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Short Communication

Removal of copper, chromium, and arsenic from CCA-treated wood onto chitin and chitosan

S. Nami Kartal *, Yuji Imamura

Laboratory of Innovative Humano-habitability, Research Institute for Sustainable Humanosphere, Kyoto University, Uji 611-0011 Kyoto, Japan

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Abstract

Chitin and chitosan are naturally abundant biopolymers which are of interest to research concerning the sorption of metal ions since the amine and hydroxyl groups on their chemical structures act as chelation sites for metal ions. This study evaluates the removal of copper, chromium, and arsenic elements from chromated copper arsenate (CCA)-treated wood via biosorption by chitin and chitosan. Exposing CCA-treated sawdust to various amounts of chitin and chitosan for 1, 5, and 10 days enhanced removal of CCA components compared to remediation by deionized water only. Remediation with a solution containing 2.5 g chitin for 10 days removed 74% copper, 62% chromium, and 63% arsenic from treated sawdust. Remediation of treated sawdust samples using the same amount of chitosan as chitin resulted in 57% copper, 43% chromium, and 30% arsenic removal. The results suggest that chitin and chitosan have a potential to remove copper element from CCA-treated wood. Thus, these more abundant natural amino polysaccharides could be important in the remediation of waste wood treated with the newest formulations of organometallic copper compounds and other water-borne wood preservatives containing copper.

Keywords: Chitin; Chitosan; Copper; Chromium; Arsenic; CCA wood preservative; Remediation; Waste wood

1. Introduction

Considerable attention has been focused on remediation of chromated copper arsenate (CCA) wood preservative-treated wood in recent years due to release of chromium, copper, and arsenic elements from treated waste wood during landfilling, burning, composting, and other disposal ways of such wood. As a result of public awareness about CCA-treated waste wood, substantial progress has been made in remediation of CCA-treated waste wood by chemical extraction with several mineral and organic acids and biodegradation using bacteria and fungi in recent years. However remediation methods are becoming costly due to the cost of chemicals and nutrient media for fungal and bacterial cultures. Eliminating or reducing the cost of chemical or biological processes will make remediation of CCA-treated waste wood more economically and environmentally acceptable.

Natural materials available in large amounts and several agricultural and fishery waste products can be considered as effective and alternative technologies for the remediation of treated waste wood. These materials have ability to retain toxic heavy metals from aqueous solutions and potential as inexpensive adsorbents. Chitin, a natural polymer extracted from crustacean shells, such as prawns, crabs, insects, and shrimps is a white, hard, inelastic, nitrogenous polysaccharide (Tikhonov et al., 1996; Ngah and Isa, 1998; Kumar, 2000; Dambies et al., 2001; Benguella and Benaissa, 2002; Dutkiewicz, 2002; Gyliene et al., 2002). Chitosan, on the other hand, is a polymer extracted from chitin using an alkaline deacetylation procedure that yields a heteropolymer (Dambies et al., 2001). Chitin and chitosan are of commercial interest due to their high percentage of nitrogen (6.9%). Amine and hydroxyl groups on their chemical structures act as chelation sites for metal ions making them useful chelating agent. Chitin and chitosan are considered as natural polymers which have excellent properties such as biocompatibility, biodegradability, non-toxicity, metal adsorption, etc. (Kumar, 2000). A recent study by Dambies et al. (2001) showed that

* Corresponding author. Tel./fax: +81-774-38-3664.
E-mail address: nami@kuwri.kyoto-u.ac.jp (S.N. Kartal).

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chitosan beads removed about 60% of Cr(VI) ions from aqueous solution. Ngah and Isa (1998); Ngah et al. (2002), and Gyliene et al. (2002) stated that chitosan could be effective adsorbent for collection of Cu(II) ions from aqueous solutions.

Although several sorption studies have been carried out on removal of metal ions by chitin and chitosan, these studies involve uptake of ions directly from aqueous solutions. The aim of our work was to determine the ability of chitin and chitosan to remove copper, chromium, and arsenic elements from CCA-treated sawdust.

2. Methods

2.1. Materials

Tsuga heterophylla (Raf.) Sarg. (Western hemlock, Pinaceae) wood treated with chromated copper arsenate Type C wood preservative (CCA-C) was supplied by Koshii Mokuzai. Ltd., Japan. CCA-treated wood was ground to pass a US standard 40-mesh screen. Chitin (powder) and chitosan (small flakes) from crab shells were obtained from Nacali Tesque Inc., Kyoto, Japan and used as received throughout this study without any preliminary purification and further modification.

2.2. Analysis of preservative retention in the sawdust

CCA-treated sawdust samples (0.1 g) were dissolved completely in 10 ml of 65% HNO_3. The sample was transferred into a conical flask equipped with a water cooler to prevent loss by volatilization during the dissolution process. The flask was then heated on a heating plate until the sample had dissolved completely (≈4 h). The solution was analyzed for copper, chromium, and arsenic content to determine the initial amounts of the elements in the samples using an X-ray fluorescence analyzer (XRF) (JSX-3220 JEOL, Nihon Denshi Detamu Ltd., Tokyo, Japan).

2.3. Remediation of CCA-treated sawdust

For bioremediation process, CCA-treated sawdust was placed into teabags made from polyester fibers and the teabags containing sawdust were sterilized with gaseous ethylene oxide before bioremediation to prevent any microbial contamination during remediation. Each bag containing sawdust of 3 g was placed in the flasks containing 200 ml of deionized water (DI) and 1 or 5 g chitin or chitosan. The flasks were agitated for 1, 5, and 10 days at 120 rpm on a rotary shaker at 27 °C. Deionized water extraction served as control. Two replicates of 3 g sawdust were removed at each time interval and rinsed three times with 300 ml of DI water at 20 °C. Remediated sawdust was oven-dried at 60 °C for 24 h and conditioned at 23 °C and 65% relative humidity (RH) for 2 weeks. Remediated sawdust was then analyzed for remaining copper, chromium, and arsenic content using an XRF analyzer as described above. The percent reduction of copper, chromium, and arsenic in the sawdust samples was calculated based on the initial amount of elements in the samples.

3. Results and discussion

The percentages of copper, chromium, and arsenic elements removed from treated sawdust following remediation with DI water, chitin, and chitosan are shown in Figs. 1 and 2. Exposure of treated sawdust to 5 g chitin-containing solution for 10 days removed about 74%, 62%, and 63% of the initial concentrations of copper, chromium, and arsenic, respectively in CCA-treated sawdust. In general, as chitin amount in the solution and duration increased, element removal from CCA-treated sawdust increased. The ratio of percentage element removed by high amount of chitin to percentage element removed by the low amount of chitin was 1.5, 1.4, and 1.9 for copper, chromium, and arsenic, respectively. Thus, the relative removal of arsenic was most affected by the chitin amount in the solution.

Chitosan was less effective in element removal from treated sawdust compared to chitin. Total percentages of copper, chromium, and arsenic removed from CCA-treated sawdust by 2.5 g chitosan-containing solution for 10 days were 57%, 43%, and 30%, respectively. In other words, the percentages of copper, chromium, and arsenic removed by 2.5 g chitin-containing solution were about 1.3, 1.5, and 2.1 times, respectively greater than those by 2.5 g chitosan-containing solution. In addition, increased chitosan amount in the solution caused no substantial difference in arsenic removal from treated sawdust.

In the order of removal of heavy metals by 2.5 g chitin or chitosan-containing solution, copper was the most removed element from CCA-treated sawdust. Studies on copper adsorption on chitosan by Ngah and Isa (1998) and Ngah et al. (2002) stated that chitosan had an excellent loading capacity of copper and high hydrophilicity of chitosan with a large number of hydroxyl and amino groups. A recent study suggested that copper amount absorbed on chitosan was higher than that on chitin from metal ions solutions (Gyliene et al., 2002). Numerous articles have been published concerning the absorption of free metal ions on chitin and chitosan from directly aqueous solutions however our study was aimed to remove complexed metal ions from aqueous solution containing CCA-treated sawdust. In our study, chitin and chitosan were found to be effective in removing copper because of their strong metal