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Endogenous minerals have influences on surface electrochemistry and ion exchange properties of biochar

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HIGHLIGHTS

- Biochars from plant or other wastes contained different mineral types and levels.
- PZNCs of the plant-based biochars were lower than that of solid waste-based ones.
- The CEC and AEC had strong positive correlation with soluble cations and anions.
- Biochar surface charges depend not only on the functional groups.
- Organic negative charges in biochar are not as stable as the inorganic charges.

ARTICLE INFO

ABSTRACT

The feedstocks for biochar production are diverse and many of them contain various minerals in addition to being rich in carbon. Twelve types of biomass classified into 2 categories: plant-based and municipal waste, were employed to produce biochars under 350 °C and 500 °C. Their pH, point of zero net charge (PZNC), zeta potential, cation and anion exchange capacity (CEC and AEC) were analyzed. The municipal waste-based biochars (MW-BC) had higher mineral levels than the plant-based biochars (PB-BC). However, the water soluble mineral levels were lower in the MW-BCs due to the dominant presence of less soluble minerals, such as $CaCO_3$ and $(Ca,Mg)_3(PO_4)_2$. The higher total minerals in MW-BCs accounted for the higher PZNC (5.47–9.95) than in PB-BCs (1.91–8.18), though the PZNCs of the PB-BCs increased more than that of the MW-BCs as the production temperature rose. The minerals had influence on the zeta potentials via affecting the negative charges of biochars and the ionic strength of solution. The organic functional groups in PB-BCs such as –COOH and –OH had a greater effect on the CEC and AEC, while the minerals had a greater effect on that of MW-BCs. The measured CEC and AEC values had a strong positive correlation with the total amount of soluble cations and anions, respectively. Results indicated that biochar surface charges depend not only on the organic functional groups, but also on the minerals present and to some extent, minerals have more influences on the surface electrochemistry and ion exchange properties of biochar.

1. Introduction

Interest in biochars has kept rising over the last few years because of their multi-functional environmental properties (Spokas et al., 2009; Teixido et al., 2013). People have produced biochars from different types of biomass waste because biochar can increase carbon sequestration when they are incorporated into soil (Ibarrola et al., 2012; Lu et al., 2012b). Moreover, it has also been found that application of biochar into soil has additional benefits, such as improving soil cation exchange capacity (CEC) and nutrient and mineral level (Qian et al., 2013; Sopeña and Bending, 2013). This means that biochars could be classified as potential soil ameliorants (Laird et al., 2010). They can also be used as heavy metal and organic contaminant absorbents in waste water and contaminated soil (Cao et al., 2011; Xu et al., 2013). These capabilities are, to some extent, related to biochar's surface electrochemistry and ion exchange properties (Inyang et al., 2010).

Several studies have been involved in the relationship between biochar composition and biochar surface electrochemistry as well as ion exchange properties. Yuan et al. (2011) suggested that functional groups, such as $–COO^-$($–COOH$) and $–O^-$($–OH$) were

responsible for the high pH and the large number of negative charges on the surface of biochars. It has also been shown that the carbonates in biochar increase the pH of amended soil, especially when biochar was generated at high temperatures (Yuan et al., 2011; Mao et al., 2012). Lee et al. (2010) suggested that pH also influenced CEC, which rose from -10 cmol kg^{-1} to 30 cmol kg^{-1} as the pH increased from 5.0 to 8.5 (Lee et al., 2010). The biochar CEC values were correlated with the increase in the oxygen atom to carbon atom ratio (O:C ratio) because a higher O:C ratio is consistent with the presence of more hydroxyl, carboxylate and carbonyl groups (Uchimiya et al., 2011). Mukherjee et al. (2011) suggests that low-temperature biochar (250 °C) contains more acid functional groups and is therefore acidic and has a large negative charge, which improves its complexation potential. These characteristics mean that low temperature biochars have higher CECs than high-temperature biochars (400 °C–650 °C) (Mukherjee et al., 2011).

These conclusions are drawn based on several specific, mainly plant-based biochars. However, there are large variations in the properties of potential feedstocks that could be employed to make biochar. We previously investigated the compositions of biochars derived from more than 20 types of waste feedstocks and found that biochars contained similar organic fractions, but very distinct inorganic fractions (Zhao et al., 2013a). It is assumed that the inorganic fractions in biochars, such as minerals, may influence the physicochemical properties of biochars.

In this study, 12 types of biochar were produced from a range of plant-based and municipal waste-based feedstocks, and then their surface electrochemical and ion exchange properties were investigated. The influence of endogenous mineral components in the biochar on these properties was analyzed. This gave us an insight into the influential effect of the total and soluble minerals on the electrochemical and ion exchange properties of different biochars and their corresponding applications.

2. Materials and methods

2.1. Waste feedstocks and biochar production

Twelve typical waste feedstocks were collected from a farm in Shanghai, China. These feedstocks were classified into either plant-based feedstocks, such as sawdust, maize straw, wheat straw, grass, waterweeds, and chlorella, or municipal waste-based feedstocks, such as shrimp hull, pig manure, chicken manure, wastewater sludge, paper waste, and egg hull. The feedstock samples were air-dried until a constant weight was obtained and then ground into particles that were less than 2 mm in size.

The biochar production method has been described previously (Zhao et al., 2013a,b). Briefly, the dried and ground feedstock samples were heated at either 350 °C or 500 °C for 4 h in a N$_2$ atmosphere. The rate of heat increase was 15 °C min^{-1}. The long holding time at the final temperature was selected in order to minimize the negative effects of pyrolysis kinetics that could result in incomplete conversion. For simplicity, the plant-based biochars and municipal waste-based biochars were referred to as PB-BC and MW-BC, respectively.

2.2. Measurement of point of zero net charge (PZNC) and zeta potential

The PZNC was measured using the potential titration method (Jiang et al., 2011). Specifically, biochar was added into de-ionized water and the pH was adjusted to between 2.0 and 12 using diluted NaOH or HCl. Then the solutions were agitated at 25 °C for 3 d to allow them to reach their equilibrium point. The equilibrium pH was measured, after which NaCl solution was added to the system and the solutions were re-agitated for 3 h. Then the pH change was recorded and the potential titration curves (pH – ΔpH) were obtained. The PZNC was the pH that corresponded to ΔpH = 0.

The zeta potential was obtained by adding about 0.1 g biochar to 50 mL de-ionized water. The suspensions were dispersed ultrasonically for 1 h in a sonicator, filtered and the pH adjusted so that it fell within the pH 2.0–12 range. Then the zeta potential was measured using a particle analyzer (Delsa Nano C, Beckman Coulter, USA).

2.3. Measurement of CEC and anion exchange capacity (AEC)

The CECs of biochars were measured using the modified BaCl$_2$–H$_2$SO$_4$ forced displacement method (Lee et al., 2010) and AEC was measured using the modified NaCl–KNO$_3$ forced displacement method (Ludwig et al., 2001; Soares et al., 2005; Lee et al., 2010). We used filter paper to wash away the residual BaCl$_2$ until no Cl$^-$ could be detected in the supernatant. The same procedure was used for AEC determination, except that a different exchanger was used.

2.4. Analysis of other physicochemical properties

Biochar pH was measured with a solid/liquid ratio of 1:20 (w/v) after the solutions had been allowed to equilibrate for 48 h. The metal elements in biochars were analyzed by digesting the biochars using the HNO$_3$/H$_2$O$_2$ hot block digestion procedure (USEPA, 1986), followed by the metal determination in solution using inductively coupled plasma method (ICP-AES, ICAP 6000 Radial, Thermo, U.K.). The water-extractable cation and anion concentrations were determined by diluting the samples with distilled water. After agitation for 24 h at room temperature, the suspensions were filtered through 0.45-μm membrane filters. The water soluble cations in the filtrate were measured by ICP-AES and the water soluble anions were analyzed using an ion chromatograph (HIC-SP/HIC-NS, Shimadzu, Japan). Chemical analysis followed USEPA approved QA/QC plan with a blank, a duplicate, and a spike every 20 samples.

3. Results and discussion

3.1. Mineral components in biochars

The biochar properties including yield, total C content, volatile matters, ash, and surface area can be seen in Table S1 in the Supporting Information. The metal profiles of these biochars were identified in our previous report showing a wide distribution and high heterogeneity in biochars derived from different feedstocks (Zhao et al., 2013a). Generally, the PB-BCs, such as sawdust, grass, and straw biochars contained low concentrations of metals, while the MW-BCs, such as manure and sludge, had much higher mineral concentrations, which were mainly Ca, Mg, S, and P. Paper and egg hull wastes contained particularly large amounts of Ca (Zhao et al., 2013a) (Fig. 1). In contrast to the high total metal concentration, lower concentrations of water soluble Ca^{2+}, Mg^{2+}, Cl$^-$, SO$_4^{2-}$ and PO$_4^{3-}$ were found in the MW-BCs than in the PB-BCs (Table 1 and 2). The discrepancy was due to the fact that these minerals in the MW-BCs were mainly present as less soluble CaCO$_3$ and (Ca,Mg)$_3$(PO$_4$)$_2$ (Zhao et al., 2013a). However, water soluble Na$^+$, especially K$^+$, has the same trend as the total Na and K, i.e., concentrations of water soluble Na$^+$ and K$^+$ were higher in the PB-BCs than in the MW-BCs (Table 1) since Na and K in both biochars were mainly present in soluble forms such as KCl (Zhao et al., 2013a). Tables 1 and 2 also show that soluble K$^+$, Na$^+$, Cl$^-$, and SO$_4^{2-}$ were