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Removal of nano- and micronized-copper from treated wood by chelating agents

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ABSTRACT

Micronized and nano-copper (Cu)-based and arsenic and chromium-free systems have received much attention for wood protection in recent years. Because they have different fixation, and micro-distribution properties, such copper systems may be more or less subject to release using known remediation methods than soluble forms of Cu. This study evaluated Cu recovery from wood treated with micronized- or nano-Cu via chemical extraction, and determined optimum release rates of Cu from micronized- and nano-Cu-treated wood compared with the release rates from soluble Cu-based wood preservatives. Chemical remediation in the study included chelating agents EDTA, oxalic acid, bioxalate, and D-gluconic acid at different durations, pH, and concentration levels to remove Cu from treated wood along with distilled water as controls. Cu removal rates increased from around 60% to over 95% when bioxalate was employed in the extraction process for all extraction durations. In extractions of nano CuO-treated wood for 24h, oxalic acid was able to remove 95% of Cu; however, bioxalate was able to remove somewhat less Cu. Bioxalate was, on the other hand, more effective than oxalic acid in removing Cu from ACQ-D, MCQ, MCA, CA-C and Cu-Et-treated wood. D-gluconic acid extractions resulted in the lowest Cu removal rate for nano-CuO. As the pH of D-gluconic acid was reduced from 10 to 2, the percentage Cu removal considerably was improved except for nano CuO. Results suggested that there is no distinctive difference in Cu removal rates among ACQ-D/MCQ, CA-C/MCA and Cu-Et wood preservatives. Nano-CuO was found to be resistant against EDTA extractions. Since it is a weak, noncorrosive, nonvolatile, nontoxic, biodegradable and inexpensive organic acid, D-gluconic acid can be used as an alternative to commercial EDTA and bioxalate in chemical remediation of Cu-treated waste wood.

Keywords: nano-Cu, micronized Cu, remediation, extraction, copper quat, copper azole, CCA

1. INTRODUCTION

Considerable attention has been focused on remediation of treated wood in recent years due to public and scientific awareness about release of toxic metals from treated waste wood disposed in landfills or by burning or composting. As a result, substantial progress has been made in remediation of preservative-treated waste wood by chemical extraction with mineral and organic acids. Methods for remediation of treated wood by various chemical, biological or thermal extraction methods are presented in a recent review by Clausen and Lebow (2011). Numerous studies on remediation of treated wood by various remediation methods have mainly focused on CCA (chromium-Cr copper-Cu arsenic-As) wood preservative due to the considerable amount of CCA-treated wood in service and in the waste stream (Kartal and Imamura 2003, Kartal *et al.* 2004a, b). Approximately, seven billion board feet of preservative-treated lumber is sold annually in U.S. Until 2004, 75% of all wood treated between the years 1980 and 2004 was treated with inorganic arsenicals. An estimated $4x10^8$ m^3 of CCA-treated wood entered service since the early 1970's (Clausen 2003; Clausen 2006). Of an estimated 160 million utility poles in North America, approximately 48 million are treated with inorganic arsenicals (Morrell 2003).

New Cu-based preservative systems that are As and Cr-free have received much attention for wood protection in recent years due to the environmental impact of heavy-metal containing wood preservatives and restrictions of CCA wood preservative for most residential applications (Lebow *et al.* 2004). As a result, novel preservative formulations without chromium and arsenic have been developed and introduced into the marketplace. Most of these new formulations use Cu as their main active ingredient because of its fungicidal properties, low cost (until recently), and low mammalian toxicity. Since 2004c, ACQ (alkaline Cu-quat), Cu-azole, and other Cu-ethanolamine based alternatives have emerged as widely available preservatives. More recently micronized-copper based systems have been introduced into the North American and European treated wood market and have gained considerable market share. Although not currently in commercial use, nano-Cu has also been evaluated as a potential preservative (Kartal *et al.* 2009).

The fixation and leaching of compounds from water-borne preservatives are extremely important since these factors greatly impact both the performance of and the environmental impact of the treated wood. Fixation of micronized Cu is believed to occur primarily through deposition in pit chambers, and on tertiary cell wall layers rather than via chemical reactions while in conventional Cu systems, fixation mechanisms rely on a number of chemical reactions such as chelate formation, ion exchange, etc. causing insoluble complexes in treated wood. Freeman and McIntyre (2008) reported that the minor amounts of free Cu^{+2} ions associated with the micronized particle formulations bind to various components of the wood by mechanisms similar to other soluble Cu preservatives such as ion exchange (Cooper 1991); however, the majority of fixation in micronized systems is believed to be simple deposition as opposed to reaction. Matsunaga *et al.* (2009) states that in preservatives containing nanoparticles, micro-distribution of the particles is different from that of wood treated with conventional aqueous preservatives because some of the particles may not be able to penetrate wood cell walls, unlike Cu ions in conventional aqueous preservatives. Matsunaga *et al.* (2011) has recently reported on the nanodistribution of copper in the pit membrane and border of a bordered pit. Kartal *et al.* (2009) showed that nano-Cu was leach resistant compared to soluble Cu oxides. Nanometer size particles smaller than the diameter of wood window pit (<10,000 nm) or the opening of the bordered pit (400-600 nm) may demonstrate complete penetration and uniform particle distribution (Freeman and McIntyre 2008). Nanoparticles have high dispersion stability, but in concentrated form, they are subject to Van der Waals forces (Clausen *et al.* 2009, Clausen *et al.* 2010). These properties may cause unexpected results from known extraction techniques and

may be subject to precipitation than other soluble or micronized forms of Cu. Due to different fixation mechanisms and micro-distribution of micronized systems when compared to water-soluble conventional systems such as CCA, CCB (Cu, Cr, Boron), ACQ, etc., both leaching of Cu from treated wood in service and removal of Cu by remediation processes are anticipated to be different in the two types of formulations.

Cu is one of the most widely used metals in the world primarily because it is highly conductive and ductile. But it is also well-known for its antimicrobial properties and has been used for centuries for control of microbial pests to crops. Due to many social and economic factors, Cu prices have soared in the past decade. While many products that use Cu are 100% recyclable, Cu used as the primary active in today's wood preservatives cannot be recycled. Rather than disposal of Cu in landfills along with the wood, Cu recovery and reuse would be an economical way to keep the costs of preservative-treatment down while benefiting the environment by diverting Cu from becoming permanently entombed in landfills. In the current study, chemical remediation processes by oxalic acid, bioxalate, D-gluconic acid and ethylene di-amine tetra-acetic acid (EDTA) as chelating agents were followed with Cu recovery from treated wood with a number of Cu-containing wood preservatives. D-gluconic acid is a non-toxic and easily biodegradable sugar acid. Since it has an ability to chelate earth alkaline elements and heavy metals, it can be used in various applications as a sequestering agent for heavy metals and as a possible extracting agent for metal-polluted soils **(**Fischer and Bipp 2002). EDTA, an archetypal synthetic chelating agent, has many applications. It forms chelates with both transition-metal ions and main-group ions. It is mostly used for leaching and remediation of heavy metals from contaminated soils and removal of many metals by reaction with EDTA is reported to be considerably efficient with certain types of soil. EDTA may be also a viable agent for the enhanced removal of Cu from CCA-treated wood waste. Chemical modification via EDTA extraction may act to reverse the fixation process of Cu in wood. Thus, EDTA extraction may be one key to unfix Cu for remediation of wood treated with Cu-based preservatives (Kartal 2003). Oxalic acid, another chelating and reducing agent, is one of the strongest organic acids. Being readily oxidized, it is useful as a reducing agent for bleaching and ink removal. A number of studies showed that the removal of Cu, Cr, and As from CCA-treated wood waste increased significantly during oxalic extraction (Clausen and Smith 1998, Kartal and Köse 2003, Kartal and Clausen 2001a, b, Clausen 2000; Clausen *et al.* 2001, Clausen *et al.* 2000, Kakitani *et al.* 2009, Kakitani *et al.* 2007). Bioxalate, on the other hand, was shown to significantly increase extraction efficiency of CCA elements over oxalic acid (Kakitani *et al.* 2007, Kakitani *et al.* 2009).

The objective of this study was to determine optimum release rates of Cu from micronized- and nano-Cu-treated wood and compare with the release rates from soluble Cu-based wood preservatives via chemical extraction. Due to the chelating abilities of above-mentioned agents, chemical remediation in the study included evaluating those chelating agents at different durations, pH, and concentration levels to remove Cu from treated wood. Distilled (DI)-water extractions were used as controls.

2. MATERIALS AND METHODS

2.1 Wood Preservatives

Commercial ACQ-D (alkaline Cu-quat - type D) (Viance, Inc., Charlotte, NC), MCQ (micronized Cu-quat) (Osmose, Griffin, GA), MCA (micronized Cu-azole), CA-C (Cu-azole - type C) (Lonza, Atlanta, GA) and CCA-C (chromated copper arsenate - type C) preservative formulations were evaluated. In addition, a quat-free form of ACQ-D (Cu-Et (Cu-

ethanolamine) (Viance, Inc., Charlotte, NC), and a nano-CuO (Cu oxide-40 nm) were tested. The solutions were adjusted in order to reach a target CuO retention level of 0.64 kg/m^3 in treated wood blocks for each preservative treatment.

2.2 Wood Specimens and Treatments

Wood blocks (19x19x19 mm) were cut from sapwood portions of southern pine (SP) lumber. The wood blocks were free of knots and visible concentrations of resins, showed no visible evidence of infection from mold, stain, or wood-degrading fungi, and had 2 - 4 growth rings per cm in cross sections. The blocks were conditioned to a moisture content of 10 - 12% in a conditioning room at 27ºC and 70%relative humidity (RH) for 2 weeks before preservative treatment. Groups of 50 pre-weighed wood blocks were vacuum-treated for 40 min at -172 kPa with each treatment according to AWPA E10 (2012). After treatment, the blocks were dry-blotted and re-weighed to determine preservative uptake. The treated blocks were conditioned for 2 weeks at room temperature to ensure that fixation was complete and then equilibrated to stable weight at 27ºC and 70% RH for 2 weeks. The blocks were then ground to pass a US Standard 40-mesh screen (420 mm) using a Grindomix GM200 (Retsch, Inc. Newtown, PA) and the ground wood was conditioned at 27ºC and 70% RH for 2 weeks before extractions.

CCA-C treated sawdust was obtained from previously treated SP stakes (19x19x450 mm) with CCA-C solution at 1.2% solution strength. For CCA-C treatments, the stakes were treated with the solution at 28 in/Hg (30 min) and 150 psi (120 min).

Table 1 shows uptake retention levels of CuO and quat in wood blocks along with Cu contents (mg/g) in wood before extractions.

Each ground sawdust sample of 4 g was placed in 100 ml-volumetric flaks along with 80 ml of each chelating agent solution for each extraction process.

2.3 Chelating Agents

Oxalic acid, bioxalate, EDTA, and D-gluconic acid (49-53% wt. in water) (Sigma, St. Louis, Missouri, USA) were used as chelating agents in the study (Figure 1). Bioxalate solution was prepared by using 0.125 mol of oxalic acid with DI-water and the pH of the solution was then adjusted to 3.2 by adding sodium hydroxide (NaOH) solution while monitoring pH changes with a basic pH-meter. DI-water extractions served as control.

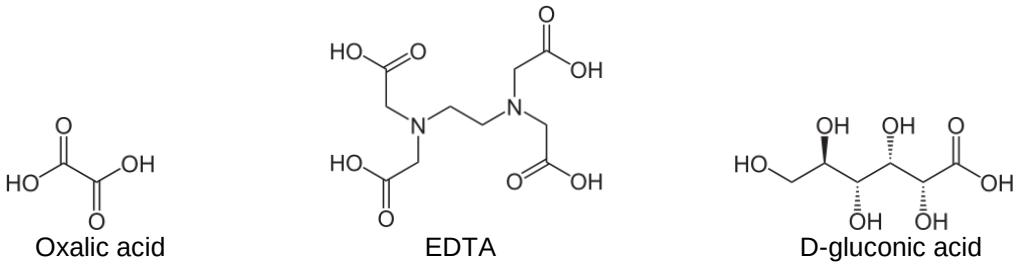

Fig. 1. Chelating agents used in the study

2.4 Extraction Processes

2.4.1 Trial-I: Oxalic acid, bioxalate, EDTA and DI-water extractions

In this trial, 1% oxalic acid (pH: 1.4), 1% bioxalate (pH: 3.2), 1% EDTA and DI-water were used to extract sawdust samples from treated blocks at room temperature for 6 and 24 h in a lab type shaker at 120 rpm. After extractions, the contents in the flasks were filtered through Whatman no. 4 filter papers using a vacuum pump, and rinsed three times with 50 ml of DI-water. Removed sawdust was oven-dried at 60ºC for 24 h and conditioned at 23ºC and 65% RH.

2.4.2 Trial-II: Effect of extraction temperature on Cu removal by DI-water

In order to determine temperature effect on Cu removal, sawdust samples were extracted by DI-water only at 20 and 50ºC for 1, 3, and 6 h in a lab type temperature-controlled shaker at 120 rpm. After extractions, the contents in the flasks were filtered through Whatman no. 4 filter papers using a vacuum pump, and rinsed three times with 50 ml of DI-water. Removed sawdust was oven-dried at 60ºC for 24 h and conditioned at 23ºC and 65% RH.

2.4.3 Trial-III: D-gluconic acid extractions

In this trial, D-gluconic acid at high (pH: 9.0) and low pH (pH: around 2) at 1, 5, and 10% concentration levels and DI-water were used. Sawdust samples from treated blocks were extracted at room temperature for 6 and 24 h in a lab type shaker at 120 rpm. After extractions, the contents in the flasks were filtered through Whatman no. 4 filter papers using a vacuum pump, and rinsed three times with 50 ml of DI-water. Removed sawdust was oven-dried at 60ºC for 24 h and conditioned at 23ºC and 65% RH.

2.4.4 Trial-IV: Oxalic acid, bioxalate, EDTA, and D-gluconic acid extractions

In this trial, 1% oxalic acid (pH: 1.4), 1% bioxalate (pH: 3.2), 1% EDTA, D-gluconic acid (pH: 2.1 and pH: 7 at 10% concentration level) and DI-water were used and sawdust samples from treated blocks were extracted at room temperature for 6 h in a lab type shaker at 120 rpm. CCA-C-treated wood sawdust samples were also tested. After extractions, the contents in the flasks were filtered through Whatman no. 4 filter papers using a vacuum pump, and rinsed three times with 50 ml of DI-water. Removed sawdust was oven-dried at 60ºC for 24 h and conditioned at 23ºC and 65% RH.

2.5 ICP analyses

Unextracted and extracted sawdust samples were then analyzed for remaining Cu by inductively coupled plasma (ICP) emission spectroscopy based on the AWPA A21 standard method (AWPA 2012) to determine percentage Cu release after extractions.

3. RESULTS AND DISCUSSION

Uptake retention of CuO in treated wood blocks before extractions is given in Table 1 for each treatment. Cu content by ICP in the blocks as mg/g for each treatment group is given in the table as footnote.

3.1 Trial-I

Table 2 shows percentage removal of Cu from treated sawdust by oxalic acid at pH: 1.4, bioxalate at pH: 3.2, EDTA and DI-water. Exposing treated sawdust samples to chelate extractions enhanced the removal of Cu compared to extraction by DI-water. No Cu removal was

seen when nano-CuO-treated sawdust was extracted with DI-water. Highest Cu removal was obtained for ACQ-D treated wood.

Table 1. Retention of CuO and quat in wood*

	CuO	Quat
Preservatives	kg/m^3	kg/m^3
ACQ-D	0.66 (0.01)	0.33 (0.01)
MCQ	0.64 (0.01)	0.32 (0.01)
MCA	0.63 (0.01)	-
CA-C	0.63 (0.01)	-
Nano-CuO	0.63 (0.01)	-
Cu-Et	0.62 (0.01)	-
CCA-C	1.44 (0.05)	-

*Uptake retention. Average of 50 wood specimens for each treatment.
Cu content in wood before extractions by ICP:
ACQ-D: 1.19 mg/g; MCQ: 1.22 mg/g; MCA: 1.29 mg/g; CA-C: 1.29 mg/g;
Nano-CuO: 0.76 mg/g; Cu-Et: 1.31 mg/g.
CCA-C retention in treated wood: 7.98 (0.26) kg/m^3.
Cu content in wood treated with CCA-C before extractions by ICP: 1.66 mg/g.

Table 2. Percentage removal of Cu from treated sawdust during extraction – Trial I

Wood	Extraction	Oxalic acid (1%, pH: 1.4)	Bioxalate (Oxalic acid 1%, pH: 3.2)	EDTA (1%)	Distilled water
preservative	duration	Average	Average	Average	Average
ACQ-D	6h	65.9	96.8	97.6	11.0
	24h	69.1	98.0	98.2	12.0
MCQ	6h	60.7	97.0	96.2	7.1
	24h	62.5	97.9	97.6	7.3
MCA	6h	63.8	95.8	97.9	3.6
	24h	65.3	97.5	99.0	5.0
CA-C	6h	58.2	96.1	97.0	8.3
	24h	60.7	96.8	98.2	9.9
Nano-CuO	6h	62.8	58.0	8.8	0.0
	24h	95.1	90.0	12.1	0.0
Cu-Et	6h	65.2	95.9	96.3	4.8
	24h	66.4	97.0	95.1	5.9

Values represent the average of duplicate samples.

It was observed that there was a distinct difference in the Cu removal between oxalic acid and bioxalate except for nano-CuO at 6h. Cu removal rates increased from around 60% to over 95% when bioaxalate was employed for all extraction durations. In extractions on nano-CuO-treated wood for 24h, oxalic acid was able to remove 95% of Cu; however, bioxalate removed slightly less Cu. As extraction time increased, Cu removal rates slightly increased except for nano CuO. Results showed that bioxalate was more effective than oxalic acid in removing Cu from ACQ-D, MCQ, MCA, CA-C and Cu-Et-treated wood because of its strong complexing properties during both 6 and 24h extraction durations. Oxalic acid, a chelating and reducing agent, is one of the strongest organic acids. Stephan *et al.* (1993), Clausen and Smith (1998), Kartal and Clausen (2001a, b), Clausen *et al.* (2000, 2001), and Clausen (2000) showed that the removal of Cu, Cr, and As from CCA-treated wood waste increased significantly during oxalic acid extraction. In a study by Kartal and Clausen (2001b), 0.8% oxalic acid extraction for 18 h removed about 23% Cu from CCA-treated particles. Clausen (2000) also found that 1% oxalic acid extraction of CCA-treated wafers for 24 h resulted in about 25% Cu removal. Kartal and Köse (2003) showed that 1% oxalic acid extraction for 24h removed around 40% Cu from CCA-C-treated wood sawdust. Kakitani *et al.* (2009) studied various extractions of CCA-treated western hemlock chips with oxalic acid and bioxalate. Their study confirmed that bioxalate was a more effective extraction solution for Cr, Cu, and As with a removal rate of 90%; however, extraction with oxalic acid removed less than 40% Cu from treated wood. In another study by Kakitani *et al.* (2006) by using CCA-treated wood, extraction efficiency reached 95.8% for Cu after a 3-h bioxalate treatment following a 1-h pre-extraction process with oxalic acid.

EDTA at 1% concentration was very effective in Cu removal for all preservatives except for nano-CuO. Interestingly, Cu removal rates in the extractions for nano-CuO were considerably lower than those for other wood preservatives tested. A previous study by Kartal (2003) showed 93% Cu removal from CCA-C treated sawdust by 1% EDTA extraction for 24h. Kartal and Köse (2003) also found similar Cu removal rate by 1% EDTA extraction. EDTA is a very effective chelating agent in removing Cu because of its strong complexing properties. However, its chelating ability was weak from sawdust treated with nano-CuO. The reason for decreased removal of Cu from nano CuO-treated wood may be strong affinity of nano-Cu for wood components, weak chelating ability of EDTA on nano-Cu, improved penetration of Cu element in treated wood, or the physical trapping of metallic copper nano-particles.

Our previous study (Kartal *et al.* 2009) showed no Cu in leachates from wood treated with nano-CuO, but the rate of leaching for $CuSO_4$ solution reached more than 20% when treated wood blocks were subjected to a 14-day-leaching course based on the AWPA E11-06 standard test (AWPA 2012) suggesting that changes in charge and Van der Waals forces might account for the low leaching of nanoCuO. Interestingly, in micronized Cu-containing wood preservatives, Cu removal rates by EDTA and DI-water were considerably higher than those in nano-Cu-containing wood preservative in the study. On the other hand, Freeman and McIntyre (2008) have reported that micronized Cu particles are physically deposited into the wood structure; however, Cu is chemically fixed in wood in soluble Cu-based wood preservative systems. They have also stated that small amounts of free Cu associated with the micronized particle formulations bind to various components of the wood by similar mechanisms as other soluble Cu-based preservatives such as ion exchange while the majority of fixation in micronized systems is believed to be simple deposition as opposed to reaction. Clausen *et al.* (2010) have stated that nano-metals may improve penetrability of the chemical into wood. If the particle size of nano-metals was smaller than the diameter of pits in the wood, complete penetration and uniform distribution would be expected. Matsunaga *et al.* (2007) observed numerous particle deposits of micronized Cu in ray tracheids and pit lumens within the wood. These deposits

created a different micro-distribution pattern in wood treated with the micronized Cu than was observed in wood treated with other Cu-based preservatives.

3.2 Trial-II

Table 3 shows percentage Cu removal from treated sawdust samples during extractions with DI-water only at three different durations and two different temperatures. DI-water was not effective in Cu removal for nano-CuO solution at all durations and temperatures due to its particulate configuration. As durations increased from 1h to 6h and temperatures from 20ºC to 50ºC, Cu removal rates increased. In general, extraction times were more dominant than extraction temperatures in Cu removal and slight changes were seen between the extractions at 20ºC and 50ºC.

Table 3. Percentage removal of Cu from treated sawdust during extraction with DI-water – Trial II

Wood preservative	Extraction duration	Extraction temperature 20°C	Extraction temperature 50°C
ACQ-D	1h	5.4	6.0
	3h	7.8	8.7
	6h	11.0	12.2
MCQ	1h	2.1	3.9
	3h	5.2	7.0
	6h	7.1	7.9
MCA	1h	0.0	0.0
	3h	1.6	1.7
	6h	3.6	3.6
CA-C	1h	2.8	2.9
	3h	6.8	6.7
	6h	8.3	8.0
Nano-CuO	1h	0.0	0.0
	3h	0.0	0.0
	6h	0.0	0.0
Cu-Et	1h	0.0	1.4
	3h	2.4	4.8
	6h	4.8	5.3

Values represent the average of duplicate samples.

3.3 Trial-III

Table 4 and Figure 2 illustrate percentage Cu removal by extractions with D-gluconic acid at two different pH levels and three different solution concentrations. The least Cu removal rates were obtained for nano CuO. As the pH of D-gluconic acid decreased from 10 to 2, percentage Cu removal considerably increased except for nano CuO suggesting that acidic pH of D-gluconic acid might play an important role in releasing Cu from treated wood. As expected, higher

concentration yielded a higher percentage of Cu removal from treated sawdust. Even though the effect of extraction time on Cu removal was distinctive for extractions at pH: 9, this trend disappeared for extractions at pH: 2. Taylor *et al.* (2001) have stated that organic acids such as citric, acetic, formic, oxalic, fumaric, tartaric, gluconic, and malic, can remove CCA components. Gluconic acid can form complexes with most metals. When symbolized as LH, only one hydrogen atom can split out from the carboxylic group yielding the gluconate anion L^-. The latter particle is classified as an active form of ligand capable of forming metal complexes (Survila *et al.* 2010). Bipp *et al.* (1998) have stated that gluconic acid is capable of dissolving the oxides, hydroxides and carbonates of polyvalent cations and forms water soluble complexes with such cations. The stability of such complexes and consequently the chelating properties of sugar acids show a great dependence on the pH value. Gluconic acid has been long used for chelant extraction of heavy metals from contaminated soils (Peters 1999, Fischer and Bipp 2002). Xue *et al.* (2010) have stated that various studies have investigated the use of organic acids such as gluconic to recover metals from municipal solid waste incineration fly ash.

Table 4. Percentage removal of Cu from treated sawdust during extraction with D-gluconic acid – Trial III

Wood	Extraction	pH: 9.0	pH: 9.0	pH: 9.0	pH: 2.1	pH: 2.2	pH: 2.5
preservative	duration	10%	5%	1%	10%	5%	1%
ACQ-D	6h	82.8	75.9	54.4	93.2	88.5	70.4
	24h	84.8	80.4	64.8	93.3	89.3	72.0
MCQ	6h	75.8	67.1	31.8	95.1	88.8	74.7
	24h	82.7	73.0	38.2	95.5	90.0	74.5
MCA	6h	75.8	67.0	34.5	94.7	87.4	69.1
	24h	80.6	71.2	37.2	93.9	87.7	72.1
CA-C	6h	83.7	78.2	39.8	92.8	88.9	73.8
	24h	85.6	80.1	43.9	93.1	88.3	72.4
Nano-CuO	6h	22.5	20.9	15.5	27.0	17.5	17.1
	24h	45.2	33.8	21.9	51.2	31.8	20.4
Cu-Et	6h	76.2	40.9	38.7	93.0	87.3	72.3
	24h	86.3	79.1	45.9	94.1	88.4	72.9

Values represent the average of duplicate samples.

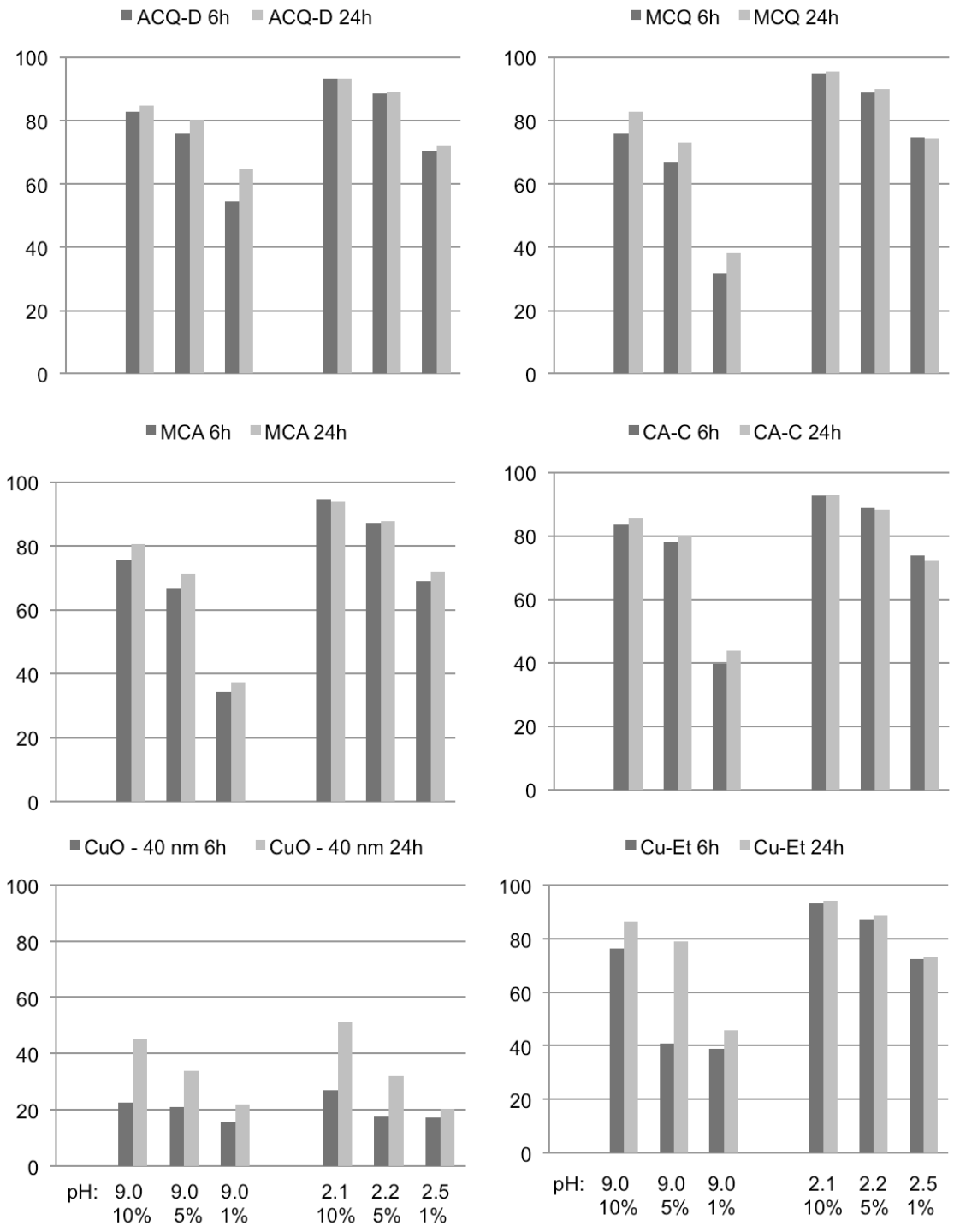

Fig. 2. Percentage removal of Cu from treated sawdust during extraction with D-gluconic acid at different pH values, concentrations and extraction durations (Trial-III)

3.4 Trial-IV

In this trial, Cu removal rates by D-gluconic acid at 10% and at two different pH levels (pH: 2.1 and pH: 7.0) for 6h were compared to the rates by oxalic acid, bioxalate, EDTA and DI-water (Table 5). The least Cu removal rates were obtained when nano CuO-treated wood sawdust was extracted with the solutions. The copper extraction rates by D-gluconic acid at the two pH levels were much lower than those by the other extractants excluding DI-water. As pH of the D-gluconic acid solution increased, less Cu was removed from sawdust samples. Except for bioxalate and EDTA, Cu removal rates in ACQ-D, MCQ, MCA, Cu-Et were higher than those in CCA-C wood preservative suggesting that Cu fixed in CCA-C-treated wood shows more resistance against oxalic acid, D-gluconic acid, and DI-water in the extractions for 6h. Overall pH effects of D-gluconic acid extraction are shown in Figure 3 for all Cu-based compounds tested as well as CCA-C wood preservative. As seen in the figure, acidic D-gluconic acid is much more favorable than alkaline conditions for removing Cu from treated wood.

Table 5. Percentage removal of Cu from treated sawdust during extraction – Trial IV

Wood preservative	Extraction duration	Oxalic acid (1%, pH: 1.4)	Bioxalate (Oxalic acid 1%, pH: 3.2)	D-gluconic acid (10%, pH: 2.1)	D-gluconic acid (10%, pH: 7.0)	EDTA (1%)	DI-water
ACQ-D	6h	65.9	93.1	93.2	86.5	95.1	11.0
MCQ	6h	60.7	92.6	95.1	89.8	95.5	7.0
MCA	6h	63.8	92.6	94.7	88.3	93.2	3.6
CA-C	6h	58.2	91.8	92.8	89.5	93.3	8.3
Nano-CuO	6h	62.8	64.0	27.0	25.4	44.9	0.0
Cu-Et	6h	65.2	94.0	93.0	90.7	94.0	4.8
CCA-C	6h	47.3	94.6	88.6	62.7	91.9	0.6

Values represent the average of duplicate samples.

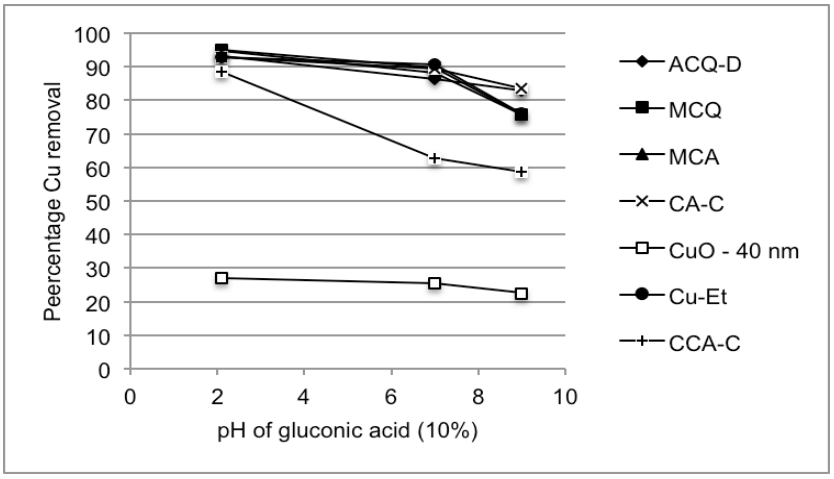

Fig. 3. Percentage removal of Cu from treated sawdust during extraction (Trial-IV)

4. CONCLUSION

From the research reported here on testing various agents for Cu removal from micronized and nano-Cu-treated wood, a number of conclusions can be drawn:

- There is no distinctive difference in Cu removal rates among ACQ-D/MCQ, CA-C/MCA and Cu-Et wood preservatives even though fixation mechanism in micronized systems (MCQ, MCA) is different from the chemistry in water-soluble systems (ACQ-D, CA-C).
- Nano-Cu was resistant against EDTA extractions where Cu removal rates were over 95% in other wood preservatives tested.
- Cu removal rates in nano-CuO compound by oxalic and bioxalate by 6h were much lower than those by 24h.
- Bioxalate (oxalic acid at pH: 3.2) was very effective in Cu removal for all wood preservatives for both extraction durations and for nano-CuO after 24h.
- As a weak, noncorrosive, nonvolatile, nontoxic, easily-biodegradable organic acid, D-gluconic acid can be used as an alternative to commercial EDTA and bioxalate in chemical remediation of Cu-treated waste wood in terms of its much lower price (€40/kg) than oxalic acid (€60/kg) and EDTA (€140/kg).

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