore the importance of kinetic approaches in assessing paper stability over time, enabling more accurate predictions of its lifespan and guiding the development of preservation strategies for archival materials and historical documents.

Indeed, the durability of paper is primarily attributed to the quality of cellulose, the raw materials used in its production, and the intrinsic structural features of cellulose itself. The microfibrils, which are the basic building blocks of cellulose's supramolecular structure, consist of a mixture of highly ordered (crystalline) domains and less ordered, amorphous regions [48]. This unique arrangement of microfibrils defines the characteristics of paper, creating a network of pores and voids within its polymeric framework. This structure not only influences the reactivity of cellulose—particularly its susceptibility to environmental factors—but also plays a critical role in determining the mechanical properties of the fibres themselves [49].

The natural ageing of cellulose is a complex process, influenced by both internal and external factors that often work in tandem to accelerate deterioration. Internal factors include substances like lignin, rosin, and alum, which are typically present in paper and contribute to its ageing. External factors, on the other hand, encompass environmental conditions such as humidity, air quality, exposure to visible and ultraviolet radiation, pollutants, and the presence of microorganisms. As paper ages, its deterioration is evident on both macroscopic and microscopic scales. On a macroscopic level, this manifests as a decline in mechanical strength and the appearance of discoloration, which may be either widespread or localised. At the microscopic level, alteration results from three primary processes: (1) recrystallisation, (2) acid hydrolysis of β -D-(1,4)-glycosidic bonds, and (3) oxidation of β -D-glucopyranose units.

Acid hydrolysis, which is more pronounced in modern paper than in ancient varieties, primarily affects the mechanical properties of the sheet by shortening the cellulose chains. This process occurs because of the cleavage of glycosidic bonds, catalysed by hydronium ions (H_3O^+) formed during the acidic hydrolysis of internal components, such as alum. Over time, this breakdown leads to a reduction in the molecular weight of cellulose, weakening its structural integrity and diminishing its strength. In contrast, cellulose oxidation is a more complex process that occurs through radical mechanisms, which are initiated by reactive oxygen species (ROS) [30]. This process involves several pathways and consecutive reactions. The deterioration typically begins with the conversion of individual β -D-glucopyranose units into unstable oxidised derivatives, which may trigger the opening of the glucose ring and/or lead to chain cleavage. Depolymerisation, facilitated by the hydrolysis of glycosidic bonds, is significantly accelerated by acidic oxidation products, such as carboxyl groups embedded within the cellulose polymer, as well as by various degradation by-products, including volatile compounds. These chemical changes contribute to the weakening of the cellulose matrix and accelerate the overall deterioration of the paper. As a result of these alteration processes, a range of low-molecular-weight products are formed, such as glucopyranose, acetic acid, and formic acid. While the mechanisms involved in acidic hydrolysis are well documented in the literature, the oxidation of cellulose via radical mechanisms initiated by reactive oxygen species remains a complex process, with many aspects still not fully understood [48]. One of the most common and visible signs of paper deterioration is yellowing, which is caused by the formation of conjugated ketonic groups. These groups have been identified as the primary contributors to the colour change that occurs in ageing paper [48]. Additionally, the presence of amino acids in the paper indicates the use of gelatine as a sizing agent, a material commonly employed in European paper production during the Middle Ages [49]. This historical connection further highlights how both the composition and the ageing processes of paper influence its long-term stability.

When examining ancient documents and manuscripts, the composition of inks plays a crucial role in determining the paper's preservation. The wide variation in ink formulations, often due to the lack of standardised recipes, significantly influences the conservation of these valuable historical records. Among the most commonly used inks was "iron gall ink", which included a variety of ingredients and recipes, each contributing differently to the deterioration of the paper [50]. Substances applied to enhance the paper's writability, such as beeswax, have also been implicated in accelerating deterioration. As an organic compound, beeswax promoted the growth of microorganisms, which led to hydrolytic damage. This damage has a profound impact on the cellulose,

often reducing its molar mass to about one-fifth of its original value [51]. Consequently, identifying such compounds through diagnostic campaigns is essential, and their removal during restoration treatments is crucial to mitigate further damage and ensure the long-term preservation of these historic documents.

Conservation and restoration of paper: from climate control to modern restoration techniques

The conservation and restoration of paper is a complex and multifaceted process that seeks to preserve the integrity of historical documents, manuscripts, and books for future generations. Figure 6 represents the types of damage that can appear on an antique sheet of paper: mould, foxing, mechanical damage, and yellowing. These deteriorations are accelerated both by both the chemical composition and pH of the paper and by environmental factors such as temperature, humidity, and light, as we will discuss later.

Effective management of environmental factors, particularly climate control, is crucial in preventing the deterioration of paper, as fluctuations in temperature and humidity can accelerate its alteration. A key aspect of this process

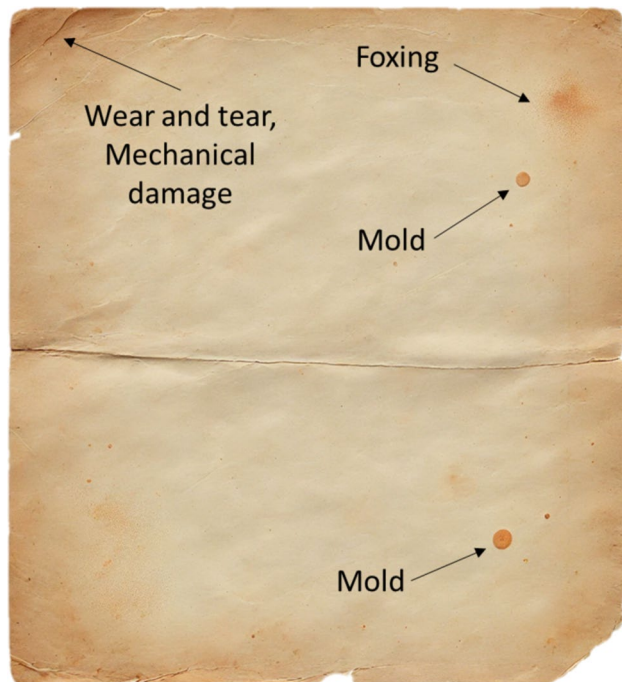


Fig. 6 Examples of damage that can occur on antique paper, including mould growth, foxing, mechanical deterioration, and yellowing. These forms of deterioration are influenced by the paper's chemical composition and pH as well as environmental factors such as temperature, humidity, and light

is understanding how cellulose breaks down over time, so researchers employ various analytical methods to assess the extent of cellulose deterioration. Among these, high-resolution imaging techniques, including scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS), are commonly used to analyse the structural and surface characteristics of cellulose. While a technique like SEM-EDS can provide an immediate analysis of the surface morphology of cellulose, along with EDS analysis of the elements present, it is necessary to sample a portion of the artefact for examination [33, 52–54]. In contrast, atomic force microscopy (AFM) in tapping mode allows for the examination of cellulose in its native state, though it may introduce tip-related artefacts that obscure structural details [29, 33, 52].

Beyond imaging techniques, non-imaging methods such as x-ray diffraction (XRD) are widely used to characterise the crystallinity and crystallite size of cellulose [34, 55]. However, XRD does not directly measure crystallinity but rather indicates the proportion of crystalline cellulose within the entire sample. Furthermore, its results may be influenced by the presence of other crystalline substances, making it difficult to isolate cellulose-specific information [29, 34, 55]. Nuclear magnetic resonance (NMR) provides valuable insights into the chemical alterations of both amorphous and crystalline cellulose. However, it requires cellulose to be dissolved in acidic or enzymatic solutions to break hydrogen bonds, rendering it a destructive technique [56, 57]. Similarly, thermo-analytical methods such as differential scanning calorimetry (DSC) and thermo-gravimetric analysis assess thermal properties by exposing samples to high temperatures, further limiting their applicability to preservation efforts [58–62]. To address the need for non-destructive techniques, methods such as Fourier transform infrared (FTIR) and Raman spectroscopy offer chemical sensitivity while preserving sample integrity, making them valuable tools for cellulose analysis [31, 63–65].

However, the most important aspect is to consider the application of a multi-analytical approach, as a single technique alone cannot fully meet conservation and preliminary analysis requirements. Each technique has its own advantages and limitations, which must be considered depending on the specific research question being addressed.

When climate control fails, diagnostic analysis takes place, and restoration becomes the only option to preserve this heritage. In the following paragraph, we will first explore the fundamental principles of environmental control for paper collections, highlighting how proper management of temperature and humidity plays a crucial role in preserving these materials. We will then discuss the latest restoration techniques that utilise modern technologies to help maintain the structural integrity of paper artefacts.

Environmental control

The alterations and deteriorations that paper undergoes over time are not solely due to the chemical composition of the material or the reactions with inks and adhesives applied to manuscripts. Paper artefacts interact dynamically with their surrounding environment, making climate control an essential aspect of preventive and long-term conservation. Figure 7 illustrates the key environmental factors with which paper interacts and that can lead to deterioration. Preventive conservation of cultural heritage aims to control these risks factors, and it is defined as "measures and actions aimed at avoiding or minimizing future damage, deterioration, and loss, and consequently, reducing the need for invasive interventions" (EN 15898:2019. Conservation of cultural property—Main general terms and definitions).

In this context, climate control falls under preventive conservation strategies, as it focuses on maintaining the optimal environmental conditions necessary to preserve paper materials effectively.

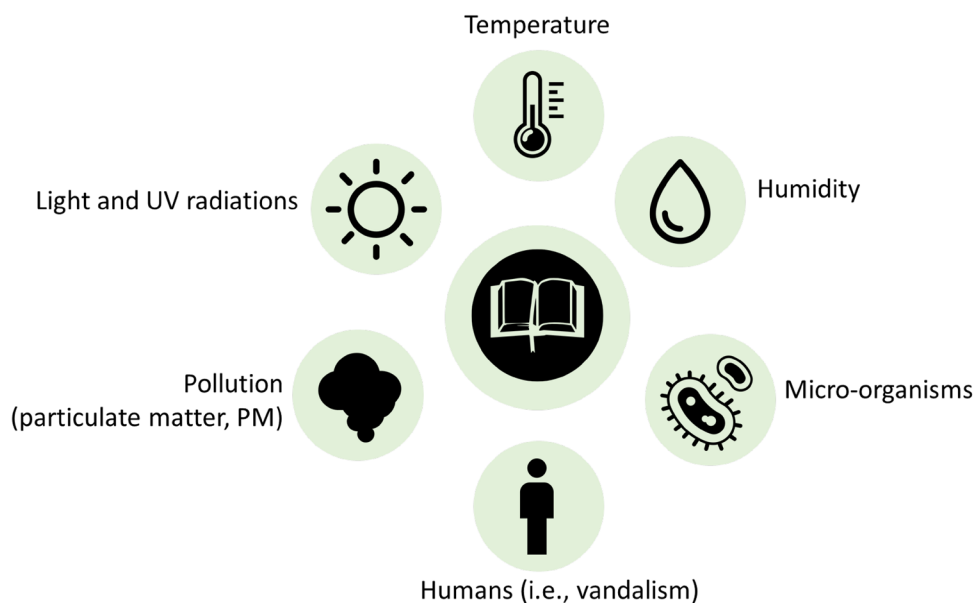
Extensive research has demonstrated the significant effects of cyclic variations in indoor conditions, outdoor climate, environmental pollution, mechanical stresses, and chemical and thermo-physical changes on cultural heritage items in libraries, museums, and historical exhibitions [66]. Studies have shown how fluctuations between indoor and outdoor climates can accelerate both deterioration and bio-deterioration processes in these collections. A schematic representation of the major risk factors for paper artefacts is shown in Fig. 6.

Acclimatisation of sensitive heritage objects to the environment in which they have been preserved for extended periods has been key in establishing climate control criteria.

This concept has been formalised in numerous standards, which recommend optimal ranges for thermo-hygrometric parameters to prevent cultural heritage deterioration. In recent studies, the idea of "historical climate" has emerged, suggesting that paper artefacts benefit from stable environmental conditions that reflect the climate in which they were originally kept. Many studies have explored the various alteration and deterioration phenomena affecting paper, including mechanical stress, chemical and photochemical reactions, and biological mechanisms. A substantial research attributes bio-deterioration of heritage cellulosic materials to fluctuations in air temperature and humidity [66, 67]. In fact, temperature and humidity are particularly critical for maintaining the balance of paper, as they directly influence the hydrolysis of cellulose, the primary concern regarding deterioration of paper collections [67]. The rate of chemical degradation is primarily driven by temperature, making these factors crucial in preserving paper's integrity [68]. Recent advancements have allowed researchers to calculate a dose-response function that depends on environmental factors such as temperature and humidity, as well as the inherent characteristics of the paper itself, such as pH and polymerisation degree. Verticchio and colleagues developed models to estimate the "time life" of a collection—essentially, the period during which a library collection remains fit for use before it becomes unfit because of the combined effects of handling and cellulose hydrolysis [68]. Furthermore, other factors like light exposure and particulate matter (PM) also impact paper preservation and must be closely monitored. Together, these factors can contribute to the growth of microorganisms and mould.

In recent years, the conversation surrounding environmental control has expanded to include the challenges posed

Fig. 7 Environmental factors critical for paper preservation, including temperature, humidity, microorganisms, human activity (such as vandalism), pollution, and light. These factors play a significant role in the deterioration of paper materials, especially when subjected to fluctuations, and these factors are interconnected, with changes in one often leading to a cascade of effects. For example, increased humidity can promote the growth of microorganisms, while temperature fluctuations can accelerate chemical degradation



by climate change. Rising global temperatures pose additional risks to paper artefacts, particularly by promoting the migration and adaptation of new species of bio-deteriorating agents. These changes, driven by global warming, intensify the risks of biodegradation and create growing challenges for the preservation of Cultural Heritage [69]. The growing concern regarding climate change further underscores the importance of proactive climate management in the preservation of paper and other sensitive materials.

The modern conservation and restoration of paper

The restoration of paper has a long history, evolving significantly from its early techniques to the advanced methods we use today. In ancient times, paper restoration primarily focused on basic interventions, often performed by scribes or conservators who applied simple manual techniques to mend tears and reinforce fragile documents. Common methods included the use of adhesives, paste, and stitching to hold fragments together, with the primary goal of preserving the readability and integrity of the text. As paper technology and knowledge of materials advanced, so did restoration methods, incorporating more sophisticated approaches such as washing, bleaching, and deacidification. These techniques, however, were often rudimentary and could sometimes contribute to further deterioration due to a lack of understanding of the long-term effects on paper. In the twentieth century, with the development of scientific methods and a deeper understanding of the chemical properties of paper, conservation practices became more specialised. Today, modern restoration techniques combine cutting-edge technologies to ensure the material integrity of the artefacts while maintaining their historical authenticity.

Deacidification of paper

In the context of paper restoration, deacidification is an essential treatment aimed at stopping the ongoing deterioration of paper caused by acidic conditions. Over time, the acids present in paper, often originating from the paper-making process itself or from materials such as inks and adhesives, can cause the cellulose fibres to break down. This leads to brittleness, discoloration, and loss of structural integrity. In restoration practice, deacidification is one of the most performed methods to prevent further damage and improve the paper's longevity [70–72].

Deacidification involves the introduction of alkaline substances to neutralise acids present in paper and ensure the retention of an alkali reserve. This reserve helps counteract any acidic compounds that may form over time, thus extending the lifespan of the paper [73, 74]. Ideally, the process

should be safe for the artwork, the environment, and the conservators, with no adverse effects on original inks, pigments, or paper fibres [23, 74]. In paper restoration—and more broadly in conservation practice—two fundamental principles guide interventions: minimum intervention and reversibility. Any treatment should be as non-invasive as possible and, when feasible, should allow for future reversibility without compromising the artefact.

Traditional deacidification methods are categorised into gaseous and liquid treatments, with the latter performed in aqueous or organic solutions [2, 72]. However, each method presents inherent risks. Aqueous treatments can cause fibre swelling and colour bleeding, particularly in delicate or water-sensitive manuscripts, while organic solvent-based methods pose concerns regarding flammability and toxicity. To address these challenges, ongoing research focuses on refining deacidification techniques. One approach explores the modification of aerosol-based treatments, adjusting the size and composition of aerosol particles to improve penetration and efficiency while minimising damage [75, 76]. Another innovative strategy, presented by Zhang and colleagues [74], involves controllable enzymatic mineralisation. Their method facilitates the deposition of calcium carbonate (CaCO_3) and hydroxyapatite, two alkaline compounds that effectively neutralise acidic content in paper. The resulting mineralised membrane is reported to be thermally stable and reversible, aligning with key restoration principles. Recent developments were made regarding the use of alkaline nanoparticles (*vide infra*), with specific deacidifying properties, applied to the cellulosic materials with the double aim of reducing the pH of the surface while improving the paper strength [77–79]. The work of Baglioni and Giorgi [80] reported that MgO nanoparticles are highly effective as a paper de-acidification agent, offering excellent physico-chemical compatibility with the substrate. Their application not only neutralises acidity but also preserves the integrity of the treated material, ensuring that no undesirable side effects, such as alterations in texture, strength, or colour, occur. This makes MgO nanoparticles a promising solution for long-term conservation efforts, maintaining the material's original properties while extending its lifespan. However, these are cutting-edge solutions that are still in the experimental phase, while even more advanced solutions are being investigated. For instance, Li and colleagues are exploring the use of bacterial cellulose impregnated with zinc oxide nanoparticles [81]. This approach not only offers deacidification but also serves as a fungal inhibitor and reinforcement for fragile paper structures.

While promising, such techniques require further testing to ensure compatibility with historical paper and adherence to conservation standards before they can be widely implemented in real-world restoration.

Cleaning

Over time, paper can accumulate dirt, stains, and pollutants that not only obscure its readability but also contribute to its deterioration and the growth of mould and micro-organisms. Various cleaning methods have been developed to address these issues while preserving the integrity of the material. These range from dry cleaning techniques, which remove surface contaminants without introducing moisture, to wet cleaning methods that can mitigate acidic deterioration and discoloration. However, these traditional methods present certain limitations, particularly in relation to the reduction of the paper's mechanical strength and the use of toxic chemical agents [82, 83]. In this paragraph, we will explore the recent advancements in cleaning methods, focusing on cutting-edge techniques that hold promise for the field of scientific conservation and restoration.

In recent years, ionic liquids have gained attention as a promising alternative due to their non-toxic and eco-friendly nature. Despite these advantages, challenges remain, especially concerning their impact on the structural integrity of the paper [83]. Ionic liquids are effective in removing lignin and hemicellulose—key components responsible for paper yellowing—but their extraction can weaken the material, as these substances also contribute to the paper's mechanical stability. However, the study by Schmitz and co-workers highlights the potential of ionic liquids as antifungal agents, demonstrating their ability to inhibit the growth of five fungal species on the paper surface [84]. His finding underscores the importance of selecting a cleaning method based on the specific conservation challenge being addressed. While ionic liquids effectively prevent fungal growth, their use may also lead to mechanical deterioration, emphasising the need for a careful balance between efficacy and material preservation. Other advanced approaches regarding laser-cleaning, enzyme-based treatments and nanomaterials have been explored to enhance the efficacy and safety of the cleaning process. Here, laser cleaning and enzyme-based treatments will be discussed, while the use of nanoparticles is addressed separately in another section because of their significant technological impact on heritage materials.

Laser cleaning of paper relies on physical effects, specifically photo-ablation, a process in which contaminant particles are ejected as photons are absorbed by the dirt material targeted for removal. This technique enables the selective elimination of unwanted substances from the surface based on differences in optical absorption. The first step in developing laser technology for paper restoration is selecting laser parameters that ensure efficient cleaning of books and documents while avoiding damage. It is crucial to fine-tune the laser output to prevent adverse effects such as carbonisation, discoloration, changes in acidity, porosity, or alterations to the paper's physical and chemical properties. Given the

fragility of paper, careful consideration of the laser type and its operational characteristics is essential to minimise the risk of damage [85–88].

A cutting-edge advancement in conservation techniques is bio-cleaning, which utilises bacterial enzymatic resources to clean artefacts. While the first applications of bio-cleaning were primarily on frescoes, recent studies have extended this approach to paper artefacts as well [89, 90]. One of the pioneering works in this field is that of Barbabietola and colleagues, who successfully applied a microbe-based procedure to remove aged glues from historical papers. They used a living bacterial cell to remove the non-desired aged glue on the ancient paper. Their research highlighted several advantages of this method, including its low environmental impact, high selectivity in targeting unwanted materials, absence of toxic agents, safety for both conservators and artefacts, and overall cost-effectiveness. Notably, the removal of aged glue has traditionally been performed through mechanical methods, which are often aggressive and lack selectivity, posing a risk to delicate artworks. While the introduction of hydrogels represents a significant improvement over chemical solvents, bio-cleaning offers an even more refined, non-invasive alternative for conservation treatments [91]. This approach represents a true revolution in the field and has the potential to be widely adopted in restoration practices. However, the use of microorganisms, enzymes, and living bacterial cells requires the expertise of highly skilled operators to ensure safe and effective application [92]. Table 6 summarises and compares the key features and limitations of the cleaning methods discussed.

New frontiers in restoration: the applications of nanoparticles

Nanoscience has brought significant advancements to conservation science, introducing nanoparticles, composite nanomaterials, and soft-condensed matter as valuable tools in the field. Research has led to the development of tailored materials designed to address specific conservation challenges. As noted by Chelazzi and Baglioni [93], material deterioration originates at the nanoscale before spreading to the entire artwork. By targeting alteration at its earliest stages, nanomaterials offer an innovative and effective approach to preserving cultural heritage.

One of the earliest applications of nanoparticles in conservation focused on the deacidification of ancient paper, using calcium hydroxide ($\text{Ca}(\text{OH})_2$) nanoparticle dispersion in non-aqueous solvents [94]. This was the very first attempt in using nanoparticles for the deacidification of paper; the success of this application led to the development of other formulations, such as the magnesium hydroxide ($\text{Mg}(\text{OH})_2$) nanoparticles to treat both artificially aged and historical documents [95]. Both studies highlighted that

Table 6 Comparison of different cleaning methods for paper artworks, highlighting their advantages and limitations. Each method—ionic liquids, laser cleaning, and bio-cleaning—offers distinct benefits

and challenges, requiring careful consideration based on the condition of the artefact and conservation goals

| Cleaning method | Pros | Cons |
|-----------------|--|---|
| Ionic liquids | <ul style="list-style-type: none"> - Eco-friendly and non-toxic alternative to traditional solvents - Effectively removes lignin and hemicellulose, reducing yellowing | <ul style="list-style-type: none"> - Can weaken the paper's mechanical strength - Requires further optimisation to balance cleaning efficiency and preservation |
| Laser cleaning | <ul style="list-style-type: none"> - Highly precise and selective removal of contaminants - Non-contact method, minimising physical stress on paper - No chemical residues left on the surface | <ul style="list-style-type: none"> - Risk of carbonisation or changes in colour, acidity, and porosity if not carefully controlled - Requires specialised equipment and expertise |
| Bio-cleaning | <ul style="list-style-type: none"> - Environmentally friendly and non-toxic - Highly selective in targeting unwanted substances - Safe for conservators and artefacts - Cost-effective compared to some chemical methods | <ul style="list-style-type: none"> - Requires skilled operators to handle microorganisms and enzymes - Application still in development for widespread use in paper conservation |

these nanoparticles significantly enhanced the deacidification process because of their high reactivity. More importantly, the treatment did not require special precautions, and the nanoparticles effectively preserved the mechanical and aesthetic properties of the artefacts. Additionally, the authors emphasised the economic advantages of this approach, as the nanoparticles can be synthesised through low-cost methods, making them a more affordable alternative to traditional deacidification techniques, which are often both time-consuming and expensive.

Beyond their essential role in deacidification, nanoparticles have also been employed for their antimicrobial and/or antifungal properties to prevent the bio-deterioration of ancient manuscripts [96, 97]. By inhibiting the growth of fungi and bacteria, these nanoparticles serve as a protective barrier, safeguarding delicate paper artefacts from biological damage. As previously mentioned, microbial bio-deterioration primarily results from the synergistic action of cellulolytic enzymes, which break down the cellulose structure, compromising the integrity of the paper. This process can also lead to the formation of rust-coloured stains and discoloration on paper surfaces, a phenomenon commonly known as “foxing” [98]. The growing interest in nanoparticles and their application as bio-protective agents stems from their unique physical and chemical antimicrobial properties. These nanomaterials have demonstrated remarkable efficacy in preventing microbial colonisation and deterioration of historical paper artefacts. Their antimicrobial activity is attributed to several mechanisms, including direct cell membrane damage, the release of metal ions that disrupt cellular functions, leakage of intracellular components such as reducing sugars and proteins, and the induction of oxidative stress. Additionally, non-oxidative mechanisms, influenced by factors such as particle size, shape, and morphology, also contribute to their effectiveness in inhibiting microbial growth [99, 100]. Among the various nanoparticles explored for antimicrobial purposes, silver nanoparticles (Ag-NPs)

and zinc oxide nanoparticles (ZnO-NPs) stand out as two of the most extensively studied. Silver nanoparticles are particularly valued for their broad-spectrum antimicrobial properties, effectively targeting bacteria, fungi, and even viruses. Zinc oxide nanoparticles, on the other hand, exhibit strong antibacterial and antifungal activity while also offering additional benefits, such as UV protection and photocatalytic properties that contribute to the alteration of organic pollutants [81, 94, 101]. These characteristics make nanoparticles a promising avenue for the long-term preservation of historical documents, minimising microbial-induced degradation without relying on more invasive or chemically aggressive conservation treatments. As research progresses, the optimisation of nanoparticle-based treatments could offer safer, more sustainable, and more efficient methods for protecting paper artefacts from bio-deterioration. [96].

A significant frontier in the field of paper conservation involves the use of nano-fibrils and nanocrystals as protective coatings for lignin-cellulosic materials [102]. These innovative materials offer a promising solution for enhancing the durability and stability of historical and archival documents while adhering to the fundamental principles of restoration—namely, reversibility and minimal intervention.

A pioneering study by Camargos and co-workers [62] introduced a novel coating material derived from elephant grass biomass. Their research demonstrated that this bio-based nano-coating provides remarkable protection against UV light, a major factor in the alteration of paper-based artefacts. Additionally, the coating is fully reversible, meaning it can be safely removed without causing damage—an essential criterion in modern restoration practices. Another ground-breaking feature of this material is its tuneable wettability, allowing conservators to tailor the surface properties according to specific preservation needs. By adjusting the formulation, the coating can be made hydrophobic, effectively shielding paper from moisture-related deterioration while maintaining breathability.

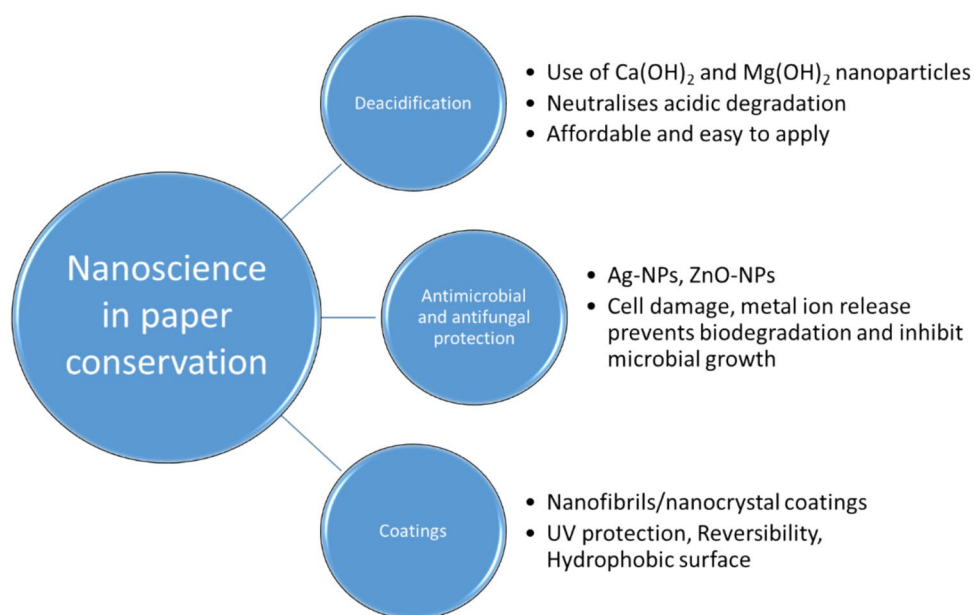
This advancement represents a major step forward in sustainable and non-invasive paper conservation. Unlike traditional protective treatments, which may involve chemical alterations or irreversible changes, nano-fibril-based coatings offer a dynamic and adaptable approach. Their ability to enhance UV resistance, control moisture interaction, and ensure reversibility makes them a highly attractive option for future conservation strategies, bridging the gap between technological innovation and the ethical principles of restoration. It is fundamental to note that nanoscience has emerged as a transformative force in the field of cultural heritage conservation, offering innovative solutions that align with the fundamental principles of restoration: effectiveness, reversibility, and minimal intervention. The application of nanoparticles and nanostructured materials in paper restoration has opened new pathways for tackling some of the most pressing challenges, such as acid-induced deterioration, bio-deterioration, and environmental damage, and these applications are summarised in Fig. 8. From deacidification treatments that prolong the lifespan of fragile documents to antimicrobial coatings that protect against fungal and bacterial colonisation, nanotechnology provides a level of precision and adaptability that was previously unattainable. Beyond these targeted treatments, the development of bio-inspired nano-coatings, such as those derived from lignocellulosic nano-fibrils, marks a significant step toward sustainable and reversible preservation methods. As research continues to push the boundaries of nanomaterials, future applications may further refine protective coatings, self-healing materials, and environmentally responsive conservation strategies.

Digital restoration

In the context of the digital era, the concept of materiality in the preservation of paper artefacts is undergoing a significant transformation. We can refer materiality to the physical and chemical composition of objects, such as the fibres in paper, inks, and pigments. As discussed in this paper, we saw that these components of the artworks are directly influenced by environmental factors, handling, and time.

However, with the rise of digital technologies, materiality has evolved to include not only the physical components of the artefact but also its digital representation and accessibility, and a brief consideration of this practice must be discussed. Digital restoration allows us to capture, manipulate, and store an artefact's visual and textual information in a format that transcends the material limits of the original object [103]. This new layer of materiality—an artefact's digital counterpart—becomes an essential aspect of preservation as it ensures the longevity of the artwork's information, even if the physical object deteriorates or is no longer accessible. While traditional material-based conservation seeks to protect the physical object from further deterioration, digital preservation protects the essence of the artefact by securing its content for future generations, regardless of the fate of the original materials. One example where digital restoration proves essential is described in the work of Savino and Tonazzini [104], which focuses on a manuscript written on both sides, suffering from bleed-through due to ink seepage through the paper fibres. In this case, traditional restoration methods cannot fully restore the manuscript to its original condition. However, digital tools can effectively remove the bleed-through pattern, ensuring that the manuscript can still be accessed and appreciated—even if in its virtual

Fig. 8 Nanoscience in paper conservation: an overview of recent applications. The diagram showcases the key applications of nanotechnology in paper preservation, ranging from deacidification techniques to advanced nano-coatings that safeguard paper surfaces against a variety of deterioration factors



form—without compromising the integrity of the undamaged portions. This shift in materiality highlights a broader understanding of cultural heritage preservation, where the emphasis is placed not only on the physical aspects of an artefact but also on its intellectual, cultural, and historical value, which can be maintained through digital means. Ultimately, digital restoration enriches our approach to heritage conservation by ensuring that cultural artefacts remain part of the collective memory, even as their physical form may fade over time.

Conclusions

The chemistry applied to the conservation of ancient paper and manuscripts provides an essential tool in the ongoing fight against their deterioration. The loss of such fragile supports, often bearing the history of humanity, would be an irreparable cultural loss that must be addressed through a combination of sophisticated conservation techniques. By examining the historical evolution of paper, from its cellulose, lignin, and hemicellulose components to the way these materials interact with environmental factors, we gain a deeper understanding of the complexities involved in preserving these invaluable artefacts. A detailed analysis of chemical pulps and their effects on paper underscores the critical role of chemical processes in both deterioration and restoration, highlighting the delicate balance required in conservation efforts.

Moreover, modern restoration methodologies—such as deacidification, nanotechnology, and other advanced chemical treatments—have introduced promising solutions that extend the lifespan of paper-based works. These techniques, while highly effective, must be carefully applied, ensuring they remain reversible and minimally invasive to maintain the integrity and authenticity of the original material.

In addition to material restoration, the digital era has brought forward significant advancements in the preservation and accessibility of cultural heritage. Digital restoration, including the creation of digital twins of artworks, enables the virtual restoration of paper artefacts, offering a highly accurate, non-invasive method to safeguard the original state of a document—even if the physical artefact is too fragile for direct interaction. This innovation allows for the preservation of the artwork's history while safeguarding the object itself from further damage. Ultimately, a multidisciplinary approach that integrates chemistry, technology, ethics, and digital restoration will continue to guide the future of paper conservation. This comprehensive strategy ensures a balanced approach, preserving the materiality and historical authenticity of artefacts while embracing new methodologies that extend their preservation and accessibility for future generations.

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Declarations

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