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Improving the decay resistance of wood by nanoparticles

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ABSTRACT

Using nanomaterials to create a new generation of novel cost-effective products is a key issue nowadays in several industries (plastics, chemistry, etc.). Nano-preparations of metals, such as zinc, silver or copper, may possess unique characteristics that are very different from the characteristic of the elemental metal or its formulations. Nanotechnology presents a tremendous opportunity to boost the field of wood preservation through implementing modern and unique metal biocides with improved properties. This study evaluated the efficacy of five different nanoparticles (zinc oxide, zinc borate, silver, copper oxide, copper borate) applied with different concentrations against Coniophora puteana and Coriolus versicolor. Tests were carried out with two different wood species (beech and pine), according to the standard EN 113. Furthermore, tests according to EN 84 were carried out to investigate the resistance of the nanoparticles against leaching. Copper nanoparticles did not provide effective protection, or only low protection against the investigated wood-decaying fungi. Zinc oxide showed good protection against the white rot Coriolus versicolor even at the lowest concentration (1 %(m/m)), while it only showed good protection against the brown rot Coniophora puteana at the highest investigated concentration (5 %(m/m)). The use of silver nanoparticles (in colloidal form) did not give protection against the brown rot Coniophora puteana, while against the white rot Coriolus versicolor it was effective even at the lowest concentration (0,5 %(m/m)). Zinc borate and copper borate nanoparticles provided high protection against both of the investigated decay fungi even at low concentrations (1 and 0,5 %(m/m), respectively). Overall, the results are diverse regarding the efficiency of the investigated nanoparticles against a brown and a white rot fungus. It can be stated that, in some cases, one of the investigated fungi showed tolerance to the nanoparticles, thus, these treatments are not recommended for general use. The generally effective nanoparticle treatments were the combinations containing borate in its chemical structure. However, only zinc oxide and silver nanoparticles showed good resistance against leaching. Unfortunately, zinc borate and copper borate showed low resistance against leaching, as after leaching the treated samples showed similar decay compared to the control samples. Thus, only zinc oxide at higher concentrations (5 %(m/m)) provided effective protection also after leaching.

1 INTRODUCTION

The utilization of wood contributes to sustainable development. The technical properties of most European wood species are in many aspects behind some competing materials, which originate from sources that are disadvantageous in aspect of sustainability (endangered tropical wood species, plastics, etc.). Utilizing nanomaterials to create a new generation of novel cost-effective products is a key issue identified by the forest products industry (TAPPI 2005). However, the utilization of nanoparticles to improve the properties of wood is not widely investigated recently. On the other hand, a lot of promising results were achieved with the use of nanoparticles in relation to the mechanical, combustion, hydrophobic and some other properties of different polymers, papers or textiles (Wang et al. 2006, Csóka et al. 2007; Chen and Yan 2012, Nypelö et al. 2012; Jiang et al. 2011; Sun et al. 2007, Textor and Mahltig 2010). Recently, there is only limited information available about the utilization of nanoparticles to improve the wood properties, but almost all results are positive. With the use of different nanoparticles, the moisture uptake is reducible, UV-protection, mechanical properties and durability are improvable (Rassam et al. 2012; Niemz et al. 2010; Yu et al. 2011; Mahltig et al. 2008). In some cases, fire resistance could be improved as well (Shabir Mahr et al. 2012). According to the careful examination of the results, mentioned above, different nanoparticles (different titanate nanotubes and nanowires, nano-sized zinc, titan dioxide, montmorillonite and other nanoclays, etc.) can be selected for the research. According to our earlier study in this field, zinc nanoparticles have an effective fungicide effect also by using very low concentrations (Bak et al. 2012).

A further study that evaluated silver formulations in combination with copper or zinc nano-metals against termites showed inhibition of termite feeding by zinc nanoparticles with and without silver (Green & Arango 2007). The potential activity of copper nanoparticles for wood protection was investigated by Weitz et al. (2011) using mini-agar slant and wood block tests with *Gloeophyllum trabeum* or *Trametes versicolor*. Weiz et al. (2011) reported that nano-copper has potential as a wood protectant, but much more research would be required to understand the properties of this material. Applying a nano-silver treatment before densification can result in optimal physical and mechanical properties of densified poplar wood (*Populus alba*) (Rassam et al. 2011). Over 20 field stake trials were carried out in well-known sites such as Gainesville, Florida or Hilo, Hawaii and the Dorman and Saucier sites in Mississippi, as well as in Australia and New Zealand. In addition, 4 ground proximity tests from Hawaii and 3 ground proximity tests from Mississippi were conducted. Micronized formulations of copper showed good performances in all field trials with standardized tests. In some tests, they performed better than the amine soluble counterparts, which were used as a control test (McIntyre & Freeman 2011).

Provided that nanoparticles of copper, boron and zinc show original properties, they may play an important role for developing new wood protection systems. In preliminary studies on nano-metal preparations, nano-zinc oxide demonstrated some unique characteristics deemed worthy of further study. Nano-preparations of metals such as zinc may possess unique characteristics that are very different from the characteristics of the elemental metal.

To improve the wood properties, immersion or mainly impregnation can be the most adequate process. In case of some nanoparticles, it is not clear already whether it is applicable and effective for improving the wood properties. On the other hand, the mode of the nanoparticle preparation might also have influence on the efficiency, because of different particle sizes and formulations. For that very reason, it is necessary to analyze the relation between these nanoparticles and wood. Nanoparticles have to be in a solution, dispersion or suspension to make possible the impregnation of wood, therefore the effect of base materials is also an influencing factor.

The objective of this study was to evaluate the preparation of different metal nanoparticles for the capacity to prevent decay by a brown rot fungus *Coniophora puteana* and the white rot fungus *Coriolus versicolor*. The novelty of the planned research was to investigate some nanoparticles which affect wood durability. An important goal of the study was to investigate the leaching resistance of the nanoparticles from wood material. Instead of surface treatments, a full cross-section treatment was planned, which could lengthen the service life of wooden products. An important objective was the expressive improvement of the durability of European wood species.

2 MATERIALS AND METHODS

2.1 Preparation of nanoparticles

Five different nanoparticles were tested in this study, namely zinc oxide (ZnO), zinc borate (ZnB), silver (Ag), copper (Cu) and copper borate (CuB). The suspensions/colloids described in the following paragraphs were used for the treatment of the samples directly.

Colloidal ZnO nanoparticles were prepared by hydrolyzing zinc acetate dihydrate in the basic KOH-methanol solution (Sun et al. 2007). With this method, ZnO nanoparticles with the average size of 3-5 nm were prepared. The concentration of the basic ZnO suspension was 5 %(m/m). This suspension was divided into three parts. One part remained in this concentration, one part was diluted with methanol to the concentration 2 %(m/m), and one part was diluted to the concentration 1 %(m/m).

The zinc borate nanoparticle suspension was produced by using a water-based mixture of 1,0 mol/dm^3 borax decahydrate and 1,0 mol/dm^3 zinc nitrate hexahydrate at 70 °C for 2 hours reaction time (Gönen 2009). With this method, zinc borate nanoparticles with the average size of 100-200 nm were prepared. The concentration of the basic ZnB nano-suspension was 2 %(m/m). This suspension was divided into three parts. One part remained in this concentration, one part was diluted with distilled water to the concentration 1 % (m/m), and one part was diluted to the concentration 0,5 % (m/m).

Silver nanocubes were prepared in aqueous solution using polyvinyl-pyrrolidon (PVP) as a protecting agent. Silver nitrate precursor was added into deionized water containing PVP in order to obtain silver colloid in the concentration 2 % (m/m) Ag. Then the aqueous solution of ascorbic acid in the molar ratio $AgNO_3/C_6H_8O_6$ = 1.2 was added dropwise into the silver nitrate solution and stirred for 1 h (Zielinska et al. 2009). With this method, Ag nanoparticles with the average size of 80-100 nm were prepared. The concentration of the basic Ag nano-suspension was 2 % (m/m). This suspension was divided into three parts. One part remained in this concentration, one part was diluted with distilled water to the concentration 1 %(m/m), and one part was diluted to the concentration 0,5 %(m/m).

In a synthesis of copper nanoparticles, aqueous solution of 0,4 M L-ascorbic acid and 0,8 M polyvinyl-pyrrolidone was directly mixed with another aqueous solution of 0,01 M copper (II) nitrate (anhydrous) and 0,8 M PVP under stirring. Then the mixture was kept in constant 45 °C without any inert gas protection. After 1 h, the initial precursor solution with light blue color changed to red colloidal slurry, indicating the formation of Cu nanoparticles. After 3 h, there was no further color change, and the process was stopped (Wu et al. 2006). With this method, Cu nanoparticles with the average size of 2-4 nm were prepared. The concentration of the basic Cu nano-suspension was 2 %(m/m). This suspension was divided into three parts. One part remained in this concentration, one part was diluted with distilled water to the concentration 1 %(m/m), and one part was diluted to the concentration 0,5 %(m/m).

2 M copper (II) nitrate (anhydrous) and 0,1 M borax decahydrate water-based solutions were mixed in borax:copper proportion of 0,25 to prepare nano-sized copper borates. Dilute $Cu(NO_3)_2$ and borax solutions were mixed at 70 °C to prevent particle growth and agglomeration and to obtain nano-sized copper borate particles. Copper (II) solutions were added drop by drop to borax solutions which were stirred at 450 rpm using a magnetic stirrer (Alp et al. 2014). With this method, CuB nanoparticles are formed in planar geometry with average dimensions of 2 μm length, 1 μm width and 100 nm thickness. Concentration of the basic CuB nano-suspension was 2 %(m/m). This suspension was divided into three parts. One part remained in this concentration, one part was diluted with distilled water to the concentration 1 %(m/m), and one part was diluted to the concentration 0,5 %(m/m).

2.2 Leaching test

The leaching test was carried out according to the standard EN 84. The impregnation was carried out according to the standard EN 113. For each concentration, test specimens kept dry and of known mass (m_0) were impregnated with the preservative. The impregnation process consisted of 15 min vacuum at 0,7 kPa, followed by the introduction of the nanoparticle suspension to the vessel and keeping the specimens at atmospheric pressure in the suspension for 2 hours. Following this impregnation treatment, the test specimens were immediately weighed to ascertain the mass after impregnation (m_1). According to these weight data, retention was calculated in kg/m^3. The impregnation was followed by the leaching procedure described in the standard EN 84. After the leaching procedure, the samples were climatized for 4 weeks at 20 °C and 65 % relative humidity.

2.3 Decay test

The decay test was carried out according to the standard EN 113. The test fungus for this study was the brown rot fungus Coniophora puteana and the white rot fungus Coriolus versicolor. The culture medium was a malt agar medium.

The species of wood used were pine sapwood (*Pinus sylvestris*) and beech (*Fagus sylvatica*). They were susceptible to attacks by fungi and had been thoroughly impregnated by the nanoparticle suspensions. The dimensions of each specimen, measured at 12 % (m/m) moisture content, were 50×25×15 mm (L×T×R). The specimens were divided into three groups:

- Treated test specimens: these impregnated specimens were subjected to attack by the wood-destroying fungi. Five treated test specimens were used for each preservative concentration, for each timber species and for each fungus species.
- Treated and leached test specimens: these impregnated specimens were subjected to attack by the wood-destroying fungi, after a leaching procedure according to the standard EN 84. Five treated test specimens were used for each preservative concentration, for each timber species and for each fungus species.
- Untreated test specimens: non-impregnated test specimens of the same wood species as the treated test specimens. They were placed in culture vessels containing the same wood-destroying fungus as for the treated test specimens.

Impregnation was carried out in descending order of concentration, starting with the highest concentration (2 or 5 %(m/m)) and ending with the diluted nano-zinc suspension (0,5 or 1 %(m/m)). For each concentration, test specimens kept dry and of known mass (m_0) were impregnated with the preservative. The impregnation process consisted of 15 min vacuum at 0,7 kPa, followed by the introduction of the nanoparticle suspension to the vessel and keeping the specimens at atmospheric pressure in the suspension for 2 hours. Following this impregnation treatment, the test specimens were immediately weighed to ascertain the mass after impregnation (m_1). According to these weight data, retention was calculated in kg/m^3. After impregnation, the samples were climatized for 4 weeks at 20 °C and 65 % relative humidity.

One culture vessel (Kolle flask) contained two treated test specimens, two treated and leached test specimens, and one untreated test specimen. After the introduction of the test specimens, the culture vessels were placed in a climate chamber at a constant temperature of 23 °C and relative humidity of 75 % for 16 weeks. Following incubation, the specimens were oven-dried and reweighed (m_2). The percentage mass loss was calculated.

2.4 Equations

The retention was calculated using the following equation:

$$R = \frac{m_1 - m_0}{V} \qquad \left[\frac{kg}{m^3}\right] \tag{1}$$

R: Amount of chemical retention of nano-zinc for wood specimens [kg/m^3]

m_1: Weight of sample after soaking [g]

m_0: Weight of sample before soaking [g]

When considering wood preservation through soaking with the nano-zinc solution, percentage weight losses were evaluated using the following equation:

$$PWL = \frac{m_0 - m_2}{m_0} \times 100 \qquad [\%] \tag{2}$$

PWL: Percentage weight loss after 16 weeks incubation [%]

m_2: Weight of sample after 16 weeks incubation [g]

m_0: Weight of sample before impregnation [g]

3 RESULTS AND DISCUSSION

3.1 Chemical retention

The amounts of chemical retention for tested specimens are shown in Table 1. There were notable differences in chemical retention based on wood species, as well as on nanoparticle concentration. Pine samples showed higher retention values for all treatments (Table 1). The retention was increasing quite proportionately with the nanoparticle concentration, according to the mean ratio of nanoparticle retention levels (Table 2). This result complied with the ratio of nanoparticle concentrations used during our experiments. It showed that the decay specimens effectively absorbed the nanoparticle suspensions/colloids.

Table 1. Average retention level of beech and pine samples for different nanoparticle suspension/colloid impregnations, at different concentrations

Treatment type	Average retention level (kg/m^3)			
	Beech		Pine	
	Normal	For leaching	Normal	For leaching
Zinc-oxide 1%(m/m)	4,21	4,15	4,60	5,02
Zinc-oxide 2%(m/m)	8,38	8,31	9,82	9,10
Zinc-oxide 5%(m/m)	22,00	22,63	27,79	25,83
Zinc-borate 0,5%(m/m)	2,83	2,80	3,40	3,38
Zinc-borate 1%(m/m)	5,66	5,59	6,58	6,35
Zinc-borate 2%(m/m)	11,59	11,47	13,69	13,73
Silver-colloid 0,5%(m/m)	2,82	2,82	3,21	3,22
Silver-colloid 1%(m/m)	5,73	5,66	6,23	6,77
Silver-colloid 2%(m/m)	11,45	11,34	12,50	12,58
Copper 0,5%(m/m)	2,85	2,84	3,58	3,51
Copper 1%(m/m)	5,68	5,76	6,77	6,85
Copper 2%(m/m)	10,97	11,28	12,77	12,13
Copper-borate 0,5%(m/m)	2,80	2,82	3,44	3,26
Copper-borate 1%(m/m)	5,63	5,62	6,46	6,57
Copper-borate 2%(m/m)	11,34	11,53	14,08	12,74

Table 2. Average retention level of beech and pine samples based on the lowest concentration, for different nanoparticle suspension/colloid impregnations, at different concentrations

Treatment type	Ratio of retention between different concentrations			
	Beech		Pine	
	Normal	For leaching	Normal	For leaching
Zinc-oxide 1%(m/m)	1,00	1,00	1,00	1,00
Zinc-oxide 2%(m/m)	1,99	2,00	2,14	1,81
Zinc-oxide 5%(m/m)	5,23	5,46	6,04	5,15
Zinc-borate 0,5%(m/m)	1,00	1,00	1,00	1,00
Zinc-borate 1%(m/m)	2,00	2,00	1,94	1,88
Zinc-borate 2%(m/m)	4,10	4,10	4,03	4,06
Silver-colloid 0,5%(m/m)	1,00	1,00	1,00	1,00
Silver-colloid 1%(m/m)	2,03	2,01	1,94	2,10
Silver-colloid 2%(m/m)	4,06	4,03	3,90	3,91
Copper 0,5%(m/m)	1,00	1,00	1,00	1,00
Copper 1%(m/m)	1,99	2,02	1,89	1,95
Copper 2%(m/m)	3,85	3,97	3,57	3,46
Copper-borate 0,5%(m/m)	1,00	1,00	1,00	1,00
Copper-borate 1%(m/m)	2,01	1,99	1,88	2,01
Copper-borate 2%(m/m)	4,05	4,09	4,09	3,91

3.2 Decay test

In general, the investigated nanoparticle treatments provided better resistance against the white rot *Coriolus versicolor* (Figure 2), compared to the results of the brown rot *Coniophora puteana* (Figure 1). According to the results, copper nanoparticles did not provide effective protection, or only low protection against the investigated wood-decaying fungi. This means that, at the highest investigated concentration (2 %(m/m)), slightly lower PWL was found in the case of *Coniophora puteana*, and in the case of *Coriolus versicolor* only 4-8 % PWL was found, beside a significantly decreasing trend in relation to the copper nanoparticle concentration. Zinc oxide showed good protection against the white rot *Coriolus versicolor* even at the lowest concentration (1 %(m/m)), while it only showed good protection against the brown rot *Coniophora puteana* at the highest investigated concentration (5 %(m/m)). The use of silver nanoparticles (in colloidal form) did not give protection against the brown rot *Coniophora puteana*, while against the white rot *Coriolus versicolor* it was effective even at the lowest concentration (0,5 %(m/m)). Zinc borate and copper borate nanoparticles provided high protection against both of the investigated decay fungi even at low concentrations (0,5 %(m/m)). Overall, the results are diverse regarding the efficiency of the investigated nanoparticles against a brown and a white rot fungus. It can be stated that in some cases one of the investigated fungi showed tolerance to the nanoparticles, thus, these treatments are not recommended for general use. The generally effective nanoparticle treatments were the combinations containing borate in its chemical composition.

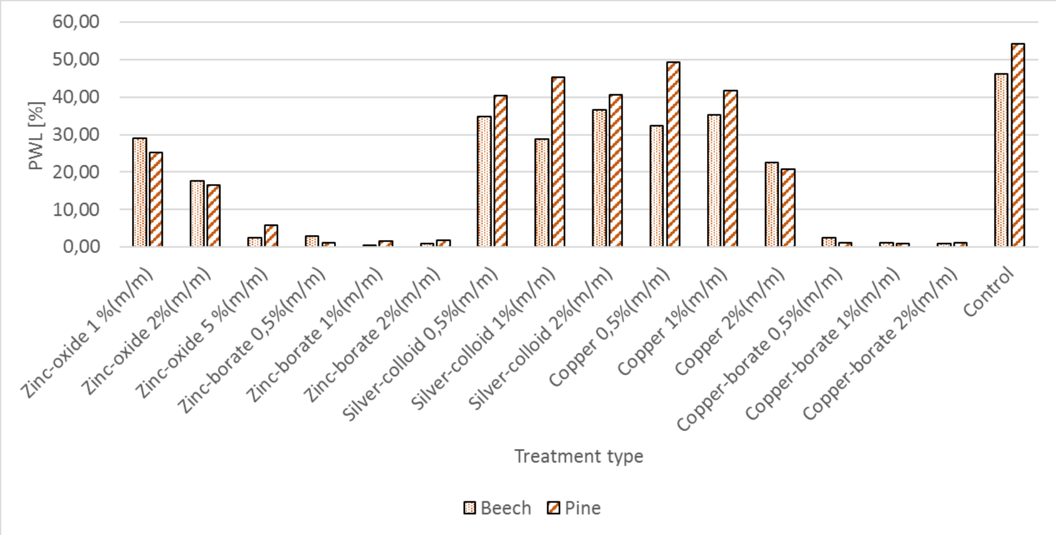

Figure 1. Percentage weight loss (PWL) of nanoparticle-treated and control samples of beech and pine, caused by the brown rot fungus *Coniophora puteana*

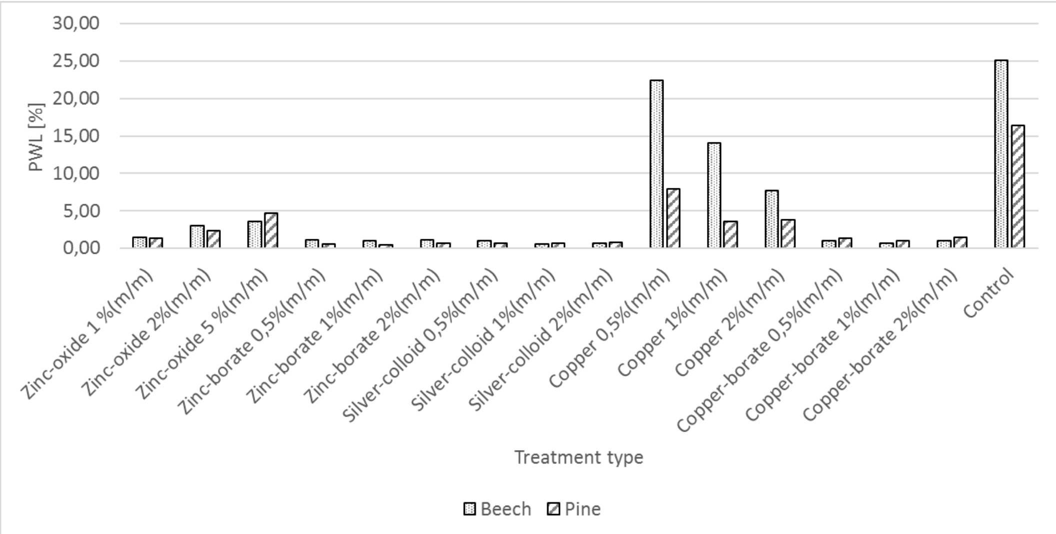

Figure 2. Percentage weight loss (PWL) of nanoparticle-treated and control samples of beech and pine, caused by the white rot fungus *Coriolus versicolor*

However, only zinc oxide and silver nanoparticles showed good resistance against leaching (Figure 3-4). Unfortunately, zinc borate and copper borate showed low resistance against leaching, as after leaching the treated samples showed similar or only slightly lower PWL compared to the control samples. Thus, only zinc oxide at the highest concentration (5 %(m/m)) provided effective protection against both investigated fungus species, also after leaching.

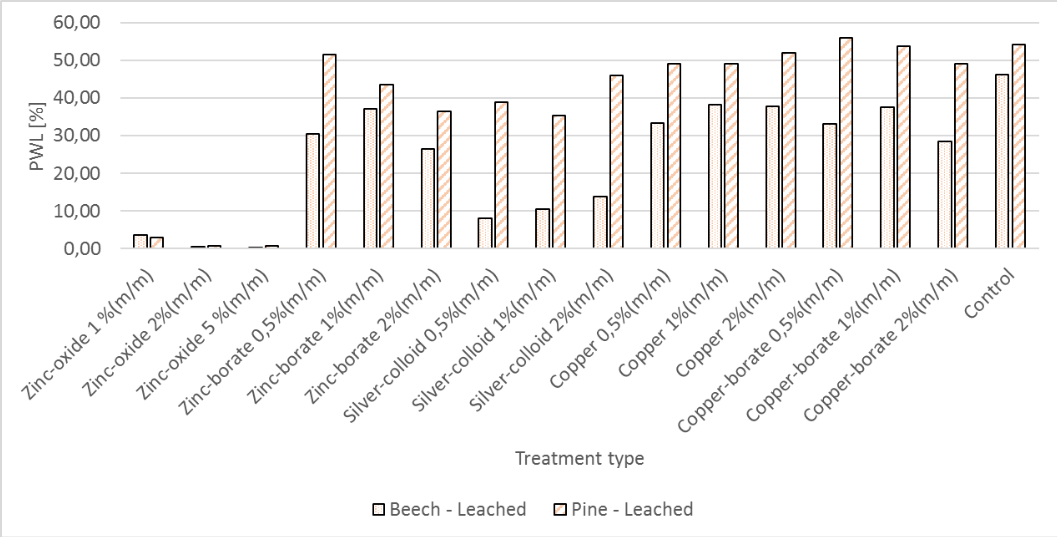

Figure 3. Percentage weight loss (PWL) of nanoparticle-treated and control samples of beech and pine after leaching procedure, caused by the brown rot fungus *Coniophora puteana*

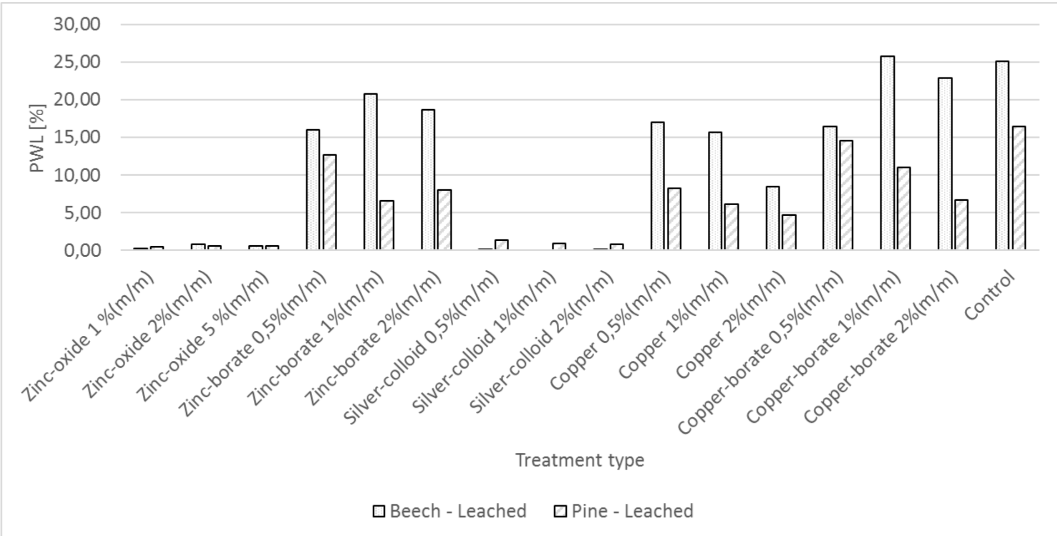

Figure 4. Percentage weight loss (PWL) of nanoparticle-treated and control samples of beech and pine after leaching procedure, caused by the white rot fungus *Coriolus versicolor*

4 CONCLUSIONS

The investigated nanoparticle treatments provided better resistance against the white rot *Coriolus versicolor* (Figure 2), compared to the results of the brown rot *Coniophora puteana*. Copper nanoparticles showed only slight protection against decay, while silver nanocolloid – only against the white rot. Borate-containing nanoparticles showed good resistance against decay, as well as zinc oxide nanoparticles, the latter rather at higher concentrations. Only zinc oxide nanoparticles and silver nanocolloids showed good leaching resistance. Summarizing, the best results were found for zinc oxide nanoparticle treatment, as it showed low PWL for both fungus species and a good leaching resistance as well.

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