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Cation exchange capacity of biochar: An urgent method modification

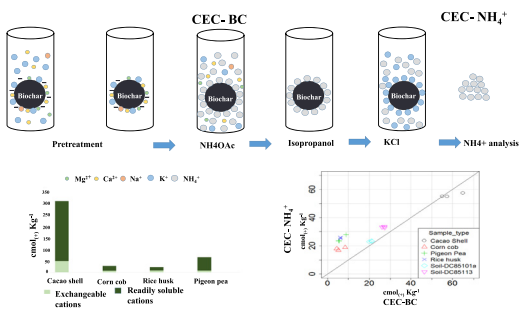
J.L. Munera-Echeverri [a,*], V. Martinsen [a,*], L.T. Strand [a], V. Zivanovic [a], G. Cornelissen [a,b], J. Mulder [a]

[a] Faculty of Environmental Sciences and Natural Resource Management, Norwegian University of Life Sciences, P.O. Box 5003, 1432 Ås, Norway
[b] Norwegian Geotechnical Institute (NGI), P.O. Box 3930, Ullevål Stadion, 0806 Oslo, Norway

HIGHLIGHTS

- The ammonium acetate (NH_4OAc) method was validated in batch for different biochars.
- CEC estimates were based on sum of base cations and displaced NH_4^+ by K^+.
- Optimal equilibration time and amount of NH_4OAc and KCl were established.
- The role of readily soluble and exchangeable cations was compared.
- Isopropanol did not penetrate all the micro-pores of some biochars.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochar, produced through pyrolysis of organic matter, is negatively charged, thus contributing to electrostatic adsorption of cations. However, due to its porous structure and contents of alkaline ashes, the determination of the cation exchange capacity (CEC) is challenging. Literature values for the CEC of biochar are surprisingly variable and are often poorly reproducible, suggesting methodological problems. Here, we modify and critically assess different steps in the existing ammonium acetate (NH_4OAc) method (pH 7), where ammonium (NH_4^+) is displaced by potassium chloride (KCl), following removal of excess NH_4OAc with isopropanol, in batch mode. We used pigeon pea biochar to develop the method and conducted a test on three additional biochars with different acid neutralizing capacity. A pretreatment step of biochar was introduced, using diluted hydrochloric acid, to decrease biochar pH to near neutral, so that 1 M NH_4OAc effectively buffers the biochar suspension pH at 7. This allows the CEC of all biochars to be determined at pH 7, which is crucial for biochar comparison. The dissolution of ashes may cause relatively large weight losses (e.g. for cacao shell biochar), which need to be accounted for when computing the CEC of raw biochar. The sum of NH_4OAC-extractable base cations provided a smaller and better estimate of the CEC than KCl-extractable NH_4^+. We hypothesize that the overestimation of the CEC based on KCl-extractable NH_4^+ is due to the ineffectiveness of the relatively large isopropanol molecules to remove excess NH_4OAc in biochars rich in micro-pores, due to size exclusion. The amount of base cations removed in the pretreatment was about three (rice husk biochar) to ten times (pigeon pea biochar) greater than the amount of exchangeable cations. The CEC values of biochar increased from 10.8 cmol/Kg carbon to 119.6 cmol/Kg carbon. These values are smaller than reported CEC values of soil organic carbon.

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1. Introduction

Biochar is a carbon-rich product made by pyrolysis of organic waste, which may be used as a soil enhancer. Particularly, in tropical soils biochar has been shown to have a positive impact on soil fertility, including

* Corresponding authors.
E-mail addresses: josemun@nmbu.no, (J.L. Munera-Echeverri), vegard.martinsen@nmbu.no (V. Martinsen).

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increased potassium (K^+) content, pH, water retention capacity, and cation exchange capacity (Jeffery et al., 2011; Liang et al., 2006; Martinsen et al., 2015), which all contribute to increased crop yield (Jeffery et al., 2017). Moreover, biochar is emerging as an alternative for heavy metal remediation in soil and water (Ahmad et al., 2014). For the assessment of the effect of biochar on soil properties and its potential as remediation agent, it is important to have reliable and accurate determination of its contribution to the soil's cation exchange capacity (CEC). However, in the literature CEC estimates for biochar are highly variable, commonly ranging from 5 to 50 $cmol_{(+)}\ Kg^{-1}$ (Agegnehu et al., 2016; Berek and Hue, 2016; Budai et al., 2014; Gamage et al., 2016; Nelissen et al., 2015; Singh et al., 2010; Song and Guo, 2012) and even reaching values as high as 69 to 204 $cmol_{(+)}\ Kg^{-1}$ (Lou et al., 2016; Mukherjee et al., 2011; Pandit et al., 2018; Yuan et al., 2011). The large variability in CEC may be due to the number of factors affecting the surface properties of biochar, such as charring temperature and feedstock (Budai et al., 2014; Suliman et al., 2016). However, it also may be attributed to errors in the analytical method, which have not yet been properly addressed. Previous research (Graber et al., 2017) summarized the potential sources of error in CEC determination of biochar, which may relate to the presence of ashes, porosity and the intrinsic hydrophobicity of biochar:

1. Incomplete saturation of exchange sites, due to hydrophobicity of biochar, which may cause poor wetting of the sample and thus underestimation of the CEC.
2. Slow diffusion of replacing cations, due to the micro-porous structure of biochar, which can prolong the equilibration time, potentially causing underestimation of the CEC.
3. Floating and non-settling particles can increase substantially the mass losses during the decantation process may cause underestimation of the CEC.
4. Release of base cations coming from the dissolution of carbonates and silicates present in ashes can interfere with the sum of exchangeable base cations (overestimation of CEC).
5. Soluble carbonates in biochar can change the pH of the replacing solution, with increasing pH causing an increase in CEC.

Methodologies, where displacement after washing is applied are commonly used for CEC analysis in soil (Bache, 1976; Rhoades, 1982) and more recently in biochar (Graber et al., 2017). Often, base cations extracted by NH_4OAc at pH 7 (Chapman, 1965; Hendershot et al., 2008; Schollenberger, 1945) are used to estimate sum of exchangeable base cations, which, in near-neutral soils, often is assumed to be equal to CEC. Alternatively, the CEC is based on displaced NH_4^+ (CEC-NH_4^+) by KCl in a subsequent step, after washing with an organic solvent, such as isopropanol or ethanol. Advantages of NH_4OAc include the avoidance of hydrolysis problems of non-neutral salts, the high wetting and penetration capacity (e.g. compared with barium chloride), and the inexpensive reagents (Schollenberger, 1945). Moreover, NH_4OAc (pH 7) allows comparison of different biochars at neutral pH, which is important, due to the pH dependency of CEC and the high variability in surface properties among different biochars (Mukherjee et al., 2011). However, biochar's CEC may differ considerably between its natural pH and pH 7. In addition, the alkalinity of biochar is highly variable and for some chars it may be needed to adjust pH with acid before using NH_4OAc (pH 7). This may cause problems such as removal of some cations, electrostatically bound to weak acid functional groups at the biochar surface, due to protonation of these groups in response to acid addition, and thus, affecting CEC based on sum of base cations (CEC-BC).

Graber et al. (2017) modified a two-step procedure for determination of CEC of biochar using 1 M NH_4OAc (pH 7), isopropanol and 2 M KCl. In brief, biochar was shaken with 1 M NH_4OAc at pH 7 in batch mode and then transferred into a mechanical extractor, where more NH_4OAc was added, before washing with alcohol and subsequently with KCl. According to these authors the method has a number of aspects which need further development, including: 1) The biochar: solution (B:S) ratio required for the saturation with NH_4^+ and displacement with K^+. 2) The equilibration time of the saturation of exchange sites with NH_4^+ and its subsequent displacement with K^+. 3) Amount of extraction steps required to get full saturation and subsequent removal of NH_4^+. In the present study we explore most of these aspects and suggest ways forward. The batch approach ensures contact between the biochar and the solution, which is important when assessing the reaction time with NH_4OAc, KCl and isopropanol and it avoids problems such as preferential flow in the column.

In our study we will critically assess (A) the B:S ratio required for the saturation with NH_4^+ and displacement with K^+, the equilibrium time with 1 M NH_4OAc and 2 M KCl, the volume of isopropanol needed to wash the excess NH_4^+, the optimal volume of 1 M NH_4OAc to sufficiently displace cations on biochar surface and the volume of KCl to replace NH_4^+ from the exchange sites, (B) to assess the relative contribution of readily soluble salts vs. exchangeable cations and (C) to compare CEC estimates based on displacement of NH_4^+ by K^+ and CEC based on sum of base cations.

2. Materials and methods

2.1. Biochar samples

Four types of biochar were used in this study: pigeon pea biochar (made at 600 °C in an earth-mound kiln at Mkushi, Zambia), cacao shell biochar (made in a locally constructed kiln at Bogor, Indonesia at 350 °C (Hale et al., 2013)), corncob biochar (made in a traditional earth-mound kiln in Zambia at 400 °C during 7 days (Cornelissen et al., 2013)) and rice husk biochar (made at 400–500 °C in a drum retort kiln at Chisamba, Zambia at 350 °C (Obia et al., 2016)). The biochar production methods are discussed in the references. In addition, two certified soils materials (NCS DC85101a and NCSDC85113 (NCS, 2017)) were included in the batch experiment. Biochar samples of about 5 L were taken to the Norwegian University of Life Sciences (NMBU), where they were crushed and sieved to 0.5 mm to 2 mm.

2.2. Biochar pretreatment

For some of the biochars, the buffered NH_4OAc (pH 7) solution may not adjust the pH to 7 (this is especially important for biochars with high alkalinity). Therefore, CEC estimates with and without pretreatment may diverge, since CEC is pH-dependent. To circumvent this problem, the biochar samples were washed with deionized water and the pH values adjusted to pH 7, using 0.05 M hydrochloric acid (HCl), thus removing readily soluble cations associated with salts, ashes and weak acid functional groups. First, 1 g of biochar (1.0 ± 0.005) and 20 ml of deionized water were added to 50 ml polypropylene tubes. The tubes were shaken at 200 rpm in a horizontal shaker overnight to ensure a proper wetting of the sample. Next, 0.05 M HCl was gradually added to the tubes until reaching pH 7.0 ± 0.3. Subsequently, the tubes were shaken during 24 additional hours. The amount of acid added was recorded and the amount of H^+ to reach pH 7 was calculated to determine the acid neutralizing capacity (ANC_{pH7}). Next, the tubes were centrifuged at 1700 *g* during 15 min, the supernatants were removed using a 10 ml pipette and the biochar slurry in the tubes was washed twice more with 20 ml deionized water and shaken for 24 h each time. The supernatant in the third washing should have EC values < 0.2 mS cm^{-1} to avoid significant amounts of base cations in the slurry prior to NH_4OAc addition, which may cause overestimation of exchangeable base cations in the NH_4OAc extracts. The total amount of water and dilute HCl used for each biochar were recorded and the supernatants were stored for analysis of base cations by inductively coupled plasma optical emission spectrometry (ICP-OES).

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