



## Research Paper

# Pretreatment of trace element-enriched biomasses grown on phytomanaged soils for bioethanol production



Mohammad Asad<sup>a</sup>, Zahra Menana<sup>a</sup>, Isabelle Ziegler-Devin<sup>a</sup>, Valérie Bert<sup>b</sup>, Michel Chalot<sup>c</sup>, Rolf Herzig<sup>e</sup>, Michel Mench<sup>d</sup>, Nicolas Brosse<sup>a,\*</sup>

<sup>a</sup> Laboratoire d'Études et de Recherche sur le Matériau Bois (LERMAB), Faculté des Sciences et Technologies, Université de Lorraine, Boulevard des Aiguillettes, 54500 Vandœuvre-lès-Nancy, France

<sup>b</sup> INERIS, Clean and Sustainable Technologies and Processes Unit, DRC/RISK, Parc Technologique Alata, BP2, 60550 Verneuil en Halatte, France

<sup>c</sup> Laboratoire Chrono-Environnement, UMR CNRS 6249, Université de Bourgogne Franche-Comté, Pôle Universitaire du Pays de Montbéliard, 4 Place Tharradin, BP 71427, 25211 Montbéliard, France

<sup>d</sup> BIOGECO, INRA, Univ. Bordeaux, 33615 Pessac, France

<sup>e</sup> Phytotech Foundation (PT-F), and AGB-Bioindikation, Umweltbeobachtung und oekologische Planung Quartiergasse, Bern, Switzerland

## ARTICLE INFO

## Keywords:

Phytoremediation-borne biomass  
Pretreatment  
Metal  
Bioethanol

## ABSTRACT

Phytotechnologies are a set of sustainable, ecological options notably for alleviating pollutant linkages induced by contaminated soils. However, concerns exist regarding the processing of trace elements (TE)-enriched biomass and the fate of TEs in the end-products. The fractionation of phytoremediation TE-enriched non-woody lignocellulosic (tobacco) and woody (birch, willow) phytoremediation-borne biomasses was studied using ethanol organosolv, soda and dilute acid pretreatments. TE distribution in the process fractions (pulp, liquid effluents and lignin) was further examined. In dilute acid conditions, a wood pretreatment performed at 170 °C in the presence of 2% w/w of sulfuric acid allowed an efficient extraction of the metals in the water effluent ( $\approx 90\%$  for Mn and Zn) producing a clean pulp. A soda pretreatment resulted in a low metal extractability, especially at high temperature. At 170 °C or above with 15% w/w of NaOH, metals were mostly recovered in the cellulosic pulp (70%–98%). Using organosolv pulping, the TE contents were in the decreasing order: pulp  $\gg$  water stream  $>$  lignin. The TE organosolv extraction in the liquid phase varied depending on the TE metal and on the species but was generally low. Metal extractability increased with the water content in the solvent of the organosolv pulping but decreased with temperature. Enzymatic hydrolyses of TE-enriched and metal-free pulps were investigated and it was concluded that the TE concentrations had little or no effect on polysaccharide enzymatic hydrolysability by cellulases. The final destination of the various fractions for valorization in a biorefinery setting is discussed, regarding their TE content.

## 1. Introduction

The management of metal-polluted soils is a worldwide challenge that often remains unanswered by conventional civil engineering methods. Brownfields (Gallego et al., 2015) and agricultural soil (Li et al., 2010) contaminated by trace elements (TE) is currently an increasing concern because of potential health risks. During the last three decades, we have witnessed the emergence of phytotechnologies for remediating contaminated soils that require far less energy and raw materials and lead to less disruption of environmental compartments of the contaminated sites (Nagendran et al., 2006; Medina et al., 2015). Currently, the development of eco-innovative soil remediation technologies is one priority of European policy.

Phytotechnologies constitute a relevant and sustainable method of using natural resources (Capuana, 2011; Chalot et al., 2012; Delplanque et al., 2013; Ruttens et al., 2011; Suer and Andersson-Skold, 2011; Witters et al., 2012; Linger et al., 2002). Several high yielding herbaceous plant species and hyperaccumulators have been assessed for the phytomanagement of polluted soils (Hao et al., 2012; Liu et al., 2011; Rivelli et al., 2012) and their effectiveness has been reviewed (Mench et al., 2010). However, the use of such TE-enriched biomass is an important issue for avoiding TE re-dissemination in the environment. Several European field trials using tobacco, birch, willow and poplar aimed to produce valuable biomass for metal or energy recovery (Kidd et al., 2015). In these projects, catalyst production and various energy-recovery techniques including combustion, torrefaction and

\* Corresponding author.

E-mail address: [Nicolas.Brosse@univ-lorraine.fr](mailto:Nicolas.Brosse@univ-lorraine.fr) (N. Brosse).

pyrolysis have been addressed. The results from combustion experiments performed at an industrial scale with willow and poplar have been reported (Chalot et al., 2012; Delplanque et al., 2013; Bert et al., 2017). In addition to cellulosic pulp, the availability of co-products (lignin and sugars) should stimulate the development of new emerging applications according to the biorefinery approach (Ragauskas et al., 2006). However, the biomass cost is one of the major factor of the viability of a lignocellulosic biorefinery contributing to 40–50% of the operating costs (Juneja et al., 2013). In this context, the use of phytoremediation-borne biomass as a feedstock for producing bioethanol and biomaterials could be of great interest. Previous studies have however demonstrated that TE concentrations in the phytoremediation-borne biomasses such as tobacco, birch and willow were significantly higher than those of the elements in reference biomass (a concentration from five to ten times higher, and occasionally even more extreme) (Migeon et al., 2009). As a consequence, some crucial questions remain unanswered about the fate of TEs in the currently used fractionation processes (the distribution between cellulosic pulp, co-products such as lignin and side stream effluents), the possible dispersion of hazardous TEs in the environment during the treatment and the impact of metal (loid)s on enzymatic hydrolysis to produce fermentable sugars.

In this study, we investigated the pretreatment of TE-enriched non-woody lignocellulosic (tobacco) and (birch and willow) woody biomasses, which has never been studied, to the best of our knowledge. Three processes (dilute acid, alkali-catalyzed and ethanol organosolv pretreatments) were evaluated, all of them being among the most widely used and studied technologies for cellulosic bioethanol production (Silveira et al., 2015). We described the fractionation of phytoremediation biomasses for the production of bioethanol, pulp and biomolecules according to the biorefinery concept, starting from TE-enriched non-woody (tobacco) and woody (birch and willow) biomasses. Metal extraction and distribution in the processed fractions (lignin, pulp, and liquid effluents) were examined in a laboratory setting. The influence of the treatment severity of the pretreatment experimental conditions on the metal extraction was investigated. The organosolv cellulosic fraction was evaluated for the sugar yield by the enzymatic hydrolysis as well as the metal effect on the enzymatic conversion of cellulose and xylan into monomeric sugars.

## 2. Materials and methods

### 2.1. Plant materials

Tobacco (*Nicotiana tabacum* L.) shoots were harvested at the Bettwiesen field trial (Zn contaminated soil) in Switzerland (Kidd et al., 2015). Willow (*Salix viminalis* cv. 'Tora') were planted on a metal-contaminated sediment disposal site in France (Kidd et al., 2015) with a dual objective, i.e., to phytoextract TE from the technosol developed on the dredged-sediments and to evaluate the potential of the sediment disposal site for energy via the production of biomass. Birch (*Betula pendula*) biomasses from naturally occurring trees were collected on a landfill made of red gypsum produced by the neutralization of waste-waters with limestone from a TiO<sub>2</sub> plant (Cristal Thann, France, sulfuric process). The red gypsum is characterized by high Mn and Fe concentrations (Assad et al., 2017). Birch was found to be the dominant (> 80%) plant species that had naturally recolonized the landfill after the deposit of red gypsum ceased in 2006. Birch and willow biomasses were collected from 4 and 3 year-old trees, respectively, at the end of winter, and chopped into 40–60 pieces. These biomasses were dried for 4–6 days at 40 °C and further milled into powder (0.05 mm) using a Retsch miller (Haan, Germany). Ethanol, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> used in this study were purchased from Sigma Aldrich and used as they were received. The enzymes were purchased from Sigma-Aldrich (St. Louis, MO). The overall processes used for the pretreatment of TE-enriched biomasses in the present paper are summarized in Fig. 1, and are fully described thereafter.

### 2.2. Acid-catalyzed pretreatment

Acid pretreatment was carried out in a 0.3 L glass-lined pressure Parr reactor with a Parr 4848 temperature controller (Parr Instrument Company, Moline, IL). Ten grams of each biomass samples were mixed with 80 mL of 0–2% (w/w) sulfuric acid at 170–200 °C for 5 min as described in Table 1. After treatment, the reactor was cooled down with tap water. The mixture was washed with distilled water and then the solid residue dried overnight at 40 °C. The filtrate was freeze-dried and collected as solid.

### 2.3. Alkali-catalyzed pre-treatment

The pretreatment was carried out in the similar reactor as acid-catalyzed pretreatment. Ten grams of each biomass samples were treated with 100 mL of NaOH solution (0.375 mol L<sup>-1</sup>). The reaction mixture was heated at 130 °C, 170 °C and 190 °C with continue stirring for 60 and 80 min as described in Table 2. The mixture was washed with water (2 × 40.00 mL) and the solid residue was dried overnight at 40 °C. The filtrates were combined and adjusted to pH 1 by the HCl (2 mol L<sup>-1</sup>) to precipitate the lignin fraction, which was collected by centrifugation and dried overnight at 40 °C. The remaining water effluent was collected as solid by freeze drying.

### 2.4. Ethanol organosolv pretreatment (EOP)

The EOP was carried out in a 1L glass-lined pressure parr reactor with a Parr 4842 temperature controller (Parr Instrument Company, Moline, IL) for metal extraction ethanol production. Twenty grams of biomass were treated with an ethanol/water mixture in a volume ratio (65:35 and 50:50) with sulfuric acid (0.5–2% w/w) as a catalyst. The 1:8 solid:liquid ratio was used, as described in Table 3. The reaction mixture was heated at ~3 °C/min with continuous stirring for 1 h. The pressure was increased to 15–20 bar depending on the temperature and ethanol concentration. The mixture was washed with 60 °C ethanol-water (8:2, 3 × 50.00 mL) and then dried overnight at 40 °C. The filtrates were combined, and three volumes of water were added to precipitate the lignin, which was collected by centrifugation and dried overnight at 40 °C. The remaining water effluent was collected as a solid after freeze drying.

The EOP was evaluated with the severity correlation, which describes the pretreatment severity (in terms of the severity factor Ro) depending on treatment time (t, min) and temperature (T, °C), where T<sub>ref</sub> = 100 °C

$$\text{Log}(\text{Ro}) = \log\{t \exp[(T - T_{\text{ref}})/14.7]\}$$

The pH effect was considered through the combined severity, defined as

$$\text{Combined severity (CS)} = \log(\text{Ro}) - \text{pH}$$

The pH can roughly be employed as a measure of the hydrogen ion concentration for sulphuric acid ethanol-water solutions (Chum et al., 1990).

### 2.5. TE analysis

Ethanol organosolv pretreated pulp, lignin, water effluent and raw tobacco, birch and willow were dried overnight at 100 °C, and then weighted aliquots (0.2 g DW) were placed in a 50 mL Erlenmeyer flask. Then, 10 mL of nitric acid was added to the flask and placed on a graphite bed at 85 °C. The flask was heated until reddish-brown fumes were no longer emitted, and then 4 mL of hydrogen peroxide (30%) was added dropwise. If some plant particles remained in the solution, an additional 4 mL of hydrogen peroxide were added to achieve total dissolution of the material. After cooling, the solution was transferred

Download English Version:

<https://daneshyari.com/en/article/5762080>

Download Persian Version:

<https://daneshyari.com/article/5762080>

[Daneshyari.com](https://daneshyari.com)