IRG/WP 09-60184

THE INTERNATIONAL RESEARCH GROUP ON WOOD PROTECTION

Section Y VVVVVVVVVVV

MICROWAVE-ASSISTED ORGANIC ACIDS EXTRACTION OF CHROMATE COPPER ARSENATE (CCA)-TREATED SOUTHERN PINE

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Paper prepared for the 41st Annual Meeting
Biarritz, France
9-13 May 2010

IRG SECRETARIAT
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ABSTRACT

The extraction effects of acid concentration, reaction time and temperature in a microwave reactor on recovery of CCA-treated wood were evaluated. Extraction of copper, chromium, and arsenic metals from chromated copper arsenate (CCA)-treated southern pine wood samples with two different organic acids (i.e., acetic acid and oxalic acid) was investigated using a microwave reactor. Oxalic acid was effective in removing 100% of the chromium and arsenic at 160°C and 30 min. reaction time. Acetic acid could remove 98% of the copper and arsenic at the same condition. Oxalic acid significantly improved the extraction efficiency of arsenic and chromium when time was prolonged from 10min. to 30min. The HSAB (Pearson acid base concept) concept was applied to explain why oxalic acid removed more chromium and less copper compared with acetic acid. Acetic acid also showed an improved ability to remove arsenic and copper when the reaction temperature was increased from 90°C to 160°C.

Keyword: CCA, recovery, microwave, extraction, HSAB

1. INTRODUCTION

Chromated copper arsenate (CCA) was the most commonly used waterborne wood preservative in the world until its removal from the U.S. residential market on December 31, 2003. However, large volumes of CCA-treated wood remain in service and according large amounts will continue to be decommissioned in coming years. Traditionally, CCA-treated wood has been primarily disposed in construction and demolition (C&D) debris landfills, with municipal solid waste (MSW) landfills as alternative disposal options. It is estimated that about 3 to 12 million tons of spent preserved wood will be removed from service in the United States and Canada in the next 20 years (Kazi and Cooper, 2006)

Disposal of the spent CCA-treated wood has become an important concern because of its residual heavy metal content, in particular the arsenic and chromium. Traditional waste disposal options for spent preserved wood, such as burning and landfilling, are becoming more costly or even impractical because of increasingly strict regulatory requirements (Townsend et al., 2004). The burning of treated wood can be extremely dangerous and even more so when the wood has been treated with CCA. Studies have shown that burning of preservative –treated wood waste emits highly toxic smoke and fumes in the environment (Solo-Gabriele, 2002). In the case of landfills, studies have shown that CCA compounds can be gradually leached out (Townsend, 2005; Moghaddam, 2008). There is an imperative need for developing techniques to recycle CCA-treated out of service wood.

Several chemical methods have been proposed to extract the metals from CCA-treated wood. Solvent extraction will dissolve the preservatives and partially remove them from the wood. The used of acid extraction to remove CCA components from wood has been extensively studied (Kartal and Clausen, 2001; Son et al., 2003; Clausen, 2003; Clausen, 2004; Gezer, 2006; Kakitani 2006; Kakitani 2007). One of the advantages for acid extraction is its potential ability to reverse the CCA fixation process, thereby converting CCA elements into their water-soluble form (Kartal and Clausen, 2001). However, a disadvantage of this recycling method is the huge amount of chemical solvents used and the long duration of the process. The prevailing treatment times reported ranged from 16 hours for sawdust (Clausen and Smith, 1998) to 24 hours for chips (Kartal and Clausen, 2001), which are considered to be major factors hindering commercial development. Therefore, to develop an economically viable industrial process, the focus of our study was on treatment time and acid concentration. Thus, the time saving potential of microwave heating led us to its application with acid extraction. The specific objectives of this study were to: (1) develop a new CCA recovery system based on the application of the microwave energy, and (2) optimize reaction time, temperature, and acid concentration for the process.

2. MATERIALS AND METHODS

The recovery of CCA metals by acid extractions was evaluated through a series of three experiments: 1) extraction of CCA in two acids (i.e., oxalic acid and acetic acid) at five concentrations (i.e. w/w: 0.25%, 0.50%, 0.75%, 1.00%, and 1.50%); 2) extraction of CCA in two acids with thee treatment times (i.e., 10min., 20min., and 30min.); and 3) extraction of CCA with two acids at three temperatures (i.e., 90°C, 125°C and 160°C). Each combination of variables was replicated three times.

2.1 Preparation of CCA-Treated Wood Samples

Southern pine chips (*Pinus sp*). were obtained from Arnold Forest Products Co. in Shreveport, La, USA and used as raw material. The chips were treated with CCA type C preservative (CCA-C, chromium as CrO_3, 45%-50%; copper as CuO, 17-21%; arsenic as As_2O_5, 30-37%) solution using a full-cell process. The wood chips were air dried (105°C), milled to sawdust, screened through a 40-mesh-size sieve. The dry sawdust was used without further treatment.

2.2 Acid Extraction in Microwave Reactor

The ratio of sawdust to diluted acid or mixed acid solution was fixed at 1g to 20 ml. The vessel was sealed and placed into the microwave reactor (Milestone, Sheton, CT). The solution was filtered after the reaction by Whatman No.4 filter paper then diluted to 100ml in a volumetric flask.

2.3. Determination of Copper, Chromium, and Arsenic Concentrations

Digestion. Solid wood residue was digested according to American Wood Protection Association Standard A7-93 (AWPA 2008). The procedure required that the CCA-bearing solid residues be accurately weighed into 100 ml test tubes. For each gram of solid residue, 15ml of nitric acid was added. A digestion blank along with the samples was also prepared. The test tubes were placed into an aluminum heating block and slowly warmed. The temperature was increased to 120 °C after the initial reaction of brown fumes subsided. The temperature was maintained until a transparent liquid was obtained. The transparent liquid was cooled to room temperature and 5ml of hydrogen peroxide was drop-wise added. If the solution was not clear after this treatment, the temperature was increased and another 5ml of hydrogen peroxide was added. The sample was continually heated until approximately 1 ml sample solution was left in the test tube. The sample was carefully transferred into a 25ml volumetric flask and then diluted with distilled water to a 25ml solution.

Analysis of Cu, Cr and As. Quantitative elemental analysis of copper, chromium and arsenic was conducted according to American Wood Protection Association Standard A21-00 (AWPA 2008). After digestion, the concentrations of copper, chromium, and arsenic in the samples were determined by inductive coupled plasma atomic emission spectroscopy (ICP-AES).

2.4 Statistical Analysis

The effect of concentration, time, and temperature on the recovery rate of arsenic, chromium, and copper from CCA-treated wood samples with various acids in a microwave reactor were evaluated by analysis of variance (ANOVA) with SAS 9.0 software (SAS 2008). The significant differences between mean values were determined using Duncan's Multiple Range Test.

3. RESULTS AND DISCUSSION

3.1 Extraction of CCA Elements of Spent CCA-treated Wood in Two Organic Acid Solutions at Five Concentrations in Microwave Reactor

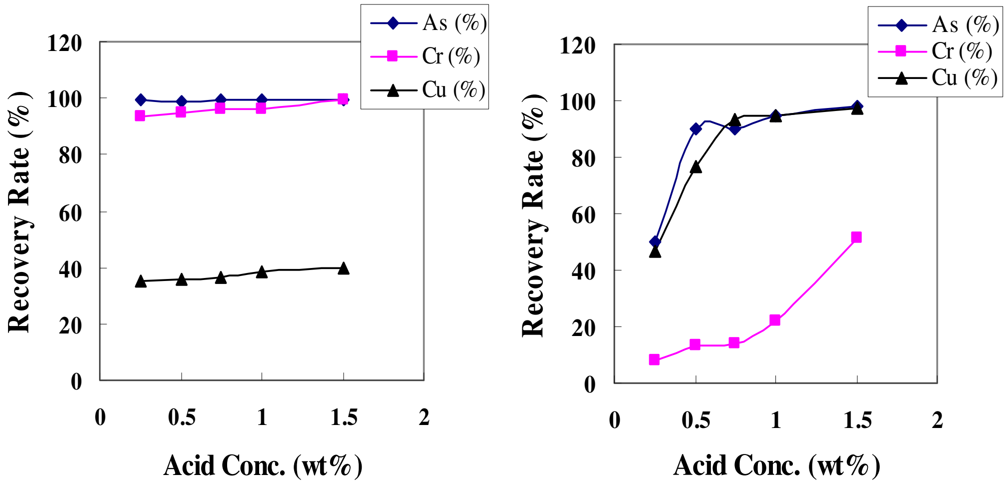
Average recovery of CCA metals from spent CCA-treated wood sawdust by acids at various concentrations in a microwave reactor are summarized in Table 1.

temperature and extraction duration were fixed at 160°C and 30min.

The significant interactions of acids and acid concentrations on CCA recovery are shown in Figure 1. It is interesting to note: 1) oxalic acid removed arsenic and chromium very effectively but not copper (Figure 1-2A). While more than 99% of arsenic and 98% chromium was extracted from the sawdust using an acid concentration of 0.5%, less than 40% of copper was extracted with a 1.50% acid concentration; 2) acetic acid extraction was highly effective on removal of arsenic and copper but not chromium (Figure 1-2B).

Table 1 CCA recovery rate in three acids and five concentrations at 160^0C and 30 min

Acid	Acid Conc.[%]	As [%]	Cr [%]	Cu [%]
Oxalic acid	0.25	99.38±0.23	98.32±0.21	35.38±0.47
Oxalic acid	0.5	99.04±0.13	98.87±0.49	35.64±1.15
Oxalic acid	0.75	99.12±0.55	98.86±0.49	36.77±9.01
Oxalic acid	1	99.38±0.26	99.32±0.36	38.62±3.41
Oxalic acid	1.5	99.66±1.45	99.69±0.29	39.22±1.49
Acetic acid	0.25	49.81±2.48	8.24±0.85	46.61±2.33
Acetic acid	0.5	89.84±2.28	13.21±1.72	76.79±2.42
Acetic acid	0.75	90.19±1.38	14.08±2.09	93.40±0.51
Acetic acid	1	94.78±0.47	22.20±1.45	94.62±0.53
Acetic acid	1.5	97.97±1.45	51.53±2.77	97.49±1.62



(A). Oxalic Acid

(B). Acetic Acid

Fig. 1 CCA metal recovery rate affected by acid type and concentration in a microwave reactor

The results indicate that more than 90% of arsenic and 77% copper were extracted from the sawdust using an acetic acid concentration of 0.5% but even at an acetic acid concentration of 1.5% less than 52% of chromium was removed.

Arsenic can be easily removed by an organic acid. Generally, arsenate anions can be exchanged by a ligand to form a strong bonded complex. Inner-sphere surface complexes are formed through strong chemical bonds between the surface functional group and arsenic (V) or arsenic (III) anions without a water molecule between them (Sparks 1995). Therefore, the acetate and the oxalate, as two strong chemical ligands, can bond with arsenic to form complexes. This was the likely pathway for the arsenic removal from the wood.

In order to understand why oxalic acid removed more chromium and less copper as compared with acetic acid, we considered Pearson's acid base concept (HSAB). In short, soft acids react faster and form stronger bonds with soft bases, whereas hard acids react faster and form stronger bonds with hard bases if all other factors are equal. Hard acids and hard bases tend to have a small atomic/ionic radius, high oxidation state, low polarizability, and high hardness (IUPAC 2006). Oxalic acid has a much stronger oxidation state than acetic acid because of its two functional groups of carboxyl which allows for oxalic acid to react faster and form stronger bonds with higher hardness of metal than acetic acid does based on the HSAB. Hardness (η) of chromium and copper is 9 and 2.5 (IUPAC 2006), $\eta_{Cr}>\eta_{Cu,}$. Therefore, oxalic acid tends to combine with chromium to form a stronger compound, and acetic acid tends to combine with copper to form a weaker compound.

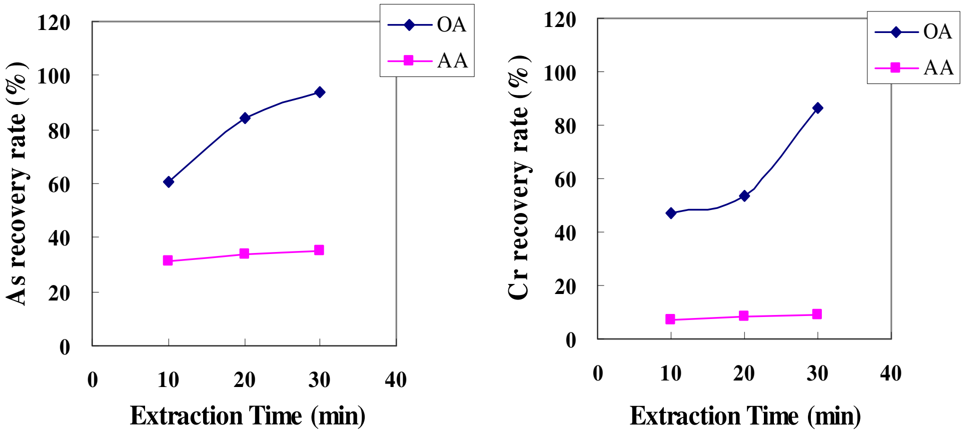
3.2 Extraction of CCA elements in Acids with Various Treatment Times.

Mean values of CCA elements recovered using two different acids at various extraction times are summarized in Table 2. The ANOVA indicated that the effects of acids and extraction time on CCA recovery were significant. The interactions of acids with extraction times on CCA recovery were also significant.

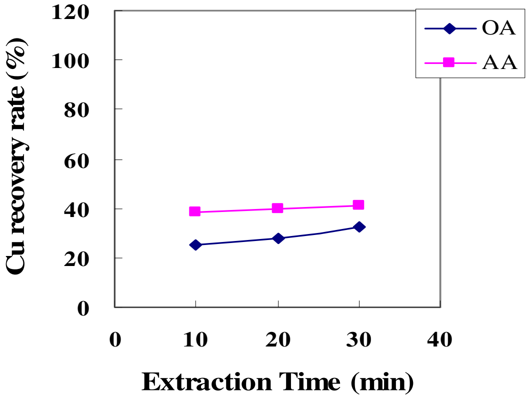
Table 2 CCA recovery rate in three acids (0.5%) and time in 125^0C

Acid	Time [min]	As [%]	Cr [%]	Cu [%]
Oxalic acid	10	60.37±2.51	47.29±0.70	25.32±1.03
Oxalic acid	20	83.96±1.57	53.53±0.57	27.61±0.65
Oxalic acid	30	94.06±2.37	86.30±0.42	32.17±0.87
Acetic acid	10	31.02±0.78	7.17±0.78	38.26±0.92
Acetic acid	20	33.99±0.64	8.23±0.64	40.07±0.64
Acetic acid	30	35.16±1.29	8.82±0.49	40.93±0.58

The significant interactions of the two acids with various extraction times on CCA recovery are shown in Figure 2. For arsenic recovery (Fig. 2A), the extraction efficiency of oxalic acid was much higher than that of the acetic acid. The CCA recovery increased from 60% to 94% as extraction times increased from 10min. to 30min., while arsenic recovery increased by 4% (31% to 35%) and 8% (48% to 55%), as extraction time increased from 10 to 30 minutes for that of acetic acid. For chromium extraction (Fig.2B), again oxalic acid was significantly more effective than that of acetic and phosphoric acid. Increased extraction time had a significant effect on chromium recovery with oxalic acid but not for acetic acid. It is interesting to note that the amounts of chromium recovered in oxalic acid between 20 to 30 min. were substantially greater than that between 10 to 20 min. (i.e., more than 32% as compared to that of 6.24%).



(A). Arsenic **(B). Chromium**



(C). Copper

Fig. 2 CCA elements recovery rate affected by acid type and time in a microwave reactor

3.3 Extraction of CCA elements in Acids at Various Temperatures

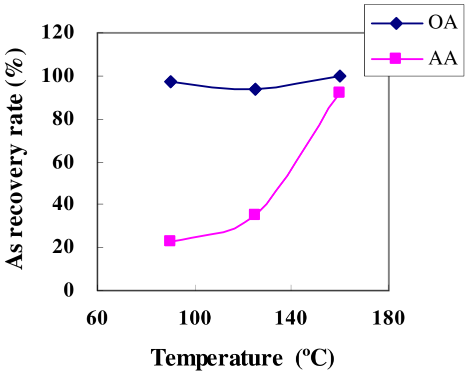
The effects of acids at various temperatures on metals recovery from CCA-treated wood are summarized in Table 3. The ANOVA showed that the effects of acid type and temperature on CCA recovery were significant. Also the ANOVA indicated that the interactions between acid type and temperature on CCA recovery rate were also significant.

The most interesting result for the effect of temperature on CCA recovery was the effectiveness of acetic acid for arsenic (Figure 3A) and copper (Figure 3C) with increasing temperature. The recovery rate increased 70% (i.e., 22% to 92%) and 62% (i.e., 32% to 94%), for arsenic and copper, respectively, as temperature increased from 90°C to 150°C. It is noted that most of the increase occurred between 130 ^{0}C to 150 ^{0}C, indicating the importance of extraction temperature for acetic acid.

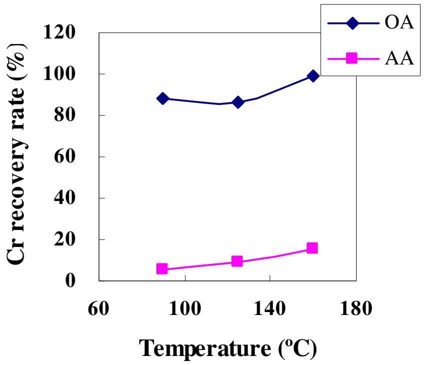
Fig. 3B shows that temperature had a minor effect on the acid extraction of chromium from CCA-treated wood.

Table 3 CCA recovery rate in three acids (0.5%) and temperature in 30min

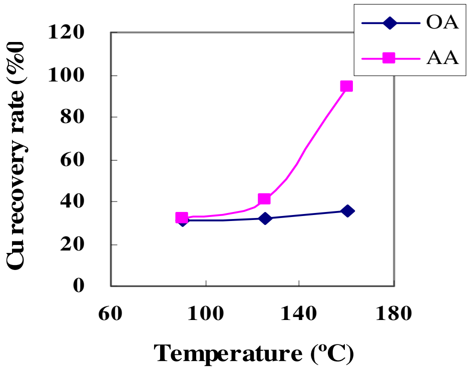
Acid	**Temperature [°C]**	**As [%]**	**Cr [%]**	**Cu [%]**
Oxalic acid	90	96.82±1.01	88.00±0.88	30.84±0.31
Oxalic acid	125	94.06±0.42	86.30±0.57	32.17±0.47
Oxalic acid	160	99.53±0.77	98.87±0.89	35.64±0.79
Acetic acid	90	22.43±2.48	5.26±0.32	31.70±0.82
Acetic acid	125	35.16±0.50	8.82±0.49	40.93±0.67
Acetic acid	160	91.84±0.21	15.29±0.37	93.89±3.49



(A). Arsenic



(B). Chromium



(C). Copper

Fig. 3 CCA elements recovery rate affected by acid type and temperature in microwave

4. CONCLUSIONS

The effect of microwave-assisted acid extraction of metals from chromated copper arsenate (CCA)-treated southern pine was studied. The results showed that diluted oxalic acid was very effective in recovering chromium and arsenic and acetic acid was effective at removing copper and arsenic at the same condition in a microwave reactor. The advantage of this approach is the reduced extraction time and one step method to achieve the complete recovery of CCA metals. Pearson's acid base concept (HSAB) concept was used to explain why oxalic acid removed more chromium and less copper as compared with acetic acid.

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