Copper extraction and recovery from alkaline copper quaternary and copper azole treated wood using sulfuric acid leaching and ion exchange resin or electrodeposition

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Abstract

A sulfuric acid leaching process was tested at pilot scale for removing copper from alkaline copper quaternary (ACQ) and copper azole (CA) treated wood waste. This process consisting in three 160-min leaching steps at room temperature using a 0.13 N H_2SO_4 solution followed by three water rinsing steps allows a removal of 95% of the initial copper presents in the treated wood. This study looks at Cu recovery and revalorisation by ion-exchange and electrochemical deposition. One chelating resin, Dowex™ M4195, has been identified for efficient Cu recovery from acidic leachate and allows ≥ 76% recovery with a maximum exchange capacity of 0.51 mmol Cu g^{-1} for ACQ-leachate and 0.39 mmol Cu g^{-1} for CA-leachate calculated by using the Langmuir isotherm. Ion exchange treatment operated in a continuous mode allowed recovery as a $CuSO_4$ solution when using H_2SO_4 as the eluent, or as a Cu-MEA solution for reuse in wood treatment when using monoethanolamine (MEA) as the eluent. Both eluents were able to solubilize ≥ 99% of the Cu trapped by the resin with a final concentration factor between 40 and 50. On the other hand, electrochemical treatment allowed for up to 92% Cu deposition at 10 A after 90 min. However, a comparison of the value of recovered Cu and the cost of the electricity required for deposition encourages use of milder conditions (3 A and 90 min). Economic analyses of the processes were completed for a plant with a capacity of 500 tons of treated wood per day (ttw d^{-1}). Accounting for direct, indirect and capital costs, the treatment of waste wood and the recovery of wood and Cu can generate a profit of 37 US\$ ttw^{-1} in case of ion exchange treatment and 65 US\$ ttw^{-1} in case of electrochemical treatment.

Key words

Copper; ACQ-treated wood; CA-treated wood; Ion exchange; Electrodeposition; Acid leaching.

1 Introduction

Wood is extensively used for exterior applications, including utility poles, railway sleepers, timbers, wooden silos, fence posts, decks, picnic tables, etc. (Mohajerani et al., 2018; Saxe et al., 2007). Copper-based preservatives have been successfully used since the 1920s to protect wood and therefore to extend its service life by 20 to 50 years (Frereman and McIntyre, 2008). Since January 2004, chromated copper arsenate (CCA-) treated wood has been voluntarily withdrawn for most residential uses, and it has since been replaced by alternative copper-based treated wood, including alkaline copper quaternary (ACQ-) and copper azole (CA-), both of which have copper present in the form of copper ethanolamine (AWPA, 2006).

Large amount of treated wood wastes are expected to be dismantled in the future (Kazi and Cooper, 2006). In North America and Europe, treated wood wastes are most often disposed of in landfilling sites or incinerated in controlled incinerators (Choi et al., 2012; Moghaddam and Mulligan, 2008). Increasing fees and stringent regulations related to solid waste landfilling and incineration encourage the development of new sustainable options that include recycling (Kumar et al., 2017; Sun et al., 2016).

An efficient acid leaching process to remove metals from treated wood has been patented in the last years (Janin et al., 2017). This process was initially developed for CCA-treated wood wastes (Coudert et al., 2014; Frighetto Ferrarini et al., 2016; Janin et al., 2009a, 2012a,b) and was then applied to ACQ- and CA-treated wood waste (Coudert et al., 2013a,b; Janin et al., 2011, 2012c). Sulfuric acid is used to chemically extract the metals from treated wood and break the metal-wood bonds. This generates acidic effluents with high metal concentrations. In the case of CCA-treated wood, the leachate contains As, Cr and Cu and requires several treatment steps for recovering the metals. CA- and ACQ-treated waste woods are less toxic to the environment than arsenic-containing treated waste wood, and their recycling has a high potential for economic revalorisation. Copper is the only metal used in the formulation, so its recovery from the treated waste wood should be more straightforward by requiring fewer treatment steps. Copper is a high-value metal with a market price on the London Metal Exchange of 6.13 US\$ kg^{-1} as of August 8, 2018. This paper examines the feasibility of Cu recovery for reuse from ACQ- and CA-treated wood waste.

2 Experimental

2.1 Copper removal from ACQ- and CA-treated wood

A pilot plant scale has been prepared to remove copper from ACQ- and CA-treated wood wastes using a sulfuric acid leaching process (Coudert et al., 2013a,b). The leaching process consists in three acid leaching steps, followed by three water rinsing steps. These steps were carried out in a 130-L capacity 316-stainless steel tank. 1” x 3” pieces of lumber were initially ground into wood chips using a wood grinder. The chips were then sieved through a 12 mm wire screen. Samples of 12 kg of the < 12 mm wood particles were then subjected to leaching using 80 L of a 0.13 N sulfuric acid (93%, Chemco Inc., Saint-Augustin, QC, Canada) solution, at room temperature (10°C) for 160 min. During leaching the wood pulp was agitated using a mixer and an immersed impeller (23 cm axial diameter). After the three leaching steps, the wood samples were rinsed three times with 80 L of cold tap water (10°C). After each leaching and rinsing step, solid/liquid separation was carried out by removing most of the liquid using an Elima-Matic Bolted Pump (6.8 m^3h^{-1} flow capacity). The wood particles and the remaining water were then transferred into a drainer and allowed to drain in open air.

2.2 Ion exchange treatment

2.2.1 Resin preparation and characterization

Three resins were evaluated for Cu recovery in this study: the strong cationic resin Amberlite™ IR120 made by Rohm and Haas (Supelco), a chelating resin containing bis-picolylamine groups made by Dow Chemical : Dowex™ M4195 (Supelco, Bellefonte, PA, USA); and Lewatit® TP207 (Fluka Analytical, Sigma Aldrich, Buchs, Germany) which is a chelating resin as well but contains imminodiacetic acid groups. The characteristics of the resins are presented in Table 1.

All three resins were first washed three times with deionized water and then were washed with 10% sulfuric acid solution (made with deionized water and 93% H_2SO_4 from Chemco Inc.). Resin density was determined experimentally in triplicate using a 100 mL graduated cylinder. The cylinder was half filled with water, then approximately 50 mL of resin beads were added to the cylinder. The cylinder weight was measured before and after addition of the resin as well as the exact volume of resin added. The values for density used in this study were the averages of the three results obtained for each resin.

2.2.2 Batch experiments

Batch experiments were conducted in 500 mL baffled shaker flasks (Cole Parmer, Montreal, QC, Canada). Resin volumes ranging from 0 to 8 mL, of resin were added to 200 mL of either ACQ- or CA-treated wood leachates. The leachates and resin beads were stirred at

250 rpm at room temperature on an oscillating shaker for 24 h to ensure that sorption equilibrium was reached. The amounts of resin added to the flasks were measured using 10 mL disposable syringes (Cole Parmer). To ensure that the volume of resin used for each batch test was correct, the resin was allowed to settle in the syringes for 5 min before addition to the leachate. After mixing, liquid samples were collected from the top of the Erlenmeyer flasks by pipette and stored for further analysis.

2.2.3 Column experiments

Continuous experiments were conducted with two different columns. The smaller column, which was used for “lab scale” experiments, was glass with an internal diameter of 2.5 cm and a height of 15 cm (Omnifit, Supelco Sigma Aldrich, Oakville, ON, Canada). The end pieces were made of polyethylene frits. The column bed height was adjustable. In these experiments, the column was filled up to 6 cm high, which corresponded to 30 mL of resin. The larger column, which was used for the “pilot scale” experiments, had an internal diameter of 2.5 cm and a height of 50 cm (Omnifit). The end pieces were also made of polyethylene frits, as used with the smaller column. The maximum bed volume of the larger column was 240 mL. For both pilot and lab scale experiments, the columns were filled with resin, and the resin bed was then backwashed with two to three bed volumes of deionized water for a final rinse. Adsorption experiments were carried out with the copper-treated wood leachate flowing upward through the resin. A 10 L beaker at lab scale or a 50 L tank at pilot scale received the column effluent during each experiment. Ten mL samples were collected at specific times from the outlet tubing to measure the outlet Cu concentration at time “t”. Additional samples were collected from the outlet beaker or tank after stirring to homogenize. These samples were used to measure the effluent concentration of Cu averaged over the time of the experiment, thus giving information about the total amount retained in the column or released to the effluent. Elution tests were carried out with flow from the top to bottom of the columns. The eluent solutions were 2 M MEA, 2 M NH_4OH or 5 M H_2SO_4 (analytical grade reagents). The flow was adjusted with a peristaltic pump (Masterflex L/S, Cole Parmer).

2.3 Electrodeposition treatment

2.3.1 Batch experiments

The leachates were treated by electrodeposition in a 12 cm x 12 cm x 19 cm (height) plexiglass cell equipped with eight vertical electrodes plates (anodes and cathodes) each with 220 cm^2 surface area. Anodes and cathode were alternately inserted 1.5 cm apart in the cell, with each connected to a DC power supply Xantrex XFR40-70 (Aca Tmetrix inc., Mississauga, ON, Canada). The cathodes were made of stainless steel or copper, while the anodes were made of titanium coated with iridium oxide (Ti/IrO_2). The cell had a working volume of 2 L. At the bottom of the cell, under the electrode pack, a 2 cm teflon-covered magnetic stirrer was used to improve mass transport between the electrodes as well as to attain homogenization in the cell. Electrodeposition tests were conducted at room temperature with current intensities ranging from 1 to 10 A. Ten mL samples were collected from the top of the cell after 15, 30, 45, 60, 75 and 90 min of treatment by pipet. Between electrochemical tests, the electrodes and the cell were washed with 5% (v/v) HNO_3, then rubbed and rinsed with deionized water.

2.3.2 Continuous experiment

Electrochemical treatment in a continuous mode was achieved using the same electrodeposition cell as for the batch experiments, with copper cathodes. Although more complicated reactors could lead to better efficiency, this reactor can easily be scaled up or down (Chen 2004) and can be adapted to both batch and continuous treatments. The DC power supply Xantrex XFR40-70 was connected to each electrode to provide the electric current in the cell, similar to the batch mode. The leachate was fed to the cell from the bottom using a peristaltic pump at a fixed flow rate of 24 mL min^{-1}, which corresponded to an 82 min retention time. The overflow left the cell over a lip at the top of the cell and was collected in a 100 L polypropylene tank below the cell. Ten mL samples were collected from the lip to get the Cu concentration at specific times as well as from the tank below to get the average effluent Cu concentration over time.

2.4 Analytical techniques

The soluble Cu concentration was measured by simultaneous inductively coupled plasma atomic emission spectroscopy (ICP-AES) coupled with a Vista-AX Charged Device Detector manufactured by Varian (Palo Alto, CA, USA). Quality controls were performed with certified liquid samples (multi-element standard, catalogue number 900-Q30-002, SCP Science, Lasalle, QC, Canada) to ensure conformity of the measurement apparatus. The pH was measured using a Fisher Acumet pH-meter (model 915) equipped with a double-junction Cole-Palmer electrode with a Ag/AgCl reference cell. The pH meter was calibrated every day with certified pH buffer solutions at pH 2, 4 and 7. Total suspended solids (TSS) were measured by filtration of 500 mL of sample through 0.45 µm glass fiber filters (Magna filters, GE Water and Process Technologies, Boulder, CO, USA). The filter was dried overnight at 60°C and was weighed before and after filtration. Dissolved organic carbon (DOC) was measured using a TOC-5000A apparatus from Shimadzu (Kyoto, Japan).

3 Results and discussion

3.1 Characteristics of the CA- and ACQ-treated wood and leachates

Copper content in treated wood samples before and after decontamination are shown in Table 2. Copper content in ACQ-treated wood was higher at 1,880 ± 100 mg/kg in comparison to CA-treated wood with 1,190 ± 170 mg/kg.

Copper removal efficiencies of 95% were measured for both types of treated wood. Residual copper levels in decontaminated wood were then 89.6 ± 22.8 mg/kg for ACQ-treated wood and 48.7 ± 13.6 mg/kg for CA-treated wood. The 95% copper removal efficiency measured at the pilot scale is even slightly higher than that measured (90%) under the same leaching conditions but at the Erlenmeyer shake flask scale (Coudert et al., 2013b).

Copper concentration in ACQ leachate (from the first leaching step) was 99 ± 22 mg L^{-1}, while in CA leachate it was 124 ± 24 mg L^{-1}. Leachate pH was in the range of 1.4 to 1.6 in both cases. The DOC was 345 ± 116 mg L^{-1} in ACQ leachate and 379 ± 130 mg L^{-1} in CA leachate. These ACQ and CA-treated wood leachates were used for the assays of copper recovery.

3.2 Copper recovery by ion exchange resins

Ion exchange is a well-established technology that is widely used for various applications, including metal finishing (Koivula et al., 2000; USEPA, 1981), water purification and softening (Prajapati et al., 1983), and wastewater treatment (Dabrowski et al., 2004). Ion exchange can provide an efficient and economical way of separating pollutants from wastewater, selectively recovering a component or concentrating a metal of interest. Copper recovery using various types of ion exchange resins has been studied by various authors. Strongly acidic resins have been widely used for heavy metal recovery and offer good efficiencies. They are made with sulfonic acid functional groups ($-SO_3H$) and usually have a high exchange capacity (Bauman and Eichhorn, 1947; Dizge et al., 2009). To enhance selectivity for metals, various resins with chelating groups have been developed. Among these resins, those bearing an imminodiacetic acid group are of interest because they can combine high metal selectivity and low manufacturing cost (Noureddine et al., 2008). The imminodiacetic group can act as a tri-dentate ligand with a free electron pair on the nitrogen (amino) atom and two carboxylic oxygen atoms available. Various resins, including Lewatit® TP207, have been studied and offer good Cu adsorption (Bulai et al., 2009; Mendes and Martin, 2004; Pagnanelli et al., 2004). Bis-picolylamine is another interesting chelating group used in the manufacture of the Dowex™ M4195 resin. Bis-picolylamine specificity resides in its very high selectivity. Electron pairs are available on three nitrogen atoms for coordination, making it a powerful ligand especially for copper and nickel (Ewing et al., 2003; Janin et al., 2009b).

Several studies report continuous ion exchange treatment in column reactors. Continuous experiments in laboratory settings allow for better reproduction of processes used in industry. Small columns are reliable tools for predicting larger-scale results and helping to determine parameters such as the volume of effluent to be treated before breakthrough, the optimal flow rates as well as the retention and elution efficiencies (Diniz et al., 2005; Dizge et al., 2009). The objectives of this study are to identify an efficient resin for Cu removal from treated wood leachate, then test it in a continuous column for adsorption and elution (Diniz et al., 2005; Janin et al., 2009b).

3.2.1 Copper sorption experiments in batch mode

Cu concentrations measured after batch adsorption on M4195, IR120, and TP207 resins are presented in Figure 1. The tests were performed with fixed amounts of leachate (200 mL) and variable amounts of the resins. Except for the fact that the initial Cu concentrations in the ACQ- and CA-treated wood leachates were different, the adsorption profiles were similar for both types of leachate. M4195 resin offered good sorption at low volume in both cases, with 76 and 77% Cu removal with only 5 mL L^{-1} of resin for ACQ- and CA-leachates, respectively. For the same volume of IR120 resin, the respective Cu removals were 49 and 42% and with TP207 resin, and the respective removals were 35 and 39%. At a higher resin volume, 40 mL L^{-1}, both M4195 and IR120 resins allowed for Cu concentration reduction below 5 mg L^{-1}, the limit value under which the effluent can be discharged to sewers in various cities in Quebec (Canada). For the same volume of TP207 resin, the final Cu concentrations were 23.1 and 9.8 mg L^{-1} in ACQ and CA leachates, respectively. The origin of copper, whether it came from CA- or ACQ-treated wood leachate, did not appear to impact the efficiency of copper adsorption. This fact suggests a future demonstration process where both types of wood and potentially others are treated simultaneously without the need to separate them.

3.2.2 Adsorption isotherms

Adsorption in a batch mode is limited primarily by the exchange capacity of the resins for the component to be recovered under specific conditions. The Langmuir and Freundlich isotherms are tools for assessing the capacities of the resins. The Langmuir isotherm applies to monolayer adsorption on a medium without interaction between the sorbed species. If the sorption obeys the Langmuir isotherm, the plot of 1 / Q_{abs} versus 1 / [Cu] is linear, where Q_{abs} is the quantity of Cu sorbed at equilibrium (in mmol g^{-1}). The isotherms are not shown, but Table 3 presents the R^2 values of the linear regressions. Q_{max}, which is the maximum quantity of Cu that can be sorbed (mmol g^{-1}), and the Langmuir constant for Cu sorption were derived from the y-intercepts and the gradients of the linear fit curves (Table 3). On the other hand, the Freundlich empirical equation does not account for adsorption in monolayers but applies to heterogeneous surfaces. If the Freundlich equation applies to Cu sorption on resins, the plot of Log (Q_{abs}) against log ([Cu]) should be linear. Linearity was effectively observed (plot not shown). The R^2 values for the Freunlich linear fits are presented in Table 3 as well as the Freundlich coefficients that were obtained from the gradient and y-intercept of the Freundlich linear fit curves. Both models offer a good fit, but, the R^2 values are higher on the average for the Langmuir isotherm. The monolayer model appeared to be a good representation of Cu sorption on both the chelating resins Dowex™ M4195 and Lewatit® TP207 and the cationic resin Amberlite™ IR120.

The maximum capacity of the ion exchange resin, Q_{max}, was determined experimentally for both the ACQ and CA treated wood leachates. The values are presented in Table 3. The theoretical maximum exchange capacity given by the manufacturer is also reported. The experimental Q_{max} varied greatly from one resin to another, ranging between 0.19 and 0.51 mmol g^{-1}. Some of the observed data differed greatly from the theoretical data provided by the manufacturers. The measured Q_{max} for TP207 resin was 0.19 mmol g^{-1} for both ACQ and CA leachates, whereas its theoretical capacity was 0.90 mmol g^{-1}. Similarly, the measured Q_{max} for IR120 resin was 0.15 mmol g^{-1} in CA leachate and 0.31 mmol g^{-1} in ACQ leachate, while the theoretical capacity was 0.88 mmol g^{-1}. For both resins, this meant that Cu sorption was 3 to 5 times less favorable with treated wood leachate compared to the ideal conditions for which the manufacturers obtained their maximum capacity.

The lower Cu adsorption capacity on Lewatit® TP207 and Amberlite™ IR120 resins was probably due to the low pH of the wood leachate. The TP207 resin bears imminodiacetic acid groups. This group is made of two carboxylic groups linked to a central nitrogen atom (amino). According to various authors, the carboxylic groups are mostly protonated at pH 1.3, as in the ACQ- and CA-treated wood leachates (McKevitt and Dreisinger, 2012; Mendes and Martins, 2004). This lowers the Cu affinity for the imminodiacetic acid group as well as its loading capacity on the resin. At this low pH, the sulfonic group is protonated as well and the surface charge of the cationic resin is lower (Dizge et al., 2009). Accordingly, the resins Lewatit® TP207 and Amberlite™ IR120 were not well suited for Cu removal from the highly acidic treated wood leachate.

The adsorption capacity of the Dowex™ M4195 is much higher than the other resins. The Q_{max} values are 0.51 mmol g^{-1} in ACQ and 0.39 mmol g^{-1} in CA-treated wood leachate. Copper sorption was more favored than Cu solubilization because of a good affinity of Cu for the sorption sites of the Dowex™ M4195 resin. Dowex™ M4195 is less affected by pH than the

Amberlite™ IR120 and Lewatit® TP207. The aliphatic nitrogen in the bis-picolylamine group is likely to be protonated at low pH, whereas the nitrogen atoms in the two pyridine groups seem to remain unprotonated. Hence, the two pyridyl nitrogens should keep their free electron pairs available for coordination of the Cu, which explains why the resin has a high exchange capacity at low pH. Diniz et al. (Diniz et al., 2002) observed a constant Cu uptake by the resin independent of the pH. In this study, at pH 1.3, the Q_{max} values calculated from the Langmuir isotherm are slightly lower than the theoretical capacity (0.51 and 0.39 mmol g^{-1} versus 0.62 mmol g^{-1} theoretically), but this may not be due to the pH. The theoretical value was measured by the manufacturer with Cu synthetic solutions, whereas the wood leachate used in this study contained Cu as well as various by-products. The DOC content in the leachate was in the range 229 to 509 mg L^{-1}. Soluble carbon came from the wood degradation during leaching, which possibly dissolved a blend of non-identified organic molecules derived from cellulose, hemicellulose, and lignin of the wood as well as from amine and azole compounds from the co-biocides used in ACQ and CA wood treatment. Two hypotheses could explain the lower Cu adsorption. First, these large organic molecules may be blocking the surface of the resin, thereby decreasing the availability of some Cu sorption sites. This is supported by the reasonably good fit of the Freundlich isotherm, which suggests heterogeneous sorption of Cu on the resin. Secondly, it is also possible that Cu in the leachate may be trapped into these large organic molecules or coordinated by functional groups in the organic compounds, especially the MEA solvent used in ACQ and CA formulation, if present in the leachate. Hence, it would reduce Cu affinity for the functional group of the resin, as observed by Ewing et al. (2003). Because that study was about the effect of various plating additives on Cu sorption on M4195, the authors put forward a possible mechanism of reduction of Cu(II) to form a Cu(I) complex with glycine. Dowex™ resin does not have affinity for Cu(I), which possibly explains the lower retention. Even under non-ideal conditions with low pH and the presence of by-products, the Dowex™ M4195 still offered a good adsorption capacity for the Cu. This resin looks promising for treating acidic wood leachate.

3.2.3 Column fixation at lab and pilot scale

The batch results showed the efficiency of the chelating resin Dowex™ M4195 for Cu adsorption from CA- and ACQ-treated wood leachates. The continuous experiments on both the lab scale (smaller column), and pilot scale (larger column), were conducted with this resin. Figure 2 presents adsorption curves of Cu at both scales with various flow rates. On the lab scale, the flow rates used were 1, 5 and 10 mL min^{-1} corresponding to 2, 10 and 20 bed volumes per hour (BV h^{-1}) respectively; 7.5 to 9.6 L of leachate were passed through the column.

At the pilot scale, the flow rates used were 480, 600 and 720 mL min^{-1}, corresponding to 2.0, 2.5 and 3.0 BV h^{-1} respectively, with a total of 57.6 to 62.4 L of effluent passed through the column. It appeared that higher flow rates (10 and 20 BV h^{-1}) led to a quick breakthrough, starting at 30 BV with a flow rate of 10 BV h^{-1} and 73 BV with 20 BV h^{-1}. The amount of Cu sorbed in the column between the start of the experiment and the start of the breakthrough represented 62% and 56% of the Cu injected in the column at 10 and 20 BV h^{-1}, respectively. These sorption rates were low; furthermore, the two high flow rate sorption curves appeared creased. Flow rates of 10 and 20 BV h^{-1} were too high for Cu sorption on the resin bed and probably led to unfavorable and disturbed flow in the column. On the other hand, the 2 BV h^{-1}

adsorption experiment at the lab scale was much better, with a Cu sorption rate of 89.6% before breakthrough (125 BV, $[Cu]_i$ = 140 mg L^{-1}). The 2 BV h^{-1} adsorption experiment at pilot scale led to even better results with 99.9% of Cu sorbed and a breakthrough appearing after 192 BV ($[Cu]_i$ = 104 mg/L, exchange capacity of 0.29 mmol Cu g^{-1} resin in continuous mode). The difference in initial Cu concentration may explain, partly, the later breakthrough at pilot scale. Secondly, the column setup was probably more efficient at pilot scale. The height/diameter ratio for the smaller column was 2.3, whereas it was 20 for the larger column, which favors better adsorption.

At 2.5 and 3.0 BV h^{-1}, breakthrough appeared respectively at 200 and 156 BV and the Cu sorption yields before breakthrough were 97.7 and 91.8%. The later breakthrough observed for 2.5 BV h^{-1} was probably due to a much lower initial Cu concentration of 79.1 mg L^{-1}, whereas it was 104 mg L^{-1} at 2.0 BV h^{-1} experiment, and 123 mg/L at 3.0 BV h^{-1}. The Cu sorption yields (the amount of Cu sorbed in the column relative to the amount of Cu introduced in the influent of the column) at 2.0 and 2.5 BV h^{-1} were very good (≥97%), whereas it was lower (92%) at 3.0 BV h^{-1}. Thus 2.0 and 2.5 BV h^{-1} flow rates were more suitable for Cu sorption at a pilot scale from copper-treated wood leachate.

3.2.4 Resin elution at lab and pilot scale

Ammonium hydroxide and monoethanolamine were used as eluents at the lab scale for Cu elution from the resin Dowex™ M4195. The cumulative Cu eluted from the resin relatively to the amount of Cu sorbed previously in the column is presented in Figure 3. The eluent flow rate used on the lab scale was 5 BV h^{-1}. Both amines were very efficient and allowed for 97.5% and

105.5% of Cu elution with NH_4OH and MEA, respectively. A result over 100% was not expected but can be explained by the way the efficiency was calculated. The amount of Cu absorbed in the column was not measured directly, but it was instead calculated theoretically, using the Cu concentration measured during the previous fixation experiment. The calculations did not take account for potential traces of Cu remaining in the resin bed prior to the fixation nor for potential Cu on wood particles trapped at the column entrance. Copper elution reached its plateau at 3.8 and 4.6 BV with NH_4OH and MEA respectively. NH_4OH allowed for a slightly quicker elution, but MEA elution was interesting as it produced a Cu-MEA solution which could possibly be reused easily for ACQ or CA wood treatment.

Pilot scale elution was conducted with sulfuric acid and MEA at 1.5 BV h^{-1} in the larger column. The results are also presented in Figure 3. Elution profiles were similar to the lab scale results. Elution efficiencies were 99.8 and 104.6% with MEA and H_2SO_4, respectively, and the plateau appeared at 3.8 BV with MEA. With H_2SO_4, the plateau was not well defined but because the efficiency was over 100% at 7.5 BV, we can suspect that the plateau was reached. Both MEA and H_2SO_4 were very good for Cu elution from resin M4195 and for recovery of Cu. Sulfuric acid is of interest for use as an eluent because it is inexpensive and produces the easily reused copper sulfate. On the other hand, elution with MEA generated a Cu-MEA solution reusable for ACQ or CA wood treatment. The copper concentration in the elution solution at the plateau at 3.8 BV was 6.96 g L^{-1}.

3.3 Copper recovery by electrodeposition

Electrodeposition, or electrolytic deposition, is another interesting technology, especially in Quebec where electricity costs are low. As environmental regulations became more stringent regarding effluent discharge during the past two decades, electrodeposition was rapidly developed for wastewater treatment applications (Chen, 2004). Electrodeposition, also called electroplating in the metal finishing industry, is based on the reduction of metals in solution. Electric current is applied in the electrochemical reactor and forces the reduction of metal species. The solid metal produced is deposited on the cathode, where the reduction occurs. The solid metal can then be collected and easily recycled. Various electrochemical wastewater treatment technologies have been developed for Cu recovery (Evans et al., 2005; Stern, 2006) based on the standard Cu^{2+}/Cu redox potential of +0.34 V. Electrodeposition was used successfully in a previous study for Cu recovery from CCA-treated wood leachate (Janin et al., 2017). However, the presence of co-preservatives required the removal of arsenic by precipitation before electrodeposition. Another objective of this study is to assess Cu recovery efficiency from raw CA- and ACQ-treated wood leachates without preliminary treatment steps. Direct electrodeposition of Cu would reduce the effluent treatment cost and possibly increase the profitability of recycling treated wood waste.

The following part of this study assesses the efficiency of Cu electrodeposition from copper-treated wood leachate in batch mode (2 L), and then, at pilot scale with 60 L of effluent.

3.3.1 Electrodeposition of copper in batch mode

Batch electrodeposition experiments were carried out for 90 min at current intensities ranging from 1 to 10 A. Figure 4 presents the residual Cu concentration in the reactor along the 90 min test periods with stainless steel electrodes. The Cu recovery efficiency ranged between 61.8 to 91.6%, going from 121 mg L^{-1} initial concentration to 46.2 mg L^{-1} at 1 A and to 10.4 mg L^{-1} at 10 A after 90 min. All the Cu deposition curves rapidly and steadily decreased, but the intensity had a large impact on the deposition efficiency. Figure 5 presents the progress of the % recovery yield (R_R) as well as the % faradic yield (R_F) over a current range of 1 to 10 A. The Cu recovery yield represents the ratio of deposited Cu relative to the solubilized Cu in the effluent available for deposition. R_F represents the amount of electrons actually used for Cu reduction relative to the amount of electrons provided to the system.

The recovery yield increased with increasing intensity, while the R_F decreased with increasing intensity as more electrons were provided to the system. Overall, the R_F was generally low and varied from 1.2 to 8.4% in this study. A low R_F is due to parasitic reactions such as water hydrolysis that are hard to avoid. However, more complex electrodeposition cells have been designed to decrease the parasitic reactions and increase the faradic efficiency. A future study on the industrial applicability of this process will look into improving the design of the electrolytic cell.

The market price of copper was 6.13 US\$ kg^{-1} as of August 8, 2018 while the cost of electricity in Quebec was 0.06 US\$ kWh^{-1}. These data were used to compare the cost of electricity strictly required in the electrodeposition cell with the value of the deposited Cu at various intensities. The results are presented in Figure 6. It was observed that above 5 A the cost of electricity was higher than the value of Cu deposited. Hence, there would be no financial interest in doing electrodeposition above 5 A. As for many recovery processes, a compromise should be reached between efficiency and economic feasibility. A current of 3 A was chosen in this study as the appropriate intensity for a continuous experiment. This condition allowed for 78% recovery of Cu with a R_F of 2.1% after 90 min. A comparative experiment at 3A and 90 min was carried out with copper cathodes. This latter experiment with copper electrodes led to better results than stainless steel electrodes, with recovery yields of 86% compared to 78% for stainless steel. Copper deposition on copper electrodes is better for recovery and was used for the following continuous experiment.

3.3.2 Electrodeposition of copper in continuous mode

Copper electrodeposition was conducted in continuous mode in the tank cell at an intensity of 3 A as identified in the previous batch study. The Cu concentration in the effluent of the electrodeposition cell during the 47 h of treatment is presented in Figure 7. A volume of 68 L of effluent was passed through the cell, with a retention time of 82 min. The Cu concentration decreased quickly in the first 20 L of treated effluent and then stabilized. The average Cu concentration in the effluent, from 20 L to the end of the experiment, was 34.8 mg L^{-1}. Copper recovery yield is also presented in Figure 7. The Cu deposition increased quickly up to 20 L of effluent passed through the cell then it plateaued around 57% of Cu deposition. The R_F (not shown) varied between 1.8 and 2.0%. This is close to the result obtained from the batch study. Again, this is low and can be enhanced by optimizing the design of the electrolytic cell.

3.4 Economic analysis

The final objective of this study is to use the data collected in the laboratory to evaluate operating costs to compare the applicability of the two technologies, ion exchange and electrodeposition, for treatment of the CA- and ACQ-treated wood leachates on an industrial scale.

The economic analysis was completed using the same model as developed for a previous study (Coudert et al., 2013a). The treatment steps included three leaching steps of 160 min each, with sulfuric acid at 0.13 N, and three rinsing steps with tap water at room temperature for 5 min each. Cost of natural gas used was calculated for drying of the remediated wood chips down to 8% humidity. The analysis accounted for countercurrent water and sulfuric acid recirculation as described in Janin et al. (2012c). The model was adapted for leachate treatment either by ion-exchange with Cu recovery as Cu-MEA solution for reuse in wood treatment or by electrolytic treatment with recovery as solid Cu. The plant capacity was accounted as 100 000 ttw yr^{-1}.

3.4.1 Ion exchange technology

Ion exchange conditions used in the economic analysis reflected the results obtained during the column experiment: an exchange capacity of 18.6 mg Cu g^{-1} resin, a contact time of 30 min (2 BV h^{-1}), a Cu recovery efficiency of 98% (99% Cu was adsorbed, from which 99% was eluted), elution with 3.8 BV at 1.5 BVh^{-1} of a 2 M MEA solution generating a 6.97 g Cu L^{-1} solution. The life time of the resin was conservatively assumed to be 400 cycles based on discussion with manufacturers. The cost of Dowex™ M4195 was 240 US$ kg^{-1} (cost obtained from the manufacturer), the cost of MEA solvent was 1.6 US\$ kg^{-1} and the value of Cu in a Cu-MEA solution was 7.7 US\$ kg^{-1}.

3.4.2 Electrodeposition technology

Electrodeposition conditions in the model were set as follow: retention time of 90 min, with 3 A intensity. The recovery yield of Cu was assumed to be 77% as observed during the batch study instead of 57% as observed during the continuous study. This choice was made as it was in better accordance with the efficiencies observed in the industry with optimized reactors. The value of Cu was 6.13 US\$ kg^{-1} value and the cost of electricity 0.05 US\$ kWh^{-1}.

3.4.3 Ion exchange and electrodeposition comparison

Table 4 presents the results of the economic analysis for leaching and rinsing of the CA and ACQ treated wood with effluent treatment by ion-exchange or electrodeposition. The costs are given per ton of treated wood (US\$ ttw^{-1}). Wood treatment cost was the same for both scenarios. However, cost of effluent treatment varied a great deal. Operating cost of electrodeposition was 34 US\$ ttw^{-1}, whereas it was 207 US\$ ttw^{-1} for ion-exchange. The higher cost was due to the use of MEA for elution; however, after the treatment MEA can be sold as a Cu-MEA solution used in the wood treatment industry (estimated 152 US\$ ttw^{-1} revenue). The model accounted for a 10% loss during the process (hence selling only 90% of the initially used MEA). The electricity cost for the process including electrodeposition was 11.6 US\$ ttw^{-1} (against 3.8 US\$ ttw^{-1} for ion exchange). Revenue came from the sale of the remediated wood chips (120\$ ttw^{-1}), the fee for waste disposal (30 US\$ ttw^{-1}), recovered Cu sale (6.13 \$ kg Cu^{-1}) and MEA sale if any. Overall, decontamination with the electrodeposition process seemed more economically profitable with 65 US\$ ttw^{-1} compared to decontamination with ion exchange process which allowed a benefit of 37 US\$ ttw^{-1}.

4 Conclusion

Treated wood inevitably reaches the end of its life. The copper-treated waste woods, like CA- and ACQ-treated wood, are usually disposed of in construction and demolition landfill as a waste. However, this waste can be converted into valuable products. A process demonstrated previously allows efficient Cu removal (95%) from the wood and, hence, wood recovery. This study showed that it is possible to recover Cu efficiently by ion-exchange (98% Cu recovery) or electrochemical treatment (78% Cu recovery) and to generate a value out of this step. Copper can be recovered either as solid Cu (higher market value) or as a Cu-MEA solution which can be reused for ACQ wood treatment. The economic analysis of the recycling process demonstrates that recycling of such waste can be profitable. This is a good argument for further development of the technology as well as for its implementation in North America.

Acknowledgments

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Nomenclature

ACQ	Alkaline copper quaternary
b	Langmuir constant
BV	Bed volume
CA	Copper azole
CCA	Chromated copper arsenate
DOC	Dissolved organic carbon
ICP-AES	Inductively coupled plasma – Atomic emission spectroscopy
IR120	Amberlite™ IR120
m and n	Freundlich coefficients
M4195	Dowex™ M4195
MEA	Monoethanolamine
n	Number of exchange electron for metal reduction
Q_{abs}	Quantity of Cu sorbed at equilibrium
Q_{max}	Maximum quantity of Cu which can be sorbed
R_F	Faradic yield
R_R	Cu recovery yield
TP207	Lewatit® TP207
ttw	Metric ton of treated wood

List of figure captions

Figure 1.	**Residual Cu concentration after sorption using various amounts of resins (Dowex™ M4195, Amberlite™ IR120 and Lewatit® TP207) from a) ACQ- and b) CA-treated wood leachate**
Figure 2.	**Cu fixation curves on M4195-filled columns at lab scale (30 mL BV column) and pilot scale (240 mL BV column) at various flow rates. $[Cu]_i$ were 139 mg L^{-1} for lab scale at 2 BV h^{-1}, 136 mg L^{-1} for lab scale at 10 BV h^{-1}, 148 mg L^{-1} for lab scale at 20 BV h^{-1}, 129 mg L^{-1} for pilot scale at 1.5 BV h^{-1}, 104 mg L^{-1} for pilot scale at 2 BV h^{-1}, 79 mg L^{-1} for pilot scale at 2.5 BV h^{-1} and 123 mg L^{-1} for pilot scale at 3 BV h^{-1}**
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Figure 6.	**Comparison of the value of Cu recovered by electrodeposition with the cost of electricity in function of the intensity applied in the electrochemical cell after 90 min for the treatment of 1 m^3 of leachate (Electricity cost of 0.06 US$ kWh^{-1})**
Figure 7.	**Cu concentration in effluent from the continuous electrodeposition treatment as well as the Cu recovery yield ($[Cu]_i$ = 80 mg L^{-1})**

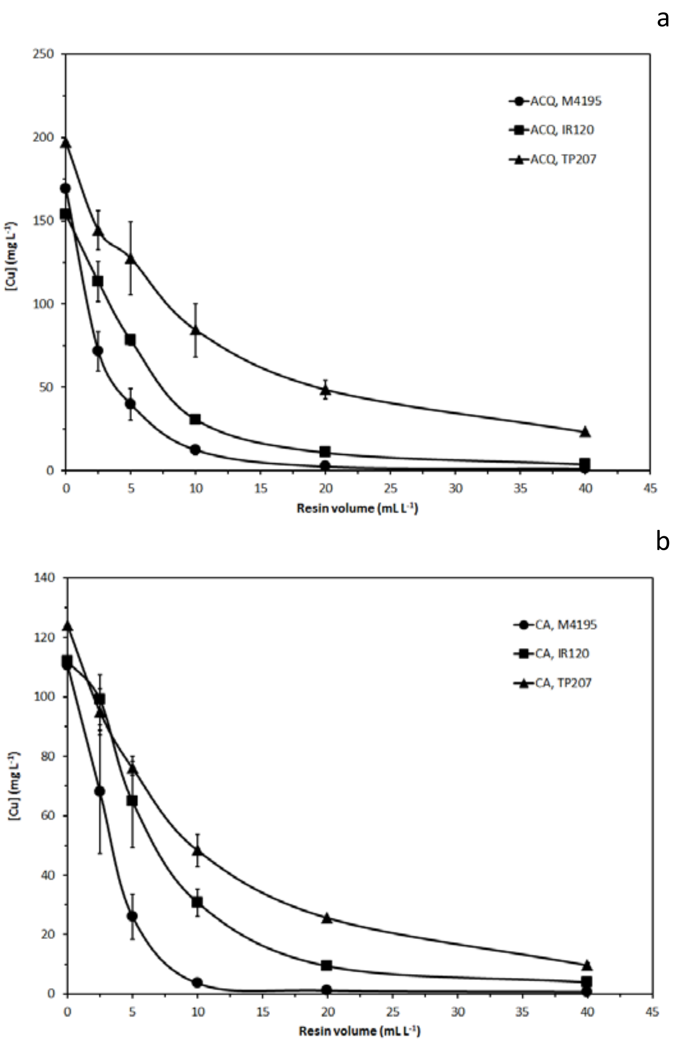
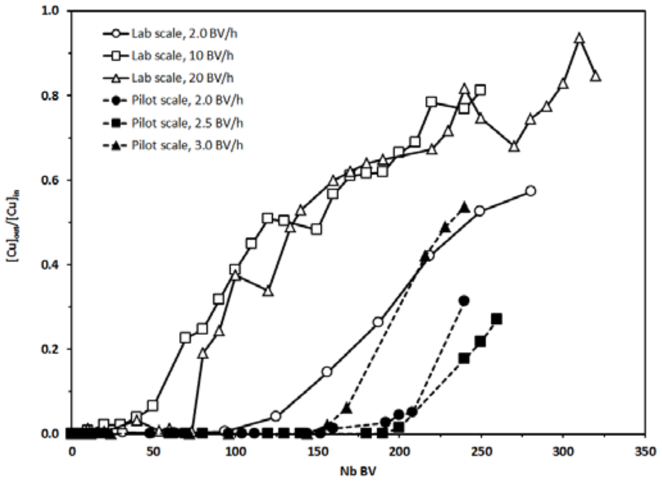

a
[Cu] (mg L^{-1})
250
200
150
100
50
0
Resin volume (mL L^{-1})
0
5
10
15
20
25
30
35
40
45
ACQ, M4195
ACQ, IR120
ACQ, TP207
b
[Cu] (mg L^{-1})
140
120
100
80
60
40
20
0
Resin volume (mL L^{-1})
CA, M4195
CA, IR120
CA, TP207

Fig. 1



1.0
0.8
0.6
0.4
0.2
0.0
$[Cu]_{out}/[Cu]_{in}$
0
50
100
150
200
250
300
350
Nb BV
Lab scale, 2.0 BV/h
Lab scale, 10 BV/h
Lab scale, 20 BV/h
Pilot scale, 2.0 BV/h
Pilot scale, 2.5 BV/h
Pilot scale, 3.0 BV/h

Fig. 2

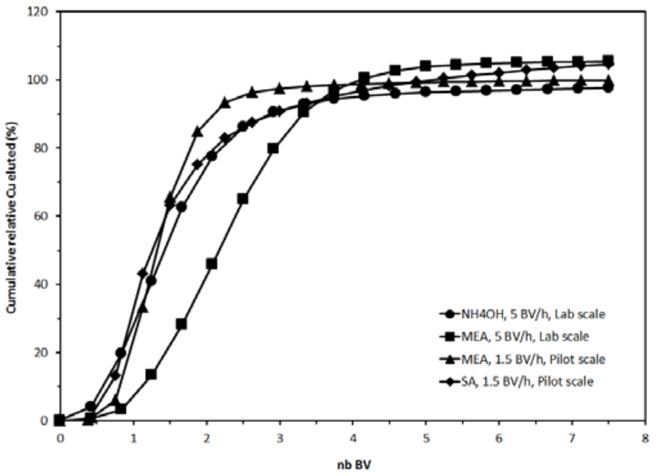
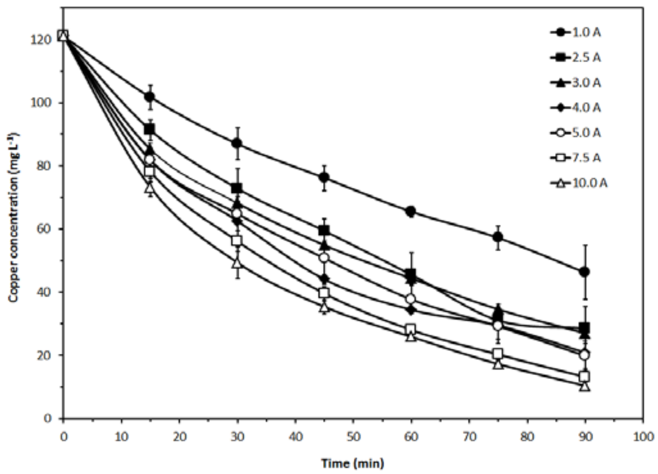

120
100
80
60
40
20
0
Cumulative relative Cu eluted (%)
0
1
2
3
4
5
6
7
8
nb BV
●NH4OH, 5 BV/h, Lab scale
■MEA, 5 BV/h, Lab scale
▲MEA, 1.5 BV/h, Pilot scale
◆SA, 1.5 BV/h, Pilot scale

Fig. 3



1.0 A
2.5 A
3.0 A
4.0 A
5.0 A
7.5 A
10.0 A
Copper concentration (mg L⁻¹)
0
20
40
60
80
100
120
Time (min)
0
10
20
30
40
50
60
70
80
90
100

Fig. 4

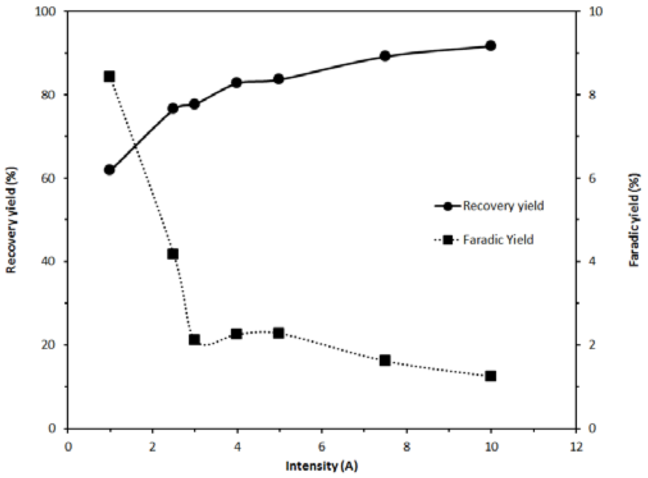

100
80
60
40
20
0
Recovery yield (%)
10
8
6
4
2
0
Faradic yield (%)
0
2
4
6
8
10
12
Intensity (A)
Recovery yield
Faradic Yield

Fig. 5

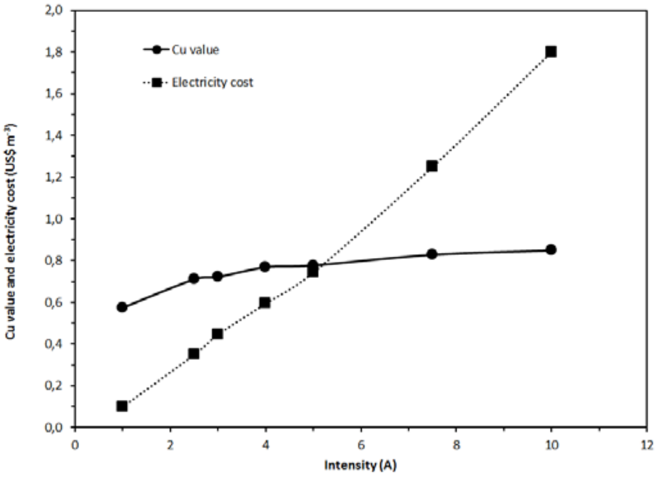

Cu value
Electricity cost
Cu value and electricity cost (US$ m⁻³)
2,0
1,8
1,6
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
0
2
4
6
8
10
12
Intensity (A)

Fig. 6

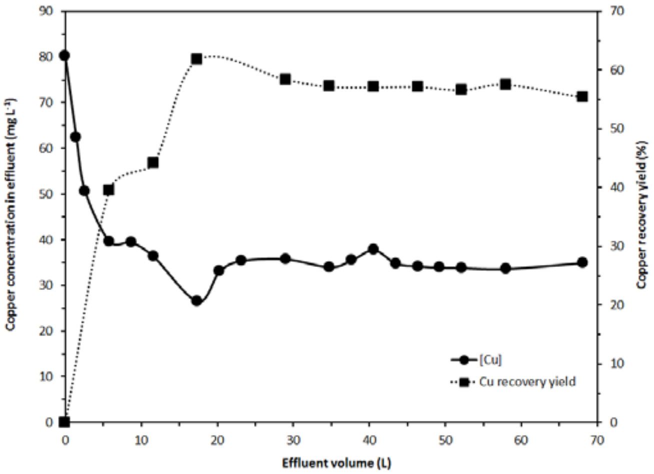

Copper concentration in effluent (mg L⁻¹)
0
10
20
30
40
50
60
70
80
90
Copper recovery yield (%)
0
10
20
30
40
50
60
70
Effluent volume (L)
0
10
20
30
40
50
60
70
[Cu]
Cu recovery yield

Fig. 7

Table 1 **Characteristics of the resins used in this study according to the manufacturers, except density which was measured experimentally**

Resin	**Amberlite IR120**	**Dowex M4195**	**Lewatit TP207**
Type	Cationic	Chelating	Chelating
Functional group	Sulfonic acid	Bis-picolylamine	Imminodiacetic acid
Bead size (mm)	0.30 - 1.18	0.37 - 0.84	0.4 - 1.25
Physical form	Amber/brown	Tan/green	Off-white
Ionic form as used	H^+	H^+	Na^+
pH range	0 - 14	n.a.	1.5 - 9
Experimental density (mg mL^{-1})	1.13	1.07	1.11
Theoretical exchange capacity (meq mL^{-1})	2.0	0.7	2.2

n.a.: not available

Table 2 **Initial and final copper contents in the ACQ- and CA-treated wood samples and copper removal yields**

Resin	Treated wood	
	ACQ	CA
Initial Cu content (mg/kg)	1 890 ± 100	1 190 ± 170
Final Cu content (mg/kg)	89.6 ± 22.8	48.7 ± 13.6
Cu removal (%)	95.2 ± 1.4	95.7 ± 1.6

Table 3 **Langmuir and Freundlich isotherms R^2 and constants ($[Cu]_i$ in ACQ leachate were 170 mg L^{-1} for M4195, 154 mg L^{-1} for IR120 and 197 mg L^{-1} for TP207; $[Cu]_i$ in CA leachate were 111 mg L^{-1} for M4195, 112 mg L^{-1} for IR120 and 124 mg L^{-1} for TP207)**

Leachate	Resin	Langmuir (R^2)	Langmuir constant (*b*) (L $mmol^{-1}$)	Q_{max} (mmol g^{-1})	Theoretical capacity (mmol g^{-1})	Freundlich (R^2)	Freundlich *n* coefficient	Freundlich *m* coefficient
ACQ	M4195	0.983	7.72	0.51	0.65	0.978	0.5055	4.26
	IR 120	0.992	3.99	0.31	1.77	0.987	0.4858	2.14
	TP 207	0.948	1.08	0.19	1.98	0.992	0.6358	0.47
CA	M4195	0.977	11.86	0.39	0.65	0.903	0.4073	4.29
	IR 120	0.996	5.33	0.15	1.77	0.903	0.3959	1.59
	TP 207	0.983	1.75	0.19	1.98	0.999	0.5833	0.68

Table 4 **Economic analysis of the ACQ and CA-treated wood decontamination process with either ion exchange or electrodeposition**

Description		**Decontamination followed by**	
		Electrodeposition (US$ ttw^{-1})	**Ion-exchange (US$ ttw^{-1})**
Direct operating costs			
Chemicals			
Sulfuric acid	(51 kg ttw^{-1} x 0.08 \$ kg^{-1})	4.1	4.1
Dowex M4195	(0.05 kg ttw^{-1} x 240 \$ kg^{-1})	0.0	11.9
MEA	(105.5 kg ttw x 1.6 \$ kg^{-1})	0.0	168.8
Labor	(0.24 h ttw^{-1} x 25 \$/h + 15% supervision)	6.8	6.8
Electricity	(0.05 \$ kWh^{-1})	11.6	3.8
Process water	(Process water is recirculated)	0.02	0.02
Natural gas	(0.84 MBtu ttw^{-1} x 3\$ MBtu^{-1}))	3.4	3.4
Maintenance and other operation fees		8.0	8.6
Total direct operating costs		33.9	207.4
Capital costs			
Total investment cost		(38.0 M US\$)	(36.1 M US\$)
Annual interest charges	(4% yr^{-1})	20.3	19.3
Depreciation	(15-yr equipment lifetime)	25.3	24.1
Other administrative fees		8.7	12.0
Total capital costs		54.3	55.4
Revenues			
Remediated wood chips sale	980 kg ttw^{-1} x 0.12 \$ kg^{-1}	117.6	117.6
Management of treated wood waste	30 \$ ttw^{-1}	30	30
Cu valorisation	0.10 kg Cu ttw $^{-1}$ as Cu-MEA solution or 0.97 kg Cu ttw^{-1} as pure Cu	5.95	0.64
MEA revalorisation	90% of MEA sold as Cu-MEA solution	0.0	151.9
Total revenues		153.6	300.1
Total	(gross profit)	65.4	37.3

Highlights

- A sulfuric acid leaching process was tested at pilot scale for removing copper from ACQ- and CA-treated wood waste.
- More than 95% of the initial copper presents in the treated wood was removed.
- Ion-exchange and electrodeposition techniques were used to recover copper presents in the acidic leachate.
- Economic analyses of the process showed that the copper extraction and recover from the treated wood can be profitable.