Optimization of a chemical leaching process for decontamination of CCA-treated wood

Amelie Janin [1], Jean-François Blais[*], Guy Mercier [2], Patrick Drogui [3]

Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, Qc, Canada G1K 9A9

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ABSTRACT

Increasing volumes of discarded Chromated Copper Arsenate (CCA)-treated wood require the development of new treatment and recycling options to avoid the accumulation of wood wastes in landfill sites, resulting in dispersion of contaminants in the environment. The aim of this study is to design an economic chemical leaching process for the extraction of arsenic, chromium and copper from CCA-treated wood. Choice of chemical reagent, reagent concentration, solid-to-liquid ratio, temperature, reaction time and wood particle size are parameters which have been optimized. Sulphuric acid was found to be the cheapest and most effective reagent. Optimum operation conditions are 75 °C with 0.2N H_2SO_4 and 150 g wood L^{-1}. Under these conditions, three leaching steps lasting 2 h each allowed for 99% extraction of arsenic and copper, and 91% extraction of chromium. Furthermore, arsenic concentration in TCLP leachate is reduced by 86% so the environmental hazard is reduced. Decontamination process cost is estimated to 115 US$ per ton of treated wood. These results demonstrate the feasibility of chemical remediation and that sulphuric acid leaching is a promising option for CCA-treated wood waste management.

1. Introduction

Chemical treatments are applied to the wood to increase their service life by protecting against insects and fungi. Obviously, the chemicals used for such a purpose are toxic to the organisms and consequently may be harmful if discharged in the environment. Chromated copper arsenate (CCA) has been commonly used for wood protection since the 70s [1]. Today's most common CCA formulation is called CCA type C, as specified by the American Wood Preservation Agency, and is made of 19% copper(II) oxide (CuO_2), 50% chromium(VI) oxide (CrO_3) and 31% arsenic(V) oxide (As_2O_5). The fixation mechanism of CCA into the wood is driven by the reduction of chromate [2] and lead to the formation of Cr(III)/As(V) cluster, Cr(III) and Cu(II) complex with the wood components as well as hydroxide compounds [2,3]. Numerous studies show that

leaching of metals occurs from in-service treated materials however arsenic and hexavalent chromium are known to be highly toxic to human life and the environment [4–7].

Another problem arises from CCA-treated wood usage: discarded CCA-treated wood still contains high metal concentrations [8]. However, since governmental organizations define treated wood material as non-hazardous waste, it is regularly dumped into landfills even if it is highly susceptible to metal-leaching and dispersion [9]. Townsend et al. [10] showed that the quantity of metals leached from CCA-treated wood can exceed the toxicity guidelines generally used for hazardous waste identification. Even if theses studies are criticized [11,12], Khan et al. [13] and Jambeck et al. [14] demonstrate the potential of arsenic release from CCA-treated wood wastes in C&D landfills or municipal landfills. Based on today's in-service CCA-treated wood and expected service life-time, Cooper [15] estimated that about 2.5 million m^3 of CCA-treated wood waste would be produced in Canada by 2020 and over 9 million m^3 in USA by 2015.

The goal of current research is to develop new CCA-treated wood waste management and recycling options [15,16]. One attractive method consists of separately recycling the wood and the metals, except for arsenic, which does not have any value except in the form of wood preservatives. This option requires wood and metal separation; in other words, a reversal of the original CCA fixation mechanism. Numerous studies have reported chemical remediation methods of CCA-treated wood using different solvents (Table 1). Wood grain size, reaction time and acid concentration

Table 1
Extraction yields of As, Cr and Cu by chemical remediation, as reported in the literature.

Wood	First leaching step	Second leaching step	Metal removal (%)			References
			As	Cr	Cu	
West spruce	Oxalic acid (1 h, 1N)	H_2SO_4 (3 h, 1N)	100	88	92	[19]
		H_3PO_4 (3 h, 1N)	98	77	75	
		H_2SO_4 (3 h, 1N)	100	90	88	
		H_3PO_4 (3 h, 1N)	100	96	99	
		H_2O_2/NaOH (3 h, 3%/1%)	97	96	86	
		Ammonia (3 h, 10%, 15 °C)	93	100	74	
		$NaHC_2O_4$ (3 h, pH 3.2)	100	100	96	
New treated wood (chips)	Sodium bioxalate		94	89	88	[20]
New treated wood	EDTA/oxalic acid	Electrokinetic extraction	88	74	97	[32]
3-year old wood	Oxalic acid					[21]
Chips		–	42	14	16	
Sawdust		–	89	62	81	
Sawdust		*Bacillus licheniformis*	100	79	99	
New treated pine	H_2O_2 (10%, 50 °C, 6 h)		98	95	94	[23]
New treated pine (2 × 2 × 2 cm)	Oleic acid (pH 2, 3 days)		97	78	97	[33]
Spruce and pine	Chitin (12.5 g L^{-1}, 10 days)		63	62	74	[34]
Sawdust	Chitosan (12.5 g L^{-1}, 10 days)		30	43	57	
West spruce	H_2SO_4 (1 N)		87	83	79	[26]
Sawdust	H_3PO_4 (1 N)		94	73	98	
	Citric acid (1 N)		63	50	70	
	Oxalic acid (1 N)		99	83	89	
West spruce	Bioxalate (oxalic acid 0.125 M + NaOH at pH 3.2)					[18]
Chips			89	88	94	
Sawdust			100	92	91	
New treated pine	Oxalic acid (1%, 24 h)					[17]
Chips		EDTA (1%, 24 h)	88	79	91	
		NTA (1%, 24 h)	83	80	87	
Sawdust		EDTA (1%, 24 h)	99	90	100	
		NTA (1%, 24 h)	98	90	99	
New treated pine	EDTA (1%, 24 h)					[22]
Chips			25	13	60	
Sawdust			38	36	93	

should be compared carefully as these parameters usually differ among various authors' experiments.

Oxalic acid has been used repeatedly by itself and in combination with additional chemical or biological agents. This acid is one the strongest organic acids available and it has chelating and reducing properties [17]. When oxalic acid was combined with sulphuric acid, phosphoric acid or sodium oxalate, it led to 98–100% removal of arsenic and 88–100% removal of chromium and copper from CCA-treated wood reduced to sawdust [18,19]. Bioxalate obtained by addition of sodium hydroxide to oxalic acid with pH control led to 88–94% removal of the three components [20]. Using oxalic acid and oxalic-acid-producing bacteria, Clausen and Smith [21] removed 100 and 99% of the arsenic and copper, respectively. Oxalic acid also performs well in extractions when it is used in combination with reactants like EDTA and NTA [17]. EDTA is a well-known chelating agent and is frequently used for metal solubilization. Nevertheless, leaching of CCA by EDTA may be inefficient. Kartal [22] obtained 38, 36 and 93% removal efficiencies, for arsenic, chromium, and copper, respectively, after 24 h of reaction with sawdust. Kazi and Cooper [23] chose to use an oxidizing agent as it allows for the reuse of Cu(II), As(V) and Cr(VI) in the wood treatment industry. Hydrogen peroxide extracted up to 98, 95 and 94% of arsenic, chromium and copper, respectively. Problems arose in these studies when reagent costs were considered, as most of the reagents used are expensive. In the remediation and recycling fields, operational costs are a major factor of development at large scale, as fees can be prohibitive.

The objective of this study is to design an efficient chemical extraction process while keeping in mind economic considerations at each step of the process design, especially when choosing the leaching reactant and operational conditions. In the province of Quebec, landfill costs 60–120 US$ t^{-1} dry wood (personal communication with Benoit Nadeau, Ministry of Environment of Quebec, 2008). Efficient chemical leaching processes involving leachate treatment and wood revalorization are possible alternatives to land filling of CCA-treated wood as well as being an important step towards sustainable waste management. We want to identify a leaching process which can be used to develop a new, competitive CCA-treated wood waste treatment facility. Effective and cheap chemical reagents need to be identified as well as optimal reagent concentration, reaction temperature, solid-to-liquid ratio and suitable wood particle size. Finally, we want to ensure that environment hazardousness of the waste be reduced and that the process be economically feasible.

2. Materials and methods

2.1. Wastes material sampling and preparation

As used treated wood available in waste discarding centers has an unknown in-service time span and varies in metal concentrations from one piece to another, it is impossible to guarantee uniformity of wood samples for analytical purposes. The choice of using relatively new CCA-treated wood has been made to ensure the homogeneity of the starting material. CCA type-C treated red pine poles were obtained from Stella Jones (QC, Canada). According to the guidelines from the Québec Ministry of Transport, 90% of sapwood or 95 mm sapwood depth must hold more than 6.4 kg CCA m^{-3}. The wood used for this study was treated in autumn

2005 and stored outside for winter. In June 2006, the poles were ground into chips using a log chipper. A grinder (Ika®Werke M20 S3 unit, Germany) was used in the laboratory to further crush the chips which were then screened through 8, 2 or 0.5 mm sieves.

In some cases, characterization experiments required only the use of wood from the treated external circumference of the log. Therefore, the chipped wood was separated by color and green pieces were manually picked out for the study. The green particles were then crushed and screened. Only the particulate fraction of the particles that passed through the 0.5 mm screen was used for the characterization tests.

2.2. Wood characterization

Metal concentrations in CCA-treated wood were determined by ICP-AES after digestion with analytical grade nitric acid (50%, $w\,w^{-1}$, 20 mL) and hydrogen peroxide (30%, $w\,w^{-1}$, 10 mL). A mass of 1.0 g of dry wood was used for wood digestion. Each wood sample was digested in triplicate to get an average metal concentration value.

The metal availability in CCA-treated wood was estimated using two standard leaching tests. These TCLP and SPLP tests were developed by USEPA in order to assess for metal mobility in wastes [24,25]. The TCLP test is used to reproduce leaching conditions in C&D landfill sites. The SPLP test reproduces acid rain conditions and estimates metal mobility when wastes are disposed in an open area. Another test is called the "Tap water test" and is used to examine metal mobility when wastes are soaked in non-acidified tap water. For all three tests, 50 g of wood were placed in 1 L plastic bottles which were filled with solvents. In the case of the TCLP test, the solvent was a diluted acetic acid solution. A mixture of diluted sulphuric and nitric acids was used in the SPLP test, and tap water was used in the Tap water test. Bottles were rotated on an eight-bottle wheel for 24 h. After filtering, the remaining acid solutions were analyzed for metals concentrations by ICP.

2.3. Wood decontamination

This study focused on the design of a cheap and operational acid-leaching process to remove arsenic, chromium and copper from CCA-treated wood. Various tests were conducted to successively measure the influence of six operating parameters to achieve high metal removal yields and to determine the most promising leaching conditions. Parameters are varied individually while all others remained fixed. Variable conditions included the choice of reagent, reagent concentration, total solid content, reaction temperature, leaching time and wood particle size.

In the first step, two inorganic acids (sulphuric and phosphoric acids), one organic acid (oxalic acid), one oxidizing agent (hydrogen peroxide) and one complexing agent (EDTA) were tested as extracting reagents. Leaching solutions were prepared using analytical grade reagents diluted in deionized water. Total Solid (TS) content was fixed at 15% and the particle size fraction was 0.5–2 mm. A mass of 10 g of sieved wood was mixed with 200 mL of leaching solution in a 500 mL baffled shaker flask (Cole Parmer, Montréal, Canada). The flasks were placed in an oscillating shaker at 200 rpm at 25 °C. The leaching time was 22 h. Liquid/solid separation was carried out using vacuum filtration on Whatman 934-AH glass fiber membranes. All pieces of glassware were washed with a detergent (Comet, Prestige Brand International) and rinsed three times with tap water and three times with deionized water.

Once the best leaching reagent was identified, a large range of acid concentrations were tested to select the most appropriate one. TS content, temperature and leaching time were kept constant throughout the series of experiments. Once the optimal acid concentration was determined, this parameter was kept constant too.

The third step involved the optimization of the solid (wood) content while the reaction temperature was maintained at 25 °C, and reaction time, at 22 h. Using the optimal reagent concentration and TS content, kinetic studies were conducted at 25 °C, 50 °C and 75 °C for 2, 4, 6, 12, 22 and 24 h to identify the best reaction time and temperature. The temperature inside the flasks was controlled by adjusting the ambient temperature in the shaker enclosure for experiments conducted at 25 °C and 50 °C. For the tests performed at 75 °C, the flasks were stirred in a temperature-controlled water bath. The flasks were corked to prevent evaporation. The temperature inside the flasks was verified occasionally using a digital thermometer. Finally, the influence of wood particle size was evaluated. All leaching experiments were carried out in triplicate.

2.4. Leaching balance and decontaminated wood characterization

In order to assess the efficiency of the leaching process, final tests were done with measurements of all inputs and outputs. The leaching operation consisted of three leaching steps plus one, two or three washing steps. Wet wood samples were weighed before and after each leaching treatment. For each wood sample, water content was calculated in triplicate by measuring the weight before and after oven-drying at 105 °C for 24 h. Leachate volumes and metal concentrations in leachates were also measured. As well, metal concentrations in the wood samples were determined before and after the leaching treatment.

2.5. Analytical techniques

The pH was determined using a pH-meter (Fisher Acumet model 915) equipped with a double-junction Cole-Palmer electrode with a Ag/AgCl reference cell. Metal concentrations were measured with an ICP-AES (Varian, model Vista-AX). Quality controls were performed with certified liquid samples (multi-element standard, catalogue number 900-Q30-002, lot number SC0019251, SCP Science, Lasalle, QC, Canada) to ensure conformity of the measurement apparatus. The Dissolved Organic Carbon (DOC) content was measured with a Shimadzu TOC-5000A apparatus. Hexavalent chromium analysis were completed by Bodycote Laboratory (Québec, Canada) using the 3500-Cr B colorimetric standard method.

2.6. Economic analysis

The operating and capital costs associated with the decontamination of CCA-treated wood were estimated for a 500 t.t.w. d^{-1} treatment plant capacity (annual operating days: 250 d $year^{-1}$; 24 h per day) and included process water treatment plant (coagulation-precipitation process using ferric chloride, hydrated lime, and polymer for As, Cr and Cu removal from the wood leachate). The estimation was conducted on the basis of the following unit prices: sulphuric acid (solution at 93%, w/w) was evaluated at a cost of 125 US\$ t^{-1}; ferric chloride, at a cost of 1610 US\$ t Fe^{-1}; polymer, at a cost of 5 US\$ kg^{-1}; labor, at an average cost of 22.5 US\$ h^{-1}; electricity, at a cost of 0.06 US\$ kWh^{-1}; hazardous waste disposal, at a cost of 300 US\$ t^{-1}; and process water (tap water), at a value of 0.5 US\$ m^{-3}. Depreciation and annual interest charges have been estimated using a 15-year equipment lifetime, and 6% annual interest rate.

3. Results and discussion

3.1. Wood characteristics

As expected, the chemical analysis of CCA-treated wood revealed high metal contents. Concentrations were 5230 ± 120 mg As kg^{-1},

Table 2
Metal concentrations ($mg\,L^{-1}$) in leachates from TCLP, SPLP and tap water leaching tests on CCA-treated wood.

Metals	Leaching tests	Unsorted wood				Green wood
		0–2 mm	2–8 mm	>8 mm	0–8 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
	Tap water	5.7 ± 0.0	4.4 ± 0.2	3.8 ± 0.1	3.3 ± 0.1	8.8 ± 0.5
Cr	TCLP	1.6 ± 0.1	0.6 ± 0.1	0.8 ± 0.1	0.7 ± 0.1	2.6 ± 0.1
	SPLP	0.9 ± 0.3	0.7 ± 0.1	0.5 ± 0.1	0.6 ± 0.1	2.0 ± 0.2
	Tap water	1.0 ± 0.1	0.6 ± 0.1	0.5 ± 0.1	0.5 ± 0.1	2.5 ± 1.7
Cu	TCLP	17.1 ± 0.5	2.3 ± 0.1	9.0 ± 0.2	11.8 ± 0.1	23.2 ± 0.5
	SPLP	3.5 ± 0.9	2.8 ± 0.1	1.9 ± 0.1	1.3 ± 0.3	4.2 ± 0.3
	Tap water	3.7 ± 0.1	2.3 ± 0.1	1.6 ± 0.2	1.1 ± 0.8	3.4 ± 0.1

$5310 \pm 70\,mg\,Cr\,kg^{-1}$ and $2620 \pm 210\,mg\,Cu\,kg^{-1}$ of wood. A key question in waste management is whether or not contaminants are easily released from wood when discarded. TCLP, SPLP and "tap water" tests allow for estimation of the contaminant availability in various conditions. Results of arsenic release during TCLP, SPLP and Tap water tests from various grain size fractions of the CCA-treated wood and from the external part of the log are shown in Table 2.

As wood particle size decreased, arsenic release increased. Hence as wood is ground into smaller pieces, specific wood surface increases and metals become more available. Arsenic concentrations in TCLP tests made with unsorted ground wood varied between 4.3 and $9.2\,mg\,L^{-1}$. In three cases out of four, the arsenic concentration surpassed $5\,mg\,L^{-1}$, meaning that this material would be considered as hazardous waste if American hazardous waste regulations were applied to CCA-treated wood. These results are consistent with those recorded by Townsend et al. [10]. They observed arsenic concentrations of over $5\,mg\,L^{-1}$ in 11 out of 13 TCLP leachate samples. This material is clearly hazardous even if unregulated.

SPLP and tap water tests conducted with unsorted ground wood led to lower arsenic release than the TCLP tests. Arsenic concentration varied between 3.9 and $5.5\,mg\,L^{-1}$ after SPLP with a pH 4.20 sulphuric and nitric acid extraction fluid and $3.3–5.7\,mg\,L^{-1}$ after tap water tests. Hence, pH 4.93 acetic acid solution (TCLP test) conducted to higher metal leaching than tap water and SPLP test, probably because of the chelating ability of the organic acid. However, arsenic was obviously released from the wood using tap water or the SPLP inorganic acids. Hence, it should be assumed, for safety principle, that arsenic is likely available for leaching in C&D landfill conditions.

The same standard tests were carried out with color-based sorting, selecting for green wood coming from the external part of the log and grinding it to under 0.5 mm. These tests simulated the slow degradation of a log after it has been discarded. It was observed that wood decomposition causes the progressive release of saw dust from the outer, highly treated portion of log. This, in turn, leads to very high metal availability. Arsenic concentrations in TCLP, SPLP and Tap water leachates from these samples reached 13.5, 11.3 and $8.8\,mg\,L^{-1}$, respectively.

Concentrations of chromium and copper released from sorted and ground treated wood during TCLP tests were 2.6 ± 0.0 and $23.2 \pm 0.5\,mg\,L^{-1}$, respectively. Chromium is relatively well bonded to the wood and is not easily released into the environment.

3.2. Selection of the leaching reagent

Different authors studied metal extraction from CCA-treated wood using one or a combination of the following: inorganic (sulphuric, phosphoric) acids, an organic (oxalic) acid, a complexing agent (EDTA) and an oxidizing agent (hydrogen peroxide) [17–19,21–23,26]. In this study, these five reagents were tested for their ability to extract metals from wood at various concentrations in the range 0.002–0.07N for sulphuric acid, 0.005–0.06N for phosphoric acid, 0.002–0.07N for oxalic acid, $1–20\,g\,EDTA\,L^{-1}$, and 0.1–10% for hydrogen peroxide. Table 3 presents the results of extraction experiments with the highest concentrations of each of the five extracting agents.

With the exception of EDTA, the higher the reagent concentration, the more effective is the extracting agent at solubilising metals. At concentrations between 5 and $20\,g\,EDTA\,L^{-1}$, metal concentrations in the leachates stay stable with less than 20% of arsenic and 4% of chromium being removed from CCA-treated wood. Metal extraction efficiencies observed in this study were lower than observed by Kartal [22], probably because this author worked with a lower particle size fraction than us. Specific surface area is greater in the case of sawdust particles than in the case of the 0.5–2 mm particle size fraction. Metal extraction is expected to increase with increasing specific surface area. On the other hand, extensive grinding increases wood preparation costs, which is why we chose not to use sawdust.

Sulphuric acid gives good extraction yields under the tested conditions. 0.07N sulphuric acid yields 67.3%, 48.2% and 100.0% extraction of arsenic, chromium and copper, respectively. In comparison, Kakitani et al. [26] obtained 87%, 83% and 79% extraction, respectively, for the same metals with 1N sulphuric acid. Performances might differ due to high sulphuric acid concentration differences. On the other hand, acid cost is low, at 9.1 US$ t.t.w.$^{-1}$, in the case where the concentration was 0.07N. This is of great interest considering the potential yield upgrade with the improvement of leaching conditions.

Hydrogen peroxide has high metal-extraction ability. We obtained 71.2%, 57.7% and 82.7% extraction yields for arsenic, chromium and copper whereas Kazi and Cooper [23] obtained respective values of 98%, 95% and 94%. The higher extraction performance in this study might be due to a higher reaction temperature, which was 50 °C whereas we used 25 °C. Under the tested conditions, hydrogen peroxide cost 4620 US$ t.t.w.$^{-1}$. In our opinion, this is far too expensive to consider further study.

As in the case of EDTA, phosphoric acid is not efficient at chromium solubilization from treated wood. Chromium extraction yield is 11% using $0.06N\,H_3PO_4$ at 25 °C and after 22 h of leaching. Kakitani et al. [26] obtained much better results with $1N\,H_3PO_4$. Again, poor metal solubilization might be due to low acid concentration but H_3PO_4 at 0.06N costs 166 US$ t.t.w.$^{-1}$. An increase in acid concentration would increase the acid cost and the overall remediation operation costs would largely surpass landfill disposal costs. This is not in agreement with our objectives.

Oxalic acid costs less than phosphoric acid and gives higher extraction yields: 79.9% of arsenic, 61.2% of chromium and 49.3% of copper were solubilized. Kakitani et al. [26] study resulted in 99%, 83% and 99% solubilization of arsenic, chromium and copper, respectively. However, sawdust was once again used. For a concen-

Table 3
Maximum yields of metal extraction (%) and associated chemical costs by leaching with various reagents.[a]

Metals	H_2SO_4	H_2O_2	H_3PO_4	EDTA	Oxalic acid
Reagent concentration	0.07N	10%	0.06N	20 g L^{-1}	0.07N
As (%)	67.3	71.2	31.1	19.7	79.9
Cr (%)	48.2	57.7	11.0	3.5	61.2
Cu (%)	100.0	82.7	92.6	99.7	49.3
Chemical cost ($ t.w.t.$^{-1}$)	9.1	4616	166	960	84.0

Note: Leaching conditions: wood content = 50 g L^{-1}, T = 25 °C, reaction time = 22 h, particle size = from 0.5 to 2 mm.
[a] Highest concentrations tested.

tration of 0.07N in the tested conditions, the cost of oxalic acid is 84 US$ t.t.w.$^{-1}$.

In order to compare cost versus efficiency of sulphuric and oxalic acids, cost was calculated on the basis of arsenic solubilization. Accordingly, to reach 60% arsenic solubilization, the cost of oxalic acid is 48 US$ t.t.w.$^{-1}$ whereas that of sulphuric acid is 8 US$ t.t.w.$^{-1}$. Therefore, the cheapest reagent is sulphuric acid although, at this stage, it does not allow for more than 67% removal of arsenic. Leaching condition optimization, especially an increase in acid concentration, might enhance sulphuric acid's metal solubilization yields.

3.3. Effect of the leaching reagent concentration

Sulphuric acid content in the leaching solution needs to be optimized for better metal extraction yields. Therefore, leaching experiments were conducted with different acid concentrations (0.002–1N) under the same conditions as before. Fig. 1 shows arsenic, chromium and copper concentrations in leachate versus acid concentration.
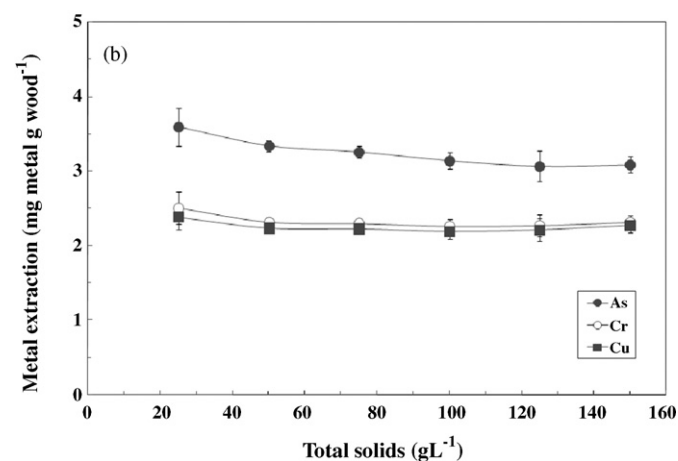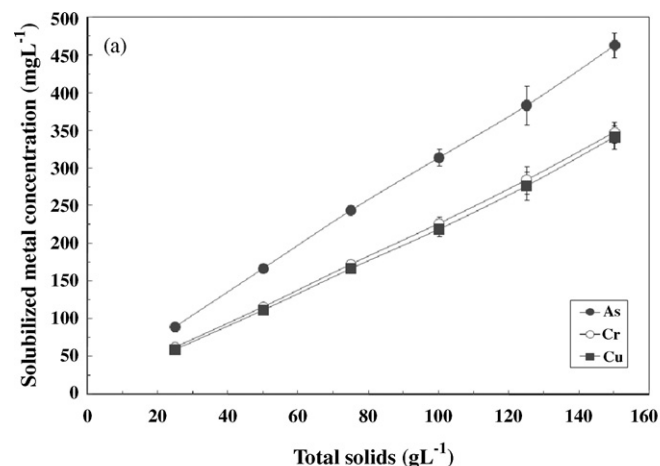
As in the previous experiment, increasing the acid concentration increased the metal extraction but between 0.5 and 1N, metal extraction did not improve. Metal leaching attained a maximum at 187 mg As L^{-1}, 151 mg Cr L^{-1} and 109 mg Cu L^{-1} corresponding, respectively, to 110, 87 and 115% extraction yields. Yield values were obtained by comparing initial content in solids measured by digestion and final concentrations in leachates for easier handling of the results. As a consequence, dissimilar analysis methods sometimes allowed for yields above 100%.

A solution of 1.0N sulphuric acid seemed to solubilize the entire content of arsenic and copper, and left a low amount of chromium in the remaining wood. Compared to Kakitani et al. [26] results, metal solubilization increased to some extent in our 22 h experi-
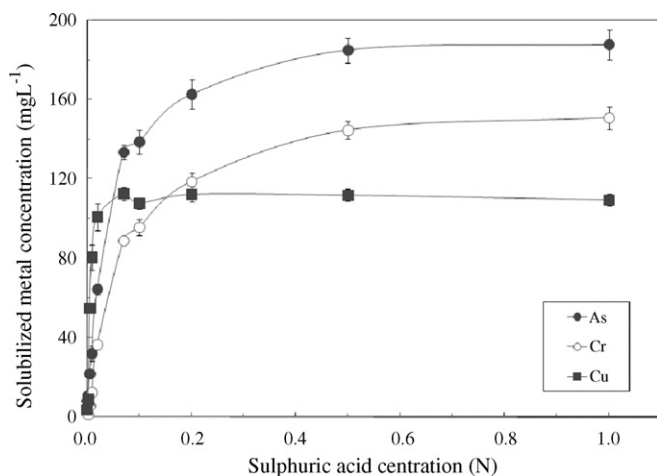
ments. Differences might come from leaching duration which was set up at 6 h in those authors' experiments. Fig. 1 shows that for acid concentrations over 0.2N, gains in metal extractions are relatively low, and cost increases greatly. Hence 0.2N sulphuric acid is a good compromise between high performance and low cost and corresponds to 20 US$ t^{-1} of dry wood within the chosen experimental conditions. The following experiments were conducted with 0.2N sulphuric acid.

3.4. Effect of total solids concentration

The total solid (TS) content is an important parameter as it greatly influences capital costs by affecting the dimensions of the leaching reactor. Leaching tests were carried out with 2.5, 5, 10, 12.5 and 15% of TS content (Fig. 2). 15% TS is the highest proportion of

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

Fig. 2. As, Cr and Cu solubilization and extraction rates from CCA-treated wood after sulphuric acid leaching at various total solids (wood) concentration. Leaching conditions: 0.2N H_2SO_4, T = 25 °C, reaction time = 22 h, wood particle size from 0.5 to 2 mm.

wood tested because 30 g wood is the largest amount that is able to sink into 200 mL of solution. With greater amounts, part of the wood would stay dry and untreated by the leaching solution.

As expected, the more wood in the reactor, the higher the metal concentration found in leachates. With 15% TS, these concentrations reached 463 mg As L^{-1}, 348 mg Cr L^{-1} and 342 mg Cu L^{-1}. As shown in Fig. 2b, extraction yields stayed stable over the solid content range meaning that, from 2.5% to 15%, the extraction efficiency does not depend on wood content. These results diverge from those of Clausen [27], who observed a decrease in performance while increasing the solid-to-liquid ratio with oxalic acid leaching. TS content was therefore set at 15% or 150 g of wood L^{-1} for the remainder of the experiments.

3.5. Effect of temperature and reaction time

Temperature and retention time are key parameters in chemical processes. To assess their effects, kinetics tests were carried out at 25, 50 and 75 °C. During the assays, 10 mL samples were withdrawn after 1, 2, 4, 6, 12, 22 and 24 h of treatment time for metal analysis. The results are presented in Fig. 3.

Cu is not influenced much by temperature but As and Cr extractions are. High temperatures speed up metal solubilization from wood and increase the extraction yield. These results are consistent with those observed by Kazi and Cooper [23] and Kakitani et al. [20]. In both of these studies increased extraction yields were observed with, respectively, hydrogen peroxide and a sodium bioxalate agent when the temperature was higher.

DOC was also measured to evaluate the effect of acid treatment on the wood structure at different temperatures. Results are shown in Table 4. Increased temperature greatly increased the DOC release during the leaching process, meaning that exposure to acid results in wood solubilization as well as metal solubilization. Control assays at high temperature without acid showed that acid is required for metal solubilization. When the acid is absent, metal release is negligible (less than 10% solubilization). Two mechanisms can coexist: acid can split apart the lignin-metal bond or it can break up the wood structure by de-polymerization of cellulose. By plotting metal concentration in leachates versus DOC (Fig. 4) it appears that the values are fairly proportional. It could be that a portion of the acid breaks apart the wood structure and solubilizes organic matter to which metals are bonded. At 75 °C metal extraction is particularly fast during the first 120 min and the reaction is almost complete after 6 h (Fig. 3). Therefore, although a high temperature usually implies high operational costs, it was decided to carry out the leaching process at 75 °C for 6 h. Under these conditions, metal concentrations in the leachate reached 697 mg As L^{-1}, 658 mg Cr L^{-1} and 368 mg Cu L^{-1}.

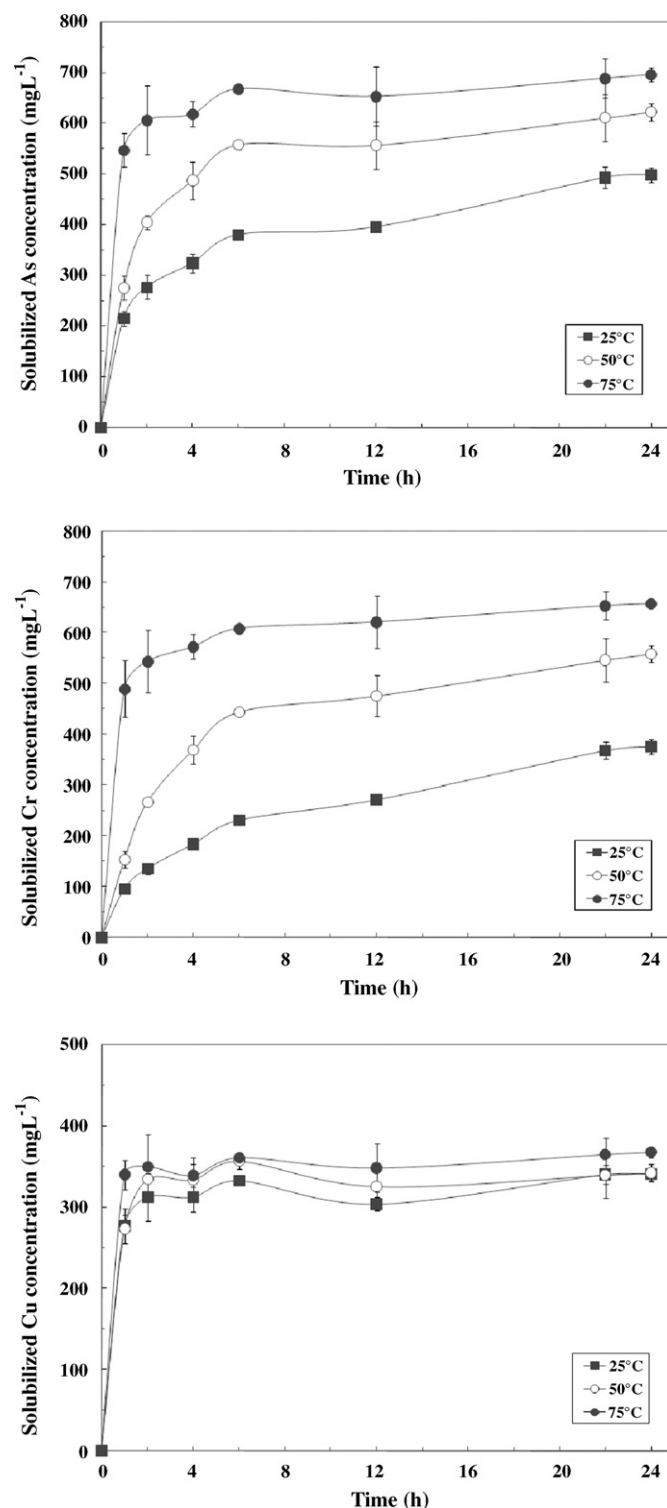### 3.6. Effect of wood particle size

Up to now, all tests have been carried out with 0.5–2 mm chopped and ground wood. The next step evaluated acid leaching with different wood particle sizes. Wood ground using the laboratory grinder was separated into 0.5–2 mm and 2–8 mm particles

Fig. 3. Kinetics 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^{-1}, 0.2N H$_2$SO$_4$, wood particle size from 0.5 to 2 mm.

ranges. The laboratory grinder produced cylindrical wood particles. The wood samples that had not been further ground in laboratory, were simply screened through an 8 mm sieve and appeared as fine flat squares. Thus, the appearance of the wood pieces depended on whether they had been chipped or ground. Table 5 presents results of leaching experiments on wood that had, and had not, been ground.
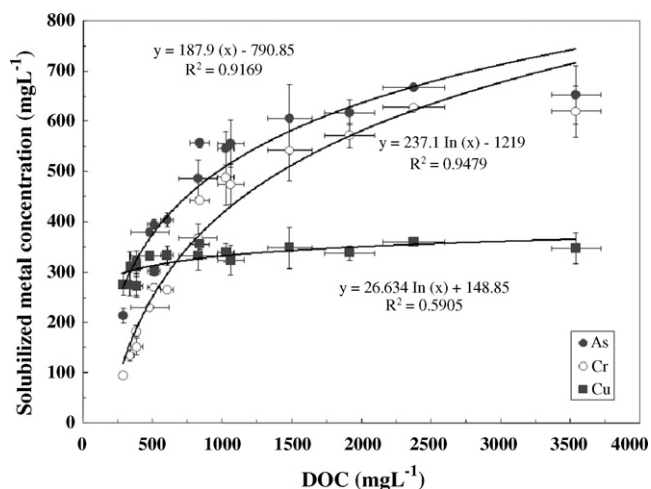
Table 4
DOC concentrations in leachates after 6 and 12 h of reaction at various temperatures (25, 50 and 75 °C).

Reaction time (h)	DOC (mg L^{-1})		
	25 °C	50 °C	75 °C
6	475 ± 138	835 ± 71	2369 ± 221
12	506 ± 45	1056 ± 94	3534 ± 178

Note: Leaching conditions: wood content = 150 g L^{-1}, 0.2N H$_2$SO$_4$, T = 75 °C, particle size = from 0.5 to 2 mm.

Fig. 4. Metal concentrations versus DOC in leachates. Leaching conditions: wood content = 150 g L^{-1}, 0.2N H$_2$SO$_4$, T = 75 °C, particle size from 0.5 to 2 mm.

The smaller the particle size, the more effective the leaching reaction owing to the higher active surface of the particles. For instance, the concentrations of metals recorded in leachates obtained from wood particles having a diameter of 0.5–2 mm were 1.2 times higher than in the case of those having a diameter measuring 2–8 mm. However, when the wood was simply chopped by the industrial chopper but not ground in laboratory, the extraction performance was much greater. Surface examination would be needed to understand why metals are more solubilized from wood particles measuring 0–8 mm. The observations made here helped to facilitate further leaching experiments as they showed that there was no need for supplementary grinding. Further mass balance experiments were conducted with chopped wood particles screened through 8 mm sieves.

3.7. Leaching process characteristics

Finally, the optimized parameters for acid leaching of CCA-treated wood are as follows:

- Wood content: 150 g L^{-1}.
- Acid type and concentration: 0.2N H$_2$SO$_4$.
- Temperature: 75 °C.
- Reaction time: 6 h.
- Wood particle size: <8 m.

In these conditions, the final leachate was highly concentrated (647 mg As L^{-1}, 629 mg Cr L^{-1}, 360 mg Cu L^{-1}). Hexavalent chromium concentration was measured to be 0.44 mg L^{-1}, hence it was assumed that chromium oxidation state was predominantly trivalent. The final pH was 1.5 while the oxidation–reduction potential was 250 mV. The concentration of organic matter in the solution reached 2370 mg COD L^{-1}.

Table 5
Metal solubilization (mg L^{-1}) based on ground and unground wood of various particle sizes.

Metals	Grinded wood 0.5–2 mm	Grinded wood 2–8 mm	Ungrinded wood <8 mm
As	572 ± 32	460 ± 15	647 ± 16
Cr	551 ± 29	437 ± 17	629 ± 16
Cu	316 ± 17	254 ± 11	360 ± 9

Note: Leaching conditions: wood content = 150 g L^{-1}, 0.2N H$_2$SO$_4$, T = 75 °C, reaction time = 6 h.

According to the Pourbaix diagram (not shown) arsenic was predicted to be in oxidation state +V. MINEQL simulations (version 4.5) were carried out with the following concentrations: 5 mM of As(V), Cr(III) and Cu(II) and 200 mM of SO$_4$$^{2-}$. Speciation calculations predicted the formation of 4 mm of CrSO$_4$$^+$ and H$_3$AsO$_4$, 3 mM CuSO$_4$, 2 mM Cu^{2+} and 1 mM of Cr^{3+} and H$_2$AsO$_4$$^-$.

The amount of sulphuric acid required to decrease the pH was 65.7 kg H$_2$SO$_4$ t^{-1}. At a unit cost of 100 \$ t^{-1} of sulphuric acid (93%), the decrease in pH involved a cost of 7.0 US\$ per ton of dry treated wood. This estimate does not take into account the possibility of recycling the acid leachate after metal recovery. Further studies should examine the feasibility of a closed-loop system to reduce operating costs.

3.8. Mass balance and wood residue characterization

As leaching parameters have been identified, the following studies examine the leaching process. It is well known that a 6-h period is needed for metals to be solubilized from CCA-treated wood. In order to ensure that all metals were solubilized and extracted from the wood with excellent yields, three short (2 h) leaching steps were tested, instead of one long (6 h) leaching step. As well, the leaching treatment was followed by one, two or three washing steps. Rinsing ensured that extracted metals, which were trapped in wood pores after acid leaching, were expelled into the liquid phase. Washings were done with 600 mL volumes of distilled water. Metal concentrations were measured in each leachate. Furthermore, the wood entering or escaping the system was digested and analyzed for metal quantification. The flow sheet of the process including the three washing steps is presented in Fig. 5.

The first observation is that, in the three cases (results not shown), water content in wood increased from 21% to 72% as the wood got wet during the first leaching step. Consequently, the weight of the wood rose from 30 to around 80 g. The leachates obtained after the two first hours of leaching had high metal concentrations. Arsenic varied between 540 and 623 mg L^{-1}; chromium, between 500 and 574 mg L^{-1} and copper, between 330 and 392 mg L^{-1}. The second and third leachates were much less concentrated than the first. Arsenic and chromium concentrations were lower than 55 mg L^{-1} in the third leachate, while the copper concentration was as low as 17 mg L^{-1}.

Also, there was no difference in metal contents in decontaminated wood produced by 1, 2 or 3 washings. This means that three leaching steps plus one washing step is enough to remove metals trapped inside wood pores. Remediated wood, as a final product, contained on average 42 mg arsenic, 438 g chromium and 31 g copper per kg of dry wood. Compared to the initial wood sample, these values represent extractions of 99, 91 and 99% of arsenic, chromium and copper from contaminated wood, respectively.

Availability of the metals in the decontaminated wood was also examined and compared with non-decontaminated wood. Results of TCLP, SPLP and tap water tests are presented in Table 6. The arsenic concentration in TCLP leachates was reduced from 6.09 to 0.82 mg L^{-1}, corresponding to an 86% reduction in arsenic mobility. More importantly, the arsenic concentration was brought down from a value exceeding the limit of hazardousness for most wastes to a much lower value. Hence, the remediated wood is no longer considered as hazardous waste. As for the SPLP and tap water tests, the reductions were 82 and 78%, respectively. Cu concentrations were also reduced in TCLP, SPLP and tap water tests. Chromium, in contrast, posed problems as its concentration in standard test leachates tended to increase somewhat. It should be mentioned that chromium concentrations were already very low in leachates produced from CCA-treated wood and that they were also low in remediated wood, having concentrations of 0.67, 1.16 and 1.20 mg L^{-1} in TCLP, SPLP and tap water tests, respectively. Finally, a
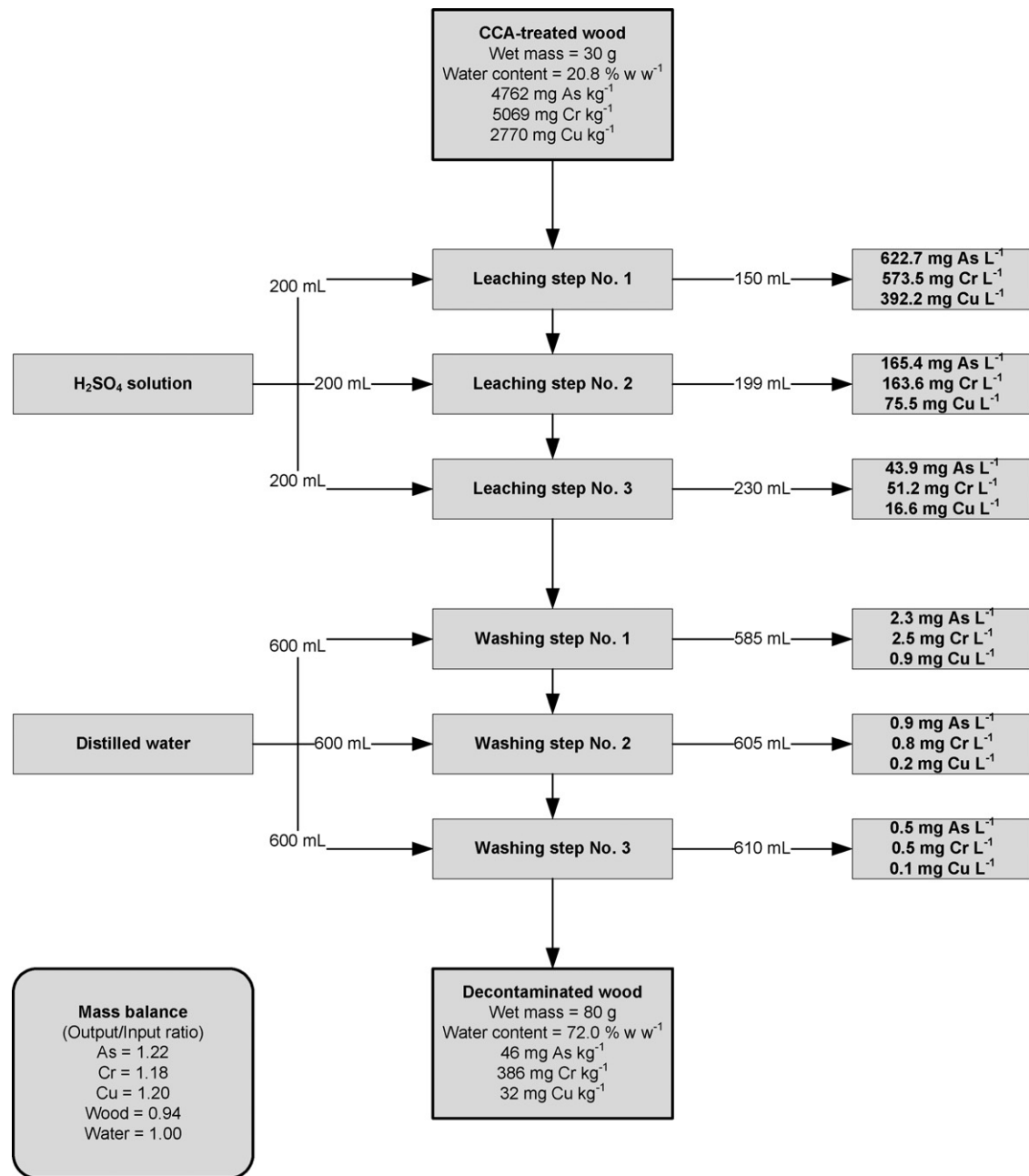
Fig. 5. Mass balance in process No. 3. Leaching conditions: wood content = 150 g L^{-1}, 0.2N H$_2$SO$_4$, T = 75 °C, reaction time = 2 h, particle size from 0.5 to 2 mm, three leaching and three washing steps.

comparison of metal content and metal mobility in freshly treated wood and in remediated CCA-treated wood showed that the acid leaching process is a great success. The remediated wood can obviously be reused for energy production through burning. Apart from that, it can be valorized and find new applications, for example, in compost production for agricultural or residential purposes [28,29],

or in bio-ethanol production where the wood can be used as a ligno-cellulosic feedstock [30,31]. On the other hand, copper and chromium have good value on the market, hence there is a potential for copper and chromium extraction from the leachate for recycling. Environmental emerging technologies like electrochemistry or ions exchange could be used for metals extraction from the liquid phase.

Table 6
TCLP, SPLP and tap water leaching test (mg L^{-1}) results for CCA-treated wood and decontaminated wood.

	TCLP			SPLP			Tap water		
	As	Cr	Cu	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	3.30 ± 0.12	0.49 ± 0.03	1.07 ± 0.07
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	0.72 ± 0.12	1.20 ± 0.07	0.23 ± 0.03
Decrease (%)	86	4	99	82	–	85	78	–	78

Table 7
Economic analysis of the CCA-treated wood decontamination process.

	Description	Cost (US$ t.t.w.$^{-1}$)
Direct operating costs		
Chemicals		
Sulphuric acid	($32.69\,t\,d^{-1} \times 125\,\$\,t^{-1}/500\,t.t.w.\,d^{-1}$)	8.17
Ferric chloride	($2.95\,t\,d^{-1} \times 1610\,\$\,t^{-1}/500\,t.t.w.\,d^{-1}$)	9.49
Lime	($42.87\,t\,d^{-1} \times 150\,\$\,t^{-1}/500\,t.t.w.\,d^{-1}$)	12.86
Labor	($132.5\,h\,d^{-1} \times 22.5\,\$\,h^{-1}/500\,t.t.w.\,d^{-1}$)	5.96
Electricity	($21.19\,MWh\,d^{-1} \times 60\,\$\,MWh^{-1}/500\,t.t.w.\,d^{-1}$)	2.54
Process water	($3796\,m^3\,d^{-1} \times 0.50\,\$\,m^{-3}/500\,t.t.w.\,d^{-1}$)	3.80
Sludge disposal	($51\,t\,d^{-1} \times 300\,\$\,t^{-1}/500\,t.t.w.\,d^{-1}$)	30.60
Maintenance	(3% of capital cost year^{-1})	6.53
Total direct operating costs		79.95
Capital costs		
Total investment cost:	27,216,000 US$	
Annual interest charges	(6% annual interest rate)	13.06
Depreciation	(15-year equipment lifetime)	21.77
Total capital costs		34.83
Total		114.78

3.9. Economic analysis

The results of the economic analysis are presented in Table 7. For this decontamination process, acid cost is estimated at only 8.2 US$ t.t.w.$^{-1}$. Hazardous sludge disposal represents the most important economic parameter with an estimated cost of 30.6 US$ t.t.w.$^{-1}$. The overall decontamination cost has been calculated at 115 US$ t.t.w.$^{-1}$ corresponding to 14.4 M US$ year^{-1}. The decontamination cost appears to be close to the landfill cost.

This economic study takes into account the treatment of the leachate. Obviously, leachates need to be treated, inevitably increasing the operational costs. On the other hand, a treated-wood recycling facility would include processes for a wood revalorization network including operations such as composting, burning and producing ethanol, and the wood would be sold for use in these applications. Chromium and copper could be removed from the leachate in revalorization processes using selective technologies such as electrolytic deposition or ion exchange, for example. Hence wood and metal recycling would generate revenues. On the whole, this study demonstrates that the sulphuric acid leaching process seems truly feasible in terms of operation costs.

4. Conclusion

Various chemical and physical parameters were varied to determine the most suitable leaching conditions in order to design an efficient process with limited costs. The best conditions were obtained using sulphuric acid 0.2N with chopped wood (<8 mm particle size) at 150 g L^{-1}, and with a 6-h leaching period at 75 °C. Temperature greatly influences extraction performances but a high process temperature does not necessarily mean high operating costs as heating energy can be provided by the remediated wood resulting from this process. Furthermore, as the extraction operation produces highly concentrated leachates, complementary studies should be focused on extraction and recycling of chromium and copper, discarding of arsenic recirculation of hot acidic water in closed loops and wood residue reuse. Overall, this study highlights the potential application of the chemical leaching process in treated-wood recycling facilities.

Acknowledgments

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