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Use of magnetic biochars for the immobilization of heavy metals in a multi-contaminated soil

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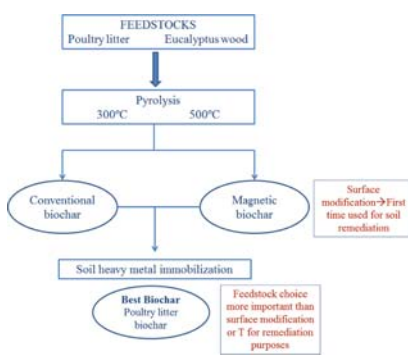
HIGHLIGHTS

- First time magnetic biochars used for remediation in a heavy metal polluted soil
- Feedstock, temperature and magnetization affects biochar's ability to immobilize metals.
- T and, particularly, feedstock choice more determinant than magnetization for soil remediation
- Poultry litter biochars better at preventing Cd, Pb and Zn leaching
- Surface modification through magnetization had an impact on plant growth.

GRAPHICAL ABSTRACT



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ABSTRACT

Modified biochars, including magnetic biochars, have been tested in water for the removal of inorganic pollutants. However, at present it is unknown if they possess benefits over conventional biochar materials in relation to land remediation. A paddy soil was collected near Liantang village in Lechang Pb-Zn mine area in Guangdong Province (China). The soil was polluted with Cd, Cu, Zn and Pb, with total contents of 1.4 mg/kg, 80 mg/kg, 1638 mg/kg and 2463 mg/kg, respectively. We prepared magnetic and conventional biochar from two feedstocks (poultry litter and Eucalyptus) at a temperature of 300 and 500 °C. A sequential extraction procedure for the speciation of heavy metals and a phytotoxicity test using rice were performed. Acid-soluble Cd in soils amended with PLB was 8 to 10% lower than in the control polluted soil. This figure was 27 to 29% for acid-soluble Zn and 59 to 63% for acid-soluble Cu. In some cases, differences were found between the heavy metal fractionation in samples amended with magnetic and conventional biochars. Plant biomass was unaffected by most treatments, but increased by 32% in the treatments containing magnetic poultry litter biochar. Our study shows that a careful choice of feedstock is of utmost importance for successful containment of heavy metals in a multi-contaminated mining area soil. An appropriate choice of feedstock (in the case of this study poultry litter vs. eucalyptus) was more determinant with respect to the mobility of pollutants than altering pyrolysis temperature or modifying surface properties through magnetization. However, surface modification through magnetization can have a significant impact on plant yield and offer comparative advantages in the management of some degraded landscapes.

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1. Introduction

Pollution by heavy metals is a common concern in soils, driven by industrialization and economic development. Higher amounts of heavy metals than soil background levels are a consequence of smelting, mining, the improper dispose of contaminated sewage sludges and other anthropogenic activities. Commonly to other developed countries, large areas of China, in particular in the Southern part of the country, are known to be polluted by heavy metals, as a consequence of the large scale mining and smelting activities occurring in this region (Li et al., 2014). Lechang Pb-Zn mine is located in an important mining area in northern Guangdong. It is well-known that soil around this mine is heavily polluted by heavy metals (Yang et al., 2008), which can transfer to vegetables and result in considerable health risks for the local population. In fact, lead (Yang et al., 2004) and cadmium (Yang et al., 2006) transfer via rice consumption is a risk to the local population of this area.

In the last years much research has been done in order to remediate heavy metal polluted soils, involving the mobilization or immobilization of the pollutants (Bolan et al., 2014). One of such alternatives is the use of pyrogenic forms of carbon. Biochar is the carbon-enriched black solid made from pyrolysis or gasification of biomass materials used as a soil amendment in agricultural and environmental applications (Guo et al., 2016). Biochar production is a process which allows upgrading materials previously considered as waste. Initially, biochar was perceived as part of a solution to mitigate global warming and its long time of residence in the terrestrial ecosystem, potentially spanning to centuries or millennia (Kuzyakov et al., 2014), sparked the interest of scientists. There has been much interest in the use of biochar in agriculture, as it can improve physical (Méndez et al., 2012), chemical and soil biological properties (Paz-Ferreiro et al., 2012), while increasing crop yields (Méndez et al., 2017; Paz-Ferreiro et al., 2015). More recently, there is an increasing appeal in using biochar for soil remediation, due to its ability to immobilize a vast range of pollutants, including heavy metals (Paz-Ferreiro et al., 2014).

The mechanisms controlling heavy metal immobilization in soils amended with biochar have been discussed before and include chemical sorption, physical sorption and precipitation (Paz-Ferreiro et al., 2014). The extent to which metal sorption is achieved is strongly determined by the intrinsic characteristics of the heavy metal (Puga et al., 2015) and by soil type (Uchimiya et al., 2011), biochar feedstock (Lu et al., 2015), biochar's maximum temperature of preparation (Méndez et al., 2014; Paz-Ferreiro et al., 2017) and the dose of biochar applied to the land (Lucchini et al., 2014).

It is possible to further improve the metal sorption efficiency of biochars, treating or modifying them after the pyrolysis process. Biochars can be activated using a steam or air flow (Trakal et al., 2014), they can be chemically modified, using hydroxides or diluted acids (Regmi et al., 2012) or magnetized (Chen et al., 2011; Reddy and Lee, 2014; Devi and Saroha, 2014; Wang et al., 2015). Biochar modification methods with the aim to improve its sportive capacity have been reviewed recently (Sizmur et al., 2017). Magnetic biochars have been tested in relatively numerous studies where it was found an enhancement of metal sorption when added to aqueous media (see for example Wang et al., 2015, Trakal et al., 2016 or Son et al., 2018). Promising results using magnetic biochars have also been achieved for the sorption of some organic pollutants (Chen et al., 2011). Similarly to other biochars, mechanisms for metal sorption in magnetic biochars include ion exchange, metal complexation through funtional groups, physical adsorption and surface precipitation (Sizmur et al., 2017). The addition of Fe-oxides can alter the active surface area of the biochar through the formation of secondary iron oxides and iron hydroxides at the biochar surface and can present themselves as a sorptive surface. In addition, magnetic adsorbents can easily and cheaply be recovered from contaminated water. Although this would not be the case after addition of magnetic biochars to the terrestrial environment, there is a need to know if the sorption capability of biochars could be improved by magnetisation (or by other surface modification methods) and be used in this context. Moreover, on occasions the performance of magnetic biochars has not been compared to the same biochars without magnetizing (Chen et al., 2011). Thus, this does not allow to make an informed decision regarding the need for pre-pyrolysis treatment.

The aim of our research is to compare biochars prepared from different feedstocks and at different temperatures and their magnetized counterparts in the context of soil remediation in a mining area polluted with various heavy metals. We aim to discern if pyrolysis temperature, choice of feedstock or surface modification (in the case of the present work through magnetization) play a more predominant role in determining the sorptive capacity of biochars. In addition, we aimed to monitor if changes in metal distribution in rice plant tissues occur as a consequence of biochar or magnetic biochar addition to the soil. Our area of study is representative of other similar polluted areas in developing countries. We hypothesize that magnetic modification of biochars, through modifications in the active BET surface area can result in an improvement of their capacity to bind heavy metals while diminishing metal toxicity to plants.

2. Material and methods

2.1. Materials

Lechang Pb-Zn mine is 4 km east of Lechang City, located in the north of Guangdong Province, China, with an area of approximately 1.5 km^2 and producing approximately 30,000 tons of tailing with a high content in lead, zinc, copper and cadmium (Shu et al., 2001). The mine area has a humid subtropical climate with a long-term average annual temperature of 19.6 °C and an average annual precipitation of 1522 mm. The major ore minerals are sphalerite, galena, pyrite and chalcopyrite. With a conventional underground operation, this ore mine was opened in 1959 and is still in operation.

The soil used for the experiment is collected from the surface layer (0–20 cm) of a paddy field in Liantang village (25°13′ N, 113°38′ E) near Lechang lead/zinc mine. The soil became polluted as a consequence of the long-term use of mining wastewater for irrigation. The soil (an Anthrosol) had an organic carbon content of 1.6%, total nitrogen content of 0.16%, pH of 4.3 and a CEC of 15.5 cmol kg^{-1}. The total Cd content was 1.4 mg/kg, total Pb 2463 mg/kg, total Zn 1638 mg/kg and total Cu 80 mg/kg, total Fe 11%. The concentrations of Cd, Pb, Zn and Cu were above the regulations in China (0.3, 250, 200 and 50 mg/kg, respectively). The soil was air dried and sieved to 2 mm to conduct the experiment.

Two raw biomass materials, eucalyptus wood and poultry litter, were used to prepare the magnetic biochars. *Eucalyptus* (*Eucalyptus urophylla* S.T. Blake) wood was collected at Heshan Hilly Land Experiment Station of the Chinese Academy of Sciences in Heshan, China (22° 84′ N and 112° 54′ E). Poultry litter was collected at the Experimental Poultry Farm of South China Agricultural University (23°09′ N and 113°21′ E) located at Guangzhou, China. Chicken at this facility are organically bred and fed with a mixture of corn, wheat bran and soybean pulp. The feedstocks was oven dried (70 °C) and grounded to pass through a 0.154 mm sieve. The preparation of the magnetic biochars was as in the method described by Chen et al. (2011). Sieved feedstocks were added into a 1 L solution containing ferrous chloride and ferric chloride (molar ratio = 1:1). A 10 M NaOH solution was added dropwise to raise suspension pH to 10, under vigorous magnetic stirring. The solution was stirred during 30 min. Afterwards, the deposit was separated by centrifugation at 3000 rpm for 10 min and pyrolyzed at 300 °C or 500 °C for six hours. The temperature was raised to the final temperature at a rate of 10 °C /min. The residues were rinsed with deionized distilled water several times until the possible desorption of organic matter from biochar was negligible. After oven-dried overnight at 70–80 °C, the magnetite/biochar samples were collected. The four