Environmental Pollution 200 (2015) 126–132

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Review

Micronized copper wood preservatives: An efficiency and potential health risk assessment for copper-based nanoparticles

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ARTICLE INFO

Article history:
Received 8 September 2014
Received in revised form
29 January 2015
Accepted 15 February 2015
Available online 23 February 2015

Keywords:
Micronized copper
Copper-tolerant fungi
Nanocopper exposure
Wood-destroying fungi
Wood preservatives

ABSTRACT

Copper (Cu) is an essential biocide for wood protection, but fails to protect wood against Cu-tolerant wood-destroying fungi. Recently Cu particles (size range: 1 nm–25 μm) were introduced to the wood preservation market. The new generation of preservatives with Cu-based nanoparticles (Cu-based NPs) is reputedly more efficient against wood-destroying fungi than conventional formulations. Therefore, it has the potential to become one of the largest end uses for wood products worldwide. However, during decomposition of treated wood Cu-based NPs and/or their derivate may accumulate in the mycelium of Cu-tolerant fungi and end up in their spores that are dispersed into the environment. Inhaled Cu-loaded spores can cause harm and could become a potential risk for human health. We collected evidence and discuss the implications of the release of Cu-based NPs by wood-destroying fungi and highlight the exposure pathways and subsequent magnitude of health impact.

1. Introduction

Wood was one of the first materials used by humans for a wide variety of applications. Moreover, this natural product is still used because of its exceptional density–strength properties, as well as being economically advantageous, sustainable, and carbon dioxide neutral. Hence, it is believed to be one of the most preferred building materials in the future (Buchanan and Levine, 1999).

Despite its positive features, wood is susceptible to different factors that cause its decay, and various biodeterioration organisms such as fungi, cyanobacteria, bacteria, protists, and insects have the capacity to decompose wood. In particular, fungi, insects, and bacteria are considered to be the principal pests of timber. Therefore, methods to improve the durability of wood have been developed since early times (Unger et al., 2001) and the chemical preservation of wood products appears to be the most common and developed strategy, with three generations' history. Health and environmental concerns with the older 1st-generation preservative systems (arsenic, penta) led to rapid and profound changes on a worldwide basis as we moved to the 2nd and 3rd generation Cu rich preservatives.

Nanotechnology, which is currently one of the most investigated areas of research, has influenced the utilization of wood preservatives because it has enabled the development of innovative metal-based biocides (Clausen, 2007; Dorau et al., 2004; Green and Arango, 2007; Kartal et al., 2009; Kim and Kim, 2006; Akhtari et al., 2013a).

More precisely, the wood preservation industry has begun to profit from formulations using particulate Cu systems, also known as micronized Cu, that contain a considerable amount of nanosized Cu (Mcintyre, 2010), which can readily penetrate into the wood (Geers et al., 2014; Matsunaga et al., 2007). Since 2006 more than 11,800,000 m^3 of wood treated with micronized Cu has been sold (Griffin, 2011), which corresponds to an annual use of 79,000 tonnes of Cu systems (Evans et al., 2008), greatly exceeding the quantities estimated for titanium dioxide NPs (Gottschalk et al., 2009).

In this review, the term Cu-based NPs will be used to indicate formulations containing a Cu nanosized fraction, according to the current nanomaterials definition (Commission Recommendation, 2011) and to recent findings (Mcintyre, 2010; Geers et al., 2014; Matsunaga et al., 2007). Cu-based NPs can be manufactured from metallic Cu or Cu compounds (e.g. Cu carbonate). Although wood preservatives based on Cu-based NPs are currently available, surprisingly there is little information on their hazard potential and

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http://dx.doi.org/10.1016/j.envpol.2015.02.018
0269-7491/

the interactions between this biocide and wood-destroying Cu-tolerant fungi are poorly understood.

The objectives of this review are the assessment of (i) the effectiveness and the risk of wood preservatives based on Cu-based NPs, (ii) to discuss the probability of Cu-tolerant fungi accumulating, and re-mobilizing Cu during their life cycle, and (iii) subsequently the magnitude of the health impact.

2. Wood preservative treatments

To date, the main fungicide used for treating wood in contact with the soil is Cu (Cu carbonate, Cu citrate), and currently there is no satisfactory alternative yet: Cu compounds are the only biocides that show a high efficiency against soft rot fungi and other soilborne fungi, which cause the greatest damage to wood products in contact with the soil (Hughes, 2004).

Cu is generally required at low concentrations by every organism in order to sustain metabolic processes for its survival, but at higher concentrations it causes serious, in some cases irreversible alterations in metabolic activities (Gadd, 1993). Furthermore, despite its excellent properties as fungicide, Cu is considered to be a toxicant with minimal effect on mammals (Lebow, 1996), although the effect on aquatic communities is relevant (Eisler, 1998; Roales and Perlmutter, 1980). The features of Cu allow it to act as a biocide, or as a growth or reproduction inhibitor for biodeteriogents. In addition, Cu is also able to cause genetic perturbation or mutation.

2.1. Potential of Cu-based NPs formulations as wood preservatives

We are currently experiencing a development of particulate-based wood preservatives, in terms of composition and size range of the particles, in order to maximize the biocidal effect and effectively protect wood in contact with the soil from biodeterioration. As discussed above, the Cu-based NPs formulations currently available have a mean particle size that is evidently nanoscale, as indicated in Fig. 1 that shows the particles from a Cu-based NPs preservative formulation.

The use of Cu-based NPs instead of bulk Cu reputedly improves the durability of wood against fungal decomposition (Kartal et al., 2009; Cookson et al., 2010; McIntyre and Freeman, 2009; Akhtari et al., 2013b) because of the following properties: (i) ability to penetrate bordered pits because they are smaller than the mean opening (300 nm), (ii) increase in the effective surface area of Cu, and enhanced dispersion stability; (iii) less viscous formulations than bulk ones, and (iv) presence of a reservoir effect that allows a continuous protection over time (Xue et al., 2014; Freeman and Mcintyre, 2013). These properties, which enable easier impregnation and deeper and more homogeneous uptake of the biocide into the wood, can be further improved by selecting specific supporting systems (e.g. surfactants) (Green and Arango, 2007). Moreover, the presence of chromium and arsenic is no longer necessary; however, leaching of the nanometal greatly depends on treatment procedure and product formulation (Kartal et al., 2009; Preston et al., 2008; Ding et al., 2013).

Finally, there is only little evidence to suggest that Cu-based NPs are more efficient against soilborne fungi or some Cu-tolerant wood-destroying fungi (Kartal et al., 2009; Cookson et al., 2010; Tang et al., 2013).

2.2. Fungicidal mechanisms of Cu-based NPs

Although the literature on the fungicidal properties of Cu-based NPs is sparse and fragmented, several studies investigated the toxic mechanisms of Cu ions.

In addition, the nanoparticles commercially available are generally poorly characterized (Altes, 2008). Furthermore, there is a substantial lack of knowledge in the underlying mechanisms on how Cu-based NPs wood preservatives function, namely whether the toxicity is exerted by the nanoparticles themselves or by the release of ions, or only in combination with secondary biocides. Thus at present the use of Cu-based NPs for wood protection is an insufficiently understood system, in regards to both the effectiveness of the treatment and its safety.

What is generally known is that the principal mode of action of Cu-based NPs can be identified as highly reactive due to their larger specific surface area (Chen et al., 2006; Oberdürster, 2000), which results in the production of reactive oxygen species (ROS), mainly peroxides, which induce a series of chain reactions and oxidative stress to the exposed organism (Heinlaan et al., 2008; Saliba et al., 2006) and cause DNA damages. As demonstrated for white rot fungi, these reactions may eventually result in the *in vitro* inhibition of lignocellulose-degrading enzymes (Shah et al., 2010). In addition, particles may interact with proteins and mitochondria damaging or disrupting them (Chang et al., 2012). Moreover, a strong ability to interact with the cell wall has been suggested (Heinlaan et al., 2008; Shah et al., 2010) and homeostatic processes may be impaired by Cu dissolution (Chang et al., 2012). These lethal interactions mentioned above are described in Fig. 2, whereas toxic mechanisms for fungi colonising wood treated with Cu-based NPs are shown at the cellular level.

Due to these features, Cu-based NPs may require lower concentrations of the metal with similar or even better efficacy than

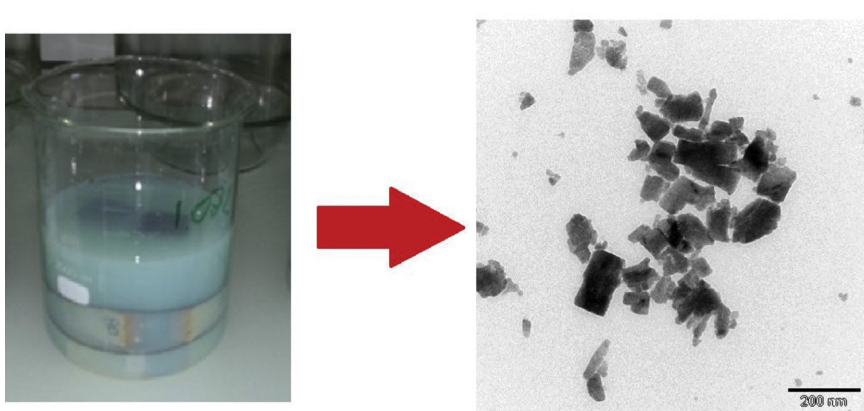

Fig. 1. Waterborne micronized copper formulations for wood preservatives: impregnation of wood samples and TEM micrograph on particles from a micronized copper formulation.