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Sorption of lead ions onto oxidized bagasse-biochar mitigates Pb-induced oxidative stress on hydroponically grown chicory: Experimental observations and mechanisms

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HIGHLIGHTS

- Chemical oxidation improved physicochemical properties of biochar.
- Oxidized biochar showed strong sorption ability to aqueous Pb^{2+}.
- Oxidized biochar reduced reactive oxygen species accumulation in chicory.
- Oxidized biochar stimulated enzymatic and non-enzymatic scavenging mechanisms.
- Oxidized biochar showed a protective effect against Pb-induced oxidative stress.

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ABSTRACT

This pilot study investigated the affinity of oxidized biochars to sorb lead ions (Pb^{2+}) in aqueous solutions, and its potentiality to serve as bio-filters to detoxify Pb-induced oxidative stress on hydroponically grown chicory. Raw bagasse was slow-pyrolyzed at 600 °C to produce original biochar (O-B), which was further oxidized by HNO_3 and $KMnO_4$ to generate HNO_3-B and $KMnO_4$-B, respectively. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), digital selected-area electron diffraction (SAED) and Fourier transform infrared spectroscopy (FTIR) analyses were performed to study physicochemical properties of pre-and post-sorption samples. Kinetic and isothermal batch sorption experiments proved the high affinity of oxidized biochar to Pb^{2+} ions. Both physisorption and chemisorption mechanisms participated mutually in sorption process. Leaf histochemistry analysis showed various dysfunctions on plants grown under severe Pb-stress including (i) induction of oxidative stress, (ii) deactivation in antioxidant enzymatic and non-enzymatic defense pathways, (iii) defects in plant water status, (iv) disruption in photosynthetic pigments synthesis, and (v) disturbance in the membrane permeability to solute leakage. Biochar filters (particularly $KMnO_4$-B) exhibited a scavenging effect against these adverse effects by reducing Pb-bioavailability. Furthermore, the chemical characteristics of biochar and its derivatives (biochar-derived humic acids) provided additional stimulating effect to plant scavenging mechanisms. This ameliorative effect of biochar filters minimized the dramatic reductions in vegetative measurements of plants grown under severe Pb-stress. Hence, this study provides insights regarding the potentiality to functionalize biochar and its derivatives for heavy metal detoxification.

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1. Introduction

Due to the global shortage in fresh water supplies, low-quality water resources should be wisely reused in agriculture (particularly in arid and semi-arid regions) to save freshwater for more economically and socially valuable uses (Mosa et al., 2016a). The global fast growing urbanization and industrialization have caused additional pressure on the available water resources through discharging of several types of pollutants (Garcia and Pargament, 2015). Unlike most biodegradable pollutants, trace elements tend to be transferred among several ecosystems to reach the food chain without being decomposed by microorganisms (Xiao et al., 2017a). Among different trace elements, lead (Pb) has received the highest attention due to its ubiquitous and hazardous effects to various ecosystems.

Phytoavailability of Pb^{2+} is associated with a broad range of deteriorations on biochemical, physiological and morphological plant indices (e.g., seed germination, root growth and elongation, chlorophyll biosynthesis, respiration, water status, nutrients uptake, and catalytic activities of various enzymes) (Shahid et al., 2014). Accumulation of Pb in plant tissues can also induce an oxidative stress arising from the production of reactive oxygen species (ROS) such as hydrogen peroxide (H_2O_2) and superoxide ($O_2^{\cdot-}$). These ROS species can cause noxious effects on the redox status of cells and lipids of membrane (Ashraf and Tang, 2017).

Unlike most classical decontamination methods (e.g. reverse osmosis, electrocoagulation, ion exchange resin, membrane separation, solvent extraction and photo reduction), biochar has proved its effectiveness in wastewater decontamination based on its low-cost, simple processing and the potential reuse of its disposals (Ahmad et al., 2018a). Biochar is a carbon-rich material derived from the thermal processing (e.g. pyrolysis) of residual biomass under inert environment (Qin et al., 2018). Beside its efficient use for wastewater reclamation, biochar has additional agro-environmental applications including soil amending (El-Naggar et al., 2018), carbon sequestration (Sheng and Zhu, 2018), and energy generation/storage (You et al., 2017).

During the thermochemical conversion of feedstock, chemical alterations in the carbonized biochar (e.g. blockage of micro-pores by molten materials and reduction in the content of active functional groups) may reduce its sorption capacity (Rajapaksha et al., 2016; Xiao et al., 2017b). Attention, therefore, has been recently directed toward the chemical activation by various solutions (e.g. acids, bases, organic solvents and surfactants) to functionalize biochar for efficient wastewater decontamination. Chemical impregnation with oxidizing agents (e.g. H_2SO_4 and HNO_3) has resulted in improving the sorption capacity of the engineered biochar through (i) increasing the content of surface oxygen-functional groups, (ii) maximizing the total surface area, (iii) changing the electronegativity of biochar surfaces and (iv) originating organo-mineral complexes (Jin et al., 2017). In this regard, $KMnO_4$ proved its effectiveness in metal ions removal comparing with other oxidizing agents as it is not only a strong oxidizing agent but also it serves as a precursor for MnO_x formation (Wang et al., 2015a).

Recent research has focused on the potential application of biochar as a growth media in hydroponic systems rather than other synthetic media (Awad et al., 2017; Karakaş et al., 2017). Other research is highlighting biochar-based filters as a safeguard against hazardous effect of water pollutants in hydroponic systems. According to a recent study, the safeguard effect of biochar filters against the toxic effect of Ni^{2+} on hydroponically grown tomato can result in alleviating dysfunctions in cell organelles through reducing its uptake and accumulation in plant tissues (Mosa et al., 2016b). The technology of biochar-based filters thus can provide a decentralized system for wastewater reclamation. Functionalizing biochar with improved sorption capacity may generate effective bio-filters for reducing the bioavailability of potentially toxic elements for hydroponically grown plants.

To date, there is gap of knowledge regarding the potentiality of biochar to serve as a bio-filter for alleviating the bioavailability of heavy metal ions. The novelty aspect of this research lies on functionalizing biochar-based filter to confer specific properties tailored in hydroponic farming systems. In addition, the functionalization of biochar may be employed in various applications other than water decontamination (e.g. releasing plant nutrients, growth regulators and plant medicines).

The main objectives of this research, therefore, are to: (1) prepare and characterize the physicochemical properties of two oxidized biochar types using HNO_3 and $KMnO_4$ as strong oxidizing agents, (2) compare the affinity of engineered biochars (the pristine and the oxidized forms) to Pb^{2+} ions under kinetic and isothermal sorption experiments, (3) evaluate the immobilization effect of the engineered biochar filters against Pb-induced oxidative stress on chicory plant, (4) study the effect of biochar filters on antioxidant enzymatic and non-enzymatic scavenging mechanisms, and (5) assess the ameliorative effect of biochar filters on physiological and morphological plant indices.

2. Materials and methods

2.1. Reagents

Potassium permanganate ($KMnO_4$), nitric acid (HNO_3), lead nitrate ($Pb(NO_3)_2$) and lead acetate ($Pb(CH_3COO)_2$) of analytical grade were purchased from Fisher Scientific. All chemical solutions were prepared using deionized water (DI, 18.2 MΩ) (Nanopure water, Barnstead), which was also used for rinsing and cleaning of samples.

2.2. Oxidized biochar preparation

Original biochar (O-B) was produced by heating 15 g of grinded air-dried raw bagasse under O_2-limited condition at 600 °C for 8 h using a high temperature tube furnace (GSL-1100). Chemical oxidation was performed by shaking 5 g of the O-B with 80 mL of each oxidizing agent (i.e. HNO_3– 2 M, and $KMnO_4$– 0.1 M, 1:16 w:v) at 150 rpm for 2 h. HNO_3-B was firstly rinsed with NaOH (0.1 M) to neutralize the pH value. Thereafter, both oxidized forms were rinsed with tape water and DI water to remove the excess of oxidizing agents.

2.3. Physiochemical characterization of chemically oxidized biochar

Using dry combustion technique, total carbon (C) and nitrogen (N) concentrations in pristine and oxidized biochar samples were determined by a Thermo Scientific Flash 2000 elemental analyzer. Microscopic features and surface morphology of engineered biochars were characterized using scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM-EDS). Scanning electron microscope (SEM) image was obtained with JEOL JSM-6400 Scanning Microscope, and the energy dispersive X-ray spectroscopy (EDS, Oxford Instruments Link ISIS) coupled with SEM to determine surface elemental composition and identifying crystalline embedded structure in biochar matrix.

The microstructure analysis of pre-and post-sorption samples were performed using transmission electron microscopy (TEM, JEOL JEM-2100). Before analysis, samples were dispersed in warm DI water for 20 min, and then deposited onto a carbon coated grid to obtain TEM micrographs. To study the crystallographic