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Role of oxygen-containing functional groups in forest fire-generated and pyrolytic chars for immobilization of copper and nickel[☆]



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ABSTRACT

Char as a carbon-rich material, can be produced under pyrolytic conditions, wildfires or prescribed burn offs for fire management. The objective of this study was to elucidate mechanistic interactions of copper (Cu^{2+}) and nickel (Ni^{2+}) with different chars produced by pyrolysis (green waste, GW; blue-Mallee, BM) and forest fires (fresh-burnt by prescribed fire, FC; aged char produced by wild fire, AC). The pyrolytic chars were more effective sorbents of Cu^{2+} (~11 times) and Ni^{2+} (~5 times) compared with the forest fire chars. Both cross-polarization (CPMAS-NMR) and Bloch decay (BDMAS-NMR) ¹³C NMR spectroscopies showed that forest fire chars have higher woody components (aromatic functional groups) and lower polar groups (e.g. O-alkyl C) compared with the pyrolytic chars. The polarity index was greater in the pyrolytic chars (0.99–1.34) than in the fire-generated chars (0.98–1.15), while aromaticity was lower in the former than in the latter. Fourier transform infrared (FTIR) and Raman spectroscopies indicated the binding of carbonate and phosphate with both Cu^{2+} and Ni^{2+} in all chars, but with a greater extent in pyrolytic than forest fire-generated chars. These findings have demonstrated the key role of char's oxygen-containing functional groups in determining their sorption capacity for the Cu^{2+} and Ni^{2+} in contaminated lands.

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1. Introduction

Past, current and future concerns related to the environmental pollution resulting from anthropogenic activities constitute one of the most critical problems faced by humans. This emphasizes a need to investigate the dynamic of contaminants in polluted lands and minimize their impact on the environment. As heavy metals are non-biodegradable elements with largely unknown and long-lasting effects on wildlife and human's health, it is essential to

develop appropriate strategies to remediate environmental pollution caused by these toxicants (Lim et al., 2005; Luo et al., 2005; Meers et al., 2005; Qiu, 2010). Heavy metals such as copper (Cu^{2+}) and nickel (Ni^{2+}) are mainly introduced into soils from sewage sludge, urban waste materials, industrial processes, and mining activities (Tembo et al., 2006). Whilst Cu^{2+} is an essential micronutrient required for plant growth, its excessive concentrations in soil similar to Ni^{2+} species may cause environmental contamination which classify them as highly toxic metals to the environment (Mamindy-Pajany et al., 2014).

Soil organic matter can regulate the fate of heavy metals and prevent their toxicity to plants and ground water by forming which are less bioavailable metal-organic complexes (Bradl, 2004). Although the application of organic amendments and carbonized materials such as manures, composts, biosolids and biochars has

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shown promising reduction effect on pollutant mobility in contaminated soils (Cao et al., 2011a,b; Karami et al., 2011), the underlying mechanisms related to their environmental interactions with inorganic pollutants still remains unclear. Among the mentioned sorbents, biochar has recently attracted substantial attention due to its potentially beneficial effects on sustainable agriculture and acting as an effective sorbent for reducing the bioavailability of organic or inorganic contaminants (Chen et al., 2007; Singh et al., 2010b). However, factors such feedstock-type (e.g. wood, green waste, paper sludge, and manure) and pyrolysis conditions (heating rate, final temperature, residence time) control each biochar's properties (specific surface area, surface chemistry and functional groups) and determine its effectiveness as a sorbent (Cao et al., 2009; Ni et al., 2011). Beesley et al. (2010) found that addition of hardwood-derived biochar to soil (8.3% w/w) can significantly decrease Cd availability, and increase Cu mobility increases, while the Pb concentration was not affected by the addition of biochar. Cao et al. (2011a,b) reported that dairy-manure biochar has an effective amendment for immobilizing both Pb and atrazine in co-contaminated soils. Park et al. (2011) noted that chicken-manure biochar has higher potential for reducing the bioavailability of Cu, Pb, and Cd than green waste biochar. However, all of the above reports focused on the sorption of contaminants to biochars at their ambient pH values, which makes it difficult to discern the contributions of different factors such as C functionality, surface chemistry, and cation exchange capacity (Ni et al., 2011).

In addition to the pyrolysis chars, forest fire-generated chars originating from the historical burning of woodlands, have been used in agricultural soil systems in Australia, USA and Germany (Skjemstad et al., 2002). Forest char is an impure form of C generated by fire through incomplete combustion of biomass and represents up to 30% of the organic C content of Australian soils (Skjemstad et al., 2002). Recent studies showed that plant-derived biochars can effectively adsorb environmentally significant ionic species like heavy metals (Singh et al., 2010a; Harvey et al., 2011). However, in contrast to other biochar feedstocks, systematic research on sorption behavior of heavy metals on plant-derived biochars is still limited (Cao et al., 2009; Harvey et al., 2011). Although some studies indicated that the high sorption capacity of biochars enables them to reduce bioavailability of metals in contaminated soils, others believe that biochars may release the absorbed metals into the soil via organic matter mineralization (Cao et al., 2009; Beesley et al., 2010). Therefore, the role of biochars as a reliable amendment remains controversial and unresolved. Additionally, the mechanisms which regulate heavy metal sorption by forest fire-generated chars (both wildfire and prescribed burning) and commercial biochars (via pyrolysis) in soil-biochar systems are not fully understood. As a result, this study aimed to investigate the effect of different forest fire-generated chars and biochars amendments on the availability of Cu^{2+} and Ni^{2+} based on their mechanistic interactions in a soil-biochar system, using sorption isotherms and a suite of spectroscopy analyses. Isotherms have been widely used to explain the behavior of metals in terrestrial ecosystems (Esfandbod et al., 2011), while Fourier Transform (FTIR) and Raman spectroscopies have been applied to elucidate gross characterization of organic substances and provide valuable information on their surface functionality (Cao et al., 2009; Cao et al., 2011a,b). The ^{13}C solid-state NMR has also been applied to characterize the composition of functional groups of soil organic matter and chars (Cao et al., 2011a,b). Previous studies have stated that FTIR and solid-state ^{13}C NMR are viable direct characterization probes to quantify C structural features and organic oxygen functionalities in organic substances like biochars (Kelemen et al., 2002). However, there is no comprehensive information available regarding the major forms of oxygen and C in biochar especially in

aged char produced during forest fire using a combination of these direct characterization methods. This study attempted to fractionate forest fire-generated chars and biochars into well-defined subcomponents and systematically characterize their structural and functional properties. In doing so, we applied a combination of spectroscopic techniques including NMR, FTIR, and Raman. To the best of authors' knowledge, this is the first study characterizing the functional groups on surface edges of forest fire-generated chars in comparison with pyrolysis chars and investigates their roles in the sorption of heavy metals in soil systems.

2. Material and methods

2.1. Preparation of forest fire-generated chars, pyrolytic chars and soil

Forest fire-generated chars, namely fresh burnt char (FC) and aged acidic char (AC), were produced during a prescribed fire in August 2013 and a wildfire in 1969, respectively. Both of these fires occurred in Peachester State Forest in south-east Queensland, Australia (26°50'S, 152°53'E). The FC was collected 3 days after a low-intensity prescribed fire, while the AC was collected approximately 44 years after an intense wildfire (Table 1). Green waste biochar (GW) produced from green waste feedstock at 450 °C in a low-temperature pyrolysis by BEST Energies P/L, Somersby, Australia (Table 1). The blue-Mallee biochar (BM) produced from blue Mallee mulch in a batch pyrolysis unit at 550 °C by Biochar Energy Systems P/L, Bendigo, Australia (Table 1). The soil sample collected from the A horizon (0–30 cm) of a loamy soil at the Gatton Horticulture Research Station, in the Lockyer Valley, Australia (27°32'S, 152°19'E) (Table 1). The soil is classified as black Vertosol equal to Udic Haplustert according to the USDA Soil Taxonomy (Soil Survey Staff, 1999) and the region has a subtropical climate (Rhodes et al., 2012). The soil was air-dried and passed through a 2-mm sieve. All char materials were air-dried and gently ground to <2 mm before mixing with the soil (Singh et al., 2012). The amended samples were prepared by mixing forest fire-generated or pyrolytic chars with soil at 5% (w/w) ratio for 7 days on an end-over-end shaker (70 rpm) to ensure uniformity (Chen and Yuan, 2010).

2.2. Physicochemical analysis of soil and char materials

Selected physicochemical properties of the forest fire-generated chars, pyrolytic chars and soil were determined, including elemental analyses, specific surface area, cation exchange capacity, and functional group biochemistry (Table 1). To determine sample's C and N contents, the soil and char samples (in triplicate) were pre-digested in sulfuric acid (H_2SO_3) to eliminate their inorganic C (carbonates) and then the total organic C (OC) and nitrogen (N) contents of the samples determined by dry combustion using TruMac CN (LECO). The specific surface area of the samples were determined using the single-point N_2 -BET method (by N adsorption isotherms at 77 K using Gemini 2360 (Micromeritics, USA)). Soil cation-exchange capacity (CEC) was determined using the silver thiourea method (Gillman et al., 2008). In order to conduct elemental analysis of Cu, Ni, Pb, Zn, P, Ca, K, Mg, and Na, the samples were digested in a mixture of nitric and perchloric acids (Miller, 1998) and then analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES; Perkin Elmer; Optima 8300).

2.3. Copper and Nickel sorption in single- and binary-solute systems

The sorption isotherm experiments were conducted in non-

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