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Rapid microwave-assisted acid extraction of chromate copper arsenate (CCA)-treated southern pine

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RAPID MICROWAVE-ASSISTED ACID EXTRACTION OF CHROMATE COPPER ARSENATE (CCA)-TREATED SOUTHERN PINE

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ABSTRACT

Recovery of heavy metals from chromated copper arsenate (CCA) treated southern pine wood samples with three different dimension was investigated by recovery with acetic acid, oxalic acid and phosphoric acid in microwave reactor. Diluted phosphoric acid mixed with acetic acid was found to be very effective to remove copper, chromium, and arsenic from spent CCA-treated southern pine sawdust at a high temperature and in a short time. No single acid can totally recover all these three metals in one step in this method. Oxalic acid was effective in removing chromium and arsenic, and acetic acid was effective in removing copper and arsenic; However, CCA cannot be recovered with the mixture of acetic acid and oxalic acid because of a possible conflict effect. The effects of mixed acid concentration, reaction time, and temperature in microwave on recovery of CCA-treated wood samples were determined. The minimal reaction condition for maximum extracting CCA elements was 2.75% phosphoric acid mixed with 0.5% acetic acid, for 10min. at 130°C. The total recovery rate of CCA can reach 100% arsenic, 93.5% chromium, and 98.5% copper in one step. Statistical analysis showed the concentration of phosphoric acid and temperatures were two important factors.

Three sizes of wood chips were also extracted in the microwave reactor. For the particle size of 0.5×0.5×0.5cm, 93.5% arsenic, 64.5% chromium, and 95.89% copper was extracted by 3.5% phosphoric acid mixed with 0.5% oxalic acid after 50 min at 130°C. Although it needs a longer time to achieve the total CCA extraction, the microwave reactor assisted acid extraction method was more effective than previous approaches.

Keyword: CCA, recovery, microwave, hydrolysis, extraction

Chapter 1. Introduction

Preservative-treated wood products are well known to significantly prolong service life, and thereby extend the forest resource and enhance its sustainability. Inevitably, however, the treated products will become unserviceable either due to mechanical damage or failure, biological deterioration, or obsolescence. 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). Chromated copper arsenate (CCA) wood preservative contains CuO, CrO_3, and As_2O_5 as specified by American Wood Protection Association (AWPA) standards (AWPA, 2009d) CCA is stabilized in the wood by means of chemical reactions called fixation (Kartal and Lebow, 2003). CCA-treated posts and sleepers have an average working life of approximately 25 years.

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 have been primarily disposed in construction and demolition (C&D) debris landfills, with municipal solid waste (MSW) landfills as alternative disposal options (Khan et al., 2006).   Wood comprises 24% of the mass of C&D waste in the United States (Tolaymat et al., 2000) and up to 60% of the wood mass in loads delivered to Florida disposal facilities may be CCA-treated wood (Solo-Gabriele et al., 2000).   However, with the increasing concern about environmental issues, traditional disposal options are becoming more costly or even impractical due to landfill tipping fees and increasingly strict regulatory requirements (Piao C., et al., 2009).

The leach-resistance of CCA is due to the chemical fixation, which renders the toxic ingredients insoluble in water. The essence of CCA fixation is the reduction of chromium from hexavalent to the trivalent state, and the subsequent precipitation or adsorption of copper, chromium, and arsenic complexes in the wood (Lebow and Kartal, 1999). The reactions that take place in the wood during fixation of CCA have a great effect on the metal species that are emitted from the wood, and the subsequent toxicity of these leachates.

 Burning of treated wood may be extremely dangerous and even more so when the wood has been treated with CCA. This is not only rises the possible environmental pollution but affect the human health. Therefore, there is great need for developing a cost-effective recycling technique to recover CCA-treated out of service wood. (Townsend, 2005; Moghaddam, 2008)

There are various methods to recycle CCA-preservative treated wood including chemical extraction, and microbiological separation. Chemical extraction seems to be quite applicable from an economic perspective, meanwhile, the chemical methods have a minimum impact on the environment. However, the recovery of treated-wood products is currently limited because of the difficulty with environmental protection requirements and regulations, and lack of a proven economically feasible process.

The biological methods used either heavy metal-tolerant fungal strains or bacteria

and chemical extraction methods. The principle of both methods is to covert insoluble heavy metals in waste wood into a soluble form through acidification with organic acids. Converted heavy metals are then leached from the wood. Thus, both the remediated wood fiber and the metals can be reclaimed. However, the microbiological method is still at an early stage.

The present situation of treated-wood recycling is reviewed in this chapter. Chemical extraction with traditional solvents, combination of traditional solvents with microbial removal, steam explosion, hydrothermal treatment, and wood liquefaction are introduced.

1.1 Current Situation of Recycling CCA-Treated Wood

Recent studies have shown that the CCA can be removed from used CCA-treated wood by low temperature pyrolysis (Helsen et al. 1997), solvent extraction (Kim and Kim, 1993; Kazi and Copper, 1999; Shiau, 2000; Kartal and Clausen, 2001; Son et al., 2003; Kartal and Kose 2003; Gezer, 2006; Kakitani 2006; Kakitani 2007), biological method (Clausen and Smith, 1998; Kartal et al. 2006), electrodialytic remediation (Ribeiro et al. 2006) and dual treatment process involving biological and chemical extraction (Clausen and Smith, 1998; Clausen, 2004). Lower temperature has been reported to be effective. However, it gives rise to very slow wood decomposition rates and thus extremely long reaction times. Solution extraction has a bright future depending on its high CCAA retention capacity. But the disadvantages of this method are the long time, the large volume of chemical solution used, and the reuse of the recycling solution (Catallo et al. 2004).

1.2 Pyrolysis Methods

Low-temperature pyrolysis has been reported to be a promising approach to the growing CCA-treated wood disposal problem (Helsen et al, 1999), with the purpose of minimizing metal release and maximizing production of pyrolysis oils. Pyrolysis oils can be used as a source of valuable chemical products (Branca et al, 2003), such as levoglucosenone (LGO), levoglucosan (LG), hydroxyacetone, hydroxyacetaldehyde, isoeugenol, guaiacol, etc. Both LG and LGO are carbohydrate thermal decomposition products. LGO is a highly functionalized compound owing to its carbon–carbon double bond, the ketone group and the glycosidic anhydro linkage. LG is also an optically active compound. Thus, LG and LGO are attractive chiral raw materials for application in organic synthesis and the pharmaceutical industry. Fu (2008) applied phosphoric acid to yield 22% (on water-free tar basis) levoglucosenone. Such data demonstrates the potential for a new pathway toward the rational utilization of chromated copper arsenate-treated wood waste. However, economic and another environmental effect should be considered.

1.3 Biological and Bioremediation Methods

The biological methods used either copper-tolerant fungal strains (Stephan et al. 1996a) or bacteria (Clausen and Smith 1998) and chemical extraction methods (Stephan et al. 1996b). The principle of both methods is to covert insoluble heavy

metals in waste wood into soluble form through acidification with organic acids. Converted heavy metals are then leached from the wood. Thus, both the remediated wood fiber and the metals could be reclaimed. Kartal et al. (2004) reported the detection of oxalic acid produced by the brown-rot fungi *Fomitopsis palustris, Coniophora uteana*, and *Laetiporus sulphureus* and bioremediation of CCA-treated wood using liquid cultures of these fungi. In this report, brown-rot fungi were first cultivated and the fermentation medium was then used as a leaching agent to remove heavy metals from CCA-treated wood (Kartal et al, 2004). Oxalic acid plays an important role in partial solubilization of the insoluble metal compounds of CCA wood preservative fixed in the wood (Green et al., 1991). Oxalate is an agent that is small enough to penetrate the cell wall structure of wood and may function in conjunction with metals in the initiation of depolymerization of wood cell components. Oxalate produced by brown-rot fungi is able to remove complex iron and other metal ions. However, microbiological method is still at an early stage.

1.4 Chemical Methods

Various chemical methods have been used to recycle CCA from spent CCA-treated wood. This chapter will focus on several groups of chemical approaches. For the chemical extraction approach, it is necessary that the extracted chemicals be in a form that can be reused, for example for the treatment of commercial products for which CCA is still registered. The CCA fixation process requires that a significant component of the chromium in the treating solution be in the hexavalent state. For this reason, oxidizing extracting systems have an advantage over non-oxidizing chemical solution such as organic and inorganic acids. Another advantage of oxidizing treatments is that they ensure that the copper and arsenic components are at the higher oxidation states (As^V and Cu^{II}) present in the original CCA treating solution. Oxidation of Cr^{III} to Cr^{VI} is a function of initial Cr^{III} concentration in the solution, pH, redox potential, and aging (James and Bartlett, 1983; Spiccia and Marty, 1986; Blesa et al., 1994; Fendorf, 1995; Milacic and Stupar, 1995). Aged precipitates of $Cr(OH)_3$ are more difficult to oxidize than freshly precipitated forms (Amacher and Baker, 1982).

1.4.1 Acid Extraction

Acid extraction has been widely studied by several researchers for removing copper, chromium, and arsenic from CCA-treated wood. (Kim and Kim, 1993; Clausen and Smith, 1998; Kazi and Copper, 1999; Shiau, 2000; Kartal and Clausen, 2001; Son et al., 2003; Kartal and Kose 2003; Gezer, 2006; Kakitani 2006; Kakitani 2007). The results indicate that exposure of CCA-treated wood to acid extraction can reverse the CCA fixation process through converting CCA elements into their water-soluble form (Kartal and Clausen, 2001).

There are several previous organic acid extraction methods summarized above in Table 1-1. Oxalic acid was preferred as the extraction solution in several studies. Clausen et al. (1998) and Son et al. (2003) both applied oxalic acid to extract metals from CCA-treated chips to achieve around 50% copper, 60% chromium and 70%

arsenic recovery rate. Citric acid and acetic acid were also used to test the extraction effect of CCA elements (Shiau et al. 2000). Gezer et al. (2006) reported that oleic acid was found to be effective to remove copper, chromium, and arsenic from CCA-treated wood samples especially at lower pH levels such as pH=2.00 and 2.50. These methods normally require at least 18 hours to finish the extraction processes. Some CCA elements still exist in the residue which might lead to environmental problems.

Table 1-1 Percentage removal of CCA-elements from treated wood using some organic acids

Acid	Acid conc/pH	During (h)	Wood source	Cu (%)	Cr (%)	As (%)	Literature
Oxalic acid	1 %	24	Sawdust	81	62	89	Clausen and Smith (1998)
Oxalic acid	1 %	18	Chips	23	65	74	Kartal and Clausen (2001)
Oxalic acid	1 %	18	Chips	55	60	75	Son et al. (2003)
Citric acid	pH: 3.5	24	Chips	42	42	38	Shiau et al. (2000)
Acetic acid	pH: 3.5	24	Chips	31	32	30	Shiau et al. (2000)
EDTA	1 %	24	Chips	60	13	25	Kartal (2003); Kartal and Kose (2003)
NTA	1 %	24	Chips	9	45	22	Kartal and Kose (2003)
Oleic acid	pH: 2	24	Chips	67	63	81	Gezer et al. (2006)
Oxalic acid with NaOH	1.6%	6	Sawdust	89	88	94	Kakitani (2006); Kakitani (2007)

1.4.2 Acid Extraction with Biological Methods

Clausen effectively used a dual remediation process for CCA-treated wood samples (Clausen, 2003; Clausen, 2004). The treatment had two steps: oxalic acid extraction and bacterial culture with *Bacillus Licheniformis* CC01. Oxalic acid concentration at 0.80% for 18h of bacterium exposure resulted in a total reduction of 78% copper, 97% chromium and 93% arsenic. This two-step process is costly and requires a long duration way.

1.4.3 Extraction with Supercritical Fluids

Several studies regarding the decontamination of CCA-treated wood using green solvent, supercritical carbon dioxide ($ScCO_2$) have been reported (Takeshita et al., 2000). The results indicate that copper can be successfully extracted from CCA-treated wood with a continuous addition of acetylacetone in $ScCO_2$. $ScCO_2$ is very attractive for environmental remediation due to its nontoxic, nonflammable and recyclable properties. El-Fatah et al. (2009) reported that hazardous metals in CCA-treated wood can be extracted using $ScCO_2$ by different chelating agents, among them Cyanex 302 was the best ligand.

The weak point of this method is that using $ScCO_2$ as the medium to remove CCA in the wood are either have lower extraction efficiency or be unsuccessful to discuss the influence of the different species of copper, chromium, and arsenic in the wood on the mechanism of extraction. The reason is that various species may present different

extraction efficiencies while under the identical extraction condition.

1.5 Relative Research

From the trend of development in recycling CCA-treated wood, single approach has been substituted by multiple procedures gradually. Various treatment methods have been applied in this recycling process. Microwave reactor is a widely applicable instrument in industry. Orozco et al. (2004) applied a microwave reactor to hydrolysis grass using dilute phosphoric acid. Kinetic analysis of the dilute acid hydrolysis of grass (to glucose) indicated that the use of microwave technology can successfully facilitate acid hydrolysis, which compare favorably with reaction rate constants found in conventional non-microwave reaction systems. The kinetic analysis would indicate that the primary advantages of employing microwave heating were to achieve a high rate constant at moderate temperatures and to prevent 'hot spot' formation within the reactor. The microwave assisted method could be an effective way to recycle CCA-treated wood.

1.6 Objectives

Although oxalic acid and other acids have been proven to recover CCA metals in relatively high extraction efficiency, the time period (Normally 18 h) and high liquid/solid ratio has limited commercial applications. Therefore, further research is needed to develop a viable and economical CCA recovery process. The objectives of this study are to:

(1) Prove that microwave is a practical way to recover CCA from spent CCA-treated wood.

(2) Develop an easy way (single step, shorter time) to recover CCA elements from southern pine in a microwave reactor;

(3) Optimize reaction factors (time, temperature and acid concentration) to achieve the maximum CCA recovery effect.

Chapter 2. Recovery of CCA Elements by A Single Acid Assisted with Microwave

2.1 Materials and Methods

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

2.1.1 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 the 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 dust was used without further treatment.

2.1.2 Acid Extraction in A 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) (Figure 2-1). The solution was filtered after the reaction using whatman No.4 filter paper then diluted to 100ml in a volumetric flask.

Fig. 2-1 Milestone Ethos EX Microwave Extraction System

2.1.3 Determination of Copper, Chromium, and Crsenic 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 remained 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).

2.1.4 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.

2.2 Results and Discussions
2.2.1 Extraction of Heavy Metals from Spent CCA-treated Wood Using Three Acid Solutions at Five Concentrations in A 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 2-1. The temperature and extraction duration were fixed at 160°C and 30min. The ANOVA indicated that the effects of acid species and concentration on CCA recovery were significant (Table 2-2). It also revealed that the interactions between acid species and concentration had significant effects on CCA recovery rate. The significant interactions of acids and acid concentrations on CCA recovery are shown in Figure 2-2.

   It is interesting to note: 1) oxalic acid removed arsenic and chromium very effectively but not copper (Figure 2-2A). 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 2-2B). 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; 3) the extraction using phosphoric acid was less effective as compared to both oxalic and acetic acids (Figure 2-2C). While the maximum recovery of copper (i.e., 79%) and

Table 2-1. CCA recovery rate for three acids and five concentrations at 160 ^{0}C 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
H_3PO_4	0.25	55.37±1.01	13.79±0.51	57.28±1.02
H_3PO_4	0.5	57.56±5.23	14.56±0.88	59.69±8.31
H_3PO_4	0.75	58.13±5.61	15.00±1.70	72.11±1.78
H_3PO_4	1	60.05±2.73	16.64±1.61	77.50±2.99
H_3PO_4	1.5	65.12±2.48	19.32±3.07	78.59±1.87

Table 2-2. ANOVA results of the effects of acid type and acid concentrations on CCA recovery rate

Source	DF	Type I SS	Mean Square	F Value	Pr > F
1. Dependent variable: As					
Conc	4	2021.29616	505.32404	84.93	<.0001
Acid	2	12371.07403	6185.53702	1039.56	<.0001
Acid*Conc	8	2775.82224	346.97778	58.31	<.0001
2. Dependent variable: Cr					
Conc	4	1591.35185	397.83796	173.64	<.0001
Acid	2	64507.71088	32253.85544	14077.6	<.0001
Acid*Conc	8	2073.44765	259.18096	113.12	<.0001
3. Dependent variable: Cu					
Conc	4	3919.70261	979.92565	74.66	<.0001
Acid	2	16376.97211	8188.48606	623.84	<.0001
Acid*Conc	8	2697.09547	337.13693	25.68	<.0001

chromium was less than 20% using an acid concentration of 1.5%. Almost 60% of total copper and arsenic were removed with an acid concentration of 0.5%, therefore, the phosphoric acid removal of copper (i.e., 20%) was slightly higher than that of arsenic (i.e., 7%) at acid concentration ranges of 0.5 to 1.5%.
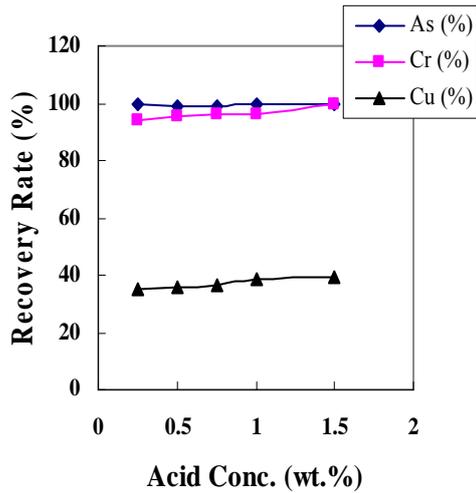
(A). Oxalic Acid
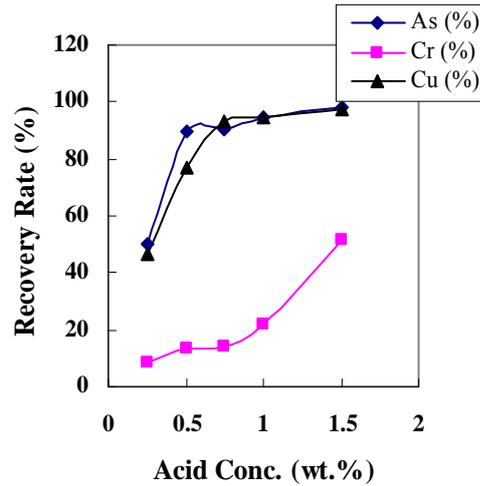
(B). Acetic Acid
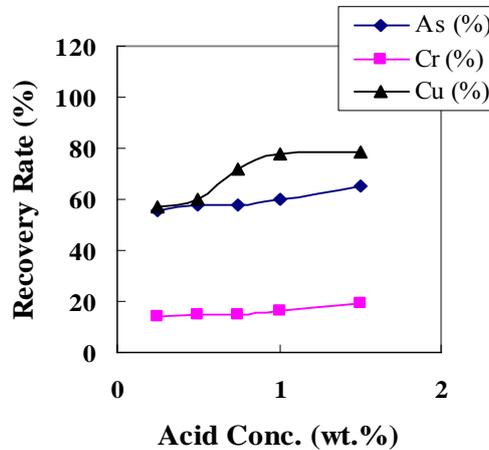
(C). Phosphoric Acid

Fig. 2-2 CCA metal recovery rate affected by acid type and concentration in a microwave reactor.

It can be explained that arsenic can be easily removed by organic acid. Generally, arsenate anions can be exchange by a ligand to form strong bonded complex. Inner-sphere surface complexes are formed through strong chemical bond between the surface functional group and arsenic (V) or arsenic (III) anions without water molecule between them (Sparks, 1995). Therefore, the acetate and the oxalate, as two strong chemical ligands, can bond with arsenic to form complexes. In this way, arsenic was removed from wood.

The HSAB (Pearson acid base concept) concept can explain why oxalic acid removed more chromium and less copper compared with the acetic acid. The gist of this theory is that soft acids react faster and form stronger bonds with soft bases, whereas hard acids react faster and form stronger bonds with hard bases, all other factors being equal. Hard acids and hard bases tend to have: small atomic/ionic radius, high oxidation state, low polarizability, high hardness (IUPAC, 2006). Oxalic acid has much stronger oxidation state than acetic acid because of its two functional groups of carboxyl which means oxalic acids 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 stronger compound, and acetic acid tends to combine with copper to form weaker compound.

2.2.2 Extraction of CCA Elements in Acids With Various Treatment Times.

Table. 2-3 CCA recovery rate for three acids (0.5%) and three time periods at 125°C.

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
H_3PO_4	10	47.97±0.84	9.27±0.83	50.37±0.85
H_3PO_4	20	53.42±1.69	12.59±0.56	56.02±0.69
H_3PO_4	30	55.39±0.97	13.17±0.67	57.23±0.32

Mean values of CCA elements recovery using three acids at various extraction times are summarized in Table 2-3. ANOVA indicated that the effects of acids and extraction time on CCA recovery were significant. Interactions of acids with extraction times on CCA recovery were also significant. The significant interactions of the three acids with various extraction times on CCA recovery are shown in Figure 2-3.

For arsenic recovery (Figure 2-3A), the extraction efficiency of oxalic acid was much higher than that of the other two acids. 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 and phosphoric acid, respectively.

For chromium extraction (Figure2-3B), 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 or phosphoric acid. It is interesting to note that the amount of chromium recovered in oxalic acid between 20 to 30 min. was substantially greater than that between 10 to 20 min. (i.e., more than 32% as compared to that of 6.24%).

The recovery of copper slightly increased as extraction time increased (Figure 2-3C). The effect of extraction time was statistically not significant. On average, phosphoric acid resulted in the highest copper recovery, while acetic acid yielded the lowest copper recovery.
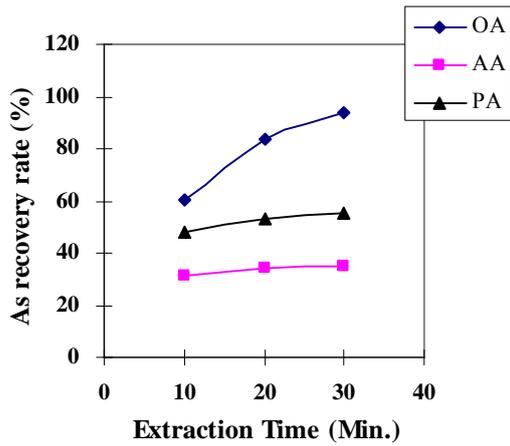
(A). Arsenic
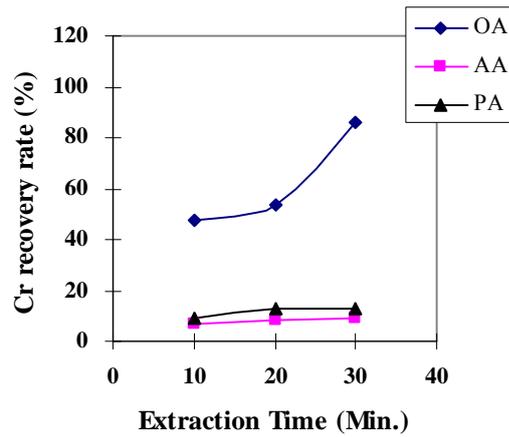
(B). Chromium
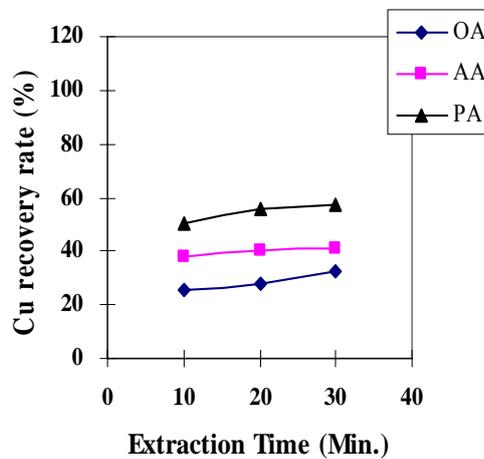
(C). Copper

Fig. 2-3 CCA elements recovery rate affected by acid type and time in a microwave reactor

2.2.3 Extraction of CCA Elements in Acids at Various Temperatures

The effect of acid type at various temperatures on metals recovery from CCA-treated wood are summarized in Table 2-4. The effect 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 temperature effect on CCA recovery was the effectiveness of acetic acid with increasing temperature. For arsenic (Figure 2-4A) and copper (Figure 2-4C) removal, 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. Most of the increased removal occurred between 130°C to 150°C, indicating the importance of extraction temperature for acetic acid. Figure 2-4B shows that temperature had a minor effect for acid extraction of the chromium from the CCA-treated wood.

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Table. 2-4 CCA recovery rate for three acids (0.5%) and three temperatures with a 30min. reaction period

Acid	Temperature [^{o}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
H_3PO_4	90	47.38±1.39	10.92±0.23	50.29±1.26
H_3PO_4	125	55.39±0.32	13.17±0.32	57.23±0.32
H_3PO_4	160	57.56±0.92	14.56±0.73	59.69±0.92

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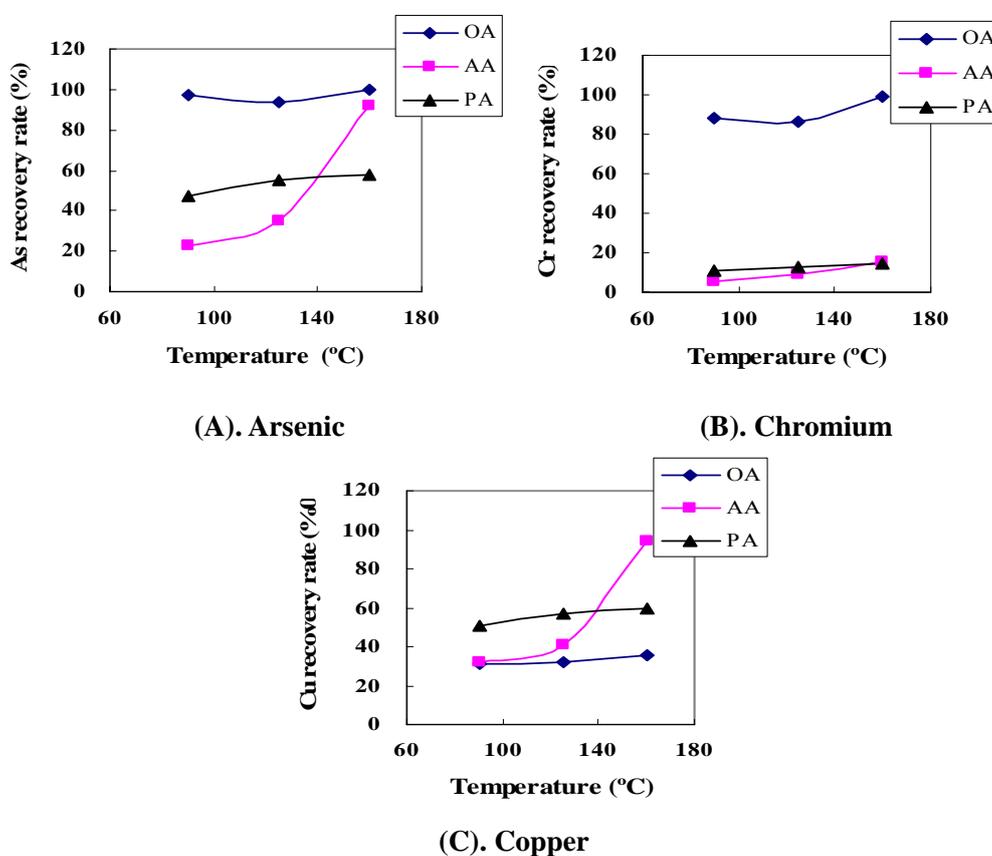
(C). Copper

Fig. 2-4 CCA elements recovery rate affected by acid type and temperature in a microwave reactor

2.3 Conclusions.

The effect of microwave-assisted single 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 conditions in a microwave reactor. The advantage of this approach is the reduced extraction time and one step method to achieve complete recovery of CCA metals.

Chapter 3. Recovery of CCA Elements by Mixed Acids Assisted in a Microwave Reactor

3.1 Materials and Methods
Please refer to section 2.1

3.2 Result and Discussions

The recovery of CCA metals by acid extraction was maximized through a series of experiments each designed to elucidate a limit facet of the problem. The study is a sequence of two experiments: 1) extraction of CCA in three acids with thee treatment times (i.e., 10min., 20min., and 30min.); and 2) extraction of CCA with three acids at three temperatures (i.e., 90°C, 125°C, and 160°C). Each combination of variables was replicated three times.

3.2.1 Behavior of Heavy Metals during Extraction of CCA-Treated Wood with Oxalic and Acetic Acid in A Microwave Reactor

The results in section 2-2 showed that diluted acid can reverse the CCA fixation process and convert CCA components into their water-soluble form. However, no single acid could totally remove the CCA elements. Because of the recovery differences of each metal ion in various acids, the recovery effect of mixed acids on CCA element needs further study.

The results of section 2-2 showed that 0.25 % oxalic acid can extract greater than 98% of the chromium and arsenic, and 0.75% acetic acid can extract approximately 90% of the arsenic and 93% copper.   Therefore, based on these data, three concentrations of acetic acid (i.e. 0.5%, 1.0%, and 1.5%) and two concentrations of oxalic acid (i.e. 0.5%, 1.0%) were chosen to do further research in which over 98% of the arsenic and chromium was removed.   However, only 30% of the copper was removed. Acetic acid had a poor extraction effect on copper when mixed with oxalic acid as indicated in Table 3-1.   The reason for this is unclear.

Table. 3-1 CCA recovery rate for two mixed acids at 160°C and 30min

Acetic acid Conc. (%)	Oxalic acid Conc. (%)	As (%)	Cr (%)	Cu (%)
1.5	1	99.65±0.24	99.88±0.49	34.57±1.02
1	1	99.67±0.45	99.89±1.03	32.93±1.18
0.5	1	99.59±0.27	99.65±0.96	31.50±0.85
1.5	0.5	99.56±1.45	99.43±1.73	31.47±0.91
1	0.5	99.21±0.65	99.37±0.83	30.60±0.79
0.5	0.5	98.78±0.79	99.38±1.28	30.11±1.32

3.2.2 Behavior of CCA Elements during Recovery of CCA-treated Wood with Oxalic, Acetic and Phosphoric Acid in A Microwave Reactor

Table. 3-2 CCA recovery rate in different concentration of mixed acid by oxalic, acetic acid and phosphoric acid at 160^oC and 30 min

H_3PO_4 Conc. (%)	Acid Conc. (%)	As (%)	Cr (%)	Cu (%)
0.5%	Oxalic acid 1	99.52	97.12	33.82
1.25%	Oxalic acid 1	99.12	97.39	36.49
2.0%	Oxalic acid 1	98.90	97.67	41.30
3.5%	Oxalic acid 1	99.58	98.77	52.14
0.5%	Acetic acid 1	94.05	23.52	95.38
1.25%	Acetic acid 1	96.66	50.03	97.38
2.0%	Acetic acid 1	99.01	72.18	97.46
3.5%	Acetic acid 1	99.52	98.10	98.60

Phosphoric acid with either acetic or oxalic acid was chosen to extract the CCA elements at 160°C and 30min. Therefore, two groups of mixed acid were applied in this experiment. 1) 1% oxalic acid mixed with four concentration of phosphoric acid (i.e. 0.5%, 1.25%, 2%, and 3.5%); and 2) 1% acetic acid mixed with four concentration of phosphoric acid (i.e., 0.5%, 1.25%, 2%, and 3.5%). From 1) The chromium and arsenic recovery rate can almost reach 100%, while there is little increase in copper extraction efficiency (from 40% to 52%) with the growing concentration of phosphoric acid. Therefore, oxalic acid mixed with phosphoric acid was still less effective to remove copper.

It was encouraging that the mixture of 1% acetic acid and 3.5% phosphoric acid can recover greater than 98% of all CCA elements. The concentration of phosphoric acid had a significant effect on chromium recovery rate from 23.52% (0.5% phosphoric acid) to 98.10% (3.5% phosphoric acid). Thus, detailed research on the concentration effect of phosphoric acid and acetic acid to CCA recovery rate was required.

3.2.3 CCA Recovery Rate in Five Concentration of Phosphoric and Acetic Acid

Since the mixture of 3.5% phosphoric and 1% acetic acid was effective to extract all CCA metals in 3.1, it was necessary to do further research on acid concentration effect to CCA extraction in a microwave reactor.

CCA recovery rate using five concentration of phosphoric acid (i.e., 0.5%, 1.25%, 2%, and 3.5%) and four concentration of acetic acid (i.e., 0.5%, 1.0% and 1.5%) at 160°C are summarized in Table 3-3. It was noted that 100% of the CCA elements could be recovered when the concentration of phosphoric and acetic acid are 2.75% and 0.5%, respectively in only 30 min. Analysis of variance (ANOVA) results indicate phosphoric acid concentration had a significant effect on the CCA recovery rate. The mean recovery rate was compared by Duncan multiple comparisons in Table 3-3. The results show below the concentration of 2.75% phosphoric acid had no significant effect to CCA recovery rate, and there was no significant effect of acetic acid concentration (0.5-2%) on CCA recovery rate. In this reaction condition, when acetic

acid concentration was 0.5% arsenic and copper showed effective but minor increases (i.e., arsenic: 93.57-99.61%, copper: 95.12-98.07%) recovery from 0.5% to 3.5% phosphoric acid. However, chromium increases drastically from 23.06% to 96.23% during the concentration change of phosphoric acid. The concentration of phosphoric acid was an important factor in this reaction. The penetration function of phosphoric acid in the microwave grows stronger when its concentration becomes larger from 0.5%-2.75%. Diluted phosphoric acid has been proven effective to hydrolyze sorghum straw in a microwave reactor which shows that phosphoric acid might have good penetration in a microwave reactor (Vazquez et al. 2007). With respect to the previous results of section 3.1, phosphoric acid alone can recover arsenic and copper effectively, but did not perform well for chromium extraction.

When mixed with diluted acetic acid, the mixed acid can totally recover CCA. Phosphoric acid and acetic acid have a synergy function in recovering CCA elements in a microwave.

Table. 3-3 CCA recovery rate in different concentration of phosphoric acid mixed with acetic acid at 160°C and 30 min.

H_3PO_4 (%)	Acetic Acid (%)	As (%)	Cr (%)	Cu (%)
3.5	2	99.52	99.30	99.02
2.75	2	99.48	99.21	99.01
2	2	98.89	74.32	98.23
1.25	2	96.77	51.77	97.99
0.5	2	95.50	25.79	96.87
3.5	1.5	99.52	99.21	98.97
2.75	1.5	99.24	97.98	98.65
2	1.5	98.66	73.33	97.98
1.25	1.5	97.79	49.36	97.56
0.5	1.5	95.01	24.57	96.22
3.5	1	99.52	98.10	98.60
2.75	1	99.06	96.37	98.56
2	1	99.01	72.18	97.46
1.25	1	96.66	50.03	97.38
0.5	1	94.05	23.52	95.38
3.5	0.5	99.61	95.35	98.01
2.75	0.5	99.01	96.23	98.07
2	0.5	98.54	70.37	97.36
1.25	0.5	96.03	48.95	96.85
0.5	0.5	93.57	23.06	95.12

Table 3-4 Effect of concentration of phosphoric acid and acetic acid on the recovery rate of CCA

Phosphoric acid (%)	n	As (%) mean*	Cr (%) mean*	Cu (%) mean*
0.5	12	94.53 D	23.78 D	95.90 D
1.25	12	96.82 C	50.03 C	97.22 C
2	12	98.78 B	73.55 B	97.80 B
2.75	12	99.26 A B	97.47 A	98.44 A
3.5	12	99.52 A	97.99 A	98.71 A
Acetic acid (%)				
0.5	12	97.42 A	66.67 A	97.29 A
1	12	97.66 A	68.5 A	97.47 A
1.5	12	98.01 A	68.67 A	97.62 A
2.0	12	98.03 A	70.08 A	98.06 A

Different letters indicates significantly different

3.2.4 The Optimum of Recovery Condition in Microwave Reactor

From section 3.1 we know that phosphoric acid mixed with acetic acid could be an effective CCA extraction solution in a microwave reactor. Also, it was shown that the lowest concentration of acetic and phosphoric acid to get the maximum CCA recovery rate was 0.5% and 2.75%, respectively, on reasonable temperature and reaction time should be optimized. Six levels of temperature (i.e., 60°C, 70°C, 80°C, 100°C, 130°C, and 160°C) and three levels of extraction time (10min., 20min., and 30min.) were chosen to optimize for reaction condition with the maximum recovery rate.

Table 3-5 CCA recovery effect at three reaction times and six temperatures

Temperature (°C)	Time (min)	As (%)	Cr (%)	Cu (%)
60	10.00	67.84	33.06	81.89
60	20.00	77.34	40.98	91.34
60	30.00	83.80	51.12	92.94
70	10.00	84.05	47.35	91.61
70	20.00	91.02	60.92	94.61
70	30.00	93.40	65.21	94.98
80	10.00	92.82	64.99	92.41
80	20.00	94.20	70.76	96.37
80	30.00	95.55	77.23	96.94
100	10.00	98.16	78.76	97.27
100	20.00	98.83	85.14	97.35
100	30.00	99.10	88.26	97.90
130	10.00	99.57	93.39	98.50
130	20.00	99.60	95.20	98.63
130	30.00	99.80	96.70	98.70
160	10.00	99.56	95.78	98.50
160	20.00	99.62	96.20	98.70
160	30.00	99.81	98.10	98.75

Table 3-5 shows the CCA recovery rate at different reaction time and temperatures. When the reaction time was 30min, the CCA recovery rate reached the maximum of 100% of all three CCA elements at 130°C. These conditions could also achieve a recovery rate of 99.7% copper, 93.5% chromium, and 98.5% arsenate in 10min. at 130°C. Analysis of variance (ANOVA) results indicate that temperature plays a more important role in this reaction than the extraction time. Higher microwave temperature tends to lead to improved recovery of elements. When the temperature is 60°C for 10 min, the recovery rate was 67.84% arsenic, 33.06% chromium, and 81.89% copper. The recovery rate was 99.7% arsenic, 93.5% chromium and 98.5% copper when the temperature was 130°C also for 10 min. Duncan test results in Table 3-6 show that the reaction time range (10-30min.) had no significant effect on the CCA recovery rate when the temperature was above 70°C. In the whole, chromium has high resistance to extraction because of the strong bonding between lignin and chromium. (Ostmeyer et al, 1988, 1989; Pizzi, 1990, 1991)

Table 3-6 Effect of temperature and time on the recovery rate of CCA

Temperature (°C)	n	As (%) mean*	Cr (%) mean*	Cu (%) mean*
60	9	76.33 D	41.72 E	88.73 C
70	9	89.49 C	57.88 D	93.71 B
80	9	94.19 B	70.99 C	95.51 B
100	9	98.70 A	84.40 B	97.44 A B
130	9	99.51 A	95.10 A	98.61 A
160	9	99.66 A	96.69 A	98.64 A
Time (min)				
10	18	90.33 A	68.91 A	93.32 A
20	18	93.42 A	74.87 A	96.30 A
30	18	95.19 A	79.60 A	96.70 A

*Different letters indicates significantly different

Table 3-7 Minimum reaction condition of all factors to obtain the maximum CCA recovery rate.

Factors	As	Cr	Cu
Acetic Acid Conc. (%)	≤0.5	≤0.5	≤0.5
H_3PO_4 Conc. (%)	2.75	2.75	2.75
Time (Min)	≤10	≤10	≤10
Temperature (°C)	100	130	80

Table 3-7 shows the minimum reaction condition of all factors to obtain the maximum CCA recovery rate. From this table, temperature and the concentration of phosphoric acid affect the maximum recovery of each metal element. When acetic acid and reaction time is 0.5% and 10min, respectively, the minimum temperature and phosphoric acid concentration to recover all CCA elements is 130°C and 2.75%. We can use temperature 80°C if the objective is only to recover copper based on the same reaction condition.

3.3 Conclusions

The effect of microwave-assisted acid extraction of metals from chromated copper arsenate (CCA)-treated southern pine was studied. The results show that diluted phosphoric acid mixed with acetic acid was very effective to recover CCA elements in microwave reactor in a shorter time. The advantage of this method is the shorter extraction time and only one step is needed to achieve the complete recovery of CCA elements. The concentration of phosphoric acid and temperature of the microwave reactor are two important factors. 2.75% phosphoric acid at 130°C and 0.5% acetic acid 10 min. are the minimal reaction conditions to achieve the maximum recovery rate. Further research such as the acetic acid concentration and time should be studied. Research on larger size chips should be done due to advance the more practical applications of this method for the future.

Chapter 4. Practical Treatment in Wood Chips Extraction

Chapter 2 and 3 showed that diluted phosphoric acid mixed with acetic acid is very effective to recover CCA elements from CCA-treated southern pine sawdust (40-mesh) in microwave reactor in shorter time. However, it is no economic and practical to recover CCA from wood sawdust. In this situation, wood chips extraction effect by microwave oven should be considered based on the industrial application.

4.1 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 the 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^oC), cut to wood chips with the size of 0.5cm×0.5cm×0.5cm, 0.5cm×0.5cm×1.0cm and 0.5cm×0.5cm×1.5cm, The dry southern pine chips was used without further treatment.

4.1.1 Acid Extraction in Microwave Reactor
The ratio of wood chips to mixed acid solution was also 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.

4.1.2 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^oC 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 remained 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).

4.2 Result and Discussions

The recovery of CCA metals by acid extraction was evaluated through a series of three experiments, the temperature of the microwave oven was set at 130 °C and the concentration of acetic acid was 0.5%: 1) three length sizes of wood chips a) 0.5cm×0.5cm×0.5cm, b) 0.5cm×0.5cm×1.0cm and c) 0.5cm×0.5cm×1.5cm); 2) extraction of CCA in 0.5% acetic acid and two concentrations of phosphoric acid (i.e. w/w: 2.5% and 3.50%); and 3) extraction of CCA at three time (i.e., 10min., 20min., and 30min.). Each combination of variables was replicated three times. The 0.5, 1.0, and 1.5cm were cut in longitude direction.

4.2.1 Behavior of CCA Elements of Different Length Size in A Microwave Oven.

In order advance microwave-assisted acid extraction technology for practical use, wood research is needed using large size wood chips. Table 4-1 shows the CCA recovery effect of three reaction times, three wood chip sizes, and two concentrations of phosphoric acid.

For all sizes of wood chips, chromium is still difficult to extract completely. Even with a reaction condition of 3.5% phosphoric acid at 130°C for 50 min. The recovery rate of chromium can achieve 54.75-64.47% when the wood chip size is decreased from 0.5×0.5×0.5cm to 0.5×0.5×1.5cm. However, at the same reaction condition the recovery rate of arsenic and copper are 85.3-93.5% and 85.55-94.89%, respectively,

Table 4-1 CCA recovery effect using three reaction times, three wood chip sizes, and two concentrations of phosphoric acid

H_3PO_4 (%)	Time (min)	0.5×0.5×0.5cm As (%)	0.5×0.5×1.0cm As (%)	0.5×0.5×1.5cm As (%)
2.5	10.00	42.11	41.17	51.48
2.5	30.00	84.36	71.61	58.65
2.5	50.00	91.26	74.40	73.74
3.5	10.00	68.22	67.79	58.01
3.5	30.00	87.70	70.68	71.91
3.5	50.00	93.52	89.91	85.30
		Cr (%)	Cr (%)	Cr (%)
2.5	10.00	12.95	10.23	22.93
2.5	30.00	43.28	37.81	26.45
2.5	50.00	52.10	40.94	34.19
3.5	10.00	33.69	33.85	26.72
3.5	30.00	52.49	37.96	34.59
3.5	50.00	64.47	60.31	54.76
		Cu (%)	Cu (%)	Cu (%)
2.5	10.00	48.33	41.86	55.82
2.5	30.00	88.28	71.42	59.03
2.5	50.00	93.84	77.79	76.13
3.5	10.00	71.38	69.80	58.17
3.5	30.00	89.84	72.36	74.25
3.5	50.00	94.89	89.81	85.55

which shows the effect of microwave oven to the larger wood size.
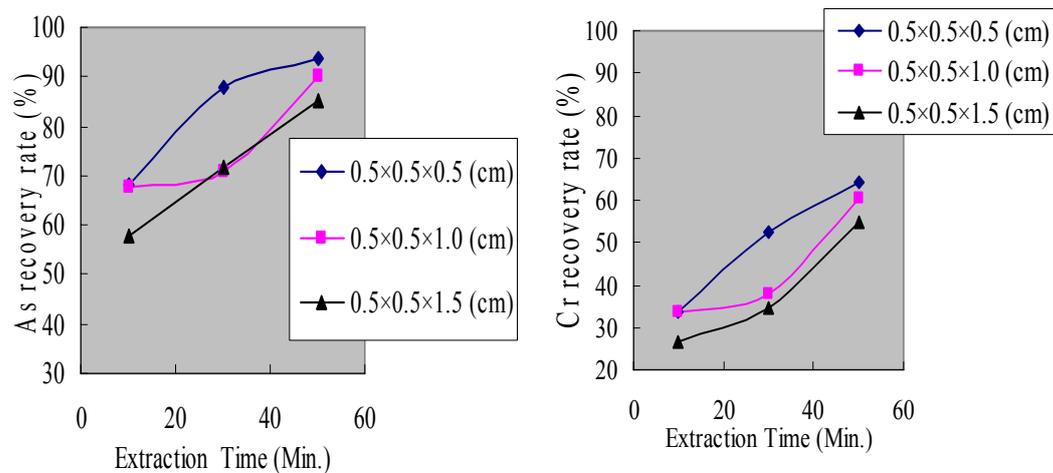
(A) As

(B) Cr
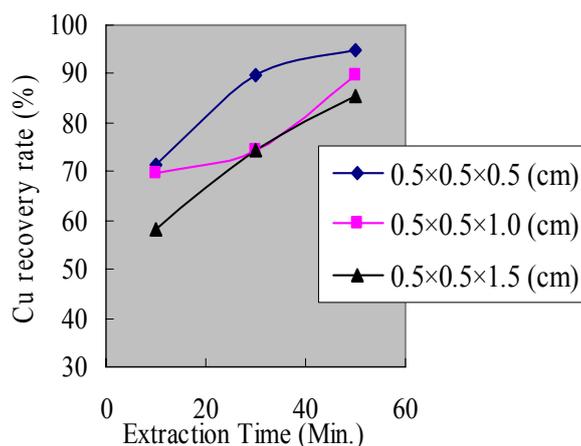
(C) Cu

Fig. 4-1 CCA element recovery rate affected by three wood chip sizes and reaction time with 3.5 % phosphoric acid in a microwave.

Figure 4-1 shows the CCA element recovery rate affected by wood chip size and reaction time using 3.5% phosphoric acid in a microwave reactor. From Figure 4-1 (A) and Figure 4-1 (C) arsenic and copper showed a similar extraction trend and recovery rate for different wood chip sizes. From 10min. to 30min., wood chip size has a significant effect on arsenic and copper recovery rate. However, after 50min. the recovery rate for all sizes was similar. The chromium recovery rate trend in Figure 4-1 (B) did not indicate an obvious sudden change from 10min. to 50min. for the three different chip sizes. Thus the extraction time has to be extended to 50min. at 130°C if all of the chromium is to be totally removed.

4.3 Conclusions

The effect of microwave-assisted acid extraction of metals using larger wood chips was studied. The results show that phosphoric acid mixed with acetic acid is very effective to recover all CCA elements in microwave reactor in short time (50min.). Thirty minutes is an ideal time for arsenic and copper extraction without consideration for total chromium. Further research such as the reuse of the extraction solution should be studied. In addition, research on a sequential extraction process should be investigated.

Chapter 5 Conclusions

Although oxalic acid and other acids have been proven to recover CCA metals in relatively high extraction efficiency, the time period (Normally 18 h) and high liquid/solid ratio has limited commercial applications. Microwave technology has been verified an effective approach to extract heavy metals from CCA-treated wood. There are several conclusions that can be derived from this study:

1. The effect of microwave-assisted single 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 conditions in a microwave reactor. The advantage of this approach is the reduced extraction time and one step method to achieve complete recovery of CCA metals. Microwave oven is an effective and fast way of extracting CCA element from spent CCA-treated wood sawdust.

2. Phosphoric acid mixed with acetic acid was very effective to recover CCA elements in microwave reactor in a shorter time. The advantage of this method is the shorter extraction time and only one step is needed to achieve the complete recovery of CCA elements. The concentration of phosphoric acid and temperature of the microwave reactor are two important factors. 2.75% phosphoric acid at 130°C and 0.5% acetic acid 10 min. are the minimal reaction conditions to achieve the maximum recovery rate.

3. Phosphoric acid mixed with acetic acid is very effective to recover all CCA elements in microwave reactor in short time (50 min.). When the wood size become larger, a longer time period is needed to achieve the object of extraction; however, it still a fast way compared to previous methods. Thirty minutes is an ideal time for arsenic and copper extraction without consideration for total chromium. Further research such as the reuse of the extraction solution should be studied. In addition, research on a sequential extraction process should be investigated.

References

Amacher, M.C., Baker, D.A (1982) Redox reactions involving chromium, plutonium, and manganese in soils. Final Report, DE-ASO8-77DPO4515. Inst. For Res. on Land and Water Resources, Penn. State University.

Branca, C., Giudicianni, P., Blasi, C.D. (2003) Ind. Eng. Chem. Res. 42 3190.

Blesa, M.A., Morando, P.J., Regazzoni, A.E., (1994). Chemical Dissolution of Metal Oxides. CRC Press Inc., USA.

Catallo, W.J., Shupe T.F., and R.P. Gambrell. (2004). Hydrothermal treatment of CCA- and penta-treated wood.   Wood and Fiber Science.   36(2):152-160.

Piao C., Shupe T.F., Nipper W.A. (2009). Recycling of Decommissioned CCA-Treated Wood Utility Poles. FOREST PRODUCTS SOCIETY 63RD INTERNATIONAL CONVENTION, 21-23 June, Boise, Idaho, poster 42, pp. 29

Clausen, C. A. and R. L. Smith (1998) Removal of CCA from treated wood by oxalic acid extraction, steam explosion, and bacterial fermentation. Journal of Industrial Microbiology & Biotechnology 20(3-4): 251-257.

Clausen, C.A (2003) Improving the two-step remediation process for CCA-treated wood: Part I. Evaluating oxalic aicd extraction Waste Management 24(4): 401-405.

Clausen, C. A (2004) Improving the two-step remediation process for CCA-treated wood: Part II. Evaluating bacterial nutrient sources.   Waste Management 24(4): 407-411.

Cooper, PA. (1993). Disposal of treated wood removed from service: the issues, In: Proceedings, Environmental Considerations in Manufacture, Use and Disposal of Preservative Treated Wood. Madison, WI, USA Carolinas-Chesapeake Section. Forest Products Society, 85-90.

El-Fatah,Abd., Goto, S.M., Kodama, A., Hirose, T (2004) Supercritical fluid extraction of hazardous metals from CCA wood. Journal of Supercritical Fluids 28(1): 21-27.

Fields, S. (2001). Caution-Children at play: How dangerous is CCA? Environ. Health Persp. 109(6): 262-269

Fendorf, S., (1995). Surface reactions of chromium in soils and waters. Geoderma (67):55 – 71.

Fu, Q. R., Argyropoulos D. S. (2008) Understanding the pyrolysis of CCA-treated wood. Part II. Effect of phosphoric acid. Journal of Analytical and Applied Pyrolysis 82(1): 140-144.

Gezer, E. D., U. Yildiz (2006) Removal copper, chromium and arsenic from CCA-treated yellow pine by oleic acid. Building and Environment 41(3): 380-385.

Green, III F., Larsen, M., Winandy. JE., Highley, TL (1991) Role of oxalic acid in incipient brown-rot decay. Mater. Organismen (26):191–213

Green, III F., Highley, T.L (1997) Mechanism of brown-rot decay: paradigm or paradox. Int Biodeter Biodegr (39):113–124

Helsen, L., Van den Bulck, E., Van den Broeck, K. and Vandecasteele, C (1997) Low temperature pyrolysis of CCA-treated wood waste: chemical determination and statistical analysis of metal input and output, Mass balances, Waste Manage.,17 (79)

Helsen, L., Van den Bulck, E., S. Mullens, J (1999) Anal. Appl. Pyrol. 52 65. James, B.R., Bartlett, R.J., 1983. Behaviour of chromium in soils. VI. Interactions between oxidation–reduction and organic complexation. J. Environ. Quality 12, 173–176.

IUPAC, (2006) Glossary of terms used in theoretical organic chemistry, accessed 16 Dec

Kartal, S.N., Lebow, S.T., (2001) Effect of compression wood on leaching and fixation of CCA-C treated red pine. J Wood Sci (33), 182 – 192.

Kartal, S.N., Munir, E., Kakitani, T., Imamura, Y (2004) Bioremediation of CCA-treated wood by brown-rot fungi Fomitopsis palustris, Coniophora puteana, and Laetiporus sulphureus. J Wood Sci (50):182–188

Kakitani, T., T. Hata, et al. (2004). "Effect of pyrolysis on solvent extractability of toxic metals from chromated copper arsenate (CCA)-treated wood." Journal of Hazardous Materials 109(1-3): 53-57.

Kakitani, T., T. Hata, et al. (2006). A novel extractant for removal of hazardous metals from preservative-treated wood waste. Journal of Environmental Quality

35(3): 912-917.

Kakitani, T., T. Hata, et al. (2007). Chelating extraction for removal of chromium, copper, and arsenic from treated wood with bioxalate.   Environmental Engineering Science 24 (8): 1026-1037.

Kazi, F., Cooper, P.A., (1999). Chemical extraction and recycling of CCA treated wood and treatment plant wastes. In: Proceedings of Canadian Wood Preservers' Association Conference, 25–26 October 1996. Vancouver, BC, Canada.

Kazi, F K. M, Cooper P A. (2006). Method to recover and reuse chromated copper arsenate wood preservative from spent treated wood. Waste Management, 26(2): 182-188.

Kim, J., Kim, G., (1993). Leaching of CCA Components from Treated Wood under Acidic Conditions. International Research Group on Wood Preservation, (Document No: IRG/WP/5004), Stockholm, Sweden.

Lebow, S.T., Kartal, S.N., (1999). Fixation effects on the release of copper, chromium, and arsenic from CCA-C treated marine piles. In: Proceedings of 95th Annual Meeting of the American Wood Preservers' Association (AWPA), 16–19 May. Ft. Lauderdale, Florida, vol. 95, pp. 168–174.

Milacic, R., Stupar, J., (1995). Fractionation and oxidation of chromium in tannery waste and sewage sludge-amended soils. Environ. Sci. Technol. 29, 506–514.

Moghaddam, A H, Mulligan C N (2008). Leaching of heavy metals from chromated copper arsenate (CCA) treated wood after disposal. Waste Management, 28(3): 628-637.

Orozco, A., M. Ahmad. (2007). Dilute acid hydrolysis of cellulose and cellulosic bio-waste using a microwave reactor system. Process Safety and Environmental Protection 85(B5): 446-449.

Ostmeyer, J. G., T. J. Elder, et al. (1988). Spectroscopic Analysis of Southern Pine Treated with Chromated Copper Arsenate .1. X-Ray Photoelectron-Spectroscopy (Xps). Journal of Wood Chemistry and Technology 8(3): 413-439.

Ostmeyer, J. G., T. J. Elder, et al. (1989). Spectroscopic Analysis of Southern Pine Treated with Chromated Copper Arsenate .2. Diffuse Reflectance Fourier-Transform Infrared-Spectroscopy (Drift)." Journal of Wood Chemistry and Technology 9(1): 105-122.

Pizzi, A (1990) Chromium Interactions in Cca Ccb Wood Preservatives .2. Interactions with Lignin. Holzforschung 44(6):419-424.

Pizzi, A (1990) Chromium Interactions in Cca/Ccb Wood Preservatives .1. Interactions with Wood Carbohydrates. Holzforschung 44(5):373-380.

Ribeiro, A.B., Rodriguez-Maroto., J.M., Mateus, E.P., Velizarova , E., Ottosen, L.M.(2007). Modeling of electrodialytic and dialytic removal of Cr, Cu and As from CCA-treated wood chips, Chemosphere (66):1716–1726

Shiau, R.J., Smith R.L. and Avellar. B. (2000) Wood Sci Technol., 34, 377-388.

Solo-Gabriele, H., Townsend, T., Messick., B., and Calitu, V. (2002). Characteristics of Chromated Copper Arsenate Treated Wood Ash. J. Hazard. Mater. B89: 213-232

Solo-Gabriele, H., M. Kormienko; K. Gary; T. Townsend; K. Stook; T. Tolaymat. (2000). Alternative chemicals and improved disposal-end management practices for CCA-treated wood (final draft). Report #00-03, Florida Center for Solid and Hazardous Waste Management, Gainesville, FL.

Sparks, D. L. (1995). Environmental Soil Chemistry. Academic Press, San Diego, CA

Spiccia, L., Marty, W., (1986). The fate of "active" chromium hydroxide, $Cr(OH)_3 \cdot 3H_2O$, in aqueous suspension. Study of the chemical changes involved in its aging. Inorg. Chem. 25, 266–271.

Stephan I, Leithoff H, Peek RD (1996a) Microbial conversion of wood treated with salt preservatives. Mater Organ 30:179–199

Stephan I, Peek R.D, Nimz H (1996b) Detoxification of salt-impregnated wood by organic acids in a pulping process. Holzforschung 50:183–187

Takeshita, Y., Sato, Y., Nishi, S. (2000) Study of extraction of metals from CCA-treated wood with supercritical CO2 containing acetylacetone: extraction of Cu by continuous addition of acetylacetone, Ind. Eng. Chem. Res. (39):4496–4499.

Townsend, T., Tolaymat, T. (2004) Leaching of CCA-treated wood: implications for waste disposal, J. Hazardous Mater. B114: 75-91

Townsend, T., Dubey, B., Tolaymat, T., Solo-Gabriele, H. (2005) Preservative leaching from weathered CCA-treated. Journal of Environmental Management, 75(2):105-113

Tolaymat, T., Townsend, T.,Solo-Gabriele, H. (2000). Chromated copper arsenate-treated wood in recovered wood. Environ. Eng. Sci. 7 (1): 19-28.

Vázquez, M., M. Oliva, et al. (2007). Hydrolysis of sorghum straw using phosphoric acid: Evaluation of furfural production. Bioresource Technology 98(16): 3053-3060.

Wang, J. S., Chiu, K.(2008). Extraction of chromated copper arsenate from wood wastes using green solvent supercritical carbon dioxide. Journal of Hazardous Materials 158(2-3): 384-391.

Vita

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