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Decontamination of CCA-treated eucalyptus wood waste by acid leaching

Suzana Frighetto Ferrarini [a], Heldiane Souza dos Santos [a], Luciana Gampert Miranda [b], Carla Maria Nunes Azevedo [a,b], Sandra Maria Maia [c], Marçal Pires [a,b,*]

[a] Postgraduate Program in Engineering and Materials Technology, Pontifical Catholic University of Rio Grande do Sul, Ipiranga Avenue, 6681, 90619-900 Porto Alegre, RS, Brazil
[b] Faculty of Chemistry, Pontifical Catholic University of Rio Grande do Sul, Ipiranga Avenue, 6681, 90619-900 Porto Alegre, RS, Brazil
[c] Institute of Chemistry, Federal University of Rio Grande do Sul, Bento Gonçalves Avenue, 9500, 91501-970 Porto Alegre, RS, Brazil

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ABSTRACT

Preservatives such as chromated copper arsenate (CCA) are used to increase the resistance of wood to deterioration. The components of CCA are highly toxic, resulting in growing concern over the disposal of the waste generated. The aim of this study was to investigate the removal of Cu, Cr and As present in CCA-treated eucalyptus wood from utility poles removed from service in southern Brazil, in order to render them non-hazardous waste. The removal was carried out by acid leaching in bench-scale and applying optimal extractor concentration, total solid content, reactor volume, temperature and reaction time obtained by factorial experiments. The best working conditions were achieved using three extraction steps with 0.1 mol L^{-1} H_2SO_4 at 75 °C for 2 h each (total solid content of 15%), and 3 additional 1 h-long washing steps using water at ambient temperature. Under these conditions, removal of 97%, 85% and 98% were obtained for Cu, Cr and As, respectively, rendering the decontaminated wood non-hazardous waste. The wastewater produced by extraction showed acid pH, high organic loading as well as high concentrations of the elements, needing prior treatment to be discarded. However, rinsing water can be recycled in the extraction process without compromising its efficiency. The acid extraction is a promising alternative for CCA removal from eucalyptus wood waste in industrial scale.

1. Introduction

Chemical treatments aim to extend the useful life of wood exposed to environmental conditions (Bull, 2001; Townsend et al., 2005; Janin et al., 2009a–c; Magalhães et al., 2012; Cookson et al., 2014). The preservative chromated copper arsenate contains the elements Cu, Cr and As and is the most widely used waterborne preservative (Hingston et al., 2001), which is inserted into wood using the vacuum pressure impregnation method. Cu and As are effective fungicides and insecticides and Cr fixes these elements in the wood (Pizzi, 1981, 1982a–c; Kazi and Cooper, 2000). The domestic use of CCA-treated wood has been banned in the USA, Europe and Canada since 2004 due to the risks associated with the presence of carcinogenic agents in the preserved wood (Townsend et al., 2004; Janin et al., 2009b; Mercer and Frostick, 2012). Moreover, with the disposing this waste in landfills, the levels of these toxic elements result in leachates values higher than the allowed amount, endangering the environment (Townsend et al., 2004; Jambeck et al., 2006; Janin et al., 2009b).

To date, there are no such restrictions in Brazil and wood treated with CCA is widely used for a number of applications, including fences, poles, posts, railway sleepers, roundwood and construction (Vidal et al., 2015).

The leaching of metals from treated wooden structures is a well-known phenomenon (Khan et al., 2006; Solo-Gabriele et al., 2004; Townsend et al., 2005) that has caused concern in the scientific community. Several factors contribute to determining the speed and amount of leached elements, including the specie of wood, the preservative application process and the pH of the medium (Cooper et al., 2001; Townsend et al., 2002, 2005; Azevedo and Chasin, 2003; Khan et al., 2006).

There are different interpretations regarding the classification of waste resulting from wood treatment processes. In countries such as Germany, the disposal of CCA-treated wood in landfills is

* Corresponding author at: Graduate Program in Material Engineering and Technology (PEGTEMA), Pontifical Catholic University of Rio Grande do Sul, Avenida Ipiranga, 6681, 90619-900 Porto Alegre, RS, Brazil.

E-mail addresses: suzana.ferrarini@gmail.com (S.F. Ferrarini), heldianedossantos@gmail.com (H.S. dos Santos), lulu.miranda@hotmail.com (L.G. Miranda), cazevedo@pucrs.br (C.M.N. Azevedo), sandramaia@iq.ufrgs.br (S.M. Maia), mpires@pucrs.br (M. Pires).

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prohibited and it must be incinerated after exhausting all possible options for reuse (Peek, 2004). In the United States, Canada and Australia, CCA-treated wood is generally discarded in sanitary landfills (Jambeck et al., 2006). In Brazil there is still no adequate classification for this type of waste, which is treated in the same manner as other solid waste (Azevedo and Chasin, 2003). Only wastewater and waste generated in wood preservation processes using inorganic preservatives containing As or Cr are considered hazardous waste (ABNT NBR 10004). However, some non-governmental organizations are pressuring the Brazilian government to classify treated wood waste as hazardous (CBCS, 2009).

Several studies have reported different methods for removing CCA from treated-wood to minimize its environmental impact when discarded (Cooper et al., 2001; Hingston et al., 2001; Townsend et al., 2002, 2004, 2005; Azevedo and Chasin, 2003; Kartal, 2003; Janin et al., 2009a,b, 2011, 2012). Among these methods, acid extraction is one of the most widely used to remove the components present in this waste. This process reverses fixing reactions by converting CCA elements into their water-soluble forms (Clausen et al., 2001). The most commonly used organic acids are citric, acetic, formic, oxalic, fumaric, tartaric, gluconic and maleic, while the most cited mineral acids are sulfuric, hydrochloric, nitric and phosphoric acids (Cooper et al., 2001; Hingston et al., 2001; Townsend et al., 2002, 2004, 2005; Azevedo and Chasin, 2003; Kartal, 2003; Silva, 2008; Janin et al., 2009a,b, 2011, 2012; Ferrarini et al., 2012a), and more recently even wood vinegar was used (Choi et al., 2012). Research carried out in Canada demonstrated that hot water extraction using moderately concentrated sulfuric acid solutions is the most cost-effective method for decontaminating CCA-treated wood (Janin et al., 2009a, 2011, 2012). Sulfur acid is used to break the lignin bond with metal or to rupture the cellulose structure and release the metals from the organic matter (Cooper et al., 2001). Janin et al. (2009a) also highlight the potential of this process and its wood-recycling possibilities. These authors pointed out that reuse of rinsing water generated in the extraction process, is little explored in the literature (Janin et al., 2012). However, this wastewater could be used to prepare the extraction solution reducing both the generation of effluent and the water consumption and, therefore making the process more efficient.

Extraction efficiency depends on the characteristics of both the elements (type and content) and wood (part and species) studied. Most wood treated in Brazil comes from forests planted with a variety of eucalyptus species, whereas the Northern Hemisphere pine wood from native forests are generally exploited. It is important to note that hardwoods such as eucalyptus, and especially their extractives, exhibit significant structural and compositional differences in relation to conifers (softwoods). This may result in different behaviors throughout leaching processes. Although Eucalyptus wood is used extensively in the production of poles for electricity and telephone networks, especially in the Southern Hemisphere, there are few studies on wood decontamination (Ferrarini, 2012; Ferrarini et al., 2012b) and recycling (Zimmermann and Zattera, 2013) with majority of studies focused on the durability and strength this wood (Araújo et al., 2012; Vivian et al., 2015).

Most research is conducted on freshly treated wood not yet in service. These samples are not representative of actual waste from wooden structures such as utility poles, which can remain in service for more than 50 years (Vidor et al., 2010). Changes in concentrations and the leaching kinetics of toxic elements are expected with ageing, caused by weather and other factors (Cooper et al., 2001).

This study aims to investigate the removal of Cu, Cr and As present in CCA-treated eucalyptus wood from utility poles in service for 14 years, in order to render them non-hazardous waste. Extraction with H_2SO_4 was optimized using factorial experiments. Standard leaching tests were also performed to classify the wood waste submitted to decontamination. Different scales and the use of rinsing water, to prepare the extraction solution, were tested in view to expand the studies to an industrial scale.

2. Methodology

2.1. Materials and reagents

All the solutions were prepared using analytical grade reagents and purified deionized water (Milli-Q®, Millipore, >18 mΩ cm). To quantify Cu, Cr and As, calibration curves were prepared using standard solutions with an initial concentration of 1000 mg L^{-1} (Titrisol, Merck). These solutions were used to prepare multi-element calibration solutions in appropriate concentration range. Rhodium was used as internal standard in the sample, blank and standard solutions at a concentration of 5 μg L^{-1}.

Wood samples were taken from CCA-treated eucalyptus utility poles removed from service in southern Brazil (Vidor et al., 2010). These poles were made from *Eucalyptus grandis* wood and had been in service for 14 years. The external portion of the treated poles (sapwood) was ground into coarse chips and then milled in the laboratory using grinders (A11 IKA, Basic and TE 600, Tecnal). The material was then sieved to obtain fine chips (<9.5 mm) as indicated in the standard methods (ABNT NBR 10005, 2004; US EPA Method 1311, 2002).

2.2. Quantification of Cu, Cr and As

In order to quantify Cu, Cr and As before and after decontamination, the wood samples were submitted to decomposition in a microwave oven. The accuracy of the methodology was tested by analyzing certified NIST (National Institute of Standards and Technology) standard reference material SRM 1575a (Trace Elements in Pine Needles from North Carolina). This material was selected for its similarity to the wood specimen.

For digestion the samples were ground using CO_2(s) to prevent loss from heating/volatilization and then sieved (particle size <425 μm). The sieved samples were treated with a mixture of 5 mL of HNO_3 + 2 mL of H_2O_2, in a tetrafluorometoxi (TFM) vessel and then heated in a microwave oven. Samples were prepared in triplicate and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) technique, using an Elan 6000 spectrometer (PerkinElmer – Sciex) (see the supplementary data, Tables S1 and S2 – Supplementary Materials, for heating program of the microwave oven used for the digestion of the samples and operational parameters of ICP-MS, respectively).

2.3. Leaching test for solid waste classification

The classification (leaching) test for treated wood waste was based on norm of the Brazilian Association of Technical Standards (ABNT NBR 10004, 2004), that regulates the procedures to obtain waste leaching in order to classify the waste for appropriate management (Maranhão et al., 2013; Lucena et al., 2014). The leaching test was applied to CCA-treated wood before (for classification purposes) and after (to check decontamination efficiency) the decontamination process. Therefore, two different regions of the wood were analyzed: a sapwood sample (outer portion of the wood), the focal point for preservative treatment for Eucalyptus species, and samples of a mixture of heartwood (inner portion) and sapwood (see the supplementary data, Fig. S1). This test simulates the leaching conditions in landfills and was chosen as a model because it better reproduces actual conditions. The test applied is