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## Extraction of Copper from Different Copper Treated Wood Wastes

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Extraction of copper from different copper treated wood wastes

By

Bradley Claude Singleton

A Thesis  
Submitted to the Faculty of  
Mississippi State University  
in Partial Fulfillment of the Requirements  
for the Degree of Master of Science  
in Forest Products  
in the Department of Sustainable Bioproducts

Mississippi State, Mississippi

May 2015

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2015

Extraction of copper from different copper treated wood wastes

By

Bradley Claude Singleton

Approved:

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Abdolhamid Borazjani  
(Major Professor/Graduate Coordinator)

---

Susan V. Diehl  
(Committee Member)

---

Micheal S. Cox  
(Committee Member)

---

George M. Hopper  
Dean  
College of Forest Resources

Name: Bradley Claude Singleton

Date of Degree: May 8, 2015

Institution: Mississippi State University

Major Field: Forest Products

Major Professor: Abdolhamid Borazjani

Title of Study: Extraction of copper from different copper treated wood wastes

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Candidate for Degree of Master of Science

There has been significant increase in production of copper treated lumber since a voluntary halt of chromated copper arsenate (CCA) for residential use by the wood treating industry. Disposal of copper treated wood wastes has become an environmental issue for companies using these products for residential applications. This study evaluated recovery of copper from sawdust of copper azole(CA),micronized copper azole(MCA), alkaline copper quat(ACQ), and micronized copper quat(MCQ) using three different extraction procedures; toxicity characteristic leaching procedure(TCLP), sonication with heated water, and sonication with room temperature water. Two extraction fluids were used, monoethanolamine (MEA) and acidic water. No significant differences in copper recovery were observed between CA, MCA, MCQ, and ACQ using acidic water in any extraction procedures. Copper recovery was significantly higher for MEA than acidic water for all preservatives. Significantly higher levels of copper were recovered for CA and MCA than ACQ and MCQ with MEA extraction fluid.

## DEDICATION

I would like to dedicate this thesis to my loving and always supporting mother, Rachel Singleton. She has always been there to help direct my path and has helped guide my life in the direction that it has taken. If it was not for her love and support I wouldn't be here today. Thank you for always pushing me to be the best of my abilities. I am truly so blessed to have you as a mother. I would also like to dedicate this thesis to my father, Jeff Singleton, who is no longer with us. I know he would be proud of the things I have accomplished. I also want to dedicate this thesis to my loving fiancé, Andrea Irvin who has always been there for me and supported me in every decision I have made.

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## CHAPTER I {TC "CHAPTER" \f C \l "1" \n}

### INTRODUCTION

There has been a significant increase in production of copper treated lumber since the voluntary halt in production of chromated copper arsenate (CCA) for residential use by the wood treating industry. Wood treated for residential applications in North America now accounts for about 70% of the approximately 18 million m<sup>3</sup> of wood treated annually (Shultz 2007, Freeman and McIntyre 2008). There are many forms of copper preservatives that are used in the treating of lumber products to increase durability as well as resistance against deterioration (Cooper 2003, Freeman and McIntyre 2008). Four of the primary copper preservatives used by industry today are Copper Azole (CA), Micronized Copper Azole (MCA), Micronized Copper Quaternary (MCQ), and Alkaline Copper Quaternary (ACQ). These copper amine based preservatives were developed to decrease the negative impact on the environment. The primary application of the copper preservatives into the lumber is done by pressure treating (Schmitt et al. 2014). Mills have to be licensed to treat lumber with any of these copper preservatives and must be registered through the EPA. All forms of copper preservatives are hazardous to the environment in large amounts. Mills are responsible for handling their treated waste wood as a hazardous byproduct. This waste wood includes anything from smaller pieces of scrap wood to sawdust. This waste wood cannot be burned in the mill's furnace because it is treated with copper preservatives. This makes disposal of wood waste

expensive and the waste is usually hauled to landfills which encounter of transportation fees as well as landfill fees.

The objectives of this research were to evaluate the effectiveness of three different extraction methods and two different solvents in recovering the copper preservatives from of the waste wood. If successful, mills could cut costs in several different ways. If the copper preservatives can be successfully leached out of the wood waste, then the wood could be disposed of on-site as well as burned in the mills furnace. This results in saving the mills money on shipping and disposal fees. Also, the copper preservatives that were leached out of the wood could be filtered and reused in the mill to treat new batches of lumber. Cleaned-up wood wastes then could be composted or burned for energy on site. This would cut down on chemical loss and therefore save money on chemical costs. These savings could have a major impact on mills, especially smaller mills that only treat their lumber with copper preservatives.

## CHAPTER II

### LITERATURE REVIEW

In recent years, the wood industry has become increasingly aware of the necessity to create environmentally favorable means of waste disposal of used wood products. Treated wood is saturated with different organic and inorganic preservatives to enhance the life of the wood and retard deterioration that can occur. Deterioration can be caused by a number of factors: micro-organisms, fungi, insects, and weather conditions. By treating the wood, it has been determined that the life of the wood in service can be increased by 20-50 years (Cooper 2003). Exterior applications that benefit from treatment include uses of wood for utility poles, decks, posts, timbers, residential construction, etc. When lumber and other wood products are used extensively in outdoor exposure, the wood can become readily degraded by the decay organisms listed above. Using treated wood would save consumers money in the long run, because of the longer service life of the wood.

#### **Copper Wood Preservatives**

Over the past century, copper-based preservatives have been widely used in the preservation of wood products, with use increasing during the 1970s and 1980s. Currently, copper compounds and formulations control algal, wood treatment antifouling pigments, and crop fungicides (Richardson 1996). Using copper preservative

formulations is advantageous due to the fact that it is relatively easy to waterborne formulate and analyze the wood penetration (Archer and Preston 2006). Because of these properties, copper compounds are one of the main biocide components used in various wood products (Archer and Preston 2006; Gadd 1993; Lesar and Humar 2008).

The most common preservative used since the 1970s in commercial and residential applications is type-C chromated copper arsenate (CCA-C). During the latter half of the 20th century the wood preservation market was dominated by the use of the CCA-treated wood. The CCA treated wood has since been voluntarily withdrawn by the industry from residential application due to health risks. The voluntary withdrawal began in 2004 after increased awareness of health-risks and environmental concerns (Freeman et al 2003; Pederson et al. 2005; Barnes 2008). Copper, although essential to organism health, can be toxic for humans and aquatic life (Gaetke and Chow 2003, Dhyan 2012). Some of the health risks associated with excessive copper exposure is liver damage, nausea, vomiting, abdominal and muscle pain, and various other disorders such as Wilson's disease. There are additional drawbacks to using copper compounds other than the health risks. Copper tolerance is exhibited in a number of fungal species; possible corrodibility to metal fasteners; and aquatic toxicity are issues. Additionally, if enough or too much copper penetrates the cell, denaturation of proteins and enzymes can occur, which will lead to cell death (Archer and Preston 2006). Today, the CCA wood is used only in critical industrial applications such as poles, piling, foundations, and support columns.

In the CCA-C formulation, the following is expressed in oxides: chromium 47.5%, copper 18.5%, and arsenic 34%. Copper is used as protection against fungi.

Chromium is utilized as a fixative for copper and arsenic in the wood. Arsenic is used to provide supplemental protection against the copper-tolerant fungi and insects. It could be concluded that CCA wood was considered a “one-size-fits-all” type of preservative treatment (Lebow et al. 2004).

In recent years, several other preservative formulations have been standardized for applications in a market that was previously dominated by the CCA preservative. This standardization was implemented by the American Wood Protection Association. After 2004, the CCA-treated wood preservative was quickly replaced by arsenic-free, copper-containing, waterborne alternatives. The first commercial copper preservatives were based on copper solubilized as an aqueous monoethanolamine or ammoniacal complex. These copper systems include alkaline copper quaternary (ACQ), copper azole (CA-B), ammoniacal copper borate (ACB), ammoniacal copper zinc arsenate (ACZA), and copper kylie (CX-A) (Lebow et al.2004). Current common treatments include (ACQ), (CA-), micronized copper quaternary (MCQ-) or micronized copper azole (MCA-)(Schmitt 2014). According to Smith(2008) “41% of preservative wood produced in the United States in 2004 was treated with ACQ, 18% with CA, and 35% with CCA.” All of these preservative formulations contain copper as the primary active ingredient, but also include inorganic or organic co-biocides instead of using chromium or arsenic. Today, the CCA-treated wood is still used as the reference standard in evaluating the biological performance of these new preservatives. CCA protects wood in a very broad range and it has been difficult to develop low toxicity, inexpensive replacements for the CCA formulation that can cover the same broad spectrum. Therefore, the new formulations and types of preservatives target specific applications. There has been a

great emphasis placed on using the minimum retentions needed to produce certain end-use applications because the replacements are more expensive and not as cost efficient as CCA. There have been studies that indicate that the CCA alternatives release components into the environment at a rate greater to or equal to that of CCA. Due to the fact that these CCA alternatives have a lower mammalian toxicity, they are less likely to cause concern in residential applications (Kong et al. 2006).

The recent commercial metallic systems, known as micronized, particulate, or dispersed preservatives, are formulated by grinding biocidal metals (water- or oil-insoluble copper compounds) down. When ground, the results include 90% or more of the particles being less than 1000nm size. Next, the particles are dispersed into a wetting agent. The most common carrier is water (Clausen et al. 2010). Polymeric dispersants, which attach to the surface of particles and keep the particles separated from each other, are the most commonly used dispersing agents. Use of dispersing/wetting agents is significant because these improve particle size reduction during milling and stabilize particles during storage and treatment. Particle size can range from 1 to 25000nm, and the particulate character can affect penetration of the wood cell walls, as well as, affect the reaction that occurs with the wood's molecular constituents (Freeman and McIntyre 2008). The presence of particles with relatively large particle size are related to the penetration and uniformity of the distribution into the wood's cellular structure. Even though larger particles are easier to prepare, particles with long axes (greater than 25000nm) may clog tracheid's and affect the uptake of additional preservative. For complete penetration and uniform distribution, the particle size of the micronized preservative should be less than the diameter of the window pit, which is typically 10,000

nm, or membrane openings in a bordered pit, typically 400-600 nm (Freeman and McIntyre 2008).

Once these particles are dispersed in water, they are then introduced under pressure into the wood. The most common insoluble copper compounds used to produce micronized copper particles is copper carbonate, however, various insoluble copper compounds can be used (Freeman and McIntyre 2008; Jin et al. 2010). Quaternary ammonium compounds [micronized copper quaternary (MCQ)] or an azole (MCA) can be used as the co-biocide. A number of patents and patent applications specifically cover the micronized copper technology as it relates to wood preservatives and the use thereof.

The variations of ACQ are Types A,B,C, and D (AWPA 2006). These all differ in the ration of CuO to quaternary compound, the type of quaternary compound used, and the solvent system used. ACQ-B treated wood exhibits a dark greenish-brown color and smells of ammonia until the wood dries. ACQ- A or D presents a light brown color with little or no odor. ACQ-C varies in color falling between ACQ-B and ACQ-D. These multiple formulas of ACQ allow for the flexibility of treating specific wood species. ACQ-B is used in the western United States because of the difficult to treat western species. The treatment in the rest of the United States is generally achieved by using amine systems (Lebow et al. 2004). ACQs are a waterborne combination of copperoxide and quaternary ammonium compounds. Although there are various formulations of the ACQ preservatives can be found in the North American market, the most common are ACQ type B for refractory species, and ACQ-D for softwoods. Alkaline copper quaternary type D is formulated with monoethanolamine (MEA; C<sub>2</sub> H<sub>7</sub> NO) with at

typical ration of CuO: MEA of 1:2.75, whereas in ACQ-B, the ammonia ratio is CuO: ammonia of 1:1. [American Wood Protection Association (AWPA) 2006].

Copper azole relies on amine copper and a co-biocide to protect wood from decay and insect infestation. CBA-A was the first copper azole formulation. CCBA-A included boric acid. More recently, CA-B formulation contains just copper at a rate of 96% with the remaining 4% of tebuconazole. Presenting a brownish-green color, the wood that is treated with either of these copper azole formulas contains no odor. The copper azole formulas are used to treat a wide range of softwood species, and these formulas are considered the AWPA standards. There is also the option of formulating copper azole as an amine-ammonia formulation when the formulation is intended for refractory species (Lebow et al. 2004).

Matsunaga et al. (2004) conducted a study using field emission scanning electron microscopy coupled with z-ray microanalysis to examine the microdistribution of copper in southern pine which had been treated with micronized copper wood preservative. The objective was to determine if the treated wood differed from that of wood treated with conventional water-borne copper preservatives. Nano-sized copper and iron particles (from grinding media) that ranged from 10-700 nm in micronized treated wood were present in pit chambers and on tertiary wall layers adjacent to the lumens of tracheids and ray parenchyma cells. Copper and iron were present, but in separate particles. Additionally, the copper found in the wood cell walls had a concentration that was higher in the middle lamella than in the secondary wall layer. The results show that the microdistribution of copper in wood treated with dispersed copper resembles that of wood treated with conventional soluble copper-based wood preservatives. However, the

amounts of copper in the cell wall components were different. Matsunga et al. 2004 has continued studies in this area.

There has been discussion that white-rot in hardwoods might be a problem for micronized formulations. White-rot organisms are inhibited more by cell-wall treatment than by cell-lumen treatment. A number of studies have been conducted and resulted in determination that the ability to control soft-rot in hardwoods is directly related to the levels of copper in the S2 layer of wood cell walls (Hale and Eaton 1986, Ryan and Rran and Drysdale 1988).

Using micronized metal allows insecticides to be mixed in the formulations. Wood that is treated with micronized copper is only slightly more corrosive than untreated lumber, and less corrosive than other water-borne copper formulations. The treated wood presents a lighter color and this allows for the use of lighter-colored paints and stains (Freeman and McIntyre 2008).

Co-biocides are included in the formulations such as quaternary ammonium compound (quat) in ACQ and some MCQ formulations at typically a CuO/quat ratio of 2:1 or tebuconazole (tcz) in CA and other MCQ formulations at typically Cu/tcz ratio of 25:1. Cu-Mea-based wood preservatives, ACQ and CA, are formulated by dissolving Cu salt in monoethanolamine (Mea) solvent at a Mea to CuO ratio of 2.75 +/- 0.25 in ACQ and 3 +/- 0.25 in CA (AWPA 2006a). Monoethanolamine has a pKa value of 9.5 (Perrin 1979). In solution, at pH<9.5, it forms a higher proportion of charged monoethanolamine and at pH > 9.5, it forms a higher proportion of neutral monoethanolamine. Mea is used because of its ability to form stable Cu-Mea coordination complexes. Depending on the solution pH and Cu to Mea ratio, Mea ligand coordinates with Cu to form monovalent

cationic, divalent cationic, and neutral Cu-Mea complexes with different metal-ligand stoichiometries (Lee and Cooper 2010a & 2010b, Sturrock 1963; Fisher and Hall 1967; Davis and Patel 1968; Srinivasan and Subramanya 1971; Hancock 1981; Djurdjevic and Bjerrum 1983; Tauler et al. 1986). ACQ and CA wood preservatives are formulated at pH close to nine. At this pH, most of the Cu is present as reactive monovalent Cu-Mea complexes (Pankras and Cooper 2012a; Pankras et al. 2012b). These complexes can effectively undergo ion exchange or complexation reaction with ionic sites present in wood immediately after wood preservative treatment. However, at pH>10, Cu forms a higher proportion of its stable, neutral complex with Mea (Davis and Patel 1968; Hancock 1981; Pankras et al. 2012a). This form of Cu-Mea complex does not react significantly with wood (Lee and Cooper 2010a, b). This suggests that Mea at pH>10 could be used for extracting Cu from copper-wood-preservative-treated wood. Absence of other metallic ingredients and higher Cu content present in ACQ, CA, and MCQ wood preservative formulations provides additional benefits to the Mea extraction of Cu. Potentially, the Cu-Mea extract may be utilized directly for making the Cu-Mea-based wood preservatives, such as ACQ and CA.

### **Leaching and Extraction**

Leaching of metals from treated wood is dependent upon a number of treating factors. CCA has been the most extensively studied preservative over the other options. It has been determined that the most rapid leaching occurs during the first months of service of the product (Moghaddam et al. 2008). Leaching is the greatest in products with high retention levels and proportions of exposed surface. Exposing wood to high water flow, low pH, and water-soluble organic acids will increase the leaching process. The greatest

loss of all treatments, regardless of the wood species and preservation type, is caused by waterlogged sites and/or sites with low pH. Additionally, forest litter that contains organic acids cause depletion (Cooper et al. 2001). Even more leaching can be caused by less efficient fixation reactions. The type of amine used in treatment directly affects the stability, polarity, and solubility of the copper amine complex. Freeman and McIntyre(2008) state that, “Cupric ions form complexes with ethanolamine through amino and hydroxyl groups in aqueous solution due to formation of a five-member ring complex.” When copper-amine complexes interact with wood by physical interaction they leach easily. It is imperative to allow copper-amine complexes to interact with wood through chemical reactions with lignin carboxylic and phenolic hydroxyl groups to permit better fixation (Kamdern and Zhang 1998, Ruddick et al. 2001).

In recent years, the development of disposal processes for copper-treated wood waste has become an issue on the forefront of the industry. Considering the industrial choice of waterborne, arsenic-free, copper-based preservatives such as ACQ and CA for treating residential lumber, future landfills will increasingly be filled with wood treated with these preservatives (Pankras et al. 2014). Currently, when wood reaches the maximum lifespan, it is either incinerated or landfilled. This is becoming an increasing problem in North America since the preferable disposal method is the landfill option. Neither burning nor incineration is ideal due to the fact that metals are being dispersed into the environment. “Acidic and reducing conditions of landfill are conducive to arsenic, chromium, and copper leaching in possible large amounts” (Townsend et al. 2004). According to Dubey et al. 2010, alternatively treated wood wastes tend to leach 4 or 10 times more copper than CCA-treated wood wastes. It is imperative that new

sustainable wood waste disposal methods be developed due to the high amounts of wood that will be dismantled in the near future. Due to potential emissions of greenhouse gases and the releasing of inorganic compounds into the environment, the landfill option is of increasing concern. With the increase of solid wastes, the landfill sites are becoming limited in the capacity of wood waste disposal. Disposal in landfills may become obsolete at some point in the future. The current view of recycling and sustainability has brought with it stringent regulations and fees regarding wood waste disposal in landfills (Dubey et al. 2010). Additionally, there can be potential emissions of preservative into the environment instead of being utilized for recycling purposes.

A process has been developed to remove metals from CCA-treated wood as well as ACQ, CA, and MCQ treated wood (Janin et al. 2009). Rigorous leaching conditions are not required and can be reduced without affecting copper-removal efficiency. It is also possible to decrease the costs related to the remediation of treated wood wastes with this method (Coudert et al. 2013b). To remove chemicals from the extract, a combination with electrolytic separation, coagulation, and precipitation processes and ion exchange technology can be used (Coudert et al. 2013). Most processes are negligent in considering the reuse of the extract or extracted wood materials. Of specific concern is the disposal of the extract contains wood preservative components. In the following study (Pankras 2014), Monoethanolamine removed 66-86% from ACQ and 65-80% from MCQ of copper by continuous column extraction.

Previous studies by Zhou (2012) on the extraction of Cu from ACQ-treated southern pine sawdust showed that 10-15 % Mea, pH>10 at room temperature extracted up to 85% of the Cu. More than 90-96% of Cu could be removed, with multiple batch

extraction or continuous column extraction processes. In a batch process, a fixed amount of preservative-treated wood is extracted using a fixed amount of Mea. Additional Cu is removed if the extracted wood is exposed to fresh solvent. The solvent can be reused to extract fresh wood although lower amounts of Cu are removed during each subsequent extraction. This process yields a low Cu to Mea ratio in the extract, resulting in a large volume of solvent consumed during the extraction process.

In continuous column extraction processes, a long column is filled with preservative-treated wood, and the fresh Mea solvent is continuously pumped from bottom to top of the column. This process has some advantages over the batch process. In the continuous column extraction process, fresh Mea is continuously available to remove Cu from the treated wood. During this process, Mea solvent can dissolve additional amounts of Cu as it moves through the column to yield higher Cu concentration in the extract (Zhou 2012).

Monoethanolamine at high pH (>10) may dissolve some of the alkali soluble wood components such as lignin and hemicelluloses into the extract. Under extraction conditions at pH>10, the neutral Cu-Mea complex should not react with these small amounts of wood components and should promote solubilization of Cu (Pankras et al. 2014). However, if this extract is reformulated into treating solution at pH 9.0 +/- 0.5, charged Mea and charged Cu-Mea complexes in the extract may react with the extracted wood components and could lead to precipitation of Cu. This potentially could affect the treatability and efficacy of reformulated Cu wood preservatives (Pankras et al. 2014).

In the past few years, a number of studies have been conducted on the feasibility of recycling preservative treated wood. In order to continue to effectively dispose of

wood waste in the future, additional studies are necessary to determine the best feasible chemical extraction processes to decontaminate wood waste. It is imperative to determine the extractants that are potentially suitable for reuse and recycling, and apply an efficient process to maximize the component removal and accumulation in solution. There is potential for the use of monoethanolamine for extracting copper from copper-wood-preserved-treated wood. This extract should be recycled along with the remaining wood after extraction. The potential uses of the remaining wood include compost bulking agent, biochemical and cellulosic ethanol application, solid fuel pellets, and developing materials for contaminant removal from the environment (Pankras et al. 2014). There are numerous studies regarding these issues, but further research is required.

## CHAPTER III

### MATERIALS AND METHODS

Five different wood samples were tested in this experiment. Four of the wood samples were treated with copper based preservatives, CA-C, MCA, MCQ, and ACQ. The fifth wood sample was untreated southern yellow pine, which was used as the control. Each of the five samples had three replications run for every test to ensure accurate results. This made a total of fifteen samples for each test run. There were two different extraction fluids used within three different treatment methods. This brought the sample total to ninety after all samples were run.

Dimensional lumber treated with ACQ, MCQ, CA, MCA were purchased from local hardware stores. Untreated lumber was also purchased to be used as a control. The lumber was delivered to the lab where it was cut using a bandsaw. Each piece of lumber was cut separately into 2.5cm by 2.5cm pieces and placed in Ziploc bags. Each Ziploc bag was labeled with the treating chemical in order to keep the samples separate. The bandsaw was cleaned between the cuts of each board to ensure there was no contamination of one type of treatment into another. The blocks were cut dimensionally to one-inch by one-inch so they would fit into the grinder. The blocks were ground separately by type of preservative into sawdust and placed back into the Ziploc bags (Figure 3.1). The grinder was wiped down and blown clean using an air gun between each type of preservative being ground to prevent cross-contamination. The sawdust

samples were then spread evenly on separate trays and placed in a vent hood. The vent hood was turned on, and the sawdust was weighed every four hours until the weight reached a continuous weight. The vent hood reaches temperatures of about 100 degrees Celsius. Allowing the samples reach a continuous weight insured that the moisture content would be as low as possible without putting the samples into an oven. The samples were then weighed again and the following formula (Figure 3.1) was used to calculate the moisture content:

$$MC = \frac{IW - DW}{DW} \times 100$$

Where IW = Initial weight

DW = Dry weight

MC = Moisture content.

Figure 3.1 Moisture content formula.

The moisture content of all the samples was measured to be between nine and ten. Since the sawdust samples were measured by weight, equalizing the moisture content ensured that the same amount of sawdust was used throughout the experiment.



Figure 3.2 Before cut, after cut, and sawdust after being ground.

### Extraction

The first solution used in the extraction experiments was acidic water. The acidic water was composed of 25 milliliters of distilled vinegar mixed in 3.7 Liters of distilled water. Using an Omega PHH-SD1 pH meter, the pH was measured to be 2.6. The acidic water was labeled as Extraction Fluid #1. One-liter bottles were used for mixing the extraction fluid and sawdust together for the extraction methods. The one-liter bottles were labeled by type of preservative as well as numerically to help keep up with the data. Ten grams of sawdust were weighed and put into each one-liter bottle. Two-hundred fifty milliliters of Extraction Fluid #1 was then measured out, and added to four one-liter bottles. Four bottles were mixed at a time because Extraction Method #1 rotor only had a capacity of four bottles (Figure 3.3). Extraction Method #1 was similar to toxicity characteristic leaching procedure (TCLP). The TCLP constantly tumbles the bottles,

resulting in mixing and shaking the contents inside. This machine is normally used to simulate leaching in landfills. Each sample was run in the TCLP for ten hours. Once the original four samples were run through the cycle, four more were placed into the TCLP, until all fifteen had been run through this method. Fifteen 250 mL bottles were labeled numerically for these solutions to be filtered into. A spreadsheet was made to keep up with the samples and corresponding numbered bottles. Whatman #40 filter paper was used to filter the solutions of wood particles. The filters were changed between each bottle. The final filtered solution was then poured into the 250 mL bottles and sealed and stored. The one-liter bottles were washed with soap and hot water so they could be used again in Extraction Method #2.



Figure 3.3 Extraction method #1.

Extraction Method #2 was sonification with room-temperature water. The Ultrasonic machine uses sound to shake the materials inside on a molecular level. The Ultrasonic can hold eight one-liter bottles at one time (Figure 3.4). Ten grams of sawdust was weighed and placed in eight of the one-liter bottles. Then, 250 mL of Extraction Fluid #1 was added. The bottles were capped and placed in the Ultrasonic for one hour. After one hour, these bottles were removed, and the next seven were measured out and placed in the Ultrasonic for an hour. Once complete, all fifteen bottles were filtered one-by-one into the 250 mL bottles. The one-liter bottles were then cleaned to be reused for Extraction Method #3.



Figure 3.4 Extraction method #2.

Extraction Method # 3 was Sonication with heated water. The Ultrasonic contains a switch to heat the water to 40 degrees Celsius. The sawdust and extraction fluid were measured, just like in Extraction Methods # 1 and # 2, and then placed in the Ultrasonic in 40 degrees Celsius water for an hour. Once all fifteen samples were run, they were filtered into 250 mL bottles.

The three extraction methods were then repeated with the exact measurements and in the same order, but with a different extraction fluid. Extraction Fluid # 2 was Monoethanolamine. Monoethanolamine should extract higher amounts of copper (Pankras et al. 2014). There has been testing conducted at the University of Toronto that extracted between 65%-85% of copper preservatives using monoethanolamine using a column extraction method (Pankras et al. 2014). All of the testing performed with Extraction Fluid #1 was replicated with Extraction Fluid #2. Extraction Fluid #2 had a pH<10 and was donated by Cox Industries.

### **Analysis**

Once all methods were complete, there were ninety samples. These samples were delivered to Dorman Hall to the soil testing lab where an inductively coupled plasma atomic spectroscopy (ICP) (Figure 3.5) machine was located. A filter system was again set up to further filter the samples to insure no wood particles would stop-up the ICP machine. Each sample was poured through its own filter then run into a .20 mL test tube. The test tubes were labeled one through ninety to keep up with the specific samples. Once the test tubes were prepared, they were analyzed using the ICP. The analytical results measured how much copper was in the solution that was extracted. The results of the ICP were presented in a spreadsheet.

An ICP machine is used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element (Stefánsson 2007). It then measures the intensity of the emission and calculates the concentration of the element.



Figure 3.5 Inductively coupled plasma atomic spectroscopy.

### **Dry Ash Test**

A dry ash test was then performed to determine how much copper was actually in the wood. Three samples were taken from each of the five types of sawdust. The samples were dried at 65 degrees Celsius for twenty-four hours, then the samples were ground

through a 20 mesh (1mm) sieve. Three reagents were required to complete the dry ash test (Figure 3.6). They are listed below:

1. 5N HNO<sub>3</sub>- In a 2 Liter volumetric flask, 640 milliliters of concentrated HNO<sub>3</sub> was mixed into approximately 1 Liter d'H<sub>2</sub>O. The bottle was then swirled to mix the solution then brought to volume with d'H<sub>2</sub>O.
2. 30% HCL- In a 2 Liter volumetric flask, 600 milliliters of concentrated HCL was mixed into approximately 1 Liter d'H<sub>2</sub>O. The bottle was then swirled to mix the solution then brought to volume with d'H<sub>2</sub>O.
3. 6N HCL- In a 2 Liter volumetric flask, 1026 milliliters of concentrated HCL was mixed into approximately 1 Liter d'H<sub>2</sub>O. The bottle was then swirled to mix the solution then brought to volume with d'H<sub>2</sub>O.



Figure 3.6 Acid used in conducting dry ash test.

One gram of sawdust per sample was weighed. Three samples for each type of sawdust brought the total to fifteen samples. Each gram was individually placed into high form crucibles that were labeled one through fifteen. The crucibles were then placed in a muffle furnace for four hours at 550 degrees Celsius. The furnace was then turned off and the samples were allowed to cool for about thirty minutes. The samples were then moved to a tray for complete cooling. A few drops of 5N HNO<sub>3</sub> were added to completely moisten and dissolve the residue. The samples were then placed on a hot plate. The hot plate was turned on level five, out of ten, and left on until the 5N HNO<sub>3</sub> dried (Figure 3.7). The samples were then returned to the furnace for an hour at 500 degrees Celsius.



Figure 3.7 Samples on the hot plate.

The samples were then removed and placed on the tray, as before, to allow cooling. Using a Manostat Autosyringe, the residue was dissolved in three milliliters of 30% HCL. The samples were then transferred to the hot plate. The samples continued heating on the hot plate for an hour on setting three. Using the Manostat Autosyringe, 3.2 milliliters of 6N HCL was added to the samples to dissolve the remaining residue.

The samples were then transferred into 100 ml volumetric flasks using plastic funnels and rubber policeman (Figure 3.8). A bottle with deionized water (DI) was used to rinse the crucible into the funnels several times to ensure quantitative transfer. The

samples were brought to volume using DI water. The samples were then filtered through Whatman #40 filter papers into 125 milliliters Erlenmeyer flasks. A subsample was then poured into plastic scintillation vial. The samples were then run through the ICP and analyzed to determine how much copper was in the sawdust.



Figure 3.8 Samples to be poured into Erlenmeyer flasks.

### **Statistical Analysis**

Statistical analysis was computed on all the data collected after the chemical analysis. The software that was used is Statistical Analysis System (SAS) computer software (SAS Institute, Cary, NC). The differences were calculated by SAS 9.3 using

Tukey's Multiple Range Test at a probability level of  $\alpha = 0.05$ . The treatments were arranged in a randomized complete block design.

## CHAPTER IV

### RESULTS AND DISSCUSSION

Extraction results varied between all three extraction methods as well as extraction fluids. Extraction method #1, using monoethanolamine as the extraction fluid removed between 464 mg/L and 888 mg/L more copper than using acidic water (Figure 4.1). The sonication method, using monoethanolamine, removed between 633 mg/L and 892 mg/L more copper than acidic water (Figure 4.2). Sonication with heated water method, using monoethanolamine, removed between 648 mg/L and 921 mg/L more copper than acidic water (Figure 4.3). These results are similar to Zhou (2012) who had 87% copper removal efficiency from ACQ-treated sawdust using monoethanolamine. These results clearly demonstrate the ineffectiveness of acidic water for copper recovery. The control samples (untreated sawdust) showed no copper recovery in any of the extraction methods, which was expected.

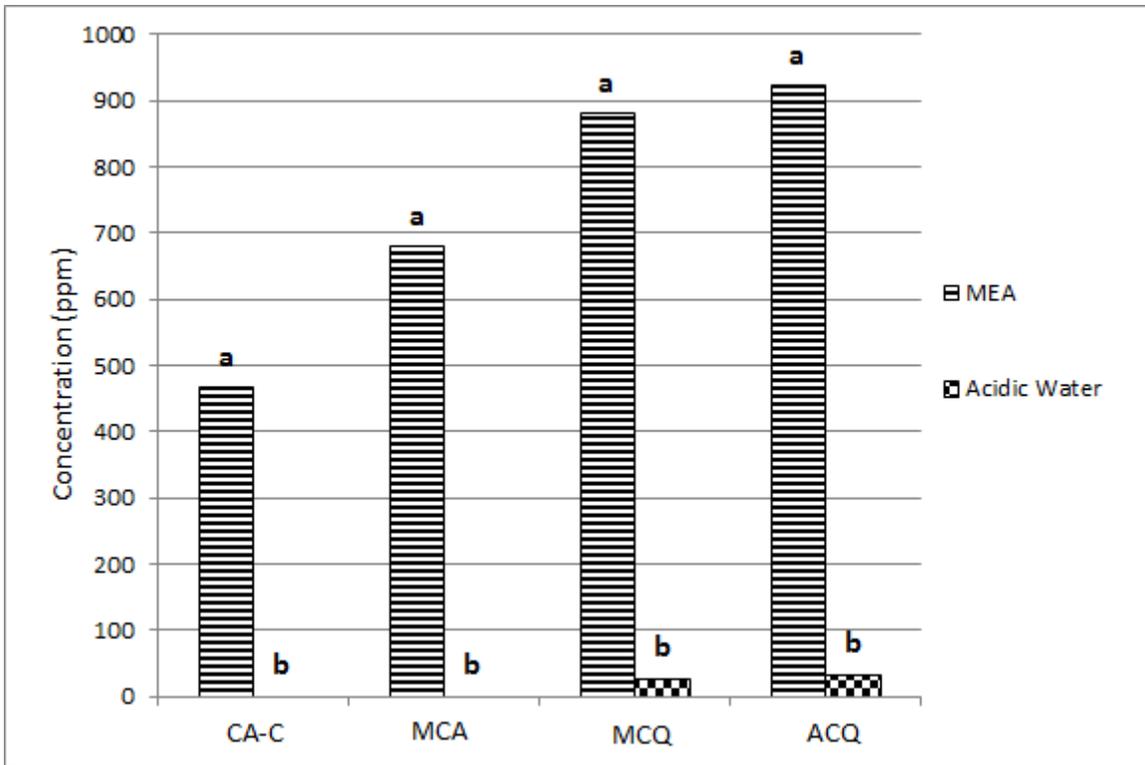


Figure 4.1 Average copper recovery amounts using extraction method #1 between monoethanolamine and acidic water.

Extraction fluids with the same letter indicate no significant difference in concentrations at the  $\alpha = 0.05$  probability level.

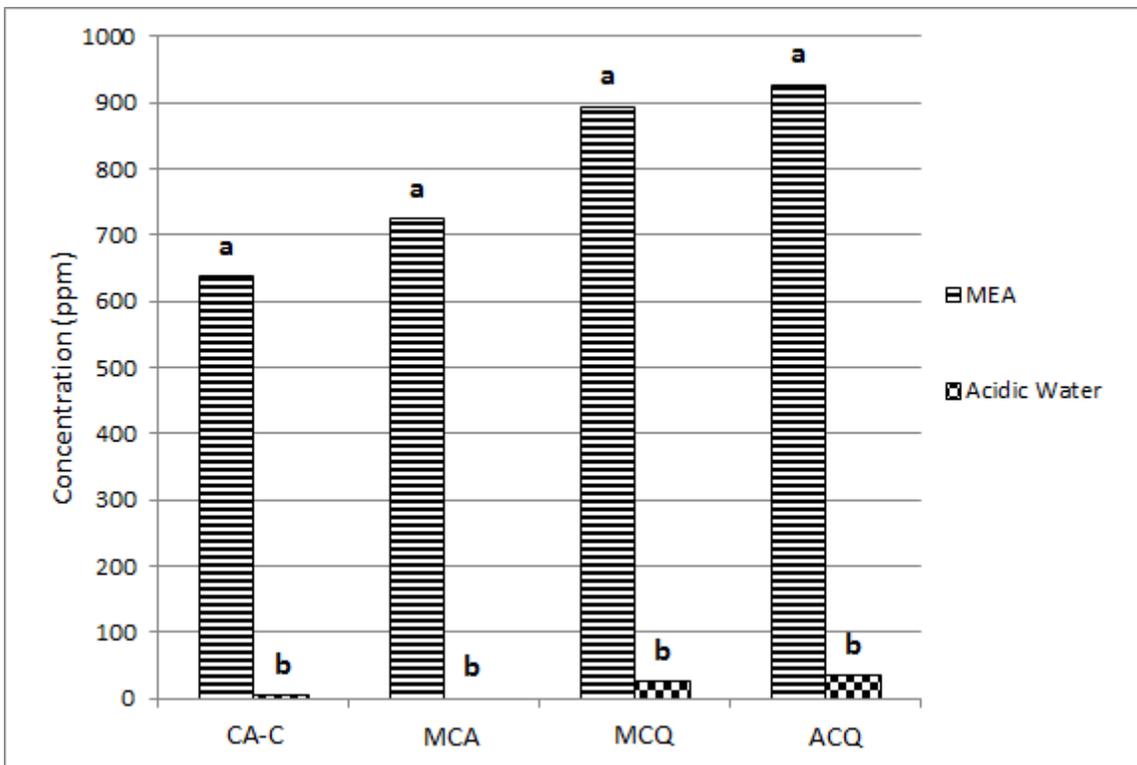


Figure 4.2 Average copper recovery amounts using sonication with room temperature water between monoethanolamine and acidic water.

Extraction fluids with the same letter indicate no significant difference in concentrations at the  $\alpha = 0.05$  probability level.

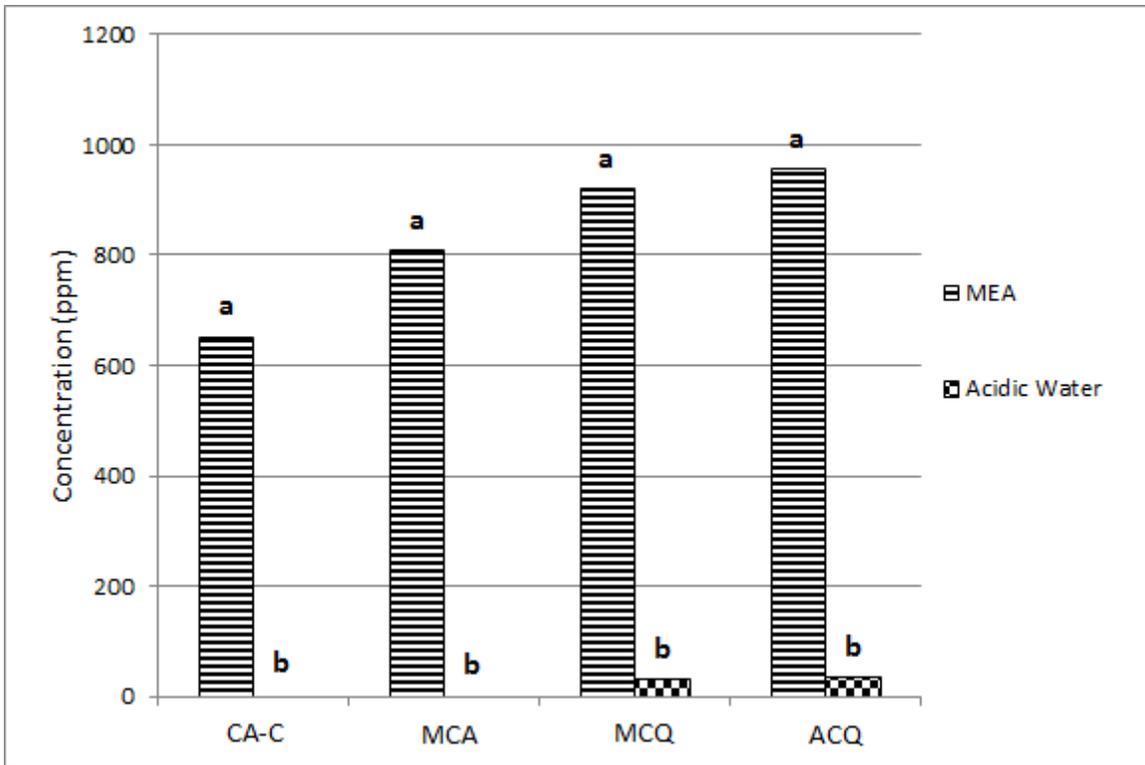


Figure 4.3 Average copper recovery amounts using sonication with heated water between monoethanolamine and acidic water.

Extraction fluids with the same letter indicate no significant difference in concentrations at the  $\alpha = 0.05$  probability level.

Figure 4.4 shows the results of copper extraction from CA-C samples using monoethanolamine as the extraction fluid. Sonication with water heated to 40 degree Celsius extracted 652 mg/L of copper. Sonication with room temperature water extracted 637 mg/L of copper, while extraction method #1 only extracted 467 mg/L. Acidic water as the extraction fluid on CA-C samples had a significantly lower copper recovery amount (Figure 4.5). Sonication with heated water removed 4.1 mg/L while sonication with room temperature water removed 4mg/L. Copper recovery was 2.8 mg/L using extraction method #1.

While different extraction fluids had significantly different recovery numbers they did have one thing in common, sonication with heated water extracted the most copper and extraction method #1 extracted the least on the CA-C samples. The increase of water temperature in the sonication method slightly increased the amount of copper extracted from the CA-C sawdust samples. Since this increase in copper recovery between sonication with heated water and sonication with room temperature water was small it is possible that much higher temperature (70 degrees C) could have increased copper recovery in the CA-C samples.

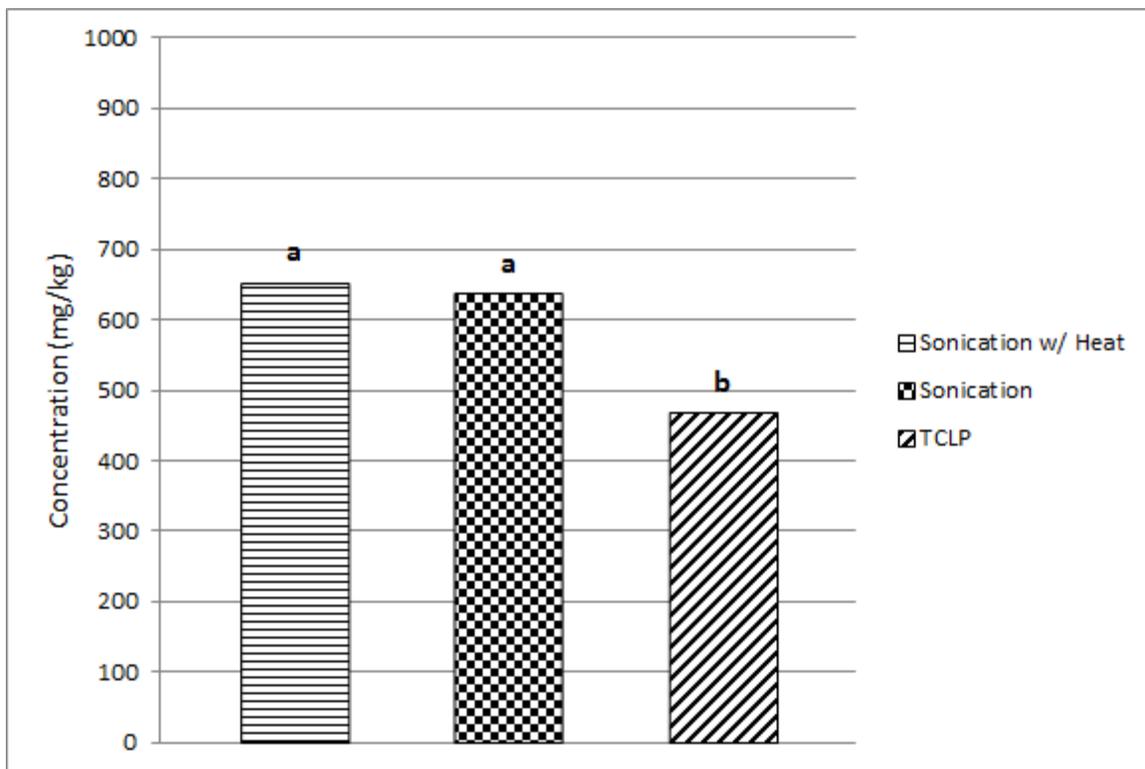


Figure 4.4 Average copper recovered from CA-C treated sawdust using monoethanolamine as the extraction fluid.

Extraction methods with the same letter indicate no significant difference in concentrations at the  $\alpha = 0.05$  probability level.

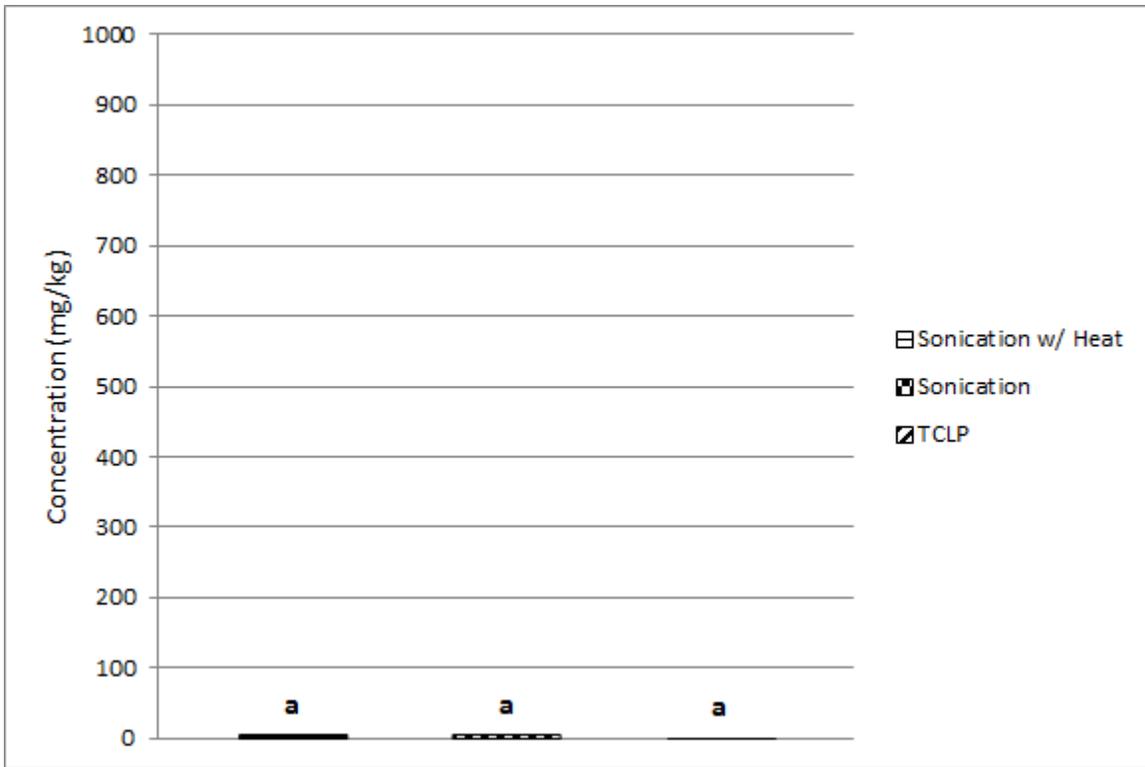


Figure 4.5 Average copper recovered from CA-C treated sawdust using acidic water as the extraction fluid.

Extraction methods with the same letter indicate no significant difference in concentrations at the  $\alpha = 0.05$  probability level.

Average results of copper extraction from MCA samples using monoethanolamine as the extraction fluid are shown in Figure 4.6. Sonication with water heated to 40 degree Celsius extracted 807.7 mg/L of copper. Sonication with room temperature water extracted 724.5 mg/L of copper, while the toxicity characteristic leaching procedure only extracted 680 mg/L. Acidic water as the extraction fluid used on MCA samples had a significantly lower copper recovery (Figure 4.7). Sonication with heated water removed 2.2 mg/L while sonication with room temperature water removed 2.1 mg/L. Copper recovery was 1.5 mg/L using the toxicity characteristic leaching procedure.

The results for the MCA samples have a very similar trend to the CA-C samples. Sonication with heated water had the highest copper recovery rate, while the toxicity characteristic leaching procedure had the lowest on the MCA samples. The higher water temperature in the sonication method with monoethanolamine increased the amount of copper extracted from the MCA sawdust samples. The increase in water temperature using acidic water as the extraction fluid seemed to have little effect on copper recovery. Copper recovery from MCA was higher than CA-C for all three extraction methods using monoethanolamine. The higher recovery rate of MCA could be due to the smaller size of copper particles used in MCA. The smaller particle size could make the copper easier to leach out of the wood.

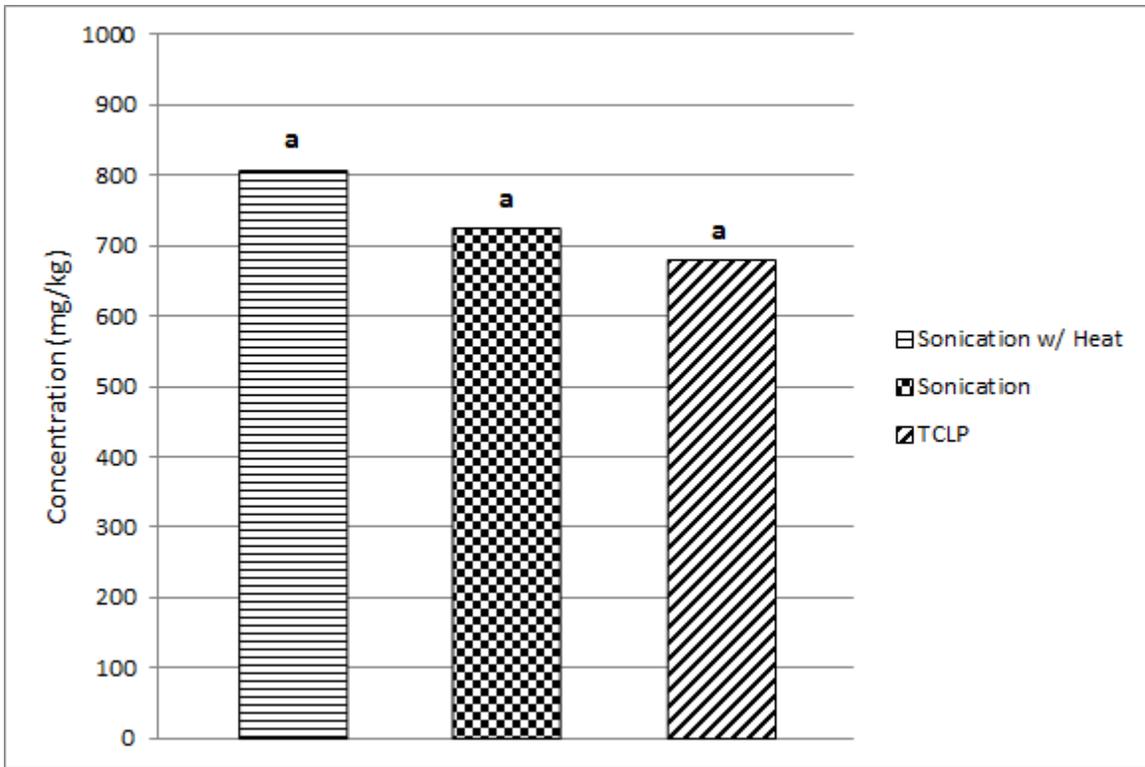


Figure 4.6 Average copper recovered from MCA treated sawdust using monoethanolamine as the extraction fluid.

Extraction methods with the same letter indicate no significant difference in concentrations at the  $\alpha = 0.05$  probability level.

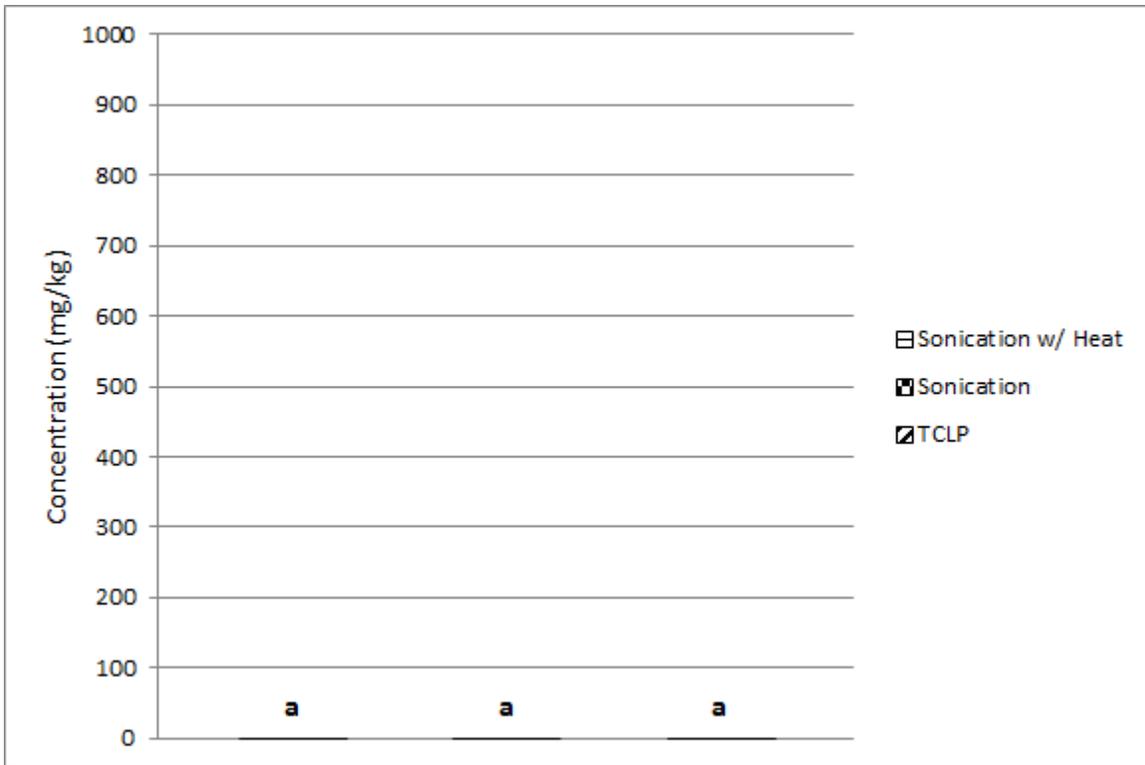


Figure 4.7 Average copper recovered from MCA treated sawdust using acidic water as the extraction fluid.

Extraction methods with the same letter indicate no significant difference in concentrations at the  $\alpha = 0.05$  probability level.

Average results of copper extraction from MCQ samples using monoethanolamine as the extraction fluid are shown in Figure 4.8. Sonication with water heated to 40 degree Celsius extracted 920.4 mg/L of copper. Sonication with room temperature water extracted 894.8 mg/L of copper, while the toxicity characteristic leaching procedure only extracted 880.3 mg/L. Acidic water as the extraction fluid used on MCQ samples had a significantly lower copper recovery (Figure 4.9). Sonication with heated water removed 31 mg/L while sonication with room temperature water removed 27.1 mg/L. Copper recovery was 27.8 mg/L using the toxicity characteristic leaching procedure.

There was not a significant difference in copper recovery on the MCQ samples between the different extraction methods using monoethanolamine, but the trend is similar to CA-C and MCA samples. Sonication with heated water had the highest concentration of recovery, while toxicity characteristic leaching procedure had the lowest recovery. Results using acidic water as the extraction fluid show sonication with heated water to have the highest recovery rate, even though the recovery rates for acidic water are very similar in all three extraction methods. MCQ results coincide with MCA and CA-C in that heating the water increases the copper recovery rate. MCQ recovery rates are higher than CA-C and MCA.

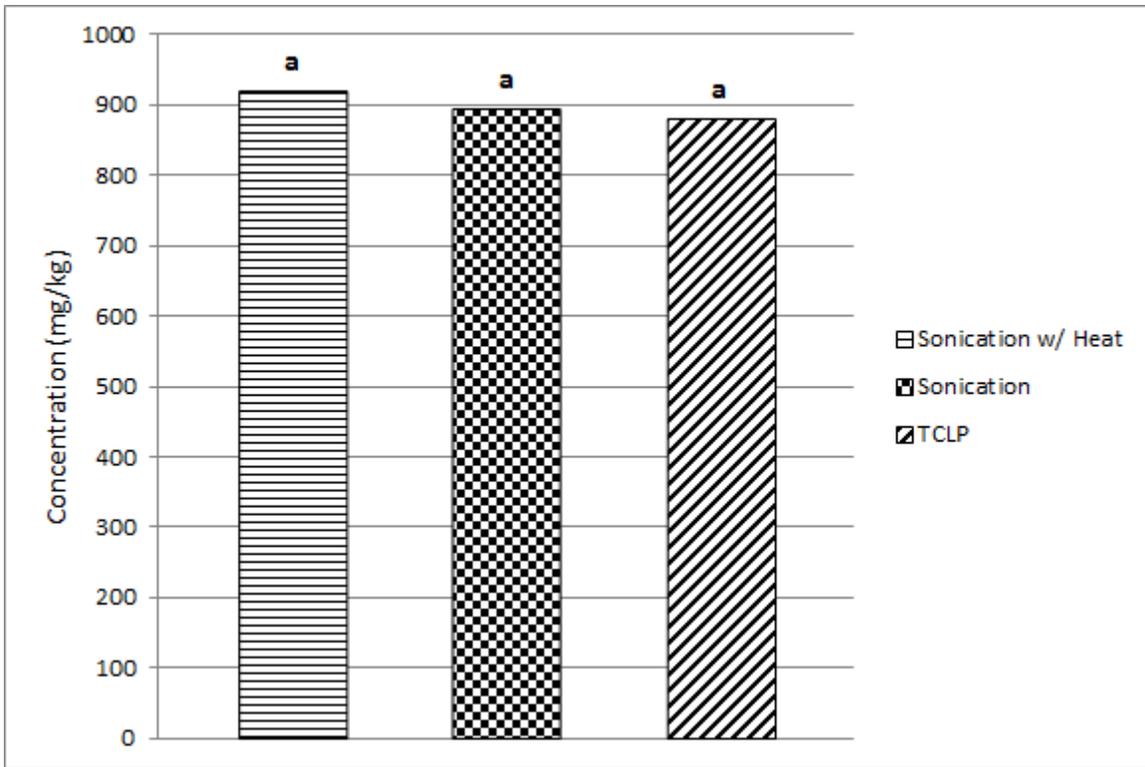


Figure 4.8 Average copper recovered from MCQ treated sawdust using monoethanolamine as the extraction fluid.

Extraction methods with the same letter indicate no significant difference in concentrations at the  $\alpha = 0.05$  probability level.

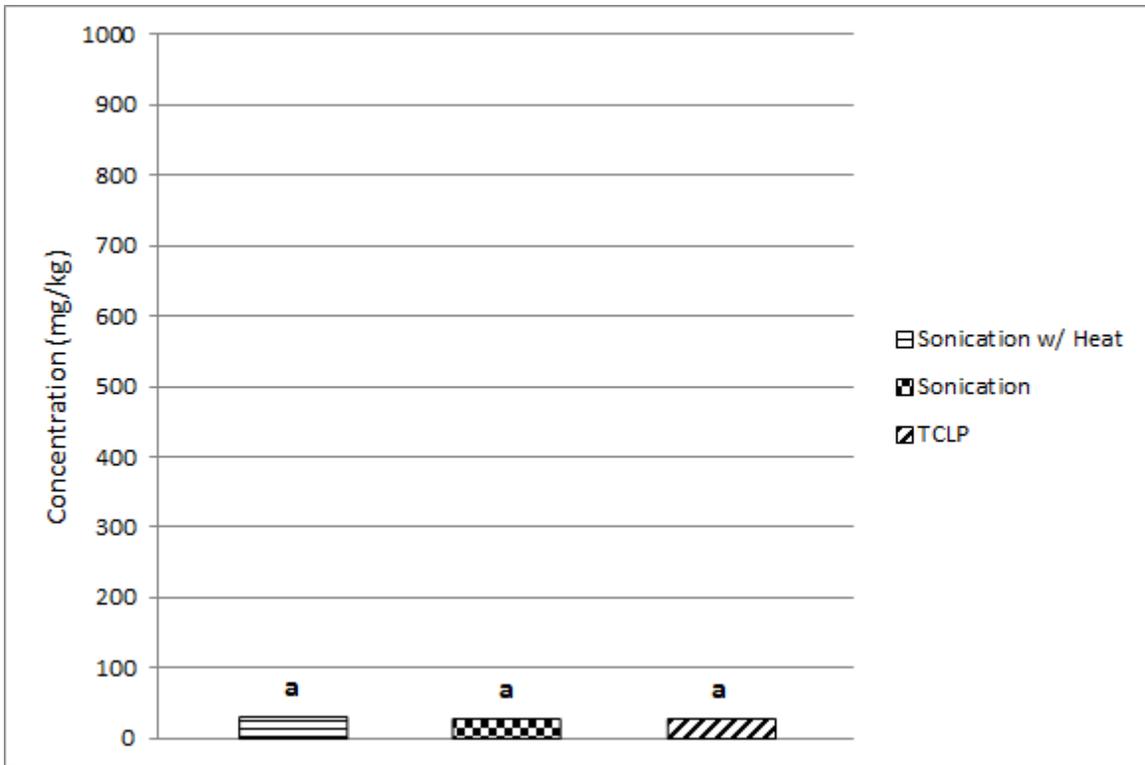


Figure 4.9 Average copper recovered from MCQ treated sawdust using acidic water as the extraction fluid.

Extraction methods with the same letter indicate no significant difference in concentrations at the  $\alpha = 0.05$  probability level.

Average results of copper extraction from ACQ samples using monoethanolamine as the extraction fluid are shown in Figure 4.10. Sonication with water heated to 40 degree Celsius extracted 957 mg/L of copper. Sonication with room temperature water extracted 927.6 mg/L of copper, while the toxicity characteristic leaching procedure only extracted 922.6 mg/L. Acidic water as the extraction fluid used on ACQ samples had a significantly lower copper recovery (Figure 4.11). Sonication with heated water removed 35.1 mg/L while sonication with room temperature water removed 35.5 mg/L. Copper recovery was 33.7 mg/L using the toxicity characteristic leaching procedure.

There was no significant difference in copper recovery on the ACQ samples between sonication with room temperature water and TCLP using monoethanolamine. Sonication with heated water had the highest recovery rate using monoethanolamine. Using acidic water, all three extraction methods had similar recovery rates. ACQ results agree with MCQ, MCA and CA-C in that heating the water increases the copper recovery rate. ACQ recovery rates are higher than MCQ, CA-C and MCA.

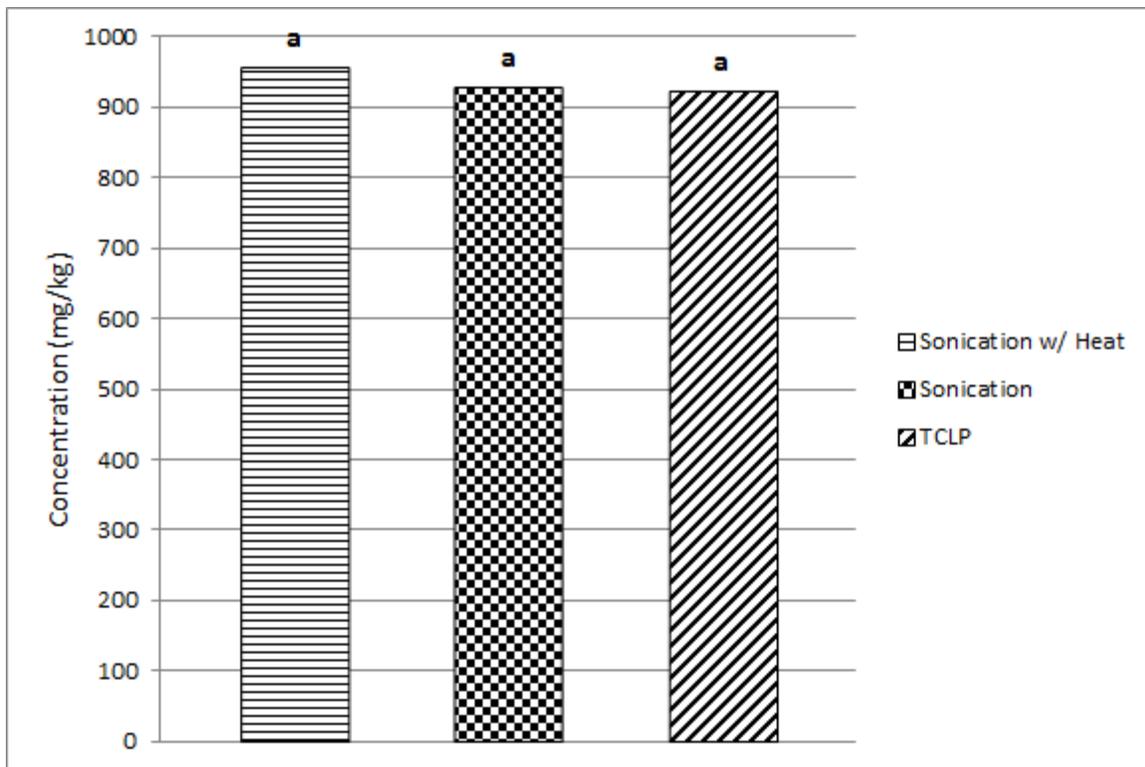


Figure 4.10 Average copper recovered from ACQ treated sawdust using monoethanolamine as the extraction fluid.

Extraction methods with the same letter indicate no significant difference in concentrations at the  $\alpha = 0.05$  probability level.

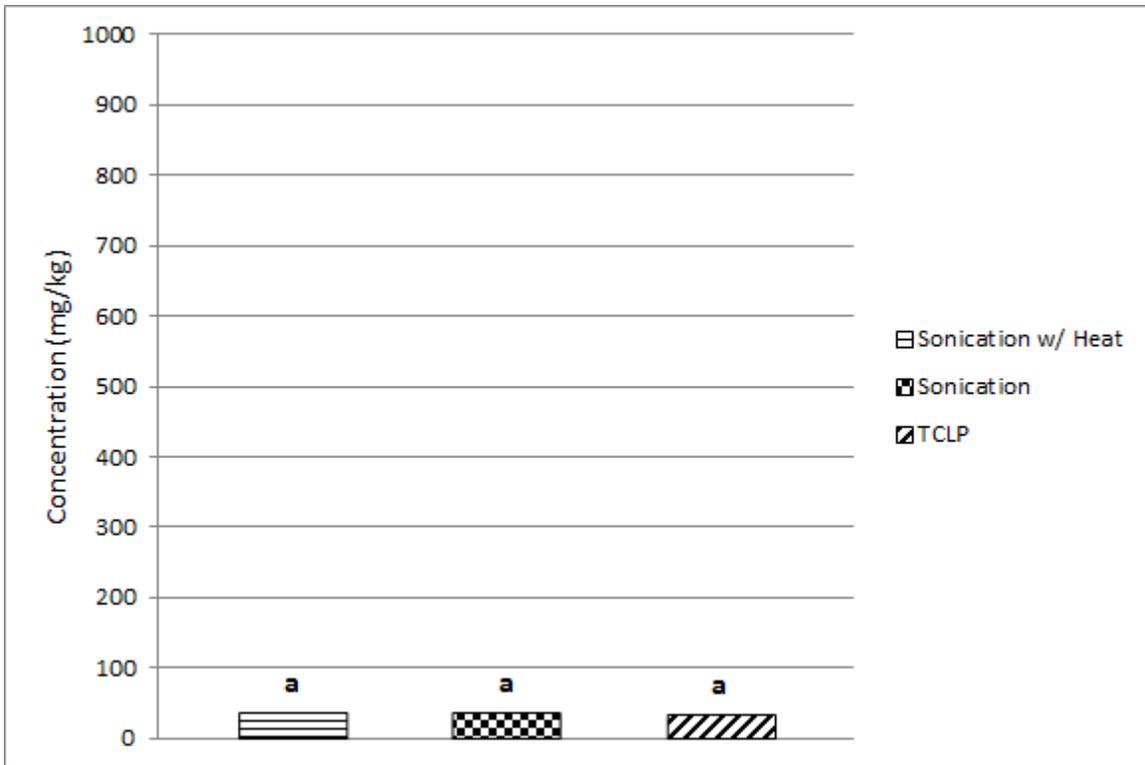


Figure 4.11 Average copper recovered from ACQ treated sawdust using acidic water as the extraction fluid.

Extraction methods with the same letter indicate no significant difference in concentrations at the  $\alpha = 0.05$  probability level.

The overall averages of Mea and acidic water show a statistical difference in the amount of copper concentration recovered (Figure 4.12). The average concentration recovered by Mea was 789 mg/kg compared to only 17 mg/kg recovered by acidic water. There was no statistical difference between extraction methods using monoethanolamine or acidic water as the extraction fluid (Figure 4.13 & 4.14). Mea extracted 834 mg/kg using sonication with heat, 796 mg/kg using sonication, and 737 mg/kg with extraction method #1. Acidic water extracted 18 mg/kg using sonication with heat, 17 mg/kg using sonication, and 16 mg/kg with extraction method #1. Figure 4.15 shows the statistical differences of copper recovered between the different wood preservatives using Mea as

the extraction fluid. MCQ and ACQ had no statistical difference between each other, while MCA and CAC were statistically different from the other preservatives. The much higher copper retention in MCQ and ACQ could have attributed to these differences (Figure 4.17). Acidic water as the extraction fluid also showed statistical differences between three of four wood preservatives (Figure 4.16).

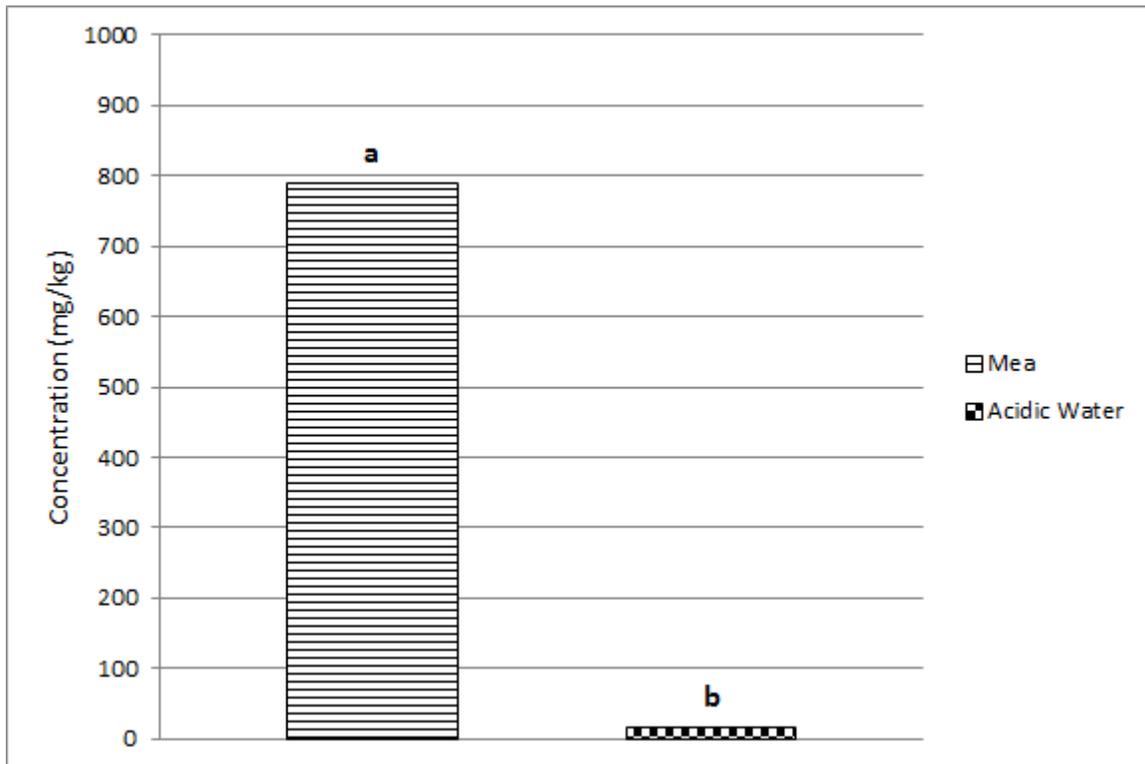


Figure 4.12 Average copper concentrations recovered between Mea and acidic water.

Extraction fluids with the same letter indicate no significant difference in concentrations at the  $\alpha = 0.05$  probability level.

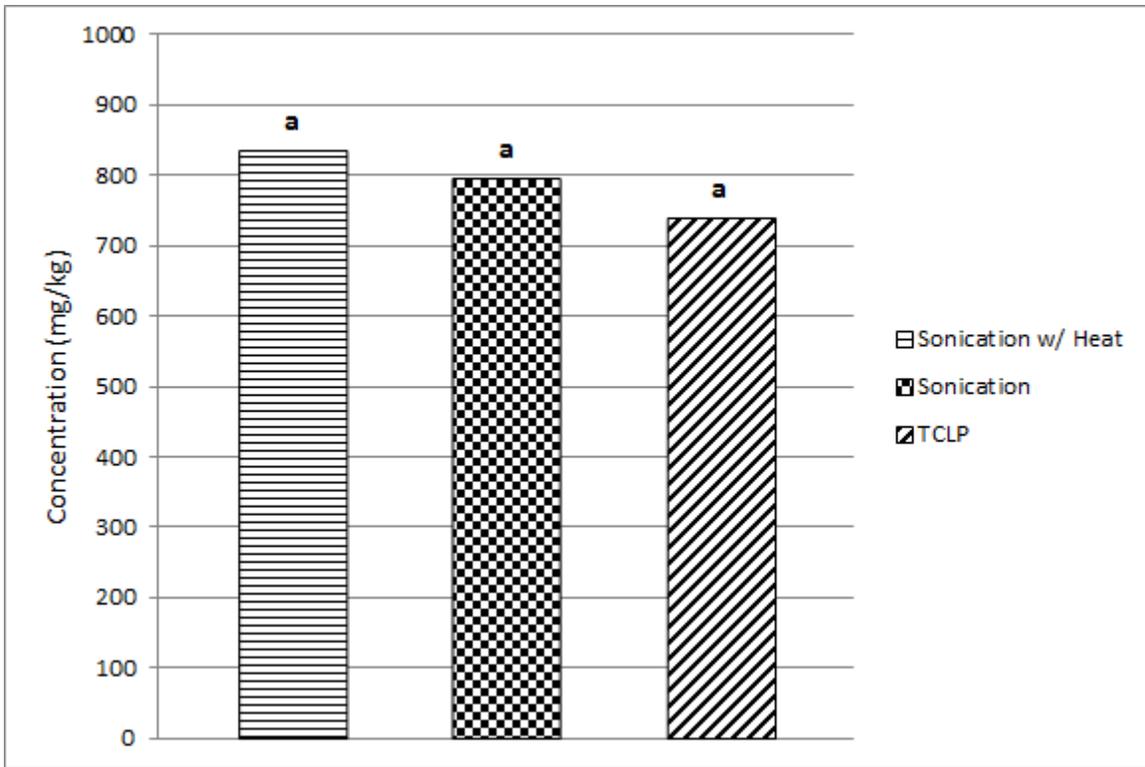


Figure 4.13 Average copper concentrations recovered using monoethanolamine with all three extraction methods.

Extraction methods with the same letter indicate no significant difference in concentrations at the  $\alpha = 0.05$  probability level.

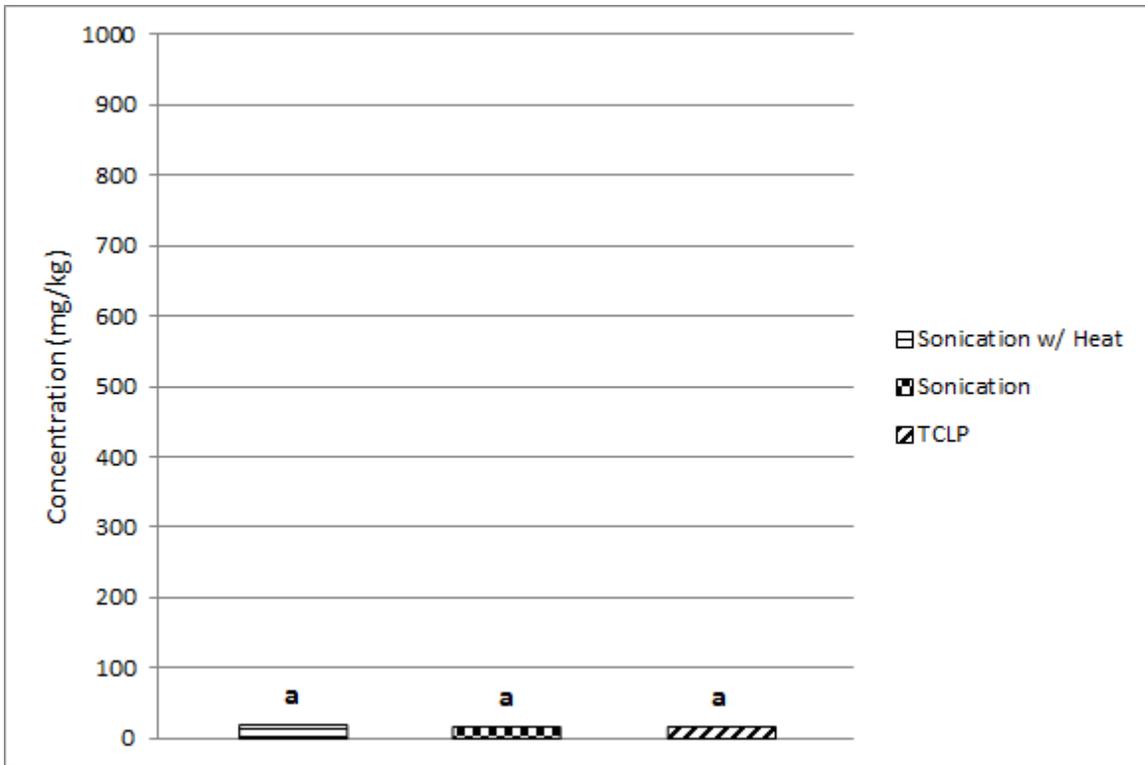


Figure 4.14 Average copper concentrations recovered using acidic water with all three extraction methods.

Extraction methods with the same letter indicate no significant difference in concentrations at the  $\alpha = 0.05$  probability level.

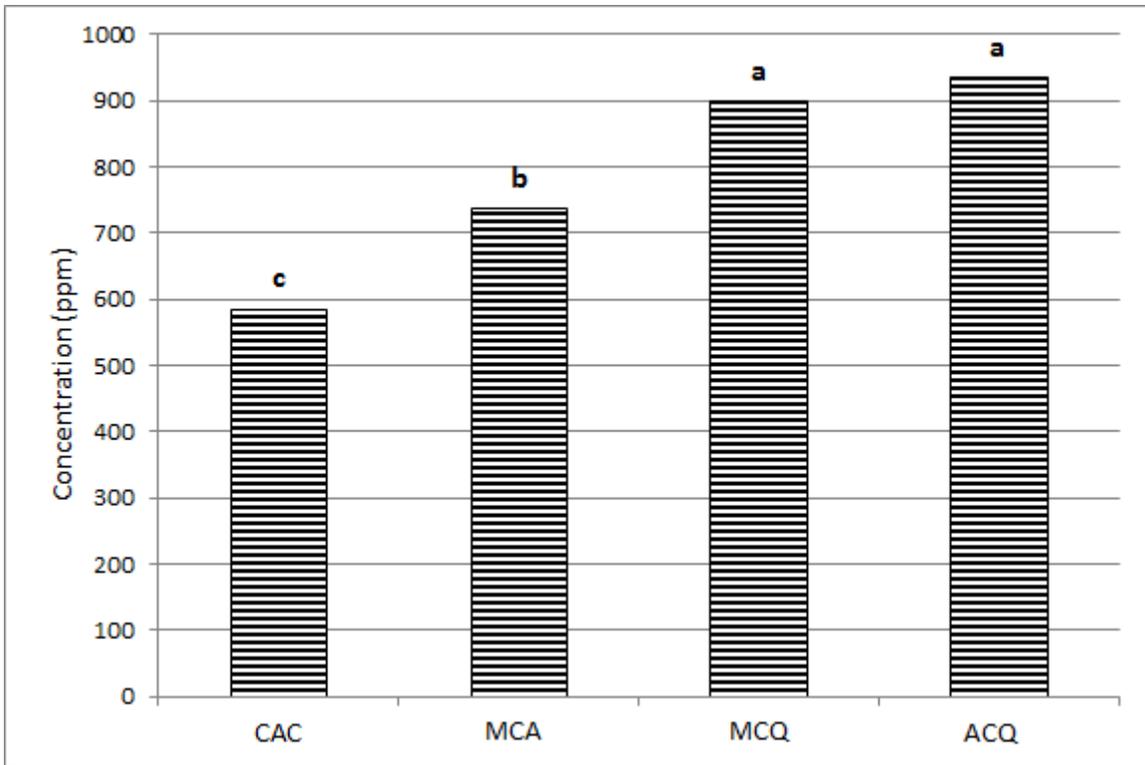


Figure 4.15 Average copper concentrations recovered from individual wood preservatives using monoethanolamine.

Wood preservatives with the same letter indicate no significant difference in concentrations at the  $\alpha = 0.05$  probability level.

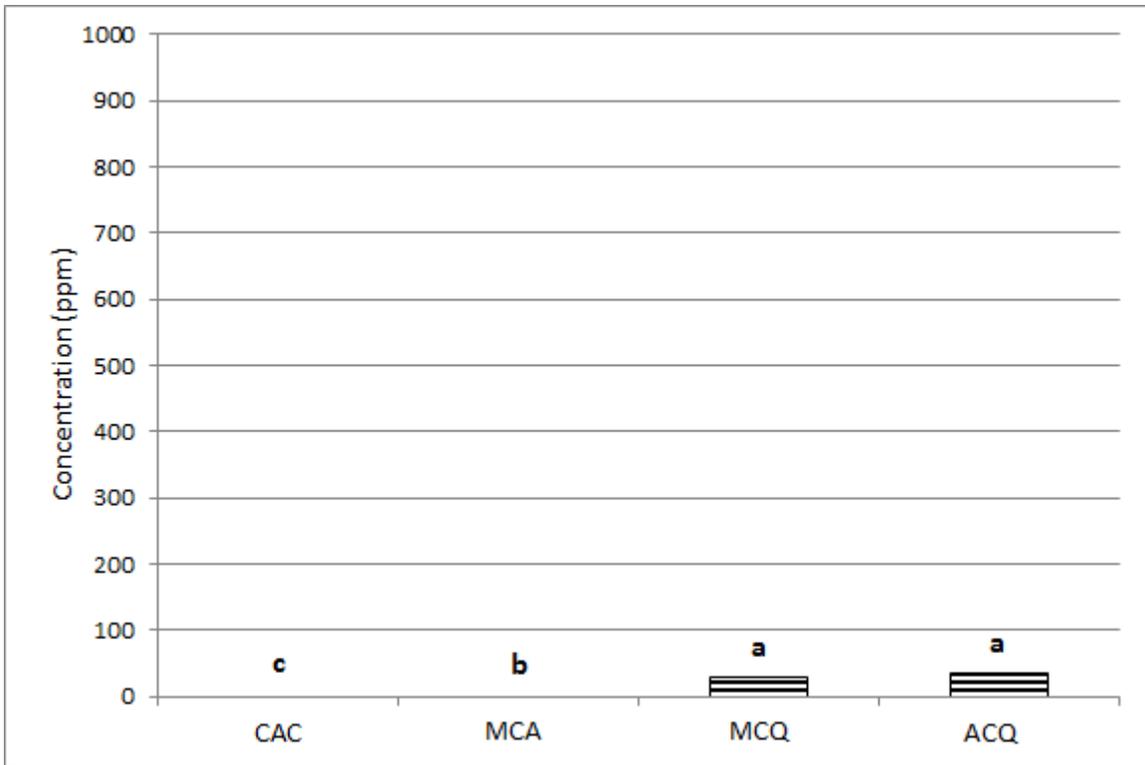


Figure 4.16 Average copper concentrations recovered from individual wood preservatives using acidic water.

Wood preservatives with the same letter indicate no significant difference in concentrations at the  $\alpha = 0.05$  probability level.

Results from the dry ash test show the average concentration of copper varied significantly between the types of preservatives (Figure 4.17). This is due to the different retention levels between the wood samples. AWPA defines retention levels in pressure treated wood as “The amount of chemical absorbed by the member in pounds per cubic foot” (AWPA 2010). Each copper preservative has their own individual retention level. These retention levels not only change between the different preservatives, but within one type of preservative as well. Certain wood is treated and rated for different uses. Wood to be used at ground contact will be treated differently and have a different retention level than wood to be used above ground, even if both are treated with the same preservative.

Average results from the dry ash test show copper concentrations to be different in each of the four preservatives samples. MCQ had the highest concentration of copper with 5,231 mg/kg. ACQ was next with 3,554 mg/kg, then MCA with 2,159, followed by CA-C with 1,972 mg/kg. The copper recovery results from all three extraction methods, with both extraction fluids, can now be compared to the data from the dry ash test (Table 1). Acidic water has a low extraction percentage for all four preservatives as well as all three extraction methods. The highest percentage extracted with acidic water was ACQ using the sonication with heat method. The ACQ copper recovery was around one percent in all three extraction methods. The MCQ copper recovery rate was a little above half a percent in all three extraction methods. MCA and CA-C both had less than one quarter of a percent copper recovery using acidic water as the extraction fluid. Monoethanolamine had much higher copper recovery percentages. Sonication with heated water had a higher recovery rate than the other two methods using monoethanolamine. MCA had the highest recovery rate with 37 percent, followed by CA-C with 33 percent, ACQ with 26 percent and finally MCQ with 17 percent. Sonication with room temperature water had the second highest copper recovery percentages out of the three extraction methods. MCA had the highest recovery rate with 33 percent, followed by CA-C with 32 percent, ACQ with 26 percent and finally MCQ with 17 percent. Toxicity characteristic leaching percentage had the lowest copper recovery percentages. MCA's recovery rate was 31 percent, followed by CA-C with 23 percent, ACQ with 25 percent and finally MCQ with 16.

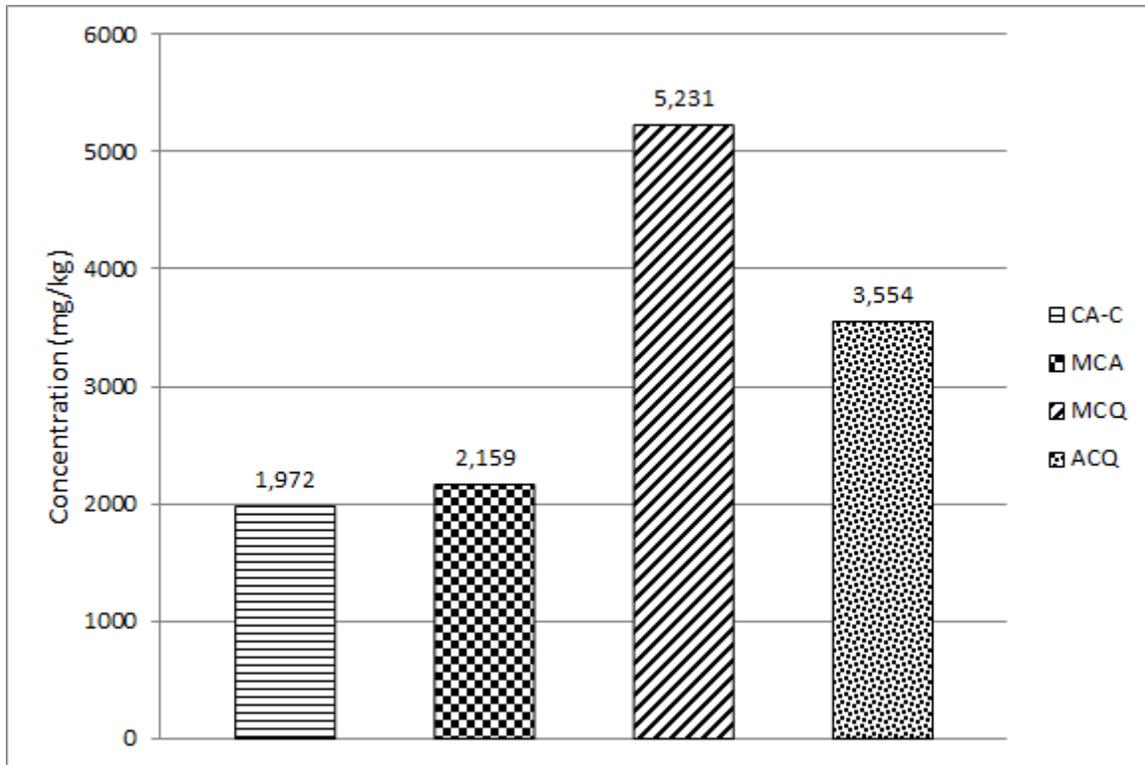


Figure 4.17 Average results from dry ash test showing the concentration of copper in each type of preservative.

Table 4.1 Results show averages of copper extracted, copper in wood, and the percent of copper extracted for each preservative and method.

Method	Samples	Copper Extracted (Acidic Water)mg/kg	Copper Extracted (MEA)mg/kg	Copper in wood mg/kg	% Extracted (Acidic Water)	% Extracted (MEA)
Sonication w/ Heat	CA-C	4.13	652.63	1972.33	0.21	33.09
	MCA	2.21	807.70	2159.00	0.10	37.41
	MCQ	31.01	920.40	5231.00	0.59	17.60
	ACQ	35.07	956.97	3553.67	0.99	26.93
Sonication	CA-C	4.08	637.20	1972.33	0.21	32.31
	MCA	2.10	724.50	2159.00	0.10	33.56
	MCQ	27.09	894.77	5231.00	0.52	17.11
	ACQ	35.54	927.63	3553.67	1.00	26.10
TCLP	CA-C	2.85	467.63	1972.33	0.14	23.71
	MCA	1.45	680.00	2159.00	0.07	31.50
	MCQ	27.83	880.33	5231.00	0.53	16.83
	ACQ	33.69	922.57	3553.67	0.95	25.96

## CHAPTER V

### CONCLUSION

The CA-C, MCA, MCQ, and ACQ samples consistently showed higher copper recovery concentrations using monoethanolamine as the extraction fluid. MCA samples had the highest copper recovery followed by CA-C, then ACQ. MCQ has the lowest concentration of copper recovered out of all preservatives using monoethanolamine as the extraction fluid. Sonication with heated water had the highest recovery rate, followed by sonication with room temperature water and then extraction method #1. The higher temperature promoted the breakdown extraction of copper from the sawdust. ACQ and MCQ lower recovery rates could be credited to the quaternary used in the two preservatives. Quaternary is a co-biocide used with copper to increase the tolerance of the wood to copper resistant bacteria and fungi. When quaternary is impregnated into the wood it fixes onto the acidic wood groups by ion-exchange mechanisms to become more leach resistant (Schmitt 2014). This in turn makes the copper particles more leach resistant and harder to extract.

Acidic water had very low copper concentration recoveries, with the highest being one percent. Therefore, acidic water is not a good extraction fluid for removing copper from treated wood. The monoethanolamine removed between 17 and 37 percent of copper throughout the different methods. Sonication with heated water was the most efficient method at copper extraction.

Expectations were to extract more copper using an economical method and extraction fluid that would be feasible for industry to apply. Based on the results from this study, the following recommendations can be made; while acidic water is cheap but it doesn't work in extracting copper from treated wood wastes; monoethanolamine was more efficient at extracting copper but in this study it still did not extract enough to be economically feasible. Further studies could be pursued with monoethanolamine to see if higher temperatures and longer time periods or different extraction methods would have a significantly higher copper recovery rate.

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