CCA removal from treated wood by chemical, mechanical, and microbial processing

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Abstract

Most preservative-treated wood produced and consumed in the U.S. is treated with toxic inorganic compounds containing copper, chromium, and arsenic. Because chromated copper arsenate (CCA) is fixed to the wood, treated wood has not been considered toxic or hazardous and is currently landfilled. Increasing public concern about environmental contamination from treated wood combined with increasing quantities of CCA-treated wood nearing the end of its service life has presented a recycling challenge for this fiber source. In this study, CCA-treated wood was processed by acid extraction, steam explosion and bacterial fermentation, and evaluated for removal of copper, chromium and arsenic. Copper was the least resistant to removal by these treatments, while chromium was the most resistant to removal. Grinding CCA wood chips into 20-mesh sawdust provided greater access to CCA components and greater removal of CCA metals by acid extraction and bacterial fermentation. Exposing CCA-treated sawdust to Bacillus licheniformis CC01 resulted in 91%, 15% and 45% removal of Cu (as CuO), Cr (as CrO₃), and As (as As₂O₅), respectively. Eighty-one percent CuO, 62% CrO₃, and 89% As₂O₅ was removed from CCA-treated sawdust by oxalic acid extraction alone. Combining acid extraction and bacterial fermentation resulted in similar rates of metal removal from CCA chips and sawdust; 80% reduction in CrO₃, 100% removal of As₂O₅, 90 and 99% removal of CuO from chips and sawdust, respectively. Processing chips by steam explosion did not enhance removal of CCA components alone or in conjunction with acid extraction and bacterial fermentation. Grinding chips following acid extraction and prior to bacterial fermentation did not enhance the ability of the bacterium to remove metals from treated or steam exploded chips. The combination of acid extraction and bacterial fermentation was successful at removing 80-100 percent of the metals from CCA-treated wood sawdust and chips.

Key Words: chromated copper arsenate (CCA), preservative, oxalic acid, Bacillus licheniformis CC01, bacteria, steam explosion
INTRODUCTION

Most of the $212 \times 10^5 \text{ m}^3$ of preservative-treated wood produced and consumed in the U.S. annually is treated with toxic inorganic compounds containing copper, chromium, and arsenic (CCA)[15]. There has been a 300% increase in demand for treated lumber between 1980 and 1993 [19]. Chromated copper arsenate-treated wood has an expected service life of 20-50 years depending on the conditions of service and the method of treatment [6, 19]. Based on current levels of production and expected service-life, Cooper [6] predicted that CCA-treated wood being removed from service annually in the U.S. will increase from 1 million cubic meters in 1990 to 16 million cubic meters by 2020. Currently, all CCA-treated waste wood is placed in approved landfills. Incineration is not an acceptable means of disposal because of potential toxicity of chemicals and metals remaining the ash. Treated wood is generally not considered a toxic or hazardous waste because the chemical components are fixed to the wood, but fungi and bacteria that can degrade CCA-treated wood are being discovered [4, 5, 20]. There is increasing public concern about environmental contamination from treated wood removed from service and placed in landfills [19]. Methods for removing CCA from treated waste wood need to be developed for both economical and environmental reasons. One possible method for recycling CCA-treated wood fiber would be to modify the fiber by removing the heavy metal components so that the wood fiber may be reused or recycled.

CCA-treated wood will begin to be removed from service in increasing quantities around the turn of the century. Developing methods now for recycling this wood resource would help alleviate potential soil and groundwater contamination in our ever-dwindling landfills. Smith and Shiau surveyed 170 composite manufacturers to evaluate whether they would consider using spent CCA-treated wood fiber in composite products. Respondents indicated that the health of mill workers and residual chemicals left in the fiber were the two most important factors in using recycled CCA fiber in their products [19]. They felt the fiber would need to be certified free of all chemicals and be approved by U.S. governmental agencies before it could be considered for use in their operations. Developing economical and efficient methods for processing this valuable fiber source need to be developed. Thorough removal of all metal components is essential for acceptance by manufacturers and the public.

Previous studies on the chemical leachability of CCA have evaluated acid extractions using citric, acetic, formic, oxalic, nitric, or sulfuric acids [13, 16, 21]. These studies have shown that the acid type has an effect on leaching rates and final concentrations of CCA in the wood, but the initial concentration of CCA in the wood does not affect leaching. Treated wood contains chromium in the largest proportion and it is chromium that has a strong affinity for wood lignin [23] making it the most resistant component of CCA to chemical extraction or microbial release [4, 22].
Certain isolates of wood decay fungi can readily decay wood that has been treated with CCA at levels intended to inhibit decay fungi. In fact, some fungal isolates can decay treated wood as rapidly as untreated wood. Previous studies [11] have suggested that oxalic acid production by decay fungi plays a critical role in the initiation of the decay process. A recent study by Stephan et al. [20] examined the leachability of chromium and copper from chromium copper-treated wood with oxalic acid at various concentrations. They showed 98% of the initial chromium could be leached at very low pH levels (0.69), but that leachability declined quickly with an increase in pH. One objective of this study was to evaluate the ability of oxalic acid to extract all components of CCA from treated wood in conjunction with other mechanical and microbial processes.

Steam explosion converts wood chips into a brown fibrous mass through a process that involves saturating the chips with steam for a specified time at a specified pressure, followed by rapid decompression [14]. A physical defibering occurs during the rapid decompression and a chemical autohydrolysis occurs during the steam treatment [19]. Some volatile degradation products, such as acetic acid, furfural, methanol, and hydroxymethyl furfural may be produced. Steam exploded material is slightly acidic (pH 3.5-4.0) due to water soluble lignin and acetic acid, but in general, all wood components are recoverable in total following this process. Steam explosion has been studied as a means of opening the chemical structure for accessibility of the carbohydrates [2]. Thus, a second objective of this study was to evaluate the ability of steam explosion to open the chemical structure of CCA-treated wood, to provide accessibility to copper, chromium and arsenic during subsequent oxalic acid extraction or bacterial fermentation.

Gram-positive spore-forming bacteria from the genus Bacillus are commonly isolated from preserved wood, possibly due to the resistance of bacterial spores to harsh conditions. They are tolerant of copper levels normally utilized to inhibit basidiomycetous fungi, the group of fungi targeted by wood preservatives [5, 17]. Fungal and bacterial tolerance of CCA varies with the amount of preservative present and the service condition [18]. Singh et al., [18] presented microscopic evidence of erosion bacteria causing degradation in failed CCA-treated timbers. Attack by erosion bacteria was throughout the diameter of the pole, while attack by aerobic soft-rot fungi was confined to the outer areas of the pole. Daniel and Nilsson, and Daniel et al. [7, 8] have documented tunneling bacteria in degraded CCA treated Radiata pine using EDAX-TEM.

Cole and Clausen [5] surveyed an experimental test plot containing CCA-treated 2 x 4s in Madison, WI for bacteria that could tolerate CCA. One isolate, identified as Bacillus licheniformis CC01, has been shown to release copper, chromium and arsenic from CCA-treated sawdust when sawdust was exposed to the bacterium in an aerated liquid culture for 3 weeks. Intracellular accumulations of copper and chromium were also detected by energy dispersive x-ray analysis (EDAX). The final objective of this study was to extend these observations by evaluating bacterial fermentation of acid extracted or steam exploded CCA wood as a means of removing 90-100 percent of the chromium, copper and arsenic from CCA-treated wood.
MATERIALS AND METHODS

Wood source

Three-year-old residential decking was chipped, homogeneously mixed and stored in watertight containers for further use. This material was originally treated to 6.4 kg/m$^3$ (0.40 pounds per cubic foot (pcf)) with chromium, copper, and arsenic formulation (CCA). In some experiments, chips were ground to 20 mesh in a Wiley mill (Figure 1).

![Figure 1. Processing protocol for CCA-treated wood.](image)

Steam explosion

Wood chips were sealed in a batch steam exploder with a 0.25 m$^3$ (0.9 ft$^3$) capacity and processed at Virginia Tech’s Brooks Forest Products Center in Blacksburg, Virginia. Chips were processed for 10 min at 205°C and $2.4 \times 10^6$ Pa (350 psi) followed by instantaneous release of pressure. Steam exploded chips were either 1) tested for release of CCA chemicals (control), 2) washed with water for 4 h and tested for remaining chemicals, 3) oxalic acid extracted, 4) further treated by exposure to B. licheniformis CC01 or 5) treated with a combination of acid and bacteria fermentation.
**Acid extraction**

One percent oxalic acid (pH 2.0) was tested for extraction of CCA chemicals. Treated wood chips, treated wood sawdust, and steam exploded chips were extracted for 24 h on a rotating platform. Wood samples were separated from the acid solution and either tested for removal of CCA chemicals or further treated with *B. licheniformis* CC01.

**Bacterial culture**

*Bacillus licheniformis* CC01, a gram positive, spore-forming, facultative anaerobe was cultured and maintained on nutrient agar (Difco) at 25°C throughout the study. Flasks (300 ml) containing 100 ml nutrient broth and 0.5 g CCA-treated chips or sawdust were inoculated with 1 ml of an 18 h nutrient broth culture of *B. licheniformis* CC01. Cultures were incubated at 25°C on a rotating table at 200 rpm for 10 d. Controls consisted of uninoculated flasks of nutrient broth and treated wood which was added before autoclaving.

**Sample collection**

CCA wood (sawdust or chipped) was separated from oxalic acid or culture filtrate by aspiration through Whatman filter paper No. 1. Wood samples were rinsed briefly with deionized water and dried at 60°C for 24 h.

**Sample analysis**

For all experiments, 0.5 g samples of dried 20-mesh sawdust were analyzed by atomic absorption (AA) spectroscopy according to AWPA [1] to determine copper, chromium and arsenic levels. For the acid extractions and bacterial fermentation experiments, 20 ml samples (acid and culture filtrate, respectively) were submitted for analysis by AA spectroscopy.

**RESULTS**

Atomic absorption analyses for copper, chromium, and arsenic following acid extraction, bacterial fermentation and steam explosion of CCA sawdust and chips are shown in Table 1. The percent reduction of each metal compared to unprocessed controls is also shown in Table 1. Exposure to the bacterium, *Bacillus licheniformis* CC01 removed 14% more Cu (91% vs. 77% reduction expressed as CuO), and 45% more As (45% vs. 0% reduction expressed as As$_2$O$_3$), but 10% less Cr (15% vs. 25% reduction expressed as CrO$_3$) from sawdust than from chipped CCA wood. Likewise, exposure of sawdust to the bacterium removed 22% more Cu (91% vs 69% reduction), and 18% more As (45% vs 27% reduction) than from steam exploded CCA chips treated with the bacterium. Steam explosion followed by bacterial fermentation removed 35% Cr, a 10% increase over
bacterial exposure to chipped CCA wood and a 20% increase over bacterial exposure to CCA sawdust.

Oxalic acid extraction of CCA sawdust removed 65% more Cu (81% vs 16% reduction), 48% more Cr (62% vs 14% reduction), and 47% more As (89% vs 42% reduction) than acid extraction of chipped CCA wood (Table 1). Likewise, acid extraction of sawdust removed more Cu, Cr, and As (8%, 61%, and 52%, respectively) than acid extraction of steam exploded chips.

Table 1. Atomic absorption analysis of copper, chromium, and arsenic following acid extraction, bacterial fermentation and/or steam explosion of CCA sawdust and chips.

<table>
<thead>
<tr>
<th>Treatments</th>
<th>CuO (ppm)</th>
<th>Percent Reduction</th>
<th>CrO₃ (ppm)</th>
<th>Percent Reduction</th>
<th>As₂O₅ (ppm)</th>
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<td>8100</td>
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<td>6923</td>
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<td>2608</td>
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<td>3100</td>
<td>62</td>
<td>500</td>
<td>89</td>
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<td>99</td>
<td>1730</td>
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<td>3300</td>
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n=3

Percent reductions of CuO, CrO₃ and As₂O₅ for individual and combined processing methods are illustrated in Figure 2. The combination of acid extraction followed by bacterial fermentation of sawdust removed 99% CuO, 79% CrO₃, and 100% As₂O₅. Table 1 shows that when CCA chips were acid extracted prior to bacterial fermentation, metal removal rates were similar to those seen in sawdust (90% CuO, 80% CrO₃, and 100% As₂O₅ reduction). Grinding CCA chips to 20-mesh following acid extraction and prior to fermentation did not enhance metal removal.
Acid extraction of steam exploded chips followed by either bacterial fermentation or grinding and then fermentation did not enhance removal of metals (Table 1). Likewise, water washing the steam exploded chips to remove some of the acids produced during the steam explosion process was not advantageous to metal removal when the chips were then exposed to the bacterium.

DISCUSSION

Copper chromated arsenate (CCA)-treated wood chips or sawdust were treated by either chemical modification (i.e., acid extraction), mechanical modification (i.e., steam explosion), or microbial modification (i.e., exposure to a bacterium) to evaluate these processes for metal removal from the wood fiber. CCA-treated wood was processed by individual methods as well as combinations of two or more methods in an effort to remove greater than 90 percent of the metals from the wood. Oxalic acid extraction followed by bacterial fermentation removed 90% CuO, 80% CrO3 and 100% As2O5 of the initial concentration of metals in chipped CCA-wood.

Spent CCA-treated wood and treated waste wood present a unique recycling challenge. CCA is fixed to the lignin component of wood by the reduction of Cr+6 to Cr+3 [12]. The strong affinity chromium has for lignin [22] aids in the retention of arsenic and copper, but the actual complexing of chromium appears to inhibit it’s removal in appreciable quantities when it is exposed to this isolate of Bacillus licheniformis [4].

Exposure of CCA-treated wood to acid and heat may partially reverse the CCA fixation process [19]. High acidity may be the key to “unfix” copper for further leaching by other processes [20]. Leachability tests with many different acids have shown some degree of success at removing various amounts of CCA metals from treated wood [13, 16, 20]. Oxalic acid, which is implicated in the wood decay process by brown-rot fungi [11], has recently been examined for leachability of chromium and copper from chromium copper-treated wood under conditions of high acidity [20]. In the current study, oxalic acid extraction at pH 2.0 was the most successful single treatment of CCA sawdust at removing copper, chromium, and arsenic. Oxalic acid extraction followed by bacterial fermentation removed 80 to 100% of the CCA chemicals from chipped wood. Oxalic acid extraction may be partially reversing the fixation process. Similar results were seen by Smith and Shiau [19] when they treated CCA sawdust with citric acid. Not only did they show that citric acid extraction of treated sawdust over 21 d could remove over 80 percent of copper, chromium and arsenic, but they also showed a dramatic effect of pH on metal removal. In extractions with citric acid, a pH of 3.5 removed chromium nearly twice as effectively as a pH of 5.0.

Since chipping is a standard process during recycling of untreated wood for composite products, it was desirable to examine processes for removal of metals that would be effective on chipped treated wood. Grinding treated wood to 20-mesh for initial experiments was merely a first step to evaluate the various processing methods under
conditions of maximum exposure to wood surface area, i.e. maximum access to metals. The ability of a process to remove metals from spent CCA-treated chips increases the likelihood of incorporating the method into existing manufacturing practices. Not only would processing chipped wood present a tremendous economical advantage over processing sawdust, but it would also provide a safer environment for workers.

Members of both *Bacillus* and *Pseudomonas* genera are ubiquitous in soils and produce pectinolytic and cellulolytic enzyme systems which may assist in releasing copper and arsenic from wood. Members of both genera are more resistant to copper than Basidiomycetes and have been isolated from preservative-treated wood [3, 10]. Tolerance levels of CCA in artificial medium showed that concentrations as high as 0.675% cause growth of these bacteria to cease, but the organisms remained viable [10]. Energy dispersive X-ray analysis suggested that *Bacillus licheniformis* CC01 accumulated copper and chromium intracellularly [5]. However, bacterial cells collected from spent medium accounted for a small fraction of the total CCA by weight of the initial test material. Most of the released metals were found in the spent culture medium (data not shown). It has been suggested that bacterial capsules or slime layers complex with elements and then release them enzymatically in small quantities [9]. Daniel and Nilsson, and Daniel *et al.* [7, 8] examined degraded CCA-treated *Radiata pine* utilizing TEM-EDAX and found copper accumulations as dense particles within the nuclear region of tunneling bacteria. They also noted that a majority of the chromium and arsenic remained as extracellular secretions. Surely, if bacteria can be isolated that have adapted to release metals from CCA-treated wood, then public concern over potential soil and groundwater contamination from landfilling spent CCA-treated wood is a valid concern.

Steam explosion as a means of opening the chemical structure of wood for accessibility to chemical components, demonstrated limited success at releasing metals from treated wood. Steam exploded chips exposed to the bacterium showed a 35% reduction in chromium, while chromium removal was nearly zero for the oxalic acid extraction alone. Further combinations of treatments following steam explosion (e.g. acid extraction and bacterial fermentation), were only successful at removing increasing quantities of copper. Smith and Shiau [19], showed that citric acid extraction for copper was similar between CCA-treated sawdust and steam exploded pulp, but chromium and arsenic were more effectively removed from acid extracted CCA-treated sawdust.

In summary, chemical, physical and microbial processes were evaluated for their ability to remove CCA chemicals from treated wood wastes. Mechanical modification of the treated fiber by steam explosion demonstrated limited success. Chemical fiber modification with oxalic acid was the single most successful treatment for removing 62% to 89% of the CCA chemicals from treated sawdust. Bacterial fermentation released 77% of the copper from chipped wood and 91% copper from the sawdust, but the microorganism was unable to release more than 45% arsenic from CCA sawdust or 35% of the chromium from steam exploded chips. Ideally, a treatment or combination of treatments should remove greater than 90% of all CCA components for the fiber to be acceptable for use in recycled composites. Overall, oxalic acid extraction was the most
successful single treatment at removing significant quantities of metals from sawdust (81% CuO, 62% CrO$_3$, and 89% As$_2$O$_5$). Clearly, combining oxalic acid extraction with bacterial fermentation by *Bacillus licheniformis* CC01 removed significant quantities of CCA metals from chipped wood. Optimizing treatment conditions i.e. exposure time to the acid and nutritional requirements of the bacterium, will be studied further to increase chromium release by these two processes.
REFERENCES


Figure 2. Percent reduction of CuO, CrO$_3$, and As$_2$O$_5$ following treatment of CCA-chips, sawdust, and steam exploded wood with oxalic acid extraction, bacterial fermentation with *Bacillus licheniformis* or acid extraction followed by bacterial fermentation.
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Section 5 Environmental Aspects

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