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Biochar based remediation of water and soil contaminated by phenanthrene and pentachlorophenol

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HIGHLIGHTS

- Biochar reduced the availability of phenanthrene and pentachlorophenol in contaminated water and soil.
- The nature of biochar and contaminant affected the efficiency of remediation process.
- Soil organic matter reduced the extractability of contaminants.

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ABSTRACT

Phenanthrene (Phe) and pentachlorophenol (PCP) are classified as persistent organic pollutants and represent serious concern for the environment as they are toxic and ubiquitous. Biochar based remediation is an emerging technology used in water and soil contamination. In this study we used poplar (BP) and conifer (BC) biochars to remediate water and soil contaminated by Phe and PCP. BP and BC were able to remove completely either Phe or PCP from contaminated water within one to three days. When biochar was confined in a porous membrane, BC and BP maintained their sorption efficiency for several remediation cycles. However, in these conditions BC allowed faster Phe removal. In soil remediation experiments, addition of two biochar rates, i.e. 2.5 and 5 mg g^{-1}, strongly reduced Phe extractability (up to 2.7% of the initially added Phe with the larger BC dose). This was similar to the behavior observed when compost was applied in order to verify the role of soil organic matter in the fate of both contaminants. PCP extractability was reduced only up to 75% (in average) in all samples including those with compost amendment. Only larger amount of biochar (20 and 50 mg g^{-1}) allowed reduction of the extractable PCP and nullified phytotoxicity of the contaminant.

1. Introduction

According to the European Biochar Certificate (EBC) “biochar is a heterogeneous substance rich in aromatic carbon and minerals. It is produced by pyrolysis of sustainably obtained biomass under controlled conditions with clean technology and it is used for any purpose that does not involve its rapid mineralization to CO_2 and preserves its capacity to become eventually a soil amendment” (Conte et al., 2015).

Due to its particular porous structure and high specific surface area, biochar is not only used as a soil amendment to increase soil fertility and to mitigate climate change by sequestering C from atmosphere to soils (Lehmann and Joseph, 2009), but it can also be a very effective sorbent for organic and inorganic contaminants in water and soil (Ahmad et al., 2014; Caporale et al., 2014; Inyang and Dickenson, 2015; Lehmann and Joseph, 2015; Tan et al., 2015) thus lowering their bioavailability and toxicity to living organisms.

Biochar is composed by different organic and inorganic fractions that can react with contaminants (Ahmad et al., 2014; Beesley et al., 2011) through different mechanisms such as partitioning, adsorption, aromatic-π and cation-π interaction, and electrostatic interactions (Ahmad et al., 2014; Inyang and Dickenson, 2015).

The interactions between biochar and contaminants change with pyrolysis temperature and nature of the parent material (Jindo et al., 2014; Mukome et al., 2013). Pyrolysis temperature strongly affects the partitioning of contaminants into non-carbonized and carbonized biochar fractions as it influences surface area and micropores development (Ahmad et al., 2014). Also the starting

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material can significantly act on biochar adsorbent properties (Jindo et al., 2014; Mukome et al., 2013). Crop residues, forestry waste, animal manure, food processing waste, paper mill waste, municipal solid waste, and sewage sludge are reported to be the most commonly used waste biomasses for biochar production (Ahmad et al., 2014). Conversion of these materials to biochar is an economical and eco-friendly tool for environmental remediation because it allows recycling of existing resources (Conte et al., 2015).

The ability to remove contaminants in aqueous solution makes biochar a suitable adsorbent for water treatment especially when multiple contamination occurs. Biochar is attractive water treatment method because it is a low cost and effective technology in waste as well as drinkable water remediation. The approach can be diversified, as demonstrated by the bulk of the literature, from the more common batch experiments to the use of biochar as an integral part of dual/multilayered/sandwich fixed-bed adsorption reactors incorporating or not conventional sand filter(s), or as a single reactor or a series of fixed-bed adsorption reactors (Gwenzi et al., 2017).

When remediation treatments are needed for xenobiotics entering soil, biochar is able to immobilize contaminant molecules. Entrapment and sorption of contaminant molecules in the carbonaceous material could be considered a detoxification process though these removal mechanisms do not provide the contaminant alteration. In order to not limit the biochar based remediation action to immobilization process several studies report the contemporary use of biochar and organic amendments such as compost. Beesley et al. (2010) investigated the capability of biochar and green-waste compost in reducing the mobility of some PAHs in soil. Both of them showed a great potential, although biochar was more efficient. A synergistic effect occurs when biochar and compost were mixed to reduce Cu and Pb concentrations in soil (Karamia et al., 2011). Furthermore, use of compost can contrast the reduced bioavailability of contaminants caused by biochar as compost can stimulate pollutant degradation (Kästner and Mahro, 1996).

The aim of the present study was to evaluate the efficiency of two different biochars, from poplar and conifer, in water and soil remediation. The attention was focused on two different organic contaminants, phenanthrene and pentachlorophenol, as representative of alarming pollutant classes such as polycyclic aromatic hydrocarbons (PAHs) and chlorophenols (CPs), respectively. The water treatment was carried out by batch experiments to define the biochar capacity of pollutant removal and by confined biochar in a semi-permeable membrane tubing hypothesizing the pollutant flux from the water into the membrane in order to simulate a remediation action of a contaminated basin.

Studies of adsorption, sequestration and reduction of bioavailability were carried out in a long-term experiment in a phenanthrene and pentachlorophenol contaminated soil with the support of phytotoxicity test checking the germination of *Lepidium sativum* seeds after biochar based remediation treatment. A combination of biochar and compost was also tested to verify a synergistic effect on pollutant degradation.

2. Material and methods

2.1. Chemicals

Reagent-grade phenathrene (Phe) (>99% purity, m.w. 178.23, H_2O solubility 1.6 mg L^{-1}) and pentachlorophenol (PCP) (>99% purity, m.w. 266.34, H_2O solubility 20 mg L^{-1}) were purchased from Sigma Aldrich (Germany). HPLC-grade solvents and all other chemicals were supplied by Carlo Erba Reagents.

2.2. Physical-chemical properties of biochar

Biochar was produced from poplar (*Populus* spp. L.) (BP) and conifer wood chips (BC). Conifer wood chips were obtained from different species (*Larix decidua*, *Pinus sylvestris* L., *Pinus nigra* A., *Abies alba* M., *Picea excelsa* L.). Biochars were provided by the Department of Agricultural and Forestry Science of the University of Palermo (Italy). The details of the gasification process as well as biochar properties (pH, elemental composition, content of ash and metals) have been already reported in De Pasquale et al. (2012). The Brunauer–Emmett–Teller (BET) analysis was carried out on biochar, previously powdered (0.5 mm), to determine surface area and pores size and volume. Infrared spectra were recorded on Perkin Elmer FT-IR spectrometer using the Diffuse Reflectance Infrared Fourier Transformed (DRIFT) analysis to highlight structural differences between biochars, in the transmittance mode by mixing with a mortar 5 mg of biochar with 95 mg of KBr. The DRIFT infrared spectra were recorded in 400–4000 cm^{-1} range, collecting 32 scans, with 4 cm^{-1} of resolution, and correcting the background noise (Novak et al., 2010). The spectra were acquired and processed using Spectrum 10 software.

2.3. Physical-chemical properties of soil and compost

Fresh soil, without no history of organic contamination, was collected from the citrus orchard located at the Department of Agriculture of University of Naples Federico II in Portici (Naples, Italy) at 0–20 cm of depth, air-dried and <2 mm sieved. The main physical-chemical soil properties were performed in triplicate following the standard techniques (Sparks, 1996) (Table S1). According to the USDA the soil was classified as a loamy sand soil (clay 27 ± 5 g kg^{-1}, sand 879 ± 42 g kg^{-1}, lime 93 ± 47 g kg^{-1}).

A compost from olive pomace (Comp), characterized in details by Altieri and Esposito (2008), was used. It consisted of 72% olive pomace, 14% wheat straw, and 14% sawdust.

2.4. Adsorption of Phe or PCP on biochars in liquid medium

Experiments to assess the capacity of BP or BC to adsorb and retain Phe or PCP from liquid matrix were performed. Glass tubes (10 mL) were used to incubate 40 mg of each biochar, BP or BC, with 1 mL of contaminant solutions (Phe or PCP). Suitable amounts of Phe or PCP stock solution (50 mg L^{-1}) in acetone were used to obtain different contaminant concentration (5, 7.5, 10, 12.5, and 15 mg L^{-1}). After 1, 3, and 7-d incubation, solutions were collected, centrifuged at 3000 rpm for 15 min, filtered (0.45 μm, Phenomenex), and analysed by high-performance liquid chromatography (HPLC) to evaluate the residual concentration of contaminants. After centrifugation solid phase was extracted by using organic solvents suitable for each contaminant, as described by Scelza et al. (2007) and Scelza (2008).

The sorption coefficients Kd and Koc were calculates as following:

$$\mathrm{Kd}\ (\mathrm{mL\ mg^{-1}}) = C_a\ (\mu\mathrm{g\ mg^{-1}})/C_s\ (\mu\mathrm{g/mL})$$

$$\mathrm{Koc}\ (\mathrm{mL\ mg^{-1}}) = \mathrm{Kd}\cdot 100/C_{\mathrm{content}}\ (\%)$$

where C_a was the contaminant adsorbed on biochar and C_s was the contaminant concentration in solution.

2.5. Adsorption of Phe or PCP on biochar confined in dialysis tubes

Very often, remediation treatments of contaminated water do not allow direct addition of biochar because it could release, in turn,