International Biodeterioration & Biodegradation 99 (2015) 95–101

Contents lists available at ScienceDirect

International Biodeterioration & Biodegradation

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

Bioremediation and decay of wood treated with ACQ, micronized ACQ, nano-CuO and CCA wood preservatives

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A R T I C L E I N F O

Article history:
Received 10 October 2014
Received in revised form
8 January 2015
Accepted 8 January 2015
Available online 28 January 2015

Keywords:
Nano-Cu
Micronized Cu
Bioremediation
Decay
Oxalic acid
Wood preservatives

A B S T R A C T

Copper (Cu) removal from wood treated with micronized, nano- or soluble forms of Cu was evaluated relative to exploration of systems that could detoxify chemicals in wood for recycling and a broader interest in bioremediation by fungi. Decay of treated wood blocks by the fungi was also studied relative to the amount of copper metal initially present, and also removed. In the fungal bioremediation tests, liquid fungal cultures were first employed to remove Cu from treated wood, and also to evaluate mechanisms that fungi use to overcome Cu-based preservatives. In most cases, when treated ground wood samples were exposed to the fungi used, Cu removal rates were over 90%; however, nano-CuO-treated wood was resistant to removal by most fungi tested. No distinct differences were seen between ACQ and micronized ACQ-treated wood in terms of Cu removal. Moderate to high mass loss associated with decay of the treated wood blocks occurred by the brown rot fungi. Mass loss was associated with moderate levels of Cu removal from the blocks, but in some blocks the removal of Cu was not correlated with mass loss. Several strains of *Serpula lacrymans* were found to remove 80–98% of the Cu from ground wood samples. Bioremediation of Cu-treated wood by fungi may offer advantages even though longer fungal remediation process durations may be needed for higher Cu releases. It might be important to develop specific remediation processes for new generation nano-Cu-based wood preservatives.

Introduction

Considerable amount of copper (Cu)-based preservative treated wood have been used in building construction and industrial products. When such wood products with preservatives reach the end of their service life, public concern regarding such waste wood and the release of biocides/metals from treated waste wood disposed in landfills or by burning or composting has increased over several decades. Various treating methods for treated waste wood are currently available i.e. reuse, landfilling, incineration, pyrolysis, liquefaction, steaming, composite production, electrodialytic, chemical and bio-remediation. Sierra-Alvarez (2009) has stated that in many countries, decommissioned wood treated with Cu-based preservatives is exempted from a hazardous designation regardless of its characteristics, and incineration and landfilling may result in environmental contamination with toxic pollutants and the release of harmful components into the atmosphere. More recently, Coudert et al. (2013) and Hse et al. (2013) have discussed that more strict regulations over the next few years are another difficulty to landfilling or incineration of wood waste treated with Cu preservatives due to reasons of health care and environmental protection. Pankras et al. (2014) has stated that landfill option for waste treated wood is a costly option and has potential risks due to emissions of preservatives from the disposal sites.

In light of this concern, the remediation of preservative treated waste wood by chemical extraction with either mineral and organic acids, chelating agents, or bioremediation using fungi and bacteria has been studied in recent years to decontaminate such waste wood before management options such as incineration and landfilling to decrease environmental concerns stated above (Kim and Kim, 1993; Stephan et al., 1993; Kamdem et al., 1998; Clausen and Smith, 1998; Kazi and Cooper 1999; Kartal, 2003; Kartal and Köse, 2003; Kartal and Imamura, 2003; Kim et al., 2004; Sierra-Alvarez, 2009; Janin et al., 2011; Coudert et al., 2013; Hse et al., 2013; Kartal et al., 2014; Pankras et al., 2014). Thus, chemical or bioremediation can be possible alternative processes to remove and

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http://dx.doi.org/10.1016/j.ibiod.2015.01.004
0964-8305/

reuse metals from wood, and create decontaminated wood. Chemical and bioremediation have been long studied and proved to be effective for the removal of preservative components. However, there is a need to develop easily managed and cost-effective methods to reduce the amount of waste treated wood tolerant wood by using effective organisms or chemicals. Kartal and Imamura (2003) and Clausen and Lebow (2011) have well reviewed several methods for remediation of treated waste wood by chemical and biological methods.

New Cu based preservative formulations without chromium and arsenic have been introduced into the treated wood market over the past decade, and these systems have much less environmental impact when compared to heavy-metal containing formulations. ACQ (alkaline Cu quat), CA (Cu azole), Cu citrate, and Cu ethanolamine as Cu-based preservatives have emerged over this period as the most widely available wood preservatives. Besides these “water-soluble copper” formulations, micronized-Cu based systems have been recently introduced into the North American and European market. Nano-CuO and nano ZnO have been also evaluated as potential preservative components by several research groups (Kartal et al., 2009; Clausen et al., 2010, 2011). Micronized and nano-particles of Cu in preservative systems may have different chemical, physical, fixation, deposition and distribution properties when compared to conventional water-soluble Cu systems (Kartal et al., 2013, 2014). Thus, remediation mechanism for Cu and other metals in micronized and nano systems might be different when compared to water-soluble forms of the respective metals.

Organisms such as fungi and bacteria play an important role in the remediation of treated waste wood under natural conditions, and some metals in treated wood can be solubilized by their extracellular enzymes or non-enzymatic oxidative systems (Kartal and Imamura, 2003; Clausen and Lebow, 2011). Previous studies on the chemical and biological remediation of CCA-treated wood showed that oxalic acid was produced by several types of fungi, and it can be secreted at different concentration levels into the culture broth depending on conditions (Kartal et al., 2004a). The copper tolerance of various fungal isolates can have a significant effect on the bioprocessing of waste wood treated with copper-based wood preservatives (Woodward and De Groot, 1999).

Various diverse mechanisms such as trapping of the metal by cell-wall components, altered uptake of copper, extracellular chelating or precipitation by secreted metabolites by organisms, and intracellular complexing by metallothioneins and phytochelatins are involved in copper tolerance (Cervantes and Gutierrez-Corona, 1994). Considerable research has suggested that copper tolerance in wood-degrading fungi is closely related to immobilization of copper by precipitating copper oxalate. On one hand, a close relationship between oxalic acid secretion and copper tolerance has been found due to copper oxalate formation in decayed wood (Murphy and Levy, 1983; Woodward and De Groot, 1999; Clausen and Green, 2003; Hastrup et al., 2005). On the other hand, a reduction in the toxicity of copper with increased acidity was observed in several fungi (Gadd and White, 1985), and others have suggested that the reduction of pH by oxalic acid had more to do with copper tolerance than with the low solubility of copper oxalate (Hastrup et al., 2005). Oxalate may function in conjunction with iron-reducing chelators to initiate depolymerization of wood cell components (Goodell et al., 1997; Goodell, 2003; Arantes et al., 2012). Because oxalate cannot reduce metals except in the presence of light (Schmidt et al., 1981), its primary role in wood depolymerization by brown rot fungi is to function in a first-phase iron solubilisation role and pH regulator (Arantes and Goodell 2014). The role of oxalate and iron-reducing chelators in the brown rot fungal chelator-mediated Fenton (CMF) system has been well-reviewed (Goodell et al., 1997; Eastwood et al., 2011; Arantes et al., 2012; Arantes and Goodell, 2014), and suggests the applicability of these types of fungi to the remediation of treated waste wood containing heavy metal ions. Most brown rot decay fungi facilitate leaching of heavy metals by secretion of organic acids and possibly iron-reducing catecholate chelators, which in addition to aiding in degradation mechanisms, may provide a source of protons to the fungus and may aid in the detoxification of metals in the environment. Our previous studies showed that the brown-rot fungi, *Fomitopsis palustris*, *Coniophora puteana*, and *Laetiporus sulphurous* had the ability to produce oxalic acid at varying concentrations which aided in the remediation of CCA-treated wood (Kartal et al., 2004a). Studies by Kartal et al. (2004b, 2006) found that the mold fungus *Aspergillus niger* removed significant amounts of Cu, Cr, and As from CCA-treated wood particles and this was attributed to oxalic acid secretion into the culture broth by the fungus during remediation process. Besides various brown-rot fungi, another brown and dry-rot fungus, *Serpula lacrymans* is also discussed in terms of its copper tolerance ability by several research groups (Schmidt and Moreth, 1996; Tsunoda et al., 1997; Woodward and De Groot, 1999; Hastrup et al., 2005; Köse and Kartal, 2010).

The primary objective of this study was to determine the release rates of Cu from micronized- and nano-Cu-treated wood as the result of fungal exposure, and compare these Cu release rates with those soluble Cu-based wood preservatives via bioremediation by fungi. The fungi employed in the study were selected on the basis of the information by previous studies on bioremediation of treated wood by fungi. A further objective was to explore how different fungi may detoxify Cu-based preservative systems in wood used in the built environment and explore potential mechanisms for Cu removal in fungal systems, which may be “copper-tolerant”, or have greater ability to invade and decay wood treated with Cu-based preservative systems. In the study, wood blocks were also exposed to the fungi strains to observe both mass and Cu losses from treated wood blocks by fungal attack during a standard decay resistance test.

Materials and methods

Wood preservatives

The following commercial wood preservatives were tested in the study (% m/m):

i) ACQ – water soluble form of Cu: Osmose Celcure AC-500 (Osmose Naturewood) (Osmose UK Protim Solignum Ltd): Quat (benzalkonium chloride) (4.8%), copper carbonate hydroxide (16.53%), boric acid (5%)
ii) Micronized ACQ – micronized form of Cu: Osmose Micro Pro, (Celcure MC) (Osmose UK Protim Solignum Ltd): Quat (benzalkonium chloride (10%), micronized copper carbonate hydroxide (17.39%), boric acid (5.23%)
iii) Nano-CuO – nano form of Cu: (NanoArc, 97.5%, 23–37 nm APS Powder, Alfa Aesar, Germany): CuO (97.5%)
iv) CCA: Osmose K-33 – water soluble form of Cu: (Osmose UK Protim Solignum Ltd) CuO (10.5%), chromic acid (29.9%), arsenic penta oxide As_2O_5 (20%), water (39.6%)

Preservative solutions were adjusted in order to reach a target elemental Cu retention level of 0.50 kg m^{-3} in treated wood blocks for each preservative treatment.

Wood blocks and treatments

Wood blocks (19 × 19 × 19 mm) were cut from the sapwood portions of Scots pine (*Pinus sylvestris* L.) lumber. The wood blocks (2 – 4 growth rings/cm) were free of knots and visible deposits of