Impact of Physical, Chemical and Biological Aspects on Degradation of Paper

Priti Yadav [1], Jothy Ch Momin[2], Pooja Rawat[3]

[1,2]Student, Department of Forensic Science, Vivekananda Global University
[3]Assistant Professor, Department of Forensic Science, Vivekananda Global University

ABSTRACT:
Paper is a thin sheet material which is produced either by chemical processing's of cellulosic fibers which is gained from different sources alike grasses, vegetable sources, wood pulp, rags, paddy straw and other fibrous materials. Paper was and still is always an important material which serves the informative script in the form of journals, books, newspaper, documents, etc. Paper being the substance obtained from the natural resources is also most easily prone to be degraded when subjected to any chemical, physical or biological conditions. The cellulosic fibers when subjected to soil can undergoes the breakdown process, as the soil contains the cellulosic bacteria's such as – Clostridium, Actinomycetes, Ruminococcus albus etc., and the deterioration process can vary with differential qualitative aspects like pH, time, mineral content of the soil, the humus composition, moisture available, presence of the organisms, etc. The paper enhances or sheds light on the process of ageing within the given consideration of all the different surrounding aspects. The ageing helps in knowing the fact of actual or the forged documents with their quality and the level of their distortion or degradation and even to know whether eaten up by any of the living organisms. It will also help us understanding the quantitative destruction of the different cellulosic fibers with their deterioration levels. So with this it will help in analyzing the whole scenario and to gather the information with qualitative and also the quantitative value data. As there have been many researches on the condition of papers when prone or put in specific conditions such as the chemical or physical or biological they behave differently as per the conditions are melting down the papers with its compensability and helping to understand the immense condition of the forgery whether happened or not.

Keywords: Moisture, pH, time, surroundings, breaking down, deterioration.

INTRODUCTION:

Degradation is the chemical breakdown process of the larger molecules to smaller ones via either biotic or abiotic factors such as microbes, helminthes, arthropods, temperature, air, humidity, chemical substances like acids or alkali etc. Paper being the biological component can be easily degraded when comes in contact with the different natural and fundamental activities. So when degraded via any of the physiologically or enzymatically means the humification process is functioned accordingly. Paper, a fundamental medium for recording and disseminating information, undergoes degradation over time due to various different environmental factors. Understanding these processes is crucial for preserving historical documents, archival materials, and everyday paper products.

1. Physical Degradation:

Physical factors such as light, temperature, humidity, and mechanical wear contribute to the deterioration of paper. Exposure to light, especially ultraviolet (UV) light, can cause photochemical reactions that weaken the paper fibers. High temperatures and fluctuations in humidity can lead to the expansion and contraction of paper, causing brittleness and loss of mechanical strength. Mechanical wear from handling and use can also cause physical damage to paper.

1.1.Environmental Factors:

1.1.1. Light Exposure: Ultraviolet (UV) light from the sun or artificial sources can cause photochemical reactions in paper. This results in fading, discoloration, and weakening of the paper fibers. Prolonged exposure to light can make the paper brittle and more susceptible to tearing.

1.1.2. Temperature Fluctuations: Extreme temperatures or fluctuations can cause paper to expand and contract. This constant movement can lead to warping, curling, and eventually breaking down the structure of the paper. High temperatures can also accelerate chemical degradation processes.

1.1.3. Humidity: High humidity levels can cause paper to absorb moisture, leading to swelling, mold growth, and weakening of the fibers. Conversely, low humidity can dry out the paper, making it brittle and prone to cracking. Fluctuating humidity levels can exacerbate these issues by causing repeated cycles of expansion and contraction.

1.2.Mechanical Stress:

1.2.1. Handling and Use: Physical handling of paper can cause wear and tear, especially in frequently used documents. This can result in creases, folds, tears, and other forms of mechanical damage. Repeated handling can also transfer oils and dirt from hands to the paper, contributing to its degradation.

1.2.2. Storage Conditions: Improper storage can lead to physical damage. Storing paper in environments that are too tight or inappropriately sized containers can cause bending, folding, or crushing. Additionally, stacking heavy items on top of paper can lead to compression and deformation.

1.2.3. Abrasive Surfaces: Contact with rough or abrasive surfaces can physically abrade the surface of the paper, causing loss of material and weakening of the structure. This is particularly concerning for valuable or fragile documents that are frequently moved or displayed.

2. Chemical Degradation:

Chemical degradation occurs when paper is exposed to reactive substances that break down its components. Acid hydrolysis is a common chemical degradation process where acids present in the paper or the environment catalyze the breakdown of cellulose fibers. Oxidation, another chemical process, involves the reaction of paper components with oxygen, leading to the formation of free radicals and further degradation of the material. Additives in the paper, such as sizing agents and fillers, can also contribute to chemical degradation over time.

2.1.Acid Hydrolysis:

This occurs when acids present in the paper or the environment catalyze the breakdown of cellulose fibers. This process is accelerated by factors such as high humidity and the presence of acidic byproducts from the decomposition of paper components. The acids cleave the glycosidic bonds in cellulose, resulting in shorter polymer chains and a reduction in the degree of polymerization. This leads to embrittlement and a decrease in the mechanical properties of the paper

2.2.Oxidation:

This involves the reaction of paper components with oxygen, leading to the formation of free radicals. These free radicals can further react with cellulose, causing chain scission and the formation of carbonyl groups, which contribute to yellowing and embrittlement of the paper. Oxidation is often accelerated by pollutants and high temperatures, which increase the rate of chemical reactions**.**

2.3.Chemical Additives:

Additives like sizing agents, fillers, and bleaching compounds can contribute to chemical degradation over time, especially if they are not properly neutralized or stabilized during manufacturing.

2.4.Factors Influencing Chemical Degradation:

Several factors influence the rate and extent of chemical degradation of paper:

- **Acidity**: The presence of acidic components in the paper or the environment accelerates hydrolysis and oxidation.
- **Humidity**: High humidity levels promote hydrolysis by providing the necessary moisture for the reaction.
- **Temperature**: Higher temperatures increase the rate of chemical reactions, leading to faster degradation.
- **Light Exposure**: Exposure to light, especially UV light, can catalyze oxidation reactions and cause photochemical degradation.
- **Additives**: Chemical additives used in paper production, such as sizing agents and fillers, can contribute to degradation if they are not properly neutralized or stabilized.

3. Biological Degradation:

Biological factors, including the presence of microorganisms such as bacteria, fungi, and insects, can cause significant damage to paper. Microbial activity can lead to the production of enzymes that break down cellulose and other organic components of the paper. Insects, such as silverfish and termites, can physically damage paper by feeding on it, leading to holes and loss of material.

3.1.Microbial Activity:

The microorganisms produce enzymes that break down cellulose and other organic components in paper. Fungi, particularly white-rot fungi, are known for their ability to decompose lignin and cellulose, leading to the degradation of paper. Bacteria can also contribute to this process, especially in moist environments..

3.2.Insect Damage:

Insects such as silverfish, termites, and booklice feed on paper, causing physical damage. They create holes, tunnels, and frass (insect debris), which compromises the integrity of the paper.

3.3.Environmental Factors:

3.3.1. Humidity:

High humidity levels provide the moisture necessary for microbial growth, accelerating the degradation process. Paper stored in damp conditions is particularly susceptible to biological degradation.

3.3.2. Temperature:

Warm temperatures can enhance microbial activity, leading to faster degradation of paper. However, extreme temperatures can also inhibit microbial growth.

3.3.3. Light Exposure:

While light exposure primarily causes photochemical degradation, it can also indirectly affect biological degradation by creating conditions that promote microbial growth.

Understanding the mechanisms of paper degradation is essential for developing effective preservation strategies. By controlling environmental conditions, using acid-free materials, and implementing proper storage techniques, the longevity of paper documents can be significantly extended. Additionally, ongoing research into the chemical and biological processes involved in paper degradation helps inform conservation practices and the development of new preservation technologies.

Here's a table summarizing the different methods of paper degradation across chemical, physical, and biological categories:

Sr. No.	Degradation Type	Method	Description	Factors Influencing
1.	**Chemical**	Acid Hydrolysis Oxidation Chemical Additives	Acids catalyze the breakdown of cellulose fibers, weakening the paper Reaction with oxygen leads to free radicals, causing yellowing and embrittlement Additives like sizing agents and fillers degrade over time, weakening paper	Acidity, humidity, temperature Oxygen exposure, pollutants, light Type and stability of additives
2.	**Physical**	Light Exposure Temperature Fluctuations Humidity	UV light causes photochemical reactions, leading to discoloration and brittleness Causes expansion and contraction, leading to warping and mechanical damage. High humidity leads to swelling and mold growth, low humidity causes brittleness Physical handling and environmental stress cause tears, creases, and other damage	Intensity and duration of light exposure Temperature range and stability Humidity levels and fluctuations Frequency and manner of handling

		Mechanical Wear		
3.	**Biological**	Microbial Activity Insect Damage	Bacteria and fungi produce enzymes that break down cellulose and other organic components. Insects like silverfish and termites feed on paper, causing holes and structural damage	Humidity, temperature, cleanliness Insect presence, storage conditions

Table 1.1. Highlights the various methods through which paper degrades and the factors that influence these processes. By understanding these mechanisms, effective preservation strategies can be implemented to protect paper documents from degradation

REVIEW OF LITERATURE

Paper degradation in certainly the most common topic to be found as most of the time the destruction happens naturally by itself. Paper degradation can be done by various different methods. There are numerous methods to degrade the paper depending on the qualities of the paper matching with the degradation process.

Lipinsky. E gave the accelerated ageing of the paper which even shows severe damages such as embrittlement, decay, and mold often occur to the paper that might threaten to lose cultural heritage. This monograph is focused primarily on hydrolysis of cellulose. However, the choice of technology for cellulose hydrolysis depends both on the state of the cellulose when it reaches the hydrolysis process and on the fermentation (or other) technology to be applied to the output of the cellulose hydrolysis process [1], [14].

However, the shelf life of papers stored in suitable conditions can be extended by hundreds of years. An experimental technique has been developed that allows a quantitative evaluation of the ratio of atmospheric oxidation to the total rate of deterioration of the paper. The results suggest that atmospheric oxidation, and not hydrolysis, may play the major role in paper ageing [2], [20], [21].

Every paper/board material shows an off-flavor or typical odor that is produced by a cloud of molecules around the product. The purpose of the analysis is to characterize the "cloud", and the transfer to a foodstuff or defined simulant for further testing [3].

A gas chromatographic investigation of volatile auto-oxidation products from sunflower oil helps in concluding about the paper reacting with the different types of oils and then resulting in their different characteristics [4].

Our study was focused on the investigation of mechanical properties (tensile strength, stretch, tensile index, zero-span tensile strength, folding endurance) of original papers (one alkaline and three different acidic samples) exposed to five methods of dry-heat and moist-heat accelerated ageing. The degree of paper deterioration upon ageing was significantly influenced by the temperature and relative humidity, along with the intrinsic chemistry of the individual paper samples [5], [10].

Aging tests documented that, contrary to alum-rosin sized paper, alkaline sized paper can last for several hundred years. The degradation of cellulose is not the result of the independent impact of individual factors, but the impact of these factors overlaps and influences each other. For better clarity and understanding, the individual factors are discussed separately [6].

The main part of this review therefore focuses upon the products arising as a result of the degradation of cellulose under alkaline, anaerobic (post-closure) conditions, at temperatures <170 °C, since these conditions predominate with respect to the long-term repository environment. Products that may be obtained under other conditions that may be experienced by the waste prior to closure of the repository (e.g. aerobic oxidative degradation) are also discussed [7].

This review is not aimed at discussing all available de-acidification techniques; this task is fulfilled by other comprehensive works. It must be said that all processes create a certain alkaline reserve after the de-acidification of documents [8].

This study aims to understand and describe whether environmental damage can be systematically isolated from mechanical damage throughout the aging process. Quasi-static tensile tests were done to characterize the effects of coupled mechanical & environmental damage on the mechanical behavior [9], [12].

A view on the kinetics of cellulose ageing is given, oriented particularly on the problem of stability and the degradation of paper, for which cellulose can be considered as a model compound. Reservations concerning the conditions of cellulose degradation are exposed, e.g. that the research efforts are focused on the degradation of cellulose at temperatures from 90°C down to room temperature at the full range of relative humidity, even if the range 30–80% is the most essential one [13], [11].

The study of the natural ageing of cellulose and all the related subjects, i.e. the question of permanence of cellulose products such as paper and the results of various processes on it, present the insurmountable obstacle that the effects of natural ageing at ambient conditions can take several years to register on certain cellulose properties, and even several decades to produce statistically significant changes [1].

The method to overcome this problem is the application of hostile environments which are far more aggressive than the normal environment paper and cellulose are exposed to the study of the natural ageing of cellulose and all the related subjects, i.e. the question of permanence of cellulose products such as paper and the results of various processes on it, present the insurmountable obstacle that the effects of natural ageing at ambient conditions can take several years to register on certain cellulose properties, and even several decades to produce statistically significant changes [2].

The method to overcome this problem is the application of hostile environments which are far more aggressive than the normal environment paper and cellulose are exposed to [1].

The attempts to compare the results of natural and accelerated ageing of paper and find parallels between them fall in one of the following three categories: comparison of properties, Arrhenius studies and comparison of products [15].

Specifies the requirements for permanent paper intended for documents given in terms of minimum strength measured by a tear test, minimum content of substance (such as calcium carbonate) that neutralize acid action measured by the alkali reserve, maximum content of easily oxidized material measured by the kappa number, maximum and minimum pH values of a cold water extract of the paper is applicable to unprinted papers [18], [19].

This paper shows the results of the Fourier Transform Infrared (FTIR) analysis of cellulose papers doped twenty years ago with 0.1 and 1 M solutions of $FeCl_3$ and $CuCl_2$ respectively and kept in polypropylene bags in the dark. Iron-treated samples appear today highly hydrolyzed and oxidized; in particular the excess of metal (treatment with 1 M solutions) brought about the formation of iron (II) oxalate, as shown by the FTIR bands at about 1620, 1358, 1313 and 814 cm-1. Washing and acid treatments removed the low-molecular weight oxidized fractions and iron oxalate, yielding the neat spectrum of oxidized cellulose. Copper-treated samples appear today only partly hydrolyzed and slightly oxidized; the excess of metal (treatment with 1 M solutions) was not fully absorbed by cellulose and appears as a saline deposit of copper chloride on the surface. However, traces of copper oxalate have been detected in the FTIR spectrum [22].

In this study, the effects of accelerated aging under different conditions, including substantially different relative humidity, were considered relative to the strength properties of the paper sheets. These include the mechanical strength, such as breaking length, tear resistance, and bursting strength of the paper samples before and after dry heat aging and hydrothermal aging [5], [10], [12].

De-acidification, oxidation, lignin effect, changes in the composition of the paper have been observed. But the main focus here is what exactly can have the degradation of the paper with its proper impact and also which can show the proper match with natural ageing of the paper.

Paper being the biodegradable component can easily be prone to the different environmental factors under different circumstances. This study further will help us to analyze the process of degradation, the depth of the degraded material, the content change of the paper and the soil, the changes in the microbial contents and the enzyme over in that duration period.

As there are differences which can be observed in the natural ageing and the artificial ageing which can be examined by different dating techniques, but restricted to some documents it becomes critical to analyze the same.

So to find out the variability and the changes in the natural ageing and also the artificial ageing and the degradation of the paper of different qualities to analyze their property and to which extent it can resemble or mimic the natural aged documents and also up to how many days it can stay further longer, since coming in contact with the microorganism can actually destroys the document over the period of time.

This is also concerned with the durability of the destroyed or degraded document and also to find out the solution for preserving these kinds of documents for longer period of time. This review of literature shed the light on the different processes of ageing and also to make an appropriate comparison with the natural and the artificial with their appropriate debating of proof.

Conclusion:

The degradation of paper through physical, chemical, and biological means poses significant challenges to the preservation of historical documents, archival materials, and everyday paper products. Each type of degradation impacts the structural integrity and longevity of paper in unique ways.

Physical degradation involves factors such as light exposure, temperature fluctuations, humidity, and mechanical stress. These factors can cause brittleness, discoloration, warping, and tearing, ultimately compromising the physical structure of the paper.

Chemical degradation is primarily driven by processes such as acid hydrolysis and oxidation. These chemical reactions weaken the cellulose fibers in paper, leading to embrittlement, yellowing, and overall deterioration. Environmental conditions and the presence of pollutants further exacerbate these processes.

Biological degradation is caused by microorganisms like bacteria and fungi, as well as insects. These biological agents produce enzymes and physically consume paper, resulting in structural damage, staining, and material loss. High humidity and poor storage conditions often accelerate biological degradation.

Result and Discussion:

This complete review paper is showing the level, time, the amount of degradation with the appropriate measurement of the degradation. This concludes the various types of degradation shows the various integrity of the paper undergoing in this process. The combined analysis of physical, chemical, and biological degradation processes reveals significant insights into the mechanisms and impacts of these factors on paper integrity. The study highlights the multifaceted nature of paper degradation and underscores the importance of understanding the various factors contributing to it. Future research should continue to explore advanced preservation techniques and materials to further protect paper artifacts from these degrading forces.

Limitations:

1. **Inaccessibility of Historical Data**: Lack of detailed historical data on paper degradation can hinder the development of effective preservation techniques.
2. **Resource Constraints**: Limited funding and resources for research and preservation efforts can restrict the scope and depth of studies.
3. **Interdisciplinary Gaps**: Collaboration between disciplines (chemistry, biology, materials science) is essential but can be challenging due to differing methodologies and perspectives.
4. **Measurement Challenges**: Accurately measuring the physical properties of paper over time can be difficult due to the delicate and variable nature of paper.
5. **Environmental Variability**: Physical degradation is highly influenced by environmental conditions, which can vary widely and unpredictably, making it hard to standardize preservation techniques.
6. **Material Inconsistency**: Differences in paper composition (e.g., fiber type, additives) make it challenging to apply generalized findings across all paper types.
7. **Complex Chemical Interactions**: Paper consists of various chemical compounds, and the interactions between them can be complex and difficult to predict.
8. **Limitations in Chemical Preservation**: While some chemical treatments can slow degradation, they might alter the paper's properties or introduce new degradation pathways over time.
9. **Detection Sensitivity**: Identifying and measuring minute chemical changes in paper can be challenging, requiring highly sensitive analytical techniques.
10. **Microbial Adaptability**: Microorganisms can adapt to different environments, making it hard to develop universal methods to prevent biological degradation.
11. **Difficulty in Identification**: Identifying the specific microbes responsible for degradation can be difficult due to the vast diversity and complexity of microbial communities.
12. **Biosecurity Risks**: Biological treatments to counteract microbial degradation can sometimes pose biosecurity risks or negatively impact the paper or its environment.

Despite these limitations, ongoing research and advancements in technology hold promise for overcoming many of these challenges and improving the preservation and longevity of paper.

Future Directions:

- **Preservation Techniques**: Developing new preservation techniques and treatments to slow down the degradation process will be a priority. This includes using polymer networks to reinforce paper and creating permanent paper with alkaline reserves1.

- **Sustainable Practices**: Research will also focus on sustainable practices in paper production and conservation, aiming to reduce the environmental impact while maintaining the quality and longevity of paper products.

Overall, the future analysis of paper degradation will involve a multidisciplinary approach, combining advanced analytical techniques, environmental studies, and innovative preservation methods to ensure the longevity and integrity of paper materials.

References:

1. Lipinsky E. Perspectives on preparation of cellulose for hydrolysis.
2. JS Arney, J AJ - 1979 - pascal-francis.inist.fr ACCELERATED AGING OF PAPER: THE RELATIVE IMPORTANCE OF ATMOSPHERIC OXIDATION
3. Donetzhuber, A., Johansson, B., Johansson, K., Lovgren, M. & Sarin, E. Analytical characterization of the gas phases in paper and board products. *Nord. Pulp Pap. Res. J.* **14**, 48–60 (1999).
4. Swoboda, P. A. T. & Lea, C. H. The flavor volatiles of fats and fat-containing foods. II-A gas chromatographic investigation of volatile autoxidation products from sunflower oil. *J. Sci. Food Agric.* **16**, 680–689 (1965).
5. B. Havlinova *et al.:* A study of mechanical properties of papers exposed to various methods of accelerated aging. Part I. The effect of heat and humidity on original wood-pulp papers, J. Cult. Herit. (2009)
6. M. Jablonský *et al.:* Considerations on factors influencing the degradation of cellulose in alum-rosin sized paper, Carbohydr. Polym. (2020)
7. C.H. Knill *et al.:* Degradation of cellulose under alkaline conditions, Carbohydr. Polym. (2003)
8. The role of magnesium species in paper de-acidification.: A review, 2023, Journal of Cultural Heritage
9. Strlič, M.; Kolar, J.; Scholten, S. Paper and durability. In *Ageing and Stabilization of Paper*; Strlič, M., Kolar, J., Eds.; Narodna in univerzitetna knjižnica: Ljubljana, Slovenia, 2005.
10. Vizárová, K.; Kirschnerová, S.; Kačík, F.; Briškárová, A.; Šutý, Š.; Katuščák, S. Relationship between the decrease of degree of polymerisation of cellulose and the loss of ground wood pulp paper mechanical properties during accelerated ageing. *Chem. Pap.* **2012**, *66*, 1124–1129.
11. Banik, G.; Brückle, G. *Paper and Water: A Guide for Conservators*; Butterworth-Heinemann: Oxford, UK, 2011.
12. Strlič, M.; Kolar, J.; Kočar, D.; Rychlý, J. Theromo-oxidative degradation. In *Aging and Stabilization of Paper*; Strlič, M., Kolar, J., Eds.; National and University Library: Ljubljana, Slovenia, 2004; pp. 101–120.
13. Barański, A. Ageing kinetics of cellulose and paper. *Restaurator* **2002**, *23*, 77–88.
14. Łojewska, J.; Lubańska, A.; Miśkowiec, P.; Łojewski, T.; Proniewicz, L.M. FTIR in situ transmission studies on the kinetics of paper degradation via hydrolytic and oxidative reaction paths. *Appl. Phys. A* **2006**, *83*, 597–603.
15. Zervos, S. Natural and accelerated aging of cellulose and paper: A literature review. In *Cellulose: Structure and Properties Derivatives and Industrial Uses*; Lejeune, A., Deprez, T., Eds.; Nova Publishing: New York, NY, USA, 2010; pp. 155–203.

16. Jacob, K. *et al.* Potentials for substituting paper by electronic media. In *Lead Markets for Environmental Innovation* (ed. Franz, W.) (Physica - Verlag HD, Heidelberg, 2005).
17. Kipphan, H. Print media and electronic media. In *Handbook of Print Media* (ed. Kipphan, H.) (Springer, New York, 2001).
18. International Standard ISO 9706:1994. I*nformation and Documentatio—Paper for Documents – Requirements for Permanence.*
19. International Standard ISO 11108:1996. *Information and Documentation—Archival Paper – Requirements for Permanence and Durability*.
20. Laguardia, L. *et al.* Investigation of the effects of plasma treatments on bio deteriorated ancient paper. *Appl. Surf. Sci.* **252**, 1159–1166 (2005).
21. Hon, D. & Shiraishi, N. *Wood and Cellulose Chemistry* 2nd edn. (Marcel Dekker, New York, 2001).
22. Calvini, P. & Silveira, M. FTIR analysis of naturally aged $FeCl_3$ and $CuCl_2$—doped cellulose papers. *E-PS* **5**, 1–8 (2008).
23. Adams, J. (2010). "Analysis of printing and writing papers by using direct analysis in real
24. time mass spectrometry," International Journal of Mass Spectrometry 30(1-3),
25. Adams, J. (2011). "Mass de-acidification annotated bibliography 1990-2010,"Library of Congress Preservation Directorate. 1-76.
26. www.loc.gov/preservation/resources/deacid/deacid_bib2011.pdf (accessed 26 Aug 2011).
27. Atalla, R. H. (1999). "3.16. Celluloses," In: Volume 3: Carbohydrates and their Derivatives Including Tannins, Cellulose, and Related Lignins, B. Mario Pinto, Volume Edi-
28. Comprehensive Natural Products Chemistry, Sir Derek Barton, Koji Nakanishi, and Otto Meth-Cohn (eds.), Elsevier
29. J.Q. Zheng *et al.* Non-additive effects of mixing different sources of dissolved organic matter on its biodegradation Soil Biol. Biochem. (2014)
30. S. Tian *et al.* Yeast strains for ethanol production from lignocellulosic hydrolysates during in situ detoxification Biotechnol. Adv. (2009)
31. R.A.A. Muzzarelli *et al.* Current views on fungal chitin/chitosan, human chitinases, food preservation, glucans, pectins and inulin: a tribute to Henri Braconnot, precursor of the carbohydrate polymers science, on the chitin bicentennial Carbohydr. Polym. (2012)
32. Z.Z. Wen *et al.* Preparation and characterization of PEGyated Concanavalin A for affinity chromatography with improved stability J. Chromatogr., B: Anal. Technol. Biomed. Life Sci. (2011)
33. O. Yildirim *et al.* Optimization of oxalic and sulphuric acid pretreatment conditions to produce bio-hydrogen from olive tree biomass Int. J. Hydrogen Energy (2022)
34. A. Esteghlalian *et al.* Modeling and optimization of the dilute-sulfuric-acid pretreatment of corn stover poplar and switchgrass (1997)
35. J.Y. Zhu *et al.* Woody biomass pretreatment for cellulosic ethanol production: technology and energy consumption evaluation Bioresour. Technol. (2010)
36. A. Rodriguez-Chong *et al.* Hydrolysis of sugar cane bagasse using nitric acid: a kinetic assessment J. Food Eng. (2004)
37. A.T.W.M. Hendriks *et al.* Pretreatments to enhance the digestibility of lignocellulosic biomass Bioresour. Technol. (2009)
38. G. Kumar *et al.* Pretreatment and hydrolysis methods for recovery of fermentable sugars from de-oiled Jatropha waste Bioresour. Technol. (2013)

39. Sustainable production of biohydrogen: Feedstock, pretreatment methods, production processes, and environmental impact 2024, Fuel Processing Technology
40. One-pot catalytic hydrolysis of sugarcane bagasse into furfural using a pressurized phosphoric acid/acetone/water system