Evaluation of the Accessibility of CCA Metals in Liquefied CCA-treated Wood Sludge for Recovery and Reuse

Hui Pan
Louisiana State University AgCenter
Calhoun, Louisiana

Todd F. Shupe
LSU AgCenter
Baton Rouge, Louisiana

Chung-Yun Hse
USDA Forest Service
Pineville, Louisiana

ABSTRACT

CCA-treated wood was liquefied with polyethylene glycol/glycerin and sulfuric acid. The heavy metals were precipitated by $Ca(OH)_2$ from liquefied CCA-treated wood.

The original CCA-treated wood and precipitated wood sludge were fractionated by a modified BCR (Community Bureau of Reference) sequential extraction procedure. The purpose of the BCR sequential extraction used in this study was to exam the accessibility of the heavy metals in CCA-treated wood for reuse. The two different size CCA-treated wood particles used for liquefaction had similar heavy metal distributions. As and Cr showed similar distributions as original CCA-treated wood and principally existed in an oxidizable fraction (As, 67%; Cr, 88%). Cu was largely present in the reducible fraction (49%) and exchangeable/acid extractable fraction (34%) in original CCA-treated wood. The distribution of As and Cr changed markedly after liquefaction. The amount of As in the exchangeable/acid extractable fraction increased from16% to 85% while the amount of Cr increased from 3% to 54%. Based on these results from sequential extraction procedures, it can be concluded that the accessibilities of CCA metals was increased markedly by the liquefaction-precipitation process. Only a small amount of heavy metals were precipitated by direct centrifugation and most were precipitated with $Ca(OH)_2$. The distributions of the heavy metals didn't vary markedly between the liquefied CCA-treated wood sludge samples obtained by filtration and centrifugation methods.

Keywords: CCA-treated wood waste, recycling, wood liquefaction, heavy metal accessibility, BCR sequential extraction

INTRODUCTION

The wood preservation industry is a $4 billion industry in the US. Approximately 150 million pounds of CCA were used in the production of preservative-treated wood in 2001, enough wood to build 435,000 houses. About 28.8 million pounds of CCA (dry oxide concentrate basis) was consumed by the U.S. treating industry in 2004 (Vlosky, 2006). Despite the decision of the US and Canadian wood preservation industry to voluntarily withdraw the use of CCA-treated wood for residential and consumer uses as of December 31, 2003 (US EPA, 2002), the use of CCA-treated wood for industrial purposes (e.g., utility poles, marine pilings) continues (Song et al., 2006; Kazi and Cooper, 2006; Block et al., 2007). With an expected average service life between 20-40 years, large volumes of this material will be coming out of service for decades to come. The environmental and human health impacts of CCA-treated wood have received increasing attention because of the toxicity of copper, chromium, and arsenic. Traditionally, CCA-treated wood has been primarily disposed within construction and demolition (C&D) debris landfills, with municipal solid waste (MSW) landfills as alternative disposal options (Khan et al., 2006). The development of environmentally friendly and cost effective recycling technology for spent CCA-treated wood, including recycling of both the wood matrix and the preservative metals, is of critical importance for both the preservative industry and the environment.

Many CCA metal removal methods, such as chemical extraction (Kartal and Clausen, 2001; Kakitani et al., 2006) and bioremediation (Clausen, 2004), have been proposed,. Very few studies have focused on both removal and reuse of CCA metals. CCA recovery is difficult because CCA fixation is largely a matter of conjecture (Bull et. al., 2000). Although much progress has been made, an in-depth knowledge of the interaction of the CCA salt and wood matrix *in situ* is still lacking. Removed CCA metals, either in extracted solution or other residues, are mixtures of three metals and are associated with other organic or inorganic substances. Knowledge of the total amount of removed CCA metals without considering their speciation is not sufficient for separation or recovery of the metals for reuse.

Sequential extraction is a chemical speciation process of identification and quantification of different species, forms or phases present in a material (Fuentes et. al., 2008). It is recognized as the best available method for gaining information on the origin, manner of occurrence, bioavailability, mobilization, and transport of heavy metals (Ma and Rao, 1997). This method has been successfully applied to a variety of matrixes, such as lake sediments, sewage sludge, and soil (Sanchez-Martin et al., 2007). To standardize the methodology used in a wide range of procedures, the Community Bureau of Reference (BCR) began an evaluation program of the sequential extraction schemes for determining metals in soils and sediments (Ure, 1991). A BCR extraction scheme is based on the defined fractions as exchangeable/acid soluble, reducible, oxidizable, and residual. The bio-availabilities or accessibilities of heavy metals exhibit a decreasing order along the sequence of the extraction process (e.g., exchangeable/acid soluble > reducible > oxidizable > residual). Considering the similarities and differences between liquefied CCA-wood sludge and sediments or soils, a modified BCR sequential extraction procedure was applied in this study to fractionate Cr, Cu, and As in liquefied CCA-treated wood sludge. The purpose of this study was to investigate the accessibilities of the heavy metals after they been removed from CCA-treated wood waste and thus to provide information for CCA metal recovery and reuse.

EXPERIMENTAL

Materials

CCA-treated wood waste was obtained from a local CCA wood treater and reduced to sawdust. The sawdust was then oven-dried and sieved to pass a 20-mesh screen before liquefaction. Polyethylene glycol with a molecular weight of 400 (PEG 400) and glycerin were used as the liquefaction reagent solvents at a weight ratio of 2/1. Sulfuric acid (95%) was used as a catalyst in the liquefaction reaction. All chemicals were reagent grade. Chemicals used in sequential extraction procedures were trace metal grade.

Liquefaction of CCA-treated wood and precipitation of CCA metals

Fig.1 shows the preparation procedures of the liquefaction and precipitation processes. In brief, CCA-treated wood particles were mixed with PEG 400/glycerin at a weight ratio of 1/3. Sulfuric acid was added at 3% of the PEG/glycerin weight. The above mixture was reacted under reflux at 150 ºC for 120 min. After the liquefaction reaction, the mixture was cooled down and diluted 6 times its volume with a acetone/distilled water (4/1, v/v) mixture. For preparation of LWS1 and LWS2 samples, the above mixture was directly subjected to centrifugation and the precipitate was oven-dried and assigned as LWS1. Then $Ca(OH)_2$ (4% of liquefied wood weight) was added to the supernatant from the above centrifugation and stirred for 2 h, centrifuged, and the precipitate was oven-dried and assigned as LWS2. For preparation of LWSF and LWSC samples, the liquefied CCA-treated wood with acetone/water solution was mixed with $Ca(OH)_2$ and stirred for 2h. The above mixture was then subjected to filtration or centrifugation to separate the liquid and the sludge. The sludge was then oven-dried and assigned as LWSF and LWSC for sample obtained from filtration and centrifugation, respectively.

Sequential extraction

A modified three-step BCR sequential extraction procedure (Rauret et al., 2000) was followed to fractionate the original CCA-treated wood particles and the sludge from liquefied CCA-treated wood. For each extraction specimen, about 0.5 g oven dried sample weighed to 3 decimal places into a 50 ml polyethylene centrifuge tube. The extraction procedures are briefly described as follows:

Step 1. A total of 20 ml acetic acid solution (0.11 M) was added to the centrifuge tube and shaken for 16 h at room temperature. The extract was separated from the solid residue by centrifugation at 3000 *g* for 20 min. The supernatant was collected for later analysis. The residue was rinsed with 10 ml distilled water by shaking for 15 min., centrifuging, and decanting the supernatant.

Step 2. A total of 20 ml freshly prepared hydroxylamine hydrochloride solution (0.5 M) was added to the residue in the centrifuge tube from step 1 and shaken for 16 h at room temperature. The separation of the extract, collection of the supernatant, and rinsing of the residue were the same as in step 1.

Step 3. First, 5 ml of hydrogen peroxide (30%) was added to the residue from step 2 in the centrifuge tube. The tubes were loosely covered to prevent substantial loss of hydrogen peroxide. Digestion at room temperature was allowed to proceed for 1 h with occasional manual shaking and followed by digestion at 85 ºC for another 1 h. The centrifuge tubes were then uncovered and heating continued to reduce the volume to 1 to 1.5 ml. Another 5 ml hydrogen peroxide was added to the tube and digested with a cover at 85 ºC for 1 h, and again, was the cover was removed and the volume reduced to 1 to 1.5 ml.

All sludge samples turned to a clear solution after the hydrogen peroxide digestion at step 3. The final extract from step 3 was diluted to 50 ml and stored for further analysis. Different from liquefied CCA-treated wood sludge samples, there was a residue that remained after hydrogen peroxide digestion for all original CCA-treated wood samples. This residue was shaken with 25 ml ammonium acetate (1.0 M) for 16 h at room temperature. The separation of the extract and rinsing of the residue were the same as described in step 1.

Step 4. For original CCA-treated wood sample, residue from step 3 was transferred to a glass digestion tube and digested with nitric acid at 120 ºC.

Digestion method for element concentration determination

To determine the pseudo-total concentration of each metal in different samples, about 0.5 g of oven-dried solid sample was digested with 10 ml nitric acid according to AWPA A7-08. To eliminate the matrix interferences from extraction reagents, liquid samples from sequential extraction step 1 and 2 were also digested according to the same method but with less nitric acid. The concentrations of As, Cr, and Cu were determined by inductive coupled plasma atomic emission spectroscopy (ICP-AES) from the digested samples.

RESULTS AND DISCUSSION

Heavy metal concentrations in different size original CCA-treated wood particles

Table 1 shows the three heavy metal contents of two different size CCA-treated wood particles. All three heavy metals showed good recovery rates from the sequential extraction procedures. The non-sieved wood particle (NWP) samples had slightly higher pseudo-total metal contents than the samples that passed through a 20 mesh (WP20) screen. However, the WP20 sample showed higher metal concentrations of the sum of 4 extraction steps than the NWP samples, which resulted in the higher recovery rates for all three heavy metals of the WP20 samples. Further experiments on size effects are ongoing to obtain sufficient data to better explain the differences on heavy metal concentrations between these two different size CCA-treated wood samples.

Except for the slight difference in the pseudo-total heavy metal contents, all three heavy metals in these two different size wood samples exhibited very similar distributions patterns for all 4 extraction fractions. Both As and Cr were principally present in the oxidizable fraction (e.g., step 3). For instance, up to 88% of Cr was present in the oxidizable fraction. In the CCA treating solution, Cr acts as a fixing agent to precipitate As and Cu onto wood when Cr^{6+} is reduced to Cr^{3+}. This function of Cr in the CCA fixation process implies that Cr easily forms a complex with wood and thus most Cr is associated with organic matter. According to current knowledge on the fixation mechanism of CCA metals in treated wood, As was precipitated in wood by Cr as $CrAsO_4$ (Bull et al., 2000). Therefore, As showed a very close trend with Cr in each fraction.

Unlike As and Cr, Cu was largely present in the reducible fraction (49%) and the exchangeable/acid extractable fraction (34%). This could contribute to the different "fixing" forms of the three heavy metals in CCA-treated wood. A extensive investigation done by X-ray absorption fine structure spectroscopy showed that Cu was not closely associated with any other heavy metals, and the authors suggested that copper hydroxide ($Cu(OH)_2$) is the only plausible inorganic fixation product in CCA-treated wood (Bull et al., 2000). Although it was reported that Cu was mainly present in the oxidizable fraction in many soil samples (Audry et al., 2006; Cuong and Obbard, 2006) and is preferentially retained on organic matter by complexation rather than ion exchange (Balasoiu et al., 2001), only about 17% of Cu existed in the oxidizable fraction in the original CCA-treated wood sample, which is substantially lower than those of As and Cr.

As described in the experimental section, little residue remained after hydrogen peroxide extraction (e.g., step3) when the original CCA-treated wood was subjected to the BCR sequential extraction procedure. Because the samples in this study were a woody material or from woody material, hot nitric acid, instead of *aqua regia* was used to extract the last fraction after step 3. The small amount of heavy metals present in this fraction could associate with wood cellulose in the crystalline region. Wood is a markedly non-uniform material. It consists of amorphous lignin, cellulose, and crystalline cellulose and thus has different accessibilities to different regions. Metals associated with crystalline cellulose represent the least amount of total fixed metals and also the most difficult portion to access or extract. Therefore, harsher conditions are required to liberate this fraction of metals than those associated with wood components in amorphous regions.

As, Cr, and Cu distributions in liquefied CCA-treated wood sludge separated by filtration and centrifugation

LWSF samples showed a negligible higher pseudo-total metal content than the LWSC samples (Table 2). The result implied that the centrifugation force used in this study could not move all of the precipitate to the bottom of the centrifuge tube. Some very fine precipitate might still be suspended in the liquefied CCA-treated wood solution after centrifugation. However, the filtration could retain more precipitate from the solution.

As listed in Table 2, the distribution of As and Cr in liquefied CCA-treated wood sludge changed dramatically as compared with that in original CCA-treated wood samples (Table 1). About 85% of As in liquefied CCA-treated wood sludge was present in the exchangeable/acid extractable fraction, which indicated that most As compounds were liberated from their association with wood components during the liquefaction reaction. The remaining 10% and 5% of As were in reducible and oxidizable fractions, respectively, which indicated that there was a small amount of As still bound to some metal oxides and decomposed wood components. Similar to As, the major change of Cr distribution was the large increase (51%) in the exchangeable/acid extractable fraction and the decrease (54%) in the oxidizable fraction compared to the original CCA-treated wood. However, Cr had a larger portion (34%) associated with organic matter in liquefied CCA-treated wood sludge as compared to As and Cu. As shown in Table 1, Cr had the largest portion in the oxidizable fraction among the three heavy metals. The heavy metals in this fraction are more resistant to acid extraction than those in exchangeable and reducible fractions (Basta et al., 2005). Other researchers also reported that Cr leached the least despite being present in the greatest proportion (Moghaddam and Mulligan, 2008). The distribution of Cu in liquefied CCA-treated wood sludge did not change markedly as did As and Cr. The amount of Cu in the reducible fraction was close to that in the original CCA-treated wood. There was a moderate increase (14%) in the exchangeable/acid extractable fraction and a decrease (13%) in the oxidizable fraction, which indicated that most copper complexed with the wood component had been liberated after the liquefaction reaction.

As, Cr, and Cu distributions in liquefied CCA-treated wood sludge precipitated with/out $Ca(OH)_2$

It is generally believed that $CrAsO_4$, a compound with low solubility, is the major fixation product of Cr and As in CCA-treated wood. Therefore, it would be expected that $CrAsO_4$ could be centrifuged and separated from diluted liquefied CCA-treated wood solution. However, the separation result was poor. As shown in Table 3, only about 1.4% As, 24.6% Cr, and 39.2% Cu (as of pseudo-total concentrations) were removed in the LWS1 without adding $Ca(OH)_2$. This result indicated that during and after the liquefaction of CCA-treated wood, when the pH of the reaction system was low and the system remained as a strong acidic environment, most As, Cr, and Cu ions stayed in soluble status. As demonstrated in a CCA metal removal mechanism by liquefaction-precipitation process we proposed in our previous study (Pan et al., 2009), $Ca(OH)_2$ functions as both a precipitant and a pH adjusting additive in the process. Without coagulation by $Ca(OH)_2$ and increased pH, it is difficult to remove the As, Cr, and Cu compounds in liquefied CCA-treated wood solution.

The distributions of all three heavy metals in LWS2 exhibited similar trends as observed with the LWSF and LWSC samples. In brief, the majorities of As and Cr were liberated from CCA-treated wood and present in the exchangeable/acid extractable fraction.

CONCLUSIONS

The sequential extraction result showed that the two different size CCA-treated wood particles used for liquefaction had similar heavy metals distributions. As and Cr had a similar distribution in the original CCA-treated wood. They principally existed in an oxidizable fraction (As, 67%; Cr, 88%). Only 1% of both As and Cr were extracted by hot nitric acid during the last extraction step. Cu was largely present in the reducible fraction (49%) and the exchangeable/acid extractable fraction (34%) in the original CCA-treated wood. The distribution of As and Cr changed markedly after liquefaction. The amount of As in the exchangeable/acid extractable fraction increased from16% to 85% while the amount of Cr increased from 3% to 54%. The distribution of Cu in liquefied CCA-treated wood sludge did not change markedly. The amount of Cu in the reducible fraction was close to that in the original CCA-treated wood. There was a moderate increase (14%) in the exchangeable/acid extractable fraction and a decrease (13%) in the oxidizable fraction. Based on these results from sequential extraction procedures, it can be concluded that the accessibilities of CCA metals increase markedly by the liquefaction-precipitation process. Only a small amount of heavy metals were precipitated by directly centrifugation and most of them were precipitated with $Ca(OH)_2$. The distributions of the heavy metals didn't vary markedly between the liquefied CCA-treated wood sludge samples obtained by filtration and centrifugation methods.

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Table 1. CCA concentration (ppm) in each fraction of the original CCA-treated wood by BCR extraction procedures.

	Step1	Step 2	Step 3	Step 4	Sum	Pseudo-total	Recovery (%)
Un-sieved CCA-treated wood particles							
As	559±91	578±54	2340±209	26±10	3503	3726±125	94
Cr	123±24	338±27	3733±390	51±16	4245	4101±123	104
Cu	853±145	1219±99	406±53	6±1	2484	2573±63	97
Pass through 20 mesh CCA-treated wood particles							
As	547±57	708±28	2471±94	17±3	3742	3508±12	107
Cr	122±13	429±23	3986±183	27±4	4564	3880±18	118
Cu	821±72	1474±68	360±48	4±1	2658	2515±91	106

Note: Results are expressed as mean ± standard deviation (3 replicates for each sample).

Table 2. CCA concentration (ppm) in each fraction of the liquefied CCA-treated wood sludge obtained from two separation methods.

	Step1	Step 2	Step 3	Sum	Pseudo-total	Recovery (%)
Liquefied CCA-treated wood sludge separated by filtration						
As	3482±180	407±37	215±12	4104	4262±201	96
Cr	2365±133	504±34	1509±42	4378	4349±166	101
Cu	1167±63	1157±40	104±4	2428	2425±113	100
Liquefied CCA-treated wood sludge separated by centrifugation						
As	3283±253	549±34	209±4	4041	4218±187	96
Cr	2423±262	582±26	1177±22	4182	4257±167	98
Cu	1248±140	997±18	85±2	2330	2319±110	100

Note: Results are expressed as mean ± standard deviation (6 replicates for each sample).

Table 2. CCA concentration (ppm) in each fraction of the liquefied CCA-treated wood sludge obtained from two-step precipitation method.

	Step1	Step 2	Step 3	Sum	Pseudo-total	Recovery (%)
Liquefied CCA-treated wood sludge from precipitation step 1[1]						
As	38±4	-	15±0.1	53	52±1	102
Cr	787±13	203±16	322±24	1312	1156±3	113
Cu	802±11	177±2	16±1	995	836±4	119
Liquefied CCA-treated wood sludge from precipitation step 2[2]						
As	2892±82	880±37	146±1	3918	3695±61	106
Cr	1915±59	949±39	869±8	3733	3534±91	106
Cu	1016±85	1107±50	135±1	2258	2130±58	106

Note: Results are expressed as mean ± standard deviation (3 replicates for each sample).

[1] Precipitation step 1 refers to the procedure in which liquefied CCA-treated wood was diluted with a solvent and centrifuged without adding $Ca(OH)_2$.

[2] Precipitation step 2 refers to the procedure in which $Ca(OH)_2$ was added to the solution, separated from precipitation step 1, and then centrifuged.

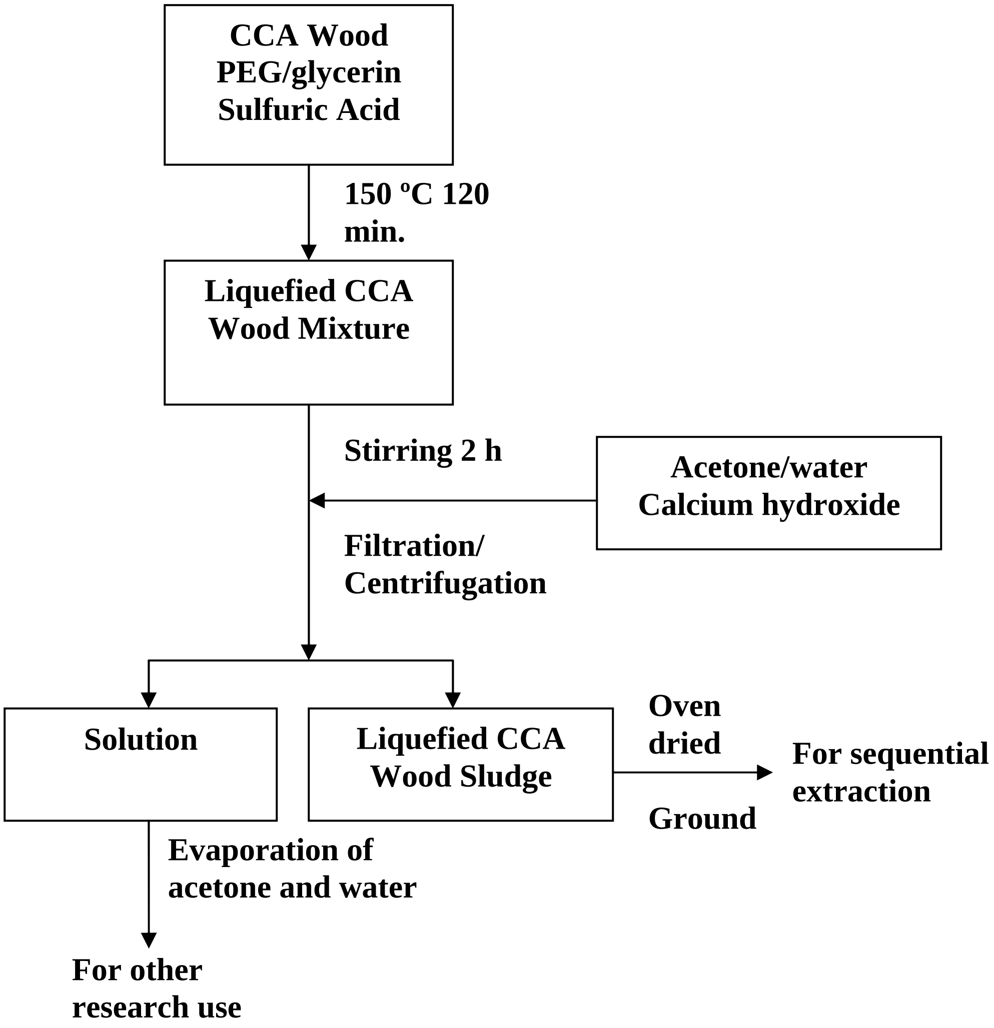

Fig. 1. Flowchart for liquefaction of CCA-treated wood and precipitation of liquefied CCA-treated wood sludge.