WOOD DECAY RESISTANCE EMPLOYING NANOPARTICLE PROTECTIVE SYSTEMS

Paula Vanesa ALFIERI[1*] and Guadalupe CANOSA[1]

[1] Laboratorio de Biomateriales, Bioremediación y Biodeterioro, Universidad Tecnologica Nacional, Facultad Regional La Plata, Calle 60 y 124, Berisso, Argentina

Abstract

In this paper, nanoparticle dispersions (nanosilver, copper nano oxide, nanozinc, and nanosilica) have been formulated to be used as protective impregnants. Since all the components of the formulations could be charged according to the pH of the medium, the solutions were formulated with the two profiles of pH=3 and pH=8 (pH changes were handled with the addition of HCl or NH_4OH at the time of application), and the interaction capacity has been analyzed. The nanoparticle dispersion medium was alcohol, and the concentrations ranged from 1 to 3% m/v. Impregnations have been performed by immersion. All formulated systems generated good protection against biotic agents due to chemical and structural modifications of the cell wall. It has been observed that the best performances were given with the presence of nanoparticles, which allowed inferring that the composite formed by nano-wood is bioactive. An issue that is also important is that the systems are easy to apply and very low concentrations are required, which translates into low costs.

Keywords: Wood; Protection; Nanoparticles; Fungi

Introduction

Wood, due to its chemical composition, is very susceptible to the action of biotic and abiotic agents; the three main ones are decay fungi, humidity, and fire.

The attack of biological agents occurs in different parts of the cell wall, depending on the type of aggressor organism and its metabolic characteristics. Wood biodeterioration is a complex phenomenon involving alterations in the physicochemical and mechanical properties of wood [1, 2]. Another issue to consider is the change in the aesthetic appearance of the affected objects. The intensity of the alterations depends on the organic components available, according to the type of substrate and the environmental conditions.

As is well known, the effectiveness of nanoparticles is essentially influenced by the medium in which they are dispersed, the size of the particles in dispersion, and the stability of the dispersion. The main limitation of dispersion can be solved by identifying a suitable medium [3, 4].

Although the nanotechnology boom has been around for years, the approach of using nanomaterials to protect wood is new. Studies are underway to develop new formulations with nanometals and metal nano-oxides as wood preservatives and/or with the incorporation of nanomaterials in wood and preservative coatings to improve their performance [5–11].

* Corresponding author: palfieri@frlp.utn.edu.ar; paulaalfieri@gmail.com

The use of nanometals and nanooxides is justified because they have several advantages over their micrometrical counterparts. The extremely small size increases the overall effective surface area, which in turn increases reactivity and efficiency [12–14]. Another advantage of nanoproducts is that their size is smaller than the size of wood pores and fibres (400-600nm). This makes possible the complete penetration of the formulation into wood [10].

Several studies have been conducted to evaluate the efficiency of different nanoparticles for wood preservation and protection. For example, zinc oxide (ZnO) is widely used in applications due to its UV stabilisation, antimicrobial, and antibacterial properties [15, 16]. Some of these studies focused on the analysis of commercially available dispersions, evaluating whether they leach into the medium and whether they improve wood properties against fungi and termites.

Therefore, in this paper, dispersions of nanoparticles (nanosilver, copper nanooxide, nanozinc, and nanosilica) in alcoholic solutions have been formulated to be used as wood protective impregnants.

Experimental part

Materials

Alcoholic dispersions of nanosilver, copper nanooxide, nanozinc, and nanosilica have been formulated to be used as protective impregnants.

The impregnating solutions were made at pH = 8±0.2 and pH = 3±0.2 since the nanoparticles could charge depending on the pH of the medium. The pH changes have been managed with the addition of HCl or NH_4OH at the time of application, so that the surface modification occurs inside the wood and the interaction capacity has been analysed.

The dispersions of the nanoparticles are alcohol-based, and the concentrations varied from 1 to 3% m/v.

The impregnations have been carried out by immersion (Table 1).

Table 1. Impregnant formulations

Id.	Agent	Solvent	Concentration
nSi	nanoSiO2	80/20 % v/v ethanol/ammonium hydroxide	1 %
nAg	nanoAg		
nZn	nanoZn	90/10 % v/v ethanol/ hydrochloric acid 37%	2 %
nCu	nanoCuO		3 %

Methods

Chemical modification study: Microscopy and FT-IR

SEM has been performed to observe the structure of the cell walls of the wood. In the case of wood impregnated with nanoparticles, the EDAX module has been used to corroborate the presence of nanoparticles. On the other hand, stained sections have been made to be observed under an optical microscope. FT-IR has been performed to confirm whether there was a reaction between the impregnating agents and wood components.

Resistance to biodeterioration

Wood samples have been exposed to fungal species representing each of the rots under laboratory conditions; two of these agents were native (*T. versicolor, P. chaquensis,* and *C. globosum*). The exposure of wood to the degrading agents has been performed following the

general guidelines of ASTM D 2017. The evaluation of the behaviour has been determined by weight loss and by micro- and macro-scale observation of the state of the substrate.

In addition, a visual analysis of the type of biocidal effect of the treatments has been performed. It has been determined that a treatment was fungistatic when there was development in the early stages of the crop but it did not proliferate over time, and fungicidal when there was immediate inhibition of growth.

Results and discussion

In figure 1 (untreated wood), the characteristic structures of conifers could be observed: cells are like perfectly ordered hollow tubes, and the punctures of the tracheid are seen.
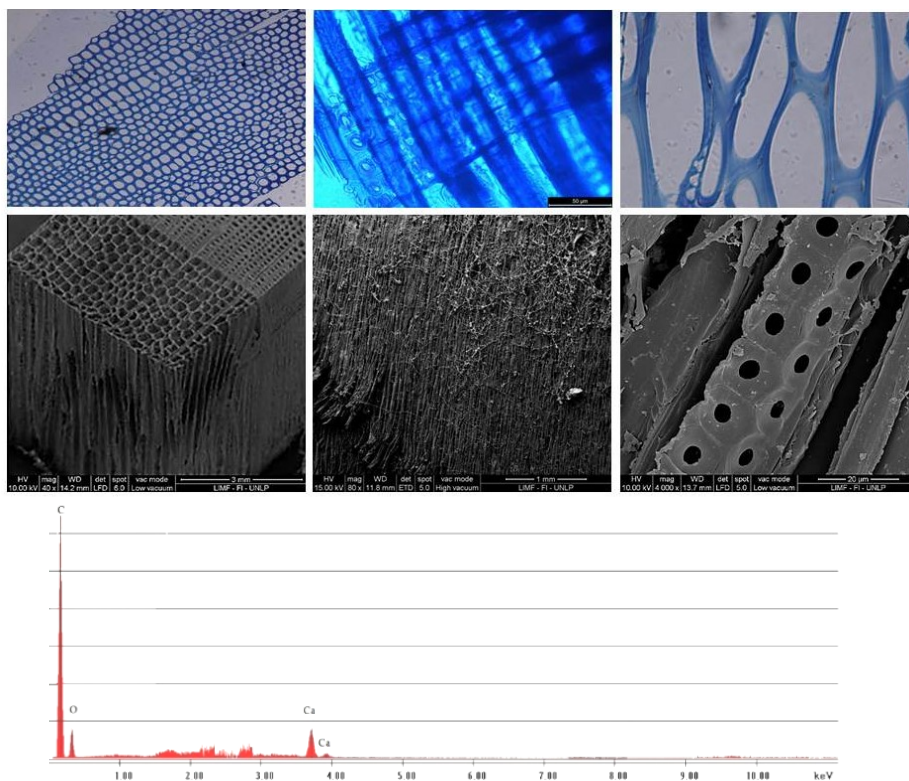
Fig. 1. Optical microscopy with and without fixation (top), Scanning Electron Microscopy (SEM) (middle) and EDAX module of untreated wood (bottom)

As for the treated woods, figure 2 displays SEM images of the nanoparticle-impregnated samples (a–d). Figure 2(I) demonstrates a clear agglomerate of nanoparticles uniformly dispersed in the wood fibers. On the other hand, in figure 2(II), the semiquantitative chemical analysis is observed by using EDAX; the peaks correspond to the nanoparticles, corroborating the efficiency of the impregnations performed.

Differences between the nanoparticles have also been observed. If it is assumed by the criterion that a greater presence of nanoparticles in the fibres implies their greater reactivity in the proposed conditions, it could be affirmed that the most reactive nanoparticles are silica nanodioxide and nanosilver.
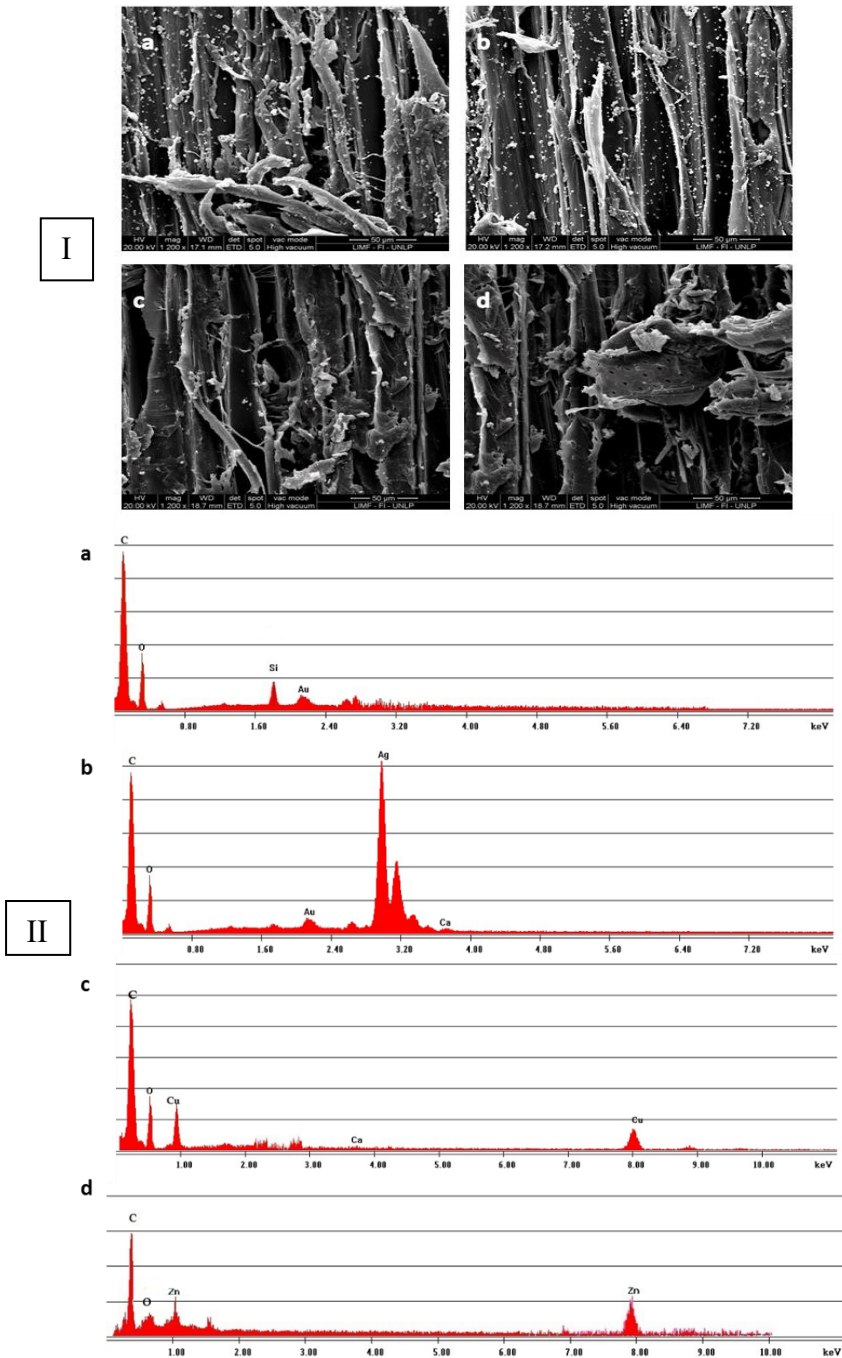
Fig. 2. (I) Scanning electron microscopy (SEM), with (II) EDAX module of samples
impregnated with nanoparticles: **a.** Si; **b.** Ag; **c.** Cu; **d.** Zn

The FT-IR spectra, figure 3, show that wood impregnated with nanosilver and silica
nanodioxide gave peaks of higher intensity in one of the two characteristic peaks of cellulose
(3400 cm^{-1}), which could indicate a higher amount of -OH available, resulting in a higher

reactivity of the system. The SEM observation of a higher particulate in the wood fibres would corroborate the hypothesis.

On the other hand, the FT-IR spectra of the nanoparticle impregnations indicate that the reactivity would be Si-Ag-Cu-Zn (Fig. 1), which was consistent with the higher presence of the particulate around the cell walls of the wood in the SEM images (Fig. 2).
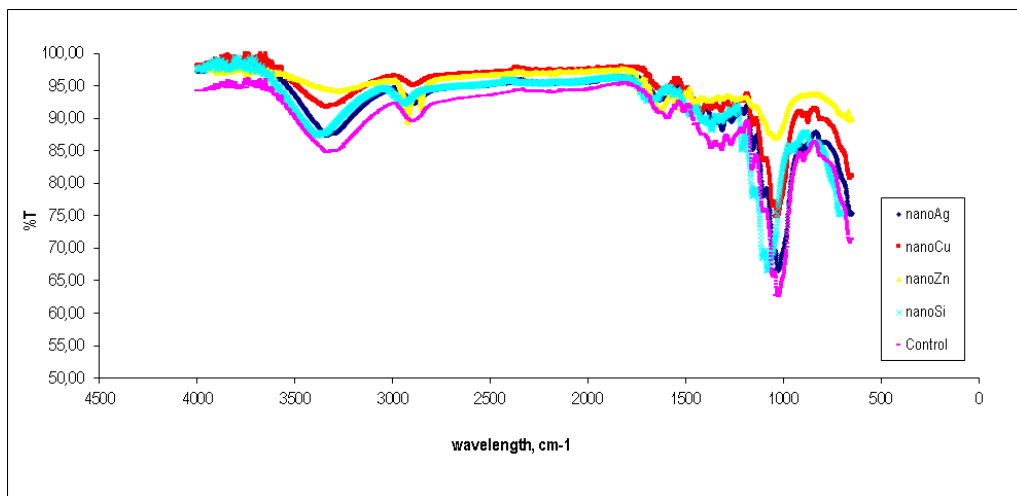

Fig. 3. Furier Transform Infrared Spectroscopy (FT-IR) of the treated with nanoparticle-based impregnants

It has also been mentioned that there was no difference between the spectra at different pHs; therefore, the fundamental reactivity of the system is in the wood and not in the impregnant. It was known that at alkaline pH, the wall structure disintegrates [17, 18]; this implies a greater exposure of the S1–S3 layers of the cell walls, where the highest concentration of crystalline cellulose and hemicelluloses has been found. The highly organised structure was due to the intramolecular formation of hydrogen bonds between the cellulose microfibrils; the hydrogen bonds are very labile and, when faced with any change in electron density, they are modified, generating new bonds [19–22]. The crystalline structure was disorganised by the reactivity and charge of the nanoparticles, increasing the energy of the system. This entropic increase causes a new polymeric microarray between the crystalline cellulose, the amorphous cellulose, and the nanoparticles, generating the chemical change of the cell wall (FT-IR and EDAX) and modifying the structure of the wood fibres (SEM).

In the cell wall, in general, chemical modification occurs between the middle lamella and S2 when the pH is acidic and between S1 and S2 when the pH is alkaline. The latter is due to the fact that at alkaline pH, the middle lamella depolymerizes or becomes laxer, leaving the innermost layers of the cell wall available [23–25]. To corroborate this, thin (1mm) and ultrathin (20m) sections were made by chemical fixation, washing, dehydration with increasing concentrations of alcohol or acetone, inclusion in resin, staining, polymerization, and cutting by microtome. Then, the structure of the cell wall was analysed by optical microscopy (OM), as shown in Figure 4.

For wood treated with silicon nanooxide (all nanoparticles gave similar images), it has been observed, in the first instance, that there were no significant changes in the cell structure between treated and untreated wood (Figs. 2-4); this was due to the low concentrations.

Regarding the difference in pH, it has been detected that treatment with nanoparticles at alkaline pH (f, g, and h) shows partial and/or total disintegration of the middle lamellae and

inclusion of the nanoparticles in the S1 and S2 layers (arrows). In the thin sections j, k, and l, could also observe uniformly distributed along the entire tracheid.
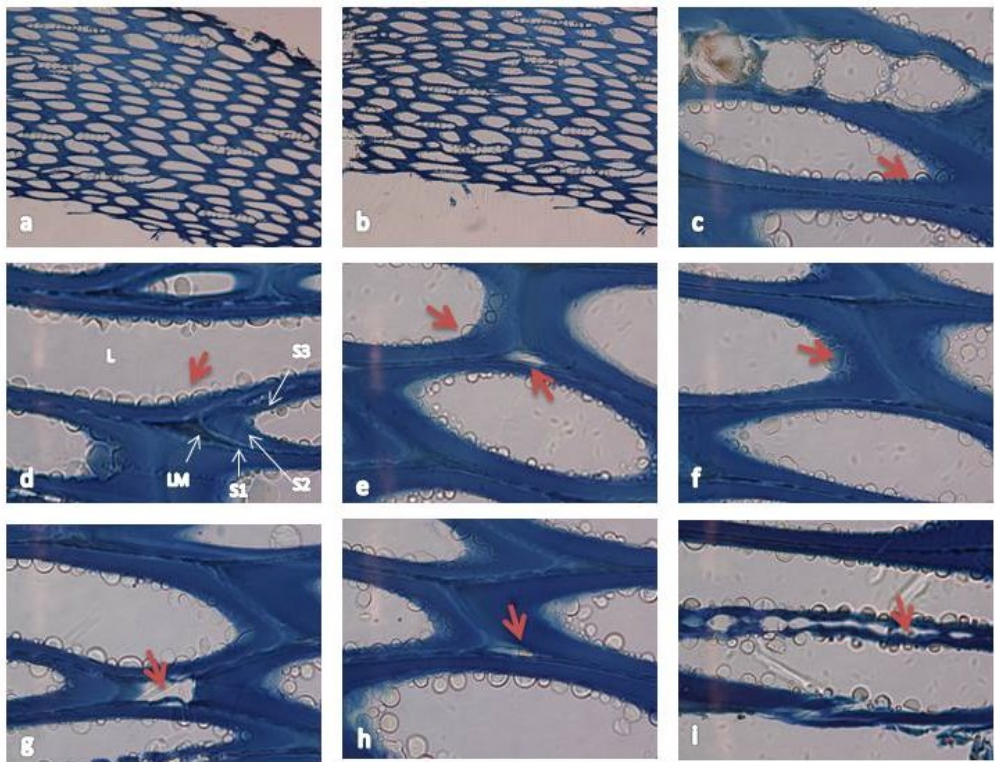
Fig. 4. Optical microscopy of ultrathin preparation (**a-i**) with fixation, dehydration, embedding in epoxy resins, ultramicrotomy, and contrast of nanoparticle treatment General view of: **a.** wood treated with nanosilver; **b.** wood treated with silica nanodioxide; **c-e.** wood treated with nanoparticles at acidic pH; the dates indicate modification in the lamellae or cell lumen (S3); **f-i.** nanoparticles at alkaline pH show modification of the S1 and S2 layers (arrows). *LM: middle lamella; *S1, S2, S3: cell wall layers; *L: cell lumen

Therefore, it has been concluded that the chemical modification at different pHs was completely different at the structural level and cell penetration, which supports the importance of pH management in the use and reactivity of nanoparticles since, with good management of the system variables (vehicle, solvent, pH, etc.), different efficiency could be obtained with the same compounds.

Structural investigations indicate that impregnation could result in the incorporation of inorganic or hybrid materials more than 4mm deep into the structure of poplar or pine wood as precipitates in the cell lumen, but without chemical modification [26]. So, special emphasis has been placed on where the change is occurring and whether the wood has been chemically modified.

According to the FT-IR spectra, the structural localization, and the structural modification of the cellulose, it could be affirmed that chemical modification of the wood occurred.

Resistance to biodeterioration

The results are shown in Figure 4, which represents the percentual weight loss for each treatment after 16 weeks of exposure to different fungi species representing the three most important types of rotting.

In all cases, the treatments reduced the mass loss, regardless of the species to which they had been exposed; therefore, it could be affirmed that all the treatments had the capacity to protect the wood from fungal degradation. The latter leads us to assume that the chemical modification effectively occurs in the different layers of the cell wall since the difference in rotting is basically given by the polymer that the fungi attack.

In the weight loss difference analysis, it could be observed that the most aggressive fungi were *P. chaquensis* (white rot degrades lignin), followed by *T. versicolor* (brown or cube rot degrades cellulose), and finally *C. globosum* (soft rot degrades middle lamellae).

From a global analysis by type of impregnant, it was possible to discriminate which group had the best performance in resistance to biotic degradation. Figure 5 shows the average mass loss after 16 weeks of exposure to the formulations. For this purpose, the weight losses of the three rots were averaged for each formulation. Nanocomposite had mass losses of $8.65\pm1.73\%$; $5.81\pm3.2\%$ and $4.65\pm0.49\%$ for *P. chaquensis, T. versicolor, and C. globosum*, respectively.

Finally, figure 5 also shows the degradation according to the metal in the formulations, where the average mass loss of the three rots has been presented. The list on the left shows the decreasing order of mass loss of the test specimens, i.e., the increasing order of performance in resistance to fungal degradation.
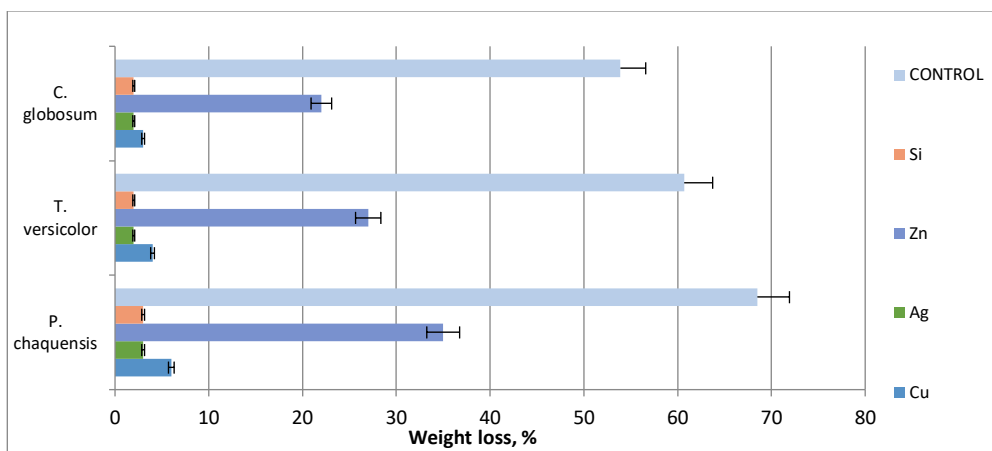

Fig. 5. Percentage weight loss for each treatment at 16 weeks of exposure for each of the species representing the three most important types of rot

In the case of nanoparticles, it has been observed that there is no polymeric formation or microarrays with wood polymers, but there is an orderly arrangement along the cell wall in the different layers. This allows inferring that the hyphae, when requested to generate the grooves between the walls (lamellae) or in the cell walls (depending on the type of rot), would meet the nanoparticles, which would prevent the recognition of the substrate (a chemically different environment), so that penetration would be unfeasible. It could be concluded that, for fungicides, there were two action mechanisms: the non-recognition of the substrate by chemical modification and steric hindrance.

It should be noted that nanozinc formulations had the worst performance. This could be because zinc is an enzymatic cofactor, so it is a compound known to biological organisms. And, since the concentrations used were low, fungi could metabolise them without any inconvenience.

Another case to highlight was the behaviour of silica nanodioxide and nanosilver. They could form an active contact polymer; as could be seen, the nanoparticles were deposited in the

different layers of the cell wall due to their high energy and surface charge (remember that because of their size they have a high surface charge and this increases by the change in pH of the formulations) and, although this energy decreases when it interacts with the wood components, leaves a "back-up" of remaining charge that, when contact with the biological membranes, would have the ability to destabilise them by electronic change of their surface, disintegrating it, or preventing the hyphae from fungal cells from continuing to proliferate [27]. This would prevent the absorption of nutrients and fungal growth.

The chemical modification allowed the generation of a new material with improved durability properties with respect to untreated wood.

Conclusions

It has been observed that the best performances of resistance to biodeterioration were given with the presence of nanoparticles, which allowed inferring that the composite formed by nano-wood is bioactive. Treatments showed excellent protective performance against biotic agents, were easy to apply (immersion), and used low concentrations, which translated into low costs.

In all cases, the nanoparticles were able to enter the wood given the stability of the emulsion by reducing the surface energy of the nanoparticles and forming non-covalent bonds (hydrogen and dipole-dipole bonds) with the alcoholic base. This situation would make the nanoparticles remain stable in the emulsion, avoiding their agglomeration and precipitation. Once they enter the wood, this equilibrium would be lost in the first instance due to the presence of water molecules that initiate the hydrolysis and condensation reactions, and in the second instance due to the attraction of the -OH of the cellulose that has just been attacked by the pH of the solution and the reactivity of the nanoparticles. This increase in the entropic energy of the system causes the whole system to tend to decrease, generating covalent bonds between the nanoparticles and the cellulose in the condensation process, generating a trimetric organic-inorganic-nanometal composite.

It was important to highlight the behaviour of silica nanoparticles, which escapes the observed pattern; this leads to the inference that its protective efficiency is given by the amount of charge and surface energy of this nanoparticle.

Acknowledgments

References

[1] E. Di Carlo, G. Barresi, F. Palla, *Biodeterioration,* Chapter 1 in **Biotechnology and Conservation of Cultural Heritage** (editors: F. Palla, G. Barresi), Springer International Publishing Switzerland, 2017, pp. 1-30, DOI: 10.1007/978-3-319-46168-7.

[2] P.V. Alfieri, M.V. Correa, *Analysis of Biodeterioration Wood Estate: Use Different Techniques to Obtain Images*, **Matéria (Rio de Janeiro)**, **23**(2), Article Number: e-12073, 2018, DOI: 10.1590/S1517-707620180002.0409.

[3] S.V. Gudkov, D.E. Burmistrov, D.A. Serov, M.B. Rebezov, A.A. Semenova, A.B. Lisitsyn, *A Mini Review of Antibacterial Properties of ZnO Nanoparticles*, **Frontiers in Physics**, **9**, 2021, Article Number: 641481, DOI: 10.3389/fphy.2021.641481.

[4] C.C. Borges, G.H.D. Tonoli, T. M. Cruz, P. J. Duarte, T. A. Junqueira, *Nanoparticles-Based Wood Preservatives: The Next Generation of Wood Protection?* **Cerne**, **24**(4), 2018, pp. 397-407, DOI: 10.1590/01047760201824042531**.**

[5] A. Can, S. Palanti, H. Sivrikaya, B. Hazer, F. Stefani, *Physical, Biological and Chemical Characterisation of Wood Treated with Silver Nanoparticles*, **Cellulose**, **26**(8), 2019, pp. 5075-5084, DOI: 10.1007/s10570-019-02416-x.

[6] M. Bak, R. Nemeth, *Effect of Different Nanoparticle Treatments on the Decay Resistance of Wood*, **Bioresources**, **13**(4), 2018, pp. 7886-7899, DOI: 10.15376/biores.13.4.7886-7899.

[7] K.S. Shiny, R. Sundararaj, N. Mamatha, B. Lingappa, *A New Approach to Wood Protection: Preliminary Study of Biologically Synthesized Copper Oxide Nanoparticle Formulation as an Environmental Friendly Wood Protectant Against Decay Fungi and Termites*, **Maderas-Ciencia y Tecnología**, **21**(3), 2019, pp. 347-356. DOI: 10.4067/S0718-221X2019005000307

[8] A.N. Papadopoulos, H.R. Taghiyari, *Innovative Wood Surface Treatments Based on Nanotechnology*, **Coatings**, **9**(12), Article Number: 866, 2019, DOI: 10.3390/coatings9120866.

[9] K.S. Shiny, S. Nair, N. Mamatha, R. Sundararaj, *Decay Resistance of Wood Treated with Copper Oxide Nanoparticles Synthesised Using Leaf Extracts of Lantana Camara L. and Nerium Oleander L.*, **Wood Material Science & Engineering**, **17**(6), 2021, pp. 727-733, DOI: 10.1080/17480272.2021.1934728

[10] S. Nair, K.K. Pandey, B.N. Giridhar, G. Vijayalakshmi, *Decay Resistance of Rubberwood (Hevea Brasiliensis) Impregnated with Zno and CuO Nanoparticles Dispersed in Propylene Glycol*, **International Biodeterioration & Biodegradation**, **122**, 2017, pp. 100-106, DOI: 10.1016/j.ibiod.2017.05.008

[11] S. Holy, A. Temiz, G.K. Demirel, M. Aslan, M.H.M. Amini, *Physical Properties, Thermal and Fungal Resistance of Scots Pine Wood Treated with Nano-Clay and Several Metal-Oxides Nanoparticles*, **Wood Material Science & Engineering**, **17**(3), 2022, pp. 176-185, DOI: 10.1080/17480272.2020.1836023

[12] L.L. Duffy, M.J. Osmond-McLeod, J. Judy, T. King, *Investigation into the Antibacterial Activity of Silver, Zinc Oxide and Copper Oxide Nanoparticles Against Poultry-Relevant Isolates of Salmonella and Campylobacter*, **Food Control**, **92**, 2018, pp. 293-300, DOI: 10.1016/j.foodcont.2018.05.008.

[13] R.J.G. Johnson, J.D. Schultz, B.J. Lear, *Photothermal Effectiveness of Magnetite Nanoparticles: Dependence Upon Particle Size Probed by Experiment and Simulation*, **Molecules**, **23**(5), 2018, Article Number: 1234, DOI: 10.3390/molecules23051234

[14] J. de Almeida, B.C. Cechella, A.V. Bernardi, A. de Lima Pimenta, W.T. Felippe, *Effectiveness of Nanoparticles Solutions and Conventional Endodontic Irrigants Against Enterococcus Faecalis Biofilm*, **Indian Journal of Dental Research: Official Publication of Indian Society for Dental Research**, 29(3), 2018, pp. 347-351, DOI: 10.4103/ijdr.IJDR_634_15.

[15] H. Yari, M. Rostami, *Enhanced Weathering Performance of Epoxy/Zno Nanocomposite Coatings Via Functionalization of ZnO UV Blockers with Amino and Glycidoxy Silane Coupling Agents*, **Progress in Organic Coatings**, **147**, 2020, Article Number: 105773, DOI: 10.1016/j.porgcoat.2020.105773.

[16] M. Turemis, I.C. Keskin, M.I. Kat, R. Kibar, K. Sirin, M. Canli, V. Corumlu, A. Cetin, *Optimizing Optical and Structural Properties of Nanocomposites by ZnO and BP-3*, **Russian Journal of Physical Chemistry A**, **92**(9), 2018, pp. 1762–1771, DOI: 10.1134/S0036024418090315

[17] G. Banvillet, G. Depres, N. Belgacem, J. Bras, *Alkaline Treatment Combined with Enzymatic Hydrolysis for Efficient Cellulose Nanofibrils Production*, **Carbohydrate Polymers**, **255**, 2021, Article Number: 117383, DOI: 10.1016/j.carbpol.2020.117383

[18] N. Le Moigne, K. Jardeby, P. Navard, *Structural Changes and Alkaline Solubility of Wood Cellulose Fibers after Enzymatic Peeling Treatment*, **Carbohydrate Polymers**, **79**(2), 2010, pp. 325-332, DOI: 10.1016/j.carbpol.2009.08.009

[19] C. Hill, M. Altgen, L. Rautkari, *Thermal Modification of Wood - A Review: Chemical Changes and Hygroscopicity*, **Journal of Materials Science**, **56**(11), 2021, pp. 6581-6614, DOI: 10.1007/s10853-020-05722-z

[20] R. Liang, Y.H. Zhu, X. Yang, J.S. Gao, Y.L. Zhang, L.P. Cai, *Study on the Ultrastructure and Properties of Gelatinous Layer in Poplar*, **Journal of Materials Science**, **56**(1), 2021, pp. 415-427, DOI: 10.1007/s10853-020-05226-w

[21] M.S. Mahr, T. Hubert, I. Stephan, M. Bucker, H. Militz, *Reducing Copper Leaching from Treated Wood by Sol-Gel Derived TiO_2 and SiO_2 Depositions*, **Holzforschung**, **67**(4), 2013, pp. 429-435, DOI: 10.1515/hf-2012-0105

[22] M. Fujita, H. Harada, *Ultrastructure and Formation of Wood Cell Wall*, Chapter 1 in **Wood and cellulosic chemistry**. **Second edition revised and expanded**, (editors; DNS Hon, N. Shiraishi), CRS Press, 2000, pp. 1-49, ISBN: 0-8247-0024-4

[23] G. Banvillet, G. Depres, N. Belgacem, J. Bras, *Alkaline Treatment Combined with Enzymatic Hydrolysis for Efficient Cellulose Nanofibrils Production*, **Carbohydrate Polymers**, 255, 2021, article number: 117383, DOI: 10.1016/j.carbpol.2020.117383.

[24] L.M. Zhang, T.T. You, T. Zhou, L. Zhang, F. Xu, *Synergistic Effect of White-Rot Fungi and Alkaline Pretreatments for Improving Enzymatic Hydrolysis of Poplar Wood*, **Industrial Crops and Products**, **86**, 2016, pp. 155-162, DOI: 10.1016/j.indcrop.2016.03.041.

[25] S. Nenkova, T. Vasileva, K. Stanulov, *Production of Phenol Compounds by Alkaline Treatment of Technical Hydrolysis Lignin and Wood Biomass*, **Chemistry of Natural Compounds**, **44**(2), 2008, pp. 182-185, DOI: 10.1007/s10600-008-9009-z.

[26] T. Hubert, M.S. Mahr, *Sol-gel Wood Preservation*, chapter in **Handbook of Sol-Gel Science and Technology. Processing, Characterization and Applications. Second edition**, (editors: L. Klein, M. Aparicio, A. Jitianu), Springer International Publishing AG, 2018, pp. 2795-2842, DOI: 10.1007/978-3-319-32101-1.

[27] L.L. Wang, C. Hu, L.Q. Shao, *The Antimicrobial Activity of Nanoparticles: Present Situation and Prospects for the Future*, **International Journal of Nanomedicine**, **12**, 2017, pp.1227–1249, DOI: 10.2147/IJN.S121956.