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Pyrolysis of Chromated Copper Arsenate-Treated Wood: Investigation of Temperature, Granulometry, Biochar Yield, and Metal Pathways

Mouna Gmar [1], Hassine Bouafif [2], Besma Bouslimi [1], Flavia L. Braghiroli [1,2] and Ahmed Koubaa [1,*]

[1] Forest Research Institute, Université du Québec en Abitibi-Témiscamingue, 445 Boul. University, Rouyn-Noranda, QC J9X 5E4, Canada; mouna.gmar@uqat.ca (M.G.); besma.bouslimi2@uqat.ca (B.B.); flavia.braghiroli@uqat.ca (F.L.B.)

[2] Centre Technologique des Résidus Industriels (CTRI), Rouyn-Noranda, QC J9X 5E5, Canada; hassine.bouafif@cegepat.qc.ca

* Correspondence: ahmed.koubaa@uqat.ca

Abstract: Chromated copper arsenate-treated (cca) wood disposal faces environmental restrictions due to its toxicity, heavy metal leaching in storage sites, and greenhouse gas emissions during incineration. Thus, finding new management methods for this contaminated wood at the end of life is crucial. This study evaluated the effect of pyrolysis temperature (300, 400, and 500 °C), particle size, biochar yield, and the behavior of arsenic (As), chromium (Cr), and copper (Cu) during treated-wood pyrolysis. The highest biochar yield was obtained at 300 °C for fine particles. The biochar retention of heavy metals decreased with increasing pyrolysis temperature. At 300 °C, the highest biochar As, Cr, and Cu retentions were 76, 91, and 83%. At 500 °C, biochar only retained 43% of the As. Additionally, heavy metal leaching from the biochar exceeded the Environmental Protection Agency's (EPA) maximum concentration limit of 5 mg/L. High-density polyethylene encapsulation of contaminated biochar reduced the leaching of As, Cr, and Cu by 96, 95, and 91%, respectively. Thus, combining pyrolysis and plastic encapsulation to produce a composite material could be a solution for reducing waste (conversion of CCA-wood into biochar) and for the safe disposal of contaminated wood.

Keywords: wood preservative; chromated copper arsenate-treated wood; pyrolysis; safe waste disposal

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1. Introduction

Wood is a very suitable material for external uses. However, it can be attacked by insects (termites, beetles, etc.), fungi (lignicolous, rotting or lignivores, molds, etc.), as well as adverse weather conditions [1]. To extend its lifetime and reduce forest harvesting, wood preservation with fungicides has been a common practice in the wood preservation industry since 1910 [2]. For example, Canada was the second-largest producer of wood preservatives globally. In addition to creosote, pentachlorophenol (PCP), and other preservatives, chromated copper arsenate (CCA) was the most widespread fabricated preservative worldwide. In 1995, CCA alone accounted for 90% of the preservatives used [3]. However, the effectiveness of preservatives cannot be assessed without considering their impacts on the environment and human health. For example, CCA used as a wood preservative in power distribution poles, railway ties, etc., is often associated with the risk of metal leaching from storage sites or landfills where they are discarded [4]. Due to its toxicity, the use of CCA-treated wood for residential use was prohibited in 2004 and is highly regulated nowadays [5]. Nevertheless, the management of CCA-treated wood waste is a major problem worldwide.

The increase in CCA-treated wood volume, the leaching, the toxic nature of the waste, and the tightening of regulations concerning its incineration are the main factors that have motivated the development of new management methods for its disposal or recovery [6]. According to the American Wood Protection Association (AWPA), three CCA formulations have been developed: types A, B, and C [7] (Table 1). The three formulations contain about 19% copper oxide (CuO) [8,9]. Type A contains a significant amount of chromium (65.5%), while types B and C contain comparable amounts of arsenic (45.1% and 34.0%, respectively) and chromium (35.3% and 47.5%, respectively) [10,11]. Type C has been the most commercially popular in the past few years (from 1980 to 2000 [11]). The arsenic pentoxide (As_2O_5) is the most problematic element present in CCA. However, Cr^{+3} is the most dominant and thermodynamically stable element under ambient redox conditions in CCA-treated wood.

Table 1. Different types of CCA formulation [8,9].

Degree of Oxidation	Chemical Formula	Type A (%)	Type B (%)	Type C (%)
Cr (VI)	CrO_3	65.5	35.3	47.5
Cu (II)	CuO	18.1	19.6	18.5
As (V)	As_2O_5	16.4	45.1	34.0

Several decontamination processes for CCA-treated wood have been developed at the laboratory level. Methods used for wood decontamination include electrodialysis [12–15], chemical [9,16], and thermal, including pyrolysis [8,17,18]. The pyrolysis of CCA-treated wood is complex due to the wood's interaction between metals and biopolymers [17]. Pyrolysis is a thermochemical conversion of biomass in an inert atmosphere that produces a solid material (biochar), a liquid (bio-oil), and non-condensable gases such as CO, CO_2, and H_2 [19]. The primary pyrolysis mechanism is the depolymerization reactions that produce volatile condensable compounds and organic non-condensable compounds [20–23]. With an increase in pyrolysis temperature, volatile compounds remain unstable. They may undergo secondary reactions such as cracking or recombination, resulting in the release of volatile compounds and the formation of lower molecular weight compounds [21,24–26].

Operating conditions such as residence time, temperature, heating rate, biomass precursor, and particle size can affect pyrolytic products' chemical composition and distribution [27]. Additionally, CCA significantly influences the thermal behavior of wood samples, especially if the CCA concentration is high. Helsen et al. [28] found that the highest char yield of CCA-treated wood was 27% at 390 °C compared to 7% at 700 °C. Cr and Cu releases were negligible, while As release was less than 10% at a pyrolysis temperature of 400 °C and residence time of 10 min. These findings are in good agreement with other studies that reported that As (V) is reduced to arsenic trioxide (As_2O_3), decomposes, and becomes volatile during pyrolysis, even at 200 °C [29,30].

Additionally, during pyrolysis, heat transfer phenomena depend on the size of wood particles [31]. Several research studies have investigated the influence of particle size on the pyrolysis mechanism [31–37]. Sadhukhan et al. [34] found that the larger the particle size, the higher the temperature gradients, which maximizes biochar production. For pyrolysis of oil mallee woody biomass at 500 °C, Shen et al. [36] found that biochar yield increased from 33 to 90% when particle size increased from 0.3 to more than 3 mm. In the case of CCA-treated wood, particle size strongly influenced the retention of As and Cr present in the biochar. Large biomass particles (9.5 cm long) had a high resistance to mass transfer to release As and Cr; therefore, biochar presents higher retention of both metals [38]. Previous studies focused on the slow pyrolysis of metal-impregnated wood to understand the behavior of metals and define the possible means of by-product recovery. Indeed, inorganic salts act as catalysts in pyrolysis reactions, which leads to increased biochar yield [16,17,28,39,40].

The final disposal of hazardous and radioactive waste is often problematic due to several technical, regulatory, and political considerations. Stabilization/solidification technologies (S/S) have been frequently used as a reliable and cost-effective technical option. This technology affects many wastes, including liquids, sludge, contaminated soils, and fly ash [41–43]. For example, all hazardous residual materials or contaminated soils with metals are treated by S/S before being disposed of in landfills in Quebec, Canada [43]. The stabilization process converts residual contaminants into a more chemically stable and leach-resistant form that contributes to their immobilization. Specifically, stabilization processes allow some form of physical solidification with organic or inorganic binders to obtain a solid inert matrix.

According to environmental regulators, this solidification technology transforms the hazardous waste into a homogeneous, leaching-resistant compound and, therefore, environmentally acceptable [42]. Wang et al. [44] focused on the S/S treatment of heavy metal contaminated soils using different binders, including Portland cement, magnesium oxide, and zeolite. After S/S treatment, the heavy metal (lead, zinc, arsenic, chromium, copper, and nickel) leaching of highly contaminated samples ranged from 0.002 to 0.225 mg/L. These low concentrations confirm the efficiency of the process. However, no studies have tested the encapsulation of biochar obtained by pyrolysis of CCA-treated wood. In addition, most studies conducted on the pyrolysis of CCA-treated wood have been limited to the prospect of pyrolysis reactions and the volatilization profile of metals. Furthermore, no studies have compared the mobility of contaminants by leaching before and after wood thermochemical conversion to determine a pathway for its recovery. Thus, this project aims to study the impact of pyrolysis at different temperatures and wood particle sizes on the mobility of contaminants (As, Cr, and Cu) and the potential disposing of CCA-treated wood by encapsulation in a high-density polyethylene matrix.

2. Materials and Methods

2.1. CCA-Treated Wood Sampling and Characterization

The CCA-treated wood waste used in this study came from shredded poles provided by Tred'si (Westbury, QC, Canada). Red pine poles were between 15 and 40 years old and had diameters ranging from 20 to 38 cm. Wood chips measured between 2 and 26.5 cm in length, 0.75 and 10 cm in width, and 0.1 and 2.4 in thickness. The CCA-treated wood was type C and composed of 45.2% CrO_3, 26.4% CuO, and 28.4% As_2O_5. Because of wood chip heterogeneity, a random sample was taken from a 5 kg bag of shredded wood received from Tred'si and crushed in a large crusher (Schutte-Buffalo Hammermill 1320, Buffalo, NY, USA) to obtain chips with a particle size ranging from 0.85 mm to 9 mm. A sample of untreated wood (red pine) was used as a control. The treated and untreated wood were milled to a particle size of 0.8 mm for the characterization tests.

2.2. Pyrolysis of CCA-Treated Wood

The slow pyrolysis of CCA-treated wood samples was carried out in an in-house pilot-scale furnace (Figure 1). Different pyrolysis temperatures (300, 400, and 500 °C) and particle sizes, as indicated by granulometry (G) ($0.85 \text{ mm} < G1 < 1.4 \text{ mm}$; $1.4 \text{ mm} < G2 < 2 \text{ mm}$ and $2 \text{ mm} < G3 < 3.35 \text{ mm}$), of CCA-treated wood were investigated. At the beginning of the pyrolysis process, the furnace was fed with 100 g of CCA-treated wood and then sealed and heated to the desired temperature. A long screw allowed the material to be transported from the inlet hopper to the outlet hopper under a nitrogen atmosphere (2 L/min) and residence time of approximately 1 h. The pyrolysis gases were condensed in a system connected to a beaker for pyrolytic oil recovery and then to an inorganic gas treatment section consisting of a mixed cellulose ester membrane filter. Gases loaded with inorganic contaminants were retained by a filter and then in nitric acid bubblers. The biochar collected in the outlet hopper was weighted, and the yield (Y) was calculated according to Equation (1):

$$Y = \frac{w_2}{w_1} \times 100 \tag{1}$$

where w_1 and w_2 are weights of treated wood (g) before and after pyrolysis, respectively.

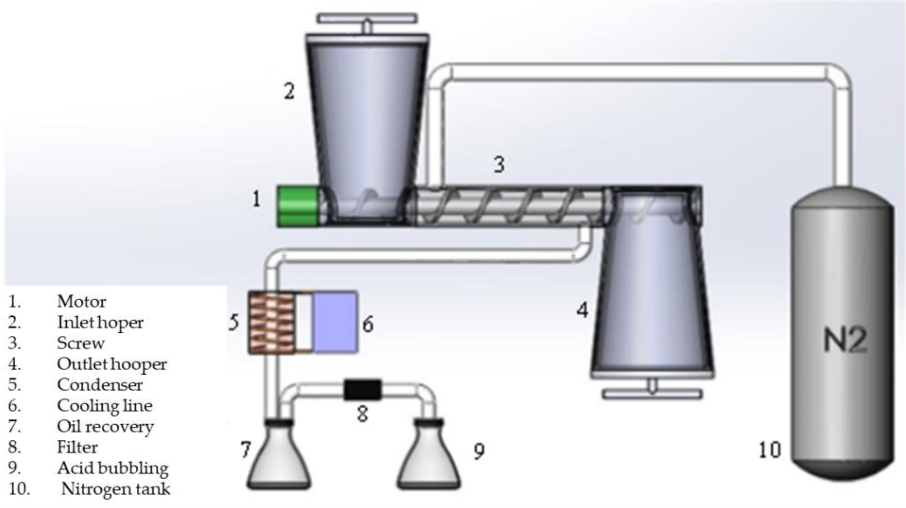


Figure 1. In-house pilot-scale furnace used for the pyrolysis of CCA-treated wood.

2.3. Characterization of Materials

2.3.1. Microstructure

The CCA-treated wood and biochar samples were analyzed by scanning electron microscopy (SEM). This analysis allows the visualization of sample microstructure and the metals' distribution in the wood and the biochar. A carbon deposit was applied to the sample before the observation to make the surface conductive and facilitate the discharge of electrons. The preparations were placed on a support and introduced into a pressure-controlled chamber of a Hitachi S-3500N Scanning Electron microscope coupled to an EDS (energy dispersive X-ray spectroscopy) spectrometer and managed by a 'Bruker' data processor for recording images, elemental maps, and chemical composition. The SEM tests were conducted at a 20 keV voltage, an amperage of 140 A, a 25 kPa pressure, and a 15 mm working distance.

2.3.2. Physical and Chemical Properties

The moisture and ash contents of untreated wood, CCA-treated wood, and biochar were measured by a Max5000XL ash analyzer (Arizona Instruments Computrac, Chandler, AZ, USA). Elemental carbon, hydrogen, nitrogen, and sulfur contents were measured using a CHNS analyzer (Perkin Elmer 2400 CHNS/O Analyzer; Waltham, MA, USA). Heavy metals (As, Cr, Cu) in the CCA-treated wood and biochar samples were quantified using inductively coupled plasma mass spectrometer analysis (ICP-MS) (Agilent Technologies, Santa Clara, CA, USA) according to Quebec's Centre of Expertise in the Environmental Analysis [45].

For sample digestion, approximately 1 g of each homogenized solid was dried at 105 °C and mixed with 4 mL of 50% (v/v) nitric acid and 10 mL of 20% (v/v) hydrochloric acid. The mixture was heated on a hot plate for 30 min without stirring (to avoid the solution boiling) and filtered for analysis. Each sample was digested in triplicate to obtain an average metal concentration value. The results of the ICP-MS analysis were used to calculate the retention capacity of heavy metals in biochar (Equation (2)):

$$Retention\ capacity\ (\%) = \frac{Concentration\ of\ a\ specific\ metal\ in\ biochar}{[Concentration\ of\ a\ specific\ metal\ in\ wood\ ]} \times biochar\ yield \qquad (2)$$

2.4. Toxicity Characterization and Leaching Procedure (TCLP)

Regulatory tests were conducted to assess the risks of metals leaching from CCA-treated wood and biochar [13]. The TCLP reproduced leaching conditions in landfill sites. The leaching solution was a mixture of glacial acetic acid and 1 N sodium hydroxide. In total, 20 g of each sample was mixed with 400 mL of the leaching solution in a plastic bottle (ratio 1:20). The mixture was agitated at 30 rotations per minute (rpm) in a leaching wheel for 18 h. After decantation, the leaching solutions were filtered and acidified before ICP-MS analysis.

2.5. Biochar Encapsulation

A twin-screw extruder (Thermo Scientific HAAKE PolyLab OS Rheodrive 7 with Rheomex OS extruding module, Thermo Electron GmbH, Karlsruhe, Germany) prepared the biochar–polymer composites, which were composed of 500 g of 80% high-density polyethylene (HDPE) and 20% biochar. The temperature was fixed at 160 °C and maintained throughout the extrusion process to ensure polymer melting. The rotational speed was about 40 rpm, whereas the filling speed was 10 rpm. At the exit, the extrudate, in the form of stretched wire, was cooled in a water tank and conveyed to a rotary mill to obtain small granules. TCLP was then applied to determine the concentration of leaching metals from the final composite HDPE-biochar.

2.6. Statistical Analyses

The data obtained from this study were statistically analyzed using the SAS (Statistical Analysis System) software, version 9.4 [46]. Biochar yield, metal retention capacity, and metal leaching rates were subjected to a two-factor analysis of variance (ANOVA) to determine the significance of pyrolysis temperature and particle size on the variables. All statistical analyses were considered significant at a threshold of $\alpha = 0.05$. For metal retention capacity and metal leaching, the dependent variables were the concentrations of arsenic, chromium, and copper in the biochar. The explanatory variables were the pyrolysis temperature and the particle size of the CCA-treated wood. Equation (3) presents the general model:

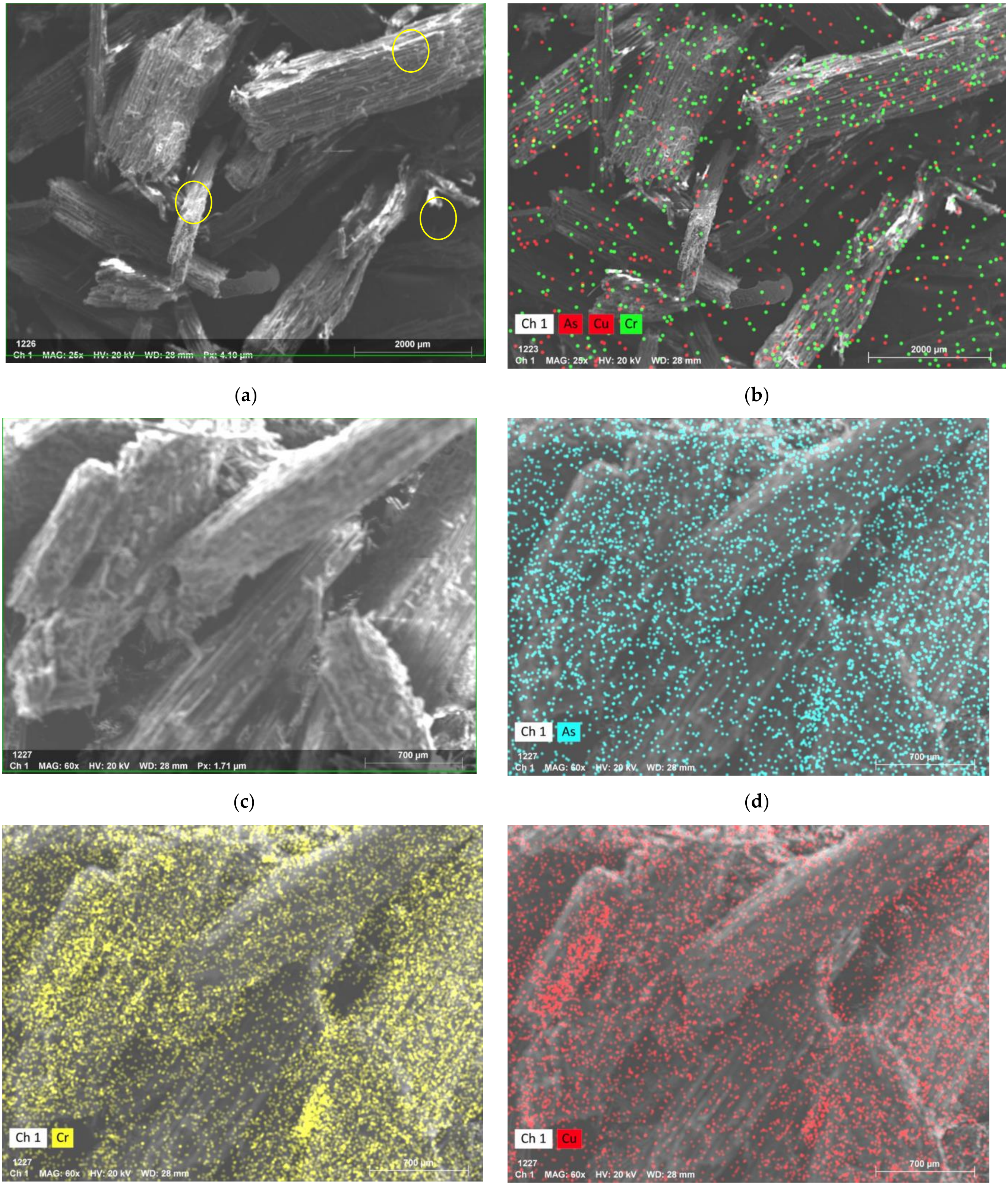
$$Y = \mu + Di + Ej + Di \times Ej + \varepsilon \tag{3}$$

where Y represents the value of the response variable; μ is the general effect (intercept); Di, Ej, and Di^*Ej are the effects of pyrolysis temperature, wood particle size, and the interaction between temperature and particle size, respectively, and ε is the residual error.

3. Results and Discussion

3.1. Microstructure of CCA-Treated Wood and Biochar

The scanning electron microscopy (SEM) images (Figure 2) illustrate the microstructure of CCA-treated wood and biochar and the distribution of metals (As, Cu, and Cr) in the CCA-treated wood structure (Figure 2a,b) and biochar (Figure 2c–f). As, Cr, and Cu appear as white spots on the wood and the biochar surface. Despite thermal degradation, the microstructure of biochar (Figure 2c) is similar to that of CCA-treated wood (Figure 2a) but with more metallic precipitates and agglomerates at its surface. The energy dispersive X-ray spectroscopy (EDS) analyses of the white spots identified arsenic, copper, and chromium as the main metallic components on both the wood (Figure 2b) and the biochar (Figure 2d–f). As, Cr, and Cu (Figure 2c–f) are abundant on the biochar surface (Figure 2c–f) due to the high initial metal concentration on the CCA-treated wood surface (Figure 2b). These observations agree with previous findings and confirm that pyrolysis promotes the precipitation and agglomeration of metals on the biochar. These inorganic elements are released from the complexes formed with the wood's lignin and cellulose to clog the biochar's pores in the form of agglomerates [47–49].



(**a**) (**b**)

(**c**) (**d**)

(**e**) (**f**)

Figure 2. Scanning electron microscopy (SEM) facias of (**a**) CCA-treated wood showing As, Cr, or Cu metals identified by circles; (**b**) the dispersion of As, Cr, and Cu in the CCA-treated wood; (**c**) Biochar showing multiple spots of metals; (**d**) The dispersion of As in biochar; (**e**) The dispersion of Cr in biochar; (**f**) The dispersion of Cu in biochar.

3.2. Physical and Chemical Properties of CCA-Treated Wood and Biochar

The moisture content of untreated wood and CCA-treated wood was similar, with an average value of 6.9%, and the biochar had an average humidity of 1.86% (Table 2). According to previous reports [50,51], biomass moisture content should not exceed 10% to not affect the quality of pyrolysis products. C, H, N, and S percentages for the untreated and CCA-treated wood samples are comparable, showing that treating wood using a metal agent (e.g., CCA) does not affect its elemental composition [50]. Measured proportions of C, H, and O in CCA-treated wood were comparable to those found in this project: 45.6%, 6.6%, and 47.8%, respectively (Table 2). The ash content was higher for the contaminated wood than the untreated one due to inorganic elements (As, Cr, and Cu).

Table 2. Characterization of untreated wood, CCA-treated wood, and biochar.

Elements/Properties	Sample Type		
	Untreated Wood	**CCA-Treated Wood**	**Biochar Produced at 300 °C**
	Elementary Analysis (%wt)		
N	0.17 ± 0.04	0.32 ± 0.03	0.27 ± 0.02
C	49.6 ± 0.10	46.1 ± 0.15	58.27 ± 0.21
H	6.74 ± 0.04	6.05 ± 0.02	4.04 ± 0.03
O *	35.2 ± 0.07	38.4 ± 0.09	28.94 ± 2.37
S	1.26 ± 0.07	0.94 ± 0.06	0.58 ± 0 01
Moisture content (%)	6.91 ± 0.03	6.85 ± 0.03	1.86 ± 0.01
Ash (%)	0.08 ± 0.02	1.42 ± 0.02	4.80 ± 0.01

* Calculated by difference.

The metal concentrations in CCA-treated wood at different particle sizes are shown in Table 3. Very high As, Cr, and Cu concentrations were found in the CCA-treated wood. Samples belonging to the G2 particle size had the highest concentration of metals, while the samples with G1 particle sizes had the lowest concentration in As, Cr, and Cu. This is due to the size dependency of mass transfer resistance, which is determined by the particle's smallest dimension. Large particles have a higher mass transfer resistance to metal release and are thus characterized by higher retention in the biochar [38].

Table 3. The concentration of metals in CCA-treated wood samples for the different particle sizes.

Particle Size (mm)	Concentration (mg/kg)		
	As	**Cr**	**Cu**
0.85 < G1 < 1.4	1539 ± 842	2856 ± 171	1585 ± 118
1.4 < G2 < 2	2850 ± 498	3580 ± 601	2107 ± 353
2 < G3 < 3.35	2478 ± 839	3461 ± 379	2019 ± 310

Several wood- and process-related factors influence the retention of metals in treated wood [1,6]. Wood-related factors include species, wood permeability, age, temperature, degree of exposure to air, and planned end-use. Process-related factors include the initial formulation and the chemicals used. Initial concentrations of As, Cr, and Cu measured in CCA-treated wood in this study differ from those reported in the literature [13,51–53]. This difference can be related to different factors affecting the metal retention capacity of the wood used. For CCA-treated wood, Kim et al. [51] and Mercer and Frostick [52] measured higher and lower concentrations than those found in this study: 4300 and 1885 mg/kg As, 4900 and 1243 mg/kg Cr, and 2800 and 1261 mg/kg Cu, respectively. According to Coudert [6], the initial levels of metals present in CCA-treated wood can directly impact its recycling or recovery.

Table 4 shows that particle size, pyrolysis temperature, and their interaction significantly affected As, Cr, and Cu concentrations. The high coefficients of determination (R^2)

of the statistical models suggest that variations in metal concentration are mainly explained by the studied factors (size, pyrolysis temperature, and their interaction). For example, 87% of the variation in As concentration is explained by the studied factors. The remaining 13% are unexplained or attributed to experimental errors or other factors. The studied factors explain 91% of the variation for the Cr and Cu concentrations.

Table 4. Analysis of variance (F values) of the effects of particle size and pyrolysis temperature on metal concentration and leaching.

Source	DF [1]	Biochar	Retention Capacity			Metal Concentration			Metal Leaching		
		Yield	As	Cr	Cu	As	Cr	Cu	As	Cr	Cu
Model	8	74.6 **	1.17 ns	8.09 **	4.03 **	14.6 **	22.2 **	22.8 **	11.9 **	7.07 **	3.49 *
Size (G)	2	145 **	0.97 ns	0.20 ns	0.27 ns	72.6 **	7.80 **	72.6 **	25.2 **	23.6 **	12.0 **
Temperature (T)	2	146 **	3.27 ns	26.5 **	13.3 **	11.3 **	5.82 *	11.3 **	12.9 **	2.58 ns	1.02 ns
TxG	4	3.25 *	0.23 ns	2.82 ns	1.28 ns	3.62 *	3.63 *	3.62 *	4.67 **	1.04 ns	0.47 ns
Error	18					-	-	-	-	-	-
R^2		0.97	0.34	0.78	0.64	0.87	0.91	0.91	0.84	0.76	0.61

[1] DF: degrees of freedom; * Significant at α = 0.05; ** Significant at α = 0.01; ns non-significant at α = 0.05.

3.3. Effect of Particle Size and Pyrolysis Temperature on Biochar Characteristics

Particle size and pyrolysis temperature have a highly significant effect on the biochar yield (Table 4). Figure 3 shows the variation in biochar yield obtained after pyrolysis for different particle sizes (0.85 < G1 < 1.4 mm; 1.4 < G2 < 2 mm; 2 < G3 < 3.35 mm) and pyrolysis temperatures (300, 400, and 500 °C). Variations in biochar yield are due to chemical interactions between wood polymers (lignin, hemicelluloses, and cellulose) and heat and mass transfer differences. On the other hand, interactions are difficult to interpret. Patwardhan et al. [54] showed that secondary reactions such as cracking occur because of inorganic elements (or catalysts). As a result, higher amounts of light compounds are obtained, resulting in lower biochar yields.

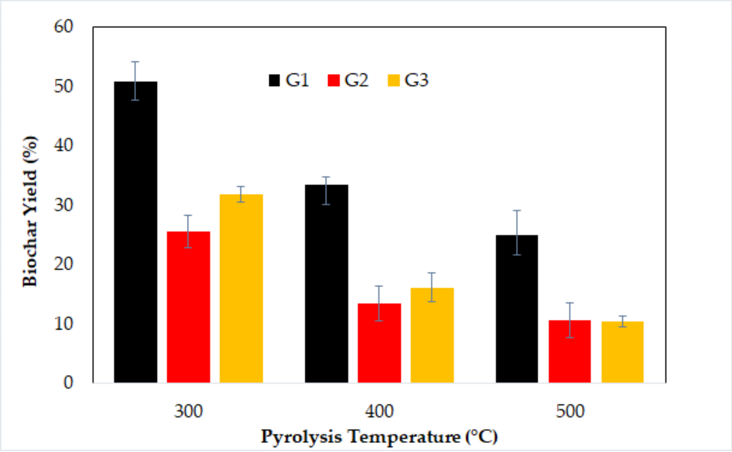
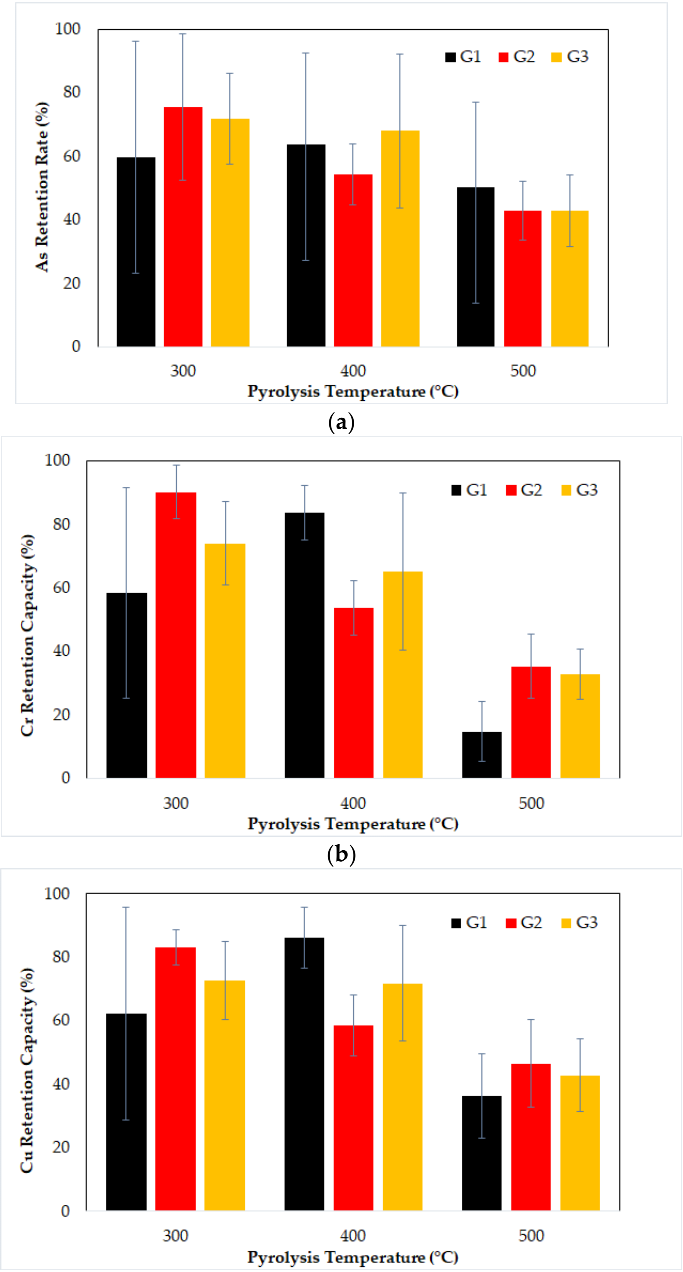


Figure 3. Biochar yield from CCA-treated wood at different granulometries (0.85 < G1 < 1.4 mm; 1.4 < G2 < 2 mm; and 2 < G3 < 3.35 mm) as a function of different pyrolysis temperatures (300, 400, and 500 °C).

The decrease in biochar yield as a function of particle size is explained by the high concentrations of As, Cr, and Cu in CCA-treated wood. For example, the concentrations of As, Cr, and Cu (1539, 2856 and 1585 mg/kg, respectively) are much lower in fine particles (0.85 < G1 < 1.4 mm) than the concentrations (2850, 3580, and 2107 mg/kg, respectively) in medium particles (1.4 < G2 < 2 mm). In addition, a significant decrease in biochar yield was observed by increasing the pyrolysis temperature from 300 to 500 °C. The loss of volatile condensable compounds released by the decomposition of hemicellulose and cellulose explains this decrease [55]. High biochar yields (up to 50%) at a low temperature (300 °C) indicate that wood thermochemical conversion was incomplete.

3.4. Effect of Pyrolysis Temperature on Metal Retention

Metal retention capacity is an indicator of the effectiveness of the pyrolysis process in stabilizing the metals present in CCA-treated wood. Thermal stabilization will concentrate metal compounds such as As, Cr, and Cu in a solid matrix (biochar). Figure 4 shows the As, Cr, and Cu retention capacities of the biochar produced at pyrolysis temperatures 300, 400, and 500 °C. With a temperature increase, the retention of the three metals decreased due to the increase in the metals' volatilization [38].



(**a**)

(**b**)

(**c**)

Figure 4. Retention capacity of As (**a**), Cr (**b**), and Cu (**c**) in biochar prepared at different particle sizes: 0.85 < G1 < 1.4 mm, 1.4 < G2 < 2 mm, and 2 < G3 < 3.35 mm, and different pyrolysis temperatures (300, 400, and 500 °C).

The ANOVA results confirm that pyrolysis temperature had a very significant effect, especially for Cr and Cu (Table 4). However, the effect of particle size does not seem to be significant during pyrolysis for any of the metals. The retention capacity of As has a lower regression coefficient (R^2 = 0.34) compared to Cr and Cu (0.76 and 0.61, respectively). Thus, 66% of the observed values are explained by factors other than those studied (particle size, temperature, and their interaction).

The other factor that may explain the model is the initial concentration of the inorganic metals in CCA-treated wood. The difference between the initial concentrations of As or Cu for the three selected samples explains the high standard deviation. These variations were in good agreement with an earlier study on CCA-treated wood [28]. This high dispersion may be due to the heterogeneous nature of the shredding of the treated poles. For example, treated sapwood can provide more homogeneous wood samples.

For the medium-sized particles (G2), As retention in biochar reached 76% at 300 °C, compared to 43% at 500 °C. Cr and Cu retention percentages at 300 °C were 91% and 83%, respectively. Additionally, the greatest amount of biochar with the highest metal concentrations was produced at 300 °C, while the smallest volume of biochar with the lowest metal concentrations was produced at 500 °C. Helsen and Van den Bulck [29] described the various reactions that can occur during CCA-treated wood pyrolysis. The As release during wood pyrolysis is governed by a reduction reaction of arsenate (As_2O_5) to arsenite (As_2O_3). This reaction occurs at about 327 °C. Heating copper and arsenic oxides volatilize part of the arsenic oxide, and the remaining part reacts with copper oxide to form mixed copper arsenates ($2\,CuO.As_2O_5$ and $Cu_3(AsO_4)_2$). Similarly, heating chromium and arsenic oxides volatilize free arsenic oxide, some of which reacts with Cr_2O_3 to form chromium arsenate ($CrAsO_4$).

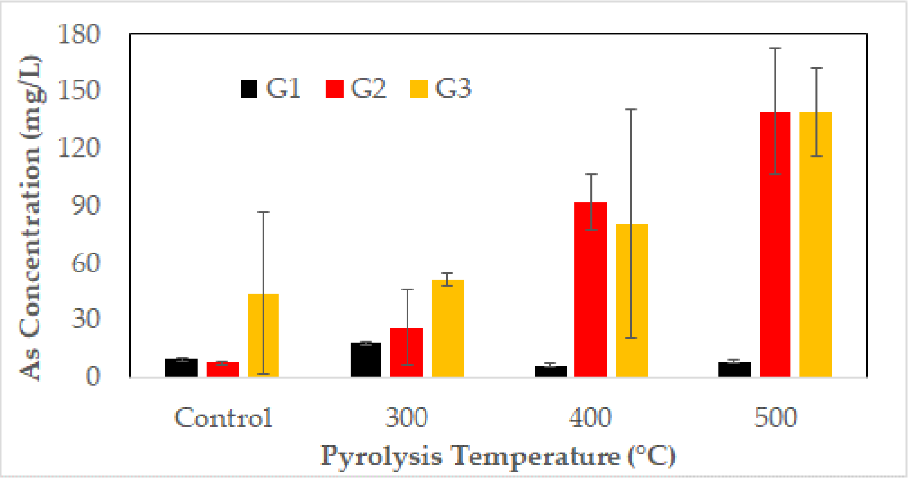
The thermal decomposition of the inorganic components of CAA-treated wood can be influenced by their interaction with the decomposition products of wood. For instance, the decomposition of arsenate is highly influenced by the presence of glucose. It might result in the acceleration of the decomposition reaction, oxidation–reduction reactions, and the formation and decomposition of arsenate esters [29].

The retention capacity for the three metals in biochar did not reach 100% at 300 °C. This difference can be explained by the extended residence time in the furnace.

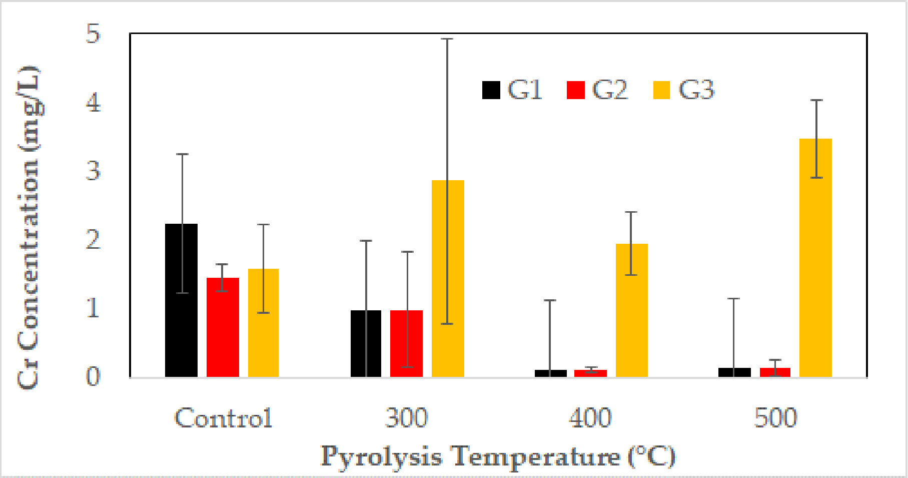
It is also important to mention that the metal retention capacity decreases slightly at 400 °C. At 500 °C, the decrease is more pronounced and suggests that the high volatilization of metal compounds occurs at higher pyrolysis temperatures [38]. However, As is a problematic compound because it volatilizes at low temperatures. At 300 °C, As is reduced to arsenic trioxide, which is retained in the biochar. However, at temperatures above 400 °C, the compound formed is no longer stable, and total As is significantly volatilized. On the other hand, chromium trioxide is the product of the decomposition of chromium arsenate, which volatilizes at lower temperatures than As following the formation of organochlorine compounds. Finally, pyrolysis at 300 °C remains safer since the retention of the three metals is more important than at other temperatures.

3.5. Metal Leaching of CCA-Contaminated Biochar

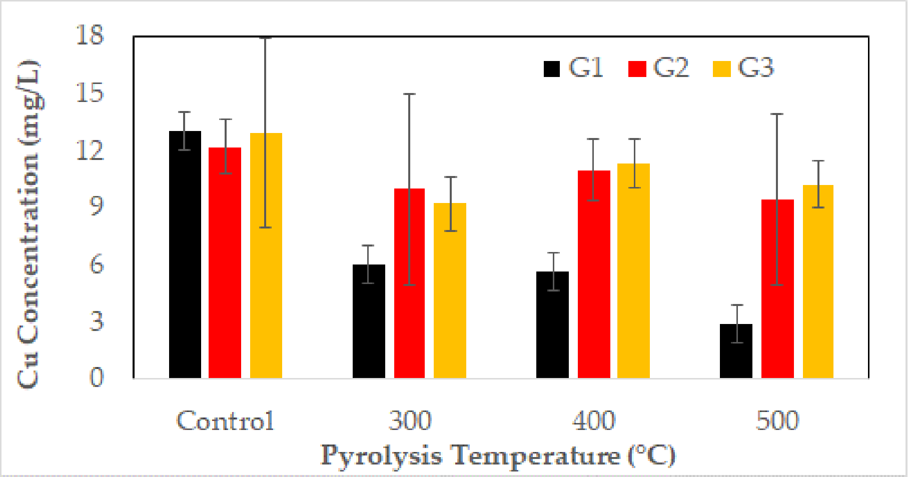
The effects of particle size on AS, Cr, and Cu leaching are highly significant (Table 4). The most leached compound is at particle sizes G2 and G3 and higher pyrolysis temperatures (Figure 5a). The effect of pyrolysis temperature was significant on As leaching but did not significantly affect Cr and Cu leaching (Table 4). The ANOVA models were highly significant, with 84%, 76%, and 61% coefficients of determination for AS, Cr, and Cu leaching, respectively (Table 4). The high coefficient of determination for As indicates that particle size, pyrolysis temperature, and their interaction explained 84% of the total variation in metal concentration. The remaining 16% of the total variation is unexplained and can be attributed to other factors and experimental errors. For Cr and Cu, the unexplained variation (24% and 39%, respectively) is higher than that for As. According to the regression coefficients, the established model explains 84% and 66% of the observed variation in As and Cr leaching.



(**a**)



(**b**)



(**c**)

Figure 5. Leaching of arsenic (**a**), chromium (**b**), and copper (**c**) as a function of pyrolysis temperature and particle size. Control is CCA-treated wood.

The high standard deviation is related to the heterogeneity of the samples despite the use of grinding and sampling techniques. However, as mentioned previously, the initial concentration of metals in the wood may depend on several other factors. For example, when subjected to low precipitation in site or storage areas, a wood sample from a younger pole will have a higher metal leaching rate than a very old pole that has already released more than 80% of the preservatives. Thus, pyrolysis temperature and CCA-treated wood particle size affected As (Figure 5a), Cr (Figure 5b) and Cu (Figure 5c) leaching from biochar. These results confirm that biochar is a hazardous waste even after thermochemical stabilization. Thus, an additional stabilization treatment is required to trap these metals. Hence, among several waste stabilization/solidification processes, encapsulating the contaminated biochar in a high-density polyethylene matrix could be an alternative for its safe disposal in landfill sites.

As previously described, leaching tests (TCLP) showed that biochar is a hazardous waste because of the high As and Cr content in leaching solutions. Before landfill disposal, hazardous waste must be stabilized and solidified according to the guidelines of the Government of Québec, Canada [43]. Based on the results of metal retention capacities, it has been demonstrated that a temperature of 300 °C and a particle size of 1.4 to 2 mm are optimal parameters for stabilizing metals in the biochar. Table 5 presents the concentrations of As, Cr, and Cu in leaching solutions for wood samples before pyrolysis, encapsulation (biochar), and after encapsulation (composites biochar-HDPE). The TCLP tests show a significant reduction in As, Cr, and Cu concentrations in leaching solutions before and after encapsulation compared with their concentrations in samples before pyrolysis. Therefore, the biochar-HDPE pressurized and agglomerated mixture is a reliable option to stabilize metals in biochar. Indeed, the residual metal contents in the leaching solutions were below tolerated limits (<5 mg/L) according to environmental regulations in Québec.

Table 5. Average metal concentrations in biochar leaching solutions before pyrolysis and before and after encapsulation, according to the TCLP test.

	Concentration of Metals (mg/L)		
	As	**Cr**	**Cu**
Before pyrolysis	9.23 ± 1.04	2.24 ± 0.27	13.0 ± 1.44
Before encapsulation	25.95 ± 19.73	0.99 ± 0.84	9.96 ± 5.20
After encapsulation	0.63 ± 0.10	0.05 ± 0.02	0.52 ± 0.04
Reduction (%)	88.4	95.0	94.8

The biochar-HDPE composite could be used for almost all wood–plastic composites' end-uses, including patios, siding, railroad ties, etc. The main advantage of such material is its dimensional stability due to biochar hydrophobicity [56]. Nevertheless, investigations on these composites in service and environmental performance are needed.

The results obtained in this study agree with those reported in the literature on the encapsulation of waste containing arsenic using other types of binders (Portland cement, asphalt concrete, an amorphous matrix of glass at a high temperature)] [57,58]. For example, Conner and Lear [57] showed that As leaching from stabilized/solidified waste was 0.016 mg/L while leaching from untreated waste was much higher (4.20 mg/L) from contaminated soils. Rechichi [58] found that the leaching rate of As was less than 5 mg/L when the waste was encapsulated in a mixture of aluminum sulfate, iron chloride, and calcium carbonate. In this study, only one formulation was tested (80% HDPE and 20% biochar) to evaluate the potential of encapsulation in the immobilization of the three metals, but further studies are needed to optimize the plastic composition and the proportions of HDPE and biochar. It could be possible to reduce HDPE proportion in the formulation to obtain acceptable metal contents in the leaching solutions. In addition, recycled plastic waste could also be a low-cost alternative for preparing the composite. Thus, two important waste problems could be minimized by this ecological solution.

4. Conclusions

Biochar obtained after pyrolysis contains large amounts of heavy metals. In addition, metal leaching increases under the effect of pyrolysis temperature. The metal retention in biochar confirmed the potential of pyrolysis for heavy metal stabilization. The pyrolysis of CCA-treated wood at 300 °C with a particle size varying between 1.4 to 2 mm reduced the contaminated biomass by 25%. It retained 75% of the arsenate, 91% of the chromium, and 83% of the copper in the biochar, while encapsulation reduced metal leaching. Further experiments should be conducted to test different HDPE/biochar and plastic waste formulations and evaluate the mobility of the three metals.

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