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Leaching characteristics of inherent inorganic nutrients in biochars from the slow and fast pyrolysis of mallee biomass

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HIGHLIGHTS

- Fast pyrolysis biochars contain less water-soluble inorganic nutrients than slow pyrolysis biochars.
- Fast pyrolysis biochars provide more plant available inorganic nutrients than slow pyrolysis biochars.
- Leaching of inorganic nutrients from large biochars is slower than that from fine biochars.
- Inorganic nutrients leaching from biochars exhibits pseudo-second order kinetics.

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ABSTRACT

This study compares the inherent leaching characteristics of inorganic nutrients, particularly alkali and alkaline earth metallic (AAEM, mainly Na, K, Mg, and Ca) species in biochars prepared from the slow and fast pyrolysis of mallee biomass particles at 500 °C. The results indicate that, compared to slow pyrolysis, fast pyrolysis produces biochars with less water-soluble AAEM species but more plant available AAEM nutrient species (through Mehlich I extraction). Pyrolysis of different biomass components results in biochars with different water-soluble and plant available AAEM nutrient species, depending on pyrolysis conditions. Biochars produced from pyrolysis of large wood particle (2–4 mm) exhibit slower water leaching kinetics and a lower plant available nutrients than those from fine wood particles (150–250 μm). Slow pyrolysis results in a reduction in water-soluble Na and K in biochars while an increment was observed for biochars produced from the fast pyrolysis of large wood. Experimental kinetic data can be broadly fitted to a pseudo-second order model. For all biochars, a significant proportion of inorganic nutrients can be recycled, demonstrating the potential of returning biochar to soil for completing the loop of nutrient recycling and enhancing the sustainability of biomass utilisation cycle.

1. Introduction

Short-rotation mallee trees are planted in Western Australia to combat dryland salinity issue in local agriculture land [1,2]. Recent studies demonstrate that mallee biomass as a byproduct from agriculture management can be used to produce biochar, bio-oil and/or bioslurry with desired fuel properties via pyrolysis [3–7]. Part of biochar produced can be used for soil application to sequestrate atmospheric carbon [8–10] and thereby reduce the overall carbon footprint for biochar/bio-oil production [9,10] as well as to deliver various agricultural benefits [10–15]. Therefore, applying biochar to soil can further enhance the synergy among food security, energy supply and environment conservation [3–6,8–13].

Biochar application for soil amendment purposes typically utilises 5–50 tonnes of biochar per hectare of land [16]. Given this large application rate, it is crucial that the majority or at least part of the inorganic nutrients taken up by biomass during its growth can be recycled or returned to the soil via biochar to improve the sustainability of the pyrolysis process. A majority of these nutrient species especially alkali and alkaline earth metallic (AAEM, mainly Na, K, Mg and Ca) species are retained in biochar during pyrolysis. A large portion of those AAEM species are water leachable thus can potentially be returned to the soil [17].

Pyrolysis conditions can have significant impacts on the leachability of AAEM species in biochar and their overall recycling [16–18]. For example, biochar prepared at a higher pyrolysis temperature generally has a higher nutrient content [17,19], but an increase in pyrolysis temperature tends to reduce the cation exchange capacity of biochar and the leachability of some

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inorganic nutrients in biochar as the nutrients become more organically bound or bound to biochar matrix at higher temperatures [17,20]. It is known that the properties of biochars produced from slow and fast pyrolysis are significantly different [21,22]. However, little has been done to compare the leachabilty and overall recyclability of the nutrients in biochars from slow and fast pyrolysis, a detailed understanding on which will enable us to engineer biochar for maximised benefits associated with its soil application.

Therefore, this work aims to compare the nutrients recyclability in biochars from slow and fast pyrolysis. A series of biochars were prepared at 500 °C from the slow and fast pyrolysis of different mallee biomass components (i.e., wood, leaf and bark). Batch leaching with fixed loading rate in water and Mehlich I extraction medium was carried out to provide new insights into the leachability of the AAEM species in biochars.

2. Experimental section

2.1. Preparation of biomass and biochar samples

Three major components, i.e. wood, leaf, and bark, of mallee biomass (*Eucalyptus loxophleba*, subspecies *lissophloia*) were separated from the whole tree and used in this study. The wood, leaf, and bark were dried at 40 °C in a lab oven, ground via a cutting mill (Fritsch Cutting Mill Pulverisette 15), and sieved to fine (150–250 μm for wood and leaf, <250 μm for bark with 80% in the size fraction of 150–250 μm) and large (2–4 mm for wood only) size fractions. The sieved samples were mixed thoroughly and stored below −4 °C prior to any experiment.

Biochars were prepared from the pyrolysis of the wood, leaf, and bark at 500 °C under slow heating and fast heating conditions, using a quartz drop-tube/fixed-bed reactor. The details of the reactor setup can be found elsewhere [23,24]. For slow pyrolysis, ~5 g of biomass sample was placed on the frit of the quartz reactor and a continuous flow of ultra-high purity Argon (2 L min^{-1}) was supplied to the reactor for 15 min before heating it up to 500 °C at a heating rate of 10 °C min^{-1} (0.17 °C/s). The reactor was held for 15 min at 500 °C before lifting it up and cooling it down to room temperature. The argon flow was maintained during the cooling process. For fast pyrolysis, the reactor was pre-heated to 500 °C, with a continuous flow (2 L min^{-1}) of argon passing through. The fine biomass (150–250 μm) was continuously fed into reactor at a feeding rate of ~0.1 g min^{-1} for ~10 min. The large wood (2–4 mm) was fed particle by particle via a water-cooled feeding probe. Based on the method detailed elsewhere [25], the heating rates of the fine and large biomass particles were estimated as ~400 and ~50 °C/s, respectively. After feeding, the reactor was held for 15 min before lifting up and cooling down to room temperature, with the argon flow continuously passing through.

2.2. Biochar leaching

The biochars were first leached via ultra-pure water (>18.2 M Ω) under batch condition at a solid to liquid ratio of ~1 g/L to quantify the water-soluble AAEM nutrients in the biochars. Briefly, ~1 g of biochar was immersed in 1 L of ultra-pure water and gently stirred with magnetic stirrer bars at room temperature. The low solid to liquid ratio used in this study eliminated the possible saturation of the AAEM species in the biochar, which may affect their leaching behaviour in water. Leachate was sampled at various leaching time using a syringe needle to minimize solid loss from the solution throughout the experiment. Leaching time was sufficiently long to ensure leaching equilibria for the AAEM species in the biochar were achieved. The biochars were also leached with Mehlich I extraction medium (0.05 N HCl acid and 0.025 N H_2SO_4 acid) at room temperature for 24 h to quantify total plant available AAEM nutrients in the biochars, following the same solid to liquid ratio used for the water leaching. The Mehlich I extraction method is well established in the field of soil science to quantify total plant available nutrients in soil, and the extraction time is generally several minutes [19,26,27]. However, due to the inherent variations between both physical and chemical properties of biochar and soil, the extraction time in this study was extended to 24 h to eliminate time-controlled mass transport factors possibly arising from different biochar structures compared to soils, as suggested in previous studies [19,20].

2.3. Sample analysis

The proximate analysis of the biomass and biochar samples was done with a Mettler thermogravimetric analyser (TGA) according to ASTM E870-82 [28]. The content of carbon (C), hydrogen (H) and nitrogen (N) of all the samples were determined with an elemental analyser (Model: Perkin–Elmer CHNSO 2400 Series II), whereas the oxygen (O) content in the samples was determined by difference on a dry and ash-free (daf) basis. The AAEM species in the biomass and biochar samples were quantified via ashing, acid digestion and quantification by an ion chromatography (IC, Model: Dionex ICS-3000), following the method detailed in a previous study [24]. The IC system was equipped with electrolytic suppression and conductivity detector. The cations (Na, K, Mg and Ca) were separated with CS12A 4 × 250 mm column and CG12A 4 × 50 mm guard column with a 20 mM methanesulfonic acid solution as eluent. The AAEM species in the leachate from the water leaching and the modified Mehlich I extraction were quantified using the same IC system. The proximate and ultimate analyses as well as the concentration of AAEM species in the biomass and biochar samples are presented in Tables 1 and 2, respectively. For the raw biomass sample, the ash and fixed carbon contents follow the order of bark > leaf > wood, whereas an opposite order is found for the content of volatile matter.

2.4. Kinetic model

The leaching profiles of the AAEM species in all the biochars in this study show a general trend which is initially rapid and followed by a slower leaching towards equilibrium. Therefore, a pseudo-second order leaching model would reasonably describe the leaching kinetics of the biochars. The second order leaching model is shown in Eq. (1) [29–31].

$$\frac{dC_t}{dt} = k(C_s - C_t)^2 \tag{1}$$

where k is the second order leaching rate constant (L mg^{-1} day^{-1}); C_s is the equilibrium concentration (mg L^{-1}) and C_t is the concentration (mg L^{-1}) of AAEM species in water at time t. Integrated rate law Eq. (2) can be obtained by integrating Eq. (1) with the boundary condition $t = 0$ to t and $C_t = 0$ to C_t. Rearrangement of Eq. (2) gives its linear form Eq. (3). The initial leaching rate can be expressed by Eq. (4) when t approaching 0.

$$C_t = \frac{C_s^2 kt}{1 + C_s kt} \tag{2}$$

$$\frac{t}{C_t} = \frac{t}{C_s} + \frac{1}{kC_s^2} \tag{3}$$

$$h = kC_s^2 \tag{4}$$

By fitting the data into t versus t/C_t, leaching parameter C_s can be obtained from the slope and k can be calculated from the intercept. The initial leaching rate h can be determined through Eq. (4).