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Characterisation of agricultural waste-derived biochars and their sorption potential for sulfamethoxazole in pasture soil: A spectroscopic investigation

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HIGHLIGHTS

- High temperature chars showed enhanced adsorptive potential, compared to low temperature chars.
- Oxygen containing acidic functional groups of biochar play negligible role in sorption.
- Biochar properties like specific surface area and aromaticity enhanced its sorption capacity.
- Amendment of pine sawdust biochar to soil significantly enhances its sulfamethoxazole sorption.

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ABSTRACT

We investigated the effects of feedstock type and pyrolysis temperatures on the sorptive potential of a model pastoral soil amended with biochars for sulfamethoxazole (SMO), using laboratory batch sorption studies. The results indicated that high temperature chars exhibited enhanced adsorptive potential, compared to low temperature chars. Pine sawdust (PSD) biochar produced at 700 °C using the steam gasification process exhibited the highest sorptive capacity (2-fold greater than the control treatment) for SMO among the three biochars used. Soils amended with green waste (GW) biochars produced at three different pyrolysis temperatures showed a small increase in SMO sorption with the increases in temperature. The NMR spectra, the elemental molar ratios (H/C, O/C) and polarity index (O + N)/C of the biochars revealed that PSD biochar possessed the highest degree of aromatic condensation compared to CC and GW chars. These results correlated well with the sorption affinity of each biochar, with effective distribution coefficient (K_d^{eff}) being highest for PSD and lowest for GW biochars. X-ray photoelectron spectroscopy results for the biochars showed a relatively large difference in oxygen containing surface functional groups amongst the GW biochars. However, they exhibited nearly identical sorption affinity to SMO, indicating negligible role of oxygen containing surface functional groups on SMO sorption. These observations provide important information on the use of biochars as engineered sorbents for environmental applications, such as reducing the bioavailability of antibiotics and/or predicting the fate of sulfonamides in biochar-amended soils.

1. Introduction

Biochar is a biomass-derived carbonaceous material produced when any form of organic biomass (e.g. forestry, crop residue, paper mill sludge, and poultry waste) is burnt without oxygen at temperatures generally between 350 °C and 700 °C through a process known as pyrolysis (Kookana et al., 2011; Singh et al., 2010). Laboratory, field studies, and traditional farming practices suggest that deliberately added biochar can have significant impact on soil fertility, crop production, and availability of nutrients (Kookana et al., 2011; Lehmann, 2007). However because of its high specific surface area, hydrophobic nature and greater degree of aromaticity, the material has been found to be quite effective in sorbing a range of organic and inorganic compounds both in water and soil systems (Sun et al., 2011; Uchimiya et al., 2011; Wang et al., 2010; Wannapeera et al., 2011; Wu et al., 2013; Xie et al., 2014; Yao et al., 2012b; Yu et al., 2006). Biochar incorporation to soil might be an effective remediation technique for pastoral land contaminated with veterinary antibiotics and other nutrients associated with faecal and urinary excretion by grazing animals (Srinivasan et al., 2014). This would potentially help to reduce the risk that these compounds are likely to pose to the receiving environment. However,

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prior knowledge on the ability of biochar to remove contaminants of interest is essential.

The sorption affinity of biochar for pesticides such as atrazine and simazine has been shown to increase with decreasing solid/solution ratio (Zheng et al., 2010). The authors attributed this to the particle size of biochar as small particle size would mean that sorption equilibrium would be reached quickly. Teixido et al. (2011) reported unconventional adsorption behavior of the veterinary antibiotic sulfamethazine on a charcoal when investigated as a function of concentration, pH, inorganic ions, and organic ions and molecules. Several authors have examined the differences in properties of the biochars produced from different feedstocks (Lian et al., 2014; Mao et al., 2013; Yao et al., 2012a,b; Zheng et al., 2010) and at different pyrolysis temperatures (Chen and Chen, 2009; Xie et al., 2014; Zheng et al., 2013) and their influence on contaminant sorption. However, these studies were confined to investigating the sorptive capacity of biochar for aqueous systems. Only a few studies have investigated the retention ability of contaminant such as steroid hormones (Sarmah et al., 2010), pesticide (Wang et al., 2010), and phenanthrene (Zhang et al., 2010) in biochar amended soils, and none so far involving veterinary antibiotic. For example Wang et al. (2010) demonstrated that biochar obtained from high temperature pyrolysis showed significant enhancement on adsorption of herbicide terbuthylazine onto soils with an enhancing factor of 63. Similarly in another separate study biochar amendment generally enhanced the soil sorption of phenanthrene (Zhang et al., 2010). In most cases, the underlying mechanisms relating to the retention capacity of various types of biochar for organic contaminants/nutrients have not been clearly understood.

Sorption of sulfonamides on biochars is poorly understood and fundamental knowledge on how biochar reacts with various organic contaminants and with soil biological constituents is important to engineer them to meet specific environmental applications, such as remediation of contaminated land (Kookana et al., 2011). SMO antibiotic, which belongs to the sulfonamide group was used as a model compound for this study given it is widely used in the treatment of livestock in NZ, and also due to its ubiquitous occurrence in surface and groundwater. For instance, SMO was detected at a concentration of up to 0.48 μg L^{-1} in surface water samples in Germany (Hirsch et al., 1999). SMO was also detected in groundwater at a concentration of 0.22 μg L^{-1} (Lindsey et al., 2001) and in monitoring well samples (Barber et al., 2009), and streams (Kolpin et al., 2002) in the USA. These studies show that there is a possibility that these chemicals be may be encountered in drinking water supply.

The overarching objective of this study therefore was to investigate the key factors responsible for antibiotic adsorption onto biochar surface, and specifically 1) to determine the effects of feedstock type and pyrolysis temperatures on the sorptive efficacy of biochar amended model soil for SMO antibiotic, and 2) to elucidate the mechanisms involved during the sorption of SMO onto biochar amended soil using a range of spectroscopic investigations.

2. Materials and methods

2.1. Soil

Matawhero silt loam soil (0–5 cm) representative of the dairy farming region of Hawke's Bay in the North Island of New Zealand was collected, air-dried, and sieved (2 mm). A full description of the soil and the methods used to determine the physico-chemical properties can be found elsewhere (Srinivasan et al., 2014).

2.2. Biochars

Biochars used in this study were prepared from greenwaste (GW), corncob (CC) and *Pinus radiata* sawdust (PSD). The feedstock for GW biochar consisted of mixture of leaves, grass clippings, twigs and plant prunings. It was produced at a three different operating temperatures (350 °C, 450 °C and 550 °C) with a mean residence time of 20 min in a low temperature pyrolysis plant by Pacific Pyrolysis (formerly BEST Energies), Australia. CC biochar was obtained from the Hawaii Natural Energy Research Institute and was produced by a flash carbonization technique at temperature > 650 °C. PSD biochar was produced by slow pyrolysis at 700 °C and was obtained from Lakeland Steel Ltd., New Zealand.

2.3. Chemicals

SMO, (>98% purity) was obtained from Sigma Aldrich, Australia. Acetonitrile (Mallinckrodt ChromAR, ≥ 99.8% purity), and dichloromethane (Mallinckrodt UltimAR, ≥ 99.9% purity) were obtained from Thermo Fischer Scientific Ltd. New Zealand. High Performance Liquid Chromatography (HPLC) grade deionised water was obtained from an onsite Arium® 61316 high performance reverse osmosis system (Sartorius Stedim Biotech GmbH, Germany).

2.4. Biochar characterisation

The biochars were homogenized and grounded to < 2 mm for most of the analyses. The pH of the biochars measured using PHM62 standard pH meter calibrated with pH 4 and 7 buffer solutions. The electron conductivity (EC) of the biochar samples were measuring using a "In House" conductance meter with a cell constant K = 0.69 cm^{-1}. The laboratory protocol, consisted of char and water (1:10) shaken for 24 h in a rotary drum shaker. Following this samples were centrifuged and the supernatant was analysed for pH and EC. The C, H, N, S, O, and ash content of the biochars (proximate analysis) were determined at the Campbell microanalytical laboratory in Dunedin (New Zealand). Exchangeable cations were determined using inductively coupled plasma mass spectrometry (ICPMS) and specific surface area (SSA) for chars was measured by Brunauer, Emmett and Teller (BET) nitrogen adsorption isotherm method. The biochars were characterized for a range of properties such as heavy metal content, surface functional groups, morphological characteristics, aromaticity and the elemental composition (including C and O species). A range of techniques such as ICPMS, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX), solid state ^{13}C nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopy (XPS) were used for this purpose. Each technique has been described in detail and is presented in the supplementary information.

2.5. Batch sorption studies

The batch sorption protocol followed was similar to the one developed by Srinivasan et al. (2014). Duplicate samples of air-dried soils (2 g) amended with the three types of biochar (sieved to < 2 mm) at two levels (0.5% and 1.0% of soil weight) were weighed into glass centrifuge tubes (35 mL) with Teflon-lined screw caps. The centrifuge tubes containing the soil and biochar were vortexed for 30 s each to ensure homogeneity. The amount of biochar added to the soil was based on biochar application rates of 5 and 10 t ha^{-1}, assuming a bulk density of 1000 kg m^{-3}, and an incorporation depth of 10 cm in the field. A stock solution of SMO antibiotic at a concentration of 1000 mg L^{-1} was prepared in methanol, covered with aluminium foil and was stored in the dark (4 °C). By adding an appropriate amount of the stock solution separately to 5 mM $CaCl_2$ solution, six different initial aqueous solution concentrations were prepared in duplicate. Aliquots of (30 mL) of SMO with six initial concentrations (1.5, 3, 5, 7.5, 10 and 15 mg L^{-1}) prepared in background electrolyte solution of 0.005 M $CaCl_2$ were added to each tube. The tubes were wrapped in aluminium foil, placed in the dark to limit photo-degradation and shaken in an end-over-end shaker (24 h). Preliminary investigation using biochar amended