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Improving the two-step remediation process for CCA-treated wood: Part I. Evaluating oxalic acid extraction

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Abstract

In this study, three possible improvements to a remediation process for chromated-copper-arsenate (CCA) treated wood were evaluated. The process involves two steps: oxalic acid extraction of wood fiber followed by bacterial culture with *Bacillus licheniformis* CC01. The three potential improvements to the oxalic acid extraction step were (1) reusing oxalic acid for multiple extractions, (2) varying the ratio of oxalic acid to wood, and (3) using a noncommercial source of oxalic acid such as *Aspergillus niger*, which produces oxalic acid as a metabolic byproduct. Reusing oxalic acid for multiple extractions removed significant amounts of copper, chromium, and arsenic. Increasing the ratio of wood to acid caused a steady decline in metal removal. *Aspergillus niger* removed moderate amounts of copper, chromium, and arsenic from CCA-treated wood. Although *A. niger* was effective, culture medium costs are likely to offset any benefits. Repeated extraction with commercial oxalic acid appears to be the most cost-effective method tested for the two-step process.
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1. Introduction

Concern about disposing of CCA-treated wood in landfills has increased because of the risk of environmental contamination. Some alternative disposal methods for this material include incineration, reconfiguration and reuse, composting with decay fungi, and acid extraction and bioleaching of metals by bacteria (Clausen, 2003). These alternative methods could divert CCA-treated material from landfills by reducing the biomass, removing and recycling the metals, or simply increasing the useful service life by reusing the material in a secondary application. All these alternative methods have one thing in common—they are costly compared with disposal in landfills.

Research on remediation of CCA-treated wood has increased during the past decade as a result of concern about chromium and arsenic disposal in landfills. CCA-treated wood is banned for use in a number of European and Asian countries and will be phased out for residential use in the United States by 2004. There are copper-based replacements for CCA in residential uses, but these products are likely to raise concerns about leaching of copper into groundwater when wood treated with this generation of preservatives begins to come out of service. A two-step remediation process, involving a combination of oxalic acid extraction and bacterial culture with the metal-tolerant bacterium, *Bacillus licheniformis*, substantially reduces the amount of copper (78%), chromium (97%), and arsenic (93%) in CCA-treated wood (Clausen, 2000; Clausen and Smith, 1998). This remediation process has been shown to be equally effective on a number of copper-based preservatives (Crawford and Clausen, 1999) and meets the need to divert wood treated with either CCA or copper-based organics from our landfills.

Chemical leaching of copper, chromium, and arsenic with acid extraction has been studied (Kim and Kim, 1993; Stephan et al., 1993, 1996; Pasek, 1994; Clausen and Smith, 1998; Kazi and Cooper, 2002). Stephan et al. (1993, 1996), Illman and Highley (1996), and Yang and Illman (1999) evaluated microbial conversion of CCA-treated wood with species of *Antrodia* and *Meruliporia*,

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brown-rot fungi known for their copper tolerance and production of high levels of oxalic acid (Clausen et al., 2000). The theory is that the high production of oxalic acid increases the acidity of the substrate, thereby increasing the solubility of the metals. Warner and Solomon (1990) reported that 100% of the copper was leached from CCA-treated wood with NaOH/citric acid buffer at pH 3.5 after 40 days of continual leaching. Minimal exposure of wood fiber to acids is desirable if fiber recovery is desired, because prolonged exposure to strong acid damages the fiber integrity by hydrolyzing carbohydrates. Clausen (2000) minimized damage of wood fiber by oxalic acid in the remediation process by optimizing the oxalic acid concentration and exposure time of the wood substrate.

Remediated wood fiber has been reassembled into medium-density particleboard panels (Clausen et al., 2001). An evaluation of the properties of particleboard made from remediated fiber showed a 28% and 13% decrease in internal bond strength and modulus of rupture (MOR), respectively, and an increase of 8% in modulus of elasticity (MOE) compared with particleboard prepared from virgin fiber. Compared with the cost of manufacturing particleboard from virgin southern pine stock, manufacturing costs using remediated wood fiber is approximately six times as expensive, mostly due to the cost of oxalic acid and the nutrient culture medium. On the other hand, savings can be incurred through extraction by avoidance of landfill fees and by recovery and reuse of the metals. With increased restrictions internationally on landfilling CCA-treated wood, landfilling costs may become prohibitive, increasing the desirability of alternative management options.

Eliminating or reducing the cost of metal extraction with oxalic acid would decrease the overall processing cost for the two-step remediation of CCA-treated wood. There are several ways to accomplish this: (1) reuse oxalic acid for multiple extractions, (2) maximize the ratio CCA-treated wood to acid, or (3) use an alternative source of oxalic acid, such as Aspergillus niger, a mold fungus commonly associated with wood. This fungus is capable of producing high concentrations of oxalic acid in culture (Cameselle et al., 1998). Sayer and Gadd (1997) have shown that A. niger can solubilize inorganic metal compounds and transform them into insoluble metal oxalates. Furthermore, when Price et al. (2001) evaluated fungi for their ability to remove metals from wastewater, they demonstrated that A. niger internally absorbs copper as a means of detoxifying its environment.

Oxalic acid has many industrial applications, including being used as a pharmaceutical purifying agent, a precipitating agent in mineral processing, a bleaching agent for textiles and wood, and in wastewater treatment. The objective of this study was to evaluate the three alternative oxalic acid extraction approaches mentioned previously to improve the economic feasibility of the two-step remediation process for CCA-treated wood.

2. Materials and methods

2.1. Treated wood

CCA-treated southern yellow pine lumber (6.4 kg/m^3 retention) was used throughout this study. The treated lumber was hammer-milled and sorted to approximately 1- to 3-mm (6- to 16-mesh) particles.

2.2. Elemental analysis

Ovendried samples, ground to pass a US Standard 20-mesh (850-μm) screen, were digested and analyzed for copper, chromium, and arsenic content by inductively coupled plasma (ICP) emission spectrometry according to American Wood Preservers' Association (AWPA) standard A-21-00 (AWPA, 2001).

2.3. Oxalic acid/CCA-treated wood ratio

One hundred grams of CCA-treated particles were extracted at ambient temperatures in 1:100, 1:20, 1:10, 1:7.5, 1:5, 1:4, and 1:3.3 (grams of wood:milliliters extract solution) 0.8% oxalic acid for 24 h with mixing at 90 rpm in an orbital shaker. A concentration of 0.8% oxalic acid (Sigma, St. Louis, Missouri, USA) was previously determined to optimally extract CCA metals from samples of CCA-treated particles (1.2 to 3.4 mm) in 18 h (Clausen, 2000). Individual extraction solutions were sampled for analysis and collected for reuse. Extracted particles were collected on a cheesecloth-covered screen, rinsed thoroughly with deionized (DI) water, and ovendried at 60 °C for 48 h. Samples were submitted for analysis of copper, chromium, and arsenic by ICP. Controls consisted of CCA-treated particles extracted in DI water.

2.4. Repeated oxalic acid extraction

Oxalic acid solutions collected as described in Section 2.3 (Oxalic acid/CCA-treated wood ratio) were used to extract fresh samples of CCA particles in ratios of 1:100, 1:20, 1:10, 1:7.5, 1:5, 1:4, and 1:3.3 wood/acid (w/v). Samples of dried particles were ground to 850 μm (20 mesh), digested, and analyzed for copper, chromium, and arsenic content by ICP. Individual extraction solutions were used for a third 24-h extraction of CCA-treated particles as described in Section 2.3. Extracted particles and controls were analyzed for copper, chromium, and arsenic by ICP.

2.5. Oxalic acid production by Aspergillus niger

One-hundred-milliliter aliquots of 2% malt broth plus 5 g CCA-treated SYP particles were placed in 300-mL Erlenmeyer flasks, autoclaved, and inoculated with A. niger. Flasks were incubated at 27 °C and 120 rpm in an orbital shaker. Three flasks were harvested on days 3, 4, 5, 6, 7, 10, 11, and 12. Culture filtrates were assayed with a commercial test for oxalate (Sigma). Particles were collected on a cheesecloth-covered screen and thoroughly rinsed with DI water before drying at 60 °C for 48 h. Dried particles were ground to 850 µm (20 mesh) and analyzed for copper, chromium, and arsenic content by ICP.

3. Results and discussion

3.1. Oxalic acid loading and reuse

Combined results evaluating the ratio of CCA-treated wood to oxalic acid concentration and use of commercial oxalic acid for multiple extractions are shown in Fig. 1. Oxalic acid (0.8%) at a ratio of 1001 (v/w) to treated wood particles was reused in three subsequent 24-h extractions, and each extraction resulted in the removal of copper, chromium, and arsenic with equal efficiency. During subsequent extractions, 65-68% copper, 48–51% chromium, and 68–71% arsenic were removed with 1:100 ratios of particles to acid. Increasing the ratio of particles to acid to 1:20 removed 53% of the copper after the first extraction. The ability of oxalic acid to remove copper after a second and third extraction was reduced to 39% and 32%, respectively, at this ratio of particles to acid. Increasing the ratio of particles to acid to 1:3.3 in the initial extraction resulted in the removal of 29% chromium and 43% arsenic. Overall, the higher the ratio of particles to acid, the less metals were removed during subsequent extractions. Increasing the ratio of CCA-treated particles to oxalic acid, and reusing the acid solution to extract fresh samples of CCA-treated particles three times for 24 h each, demonstrated that increased particle loading and reuse of extraction solution steadily decreased the percentage of metals removed.

3.2. Oxalic acid production by Aspergillus niger

By day 10 of incubation, in cultures containing CCA-treated wood and *A. niger*, increasing oxalic acid concentrations resulted in decreases in residual copper, chromium, and arsenic from the wood fiber (Table 1). A maximum of 84% copper was removed from CCA-treated particles exposed to *A. niger* for 10 days. A maximum of 46% chromium and 54% arsenic were removed from CCA-treated particles after 12 days,

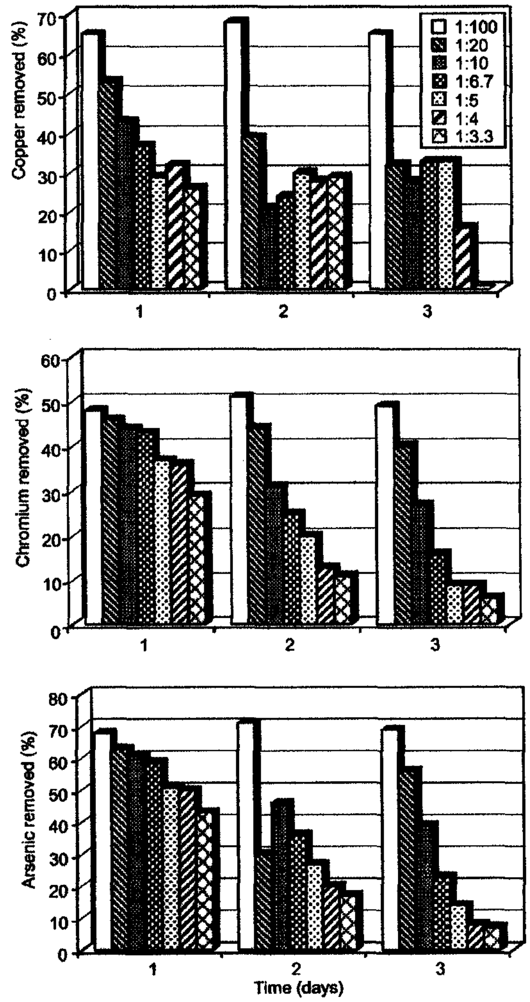

Fig. 1. Percentage copper, chromium, and arsenic removed during three sequential 24-h extractions reusing oxalic acid solutions at various ratios (v/w) to fresh CCA-treated particles.

Table 1
Oxalic acid (OA) production and metal removal from CCA-treated particles by Aspergillus niger with time, determined by inductively coupled plasma (ICP) elemental analysis

Time (days)	OA produced (mM)	Amount of metal removed					
		Copper		Chromium		Arsenic	
		mg/g	%	mg/g	%	mg/g	%
0		1.61		3.58		2.71	
3	33	0.54	63	2.18	24	1.69	40
4	36	0.63	60	2.96	23	1.8	39
5	35	0.41	61	2	26	1.25	41
6	31	0.46	69	2.2	39	1.37	50
7[a]	41	0.56	65	2.96	25	1.79	42
10[a]	157	0.2	84	1.89	38	1.17	52
11[a]	139	0.22	82	1.86	36	1.14	50
12[a]	107	0.32	79	1.93	46	1.21	54

[a] *A. niger* growth was visible in culture as submerged hyphal growth.

although there was not a steady upward trend in arsenic and chromium removal beyond day 6 of incubation. *A. niger* may have been affected by increasing concentrations of arsenic (348 mg/l) and chromium (246 mg/l); these metals were released from the treated wood by day 6. Increased copper removal beyond day 7 coincided with both visible growth of *A. niger* in the form of submerged hypha and increased production of oxalic acid.

Sporulation was prevented by vigorously aerating *A. niger* cultures at 120 rpm; spores of *A. niger* can cause allergic reactions in sensitized individuals and would be undesirable in a remediation process or resulting product. The ability of *A. niger* to resolubilize precipitated inorganic compounds has previously been evaluated as a means of toxic metal immobilization (Sayer and Gadd, 1997), wastewater remediation (Price et al., 2001), and land reclamation (Gharieb et al., 1998). Gharieb et al. (1998) proposed that the complexing activity of organic acids produced by the mold fungus with calcium was the mechanism of solubilization and resulted in the precipitation of calcium oxalate. Similarly, insoluble calcium and copper oxalate precipitates are common in wood decayed by brown-rot fungi. Many brown-rot fungi are copper tolerant (Clausen et al., 2000). Copper-tolerant brown-rot fungi produce and accumulate high concentrations of oxalic acid. Organic acid solubilization of insoluble inorganic compounds may be the method by which *A. niger* partially removed copper, chromium, and arsenic from CCA-treated wood.

4. Conclusions

Oxalic acid extraction is an important first step in the two-step remediation process; neither acid extraction nor bacterial exposure alone is as effective as they are in combination. Using commercial oxalic acid to repeatedly extract CCA-treated particles appears to be the most cost-effective method for acid extraction. The CCA-treated wood to acid ratio was optimized at 1:100 (w/v). The ability of *Aspergillus niger* to produce oxalic acid and effectively remove significant amounts of copper from CCA-treated wood indicates that there are natural alternatives to using commercial oxalic acid for the acid extraction of CCA-treated wood, although in this study, it added 10 to 12 days to the length of the process. Oxalic acid extraction alone was not as effective at removing copper, chromium, and arsenic from CCA-treated wood as the two-step remediation process that involves acid extraction followed by bioleaching with a metal-tolerant bacterium (Clausen, 2000). Metals separated from the wood fiber are available for recovery from the extraction fluid. Wood fiber separated from the metals has been reassembled into particleboard panels in the laboratory (Clausen et al., 2001). Future research will evaluate scaling-up optimized parameters of the two-step remediation process.

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