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PREPARATION AND APPLICATION OF SILVER AND ZINC OXIDE NANOPARTICLES IN WOOD INDUSTRY: THE REVIEW

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ABSTRACT

Wood products are widely used in exposures convenient for their degradation by bacteria, fungi, insects, atmospheric agents, and fire. In such situations they should be protected by structural arrangements, modification methods or chemical preservatives. The efforts to replace traditional preservatives, e.g. creosote, chlorinated hydrocarbons or heterocycle, having harmful impact on the human health and also contaminating the environment have been made in recent years. Close look at metallic nanoparticles, their production, properties and application as eco-friendly preservatives for wood protection is presented in this paper. Simultaneously, several suggestions of enhancing the functionality and antimicrobial properties of wood and wood-based materials surfaces treated with silver and zinc oxide nanoparticles are provided.

Key words: wood preservation, wood-based composites, metallic nanoparticles, nano silver, nano zinc oxide.

INTRODUCTION

Wood is widely used material with numerous application possibilities in interior and exterior due to its appearance, relatively low cost, natural character, acceptable functional, aesthetical and environmental properties, and renewability. Elemental wood components – cellulose, hemicelluloses, lignin, and extractives – are susceptible to damage and degradation caused by activity of bacteria, moulds, decaying-fungi and insects, as well as due to weathering and fire (AUCLAIR *et al.* 2011, REINPRECHT 2016). The primary biotic decomposers of wood are basidiomycete decaying-fungi, which attack and degrade wood and wood products (AKHTARI *et al.* 2013). Surfaces of wood in exterior and wet interior are often attacked by molds if left without maintenance (PRESTON 2000).

Recently, preservation of wood and wood products against microbial attacks is in transition, because traditional substances used as a wood preservatives (creosote, oil-borne pentachlorphenol, water-borne metallic arsenicals, principally chromated copper arsenate – CCA, *etc*.) are no longer available because of their harmful effect on human health and environmental toxicity (SCHULTZ *et al.* 2007).

However, not only solid wood but also wood-based composites, for example, wood-plastic composites (WPC), particleboards (PB), oriented strand boards (OSB) or laminated veneer lumbers (LVL), are susceptible to microbial attacks. Wood substance in such composites is solely responsible for their susceptibility to microbial attacks (FARAHANI and BANIKARIM 2013). Similarly to solid wood, wood-based composites are widely applied in various interior and exterior expositions, therefore it is necessary to enhance their antimicrobial properties and also antimicrobial properties of their surfaces (NOSÁĽ and REINPRECHT 2017).

Furthermore, the surface of wood exposed to sunlight can photodegrade. Photodegradation is the main cause of the discoloration and degradation of wood exposed outdoors. UV and visible rays can penetrate several micrometres into the wood structure. Lignin in the presence of UV radiation (< 300 nm) decomposes into the radicals, which induce other degradation of lignin and hemicellulose polymers on the wood surface (AUCLAIR *et al.* 2011) in connection with its yellowing and red-browning. Prevention of photodegradation is basic requirement for the wood surface treatments in order to maintain its stable appearance. Thus, coating systems for surface treatment of wood and wood products should contain suitable UV additives (LANDRY *et al.* 2015, REINPRECHT and PÁNEK 2015).

Metallic nanoparticles, *i.e.* solid particles containing metal atom which all three external dimensions are in the size between 1 and 100 nm, have the potential to be adequate substitute through the development of a new, improved, environmental-friendly biocide. Silver and zinc oxide nanoparticles fulfil requirements for wood preservation against biotic damaging agents and UV light. Basically in nanoscale, materials exhibit new and considerably enhanced physico-chemical, and biological properties as well as distinct phenomena and functionalities as result of a small particles size (SIRELKHATIM *et al.* 2015). Metal particles reduced to nano-level increase their effectiveness against microbes on account to their enlarged surface area and therefore enlarged surface able to interact with microbe cells (LI *et al.* 2010, AKHTARI *et al.* 2012, 2013).

SILVER NANOPARTICLES FOR WOOD PRODUCTS

The silver nanoparticles (Ag-NPs) play an important role in the field of biology and medicine thanks to their biological, and physico-chemical properties. Silver products have strong inhibitory effect against a wide spectrum of microbial activities. Silver nanoparticles are accounted to own anti-bactericidal (IŽDINSKÝ *et al.* 2017), anti-mould (ZHANG *et al.* 2008), anti-decaying-fungi (AKHTARI *et al.* 2012, REZAEI *et al.* 2011), anti-inflammatory (WONG *et al.* 2009), anti-viral (CASTRO-MAYORGA *et al.* 2017).

Importance of Ag-NPs in practice

The Ag-NPs represent the group of antimicrobial agents of new generation. Ag-NPs has better antimicrobial properties than bulk, because of their small size and increased surface area through which they can interact with microbe cells (FRANCI *et al.* 2015, MARAMBIO-JONES and HOEK 2010) proposed most common mechanism of cytotoxicity: (1) silver nanoparticles directly damage the cell membranes, (2) silver nanoparticles in ion form generate of reactive oxygen species (ROS), and (3) free silver ions uptake is followed by disruption of ATP production and DNA replication (Fig. 1).

The Ag-NPs have high efficiency against both the Gram-positive and the Gram-negative bacteria (*Escherichia coli, Bacillus subtilis, Streptococcus aureus, Streptococcus mutans, Staphylococcus epidermis, Pseudomonas aeruginosa etc.*) (SONDI and SALOPEK-SONDI 2004, YOON *et al.* 2007, KIM *et al.* 2007, LEE *et al.* 2008, ZHANG *et al.* 2008, LIN *et al.* 2014, LEFTA *et al.* 2016, SALOMONI *et al.* 2017). The Ag-NPs are active against bacteria already at low concentrations (LI *et al.* 2010, SUCHOMEL *et al.* 2015) – as it is documented in Table 1. Moreover, the Ag-NPs are distinguished also with considerable efficiency against molds named as microscopic-fungi (*Aspergillus niger, Penicillium brevicompacum, Candida albicans, Trichophyton mentagrophytes, etc.*) (VERTELOV *et al.* 2008, ZHANG *et al.* 2008; KIM *et al.* 2009, CHANDRA SAI *et al.* 2015; FATMA *et al.* 2015).

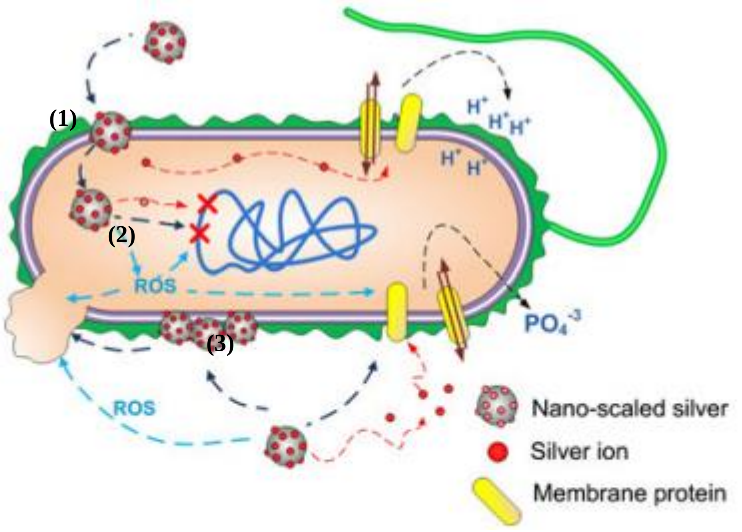

Fig. 1 Interaction of Ag-NPs with microbial cell: (1) it directly damage the cell membrane, (2) its ion form generate of ROS, and (3) its free ion uptake is followed by disruption of ATP production and DNA replication (MARAMBIO-JONES and HOEK 2010).

Tab. 1 Minimal inhibitory concentration of Ag-NPs against selected bacteria (SUCHOMEL *et al.* 2015).

Group of bacteria	Species of bacterium	Minimal inhibitory concentration of Ag-NPs (mg/L)
Gram-negative	*Escherichia coli*	2.5
	Pseudomonas aeruginosa	2.5
	Klebsiella pneumoniae	5.1
Gram-positive	*Enterococcus facalis*	5.1
	Staphylococcus aureus	2.5
	Staphylococcus epidermis	1.3

Recently, the Ag-NPs are used as antimicrobial and disinfect agent mainly in biomedicine (PANÁČEK *et al.* 2006, ECKHARDT *et al.* 2013, LIM *et al.* 2015, SALAR *et al.* 2015, BAUER *et al.* 2016, EBRAHIMINEZHAD *et al.* 2016, GALLO *et al.* 2016) and in textile industry (BUDAMA *et al.* 2013, HEBEISH *et al.* 2014). Silver can be incorporated into textiles using different methods: in production process of individual fibers or after preparation of the final textile product through its chemical modification (FILIPOWSKA *et al.* 2011). In order to improve the quality of indoor air and water purifying, the filter materials, *i.e.* polyester fibers, polyurethane (PU), and latex, are coated with the Ag-NPs as a disinfectant (SKWARCZYNSKI and SKWARCZYNSKA-KALAMON 2016). The Ag-NPs are also used in cosmetics, packaging materials (CARBONE *et al.* 2016) and other materials for household.

Ag-NPs synthesis

The Ag-NPs can be prepared by chemical, physical and biological methods. The most common methods for Ag-NPs synthesis are chemical methods, especially chemical reduction of silver compounds such as silver nitrate ($AgNO_3$), silver perchlorate ($AgClO_4$), and silver tetrafluoroborate ($AgBF_4$). The salts are reduced by strong reducing agent – elemental hydrogen, sodium borhydride ($NaBH_4$), sodium citrate, polyethylene-glycol block co-polymers in aqueous or non-aqueous solution (SHAKEEL *et al.* 2016). To prevent agglomeration of Ag-NPs, suitable stabilizer is present in a solution such as sodium nitrate ($NaNO_3$) and aminosilanes (NOGUEIRA *et al.* 2014). Chemical reduction methods that have been used for Ag-NPs synthesis from silver precursors differ in the selection of the relative quantities, reducing agent and reagent concentrations, mixing rate, temperature, and duration of reaction. Nanoparticles size and shape depends on the reaction conditions (JIANG and YU 2010). The Ag-NPs can be synthesized in various shapes as shown in Figure 2.

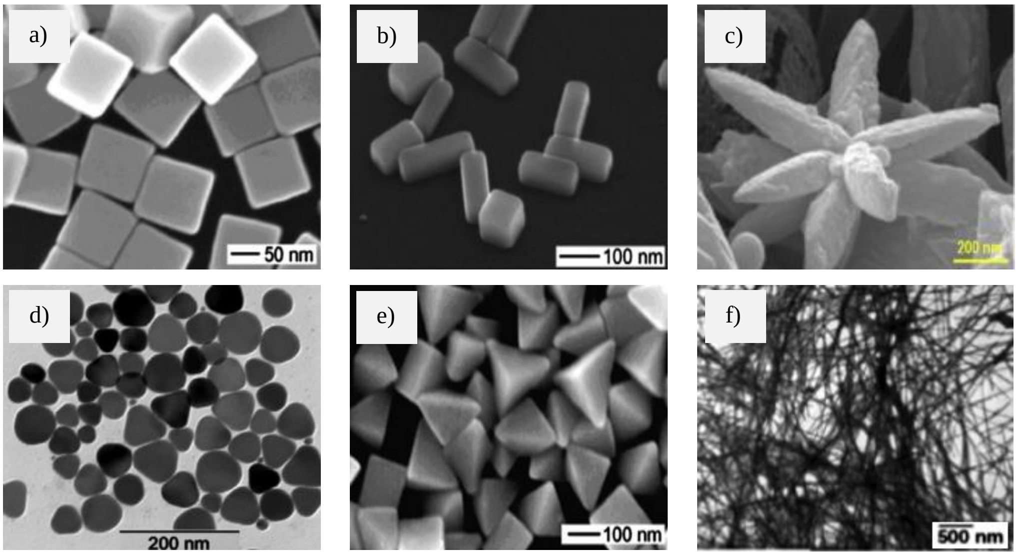

Fig. 2 Silver nanostructures: a) nanocubes, b) nanobars, c) nanoflowers, d) nanoprisms, e) nanopyramids, f) nanowires (KHODASHENAS and GHORBANI 2015)

Many research look into the possibility to prepare Ag-NPs via biological methods. Biosynthesis (green synthesis) of Ag-NPs has received large attention due to increasing demand for eco-friendly agents and stabilizers (GE *et al.* 2014). The biological methods use biomolecules (proteins, enzymes, amino acids, carbohydrates), which replace toxic and many times expansive reduction agents (BAUER 2016). In the biosynthesis, extracts from various plant and plant parts are used (Table 2) such as leaves (SANTOSH *et al.* 2013, NARAYANAN 2014), roots (RAO *et al.* 2016), seeds (THOMBRE *et al.* 2014), bark/peel (BANKAR *et al.* 2010), fruits (MOLDOVAN *et al.* 2016), flowers (VIDHU and PHILIPS 2014) and wood (LIN *et al.* 2014). Similarly can be applied products of bacteria (BHATIA *et al.* 2016), fungi (GAJBHIYE *et al.* 2009), yeasts (FERNÁNDEZ *et al.* 2016), actinomycetes (GHASEMINEZHAD *et al.* 2012) and algae (SHANKAR *et al.* 2016). The Ag-NPs biosynthesis are stimulated by phenols, carbonyl groups, flavonoids, alkaloids, terpenoids, proteins, pigments and other reduction agents/stabilizers contained in plant extracts (KHARISSOVA *et al.* 2013, LIN *et al.* 2014, AJITHA *et al.* 2015, DU *et al.* 2016, ISMAIL *et al.* 2016, LATEEF *et al.* 2016).

Possibilities for application of Ag-NPs in wood industry

More compositions of Ag-NPs have been tested as a substituent of traditional wood preservatives. One of the first investigations into the potential use of silver as biocide for wood protection were made by DORAU *et al.* (2003), which observed high efficiency of colloidal and ionic silver against microbes when impregnated into the wood structure. Moreover, ascertained that the wood impregnation with Ag-NPs compositions has no negative effect on its mechanical properties like modulus of rupture (MOR), modulus of elasticity (MOE), and compression strength parallel to the grain.

NASROLLAHI *et al.* (2011) observed also the antifungal activity of Ag-NPs (0, 5, 10, 50, 100 ppm added in Lysogeny broth medium) against the *Candida albicans* and *Saccharomyces cerevisae*, when Ag-NPs was able to destroy the fungal cells with pore in their cell membrane. REZAEI *et al.* (2011) protected poplar wood (*Populous deltoides*) against the white-rot fungus *Trametes versicolor* using 200 and 400 ppm concentrations of

Ag-NPs. The silver nanoparticles were not able to fully inhibit fungal growth, nevertheless the weight losses (WL) of treated wood decreased at decay from 41.8% to 36.1% or to 29%.

Tab. 2 Examples of plants used for green synthesis of silver nanoparticles (Mohammadlou *et al.* 2016, Moldovan *et al.* 2016, Santosh *et al.* 2013, Narayanan 2014).

Plant species	Used plant part	Ag particle size (nm)
Medicago sativa	Leaves	2–3
Pseudocydonia sinensis	Fruit	15–20
Murraya koenigii	Leaves	40–80
Terminalia chebula	Fruit	25
Viola serpens	Leaves	80–90
Ocinum tenuiflorum	Leaves	7–15
Ammannia baccifera	Leaves	10–30
Hibiscus cannabinus	Leaves	9
Vitex negundo	Leaves	5–47
Piper pedicellatum	Leaves	2–30
Moringa aleifera	Flowers	14
Artocarpus heterophyllus	Seeds	10
Aloe vera	Leaves	20
Emblica officinalis	Fruit	10–20
Leucas aspera	Bark	29–45

Likewise, Moya *et al.* (2014) found that Ag-NPs applied at 50 ppm concentration by pressure impregnation significantly suppressed the decay activity of the white-rot fungus *T. versicolor* in tropical woods *Acacia magnium, Cedrela odorata* and *Vochysia guatemalensis*, as their WL after 4 months decreased from 25–50 % to less than 5 % for all of the species. Similarly, Moya *et al.* (2017) studied the effectiveness of Ag-NPs at concentration 50 ppm against brown- and white-rot fungi acting on nine tropical woods. The results showed improvement of the durability and resistance of these individual tropical wood species to the white-rot fungus *T. versicolor*, but their resistance against the brown-rot fungus *Lenzites acuta* appeared to be a lower. Smaller efficiency of Ag-NPs against brown-rot fungi documented also Pařil *et al.* (2017) when their 1000 ppm and 3000 ppm concentrations did not inhibit but only suppressed the growth of the fungus *Poria placenta*, when WL of wood samples decreased on 13% or 7%.

Also wood-based composites, such as particleboards (PBs), could be preserved from action of wood-decaying fungi. PBs treated with 100 $mL{\cdot}kg^{-1}$ and 150 $mL{\cdot}kg^{-1}$ of 200 ppm Ag-NPs suspension showed significant inhibitory effect on *T. versicolor* growth, as well as a preventive effect toward decays of PBs, when reducing the WL about 10% (Taghiyari *et al.* 2014).

The Ag-NPs could find their application also as an antimicrobial agent in surface treatments of various materials including wood, wood-based composites, and paper. Thin gel-films of SiO_x with content of Ag-NPs created on wood polymer composites (WPC) by plasma and sol-gel technology can be effective against bacterial growth (Gerullis *et al.* 2018). Likewise, the addition of silver nanoparticles in melamine-formaldehyde (MF) coating in amount of 0.5 wt.% during WPC production has positive effect on antifungal and antibacterial activity (Wang *et al.* 2017). Kim and Kim (2007) also modified the MF with Ag-NPs for the impregnation of overlay papers applied as a coating of laminate flooring. Results of their work showed that substitution of 3% of water addition in MF production with colloidal silver at 20 ppm concentration can create highly antibacterial surface with almost 99 % bacterial reduction on the laminated surface.

Silver treated wood-building materials can also be active against microorganisms. For example, the Ag-NPs in urethane alkyd resin completely inhibited bacterial growth (Naik and RATNA 2015). However, by KÜNNIGER *et al.* 2014, the initial concentration of Ag-NPs below 50 ppm in commercial coatings may not be sufficiently efficient against microbial growth. On the other hand, the addition of Ag-NPs at only 14 ppm concentration into the surface finishing of acrylic and polyvinyl acetate resins applied onto the building materials slowed growth of the molds *Aspergillus brasilensis* and *Penicillium funiculosum* as observed LIN and CHEN (2017). DOMINGUEZ-WONG *et al.* (2014) demonstrated the antibacterial activity of Ag-NPs when added into a vinyl-acrylic based indoor waterborne coating; nevertheless it is necessary to say that with lowering humidity and temperature, its antimicrobial activity dropped significantly.

To achieve antimicrobial properties of other wood products, for example papers commonly used as a packaging material. In the paper production, the cellulose fibres are impregnated with solutions of Ag-NPs having optimal concentrations from 5 ppm to 10 ppm. This technology appeared to be efficient for 100% inhibition of both the Gram-positive and the Gram-negative bacteria (AMINI *et al.* 2016).

The Ag-NPs can also be used in reducing the pressing time of PBs thanks to their heat-conductive nature. TAGHIYARI *et al.* (2011) achieved the pressing time reduction up to 10.9% (from 202.5 s to 180.5 s) by adding Ag-NP at 200 ppm to the urea-formaldehyde (UF) resin before mixing with wood particles in volume of 100 and 150 mL/kg of wood particles, based on dry wood basis. Furthermore, the addition of Ag-NP improved more of mechanical and physical properties of PBs. However, due to a higher thermal conductivity of silver nanoparticles, their addition to the resin may result in the depolymerisation of part of the resin bonds in the surface layers of PB and consequently reduce its hardness (TAGHIYARI and MORADIYAN 2014).

ZINC OXIDE NANOPARTICLES FOR WOOD PRODUCTS

Zinc oxide has a long history of use in numerous application in wood products as a UV stabilizer in coatings, as an antifouling agent in pigments, and mould growth inhibitor in latex paints for paper (CLAUSEN *et al.* 2011). The zinc oxide nanoparticles (ZnO-NPs) have been reported to have considerable activity against microbes (REINPRECHT *et al.* 2015, AKHTARI *et al.* 2013, and MARZBANI *et al.* 2015), and they are also effective UV absorbers with partially hydrophobic properties predetermined for use as a protection against wood degradation caused by abiotic agents such as UV-light and humidity changes (FENG *et al.* 2004).

Importance of zinc oxide nanoparticles in practice

A high antimicrobial efficiency of ZnO-NPs was observed already before several years, although their antimicrobial mechanism is still not well known. The direct or electrostatic interaction between ZnO-NPs and live cells of microorganism, the cellular internalization of ZnO-NPs, and the production of active oxygen substances (oxidative stress) such as H_2O_2 in cells due to metal oxides have been suggested as the possible causes of cell membrane disruption (XIE *et al.* 2011). ZnO-NPs are effective antibacterial agents against both the Gram-positive and the Gram-negative bacteria (*Escherichia coli, Staphylococcus aureus, Streptococcus pyogenes, Enterococcus faecalis, Bacillus subtillis, B. atrophaenus, Salmonella typhimurium, Klebisella pnumoniae, etc.*) (JONES *et al.* 2008, TAM *et al.* 2008, WAHAB *et al.* 2010, YAMAMOTO 2001, JALALA *et al.* 2010). Bactericidal effect of ZnO-NPs on the Gram-positive and the Gram-negative bacteria are already evident at concentrations of 1.9 mg/mL and 3.5 mg/mL, respectively (Tab. 3). However, a minimum inhibitory concentration of ZnO-NPs varies already at lower values, it means from 0.005 mg/mL to 1.7 mg/mL (EMAMI-KARVANI and CHEHRAZI 2011, SIDDIQUE *et al.* 2013, MOSTAFA 2015).

Tab. 3 Minimal inhibitory and bactericidal concentrations of ZnO-NPs against selected bacteria (SIDDIQUE *et al.* 2013)

Species of bacterium	Minimal inhibitory concentration of ZnO-NPs (mg/mL)	Minimal bactericidal concentration of ZnO-NPs (mg/mL)
Escherichia coli	1.7	3.5
Bacillus subtillis	0.8	2.3
Staphylococcus aureus	0.6	1.9
Staphylococcus epidermis	1.3	3.1

NAVALE *et al.* (2015) observed activity of ZnO-NPs against molds *Aspergillus flavus* and *A. fumigatus*. Many studies confirmed antifungal activity of ZnO-NPs also against other microscopic fungi, such as *Phanerochaete salmonicolor, Botrytis cinerea, Penicillium expansum, Candida albicans, Fusarium oxysporum* (ARCINEGAS-GRIJALBA *et al.* 2017, HE *et al.* 2011, NARENDHRAN and SIVARAJ 2016)

The ZnO-NPs with their antimicrobial, physical and chemical properties, to which belong a good chemical stability, absorbance of wide radiation spectra and high photostability, are multifunctional material for protection of wood and other organic materials, and also for improving their properties. The ZnO-NPs are due to their antimicrobial properties widely used in production of different types of pharmaceuticals, mainly in form of ointments and creams against infections. Likewise, ZnO-NPs in combination with SiO_2 in textiles provide absorbance of UV-light, enhance the hydrophobicity and bacterial reduction (KOLODZIEJCZAK-RADZIMSKA and JESIONOWSKY 2014, BOGUTSKA *et al* 2013). The ZnO-NPs are incorporated in many optoelectronic, photoelectronic devices, in emitters of surface acoustic waves, sensors or UV lasers, and in production of display technology, photodiodes, and semiconductors for voltage stabilization and regulation purposes (VASEEM *et al.* 2010, TSONOS *et al.* 2011, UIKEY and VISHWAKARMA 2016).

ZnO-NPs synthesis

The ZnO-NPs can be synthesized by various chemical, mechano-chemical, physical or biological methods. The selected method depends on demands of their future use. One of the most used ZnO-NPs synthesis method is the mechano-chemical method, which does not require any organic solvents to control the nanoparticles growth. The mechano-chemical method involves high-energy dry milling at low temperature. $ZnCl_2$ and Na_2CO_3 powders are used as reagents and NaCl as a reaction medium for separation of the nanoparticles. Formed precursor $ZnCO_3$ is calcinated at the temperatures of 400 °C and 800 °C. Resulting particles size depends on milling time and calcination temperature (MATEI *et al.* 2014). Depending on synthesis method and its conditions, various shapes, structures and sizes of nanoparticles can be produced. Basically, their chemical and physical properties depend on used solvent type, precursor type ($ZnCl_2$, $Zn(NO_3)_2.6H_2O$, $Zn(CH_3COO)_2$, $Zn(NO_3)_2$, $ZnSO_4$), pH value, synthesis temperature. The ZnO-NPs can also acquire different shapes, for example, nanorods, nanotubes, nanospheres, nanorings, nanowires, nanoconsoles or nanospirals (Fig. 3). Every nanostructure has its specific physicochemical properties (WANG 2004).

Similarly to the Ag-NPs synthesis, researchers look into the possible green way of ZnO-NPs synthesis. In the green synthesis, chemical "contaminants" used as a reducing agents or stabiliser are substituted by different biological entities such as extracts, enzymes or proteins obtained from various plant species and plant parts (Tab. 4), such as leaves (FATIMAH *et al.* 2016, JAYARAMBABU *et al.* 2018), roots (NAGAJYOTI *et al.* 2015), seeds (QU *et al.* 2011), bark/peal (KARNAN and SELVAKUMAR 2016), fruits (RAMESH *et al.* 2014) and flowers (DOBRUCKA and DLUGASZEWSKA 2016), as well as from bacteria (KUNDU *et al.* 2014) algae (AZIZI *et al.* 2014) and fungi (RAJAN *et al.* 2016).

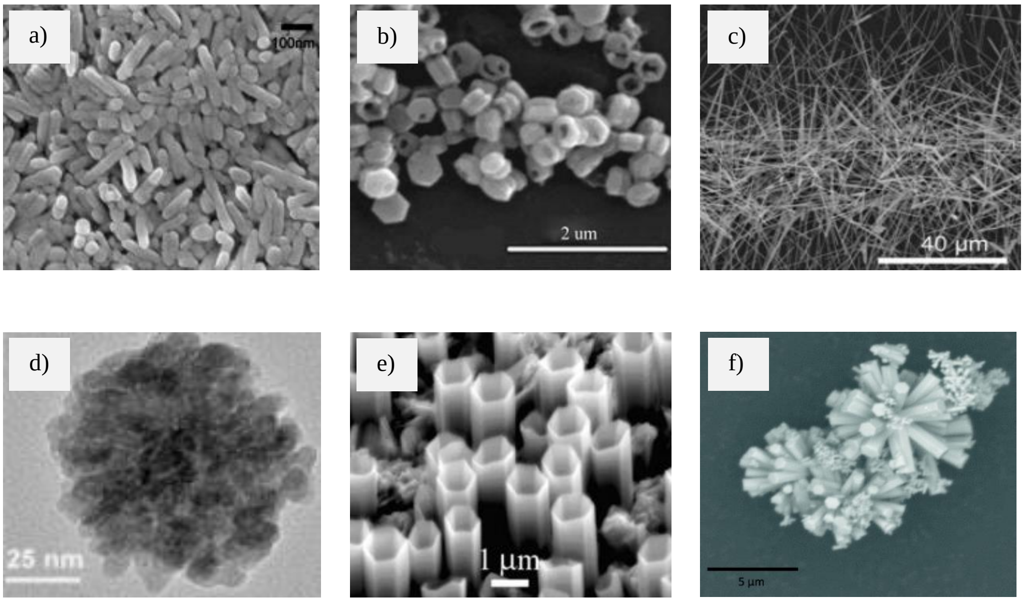

Fig. 3 ZnO nanostructures: a) nanorods (LEE *et al.* 2008), b) nanorings (PENG and BAO 2008) c) nanowires (KONG *et al.* 2018), d) nanospheres (TIAN *et al.* 2017), e) nanotubes (YUAN *et al.* 2007), f) nanoflowers (AKHTAR *et al.* 2017)

Tab. 4 The examples of plants for green synthesis of ZnO nanoparticles (AGARWAL *et al.* 2017, GAWADE *et al.* 2017, RATHNASAMY *et al.* 2017, SANTOSHKUMAR *et al.* 2017)

Plant species	Used plant part	ZnO particle size (nm)
Azadirachta indica	Leaves	18
Aloe Vera	Leaves	8–20
Phyllanthus niruri	Leaves	25
Rosa canina	Fruit	25–200
Ocimum basilicum	Leaves	50
Moringa oleifera	Leaves	16–20
Nephelium lappaceum	Peel	50
Plectranthus amboinicus	Leaves	50–180
Solanum nigrum	Leaves	20–30
Cocus nucifera	Coconut water	20–80
Vitex negundo	Flowers	10–130
Trifolium pratense	Flowers	60–70
Passiflora caerula	Leaves	30–50
Carica papaya	Leaves	50
Calotropis procera	Leaves	15–25

Possibilities for application of ZnO-NPs in wood industry

The ZnO-NPs as an effective antimicrobial agent and UV absorber are predetermined to be potential wood protectives against various wood degrading agents. Anti-fungal resistance of wood can be improved when it is modified with ZnO-NPs, or the zinc oxide nanoparticles are incorporated into glues or coatings. REINPRECHT *et al.* (2015) reported anti-fungal effect of nano-ZnO against the wood-decaying fungi *Trametes versicolor* and *Coniophora puteana*, if it was used at modification of lime wood (*Tilia cordata*) either alone or together with ethylmethacrylate-methylacrylate copolymer.

Action against the above mentioned decaying-fungi observed also AKHTARI *et al.* 2013. Using FTIR spectroscopy, they observed chemical changes at a lower scale at samples treated with ZnO-NPs than untreated ones. A slight decrease in WL about 9% for samples of *Pinus nigra* impregnated with ZnO-NPs according to the full-cell process was observed by LYKIDIS *et al.* (2013). HARANDI *et al.* (2016) determined that samples of *Populus alba* treated with 1% and 2% ZnO treated polyvinyl-butyral have a good resistance against the white-rot fungus *T. versicolor*. However, there was a significant difference in antifungal properties of ZnO-NPs in the dark and light conditions; WL of samples in the dark conditions varied between 24.2% and 4.6%, and on contrary, under the light conditions only between 1.23% and 0.81%. Additionally, wood impregnation with zinc oxide nanoparticles has no negative effect on MOR, MOE and compression strength parallel to grain (LYKIDIS *et al*. 2013).

Biological resistance of wooden composites, for example, WPC, PB, OSB, LVL or plywood, can also be improved by ZnO-NPs addition into their structure. WPC are often exposed outdoors and susceptible to degradation by bacteria and fungi. Thus, decay resistance of WPC is important. FAHRANI and BANIKARIM (2013) observed improved decay resistance of WPC against decaying fungi *T. versicolor* and *C. puteana* when their WL were minimal, near to 0% at 3 wt.% addition of ZnO-NPs. Alike, when immersion styrene solution was modified by ZnO-NPs, noticeable enhanced resistance of WPC against wood-decaying fungi was observed (HABIBADZE *et al.* 2014) – WL of samples treated with 0.5 and 1.5 wt.% content of ZnO-NPs was lowered about 15 and 22% at action the white-rot fungus *T. versicolor* and about 8% – 14% at action the brown-rot fungus *C. puteana*, respectively. Decay of PBs by wood-decaying fungi was evidently suppressed when UF glue was modified with 15 wt.% ZnO-NPs (MARZBANI *et al.* 2015), and similarly using MUF glue modified with 6 to 24 wt.% ZnO-NPs (REINPRECHT *et al.* 2018).

The ZnO-NPs were tested as an additive for modification of resins used for wood and wood-based composites surface treatment with the aim to achieve antimicrobial properties of their surfaces and to enhance their protection against weathering (CLAUSEN *et al.* 2010, NOSÁĽ and REINPRECHT 2017). LI *et al.* (2009) set optimal concentration of ZnO-NPs in polyuretane (PU) resin at 2 wt.% content. They observed excellent antibacterial activity of such treated wood surfaces, especially against the Gram-negative bacteria (*E. coli*), and also significant improvement of their mechanical resistance. Optimal 2 wt.% concentration of ZnO-NPs in PU resins confirmed EL SAEED *et al.* (2015) – when PU resin modified with 0.1 to 1.5 wt.% content of zinc oxide nanoparticles was characterized with 15% to 90% inhibition of both the bacterial groups, while at 2 wt.% addition of ZnO the bacterial growth was completely stopped. Moreover, contact angle, wetting properties, corrosion resistance, and mechanical resistance of treated surfaces are significantly enhanced as well. SALLA *et al.* (2012) added ZnO-NPs into modified maleic anhydride polypropylene (MAPP), and such modified resin applied onto the wood surface restrict the colour changes and photodegradation of *Hevea brasiliensis* wood (Fig. 4).

The ZnO-NPs based coatings create a protective layer against moisture on wood products. MAKARONA *et al.* (2017) coated wood samples of two coniferous and deciduous wood species with ZnO-NPs modified coatings. Nanostructure on the wooden surfaces enhanced the resistance of samples to water sorption. The enhanced resistance of samples were noticeably below the average values of untreated wood. CRISTEA *et al.* (2010) prepared and tested exterior waterborne acrylic latex coating for wood with nano-ZnO as a UV absorber added in 2 wt.% content. Wood treated with this coating has shown very good hydrophobicity, and in addition a good photostability and a high gloss retention.

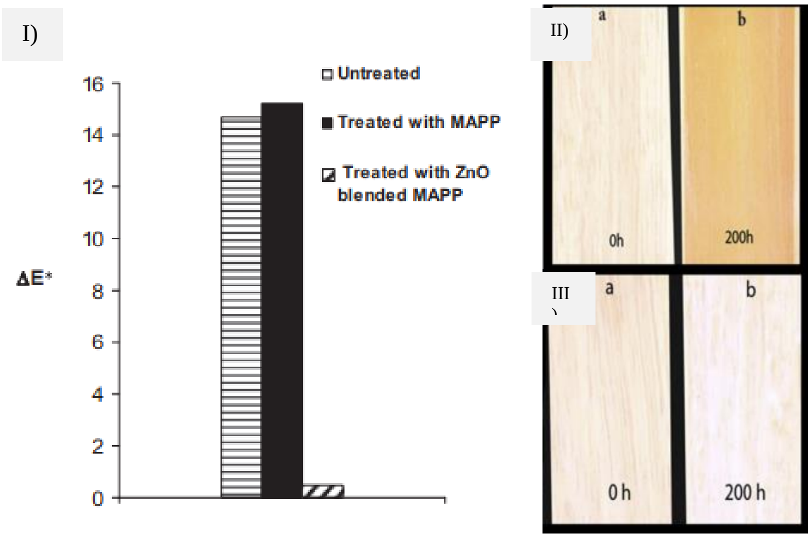

Fig. 4 Comparison of the total colour difference ΔE (I) of wood samples treated with MAPP (II) and with ZnO-NPs modified MAPP (III) after 200 h of UV exposure (SALLA *et al.* 2012).

The ZnO-NPs can be added as well as into impregnating MF resin used for surface lamination of PBs or other wooden composites, with the aim to create on them anti-microbial or even anti-microbial-active surfaces. In the experiment of NOSÁĽ and REINPRECHT (2017), the zinc oxide nanoparticles added to MF resin in content of 0.1 – 3 wt.% suppressed the activity of bacteria (*S. aureus*, *E. coli*) and molds (*A. niger*, *P. brevicompactum*) on the top surfaces of laminated PBs – it means, the ZnO-NPs presented as a good anti-bacterial and anti-mould substance. Furthermore, such modification of MF resin had no negative effect on chemical resistance of the laminated surfaces and only negligible in a negative trend effected their mechanical resistance.

CONCLUSIONS

Wood due to its chemical structure, composed of polysaccharides, lignin, and extractives, is oftentimes degraded by diverse biotic and abiotic agents what has a negative impact on its quality and functionality. Thus, wood products need to be protected – preferentially with optimal design, but under more damaging conditions with chemical preservatives or by using thermal, chemical or biological modification methods. Today, traditional chemical preservatives, mostly arsenic, chromium and organic based, are on the remission due to their harmful effect on health and the environment.

Nanotechnologies are on the expansion as well as in the field of wood protection with chemical preservatives. Many research works mentioned metallic nanoparticles to be a highly effective against the wood-degrading agents. Based on our ascertainment introduced in the article, we assume that nanoparticles of silver and zinc oxide could be applicable at substitution of some traditional wood preservatives with their lower impact on health and environment. Also, the production of these metallic nanoparticles has a tendency to become environmentally friendly when harmful chemical substances used as a reagents and stabilizers are being replaced by biomolecules such as proteins, enzymes or amino acids obtained from natural extracts. Moreover, silver and zinc oxide nanoparticles are characterized by the ability to protect the wood against degrading external effects already at low concentrations, and this ability remains unchanged even in ecological way of metallic nanoparticles production.

However, more detailed research into the final properties of wood products treated with metallic nanoparticles needs to be done to make it possible to say with certainty that they could adequately substitute traditional preservatives.

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