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Research article

Acidification with nitric acid improves chemical characteristics and reduces phytotoxicity of alkaline chars

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ABSTRACT

Charred organic matter is recently receiving attention for its potential use as soilless growth medium. However, depending on its origin and on the manufacturing technology, it can result toxic for plants. This fact implies that a detoxifying treatment ought to be devised in order to reclaim char in this way. We have studied three materials which combine these factors: two pyrolyzed biochars, one from forest waste (BCH-FW) and another from olive mill waste (BCH-OMW), and one hydrothermally carbonized hydrochar from forest waste (HYD-FW). These materials are suspicious of phytotoxicity due to their high pH, high salinity, or presence of organic toxics. For these new materials, it is mandatory to select fast and reliable bioassays to predict their potential phytotoxicity. In order to achieve this goal water extracts of the three chars were subjected to bioassays of seed germination and bioassays of seedling growth in hydroponic conditions. The biochar from olive mill waste and the hydrochar, but not the biochar from forest waste, showed considerable phytotoxicity as seed germination and plant growth were negatively affected (e.g. BCH-OMW reduced seed germination by 80% and caused early seedling death). In order to adjust pH and electrical conductivity for plant growth, treatments of acidification and salt leaching with optimal diluted HNO_3 solutions (0.3 N, 0.2 N, and 0.75 N for BCH-OMW, BCH-FW, and HYD-FW, respectively) as calculated from titration curves, were conducted. The acid treatment reduced electrical conductivity in BCH-OMW (from 9.2 to 4.5 dS m^{-1}), pH (maximum in BCH-FW from 9.6 to 6.2) and water soluble carbonaceous compounds (maximum in HYD-FW from 5969 to 2145 mg kg^{-1}) in the three chars, and increased N content (maximum in BCH-OMW from 50 to 6342 mg kg^{-1}) in the three chars. Bioassays on acid-treated chars demonstrated the absence of phytotoxicity and even stimulation of seedling growth over the control (increase of 86% and 56% for BCH-FW and HYD-FW, respectively). We conclude that acidification of chars with diluted HNO_3 is a viable technique to conform chars to standards for plant growth purposes.

1. Introduction

In horticulture plants are often grown on soilless organic or inorganic media. When we consider the use of new materials as substrate or substrate constituents for containerized soilless plant production, adequate physico-chemical (pH and electrical conductivity [EC]) and chemical (absence of toxic levels of organic compounds) characteristics are of chief importance (Bunt, 1988).

Salinity can cause osmotic stress and nutrient imbalance and alkalinity can lead to the insolubilization of important nutrients. These negative effects are most prominent during the early stages of seedling growth when the plant is particularly sensitive to stress (Marschner, 1995). Leaching salts by pouring water has been proposed to decrease salinity in organic materials such as composts (Fornes et al., 2010). Its efficiency in displacing salt depends on physical properties such as particle size, intra- and inter-particle porosity, hydrophobicity, etc. (Rose, 1973).

Lowering the pH of alkaline materials has been achieved by amending with elemental sulfur or sulfates (García de la Fuente et al., 2007), by mixing with acid materials such as *Sphagnum* peat (García-Gómez et al., 2002), and by adding sulfuric acid

Abbreviation: AR, adequate range; BCH-FW, biochar from forest waste; BCH-OMW, biochar from olive mill waste; CBC, char buffering capacity; CC, container capacity; EC, electrical conductivity; GI, germination index; HYD-FW, hydrochar from forest waste; LE, leaching efficiency.

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(Costello and Sullivan, 2014).

Dry pyrolysis and wet hydrothermal carbonization (HTC) of organic matter are technologies which allow to obtain biochar and hydrochar (Libra et al., 2011). Although biochar has been scarcely studied as a constituent of growth media the available data are promising (Graber et al., 2010; Méndez et al., 2015; Nieto et al., 2016; Steiner and Harttung, 2014; Vaughn et al., 2013). Hydrochar has not been practically assayed for soilless plant cultivation. Gruda (2012) argued that 'only innovative approaches will ensure a continuously positive and sustainable development of growth media'. Two additional benefits of the use of biochars are their ability to sequester C and to reduce greenhouse gas emissions (Xiang et al., 2015), since these materials take hundreds of years to decompose (Kuzyakov et al., 2009). Moreover, it has been recently demonstrated that alkaline and saline biochars can chemically trap atmospheric CO_2 (Fornes et al., 2015). Hydrochar, however, has a high proportion of labile C and decomposes faster than biochar although it maintains long mean residence times (Libra et al., 2011).

To be a good growth medium constituent, char physico-chemical (pH and EC) properties must meet the adequate ranges (AR; pH = 5.5 to 6.3; EC < 3.5 dS m^{-1}) proposed by different authors (Abad et al., 2001; Bunt, 1988) Biochars are usually markedly alkaline (Bargmann et al., 2013) whereas hydrochars are often acidic with some exceptions (Bargmann et al., 2013; Fornes et al., 2015). EC is often low in hydrochars (Fornes et al., 2015) and variable in biochars from different feedstocks (Fornes et al., 2015; Ma and Matsunaka, 2013). As saline biochars have not yet been suggested for horticultural purposes, it is important to study the feasibility of salt leaching in them. With respect to char alkalinity, it does not seem advisable to use elemental sulfur to acidify saline biochars because it might increase EC (García de la Fuente et al., 2007). Additionally, concerns on the phytotoxicity of some char types (mainly hydrochars) due to the presence of toxic soluble and volatile organic compounds have been expressed (Bargmann et al., 2013; Busch et al., 2011). This phytotoxicity varies depending on the raw material used for charring (Bargmann et al., 2013) and on the post-handling of the char (Buss and Mašek, 2014). The variability in physico-chemical characteristics and pollutant content with potential phytotoxicity (Yargicoglu et al., 2015) makes it difficult to predict the impact of chars on plant performance. This accentuates the importance of screening chars for phytotoxicity prior to application.

Seed germination bioassays are fast and easy systems to test potential phytotoxicity of organic materials (Bargmann et al., 2013; Zucconi et al., 1981). Nevertheless, germination and seedling growth are different physiological stages, both being sensitive to abiotic stress. Seed germination depends on the initial physical mechanisms of water uptake by seed tissues and breakdown of the seed coat and later on metabolic activation. During seedling growth, root and shoot coordinate their development by exchanging chemical signals and nutrients. Hence, a stress factor negatively affecting seed germination might not affect seedling growth and vice versa. This is the reason of conducting phytotoxicity bioassays which test seedling growth along with seed germination.

The aims of this study were: 1) to test the potential phytotoxicity of two biochars, one from forest waste (BCH-FW) and another from olive mill waste (BCH-OMW), and one hydrochar from forest waste (HYD-FW), and 2) to improve the negative characteristics of the materials by applying viable techniques for the growers. To reach these objectives, the effectiveness of dilute nitric acid on removing phytotoxicity was checked by carrying out two bioassays based on seed germination and on seedling growth. This would allow to predict whether the raw or the improved chars are reliable when used as growth media.

2. Material and methods

2.1. Biochars and hydrochar

The origin, physico-chemical and chemical characteristics, and some other specific properties of the three chars used in this study (BCH-FW [BioCHar from Forest Waste]; BCH-OMW [BioCHar from Olive Mill Waste]; HYD-FW [HYDrochar from Forest Waste]) were previously published by Fornes et al. (2015). Briefly, BCH-FW was the small particle (≤6 mm) waste obtained after the pyrolytic charring of hard woods (i.e. *Quercus* sp.) in a traditional kiln. It was alkaline, non-saline and nutrient poor. BCH-OMW was produced from the olive mill waste (largely olive stone mixed with olive pulp) obtained after the industrial extraction of olive oil. This waste was charred in a pyrolytic-like process in the olive oil extracting facilities. The charring process was conducted in a firebrick oven. The resulting material was granular (with a particle size ≤ 6 mm), highly saline and alkaline and rich in several nutrients, particularly potassium. HYD-FW was produced from forest waste with some minor proportion of garden waste. These wastes were subjected to hydrothermal carbonization. This material was unstructured and powdery when dry but it would aggregate in larger particles when wet. It was close to neutrality and non-saline with a substantial proportion of soluble and easily decomposable carbon compounds.

2.2. Column preparation and leaching of BCH-OMW

To study the workability of reducing EC in saline BCH-OMW, a column experiment was carried out as described by Fornes et al. (2010). Briefly, three methacrylate columns (40 cm in height and 5.3 cm in internal diameter), fastened in vertical position, were filled with 883 mL of biochar with a moisture content equivalent to container capacity (CC; 420 mL of water per litre of biochar; 371 mL per 883 mL of biochar in the column), determined at 2 kPa suction following De Boodt et al. (1974).

Fractionated volumes (0.5 x CC) of distilled water were sequentially poured through the columns, and leachates separately collected and analysed for pH and EC. The total volume of water poured through the columns in the assay was 3710 mL (20 × 186 mL).

Leaching efficiency (LE, %) was calculated using equation $LE = 100 \times [1 - (X/X_0)]$ where X = EC (dS m^{-1}) in the char after leaching, and X_0 = EC (dS m^{-1}) in the char before leaching.

2.3. Titration curves and char acidification

Char titration curves and char buffering capacity (CBC; meq H^+/L char/pH unit) were obtained using a modification of the method proposed by Costello and Sullivan (2014). They were used to determine the dose of H^+ required to reach the desired char pH. We used HNO_3 as a source of H^+ in order to enrich chars with N and, in so doing, raise their fertilizing potential. We express the results on a volume basis, as is the usual in soilless growth media studies, and not on a weight basis.

Briefly, 200 mL of 0 (distilled water), 0.0125 N (125 meq H^+/Kg char), 0.025 N (250 meq H^+/Kg char), 0.05 N (500 meq H^+/Kg char), 0.075 N (750 meq H^+/Kg char), 0.1 N (1000 meq H^+/Kg char), 0.15 N (1500 meq H^+/Kg char), 0.2 N (2000 meq H^+/Kg char), 0.25 N (2500 meq H^+/Kg char), and 0.3 N (3000 meq H^+/Kg char) HNO_3 solutions were added to 20 g of each char. In addition, 4 drops of chloroform were added to the suspensions prepared in this way to prevent microbial activity. Suspensions (in triplicate) were incubated at room temperature and gently shaken for 4 days, which was considered the necessary interval to reach pH stabilization (Costello and Sullivan, 2014). After this, suspensions were filtered