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Removal of copper, chromium and arsenic from preservative-treated wood by chemical extraction-fungal bioleaching

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ABSTRACT

Large volumes of preservative-treated wood containing toxic Cr, Cu and As salts are decommissioned worldwide. This study investigated the effectiveness of solid-state fermentation with copper-tolerant brown-rot fungi for the remediation of wood treated with chromated copper arsenate (CCA) and acid copper chromate (ACC) formulations. Treatment of CCA- and ACC-wood with the most effective strain, *Antrodia vaillantii* FRLP-14G, attained extensive leaching of As and/or Cr, but Cu elimination was poor (<18%). Additional research showed that a variety of organic acids, including citrate, are effective Cu extractants. Based on these findings, a process combining chemical extraction and subsequent fungal treatment was developed that proved highly effective in removing inorganic pollutants from CCA-wood. Extraction of CCA-wood with citric acid (30 mM, pH 3.10) followed by a 28-day solid-state fermentation period removed 87% Cu, 80% Cr, and 100% As. These results indicate the potential of the two-stage process for the remediation of preservative-treated wood.

1. Introduction

Copper-based preservatives are widely used to increase the resistance of timber against fungal decay in outdoor applications. Chromated copper arsenate (CCA) is the most common preservative found worldwide in treated wood which is currently in service. In the year 1997, approximately 58,000 tons of the chemical were utilized in the USA to produce 12.7 million m^3 of treated wood product (AWPI, 1997). CCA treating solutions usually consist of a mixture of hexavalent chromium (CrO_3), divalent copper (CuO), and pentavalent arsenic (As_2O_5) oxides. The Cu in treated timber serves as the fungicide, whereas the As protects the wood against attack by insects. Chromium promotes fixation of the Cu and As in the wood through the formation of sparingly soluble metal complex, such as $CuCrO_4$ and $CrAsO_4$ (Pizzi, 1982). Although preservative chemicals are fixed within the treated timber by chemical binding with wood compounds and by precipitation reactions, leaching of inorganic pollutants has been reported to occur during the service life of treated timber (Hingston et al., 2001). Increasing concern about the potential public health and ecological risks associated with the release of As, a known human carcinogen, has led to significant restrictions in the use of As-based preservative formulations. As a result, a variety of arsenic-free copper-based preservatives such as acid copper chromate (ACC), alkaline copper quaternary, and copper boron azole have been introduced to replace CCA in wood preservation. All of these formulations rely on copper as their primary active ingredient because copper is an excellent fungicide and has relatively low mammalian toxicity. The appearance, strength properties, and handling characteristics of wood impregnated with these CCA alternatives are very similar to those of CCA-treated wood (Lebow, 2004).

Disposal of decommissioned timber treated with preservatives based on Cr, Cu and As is of increasing concern because of the high concentrations of toxic inorganic contaminants present in the treated wood and the large volumes of waste wood currently generated. CCA levels in treated wood vary widely depending of the expected use and decay hazard. In the USA, as an example, minimum retention standards for treating Southern Pine with CCA range from 4 kg/m^3 to as much as 40 kg/m^3 wood (AWPA, 1999). Consumption of CCA-treated wood has increased steadily since the early 1970s (Micklewright, 1998). With an average service life of 20 to 25 years, increasing volumes of decommissioned wood treated with inorganic preservatives should be expected in the coming decades. In the USA and Canada, 3–4 million m^3 of CCA-wood are currently decommissioned annually, and this amount is expected to increase to 16 million m^3 by 2020 (Cooper, 2003). Disposal of CCA-treated wood is also a growing problem in Europe (Helsen et al., 1998).

In numerous countries, including the USA, decommissioned wood treated with CCA and other Cu-based preservatives is exempted from a hazardous designation regardless of its characteristics, and common methods to dispose of this type of wood waste are combustion and land disposal in mixed municipal waste landfills and construction and demolition debris landfills. There is a growing concern that these waste management practices may

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result in environmental contamination with toxic pollutants. Numerous studies have confirmed that combustion of CCA-treated wood wastes can lead to the release of arsenic into the atmosphere (Hirata et al., 1993; McMahon et al., 1986). Decay of CCA-wood in microbial-active landfills might result in contamination of soil and groundwater with toxic pollutants. The ability of a wide variety of microorganisms to promote metal leaching from CCA-wood is well documented (Clausen and Smith, 1998; Clausen, 2004; De Groot and Woodward, 1998; Kartal et al., 2004a; Stephan et al., 1996). Mixed municipal waste landfills rely on microbial processes to attain waste stabilization, but construction and demolition debris disposal facilities can also be biologically active and they often lack a liner system to protect underlying groundwater.

In view of these developments, alternative waste management practices are needed to address current and future disposal issues associated with discarded CCA-treated wood. Solid-state fermentation with Cu-tolerant, brown-rot fungi is a promising approach for the remediation of decommissioned wood treated with Cu, Cr and/or As. Degradation of wood polysaccharides by brown-rot fungi can yield high levels of polycarboxylic acids (e.g., oxalic and citric acid) (Dutton et al., 1993; Takao, 1965), which are well known for their highly acidic character and metal chelating properties (Gadd, 1999). Fungal leaching of heavy metals has been demonstrated in a variety of materials including low-grade minerals (Gadd, 2004; Torma, 1988), preservative-treated wood (Kartal et al., 2004b, 2006; Stephan et al., 1996), and other metal-contaminated wastes (Gadd, 2004).

The objective of this study was to investigate the ability of selected brown-rot fungi to decay wood containing high concentrations of inorganic preservation chemicals (Cu, Cr and/or As) and to promote the mobilization of these hazardous contaminants. The brown-rot isolates utilized were selected in a screening program including 34 wood-degrading fungi for their excellent metal leaching efficiency and high tolerance to Cu toxicity (Sierra-Alvarez, 2007). Leaching experiments with synthetic solutions containing organic acids similar to those produced by fungi or strong inorganic acids were also conducted to evaluate their effectiveness in the treatment of metal-contaminated timber and to devise approaches to decrease residual metal levels in fungal-treated wood. The knowledge gained was utilized to develop a two-step process for the remediation of preservative-treated wood, involving a combination of citric acid extraction and bioleaching with a metal-tolerant brown-rot fungal culture which provided extensive removal of inorganic pollutants from CCA-wood.

2. Materials and methods

2.1. Microorganisms and culture media

Three brown-rot fungal strains were utilized in this study. *Antrodia vaillantii* (syn. *Fibroporia vaillantii*) strain DFP-7919 was kindly supplied by CSIRO Division of Forest Products, Clayton, Australia. *A. vaillantii* strain FPRL-14G and *Poria placenta* (syn. *Postia placenta*) strain FPRL-280 were a gift of the Forest Products Research Laboratory, Princes Risborough, UK.

Fungal cultures were cultured in agar-malt extract medium (per liter: 25 g of agar and 40 g malt-extract). Cultures were maintained in the same growth medium at 4 °C. Solid-state fermentation experiments were inoculated with fungal mycelium pregrown on sterile rye for approximately 2 weeks. Rye grain was cooked for 5 min and then allowed to soak overnight. Erlenmeyers (100 ml) were supplied with soaked rye (2 g dry weight (dwt)) and distilled water (8 ml), and they were autoclaved at 121 °C for 60 min. After cooling, Erlenmeyers were inoculated with one mycelium plug (diameter 6 mm) obtained from a 7 to 14-day old solid culture. All experiments involving fungal incubation were conducted in triplicate at a temperature of 27 °C and a relative humidity (R.H.) of 70%. The standard deviation values were generally under 5% of the mean value.

2.2. Preservative-treated wood

2.2.1. Wood treated with acid copper chromate (ACC)

Scots pine (*Pinus sylvestris* L.) sapwood was obtained from a local sawmill. Scots pine wood chips (15–25 mm) were dried overnight at 60 °C and their weight was determined. The wood chips were impregnated with a commercial aqueous ACC solution containing Cr (71.3% as CrO_3) and Cu (28.7% as CuO). The wood chips were degassed under vacuum (2.0–2.4 KPa) in a desiccator for 10 min to facilitate subsequent liquid uptake. Afterwards, the impregnation solution was allowed to flow into the desiccator until the wood chips were submerged. After 2 h, the wood chips were withdrawn, blotted lightly, and weighed. The treated wood was fixed for 3 weeks at 27 °C in a sealed plastic bag, and then dried in a drying oven at 23 °C. The concentrations of Cr and Cu in the wood chips were 6.09 ± 0.05 and 4.68 ± 0.02 g/kg wood dwt, respectively. The corresponding ACC-retention (9.1 kg/m^3 wood) is in the range of the retentions in treated wood for use above ground. A sample of treated wood chips was milled under liquid nitrogen and sieved to yield wood meal with a particle size <40 mesh (equivalent to <0.42 mm). The wood meal sample was utilized in some of the chemical extraction experiments.

2.2.2. Wood treated with CCA

Spruce (*Picea abies*) sapwood was obtained from a local sawmill. The sapwood sample was chipped and sieved, and the wood chip fraction ranging in length from 15 to 25 mm was used. Wood chips were treated with a commercial CCA preservative solution containing Cu (18.5% as CuO), Cr (47.5% as CrO_3), and As (34.0% as As_2O_5) as described above for the ACC-wood chips. The concentrations of Cu, Cr and As in the treated wood chips were 1.01 ± 0.01, 1.39 ± 0.03, and 1.29 ± 0.02 g/kg wood dwt, respectively. The corresponding CCA-retention (2.6 kg/m^3 wood) is in the range of the retentions in treated wood for use above ground.

2.3. Solid-state fermentation experiments

Batch reactors were supplied with treated wood chips (20 g dwt) impregnated with demineralized water to 150% moisture (based on wood dwt). The reactors were autoclaved for 60 min at 121 °C, allowed to cool down and then inoculated with rye colonized by the selected brown-rot strain (2 g) suspended in 10 ml of sterile water. The rye inoculum was not ground prior to inoculation. In some experiments, CCA-wood chips were extracted with citric acid prior to biological treatment. Wood chips were extracted with 30 mM citric acid pH-3.1 (10 ml/g wood dwt) for 5 h in a shaker (150 rpm) at 30 °C. Non-inoculated controls were run in parallel to determine mass and metal losses by abiotic mechanisms.

Samples of the colonized wood chips were obtained periodically under aseptic conditions during the course of the experiments. Wood chips were extracted with distilled water (10 ml/g wood dwt) as described below, and the resulting leachate was analyzed for Cu, Cr and/or As content. In some experiments, sterile-incubated and biotreated wood chips were first extracted with water and then with 10 ml of citric acid (30 mM, pH 3.10) per g wood dwt.

2.4. Chemical leaching of metals from preservative-treated wood

Leaching of Cu, Cr and As by direct extraction of preservative-treated wood with 0.15 M solutions of HCl, H_2SO_4 and different