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Copper Arsenate (CCA)-Treated Southern Pine Wood**

Bin Yu¹, Chung Y. Hse², Todd F. Shupe¹

¹ Louisiana Forest Products Development Center, Louisiana State University AgCenter,
70803, Baton Rouge, LA USA

² USDA Forest Service, Southern Research Station, 71360, Pineville, LA USA,

¹ Louisiana Forest Products Development Center, Louisiana State University AgCenter,
70803, Baton Rouge, LA USA

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IRG SECRETARIAT
Box 5609
SE-114 86 Stockholm
Sweden
www.irg-wp.com

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Bin Yu¹, Chung Y. Hse², Todd F. Shupe¹

¹Louisiana Forest Products Development Center, Louisiana State University AgCenter, USA,
byu2@lsu.edu

²USDA Forest Service, Southern Research Station, 71360, Pineville, LA USA,
chse@fs.fed.us

¹Louisiana Forest Products Development Center, Louisiana State University AgCenter, USA
tshupe@agcenter.lsu.edu

ABSTRACT

The 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 three different acids (i.e., acetic acid, oxalic acid, and phosphoric acid) was investigated using in microwave reactor. Oxalic acid was effective in removing 100% of the chromium and arsenic at 160°C and 30 min., and acetic acid could remove 98% of the copper and arsenic at the same conditions. Oxalic acid greatly improved the extraction efficiency of arsenic and chromium when time was prolonged from 10min. to 30min. Acetic acid also showed improved ability to remove arsenic and copper when the reaction temperature was increased from 90°C to 160°C.

Keyword: CCA, recovery, microwave, extraction

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, large volumes of preservative-treated wood are decommissioned each year. It is estimated that about 3-4 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 a major concern because of its residual toxic components, particularly arsenic and chromium. Conventional 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). Moreover, there is concern regarding landfill capacity. Therefore, there is an urgent need for developing techniques for recycling CCA-treated out of service wood.

Several chemical methods have been proposed to extract the metals from CCA-treated wood. Solvent extraction can dissolve the preservatives and partially remove them from the wood. The use 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 based on its potential ability of reversing the CCA fixation process, thereby converting CCA elements into their water-soluble form (Kartal and Clausen, 2001). However, among the disadvantages of this recycling method are the huge amount of chemical solvents used and the long duration of the process. The prevailing treatment times reported ranged from 16 h for sawdust (Clausen and Smith, 1998) to 24 h 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 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 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 three 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 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 CrO₃, 45%-50%; copper as CuO, 17-21%; arsenic as As₂O₅, 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 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).

2.4 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 three 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. 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). It is 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 1.

Table 1 CCA recovery rate for three acids and five concentrations at 160°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 ₃ PO ₄	0.25	55.37±1.01	13.79±0.51	57.28±1.02
H ₃ PO ₄	0.5	57.56±5.23	14.56±0.88	59.69±8.31
H ₃ PO ₄	0.75	58.13±5.61	15.00±1.70	72.11±1.78
H ₃ PO ₄	1	60.05±2.73	16.64±1.61	77.50±2.99
H ₃ PO ₄	1.5	65.12±2.48	19.32±3.07	78.59±1.87

Table 2 ANOVA results of the effects of acids 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

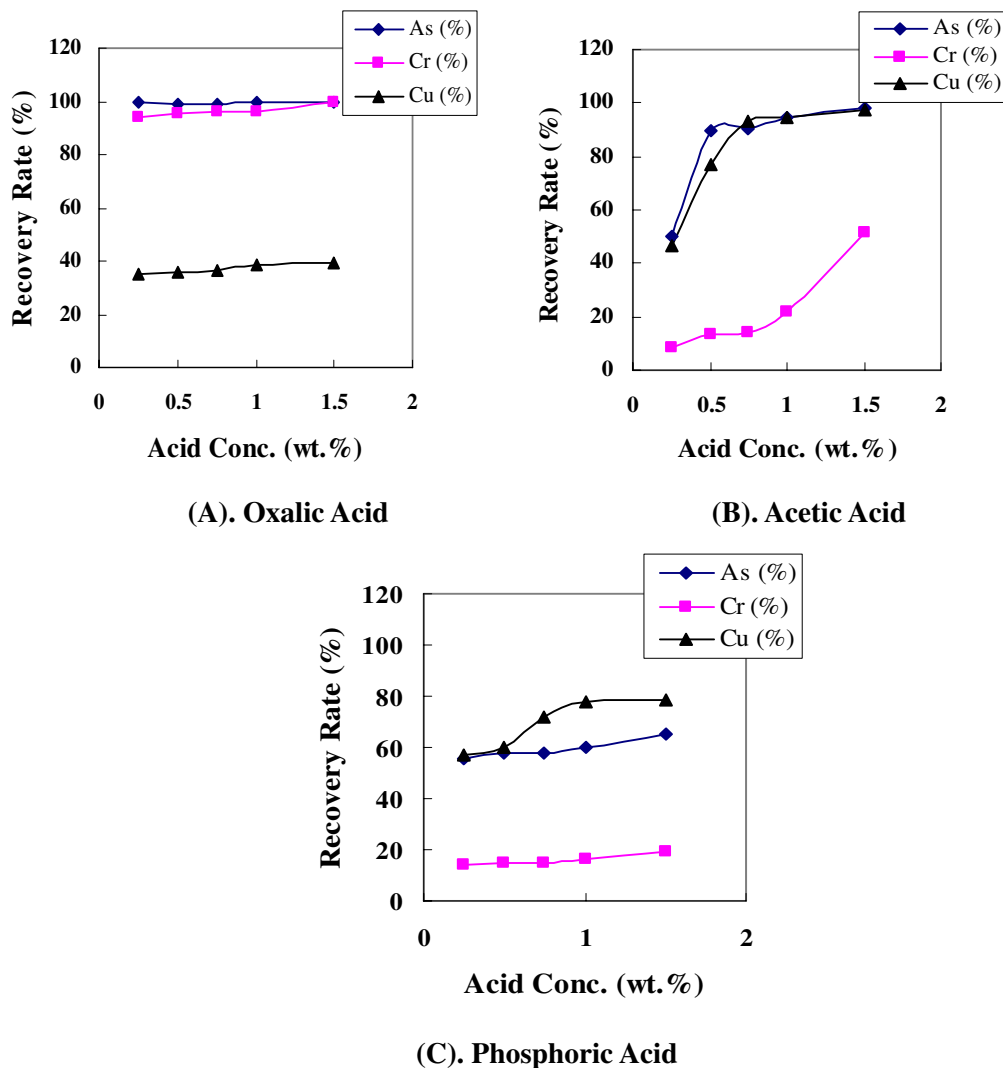


Fig. 1 CCA metal recovery rate affected by acid type and concentration in a microwave reactor.

It is interesting to note that: 1) oxalic acid removed arsenic and chromium very effectively but not copper (Figure 1A). 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 1B). 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; and 3) the extraction using phosphoric acid was less effective as compared to both oxalic and acetic acids (Figure 1C). While the maximum recovery of copper (i.e., 79%) and arsenic (i.e., 65%) were obtained with an acid concentration of 1.5%, respectively, the recovery of 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%. Thereafter, 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%.

3.2 Extraction of CCA elements in acids with various treatment times.

Mean values of CCA elements recovery using three acids at various extraction times are summarized in Table 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.

Table 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 ₃ PO ₄	10	47.97±0.84	9.27±0.83	50.37±0.85
H ₃ PO ₄	20	53.42±1.69	12.59±0.56	56.02±0.69
H ₃ PO ₄	30	55.39±0.97	13.17±0.67	57.23±0.32

The significant interactions of the three 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 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 (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 or phosphoric acid. It is interesting to note that the amounts 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 2C). However, 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.

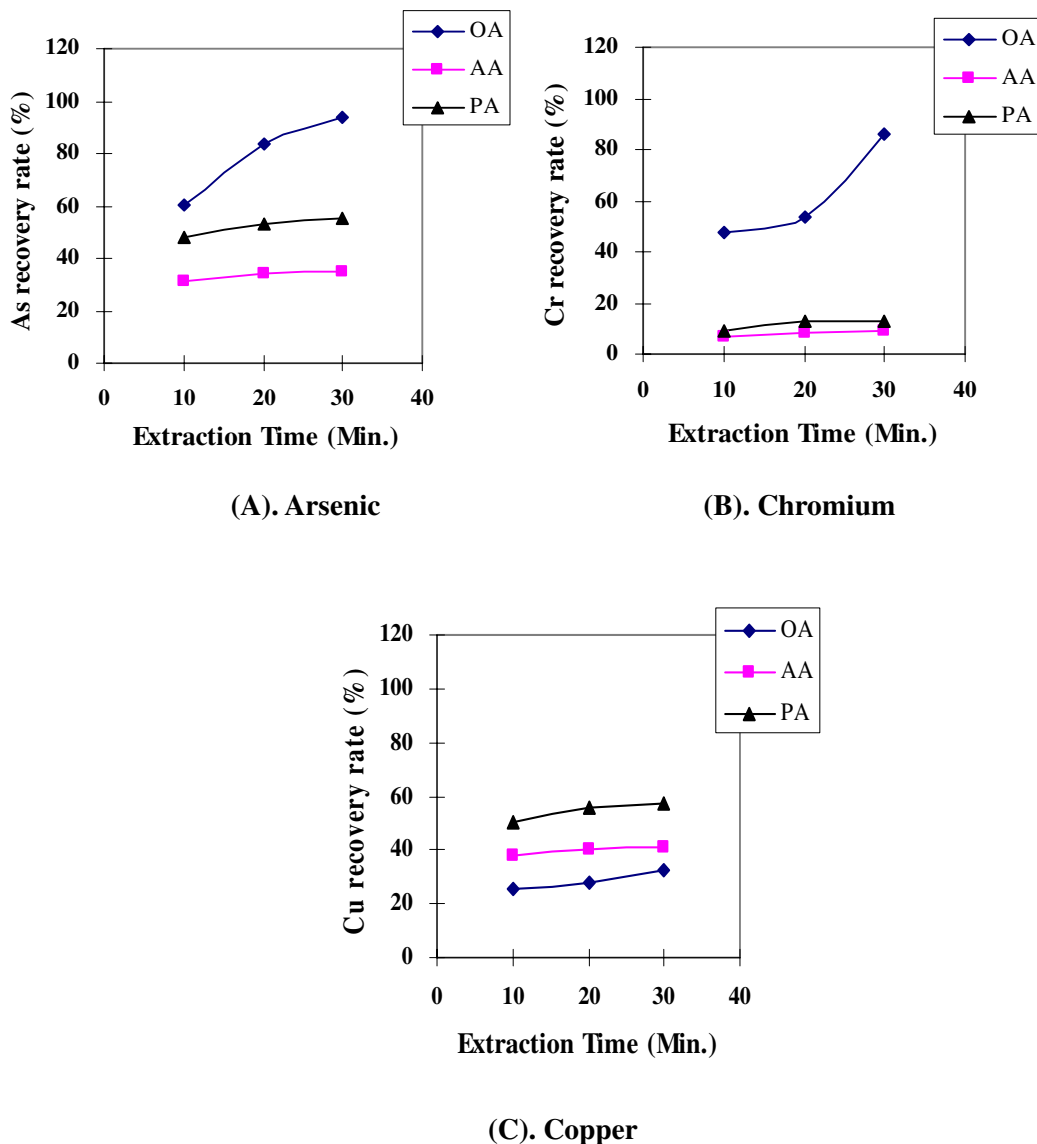


Fig. 2 CCA elements recovery rate affected by acid type and time in a microwave reactor.

3.3 Extraction of CCA elements in acids at various temperatures

Effects of acids at various temperatures on metals recovery from CCA-treated wood are summarized in Table 4. 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 temperature effect on CCA recovery was the effectiveness of acetic acid with increasing temperature. For arsenic (Figure 3A) and copper (Figure 3C) 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.

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

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

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
H ₃ PO ₄	90	47.38±1.39	10.92±0.23	50.29±1.26
H ₃ PO ₄	125	55.39±0.32	13.17±0.32	57.23±0.32
H ₃ PO ₄	160	57.56±0.92	14.56±0.73	59.69±0.92

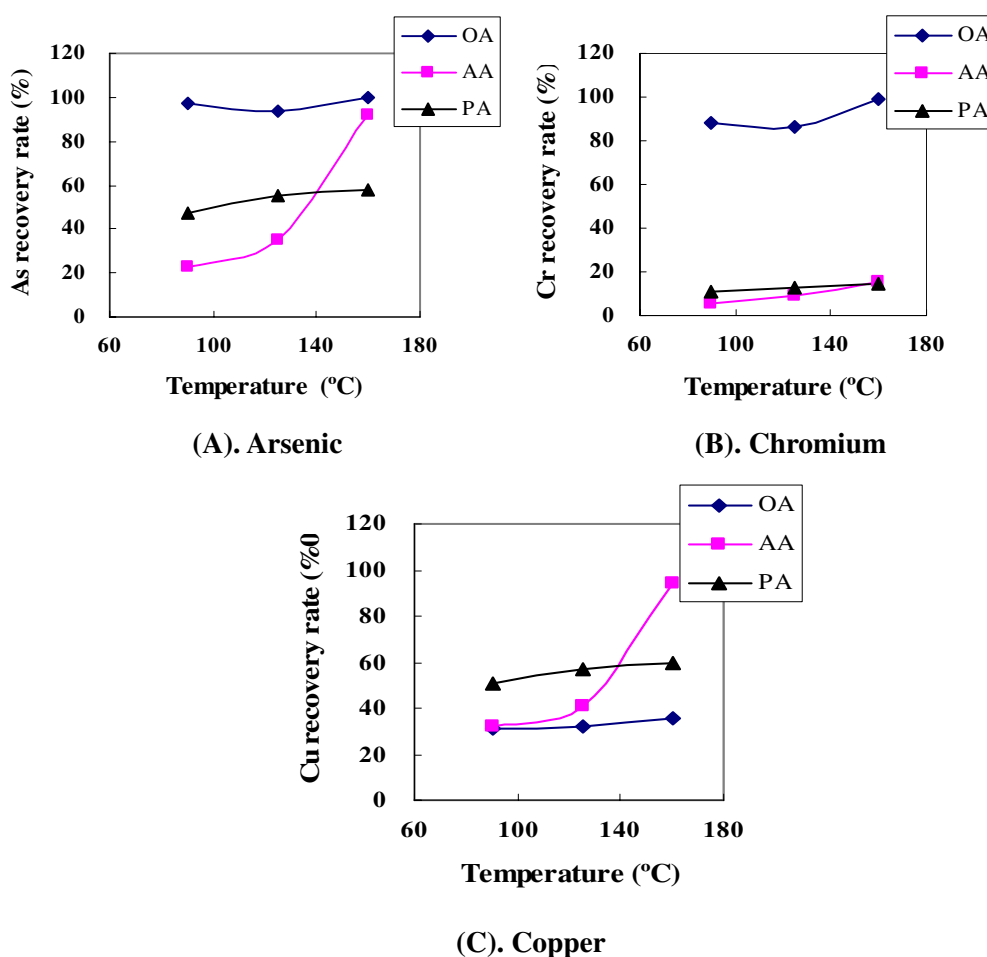


Fig. 3 CCA elements recovery rate affected by acid type and temperature in microwave.

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 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. Research on larger size southern pine chips should be done to further develop a more practical application of this method

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