

# CONTRIBUTIONS CONCERNING THE TREATMENT OF BIRCH VENEER WITH LIGNINS MODIFIED AND COPPER COMPOUNDS

## CONTIBUȚII PRIVIND TRATAREA FURNIRULUI DE MESTEACĂN CU LIGNINE MODIFICATE ȘI COMPUȘI AI CUPRULUI

CĂPRARU Adina-Mirela<sup>1</sup>, UNGUREANU Elena<sup>1</sup>,  
TRINCĂ Lucia Carmen<sup>1</sup>, POPA I. V.<sup>2</sup>  
e-mail: mirelacapraru@yahoo.com

**Abstract.** *This work presents experimental data on the interaction of birch veneer and copper complexes of some commercial products, lignin's Protobind unmodified and modified by hydroxymethylation and epoxydation. The treatments with these compounds were based in a first stage for its successful immersion in solutions of copper chloride or tetra amino copper hydroxide, followed by impregnation with unmodified or modified lignin's, with a concentration of 5% dissolved in ammonia solution or furfuryl alcohol to achieve in situ of the complexes between the two partners. The efficiency of the treatment was evaluated consecutive by periodically evolution with distilled water to determine the veneer samples impregnated, UV-VIS absorption elution products, and their toxicity experiments by determining the germination of tomato seeds. The results show that the stability of treatment depends on the nature of lignin compound and its ability to copper ion complexity, which ensures optimal interaction with the wood surface.*

**Key words:** lignin, hydroxymethylation, epoxydation, veneer, biocides.

**Rezumat.** *Lucrarea prezintă date experimentale privind interacțiunea furnirul de mesteacăn și complexii cuprici ai unor produse ligninice comerciale - Protobind nemodificate și modificate prin hidroximetilare și epoxidare. Tratamentele cu acești compuși aplicate furnirului de mesteacăn s-au bazat într-o primă etapă pe imersarea succesivă a acestuia în soluții de clorură de cupru sau hidroxid tetraaminocupric, urmată de impregnarea cu lignine nemodificate sau modificate, de concentrație 5 % dizolvate în soluție de amoniac sau alcool furfurilic, pentru realizarea în situ a complexilor între cei doi parteneri. Eficiența tratamentului a fost evaluată consecutiv prin eluarea periodică cu apă distilată a epruvetelor de furnir impregnate și determinarea absorbției în UV-VIS a produselor de eluție, precum și prin determinarea toxicității acestora în experimentele de germinare a semințelor de tomate. Rezultatele obținute evidențiază că stabilitatea tratamentului depinde de natura compusului ligninic și capacitatea sa de complexare cu ionul cupric care asigură interacțiunea optimă cu suprafața lemnoasă.*

**Cuvinte cheie:** lignină, hidroximetilare, epoxidare, furnir, biocizi.

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<sup>1</sup> University of Agricultural Sciences and Veterinary Medicine Iasi, Romania

<sup>2</sup> "Gheorghe Asachi" Technical University Iasi, Romania

## INTRODUCTION

Lately, one may notice constant interest regarding finding solutions for increasing the resistance of wooden products towards destructive agents, through methods that are acceptable from a viewpoint of compatibility with the environment. It is known that “*products of secondary metabolism of plants*”, namely lignin and polyphenols, are included in the defense mechanisms that plants have developed against pathogenic or non-pathogenic microorganisms. On the other hand, the aforementioned compounds may result as subproducts of the industry of chemically treated wood or from technologies of complex biomass capitalization. On this direction, interaction between birch veneer and a series of biocide compounds has been studied (Ungureanu E. et al., 2007, 2008; Căpraru A. M., 2010). Large scale use of this lignocellulose compound in various fields and its relatively reduced stability during the action of environmental factors implies usage of chemical compounds in order to ensure partial or total protection against the attack of biological agents. Products that are toxic to microorganisms and insects but largely incompatible with the environment are presently used for wood protection. There are known chemical protection agents in water system, their efficiency relying on the presence of copper. Part of the copper ions are fixated in the wooden sub layer through the hydroxyl or carboxylic groups in the wood, which are found in ionized state under conditions of high pH (Măluțan Th. et al., 2007). Considering the resistance of lignin at the attack of biotic agents and the toxicity of copper ions, the study hereby targeted the way in which the biostability of birch wood is influenced by systems created from regenerable products: chemically modified/unmodified lignin (Căpraru A.M. et al., 2008, Măluțan Th. et al., 2007, 2008) in the absence or presence of copper ions.

## MATERIAL AND METHOD

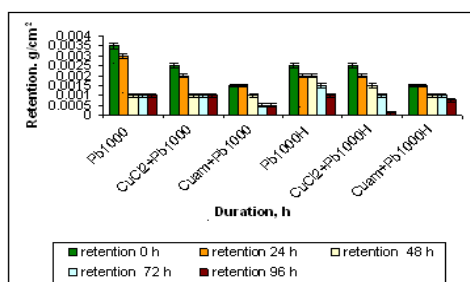
We used birch veneer samples (1x10 cm) and five lignin types: wheat straw lignin (L1), grass lignin (L2) and three commercial products: Protobind 1000 (Pb1000), Protobind 2000 (Pb2000), Protobind 3000 (Pb3000), 5 % dissolved in ammonia 0.1 N or alcohol furfuryl of 5% concentration. Unmodified products (marked as –N) offered by Granit Company (Switzerland) during Ecobinders research program as well as hydroxymethylated and epoxydation lignin in lab conditions (marked as –H and –E) were tested. To this end birch veneer samples were weighed in advance in order to determine the weight of each sample before and after impregnation with established solutions. Impregnation was performed with 5% solutions of unmodified and hydroxymethylated and epoxydation lignin products obtained by dissolving them in a 0.1 N ammonia solution or furfuryl alcohol. After impregnating with cupric solutions (cupric chloride ( $\text{CuCl}_2$ ), Cuproxam (Cuam) and lignin products, the samples were dried in laboratory conditions (25 °C) and were weighed to establish mass increase. The stability of the treatment was evaluated by immersing the samples in distilled water for varying durations (24, 48, 72 and 96 hours) and collecting elutes. After elution we have determined samples' mass loss and the separate elutes were characterized with respect to UV absorption at 280 nm (those derived from samples of lignin or derivatives) and toxicity in tomato seed germination. The UV absorption was

determined using UV/VIS - Jasco 550 spectrophotometer. To assess the toxicity degree tomato seeds germination tests were carried out. Thus, in Petri dishes with 10 cm in diameter the filter paper was introduced as support along with 10 mL of elute.

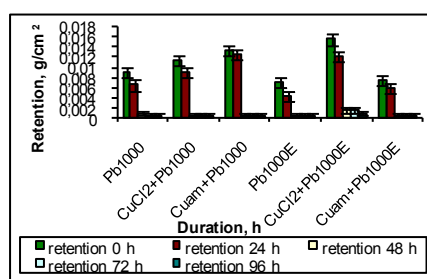
Thus, in Petri dishes with 10 cm in diameter of, were introduced as filter paper and 10 mL of elute, adding the tomato after 10-seed to determine the percentage germinated seeds (as a measure of toxicity) after 96 hours was used as a control sample of distilled water. The experimental data were subjected to statistical processing using The Unscrambler software.

## RESULTS AND DISCUSSIONS

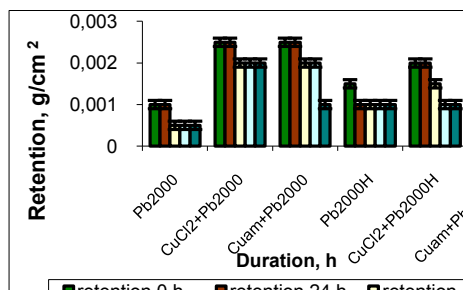
The data presented in figure 1 and 2 refer to treatments with products Protobind 1000 modified lignin is, modified and their complexes with cupric ions.



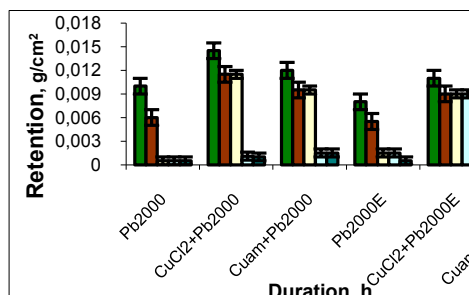
**Fig. 1** - Variation of retention degree of Pb1000 lignin unmodified/hydroxymethylated and their complex with copper ions depending on the elution duration



**Fig. 2** - Variation of retention degree of Pb1000 lignin unmodified/epoxydated and their complex with copper ions depending on the elution duration



**Fig. 3** - Variation of retention degree of Pb2000 lignin unmodified/hydroxymethylated and their complex with copper ions depending on the elution duration



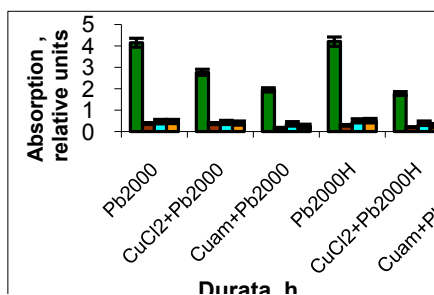
**Fig. 4** - Variation of retention degree of Pb2000 lignin unmodified/epoxydated and their complex with copper ions depending on the elution duration

In the case of test tubes treated with modified Protobind products and copper complexes, a larger quality of lignin is retained by the veneer surface, because of increased functionality. Moreover, this fact is also confirmed by a greater stability of copper ion complexes of these derivatives. The amount of lignin retained on the wooden surface reaches around  $0.0015 \text{ g/cm}^2$  for most veneer samples treated with modified lignins. The use of these in the presence of copper

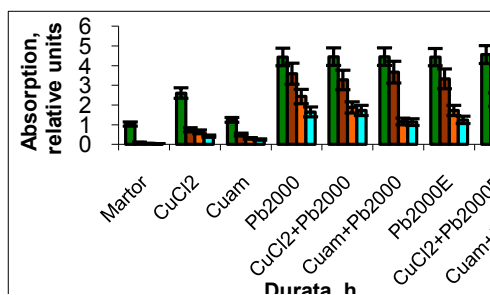
ions leads to a retention rate growth reaching  $0.0035\text{g}/\text{cm}^2$  (figures 3 and 4). These studies have been concluded by noticing that the retention level is influenced by the products' nature, by their functionality and complexity degree. The modification of lignin products plays in this case a very important role in wood protection, these products sticking efficiently to the surface and thus offering increased stability in case of increased atmospheric humidity as well as repeated elution.

### Characterization of watery extracts

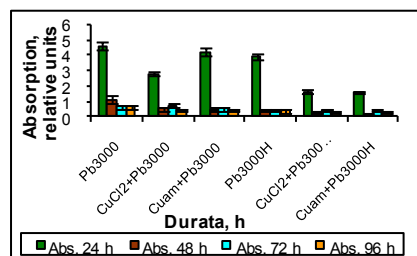
In figures 5 and 6, time-dependent absorption variation in UV-VIS of elution products is presented for samples treated with unmodified/modified lignins and cupric compounds.



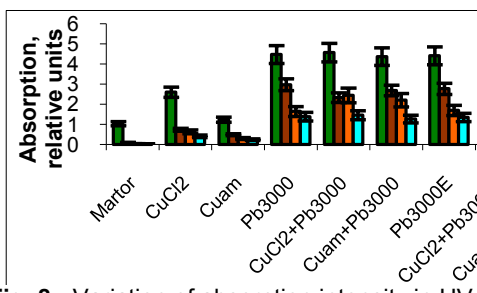
**Fig. 5** - Variation of absorption intensity in UV of leachates depending on elution time for the samples treated with Pb 2000 and Pb2000H lignin and their complexes with copper ions



**Fig. 6** - Variation of absorption intensity in UV of leachates depending on elution time for the samples treated with Pb 2000 and Pb2000E lignin and their complexes with copper ions



**Fig. 7** - Variation of absorption intensity in UV of leachates depending on elution time for the samples treated with Pb3000 and Pb3000H lignin and their complexes with copper ions

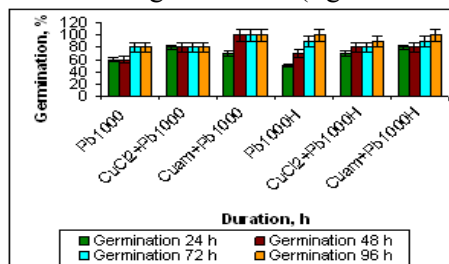


**Fig. 8** - Variation of absorption intensity in UV of leachates depending on elution time for the samples treated with Pb3000 and Pb3000E lignin and their complexes with copper ions

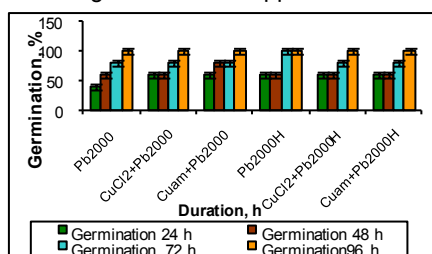
Most of the studied products elude after the first 24 hours, and then the absorption values remain constant until the end of the treatment. Absorption values are low in the case of modified Protobind samples and their complexes with copper ions where a direct correlation between retention and absorption value is also noticed (figures 7 and 8).

## Determination of the toxicity of solutions eluted from unmodified and modified lignin extraction with distilled water results

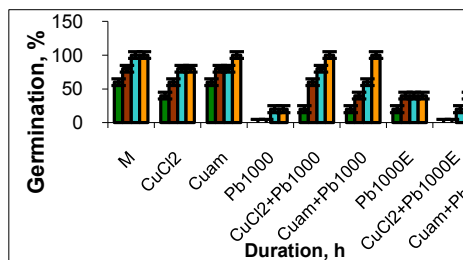
Solutions separated after various durations of successive water immersion of birch veneer test tubes were tested from a toxicity viewpoint in experiments of tomato seed germination (figures 9-12).



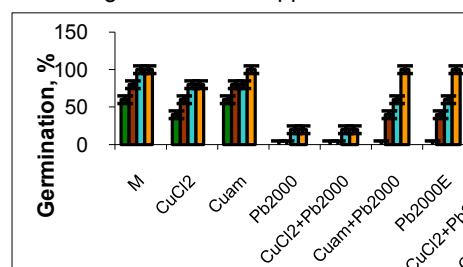
**Fig. 9** - The evolution of germination degree of tomato seeds in the presence of leachates resulted after the elution of the veneer treated with Pb1000 and Pb1000 H lignin and with copper ions



**Fig. 11**-The evolution of germination degree of tomato seeds in the presence of leachates resulted after the elution of the veneer treated with Pb 2000 and Pb2000H lignin and with copper ions



**Fig. 10** - The evolution of germination degree of tomato seeds in the presence of leachates resulted after the elution of the veneer treated with Pb1000 and Pb1000E lignin and with copper ions



**Fig. 12** - The evolution of germination degree of tomato seeds in the presence of leachates resulted after the elution of the veneer treated with Pb1000 and Pb1000H lignin and with copper ions

The toxicity of elution products is insignificant in the case of products eluted after 72 and 96 hours, and seed germination reaches 100% in most cases. The best percentage has been achieved at solutions resulted from elution of test tubes that were treated with hydroxymethylated lignin's and copper based compounds, where the germination capacity presents values above 70% from the first solutions resulted after 24 hours. Thus, after the experiments, it results that there is a strong tie between the three parameters measured within this study. It can be affirmed that there are direct correlations between retention and the absorbance value determined in the UV-VIS field, but also between the germination capacity and the other two studied parameters. From the registered data, it results that the toxicity of elution products varies depending on the used chemical agent and toxic effects are reduced along with the decrease of concentration so they cannot be considered significant.

## CONCLUSIONS

1. The stability of treatments that were performed with modified lignin's and their complexes with copper ions was kept track of by successive elution with water of the wooden support impregnated with the aforementioned chemical species and it was concluded that the retention level is influenced by the nature of the products, by their functionality and their complexation degree.

2. By UV-VIS, spectroscopy there was obtained a direct correlation between the absorption of elution products and the retention degree. Significant draining of treatment agents is encountered during the first 24 hours, and then there are no more important losses.

3. The germination capacity of tomato seeds in the presence of solutions resulted from successive water extraction of wooden support treated with products with potentially biocide action does not highlight any significant toxic effects; hence the existence of the premise of achieving biocide systems compatible with the environment.

## REFERENCES

1. **Cazacu G., Totolin M. I., 2010** - *Lignina, sursă de materii prime și energie*. Ed. Pim, Iasi, 148-170;
2. **Căpraru Adina Mirela, Ungureanu Elena, Popa V.I., 2008** - *Aspects concerning the interaction between birch veneer and different compounds with biocide potential action*. EEMJ, (7), 5, 525-530;
3. **Căpraru Adina Mirela, Ungureanu Elena, Popa V.I., 2009** - *Aspects concerning some biocides systems based on natural aromatic compounds aromatic compounds and their copper complexes*. 15<sup>th</sup> International Symposium on Wood, Fibre and Pulp Chemistry, Oslo, Norway, 50-55;
4. **Măluțan Th., Nicu R., Popa V.I., 2008** - *Contribution to the study of hydroxymethylation reaction of alkali lignin*. Bio/Resources (1), 13-20;
5. **Măluțan Th., Popa V. I., 2007** - *Protecția lemnului prin metode specifice*. Ed. Cermi, Iași, 141-154;
6. **Ungureanu Elena, Popa V. I., 2007** - *On the biological stability of wood in the presence some bioprotection agents*. Cellulose Chemistry and Technology, 41(7-8), p. 429-436, 2007;
7. **Ungureanu Elena, Căpraru Adina Mirela, Popa V.I., 2008** - *Aspects concerning some bioprotection agents based on natural aromatic compounds and their copper complexes*. Coste 50/ILI joint meeting, 27-29 october, Elveția, p. 40;