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Cation Exchange Capacity of Biochar: An urgent method modification

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A better understanding of the cation exchange capacity (CEC) values of biochar and its acid neutralizing capacity (ANC) is crucial when tailoring a single biochar for a particular soil and crop. Literature values for the CEC of biochar are surprisingly variable, commonly ranging from 5 to 50 cmol+/Kg even as high as 69 to 204 cmol+/Kg and often poorly reproducible, suggesting methodological problems. Ashes and very fine pores in biochar may complicate the analysis and thus compromise the results. Here, we modify and critically assess different steps in a common method for CEC determination in biochar and investigate how the measured CEC may be affected by slow cation diffusion from micro-pores. We modified the existing ammonium acetate (NH4-OAc) method (buffered at pH 7), based on displaced ammonium (NH4+) in potassium chloride (KCl) extracts after removing excess NH4-OAc with alcohol in batch mode. We used pigeon pea biochar (produced at 350 °C; particle size 0.5mm to 2mm) to develop the method and we tested its reproducibility in biochars with different ANC. The biochar sample (1.00g) was pH-adjusted to 7 after 2 days of equilibration, using hydrochloric acid (HCl), and washed with water until the conductivity of the water was $<200\mu$ Scm-1.Thus, we removed the soluble ash component, while simultaneously allowing the NH4-OAc to buffer at pH 7. To assess the importance of diffusion limitation of replacing cations (NH4+ and K+) in micro-pores, we equilibrated the biochar with NH4-OAc for 1 and 7 days, and after washing with alcohol, for 1, 3 and 7 days with KCl. The effects of the washing volume of alcohol (15, 30 and 45 ml) and of the biochar to NH4OAc solution ratio (1:15, 1:30 and 1:45) were also tested. The CEC values were corrected for dry matter content and mass losses during the process. Results indicate that the measured CEC values of the modified method were highly reproducible and that 1 day shaking with NH4OAc and KCl is enough to saturate the exchange sites with NH4+ and subsequently with K+. The biochar to NH4OAc solution ratio did not affect the measured CEC. Three washings with at least 15 ml alcohol are required to remove excess NH4-OAc. We found the CEC of biochar with the displacement method from pigeon pea, corncob, rice husk and cacao shell to be 26.4(\pm 0.3), 19.2(\pm 0.5), 20.5(\pm 0.4), 46.5 \pm (0.2) cmol+/Kg, respectively. The selected batch experiment allows a large sample throughput, less laboratory equipment is needed and shaking ensures better contact between the extracting solution and the exchange sites.