Environmental Pollution 230 (2017) 329–338

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

The role of tailored biochar in increasing plant growth, and reducing bioavailability, phytotoxicity, and uptake of heavy metals in contaminated soil☆

Badr A. Mohamed [a, b], Naoko Ellis [a], Chang Soo Kim [a, c], Xiaotao Bi [a, *]

[a] Department of Chemical and Biological Engineering, University of British Columbia, Vancouver, BC V6T 1Z3, Canada
[b] Agricultural Engineering Department, Cairo University, Giza, Egypt
[c] Clean Energy Research Center, Korea Institute of Science and Technology, 14 gil 5 Hwarang-no Seongbuk-gu, Seoul, 136-791, South Korea

A R T I C L E I N F O

Article history:
Received 4 December 2016
Received in revised form
18 June 2017
Accepted 22 June 2017

Keywords:
Microwave-catalytic pyrolysis
Engineered-biochars
Potassium phosphate (K_3PO_4)
Clinoptilolite
Nutrients
Heavy metals bioavailability

A B S T R A C T

Microwave-assisted catalytic pyrolysis was investigated using K_3PO_4 and clinoptilolite to enhance biochar sorption affinity for heavy metals. The performance of resulting biochar samples was characterized through their effects on plant growth, bioavailability, phytotoxicity, and uptake of heavy metals in a sandy soil contaminated with Pb, Ni, and Co. The produced biochars have high cation-exchange capacity (CEC) and surface area, and rich in plant nutrients, which not only reduced heavy metals (Pb, Ni, and Co), bioavailability and phytotoxicity, but also increased plant growth rate by up to 145%. The effectiveness of biochar in terms of reduced phytotoxicity and plant uptake of heavy metals was further improved by mixing K_3PO_4 and clinoptilolite with biomass through microwave pyrolysis. This may be due to the predominance of different mechanisms as 10KP/10Clino biochar has the highest micropore surface area (405 m^2/g), high concentrations of K (206 g/kg), Ca (26.5 g/kg), Mg (6.2 g/kg) and Fe (11.9 g/kg) for ion-exchange and high phosphorus content (79.8 g/kg) for forming insoluble compounds with heavy metals. The largest wheat shoot length (143 mm) and lowest extracted amounts of Pb (107 mg/kg), Ni (2.4 mg/kg) and Co (63.9 mg/kg) were also obtained by using 10KP/10Clino biochar at 2 wt% load; while the smallest shoot length (68 mm) and highest extracted amounts of heavy metals (Pb 408 mg/kg, Ni 15 mg/kg and Co 148 mg/kg) for the samples treated with biochars were observed for soils mixed with 1 wt% 10Clino biochar. Strong negative correlations were also observed between biochar micropore surface area, CEC and the extracted amounts of heavy metals. Microwave-assisted catalytic pyrolysis of biomass has a great potential for producing biochar with high sorption affinity for heavy metals and rich nutrient contents using properly selected catalysts/additives that can increase microwave heating rate and improve biochar and bio-oil properties.

1. Introduction

Soil contaminations by organic and/or inorganic contaminants in many areas around the world pose severe environmental problems (e.g., toxicity, water pollution, food pollution, human and animal health, etc …) and increase the risks to humans and biota (Beesley et al., 2011; Bolan et al., 2014). High concentrations of heavy metal(loid)s (e.g., As Cd, Cu, Pb, Co, Ni and Zn) have been reported in many countries around the world (Bolan et al., 2014). Unlike organic contaminants, heavy metals do not degrade easily either through microbial or chemical degradation and, as a result, the concentration of these metals or metalloids will last for a long period of time (Adriano et al., 2004; Bolan et al., 2014). Significant amounts of heavy metals in contaminated soils are associated with mining and mineral processing (Wingenfelder et al., 2005). Previous studies have also found that heavy metals such as Pb, Ni, and Co can reduce the plant germination and pose significant inhibitory effects on roots, stems and leaves of various plant species (Munzuroglu and Geckil, 2002; Kukier and Chaney, 2004). One inexpensive rehabilitation method is to stabilize mine tailings through vegetation. However, because of the toxicity, low soil fertility, low water holding-capacity and unfavourable soil

☆ This paper has been recommended for acceptance by Dr. Yong Sik Ok.
* Corresponding author.
E-mail address: tony.bi@ubc.ca (X. Bi).

http://dx.doi.org/10.1016/j.envpol.2017.06.075

structure, amendments should also be used to improve soil physiochemical properties (Fellet et al., 2011). An engineering approach to remediate heavy metals cost-effectively is to immobilize pollutants and heavy metals while improving plant growth through providing nutrients to plants in situ, and promoting ecological restoration (Vangronsveld et al., 2009; Beesley et al., 2011; Mohan et al., 2014).

Biochar is a byproduct obtained from thermochemical conversion of biomass at high temperatures (>300 °C) (Mohan et al., 2014) and has been successfully tested for its ability to retain different heavy metals and organic contaminants (Cao et al., 2009; Mohan et al., 2014). Biochar can be applied to soil to serve as an amendment and remediate agent to immobilize and reduce the bioavailability and toxicity of heavy metals in contaminated soils through ion-exchange, metal ion surface complexation, co-precipitation and physical adsorption (Fellet et al., 2011; Bolan et al., 2014; Mohan et al., 2014). Many natural and synthetic amendments can reduce extractability of heavy metals from contaminated soils. However, they cannot improve soil productivity, microbial activity, and plant growth (Karapinar and Donat, 2009; Bolan et al., 2014). It is easier to reduce extractable metals in contaminated soils than to improve plant growth (Brown et al., 2005; Crombie et al., 2014).

Biochars have been demonstrated to retain both nutrients and organic/inorganic contaminants (Mohan et al., 2014). Moreover, biochars with high cation-exchange capacity (CEC) are considered the most suitable for soil remediation in contaminated soils (Beesley et al., 2011). Most biochars used in heavy metal adsorption/removal are produced from either slow pyrolysis with low surface area (5–25 m^2/g) or fast pyrolysis without any pretreatment or modification (Beesley et al., 2011; Bolan et al., 2014; Mohan et al., 2014). To improve soil physiochemical properties of contaminated soils, biochars need to be further treated by activation or blending with other nutrients to increase CEC, pH and surface area (Beesley et al., 2011; Uchimiya et al., 2011; Li et al., 2016).

Microwave heating can produce biochars of increasing porosity and higher surface area than that from conventional heating due to higher heating rate and different heating mechanism. In microwave-assisted pyrolysis, water is vaporized from the depth of the particle prior to the organic contents being volatilized. As a result, volatiles releasing rate at low temperatures is expected to be higher than conventional heating (Fernández et al., 2011). However, there have been no reports on the economic viability of microwave heating compared to conventional heating for large-scale applications of biochar production. In addition, microwave heating in general produces lower biochar yield than conventional heating, though can be controlled by reducing the microwave power level (Lam and Chase, 2012). The fact that most biomass materials are poor in absorbing microwaves requires the addition of microwave absorbers to increase microwave heating rate and efficiency. On the other hand, catalyst has been explored to improve bio-oil quality because of its high oxygen content, high acidity and viscosity (Mohamed et al., 2016a). It is thus desirable to identify solid additives which can serve as a catalyst to improve the bio-oil quality, a microwave absorber to improve microwave absorption rate, and a nutrient to improve the quality of biochar byproduct.

Many low-cost natural adsorbents have been used for removing pollutants such as natural zeolites which can effectively immobilize many heavy metals (e.g., Cd, Pb, Fe, Co, Cr, Ni, Hg and Zn) from contaminated sites (Bailey et al., 1999; Babel and Kurniawan, 2003; Wingenfelder et al., 2005; Karapinar and Donat, 2009). It was also found that natural zeolite (clinoptilolite) possesses a great potential for heavy metals immobilization in contaminated soils and improves plant productivity (Reháková et al., 2004; Jha and Hayashi, 2009). The unique structure of clinoptilolite makes it an ideal candidate for sorption and ion-exchange processes, to be used as a carrier for slowly releasing fertilizers, and as a remediation agent in contaminated soils (Reháková et al., 2004). Clinoptilolite is also the most common natural zeolite used in agriculture due to its high CEC, the relatively high absorption rate of moisture and dehydration capacities (Polat et al., 2004). It is known that phosphorus as a major nutrient for plants is a good immobilizer for heavy metals and metalloids such as As, Pb, Cd, Co, Ni and Zn (Ryan et al., 2004; Brown et al., 2005; Liu and Zhao, 2007; Bolan et al., 2014).

Phosphorus immobilizes heavy metals and organic contaminants through forming insoluble or sparingly-soluble metal phosphates with enhanced geochemical stability (Ryan et al., 2004; Cao et al., 2008, 2011). A laboratory study found that phosphorous considerably reduced the phytotoxicity of Pb, Cd and Zn in a highly contaminated soil, and increased plant yields compared to soil without treatment (Brown et al., 2005). An experimental field study also found that the addition of phosphate to a contaminated soil with Pb under field conditions reduced Pb bioavailability and improved the stability of Pb-compounds (Ryan et al., 2004).

Microwave-assisted catalytic pyrolysis was exploited in our lab recently as a novel approach to improve bio-oil quality and to tailor a highly efficient biochar with increased heavy metal immobility by using additives such as clinoptilolite and K_3PO_4. The catalytic activity of these selected materials on pyrolysis products properties has been investigated and clearly discussed in previous work (Mohamed et al., 2016b). Those additives are pre-mixed with biomass samples and remain within biochar to serve as a source of slow-release nutrients for plants and act as a remediate agent. From our previous work, it is noted that microwave catalytic pyrolysis could produce biochars with higher quality (e.g., high surface area, rich in nutrients and high sorption affinity) at reduced microwave heating time. However, there are many challenges related to microwave catalytic pyrolysis such as selecting the proper additives/catalysts mixture, which is the key for promoting different pyrolysis reactions, increasing the dielectric heating rate and scaling up the microwave catalytic pyrolysis reactor.

The overall goal of this investigation is to use the multifunctional catalysts/additives for biomass pyrolysis: (1) as a good microwave absorber for accelerating the microwave heating rate; (2) as a catalyst to improve the quality of bio-oil and biochar; and (3) as a nutrients/soil conditioner embedded in biochar to increase its performance as a fertilizer and soil remediate. This paper reports the performance of produced biochars by assessing the capacity of these biochars to reduce bioavailability, phytotoxicity and uptake of heavy metals by wheat plants and determining the efficacy of these biochars to increase soil fertility and plant growth in contaminated soil.

2. Materials and methods

2.1. Catalytic microwave pyrolysis and biochars preparation

Biochars used in this study were produced from microwave-assisted pyrolysis of switchgrass at 400 °C and 750 W in a 2.45 GHz single mode microwave oven. Different catalysts/additives with different loads were used to accelerate heating and promote the pyrolysis reactions. Because of the poor microwave absorption rate of pure switchgrass (maximum temperature <160 °C after 30 min of microwave irradiation), no biochar was produced from switchgrass without catalysts/additives. K_3PO_4 and clinoptilolite ($(K,Ca,Na)\ 2O\text{-}Al_2O_3\text{-}10SiO_2\text{-}6H_2O$) were mixed with switchgrass at different percentages (10 or 30 wt%) to promote pyrolysis reactions and improve the quality of the produced biochars (10 KP, 30 KP, 10Clino, 30Clino).

Different loads were selected because 10 wt% was the lowest