Designing and Development of Novel Chelating Method for Extraction of Heavy Metals from Chromated Copper Arsenate (CCA)-treated Wood

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Most wood material used for houses, utility poles, ground sills and other structural materials in damp conditions are generally treated with preservatives to enhance the durability. Some wood preservatives include chromated copper arsenate (CCA), ammoniacal copper quaternary compound-based wood preservative (ACQ), and copper azole compound-based wood preservative (CuAz) and other water-borne wood preservatives.

Among wood treated with preservatives, CCA-treated wood has been widely used because of its high performance against attack from fungi with a very wide antimicrobial spectrum and from termites, as well as against weathering over long periods of time. Although treatment with CCA has held the majority of the market share for pressure-treated wood preservation for a long period, increasing environmental regulations and disposal problems, particularly during wood combustion, have resulted in manufacturers limiting production of CCA-treated wood.

The present study focuses on designing and development of a novel solvent, in particular chelate, extraction process, which can easily and efficiently remove toxic metals of chromium, copper and arsenic from CCA-treated wood, and copper from ACQ-treated wood and CuAz-treated wood.

The extractability of CCA metals with various types of solvents, inorganic and organic acids, was studied [1] at first. The solvents of sulfuric, phosphoric, citric and oxalic acid, were relatively effective to remove CCA metals but these were too severe for wood. Thus more moderate solvent extraction condition should be needed.

The behavior of arsenic during pyrolysis of CCA-treated wood and the effect of pyrolysis on the extractability of CCA metals were studied [2, 3]. It was found that there are two possible ways of release of arsenic during pyrolysis. The first possible pathway is caused by reacted arsenic compound, $CrAsO_4$, which appears to be released at around 400-500°C. The second possible pathway is caused by unreacted arsenic compound, As_2O_5, in CCA-treated wood, which appears to be released at a much lower temperature than chromium arsenate, possibly 200°C.

Based on this result, pyrolysis of CCA-treated wood was conducted carefully without loss of arsenic. The results showed that the resistance of CCA metals to extraction increased drastically after pyrolysis. The toxic metals in CCA-treated wood were highly stabilized by heating at 300°C for 60 min. Immobilization of toxic metals in the residue was promoted by pyrolysis, resulting in the transformation of toxic metals to various types of stable compounds.

Various types of two-step extraction were designed and tested on CCA-treated wood instead of simple solvent extraction [4]. Among them, we found the best combination was oxalic acid as the 1st step and bioxalate (BO) solution, pH adjusted oxalic acid with sodium hydroxide, at pH=3.2 as the 2nd step. The latter conditions efficiently removed almost all CCA metals, approximately 90%, from treated wood powder in 3 hours extraction following the 1 hour pre-extraction by oxalic acid. However, the bioxalate solution under alkaline conditions (pH=11.2) proved ineffective.

Application of one-step metal extraction, that would effectively remove CCA metals from treated wood powder or chips with BO, was conducted [5]. A BO solution consisting of 0.125 M oxalic acid adjusted to pH 3.2 with sodium hydroxide was tested for its ability to extract chromium, copper and arsenic, from CCA-treated wood in single step (at 75°C). The extraction proceeded efficiently with 6 hours of treatment, and was insensitive to the differences in chemical characteristics, including solubility of individual metals. The preferential extractability for copper from CCA-treated wood was observed, although acid extraction, in general, tends to extract arsenic preferentially. After 6 hours of treatment, approximately 90% of chromium, copper and arsenic were effectively removed from CCA-treated wood.

The characteristics of the BO chelating extraction process for CCA metals were studied as a function of solvent pH, BO concentration, extraction temperature and liquid to solid ratio, and with various alkaline metal hydroxides as pH-adjusting reagents. The experimental results showed that the extraction efficiency was highly affected by BO solvent characteristics.

The solubility of chromium, copper and arsenic depends on pH of the BO solvent. Decreased pH clearly increases the solubility of chromium and arsenic, while copper had high solubility at higher pH. The solubility of chromium and arsenic was also highly affected by BO concentration in the solvent, while copper is dissolved at a wide range of concentrations (0.0125-0.125M). Higher temperatures increased the solubility of chromium and arsenic, while copper was easily dissolved at a wide range of temperatures from 25 to 75°C. Higher liquid to solid ratios were preferable for obtaining good stirring efficiency and preventing re-absorption of CCA metals into wood. Various alkaline metal hydroxides (lithium, sodium and potassium) and sodium carbonate, as pH-adjusting reagents for BO solvent were found to be almost equally effective. Based on the present data, the recommended extraction conditions are pH=2.2 to 3.2, oxalic acid concentration of 0.125M adjusted with sodium hydroxide, and 75°C (Table 1).

Table1 Recommended condition for extraction of CCA metals by using BO chelating process

	Metals			***Total***
	Cr	Cu	As	***Cr, Cu, As***
pH	1.0-3.2	2.2-5.2	1.0-3.2	***2.2-3.2***
Concentration (M)	1.25×10^{-1}	1.25×10^{-2}-1.25×10^{-1}	1.25×10^{-1}-6.50×10^{-2}	$\boldsymbol{1.25 \times 10^{-1}}$
Temperature (°C)	75	25-75	75	***75***
Liquid/solid ratio (ml/g)	10-20	15-20	15-20	***15-20***
Duration of extraction (hr)	3-6	4-6	4-6	***4-6***

The characteristics of the extraction processes of CCA-treated wood with two-stage BO, adding sodium hydroxide during simple oxalic acid extraction and adjusting pH to 3.2, were investigated [6]. BO was reconfirmed to be an effective agent for removal of chromium, copper and arsenic. Simple oxalic acid was effective for chromium and arsenic, but ineffective for copper, while sodium hydroxide was ineffective for chromium and copper, but relatively effective for arsenic. It is important to note that the addition of sodium hydroxide to a simple oxalic acid solution during the extraction process resulted in a dramatic increase in the extraction efficiency of copper (up to 90%), compared to simple oxalic acid extraction. Thus, extraction with BO, with addition of sodium hydroxide to the oxalic acid solution not only before but also during extraction process, was concluded to be a highly effective method for removal of CCA metals.

We additionally tested BO extraction process for wood treated with other copper based preservatives such as ACQ and CuAz or a mixture of CCA, ACQ and CuAz-treated wood in single step. The extraction proceeded efficiently with 6 hours of treatment, and was insensitive to the differences in chemical characteristics, including solubility of individual metals. After 6 hours of treatment, approximately 90% of chromium, copper and arsenic were effectively removed from a mixture of CCA, ACQ and CuAz and 90% of copper from ACQ- and CuAz-treated wood chip. These results demonstrate that the solvent extraction technique using pH adjusted BO solution with sodium hydroxide is a suitable method for pollution minimization by various types of wastes contaminated with heavy metals and arsenic.

Cheating extracrtion of CCA-, ACQ-, and CuAz-treated wood was successfully conducted by novel chelating reagent of BO. Oxalic acid has long been known as one of the most popular and important organic acids in the field of wood preservation. Now we would like to add a new knowledge in this field. Thus oxalic acid found new role for purification of CCA-treated wood waste as a BO chelating reagent.

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