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OPTIMIZATION AND ECONOMICAL STUDY OF A CHEMICAL LEACHING PROCESS FOR DECONTAMINATION OF CCA-TREATED WOOD WASTE

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Abstract

Increasing volumes of discarded chromated copper arsenate (CCA)-treated wood requires the development of new treatment and recycling options to avoid wood waste landfill as well as dispersion of contaminants in the environment. This study intends to design an economical chemical leaching process for extraction of arsenic, chromium and copper from CCA-treated wood. Chemical reagent, reagent concentration, solid to liquid ratio, temperature, reaction time and wood particle size were optimized. Sulphuric acid is found to be the cheapest and most effective reagent. Optimum operation conditions are 75°C with 0.2 N H_2SO_4 at 150 g wood/L. 99% extraction of As and Cu and 91% Cr were removed from the wood. Chemical cost has been estimated at 7$/t of dry wood whereas energy is almost cost-free as it is provided by decontaminated wood. Furthermore, the resulting arsenic concentration following a toxicity characteristic leaching procedure (TCLP) is reduced from 6.09 mg/L to 0.82 mg/L. Environmental hazard is greatly reduced, hence decontaminated media could find new applications and be recycled. These results demonstrate the feasibility of chemical remediation. Sulphuric acid leaching is a promising option for CCA-treated wood waste management.

1. Introduction

Worldwide waste volumes increase yearly and their disposal is becoming an issue. Industries are facing global challenge and have to develop new waste management strategies (United Nations 2002). The treated wood industry is not an exception. CCA-treated waste will reach 2.5 million m^3 yearly in Canada in 2020 and 9 million m^3 in USA in 2015 according to Cooper (2003). Discarded CCA-treated wood still contains high metal concentrations (Cooper et al. 2001) but as governmental organisations define treated wood material as non hazardous waste, it typically goes into landfills or is being incinerated. Landfill causes contaminant dispersion through leaching (Jambeck et al. 2007) whereas incineration implies serious considerations of ash disposal and gas emissions (Song et al 2006). Today's research is looking at innovative CCA-treated wood waste management and recycling. An attractive way is by recycling wood and metals separately except for arsenic that does not have any economic value. This option implies

the separation of wood and metals and the reversal of the original CCA fixation mechanism. Numerous studies reported chemical remediation of CCA-treated wood with different solvents. Oxalic acid has been used repeatedly by itself or combined with additional chemical or biological agents. Using oxalic acid with sulphuric acid, phosphoric acid or sodium oxalate led to 98-100% removal of As and 88-100% removal of Cr and Cu from CCA-treated wood reduced to sawdust (Kakitani et al. 2006a,b). Bioxalate obtained by the addition of sodium hydroxide to oxalic acid with pH control leads to an 88-94% removal of the three components (Kakitani et al. 2007). Combining oxalic acid and oxalic acid-producing bacteria, Clausen and Smith (1998) removed 100% and 99% of As and Cu, while this acid used with reagents such as ethylenediaminetetraacetic acid (EDTA) or nitrilotriacetic acid (NTA) also leads to very high extraction performances (Kartal and Kose 2003). EDTA is a well known chelating agent and is frequently used for metal solubilization. Nevertheless, leaching of CCA by EDTA is deceiving and solubilizes less than 40% of As and Cr (Kartal 2003). Kazi and Cooper (2006) chose to use an oxidizing agent as it allows the reuse of Cu(II), As(V) and Cr(VI) in the treated wood industry. Hydrogen peroxide extracts up to 98, 95 and 94% of As, Cr and Cu, respectively. In spite of their extraction efficiency for metals, the complexity of these methods, high chemical consumption and relatively higher treatment cost constitute major barriers to their application at an industrial scale. In remediation and recycling fields, the overall operation fees of the process is a major factor of development at a large scale as high cost can be prohibitive. Hence the objective of this study is to design a high-quality extraction cost efficient leaching process. The goal of this work is to develop an economical process based on sulphuric acid leaching, a potential alternative to CCA-treated wood landfills. In the province of Quebec, landfill costs 60 to 120 US$/t dry wood (Ministry of Environment of Quebec, 2006). The objective is to develop a new environment-friendly process that costs less than 100 US$/t dry wood.

2. Materials and Methods

Wood sampling and preparation

As used treated wood available in waste discarding centres has unknown in-service time and has metal concentrations varying from one log to another it is impossible to obtain large amounts of uniform wood for laboratory purposes. The choice of using relatively new CCA-treated wood has been made to ensure homogeneity of the starting material. CCA type-C treated red pine was obtained from Stella Jones (QC, Canada). The logs were grinded into chips by a log-cutter. Further crushing was achieved in laboratory by a grinder when necessary, and was then sifted through 8, 2 or 0.5 mm sieves. In some cases, characterization experiments only require the treated external circumference of the log. Therefore the chopped wood was separated by color and green pieces were manually picked out. The green particles were then crushed and screened. Only the granulometric fraction of the particles inferior to 0.5 mm was used for characterization tests.

Wood characterization

Metal concentrations in CCA-treated wood were determined by digestion with nitric acid (50% w/w) and hydrogen peroxide (30% w/w). Each wood sample was digested in triplicate to get average metal concentration values.

The metal availability in CCA-treated wood was estimated by two standard leaching tests. The Toxicity Characteristic Leaching Procedure (TCLP) and the Synthetic Precipitation Leaching Procedure (SPLP) were developed by USEPA (USEPA 2002a,b) in order to assess for metal mobility in waste. The TCLP test intends to reproduce leaching conditions in C&D landfill whereas the SPLP test reproduces acid rains and attests for metal mobility when waste is disposed of in open areas. For the two tests, 50 g of wood were placed in 1 L plastic bottles and filled with solvent. Solvents were diluted acetic acid solution in the case of the TCLP test, diluted sulphuric and nitric acid in the case of the SPLP test. Bottles were rotated on an eight-bottle wheel for 24 h. After filtering, the remaining acid solutions were analyzed for As, Cr and Cu concentrations.

Wood remediation treatment

To measure the influence of leaching parameters, a mass of 10 g of sieved wood (2 to 8 mm) was mixed with 200 mL of an acid solution in baffled shaker flasks. The flasks were placed onto an oscillating shaker at 200 rpm for 24 h at 25°C. Liquid/solid separation was carried out using vacuum filtration on glass fibre membranes. Acid concentration, solid content, and temperature were varied one at a time for optimal value identification. Initial conditions were 25°C for 24 h with 50 g/L of 0.5 to 2 mm chipped wood. H_2SO_4 concentrations ranged from 0.002 to 1.00 N. Then total solid (TS) content varied from 25 to 150 g/L using the optimal H_2SO_4 concentration determined previously. Finally a kinetics study was conducted at 25, 50 and 75°C using the optimal acid concentration and wood content selected previously. Temperature in the flasks was controlled by adjusting ambient temperature in the shaker enclosure for 25 and 50°C experiments. For 75°C tests, flasks were stirred in a temperature-controlled water bath. The flasks were corked to prevent liquid evaporation. Final optimization tests intend to measure the influence of granulometry. Leaching with 0.5 to 2 mm grinded wood and 0 to 8 mm wood was conducted. All leaching experiments were carried out in triplicate.

Leaching balance and decontaminated wood characterization

In order to assess the leaching process, final tests were done with measurements of all incomes and outcomes. The leaching operation consisted of three leaching steps and three washing steps. Wood samples were weighted before and after leaching treatment. For each wood sample, water content was calculated in triplicate by measuring the weight before and after drying in an oven at 105°C for 24 h. Volumes and metal concentrations in leachates were also measured. Metal concentrations in wood were determined as well before and after the leaching treatment.

Analytical techniques and economical aspects

Metal concentrations were measured by an ICP-AES. Quality control was performed with certified liquid samples to ensure conformity of the measurement apparatus. TS concentrations were determined according to method 2504B (APHA 1999). The dissolved organic carbon (DOC) was measured by a Shimadzu TOC-5000A apparatus.

The sulphuric acid costs associated with the decontamination of CCA-treated wood were calculated on the basis of the 100 US$/t for a solution at 93% w/w.

3. Results and Discussion

Wood characteristics

As expected, the chemical analysis of CCA-treated wood revealed high metal contents. Concentrations were 5,230 ± 122 mg As/kg, 5,306 ± 73 mg Cr/kg and 2,616 ± 209 mg Cu/kg of wood. A key question in waste management is whether contaminants are easily released from wood when discarded. Results of arsenic release during TCLP and SPLP for various grain size fractions are shown in Table 1. As wood particle size decreased, arsenic release increased. Arsenic concentrations in TCLP tests done with unsorted ground log varied between 4.3 and 9.2 mg/L. In three cases out of four, arsenic concentrations surpassed 5 mg/L meaning that this material would be considered hazardous waste if American Hazardous Wastes Regulations were applied to CCA-treated wood. These results are consistent with those recorded by Townsend et al. (2004). They observed arsenic concentrations in TCLP leachates over 5 mg/L in 11 samples out of 13. This material is clearly hazardous even if unregulated. On the other hand, the same standard tests were carried out with green-sorted wood coming from the external part of the log and grinded under 0.5 mm. These tests simulate the slow degradation of logs when discarded. As wood logs age, decomposition arises from the external part of the wood that is, from the highest As, Cr and Cu containing log fraction. In these samples, arsenic concentration in TCLP leachates reached 13.5 mg/L. Hence this contaminant is readily available in C&D landfill conditions.

Table 1. Metal concentrations (mg/L) in leachates from TCLP and SPLP leaching tests on CCA-treated wood

Metals	Leaching tests	Unsorted wood				Green sorted wood
		0 to 2 mm	2 to 8 mm	> 8 mm	0 to 8 mm	< 0.5 mm
As	TCLP	9.2 ± 0.2	4.3 ± 0.2	6.5 ± 0.1	6.0 ± 0.2	13.5 ± 0.1
	SPLP	5.5 ± 1.3	5.5 ± 0.0	4.6 ± 0.3	3.9 ± 0.5	11.3 ± 0.4

Effect of the leaching reagent concentration

Leaching experiments were conducted at 25°C for 24 h with 50 g/L of wood with acid concentrations varying from 0.002 to 1 N. Figure 1 shows As, Cr and Cu concentrations in leachate versus acid concentration.

As reported in previous studies, increasing the acid concentration raised the metal extraction but it appeared that between 0.5 and 1 N, metal extraction was not improved. Metal leaching reaches a maximum at 187 mg As/L, 151 mg Cr/L and 109 mg Cu/L corresponding respectively to 110, 87 and 115% extraction yields. Yield values were obtained by comparing initial content in solid measured by digestion and final concentrations in leachates for easier handling of the results. As a consequence,

dissimilar analysis methods occasionally allow yields above 100%. Hence, at 1.0 N sulphuric acid seemed to solubilize the entire content of As and Cu in the wood. Over 0.2 N sulphuric acid concentration, benefits in metals extraction are relatively low while costs are increasing substantially. Therefore the use of 0.2 N sulphuric acid is an attractive cost-benefit solution. It corresponds to 20 $/t of dry wood with 5% TS.

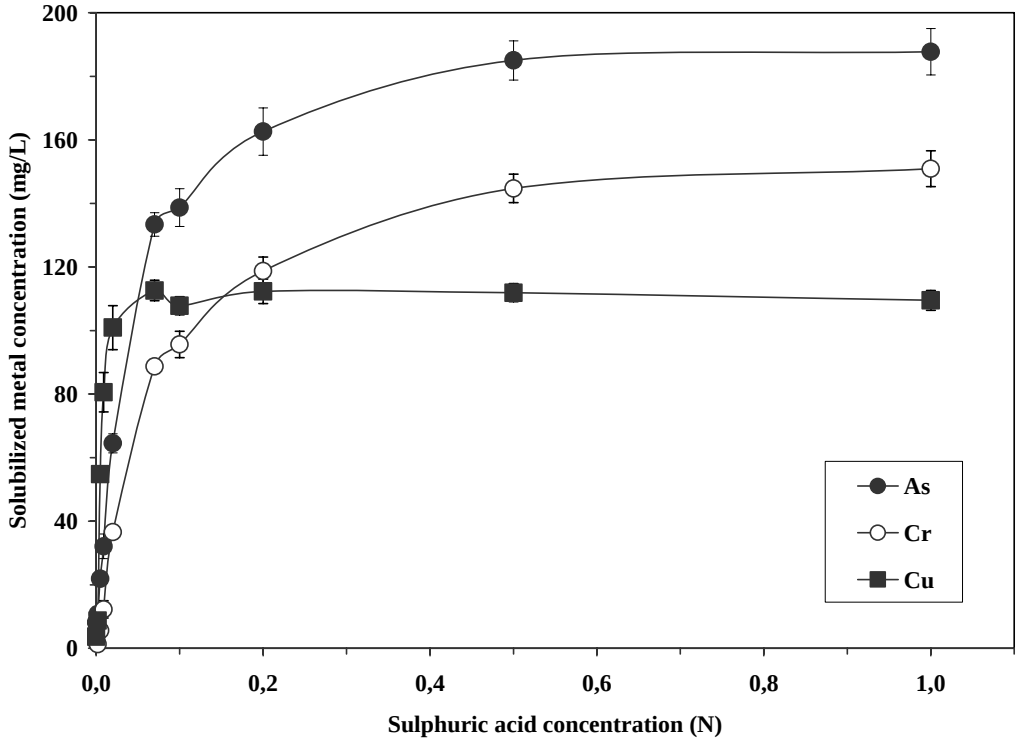

Figure 1 **As, Cr and Cu solubilization from CCA-treated wood after sulphuric acid leaching. Leaching conditions: wood content = 50 g/L, T = 25°C, reaction time = 22 h, wood particle size from 0.5 to 2 mm**

Effect of total solid concentrations

The TS content is an important parameter as it greatly influences capital costs by varying the dimensions of the leaching reactor. Leaching tests were carried out with 2.5, 5, 10, 12.5 and 15% of TS content. 15% TS is the maximal concentration tested as 30 g corresponds to the largest volume of wood able to sink into 200 mL. As expected, the larger the wood content in the reactor, the higher the metal concentrations in leachate. With 15% TS, concentrations in leachates reached respectively 463 ± 17 mg As/L, 348 ± 13 mg Cr/L and 342 ± 15 mg Cu/L. Figure 2 presents the extraction yield over the solid content range. It shows that by using sulphuric acid, the extraction efficiency did not depend on the solid to liquid ratio. These results diverge from Clausen (2004), who observed a decrease in performance while increasing this ratio. TS content was then set up to be 15% or 150 g of wood/L during metal extraction using sulphuric acid.

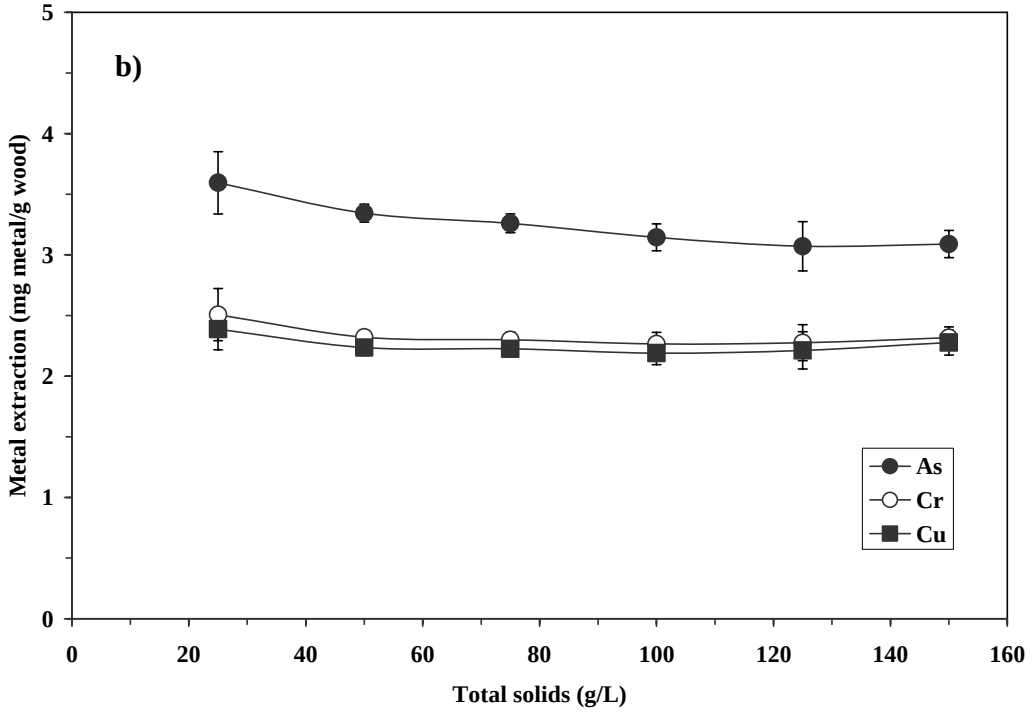

Figure 2: As, Cr and Cu extraction rates from CCA-treated wood after sulphuric acid leaching for various total solid (wood) contents. Leaching conditions: 0.2 N H_2SO_4, T = 25°C, reaction time = 24 h, wood particle size from 0.5 to 2 mm.

Effect of temperature and reaction time

Temperature and retention time are key parameters in chemical processes. To assess the influence of these parameters, kinetics tests were carried out over 24 h at different temperatures: 25, 50 and 75°C. The results are presented in Figure 3. Cu was not much influenced by temperature while As and Cr extraction was especially sensitive to temperature. High temperature speeded up metal solubilization and increased the extraction yield. These results are consistent with those recorded by Kazi and Cooper (2006) and Kakitani et al. (2007). The authors observed that the yield of metal extraction increased with hydrogen peroxide and sodium bioxalate, respectively, when leaching reactors were heated. At 75°C metal extraction was particularly fast during the first 120 minutes and the reaction was almost complete after 6 h (Figure 2). Therefore, even if high temperature causes high operational costs, it was decided to operate the leaching at 75°C for 6 h. In these conditions, metal concentrations in leachates reached 697 ± 14 mg As/L, 658 ± 2 mg Cr/L and 368 ± 7 mg Cu/L.

DOC was also measured to evaluate the effect of acid treatment at different temperatures on the wood structure. An increase in temperature led to higher DOC release. After 12 h, DOC was measured at 506 ± 45 mg/L, 1056 ± 94 mg/L and 3534 ± 178 mg/L at 25, 50 and 75°C respectively. Thus acid induces wood solubilization as well as metal solubilization. Control assays at high temperature showed that metal release was negligible (less than 10% solubilization) in the absence of acid. Hence acid was required

for metal solubilization. Two mechanisms can coexist. Acid can split the lignin-metal bond apart or it can break the wood structure by splitting lignin-lignin bonds.

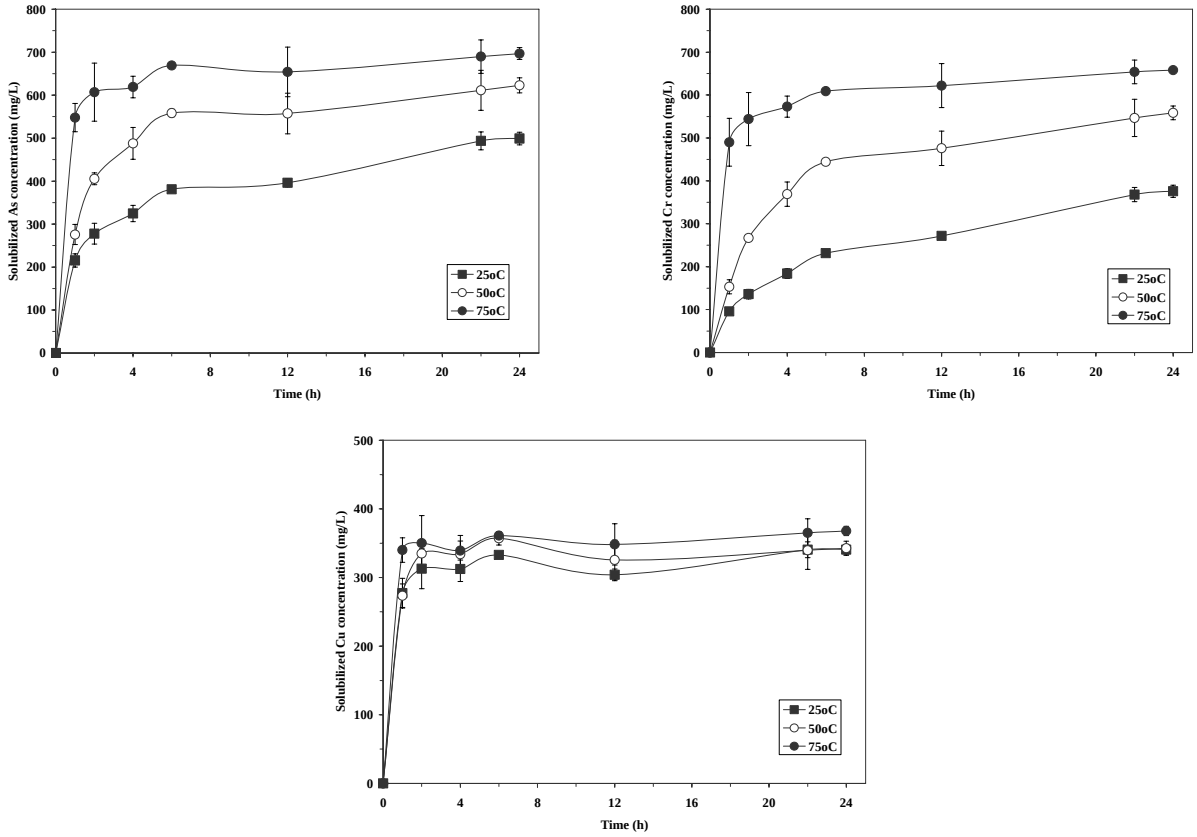

Figure 3. Kinetic of As, Cr and Cu solubilization from CCA-treated wood during sulphuric acid leaching at various temperatures (25, 50 and 75°C). Leaching conditions: wood content = 150 g/L, 0.2N H2SO4, wood particle size from 0.5 to 2 mm.

Effect of wood particle size

Up to now, all tests were carried out with 0.5 to 2 mm chopped and grinded wood. This step intended to compare 0.5 to 2 mm grinded wood and 0 to 8 mm chopped. While using the laboratory grinder, the particles of wood resembled little cylindrical wood pieces whereas industrially chopped wood resembles fine squares. It was observed that when wood was simply chopped by the industrial chopper but not grinded in laboratory, the extraction performance was greater than with grinded wood. Surface examination would be needed to understand why metals from 0 to 8 mm wood squares had a greater solubilization. Nonetheless, these observations facilitated further leaching experiments as there is no need for supplementary grinding. Chopped and screened through 8 mm sieve was the retained parameter for the leaching process.

Leaching process characteristics

Finally, the optimal parameters for acid leaching of CCA-treated wood are as follow:

- Wood content : 150 g/L;
- Acid type and concentration : 0.2 N H_2SO_4;
- Temperature : 75^oC;
- Reaction time : 6 h;
- Wood particle size : < 8 mm

In these conditions, the final leachate was highly concentrated (647 ± 16 mg As/L, 629 ± 16 mg Cr/L, 360 ± 9 mg Cu/L). pH was 1.5 while redox potential was 250 mV. The concentration of organic matter in solution reached 2,370 ± 221 mg DOC/L. The amount of sulphuric acid required to decrease the pH was 65.7 kg H_2SO_4/t, corresponding to 7.0 $ per ton of dry treated wood. This estimate did not take into account the possibility of recycling the final acid leachate after metal recovery. Further study should examine the feasibility of a closed loop system to reduce chemicals costs.

Mass balance and characterization of decontaminated wood

Following the identification of the leaching parameters, the study examined the whole process through mass balance study. As previously demonstrated, a 6-h period is needed for metal solubilization from CCA-treated wood. In order to insure that all metals are solubilized and extracted from the wood with excellent yields, three short leaching steps (2 h) were tested, instead of only one long leaching step (6 h). Moreover, the leaching treatment was followed by three washing steps. Rinsing ensures that extracted metals that are trapped into wood pores after acid leaching, are expelled in the liquid phase. Washings were done at 5% TS in distilled water. The flow sheet of the process is presented in Figure 3. The first observation is that water content in wood increased from 21% to 72% as the wood got wet during the first leaching. The leachates obtained after the two first hours of leaching have high metal concentrations. As, Cr and Cu concentrations were respectively 623, 573 and 392 mg/L. The second and third leachates were much less concentrated. As and Cr concentrations were 44 and 51 mg/L in the effluent of the third leaching step, while Cu concentration was 17 mg/L. Final remediated wood contained in average 46 g As/kg dry wood, 386 g Cr/kg of dry wood and 32 g Cu/kg dry wood. Compared to the initial wood sample, this represents 99, 92 and 99% As, Cr and Cu extracted from contaminated wood, respectively. Availability of the metals in the decontaminated wood was also examined and compared with non-decontaminated wood. Mean arsenic concentration in TCLP leachate decreased from 6.09 to 0.82 mg/L, corresponding to an 86 % reduction, but especially went from a value higher than the limit of wastes hazardousness to a value much lower. In SPLP tests, arsenic concentration reduction was 82 %.

Table 2. TCLP and SPLP leaching test results for CCA-treated wood and decontaminated wood

	TCLP			SPLP		
	As	**Cr**	**Cu**	**As**	**Cr**	**Cu**
CCA-treated wood	6.09 ± 0.23	0.70 ± 0.05	11.82 ± 0.15	3.89 ± 0.55	0.59 ± 0.11	1.27 ± 0.26
Decontaminated wood	0.82 ± 0.14	0.67 ± 0.44	0.13 ± 0.05	0.69 ± 0.07	1.16 ± 0.02	0.19 ± 0.00
Decrease (%)	86	4	99	82	-	85

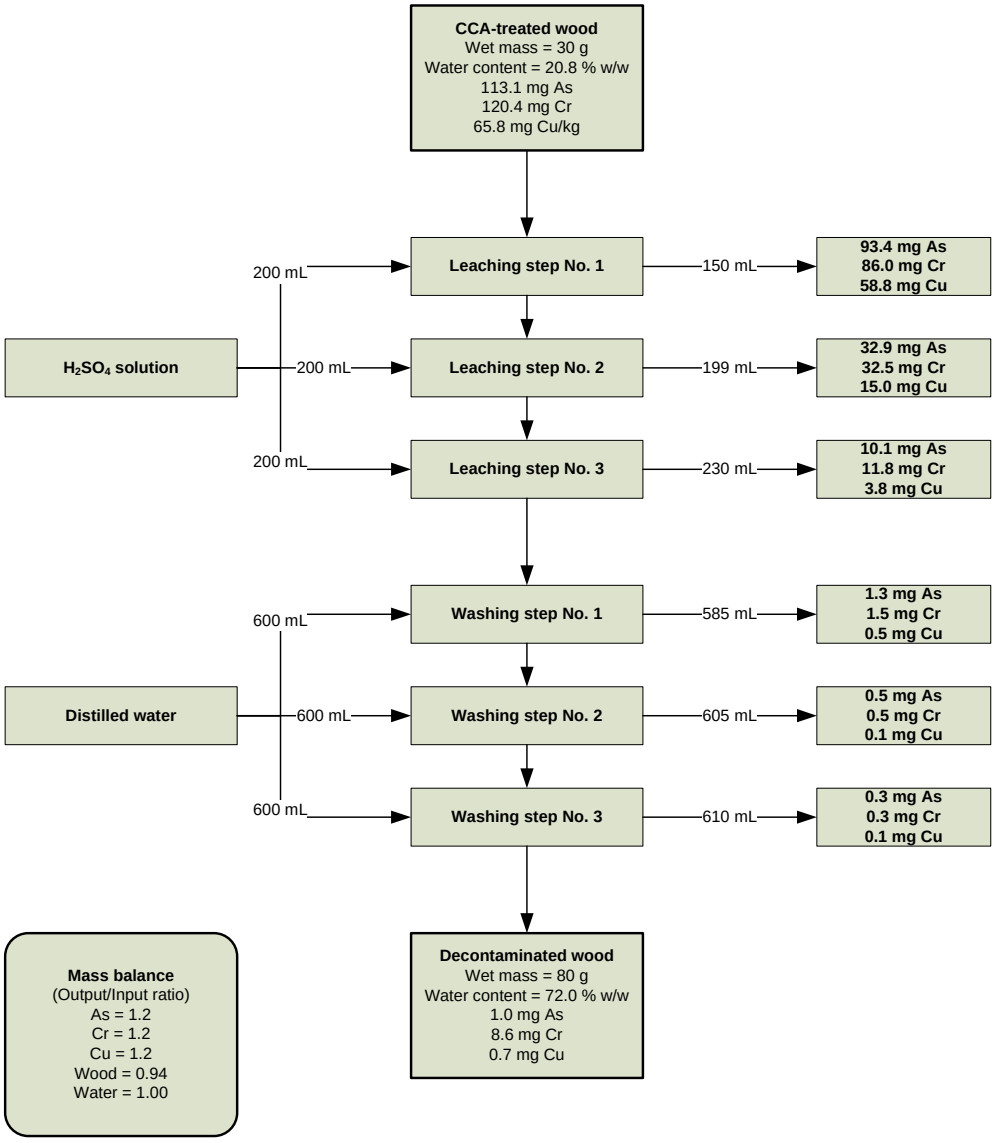

Fig. 4. Mass balance of leaching process. Operation parameters: wood content = 150 g/L, 0.2 N H_2SO_4, T = 75°C, reaction time = 2 h, particle size from 0 to 8 mm, three leaching and three washing steps.

4. Conclusions

Various chemical and physical parameters were tested to determine the most suitable leaching conditions to design an effective process with limited costs. The best conditions are obtained using sulphuric acid at 0.2 N with chopped wood (< 8 mm particles size) at 150 g/L, and with a 6-h leaching period at 75°C. Temperature greatly influenced extraction performances but high process temperature did not necessarily mean high operating costs as heat can be provided by the remediated wood produced.

Finally, when comparing wood metal contents and metal mobility in new CCA-treated wood and remediated CCA-treated wood, this acid leaching process was a great success. Moreover, this process implies low costs; the acid cost estimated at approximately 7 $/t of dry wood. Electricity costs associated with stirring were not calculated as it depends on reactor design. Additionally, as the extraction operation produces highly concentrated leachate, complementary studies should focus on extraction and recycling of Cr and Cu, discard of As. Coagulation, precipitation, electrodeposition and ion exchange resins technologies will be evaluated for metal selective recovery from CCA treated wood leachate. Either electrodeposition or ion exchange resins could allow metals recovery in worthwhile forms. On the other hand recirculation of hot acidic water in closed loops will be assessed as this would reduce effluent outcome and acid cost. Overall process costs will be calculated when leachate treatment operation charges are identified.

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