

SCALED-UP REMEDIATION OF CCA-TREATED WOOD

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ABSTRACT

Bioremediation is a novel approach to recycling waste wood treated with chromated copper arsenate (CCA). Remediating CCA-treated waste wood diverts this fiber source from our landfills and provides tangible secondary products from the cleaned fiber. On a laboratory scale, this method, which utilizes oxalic acid extraction and bioleaching with a metal-tolerant bacterium, removed up to 78% Cu, 100% Cr, and 97% As from 1 kg chipped CCA-treated southern pine. The two-step sequence of oxalic acid extraction and bioleaching removed more metals than did either acid extraction or bioleaching alone. Scale-up parameters on 11 kg of particulate, flaked, or chipped CCA-treated wood were evaluated in a 150-L reactor. This process removed 79% Cu, 70% Cr, and 88% As from particulate wood, 83% Cu, 86% Cr, and 95% As from flaked wood, and 65% Cu, 64% Cr, and 81% As from wood chips. Metals released from CCA-treated wood during bioremediation are potentially recoverable from a liquid medium for reuse or disposal. Remediation methodologies remain cost prohibitive, but they may become economically competitive in the event landfill restrictions are imposed domestically.

Keywords: remediation, CCA-treated wood, acid extraction, bioleaching, *Bacillus licheniformis*

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INTRODUCTION

Chromated copper arsenate (CCA) has been the most commonly used wood preservative in North America for the past 25 years [1], resulting in large volumes of this material entering our landfills after removal from service. It is estimated that 18 billion cubic feet ($5.1 \times 10^8 \text{ m}^3$) of CCA-treated wood will be removed from service by the year 2020 [2]. A number of approaches to remediate CCA-treated wood have been developed in an effort to divert treated waste wood from landfills. Alternative disposal methods including, but not limited to, incineration, reconfiguration and reuse, composting with decay fungi, acid extraction, and bioleaching of metals by bacteria were reviewed by Clausen [3]. Alternative disposal strategies could divert CCA-treated material from landfills by reducing the biomass, removing and recycling the metals, or simply extending the useful service life of this material through reuse in a secondary application. No alternative to landfilling has been readily adopted due to the inherent costs and lack of means to handle, transport, sort, and process this waste material. Nevertheless, it is important to continue to investigate and develop new methods to remediate treated wood as well as evaluate scale-up of existing remediation methods so that this technology can be readily transferred into the marketplace in the event domestic landfill restrictions similar to those in Europe are imposed in the future.

A two-step remediation process, involving a combination of oxalic acid extraction and bacterial culture with the metal-tolerant bacterium, *Bacillus licheniformis*, substantially reduced the amount of copper (70%–78%), chromium (81%–97%), and arsenic (93%–100%) in CCA-treated wood on a laboratory scale [4,5]. This remediation process, which has been shown to be equally effective in the laboratory on a number of copper-based preservatives [6], allows for recycling of both the wood fiber and metals. The objective of this study was to scale up the two-step remediation method of Clausen [4] to evaluate the effectiveness of the process on larger volumes of particulate, flaked, and chipped CCA-treated southern yellow pine.

MATERIALS AND METHODS

Treated Wood

CCA-treated southern yellow pine was used for all three trials in this study. In trial I, 11.6 kg of treated lumber (Brunsell Lumber, Madison, WI), hammer-milled and sorted to an approximate particle size of 3 by 8 mm, was processed. In trial II, flaked southern pine (0.5 mm thick by 11 cm long by varying widths) was treated with CCA-C using a full cell treatment process to a nominal retention of 6.4 kg/m^3 . In trial II, 11.8 kg of treated flakes was processed. In trial III, 11.3 kg chipped southern pine (3 by 2 by 0.3 cm), treated with CCA-C using a full cell process to a nominal retention of 6.4 kg/m^3 , was processed.

Remediation Process

Processing Equipment

The processing equipment consisted of a 300-L fermentor connected to a 150-L stainless steel recirculating tank (Figure 1). In each of three trials, the wood was confined in a polypropylene bag and placed inside the recirculating tank (Legion Utensils Co., Inc., Long Island City, NY). The bag used for particulate wood was manufactured from woven polypropylene filter fabric (Astrup, Chicago, IL), and the bag used for the flaked and pulp chipped wood was manufactured from nominal 1- by 2-mm polypropylene mesh (McMaster-Carr, Elmhurst, IL). Both bags were manufactured by Gallagher Tent and Awning (Madison, WI) and designed to fit the dimensions of the 58.4-cm-high by 58.4-cm-diameter recirculating tank.



Figure 1 Fermentator (left) connected to recirculating remediation tank (right).

Design, Inc., Allentown, PA) at 121°C for 20 min. Medium was cooled to 65 °C–70°C and pumped into the remediation tank. Medium was further cooled to 27°C, adjusted to 125 L volume, and pH was adjusted to 5.5–5.6 with saturated NaOH. Antifoam A (Sigma, St. Louis, MO) was added before the tank was inoculated with 1 L of inoculum prepared as follows. Bacterial inoculum preparation consisted of aseptically inoculating *Bacillus licheniformis* CC01 into 100 mL of nutrient medium, incubating for 15 h at 27°C, transferring 100 mL of the 15-h culture into 1 L of nutrient medium, incubating for 8 h at 27°C, and transferring 1 L of the 8-h culture into 125 L of nutrient medium in the remediation tank of cooled medium. Inoculum contained 6×10^7 colony forming units per milliliter (CFU/mL).

The inoculated medium was recirculated (50 L/min) with a uniform spray over the surface of the wood at 27°C for 7 to 9 days. Filtrate samples were taken periodically during the incubation for bacterial counts and elemental analysis. Wood samples were submitted for elemental analysis following bioleaching. Spent nutrient medium was collected for either disposal as hazardous waste or future studies on metal recovery. An uninoculated control was subjected to oxalic acid-extraction, drained, and incubated for 7 days in DI water. Samples of filtrate and wood were taken periodically for elemental analysis.

Microbial Growth Analysis

Samples of nutrient medium were taken periodically during the 7-day incubation and streaked for purity on nutrient agar (Difco, Detroit, MI). A plate count was also conducted on nutrient agar plates to determine CFU/mL of inoculum and time of peak growth of the bacterium [8].

Acid Extraction

Oxalic acid, (125 L, 0.8%, pH 1.52) (Sigma, St. Louis, MO) in deionized (DI) water was added and recirculated with a uniform spray over the surface of the immersed bag of wood at 50 L/min and 27°C for 18 h. The optimal ratio ($\leq 1:10$) kg of treated wood to liters of acid was previously determined [7]. Acid extract and wood were sampled at T_0 and T_{18} h for elemental analysis. Following extraction, the acid was drained for 1 h and the volume recovered was recorded (Table 1).

Bioleaching

Nutrient medium (Difco, Detroit, MI) was prepared according to manufacturers' directions to give 0.8% concentration and sterilized in a 300-L fermentor (Fermentation

Table 1 Processing conditions for three CCA-treated chip types and elemental analyses of filtrates and processed wood samples^a

Wood geometry	Process	Time	pH	Wood weight (kg)	Filtrate volume (L)	Total metals in filtrate (g recovered)			Metals in wood samples (mg/g) ^b			
						Cu	Cr	As	Cu	Cr	As	
Particle	Acid extraction	0	1.52	11.61	125				1.45 (0.03)	2.67 (0.05)	2.55 (0.03)	
		18 h	1.44		91	3.76	17.70	21.11	1.28 (0.05)	1.30 (0.03)	0.90 (0.15)	
	Bioleaching	1 d	5.60		125							
		7 d	6.23		125	20.58	7.08	6.70	0.30 (0.01)	0.79 (0.02)	0.30 (0.01)	
	Flake	Acid extraction	0	1.50	11.79	125				2.66 (0.10)	5.19 (0.26)	4.61 (0.33)
			18 h	1.58		109	5.12	24.83	28.27	2.23 (0.11)	1.54 (0.06)	0.81 (0.01)
Bioleaching		1 d	5.30		125							
		7 d	6.11		125	12.17	5.36	4.51	0.46 (0.04)	0.72 (0.03)	0.22 (0.02)	
Pulp chip	Acid extraction	0	1.56	11.34	125				1.88 (0.21)	5.13 (0.09)	4.58 (0.06)	
		18 h	1.62		110	2.75	21.04	24.58	1.87 (0.16)	3.00 (0.09)	1.94 (0.05)	
	Bioleaching	1 d	5.15		125							
		7 d	6.13		125	12.84	13.16	13.36	0.65 (0.04)	1.87 (0.06)	0.89 (0.02)	

^an = 3.^bStandard error in parentheses.

Elemental Analysis

Oven-dried wood samples, ground to pass a U.S. Standard 20-mesh (850- μ m) screen, were digested and analyzed in triplicate for copper (Cu), chromium (Cr), and arsenic (As) content by inductively coupled plasma (ICP) emission spectrometry according to American Wood Preservers' Association standard A-21-00 [9]. Filtrate samples were submitted in triplicate for ICP analysis for copper, chromium, and arsenic.

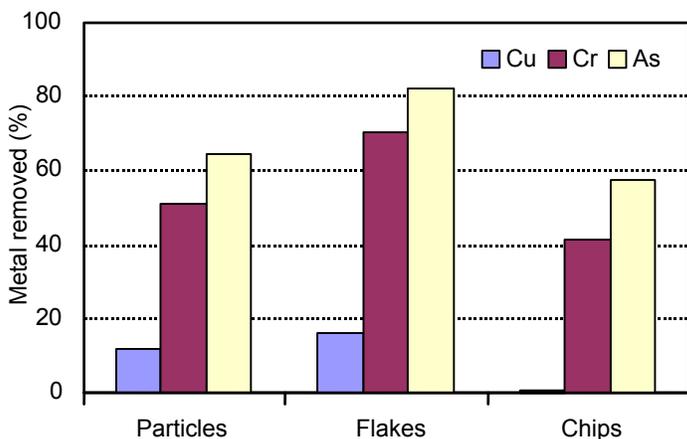


Figure 2 Metals removed by acid extraction of CCA-treated particles, flakes, and chips.

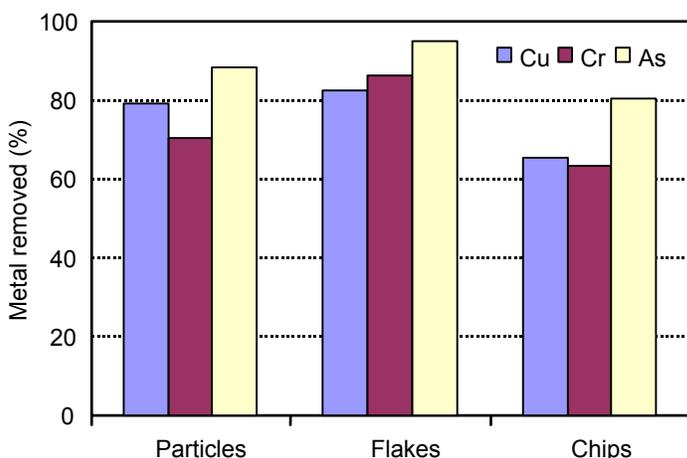


Figure 3 Percentage of Cu, Cr, and As removed after 7 days of bioleaching with *Bacillus licheniformis*.

copper was removed during bioleaching than by acid extraction alone. Residual acid in the uninoculated control extracted 12% to 35% additional Cu, Cr, and As during the subsequent 7 days (results not shown). That compares to 22% to 65% additional metal removal by bioleaching in the same time frame.

Trial I

The cumulative percent removal of CCA components—12% Cu, 51% Cr, and 65% As following acid extraction and 79% Cu, 70% Cr, and 88% As following bioleaching—are similar to results seen in bench-scale studies for this method [3–5]. Bioleaching with *B. licheniformis* clearly increased the removal of all three CCA components and preferentially copper. The filter fabric bag and small wood particle size moderately hampered exchange of acid and medium from the inside to the outside of the bag during recirculation. The bag also inhibited drainage following the acid extraction, which, in turn, required more sodium hydroxide to adjust the pH for the bioleaching portion of the process. Opening the remediation tank several times for pH adjustment eventually led to microbial contamination. Foaming was minimal and confined to the inside of the bag until day 7 of incubation, when signs of contamination were noted on a plate of nutrient agar streaked for purity and on the bag and sides of

RESULTS

Conditions for remediation of CCA-treated southern yellow pine and elemental analyses of filtrates and wood samples are summarized in Table 1. Extrapolating total metals recovered in large volumes of filtrate is subject to experimental error. Residual metals in processed wood samples are a better indicator of the success of the remediation process. The extent of metal removal following acid extraction is shown in Figure 2. Copper extraction was the lowest, particularly for pulp-chipped wood. Flaked wood showed the highest extraction of chromium (70%) and arsenic (82%) of the three material geometries tested, presumably because of the increased surface area exposed to the acid.

Figure 3 shows the total percentage of each metal removed from CCA-treated particles, flakes, and chips following step 2, bioleaching. Greater percentages of each metal were removed from particles, flakes, and chips following bioleaching than following acid extraction. Increases in the removal of copper by *B. licheniformis* were most dramatic; 65% to 68% more



Figure 4 Remediated particles were rinsed with DI water. Evidence of mold growth, which occurred on day 7 of incubation, were evident on the bag above the liquid line (arrow).



Figure 5 Mesh bag and larger wood configurations changed dynamics of surface spray, resulting in foaming that filled remediation tank.

extraction (Figure 2). Growth of the bacterium peaked on day 6 post-inoculation, at 2.5×10^9 CFU/mL. Because no contamination was detected, this trial was continued for two additional days to determine if additional metal removal would occur, but it did not. The proportion of metals removed from pulp-chipped southern pine was 65%, 64% and 81% for copper, chromium, and arsenic, respectively (Figure 3). Remediated chips were thoroughly rinsed with DI water and air-dried before storage.

the remediation tank above the liquid level (Figure 4). Remediated particles were thoroughly rinsed with DI water and air dried before storage.

Trial II

Following the 18-h oxalic acid extraction, flaked pine samples showed 16% removal of Cu, 70% removal of Cr, and 82% removal of As (Figure 2). Following bioleaching, the cumulative proportion of Cu, Cr, and As removed was 83%, 86%, and 95%, respectively (Figure 3). Flaked CCA was more voluminous than particulate CCA. While the mesh bag allowed for equal and unencumbered exchange of medium between the inside and outside of the bag, the flakes had to be settled into a flat configuration. The spray of medium on flat flakes changed the uniformity of the medium spray and may have increased foaming. Despite adding additional antifoam A, foam filled the remediation vessel (Figure 5). Remediated flakes were thoroughly rinsed with DI water and air dried before storage.

Trial III

Results showed that pulp-chipped southern pine had 0.5% removal of Cu, 42% removal of Cr, and 58% removal of As following the 18-h oxalic acid

DISCUSSION

Eleven-kg batches of CCA-treated wood were remediated with a two-step process involving oxalic acid extraction for 18 h followed by bioleaching for 7 days. Special attention to details, such as handling increased quantities of raw materials, maintaining aseptic conditions, adequate inoculum, and ensuring robust microbial growth, is essential when scaling up a microbial process. In an industrial scale-up of a fungal-based remediation process for CCA-treated wood using the brown-rot fungus *Antrodia vaillantii*, Leithoff and Peek [10] cited difficulties in regulating humidity and contamination by bacteria that were capable of totally inhibiting growth of this fungus. In our study, acid extraction combined with the presence of soluble metals in the filtrate discouraged, but did not entirely eliminate, growth of potential microbial contaminants, e.g., mold fungi. Similarly, overwhelming the system with a bacterial inoculum with a short regeneration time provided an opportunity for the *Bacillus* to out-compete potential contaminants for nutrients, especially those susceptible to the toxic components of CCA.

We were successful in sanitizing and maintaining aseptic conditions for the 7 day's duration of the remediation process. Uninoculated controls, however, could not be tested under these conditions without contamination. Therefore, following acid extraction, controls were incubated in DI water for 7 days to determine if residual acid would continue to extract metals, specifically copper. Residual acid from the saturated wood did continue to extract additional metals, but to a lesser degree than did bioleaching. It was previously shown that neither oxalic acid extraction alone for 18 h nor bioleaching with *B. licheniformis* for 7 days alone were as efficient at metal removal as was acid extraction followed by bioleaching [5].

The bacterial inoculum (10^8 CFU/mL) was unable to enter log growth phase as quickly as anticipated, which may have allowed for some contamination on the final day of the remediation process, despite the fact that elevated levels of copper, chromium, and arsenic were present in the nutrient medium. Likewise, adjusting pH, adding antifoam one or more times, and sampling the wood and filtrate were also factors that increased the potential for contamination of the otherwise sanitized but not sterilized system.

The polypropylene filter fabric bag used to contain the particulate wood somewhat hindered the free exchange of liquid (both acid and nutrient medium) between the inside and outside of the bag. It also slowed drainage of the acid following the extraction step; 91 L of acid was recovered from the particulate wood after draining the vessel for 1 h. Conversely, the open-weave mesh polypropylene bag used to contain the flaked and chipped wood allowed for unencumbered liquid exchange and rapid drainage of acid following the extraction process; 109 L and 110 L of acid were recovered from flakes and chips, respectively, following 1 h of drainage.

The configuration of the wood played a role in the fluid dynamics of the remediation process. While the surface area and thickness of flaked wood were clearly advantageous to the removal of metals by both acid extraction and bioleaching, they enhanced foaming and limited uniform coverage of wood by the spray of liquids through the recirculating nozzle. However, once the wood became saturated during the acid extraction and remained submerged for the duration of the process, the surface spray of liquids probably played a minor role compared to mixing of the vessel contents.

From an economic perspective, the two-step process described here remains prohibitively expensive. For example, the cost of manufacturing particleboard from virgin southern pine stock is approximately \$0.28/kg. Particleboard made from wood fiber remediated by the two-step process would be over 6 times more, due to the cost of oxalic acid (\$0.02 to 0.07/kg) and the nutrient medium (~\$1.79/kg). Collection, sorting, and transportation costs for treated wood have not been determined for this remediation process. Savings incurred by recovery and reuse of the metals are not addressed here.

With increased restrictions internationally on landfilling CCA-treated wood, domestic landfilling costs may also become prohibitive. Currently, the landfill tipping fee for CCA-treated wood in the midwestern United States is approximately \$33/1,000 kg [11]. In California, the average cost for regulating treated wood waste as hazardous waste has been estimated at \$291/1,000 kg, which would represent a 500% increase over the current non-hazardous disposal fee of \$61/1,000 kg [12]. This would be comparable to disposal of CCA-treated wood in special landfills in Europe, which can cost over \$300 USD per 1,000 kg (personal communication).

The process described here was not optimized to provide ideal growth conditions for *B. licheniformis*. Aeration was only provided by recirculating liquid, pH was not continuously controlled, and sanitary conditions can only delay eventual contamination. A system that merely controls temperature and aerates by recirculating and spraying liquid would be considered one of the simplest process designs for wood remediation. Nevertheless, the robustness of the process indicates acid extraction and *B. licheniformis* growth can effectively remove metals from CCA-treated wood.

CONCLUSIONS

Sample thickness and surface area of CCA-treated wood samples affected metal removal during both oxalic acid extraction and bioleaching processes. Flaked wood, which was thin and had a large surface area, was most amenable to metal removal, followed by small particulate wood (3 by 8 mm). The lowest metal removal rate, seen in pulp-chipped wood, may be improved by increasing acid extraction time. Circulating oxalic acid helped sanitize both the tank and wood, but it did not totally prevent contamination of the remediation process by day 6, despite elevated levels of copper, chromium, and arsenic in the nutrient medium. Similar to previous bench-scale studies, oxalic acid extraction removed a greater amount of chromium and arsenic, while the bacterium was most effective at removing copper. The two-step processing sequence is more efficient than either acid extraction or bioleaching alone. The results of this study show that scaling-up the bioremediation process to 11–12 kg batches of CCA-treated wood removed metals with an efficiency similar to that seen in 1-kg batches at the optimized 1:10 ratio (w/v) of solid to liquid [13], even for chipped and flaked wood.

ACKNOWLEDGMENTS

The authors would like to thank Dan Foster, Chemist, for elemental analyses, and Brian Schlitt for technical assistance.

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In: Proceedings of Environmental Impacts of Preservative-Treated Wood February 8 - 11, 2004; Orlando, Florida, USA. Florida Center for Environmental Solutions Gainesville, Florida; (pre-conference Proceedings) 1 CD-Rom pp 1-10