Leachability and decay resistance of particleboard made from acid extracted and bioremediated CCA-treated wood

S. Nami Kartal *, Carol A. Clausen

USDA Forest Service Forest Products Laboratory. One Gifford Pinchot Dr, Madison, WI 53705-2398, USA

Received 3 November 2000; received in revised form 14 February 2001; accepted 20 February 2001

Abstract

Composite manufacturing appears to be one of the most suitable recycling options for chromated copper arsenate (CCA)-treated waste wood. However, in many applications it would be beneficial to remove much or all of the CCA from the wood prior to composite production. This paper evaluates the effect of remediation processes, namely oxalic acid (OA) extraction and Bacillus licheniformis fermentation, on leaching of copper, chromium, and arsenic from particleboard made from remediated wood particles and also investigates decay resistance of the particleboard. Oxalic acid extraction and bioremediation by B. licheniformis affected the chemical properties of wood particles and significantly increased leaching of elements from CCA-treated wood particles. The particleboard containing OA-extracted and bioremediated particles showed generally high leaching losses of remaining elements. Exposure of particleboards to decay fungi in soil block tests indicated that boards containing CCA-treated particles were most resistant to fungal degradation. Also, for a given board type, Gloeophyllum trabeum resulted in greater weight losses than Postia placenta and Trametes versicolor after 12-week exposure. We concluded that bioremediation of CCA-treated wood is a promising method of safely reusing treated fiber, although chemical extraction diminished the properties of composites prepared from this material. Published by Elsevier Science Ltd.

Keywords: Treated-waste wood; Remediation; Acid extraction; Bacterial fermentation; Composite; Bacillus licheniformis; Gloeophyllum trabeum; Postia placenta; Trametes versicolor

1. Introduction

Chromated copper arsenate (CCA) is currently a major commercial wood preservative for many applications in the United States. By 1995, $67 \times 10^6$ kg ($147 \times 10^6$ pounds) of water-borne preservatives were utilized for wood treating purposes and over 90% of this was CCA (Solo-Gabriele et al., 1999). Approximately $17 \times 10^6$ m$^3$ ($600 \times 10^6$ ft$^3$) of CCA-treated wood are generated annually (Cole and Clausen, 1996). It is estimated that the quantity of CCA-treated wood removed from service will increase to $12 \times 10^6$ m$^3$ ($430 \times 10^6$ ft$^3$) by the year 2004 (McQueen and Stevens, 1998). Cooper (1993) predicted that CCA-treated wood being removed from service annually in the United States would increase to $16 \times 10^6$ m$^3$ ($570 \times 10^6$ ft$^3$) by 2020.

Currently, some options for dealing with spent CCA-treated wood include reuse, recycling, incineration, use as fuel, and landfill disposal (Huang and Cooper, 2000). Recycling of treated wood waste into wood-based composites is a relatively low-cost alternative to disposal into the environment (Vick et al., 1996). Recycling treated wood into composites is not a new concept. Several studies have recently concentrated on wood-based and wood-cement based composites from CCA-treated wood and compatibility of copper, chromium, and arsenic with adhesives and cement in composites (Boggio and Gertjejansen, 1982; Hall et al., 1982; Huang and Cooper, 2000; Kamdem and Munson, 1996; Munson and Kamdem, 1998; Schmidt et al., 1994; Vick et al., 1996). However, concerns about introducing preservatives into manufacturing facilities and concerns about leaching from composites made from waste treated wood have limited this management option.
Extraction of the CCA elements from the wood fiber can increase recycling opportunities for the remaining wood pulps. One novel method for recycling CCA-treated wood fiber would be to modify it by removing all or much of the heavy metal components so that both the wood fiber and the metals could be reclaimed. Acid extraction, one option for removal of copper, chromium, and arsenic from treated wood fiber, has been explored by several researchers using different acids (Kim and Kim, 1993; Pasek, 1994; Stephan et al., 1993). Clausen and Smith (1998) and Stephan et al. (1996) showed that the removal of copper, chromium, and arsenic from CCA-treated wood waste increased significantly during oxalic acid (OA) extraction. OA, the strongest organic acid (pK_a: 1.23), has also been implicated directly and indirectly in the brown-rot decay process. OA is also involved with pH reduction and acid-catalyzed hydrolysis of the wood substrate, especially hemicelluloses (Green et al., 1991; Green and Clausen, 1999; Green and Hightley, 1997). Bacterial fermentation is another possible method for removal of heavy metals from treated wood since some bacteria are extremely tolerant of toxic metals (Cole and Clausen, 1996; Daniel et al., 1987; Daniel and Nilsson, 1985). The mode of action for bacterial removal of heavy metals is often conversion of CCA elements into their water-soluble form. Once converted, copper, chromium, and arsenic can be removed from the wood through a washing process (Felton and DeGroot, 1996). Clausen (1997), Clausen and Smith (1998), Cole and Clausen (1996), and Crawford and Clausen (1999) showed that Bacillus licheniformis isolated on CCA-treated wood had a great potential to remove toxic metals when treated wood sawdust was exposed to this organism in liquid culture. Clausen and Smith (1998) and Cole and Clausen (1996) suggested that besides the advantage of enabling reuse of “cleaned” treated fiber, fermentation of CCA-treated wood by bacteria reduces the risk of soil and groundwater contamination from landfilling spent CCA-treated wood.

Previous research on the physical and mechanical properties of particleboard made from CCA-treated and remediated wood waste showed that particleboard properties were diminished either due to the remedial treatments or interference of OA with the UF resin (Clausen et al., 2000). Several studies on mechanical properties of wood-based composites made from CCA-treated particles suggest that the properties were lower than those of untreated particles due to either the surface modification by the preservative treatment or the interaction between resin and metals in preservative (Gertjejansen et al., 1988; Vick et al., 1990, 1996; Vick, 1980). The objectives of the present work were to evaluate (i) the leachability of copper, chromium, and arsenic from particleboard made from CCA-treated and remediated wood fibers, (ii) residual decay resistance of the particleboard made from recycled and remediated fibers, and (iii) effect of OA extraction and bioremediation by B. licheniformis on the properties of wood particles and particleboard.

2. Materials and methods

2.1. Remediation of CCA-treated wood particles

For OA extraction, 2 kg of CCA-type C treated wood particles (6.4 kg m⁻³ retention) (hammermilled to 6-16 mesh (3360-1190 µm)) were extracted with 18 L of 0.8% OA (pH: 1.7) (Sigma Chemicals, St. Louis, MO) for 18 h at 25°C in 18 L polypropylene containers.

In order to bioremediate the particles, OA was siphoned off and 18 L 0.8% nutrient broth (Difco, Detroit, MT) prepared according to manufacturer’s directions, were added and inoculated with 500 ml of an 18-h culture of B. licheniformis CC01, a gram-positive spore-forming and copper-tolerant bacterium. This Bacillus isolate grows at temperatures ranging from 10°C to 55°C and at pH 3-10 in nutrient broth (Clausen and Smith, 1998). Inoculated containers were then incubated at 28°C and stirred at 100 rpm for 10 days. Spent medium was siphoned off and bioremediated chips were collected on cheesecloth covered screens and oven dried at 60°C (Clausen, 2000; Clausen and Smith, 1998).

Three additional types of particles were evaluated: (1) untreated southern yellow pine (SYP) particles, (2) SYP particles treated to 6.4 kg m⁻³ with CCA-type C, and (3) SYP particles treated to 6.4 kg m⁻³ with CCA-type C followed by an OA-extraction as described above.

2.2. Particleboard manufacturing

Two 406 × 406 mm particleboard panels by 6.4 mm thick, with an approximate specific gravity of 0.80, were manufactured per particle type. Nine hundred grams of each of four particle types (untreated SYP, CCA-treated SYP, OA-extracted SYP and bioremediated SYP) were blended with 10% urea formaldehyde (UF) resin (Southern Adhesives’ 9-2035, Lenoir, NC, USA). The UF resin was applied in a rotating drum blender using an atomizing Binks spray gun. Particleboard panels were formed by hot-pressing for 5 min to an internal temperature of 121°C. The boards were then trimmed to 406 × 406 mm and conditioned at 20°C and 65% relative humidity (RH) for 2 weeks (Youngquist, 1999).

2.3. Chemical composition and pH of particles and particleboard samples

A single homogenous sample of each type of wood particle was analysed for Klason lignin, acid soluble lignin, acetyl content, carbohydrate composition and pH. For lignin content in wood, particles were milled to pass a US Standard 30-mesh (589 µm) screen and vacuum dried at 45°C. Approximately, 100 mg of sample was hydrolyzed with 1.00 ml 72% H_2SO_4 for 1-h at 30°C. Samples were diluted to 4% H_2SO_4 with deionized water, fucose was added as an internal
standard, and a secondary hydrolysis was performed. A standard mixture of sugars was hydrolyzed in parallel with each batch of samples. Losses during primary hydrolysis were minimal and were ignored. Following secondary hydrolysis, samples were immediately filtered and three washes with 5 ml deionized water were collected in 100 ml volumetric flasks and brought to volume with water. Acid-soluble lignin was estimated by the absorbance of the hydrolysate at 205 nm. The acid-insoluble lignin residue (Klason lignin) was washed an additional six times with 10 ml hot deionized water and quantitated gravimetrically. Klason lignin values were corrected for ash content gravimetrically following incubation of the lignin at 575°C for less than 3 h.

To determine acetyl content in wood, approximately 100 mg sample was deacetylated by incubation for 2 h at 60°C in 5 ml of 100 mM sodium hydroxide with 0.134 mM propionic acid added as an internal standard. Hydrolysates were diluted 100-fold with deionized water and their acetate contents were determined by anion exchange high performance liquid chromatography (HPLC) using suppressed conductivity detection. The chromatographic separation was achieved with IonPac AG-11 guard and AS-11 analytical columns connected in series by elution with 0.10 mM sodium hydroxide at a flow rate of 2.0 ml min⁻¹.

Wood sugars were determined by subjecting the samples to acid hydrolysis, and then analyzing the hydrolysates using anion exchange HPLC with pulsed amperometric detection. Sugar separation was achieved with Carbo-Pac PA1 guard and analytical columns connected in series. Sugars were quantitated using an internal standard method and results were reported in terms of percent of the original sample mass (Davis, 1998).

For pH of wood particles and particleboard samples, one part (by weight) of ground sawdust (to pass a US Standard 40-mesh (420 pm) screen) was placed in three parts of deionized water. The sample and water were mixed until the sawdust was wet. pH was measured after 10 min and 24 h.

2.4. **Water absorption and thickness swelling**

Particleboard samples (152 x 152 mm) were evaluated for water absorption and thickness swelling at 2, 24, and 336-h according to ASTM D 1037-96a test method (ASTM, 1998). Water absorbed from the increase in weight during submersion and thickness swelling, as a percentage of the conditioned thickness at 20°C and 65% RH were calculated.

2.5. **Leaching**

CCA leaching performance was evaluated on particleboard samples and wood particles using a modified AWPA E11-97 test method (AWPA, 1999a). The board samples with dimensions 19 x 19 x 6.4 mm were cut from the particleboard panels. Samples of wood particles used for particleboard manufacture, equal to the particle weight in the particleboard samples, were exposed to the same leaching test for comparison. Wood particles and particleboard samples were put into glass containers and leached with deionized water using the water-to-wood ratio specified by AWPA E11-97 test method (AWPA, 1999a). The water was replaced after 6 h, 1 day, and 2 days, and every 2 days thereafter for a total of 14 days. Water samples were collected after each water replacement and the water samples were analyzed for copper, chromium, and arsenic with a Perkin Elmer 5100 PC Atomic Absorption Spectrometer (AAS) (Perkin Elmer, Norwalk, CT, USA) using flame atomization for higher concentrations and graphite furnace atomization for lower concentrations of the elements to estimate total amounts of CCA elements leached from the board samples and wood particles (AWPA, 1999a). The results were expressed as percentage of copper, chromium, and arsenic leached, relative to the amounts contained in the board samples and wood particles originally. Two replicate leaching tests were completed for each board sample and wood particle type.

2.6. **CCA retention**

Before and after the leaching course, the particles and particleboard samples were ground to pass a US Standard 30-mesh (589 µm) screen and analyzed for amount of copper, chromium, and arsenic by X-ray fluorescence spectroscopy according to AWPA A9-99 test method (AWPA, 1999b). The percent reduction of copper, chromium, and arsenic in OA-extracted and bioremediated particles was calculated based on the initial amount of elements in CCA-treated particles.

2.7. **Decay resistance**

Particleboard samples, 19 x 19 x 6.4 mm, unleached and leached for 14 days, were subjected to a modified decay resistance test. Four replicate samples of each particleboard type were dried to constant weight, steam-sterilized at 100°C, and exposed to two brown rot fungi, *Gloeophyllum trabeum* (Mad 617) and *Postia placenta* (Mad 698) and the white rot fungus, *Trametes versicolor* (Mad 697) in a modified soil-block test according to AWPA E10-91 test method for solid wood (AWPA, 1999c). After 12 weeks of incubation at 27°C and 70% RH, the surface fungus mycelia was removed, the samples were dried to constant weight at 60°C, and weight losses determined as percentage of total particleboard mass.

3. Results and discussion

3.1. **Effect of remediation on wood particles and particleboard samples**

The comparative chemical composition of untreated, CCA-treated, OA-extracted, and bioremediated particles
Basidiomycetes and has been isolated from CCA-treated wood (Clausen, 1996; Clausen and Smith, 1998; Greaves, 1973).

3.2. Water absorption and thickness swelling

Percentage water absorption and thickness swelling after 2, 24, and 336-h submersion are shown in Table 3. The board samples with CCA-treated particles were the most resistant to water absorption and initial thickness swelling, but after 24-h submersion, thickness swelling was 25.7% and water absorption was 42.5% for the same particle-board samples. Water absorption and thickness swelling rates were similar in control particleboard samples and particleboard samples containing bioremediated fibers. Two, 24, and 336-h water absorption and thickness swelling test results showed that control particleboard samples had the greatest absorption and swelling rates compared to the boards made from CCA-treated and OA-extracted particles. The decreased rates in particleboard samples containing CCA-treated particles are assumed to be an effect of CCA preservative elements, which may decrease wettability of wood (Maldas and Kamdem, 1998).

3.3. Leachability of CCA elements

The percentage of copper, chromium, and arsenic leached from the wood particles is shown in Fig. 2. The leaching rate and total percentage of copper released from OA-extracted particles were considerably higher than those from CCA-treated and bioremediated particles (Table 4). The percentage of copper leached from OA-extracted particles was between 2.8% and 9.6% for each leaching time (Fig. 2).

Compared to copper, the leaching rate of chromium was much greater after 6-h and 1-day of leaching, although the total percentage of chromium released from OA-extracted particles was smaller (Fig. 2). Total percentage of chromium leached from CCA-treated particles over 14 days was 2.6%, whilst 56.2% of the remaining chromium leached from OA extracted particles and an additional 26.5% of chromium remaining following OA extraction leached from the bioremediated particles (Table 4).

Unexpectedly high levels of arsenic leached from CCA-treated particles compared to copper and chromium leaching rates (Fig. 2 and Table 4). While the total percentage of arsenic released from CCA-treated particles exceeded Cu and Cr by 4 to 6-fold, arsenic in OA-extracted particles was 1.8-1.6 times less than copper and chromium in the same type of particles, respectively.

As seen in Table 4, the total percentage of elements leached from OA-extracted and bioremediated particles was considerably higher than the total percentage of elements leached from CCA-treated particles. It may be concluded that exposure of CCA-treated particles to OA-extraction and bacterial fermentation may reverse the CCA fixation process (Smith and Shiau 1997; Stephan et al., 1993).

Fig. 3 and Table 4 show the percentage of copper, chromium, and arsenic released from the particleboard samples during the leaching course. The total percentage of copper released from the boards with CCA-treated particles was insignificant compared to that of the other types of particleboard. Compared to CCA-treated particles, the total percentage of copper removed from the particleboard was smaller. In the particleboard samples containing OA-extracted particles, the total percentage of copper leached decreased 42.6% compared to the OA-extracted
Table 3
Water absorption and thickness swelling in particleboard samplesa

<table>
<thead>
<tr>
<th>Particleboard type</th>
<th>Water absorption (%)</th>
<th>Thickness swelling (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6-h</td>
<td>24-h</td>
</tr>
<tr>
<td>Control particleboard</td>
<td>53.6</td>
<td>65.6</td>
</tr>
<tr>
<td>CCA particleboard</td>
<td>19.1</td>
<td>42.5</td>
</tr>
<tr>
<td>OA particleboard</td>
<td>27.8</td>
<td>47.3</td>
</tr>
<tr>
<td>Bioremediated particleboard</td>
<td>49.0</td>
<td>74.5</td>
</tr>
</tbody>
</table>

*aEach value represents the means of 4 replications. Values in parentheses are standard deviations.

Table 4
Total CCA components leached from particles and particleboards based on original amounts of componentsb

<table>
<thead>
<tr>
<th>Particleboard type</th>
<th>CCA components before leaching</th>
<th>Total leached CCA components</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CuO %</td>
<td>CrO3 %</td>
</tr>
<tr>
<td>CCA-treated particles</td>
<td>0.26</td>
<td>0.48</td>
</tr>
<tr>
<td>OA-extracted particles</td>
<td>0.20</td>
<td>0.17</td>
</tr>
<tr>
<td>Bioremediated particles</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>CCA particleboard</td>
<td>0.22</td>
<td>0.36</td>
</tr>
<tr>
<td>OA particleboard</td>
<td>0.18</td>
<td>0.12</td>
</tr>
<tr>
<td>Bioremediated particleboard</td>
<td>0.09</td>
<td>0.07</td>
</tr>
</tbody>
</table>

bEach value represents the means of 2 replicates of 6 samples. Values in parentheses are Standard deviations.

Particles. In contrast to these results, the total percentage of copper leached from particleboard samples containing bioremediated particles increased 32.1% compared to the same type of particles. The percentage of chromium released from the boards made from CCA-treated and OA-extracted particles was not significantly different than that from the particles (Table 4). However, percentage of chromium released from the board samples containing bioremediated particles increased 17.3% compared to bioremediated particles.

In contrast to copper and chromium leaching rates, more arsenic was released from particleboard samples with CCA-treated and OA-extracted particles than the comparable particles. The arsenic leached increased 40.5% in board samples made from CCA-treated particles, while the total percentage of arsenic released from the board samples containing OA-extracted particles was approximately 2 times greater than that released from the particles.

Kamdem and Munson (1996) showed that the particleboard prepared with UF resins leached more CCA components than phenol formaldehyde (PF) resins because UF resins are not water resistant. Our results also showed that leaching of particleboard samples containing OA-extracted and bioremediated particles resulted in high release rate of CCA components compared to CCA-particleboard samples. We conclude that the remediation processes used in this study created chemical modification on the surfaces of wood particles, essentially reversing CCA fixation. Leaching of residual CCA was even greater after particles (CCA-treated, OA-extracted, and bioremediated) were glued with UF resin, indicating the resin further interfered with fixed CCA components (Table 4).

3.4. Decay resistance of particleboard samples

Average weight losses of the particleboard samples exposed to decay fungi for 12 weeks are given in Table 5. The leaching procedures applied for 14 days had a considerable effect on weight losses due to removal of preservative components found in the particles originally.

Of the tested fungi, Gloeophyllum trabeum caused most significant weight losses in all particleboard samples. The greatest weight losses were seen in control particleboard samples and particleboard samples containing bioremediated particles. In unleached particleboard samples containing CCA-treated particles, weight loss (5.9%) was much lower than those of the other particleboard samples. A visual inspection revealed that the entire surfaces of all samples were covered with fungal mycelium. Macroscopically, G. trabeum caused dark-colored discolorations on the surfaces of all leached samples except board samples containing CCA-treated particles. The upper and lower surface layers of all leached samples were also easily colonized by the fungus.

Unleached and leached particleboard samples containing CCA-treated particles had the lowest weight losses after a 12-week exposure to Postia placenta. Although weight losses in leached control particleboard samples and particleboard samples with OA-extracted and bioremediated
particles were greater than 20%, weight losses were remarkably lower in un-leached samples compared to leached samples. It appears that *P. placenta* cannot readily penetrate the UF resin in un-leached control samples to gain access to the wood fiber. This is illustrated by increased weight losses for all leached samples, which is related to the water absorption and corresponding thickness swell of particleboard manufactured with UF resin. Sample swelling provides greater access to wood fiber. Macroscopic examinations revealed that *P. placenta* showed good mycelial growth on the surfaces of all leached and un-leached samples.

Compared to *G. trabeum* and *P. placenta*, *Trametes versicolor* caused lower weight losses in leached particleboard samples because white-rot fungi preferentially decay hardwoods. However, weight losses in un-leached samples were slightly greater that those of control samples and particleboard samples with OA-extracted and bioremediated particles exposed on *P. placenta*. Particleboard samples made from CCA-treated particles showed the greatest resistance to *T. versicolor*. Macroscopically, this fungus did not show good mycelial growth on the surfaces of all samples in contrast to *G. trabeum* and *P. placenta*.

4. Conclusions

This study shows that OA extraction and *B. licheniformis* fermentation remediates CCA-treated waste wood via partial removal of active chemical components of CCA. Particleboard made from CCA-treated wood particles seems to be compatible with UF-bonded boards with regard to water absorption, thickness swelling, leachability of CCA elements, and biological efficacy against brown-rot and white-rot decay fungi; however, arsenic leaching is relatively high. On the other hand, the particleboard samples made from remediated particles show high leaching losses of residual CCA components. Clearly, leachability of residual chemicals from particleboard made from treated waste wood is not desirable either in use or upon disposal. Also, increased leachability of residual chemicals results in decrease decay resistance as indicated by the results in this study. On the other hand, thorough removal of CCA from treated waste wood prior to particleboard manufacture would produce a desirable product for indoor use. It may be concluded from increased leaching of residual elements that remediated particles may have little potential for composite production unless metals are fully removed from fibers before composites are manufactured.

Since UF resins are not water resistant, alternative adhesive systems might be desirable for composite production from remediated fibers depending on their intended use in order to reduce leaching of CCA components. For example, use of inorganic matrix systems such as cement might result in improved properties allowing compatibility between CCA-treated and bioremediated fibers and cement. Remediated wood fibers would also provide an excellent source as reinforcing fillers in thermoplastic composites. Utilizing bioremediated fibers in composite production with proper manufacturing processes can decrease interference with CCA elements and adhesive bonding. Furthermore, remediation of CCA-treated waste wood prior to composite production would decrease concerns about the safety of workers.

Acknowledgements

The authors would like to thank Dan Foster, Analytical Chemist, for conducting atomic absorption spectroscopy.
Table 5
Weight losses in particleboard samples after 12-week exposure against wood degrading fungi

<table>
<thead>
<tr>
<th>Particleboard type</th>
<th>Average weight loss (%)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G. trabeum</td>
<td>P. placenta</td>
<td>T. versicolor</td>
</tr>
<tr>
<td>Control particleboard</td>
<td>21.6 (1.9)</td>
<td>4.4 (3.7)</td>
<td>8.1 (1.7)</td>
</tr>
<tr>
<td>Unleached</td>
<td>38.2 (8.2)</td>
<td>22.0 (3.8)</td>
<td>11.4 (1.1)</td>
</tr>
<tr>
<td>Leached</td>
<td>5.9 (4.9)</td>
<td>0.3 (0.7)</td>
<td>-0.7 (0.8)</td>
</tr>
<tr>
<td>CCA particleboard</td>
<td>26.7 (8.1)</td>
<td>2.7 (0.3)</td>
<td>1.67 (0.8)</td>
</tr>
<tr>
<td>Unleached</td>
<td>13.8 (4.2)</td>
<td>0.6 (0.7)</td>
<td>2.5 (1.8)</td>
</tr>
<tr>
<td>Leached</td>
<td>31.4 (5.9)</td>
<td>25.6 (2.7)</td>
<td>8.7 (0.8)</td>
</tr>
<tr>
<td>OA particleboard</td>
<td>19.9 (3.2)</td>
<td>0.1 (2.2)</td>
<td>7.5 (1.7)</td>
</tr>
<tr>
<td>Unleached</td>
<td>40.5 (1.3)</td>
<td>26.9 (3.8)</td>
<td>10.3 (3.0)</td>
</tr>
<tr>
<td>Leached</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Each value represents the means of 4 replications. Values in parentheses are standard deviations.

References


