SCALE-UP OF A CHEMICAL LEACHING PROCESS FOR DECONTAMINATION OF CCA-TREATED WOOD WASTE

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Summary

This study intended to develop the scale-up of a sulphuric acid process for extracting . CCA components from waste treated wood. Various durations of wood leaching with 80 L of 0.1 M sulphuric acid solution at 75°C with 15 kg of CCA-treated wood were tested. Three leaching steps of 2 h gave the best results (99% removal of As and Cu and 96% removal of Cr). After decontamination, the wood contained 26 ± 13 mg As/kg, 280 ± 110 mg Cr/kg and 15 ± 5 mg Cu/kg. The reproducibility of the process was high; hence the experimental setup was applicable. Moreover, the results of leaching obtained at pilot scale were very similar to the results obtained at lab scale. Wood decontamination produced leachate containing 63 to 745 mg As/L, 75 to 773 mg Cr/L and 27 to 524 mg Cu/L. The precipitation of the leachate with sodium hydroxide and ferric chloride at the pilot scale allowed almost complete metals removal and the final effluents contained less than 1 mg/L of arsenic and less than 5 mg/L of chromium and copper.

1. Introduction

CCA preservative was widely used for treatment of residential and industrial wood products as it protects the wood against decay, insects and weathering degradation when used for exterior applications. CCA was voluntarily withdrawn in Canada for treatment of residential products in December 2003 (Pedersen et al. 2005). However, much of the treated wood remaining in service is treated with CCA and it is still an important preservative for treatment of commercial/industrial products such as poles. Hence, the volume of discarded CCA-treated wood waste is actually increasing. This material is disposed of in landfill or burning facilities; however toxic metals dispersion is an issue (Jambeck et al., 2007; Solo-Gabriele and Townsend, 1999; Song et al. 2006). There is considerable industry and regulatory interest in finding appropriate technologies to manage these waste materials. Landfill costs are high and are actually rising as the landfill space becomes limited. Previous studies identified a process involving sulphuric acid leaching for metals removal from the discarded CCA-treated wood (Janin et al. 2009a,b; Janin et al. 2008). It includes chemical treatment of the wood and of the effluent containing the contaminants. This process was successfully tested at lab scale; it appeared efficient and possibly economically viable. Hence, it is interesting to evaluate this process at a larger scale. The objective of this study was to test wood leaching and leachate precipitation at an 80 L scale and to compare it with a lab scale test.

2. Methodology

Various samples of CCA-treated wood were collected from Hydro-Québec (IREQ, Varennes, QC, Canada) and Stella Jones (Delson, QC, Canada). An unweathered sample was collected in 2005 in Stella Jones (CCA 2005) while a 1 year weathered sample (CCA 2008) was collected from Hydro-Québec. All samples were wood pole sections (4 to 6 feet long). "CCA 2005" sample was ground directly whereas "CCA 2008" pole sections were first cut into 15 cm thick slices using a chain saw. Then, each individual slice was sectioned again in order to remove the untreated core of the pole. Then, the treated wood pieces were ground first to generate 10 to 200 mm particles. Finally, the wood chips of the three samples were sieved through 12 mm wire mesh and < 12 mm wood chips were used for the decontamination tests.

At the lab scale, the leaching and rinsing steps were completed in 500 mL baffled shaker flask (Cole Parmer, Montréal, QC, Canada). 30 g of sieved wood was mixed with 200 mL of leaching solution. The leaching solutions were prepared using analytical grade sulfuric acid diluted in deionised water to 0.1 M. The flasks were stirred at 150 rpm in a temperature-controlled water bath at 75°C during a 2-h period. The flasks were fitted with a cork to prevent evaporation. Solid/liquid (S/L) separation was carried out using a vacuum filtration system on Whatman 934-AH glass fiber (1.5 µm pore size) membranes.

At pilot-scale, the leaching and the rinsing steps were conducted in a 130-L capacity 316-stainless steel tank. The lid was truncated to allow coverage of the tank while the impeller and shaft were immersed in the tank. The 192 in-oz torque Lightning Batch Mixer was used at 70 rpm for wood and liquid mixing with a 23 cm diameter axial flow impeller. Heat was provided by an E20-SP Garland electric stock pot heater. 12 kg of wood was added to the 80 L of 75°C tap water. Rinsing step was conducted similarly with 80 L cold tap water. Tap water and wood were mixed for 15 min using the axial flow impeller. After the leaching or the rinsing, the liquid was removed by pumping (1" Elima-Matic Bolted Pump with 6.8 m^3/hr flow rate capacity). A stainless steel sump filter was added to the inlet tube to avoid pumping the wood. However, this sump filter tended to become fouled and required regular wood removal from its surface. Remaining leachate and wood were transferred into a Plexiglas drainer with glass fiber screen and allowed to dry overnight.

At the pilot scale, the leachate treatment consisted of precipitation-coagulation. This treatment was conducted in a 136 L settler tank with cone-shaped bottom and sludge outlet. Ferric chloride (131.5 g Fe/L, $FeCl_3$, Laboratoire Mat, Québec, QC, Canada) was added to the leachate or to the rinsing water and mixed with a RZR 2020 Heidolph mixer with 12.7 cm impeller. Sodium hydroxide (100 g NaOH/L) was added using a peristaltic pump while pH was measured using a Fisher Acumet handheld pH meter (Fisher Scientific, ON, Canada). When pH approached 7, the solution was homogenised for about one hour until the pH stabilized. Afterward, the mixer was stopped and the polymer Magnafloc 10 (Ciba Specialty Chemicals Canada, Mississauga, ON, Canada) was added to the solution as a1 g/L solution. The mixture was stirred very slowly for 1 min then allowed to settle overnight. The sludge settled in the cone-shaped bottom. The supernatant was collected by pumping from the top while the sludge were collected using the bottom outlet. Samples were collected from the sludge and the supernatant for analysis.

Soluble metals were analyzed using a Vista-AX CCO with a simultaneous inductively coupled plasma atomic emission spectroscopy (ICP-AES) apparatus manufactured by Varian (Palo Alto, CA, USA). Metal concentrations in treated wood were determined by ICP-AES after digestion with analytical grade nitric acid (50% w/w, 20 mL) and hydrogen peroxide (30% w/w, 10 mL) (Method MENVIQ.89.12/213.Mét 1.3). A 1.0 g (dry mass) sample of wood was digested. Each wood sample was digested in triplicate to get an average metal concentration value. Quality controls were also performed with certified liquid samples (multi-element standard, catalogue number 900-Q30-002, lot number SC0019251, SCP Science, Lasalle, QC) to ensure conformity of the measurement apparatus.

3. Results and discussion

The characteristics of the three wood samples and the metal contents are presented in Table 1. As explained in the methodology, the untreated core of the pole was removed from the 2008 CCA samples whereas the 2005 sample included the treated and untreated section of the log. This might explain the slightly lower metals concentrations observed in the CCA 2005 sample. It contained 5 230 ± 120 mg As/kg, 5 310 ± 70 mg Cr/kg and 2 620 ± 210 mg Cu/kg of dry wood. The 2008 CCA sample had higher metal content: 5 397 ± 618 mg As/kg, 6 478 ± 864 mg Cr/kg and 3 445 ± 405 mg Cu/kg. The moisture content was 18.4 ± 2.0% for the oldest wood and 24.2 ± 0.8% for the newest wood.

Table 1 Initial characteristics of the CCA-treated wood used for the pilot scale and lab scale experiments

Treatment year	Moisture content (%)	Metal content (mg/kg)		
		As	Cr	Cu
2005	20.8 ± 0.0	5 230 ± 120	5 310 ± 70	2 620 ± 210
2008	24.2 ± 0.8	5 397 ± 618	6 478 ± 864	3 445 ± 405

A previous lab scale study identified the optimal duration of the leaching step with sulphuric acid being 6 h. It was observed at lab scale that as well as duration, the number of steps was important. Hence, one of the objectives of this work was to test one leaching of 6 h duration, two leaching of 3-h duration each and finally three leaching steps of 2-h duration in the 130 L tank. The results are presented in Table 2. As expected, the remaining metal contents clearly decreased with increasing number of leaching steps. Arsenic content was 103 ± 62 mg/kg after one leaching step of 6 h, whereas it decreased to 95 ± 46 mg/kg and 26 ± 13 mg/kg after, respectively, two leaching steps of 3 h and three leaching steps of 2 h each. The same tendency was observed for chromium

(572 ± 221 mg/kg, 544 ± 64 mg/kg and 280 ± 110 mg/kg after three leaching steps) and copper (48 ± 11 mg/kg, 48 ± 8 mg/kg and 15 ± 5 mg/kg after three leaching steps). In fact, each leaching step provided fresh acid which helped splitting of the metal-to-wood bonds and fresh water which allowed dilution and metals to diffuse out of the wood pores. The three step leaching process was clearly more efficient than the single 6-h leaching process.

Table 2 **As, Cr and Cu contents in the remediated wood after 1, 2 or 3 leaching steps at pilot scale with average values and standard variations (CCA 2008 sample, leaching with 0.1 M H_2SO_4 and 15% slurry density at 75°C, followed by three rinses)**

Assays	**Leaching conditions**	**Metal content (mg/kg)**		
		As	**Cr**	**Cu**
P1	1 x 6 h	147	728	56
P2		59	415	40
Average (P1-P2)		103 ± 62	572 ± 221	48 ± 11
CV (%)		60	39	24
P3	2 x 3h	147	728	56
P4		59	415	40
P5		79	489	49
Average (P3-P5)		95 ± 46	544 ± 164	48 ± 8
CV (%)		49	30	17
P6	3 x 2h	11	154	9
P7		34	335	17
P8		32	352	19
Average (P6-P8)		26 ± 13	280 ± 110	15 ± 5
CV (%)		50	39	35

Reproducibility is an important characteristic of a process and usually, it is especially sensible to scale up the process. It was necessary to check for affordable reproducibility with the pilot scale setup in order to build confidence with further results. The measurement of the metal contents in wood, the averages, the standard deviations and the coefficient of variation are presented in Table 2. As expected, the standard deviations were largely higher than the variations obtained at small scale (results not shown) and are between 49 and 60% for arsenic, 30 to 39% for chromium and 17 to 35% for copper. This was simply due to the fact that the operator had lower control on the experimental conditions at pilot scale than at lab scale, especially on the stirring and on the temperature. Arsenic variation was higher than that of chromium, which was itself higher than copper variation. This is in accordance with the results of the previous study, which attested for a greater influence of the leaching temperature on arsenic and chromium solubilisation from the wood using sulphuric acid. Chromium, and more specifically arsenic were more difficult to solubilise from the wood than copper. Hence copper has less variation of the leaching parameters.

Moreover, the results of the three assays P3 to P5 which included two leaching steps were more reproducible and had lower relative variation (49%, 30% and 17% variation for As, Cr and Cu respectively) than the results of the P6 to P8 assays which included three leaching steps (50%, 39% and 35% variation). In fact, increasing the complexity of the process usually lowers reproducibility. Higher variation of the P6-P8 results came from the higher number of leaching steps. However, the results of the three leaching decontamination tests P6 to P8 assays still offered good results, with acceptable standard deviations; therefore the experimental setup used for those experiments was acceptable.

The evolution of arsenic, chromium and copper contents in the wood during the process are presented in Figure 1. Metals contents decreased rapidly during the first and second leaching steps. Most of the metals are solubilised in presence of sulphuric acid whereas the rinsing steps are used as a finishing treatment to extract the metals solubilised during the leaching steps. Finally, the removal of arsenic was 99.5% in average. It was 95.7% for chromium and 99.6% for copper.

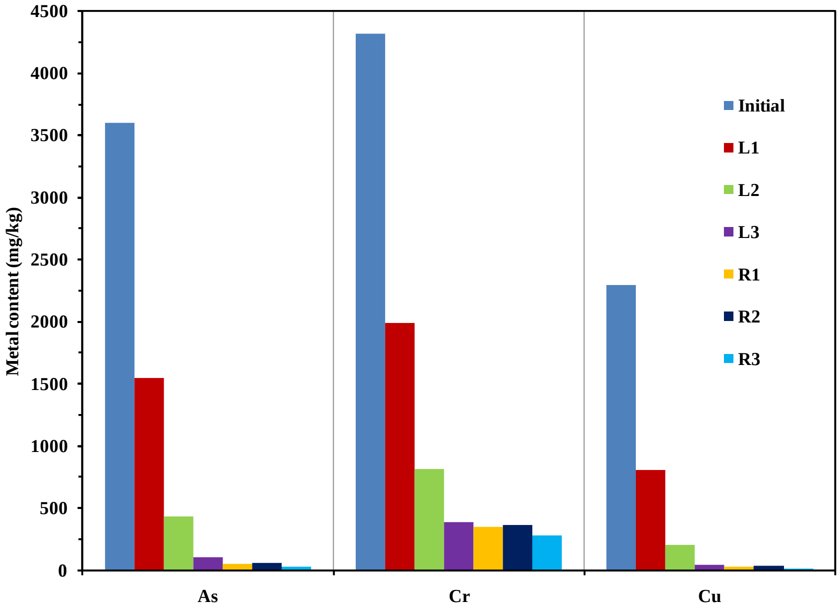

Figure 1 **Arsenic, chromium and copper content in the wood after each step of the process (average values, P6 to P8 assays : 3 leaching of 15 kg wood during 2h with 80L of 0.1 M H_2SO_4 solution, at 75°C followed by 3 rinses with 80L tap water at room temperature)**

The scale-up of a process inevitably required comparison between the lab scale results and the pilot scale results (Euzen, Trambouze and Wauquier, 1993). Table 3 presents the metals contents in leachate, rinsing water and in the final wood during the decontamination process lab scale and at pilot scale. This table compares the two kinds of experiment although wood sample used for lab scales assays was CCA 2005 whereas CCA 2008 was used for the pilot scale assays. The two wood poles were ground differently and initial metals contents in wood were different. However, in both experimental setups, the metals solubilisation performances were similar. Removal yields of arsenic were 99.7% and 99.5% at lab and pilot scale respectively, 92.4% and 95.7% for chromium and 98.8% and 99.6% for copper. In lab scale assays, the first leaching step released, in average, 151 mL of leachate containing 578 mg As/L, 533 mg Cr/L and 380 mg Cu/L. In the pilot scale assays, the volume was on average 53 L with concentrations of 745 mg As/L, 773 mg Cr/L and 524 mg Cu/L. Higher metals concentration in leachate came from higher metal content in wood. In both setups, most of the metals were removed from the wood in the first leaching step. At lab scale, solubilisation from the first step represented 70% to 75% of the total amount of metals solubilised. Similarly, it represented 67% to 74% at pilot scale. Results of both setups were comparable.

Leaching of the CCA-treated wood produces leachates which contain high metal concentrations. Previous lab scale assays identified precipitation-coagulation as an efficient technique for arsenic, chromium and copper removal from the leachates, although, the addition of ferric chloride was necessary for arsenic removal. $FeCl_3$ addition, followed by pH increase up to 7 with sodium hydroxide, allowed the production of solid $FeAsO_4.2H_2O$ and the adsorption of arsenic onto solid iron hydroxide, $Fe(OH)_3$ (Janin et al. 2009b). The same technique was applied at pilot scale to the leachate coming out of the first, second or third leaching steps. The results are presented in Table 4. It was observed that precipitation-coagulation was very efficient at pilot scale. The results were similar to what was observed at lab scale. It allowed over 99% removal of the three metals in all leachates. After coagulation treatment, the effluent had arsenic concentration below 1 mg/L and chromium and copper concentration less than 5 mg/L in all effluents. Hence, discharge of those effluents in Québec City urban sewers would be permitted as it respects municipal guidelines (Ville de Québec, 2003).

Table 3 **Metal concentrations in leachates and rinsing waters at lab scale (0.03 kg of CCA 2005 wood sample in 0.2 L) and pilot scale (Assays P6-P8; 15 kg CCA 2008 wood sample in 80 L) as well as metal content and metal removal yields in wood after decontamination**

Metals		**Lab scale (CCA 2005)**			**Pilot scale (CCA 2008)**		
		As	**Cr**	**Cu**	**As**	**Cr**	**Cu**
Initial metal content (mg/kg)		4 762	5 070	2 770	5 397	6 478	3 445
Concentration (mg/L)	1st leaching	578 ± 40	533 ± 36	380 ± 18	745 ± 121	773 ± 103	524 ± 73
	2nd leaching	164 ± 8	162 ± 8	77 ± 1	192 ± 27	197 ± 26	102 ± 15
	3rd leaching	41.6 ± 2.1	48.6 ± 2.7	16.9 ± 0.7	63.2 ± 0.4	75.5 ± 1.3	27.7 ± 2.2
	1st rinsing	2.58 ± 0.28	2.65 ± 0.19	1.19 ± 0.33	10.0 ± 2.7	12.1 ± 3.8	3.59 ± 0.96
	2nd rinsing	0.75 ± 0.21	0.70 ± 0.14	0.26 ± 0.08	3.49 ± 1.02	4.54 ± 1.59	1.19 ± 0.59
	3rd rinsing	0.49	0.49	0.16	1.23 ± 0.25	1.63 ± 0.43	0.32 ± 0.06
Metals in remediated wood (mg/kg)		16	386	32	26 ± 13	280 ± 110	15 ± 5
Metal removal yields (%)		99.7	92.4	98.8	99.5	95.7	99.6

Table 4 **Metal contents in leachates (P6 to P8 assays, 3 x 2 h leaching with 0.1 M H_2SO_4) and in effluents after precipitation with $FeCl_3$ (2.88 g/L for 1st leachate, 1.82 g/L for 2nd leachate and 0.91 g/L for 3rd leachate) and Magnafloc 10 (5 mg/L for 1st leachate and 3 mg/L for 2nd and 3rd leachate)**

Metals		**1st leachate**	**2nd leachate**	**3rd leachate**
Arsenic	Leachate (mg/L)	698 ± 150	223 ± 39	76.1 ± 12.1
	Effluent (mg/L)	0.56 ± 0.48	0.43 ± 0.53	0.16 ± 0.13
	Removal (%)	99.9 ± 0.1	99.8 ± 0.2	99.8 ± 0.1
Chromium	Leachate (mg/L)	690 ± 151	230 ± 39	89.3 ± 11.7
	Effluent (mg/L)	0.62 ± 0.41	0.40 ± 0.44	0.17 ± 0.15
	Removal (%)	99.9 ± 0.1	99.8 ± 0.2	99.8 ± 0.2
Copper	Leachate (mg/L)	467 ± 93	123 ± 23	44.3 ± 12.0
	Effluent (mg/L)	2.37 ± 1.46	0.68 ± 0.38	0.30 ± 0.13
	Removal (%)	99.6 ± 0.1	99.4 ± 0.3	99.3 ± 0.2

4. Conclusions

Preliminary results of the scale-up of the chemical decontamination process for CCA treated wood waste were successful. Lab scale and pilot scale results were comparable, except that reproducibility at larger scale was lower. Efficiency was as high in the 80 L setup as in the 0.2 L setup and led to 99% removal of As and Cu and 96 % removal of Cr. Also, the precipitation-coagulation experiments carried out on the leachates did not seem to be influenced by the size of the equipment, the efficiency was very good (> 99% removal of As, Cr and Cu).Those experiments were interesting, however the complete scale-up development need to go through the decontamination of various samples. Up to now, only one sample has been treated. Further study needs to look at decontamination at pilot scale of samples with varying metals contents and ages in service.

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6. Literature

J.P. Euzen, P. Trambouze and J.P. Wauquier. 1993. Scale-up methodology for chemical processes. Édition Technip, Paris.

J. Jambeck, K. Weitz, H. Solo-Gabriele, T. Townsend, S. Thorneloe, CCA-treated wood disposed in landfills and life-cycle trade-offs with waste-to-energy and MSW landfill disposal, Waste Manag. 27 (2007) 21-28.

A. Janin, J.F. Blais, G. Mercier and P. Drogui (2008) Optimization and economical study of a chemical leaching process for decontamination of CCA-treated wood waste. Canadian Wood Preservation Association 29th meeting, 29 octobre 2008, Vancouver (BC).

A. Janin, J.F. Blais, G. Mercier, P. Drogui, Optimization of a chemical leaching process for decontamination of CCA treated wood, J. Hazard. Mat. 169 (2009a) 136-145.

A. Janin, J.F. Blais, F. Zaviska, P. Drogui, G. Mercier, Selective recovery of metals in leachate from chromated copper arsenate wastes using electrochemical technology and chemical precipitation, Hydrometallurgy 96 (2009b) 318-326.

A.J. Pedersen, I.V. Kristensen, L.M. Ottosen, A.B. Ribeiro et A. Villumsen. Electrodialytic Remediation of CCA-Treated Waste Wood in Pilot Scale. *Eng. Geol.* 77 (2005) 3-4, 331-38.

H. Solo-Gabriele and T. Townsend. Disposal practices and management alternatives for CCA-treated wood waste. Waste Manage. Res. 17 (1999) 378-389.

J. Song, B. Dubey, Y.C. Jang, T. Townsend and H. Solo-Gabriele, Implication of chromium on disposal of discarded CCA- treated wood, J. Hazard. Mater. 128 (2006) 280-288.

Ville de Québec, Règlement sur la quantité et la qualité des eaux usées, Règlement R.V.Q. 416, Québec, QC, Canada, 2004, 19 p. (in French).