AMERICAN WOOD PROTECTION ASSOCIATION

Rapid Recovery of Metals in CCA-treated Wood

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ABSTRACT

The recovery of heavy metals from chromated copper arsenate (CCA)-treated southern pine wood particles was investigated using binary acid solutions consisting of two of acetic, oxalic, and phosphoric acids in a microwave reactor. Formation of an insoluble copper oxalate complex in the binary solution containing oxalic acid was the major factor for low copper removal. Furthermore, the possible complexation of acetic/oxalic acid in the organic phase, the decomposition of oxalic acid in acetic acid at high temperatures, and the promotion of the formation and precipitation of the copper oxalate by phosphoric acid may induce an antagonistic effect which adversely influenced the effectiveness of the copper extraction. It was found that the addition of acetic acid into phosphoric acid enhanced the chromium recovery rate of the mixed acid solution. This synergistic effect of mixed acetic acid and phosphoric acids is considered one of the most interesting and significant discoveries in the study. The minimal reaction conditions for extracting the maximum percentage of metals was 2.75% phosphoric acid, 0.5% acetic acid, and 130°C. The total recovery rate approached 100% for arsenic, 96.7% for chromium, and 98.6% for copper in a one step process.

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 approximately 12 million m3 per year of spent CCA treated wood will be removed from service in the United States and Canada in the next 20 years (Kazi and Cooper 2006). Disposal of this material has become a major concern because of its residual toxic chromated copper arsenate (CCA) content, in particular the arsenic and chromium. Previous studies have shown that CCA compounds can be gradually leached into the environment (Townsend et al. 2005; Moghaddam and Mulligan 2008). Conventional waste disposal options for spent preserved wood, such as land-filling, are becoming more costly or even impractical because of increasingly strict regulatory requirements and liability concerns. The burning of treated wood may be extremely dangerous to the environment and human health, particularly if the wood has been treated with CCA. There is an urgent requirement for the development of techniques to effectively recycle decommissioned CCA-treated wood.

Fixation is a chemical process in which the preservative chemically bonds to the wood. It is well recognized that exposure of CCA-treated wood to an acid solution can re-oxidize the chromium thereby converting the CCA elements into their water-soluble form. Thus, acid extraction using different acids and wide ranges of reaction conditions has been extensively studied for removal of CCA from out-of service CCA-treated wood (Shiau *et al*. 2000; Clausen 2004; Humer *et al*. 2004; Kazi and Cooper 2006; Gezer *et al*. 2006; Kakitani *et al*. 2007; Janin *et al*. 2009). These studies have shown that the recovery of CCA elements from CCA-treated wood can be obtained with many organic acids, such as oxalic, acetic, citric, and formic acids; however, the acid extraction process is slow. Therefore, cost-effective acid extraction methods are lacking.

Our recent studies on removal of CCA elements from spent CCA-treated wood have focused on the application of the microwave energy to facilitate acid extraction. A preliminary study (Yu *et al*. 2009) has shown: (1) microwave-assisted acid extractions with oxalic, acetic, and phosphoric acids have reduced the reaction times from hours to minutes compared to the conventional methods, (2) oxalic acid effectively removed arsenic and chromium but not copper, (3) acetic acid extraction was highly effective for the removal of arsenic and copper but not for chromium, and (4) extraction using phosphoric acid was less effective as compared to both oxalic and acetic acids. These results indicated that none of the individual acids were able to effectively remove all three CCA elements simultaneously, but showed a potential complementary effect for

extraction. For instance, oxalic acid removed chromium very effectively but not copper, and acetic acid effectively extracted copper but not chromium. The results strongly suggested the opportunity for a two-acid process by either a synergistic extraction effect of the combined acids or a two-step process of consecutive acid extraction. In this study, two acids were mixed, and the extraction potential was evaluated. The acids studied were oxalic, acetic, and phosphoric. The objective of this study was to develop a cost-effective microwave-based dual acids extraction system to maximize removal of CCA elements from spent-CCA-treated wood. This was addressed by optimizing of the acid combinations and concentration, extraction times, and reaction temperature to minimize any environment impact.

MATERIALS AND METHODS

Materials

CCA-treated southern pine (*Pinus* sp) guard rail posts were obtained from Arnold Forest Products Co. in Shreveport, La. The posts were reduced to sawdust on a table saw. The sawdust was screened to collect sawdust that passed through a 40-mesh sieve and retained on a 60-mesh sieve and then dried to a constant weight in an oven maintained at 50 ^{o}C. The dried sawdust was stored in heavy duty zip lock polyethylene bag and used without further treatment. All acids used were of reagent grade and obtained from commercial sources. Deionized water was used to dilute the acid.

Acid Extraction in a Microwave Reactor

The acid extractions were carried out in a Milestone MEGA 1200 laboratory microwave oven. Unless otherwise stated, 1 g of wood meal was weighed into a 100 ml Teflon reaction vessel with a magnetic stirring bar. The acid solutions were prepared in percentage concentration by weight of acid in grams per volume of deionized water (g/v). Twenty ml of a designated concentration and mixed ratio of the binary acid solutions of acetic/oxalic, acetic/phosphoric, or phosphoric/oxalic acids were then added to the reaction vessel and thoroughly mixed. The reaction vessel was then placed on the rotor tray inside the microwave cavity. The temperature was monitored using an ATC-400FO automatic fiber optic temperature control system. Based on monitored temperature, the output power was auto-adjusted during acid extraction. In this study, the temperature was increased from room temperature to 160 °C at a heating rate of 32.5 °C/min. and then was kept constant for 30 min., unless otherwise noted. After a cooling period of 30 min at the end of acid extraction, the extracted liquids were vacuum-filtered through Whatman No. 4 filter paper and then diluted to 100 ml in a volumetric flask for determination of the CCA elements. The solid wood residue retained on the filter paper was oven-dried and then subjected to acid digestion prior to the determination of chromium, arsenic, and copper. Samples were digested in accordance with American Wood Protection Association Standard A7-04 (AWPA, 2008). The procedure required that the solid residues be accurately weighed into 100 ml test tubes. For each gram of solid residue, 15 ml 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 the temperature was increased and maintained at 120 °C until a transparent liquid was obtained. The transparent liquid was cooled to room temperature and 5 ml of hydrogen peroxide was drop-wise added. If the solution was not clear after this treatment, the temperature was increased and another 5 ml of hydrogen peroxide was added. The sample was continually heated until approximately 1 ml of sample solution remained in the test tube. The sample was carefully transferred into a 25 ml volumetric flask and then diluted with distilled water to a 25 ml solution for the determination of the chromium, arsenic, and copper in the residue. The concentration of chromium, arsenic, and copper in both samples (i.e., acid extracted solution and digested solution) was determined by inductive coupled plasma atomic emission spectroscopy (ICP-AES). The recovery rate of the elements in acid extraction was then determined by the following equation:

$$\text{Recovery rate (\%)} = Ws/(Ws+Wr)*100\%$$

Where Ws is the weight of the CCA elements in acid extracted solution and Wr is the weight of CCA elements in the wood residue

Statistical Analysis

Data 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.

RESULTS AND DISCUSSION

Recovery of Metals from CCA-treated Wood with Binary Oxalic and Acetic Acid Solutions in a Microwave Reactor

CCA recovery rate for binary acid solutions consisting of the oxalic and acetic acids are summarized in Table 1. All mixed acids resulted in more than 98 and 99% recovery for arsenic and chromium, respectively. However, it should be noted

that average copper recovery ranging from 30.1 to 34.6% was surprisingly ineffective based on the previous finding that 97.5% copper removal was attained with only acetic acid extraction in a microwave reactor (Yu *et al*. 2009). This result strongly suggests possible physical interactions as well as chemical reactions in the binary acid solution hindered the reactive extraction of acetic acid. The formation of an insoluble complex of oxalic acid and copper during acidification of CCA-treated wood with organic acids is well recognized (Bull 2001; Humer *et al*. 2004; Kakitani *et al*. 2009; Pizzi 1982, 1990). Furthermore, in a liquid-liquid equilibrium involved in the reactive extraction of an organic acid, the formation of mixed acid complexes containing acetic and oxalic acids in the organic phase have been reported (Kirsch and Maurer 1998). In addition, it was reported that in anhydrous acetic acid at high temperatures, oxalic acid can decompose quickly (Pszonicki and Tkacz 1976). Thus, it is possible that the mixed oxalic and acetic acids solution may have induced an antagonistic effect and adversely influenced the effectiveness of the copper extraction, suggesting that the binary mixed solution of oxalic and acetic acid is not suitable for CCA extraction.

Recovery of CCA-treated Wood with Phosphoric Acid and Oxalic or Acetic Acids in a Microwave Reactor

Table 2 summarizes the average removal of CCA elements using binary acid solutions consisting of phosphoric acid with either acetic or oxalic acid. In the mixed phosphoric and oxalic acids solution, the recovery rate of chromium and arsenic approached 100%. However, the highest copper recovery rate was 52%, which is slightly higher than that of 39% but substantially less than that of 79% obtained, respectively, in the simple oxalic acid and phosphoric acid extraction in a microwave reactor in a previous study (Yu et al., 2009). This result indicates that the extraction efficiency of phosphoric acid in the binary solution appears to be ineffective for copper recovery suggesting that the binary solution of oxalic and phosphoric acid is not suitable for CCA extraction. In a two-step extraction process using oxalic acid as the first step with a 1-h pre-extraction followed by a 3-h extraction with phosphoric acid in the second step, Kakitani *et al*. (2006) also concluded that the use of inorganic acids under the experimental conditions were ineffective for remediation of CCA-treated wood.

Table 1: CCA recovery rate for mixed acids extraction consisting of acetic acid and oxalic acid at various concentrations extracted with microwave reactor at 160°C for 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

*Each recovery rate is an average of 3 sample replications.

Table 2: CCA recovery rate for mixed acids consisting of phosphoric acid with acetic acid or oxalic acid at various concentrations extracted with microwave reactor at160°C for 30 min.

H_3PO_4 Conc. (%)	1% acid Conc.	As (%)*	Cr (%)*	Cu (%)*
0.5%	Oxalic acid	99.52±0.23	97.12±0.21	33.82±1.15
1.25%	Oxalic acid	99.12±0.13	97.39±0.49	36.49±1.05
2.0%	Oxalic acid	98.90±0.55	97.67±0.49	41.30±2.01
3.5%	Oxalic acid	99.58±1.05	98.77±1.03	52.14±1.49
0.5%	Acetic acid	94.05±2.28	23.52±1.72	95.38±2.42
1.25%	Acetic acid	96.66±1.38	50.03±2.09	97.38±1.02
2.0%	Acetic acid	99.01±0.60	72.18±1.45	97.46±0.67
3.5%	Acetic acid	99.52±0.91	98.10±1.37	98.60±0.93

*Each recovery rate is an average value of 3 sample replications.

In the mixed solution consisting of phosphoric acid and acetic acid, the arsenic and copper were recovered at high efficiency as expected. But the recovery of chromium is the most interesting result in the study. Yu *et al*. (2009) found that extractions with neither acetic acid nor phosphoric acid alone can effectively recover chromium. In this present study, the addition of 1.0% acetic acid into a series of concentrations of phosphoric acid enhanced the chromium recovery rate of the mixed acid solution (i.e., removal of chromium increased as the phosphoric acid increased). It should be noted that all three CCA elements were recovered in high efficiency with the maximum chromium recovery rate of 98.1% when phosphoric acid concentration was 3.5%. This synergistic effect of mixed acetic acid and phosphoric acids is considered one of the most interesting and significant discoveries in the study. The potential for the development of this binary acid solution into a highly efficient CCA recovery system is apparent. The results suggest that the optimization of process variables such as reaction temperature, reaction time, concentrations and mix ratio is needed for a highly efficient CCA recovery system.

Optimization of the Synergistic Effects of the CCA Recovery Rate of a Phosphoric and Acetic Acid System

Table 3 summarizes the CCA recovery rate for the combination of five phosphoric acid and four acetic acid concentrations in microwave extraction at a fixed temperature at 160 oC for 30 min. Analysis of variance (ANOVA) indicates phosphoric acid concentration had a significant effect on the CCA recovery rate, but the effect of the acetic acid concentration was not significant within the concentration range evaluated. The results of the Duncan's multiple range tests for significant means are summarized in Table 4. The average recovery rates were 99.3%, 97.5%, and 98.4% for arsenic, chromium, and copper, respectively, when the concentration of phosphoric was 2.75% regardless of the concentration of the acetic acid. The results also show that there was no significant improvement in average chromium recovery rate by raising phosphoric acid concentration above 2.75%, however, the chromium recovery decreased significantly with a decrease in phosphoric acid concentration below 2.75%. This concentration (i.e., 2.75%) was elected for additional studies in the following process optimization experiment.

It is important to note that even though the effect of acetic acid concentration was statistically not significant, the recovery rate of greater than 99% was attained for all CCA elements as acetic acid concentration increased to 2.0%. The additional capability of further increase in recovery rate is considered important in the development of a scaled up extraction process.

The concentration of phosphoric acid is an important factor in this binary acid extraction. The significant effect of phosphoric acid concentration on CCA recovery rate (Table 4) shows greater average extraction rate change as the phosphoric acid concentration increased for chromium extraction as compared to that of arsenic and the copper even though the maximum chromium recovery is consistently lower than those of the other elements. Chromium has the highest resistance to extraction because of its strong bonding with lignin (Pizzi 1990). However, it is not fully clear how the addition of acetic acid into phosphoric acid resulted in an enhancement regarding the recovery of chromium. Nevertheless, the use of chemical activation of wood with phosphoric acid has been known for many decades and has been applied to different cellulose and lignocellulosic materials for the preparation of activated carbon (Zuo *et al*. 2009; Jogtoyen and Derbyshire 1998) and flame-retardant products (Inagaki *et al*. 1976). Studies have shown that during thermal treatment the phosphoric acid treated lignocellulosics begin to lose carbonyl and methyl groups in hemicelluloses at 50 ^{o}C, composition of lignin starts to change at 100 ^{o}C, and substantial oxidation of cellulose to form ketones occurs at 150 ^{o}C (Jogtoyen and Derbyshire 1998).

Also, the bond cleavage reaction of the biopolymer chains occur around 150 ^{o}C (Solum *et al*. 1995). Furthermore, it was shown that the treatment of cellulose with phosphoric acid also resulted in reduced substrate crystallinity and increased accessibility (Nilsson *et al*. 1995; Saito *et al*. 1994).

Thus, it is possible that these characteristic reactions of phosphoric acid may each contribute to a different degree toward chromium recovery. For instance, the composition and structural changes in lignin induced by phosphoric acid treatment may weaken the bond binding the metal-lignin complexes to increase the chromium removal. Furthermore, decreased crystallinity and cellulose surface exposure by solubilization of hemicelluloses by the phosphoric acid treatment may result in increasing access for acetic acid to enhance the recovery rate. Additional studies on the influence of particle size on metal recovery rate with a focus on the accessibility factor as well as the effect of phosphoric acid treatment on the distribution of hemicelluloses and lignin compositions between acid solution and extracted wood residues are in progress. These studies should provide additional new data to elucidate the synergistic effect of the binary solution.

Table 3: CCA recovery rate for mixed acids consisting of phosphoric acid and acetic acid at various concentrations extracted in microwave reactor at 160°C for 30 min.

Phosphoric Acid(%)	Acetic Acid(%)	As (%)*	Cr (%)*	Cu (%)*
3.50	2	99.52	99.30	99.02
2.75	2	99.48	99.21	99.01
2.00	2	98.89	74.32	98.23
1.25	2	96.77	51.77	97.99
0.50	2	95.50	25.79	96.87
3.50	1.5	99.52	99.21	98.97
2.75	1.5	99.24	97.98	98.65
2.00	1.5	98.66	73.33	97.98
1.25	1.5	97.79	49.36	97.56
0.50	1.5	95.01	24.57	96.22
3.50	1	99.52	98.10	98.60
2.75	1	99.06	96.37	98.56
2.00	1	99.01	72.18	97.46
1.25	1	96.66	50.03	97.38
0.50	1	94.05	23.52	95.38
3.50	0.5	99.61	95.35	98.01
2.75	0.5	99.01	96.23	98.07
2.00	0.5	98.54	70.37	97.36
1.25	0.5	96.03	48.95	96.85
0.50	0.5	93.57	23.06	95.12

*Each recovery rate is an average value of 3 sample replications.

Table 4: Summary of the Duncan's multiple range tests for significant means on the effect of concentrations of phosphoric acid and acetic acid on the CCA recovery rate.

Phosphoric acid (%)	n**	As (%) mean*	Cr (%) mean*	Cu (%) mean*
0.50	12	94.53 D	23.78 D	95.90 D
1.25	12	96.82 C	50.03 C	97.22 C
2.00	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 (%)				
0.50	15	97.42 A	66.67 A	97.29 A
1.00	15	97.66 A	68.5 A	97.47 A
1.50	15	98.01 A	68.67 A	97.62 A
2.0	15	98.03 A	70.08 A	98.06 A

*Different letters indicates significantly different: **n indicates number of samples.

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 is very effective to recover CCA elements in a microwave reactor in a short period. The advantage of this method is a shorter extraction time and a one step process to achieve the complete recovery of CCA elements. The concentration of phosphoric acid and temperature of the microwave reactor were two important factors. A binary acid solution consisting of 2.75% phosphoric acid and 0.5% acetic acid, and temperature of 130 ^{0}C is the minimal reaction condition to achieve the maximum recovery rate of all CCA elements. Further research such as the acetic acid concentration, reaction time, and temperature should be studied. Also, research on larger sized wood chips should be done to enhance the practical application of this method.

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