

Biochar-Ion Interactions: An investigation of biochar charge and its effect on ion retention

David Waters^A, Jason Condon^B, Lukas Van Zwieten^C and Sergio Moroni^B

^AEH Graham Centre for Agricultural Innovation, Wagga Wagga Agricultural Institute, Pine Gully Road, Wagga Wagga NSW 2650, Australia

^BEH Graham Centre for Agricultural Innovation, Charles Sturt University Locked Bag 588, Wagga Wagga NSW 2650, Australia

^CIndustry and Investment NSW, 1243 Bruxner Highway, Wollongbar NSW 2477, Australia

Abstract

The method of measuring exchangeable cations as an approximation for cation exchange capacity was examined using a cow manure and green waste biochar. Both biochars were pre-treated by shaking with water over a range of times. Leachates were analysed, and the pre-treated biochars were then treated with two solutions (0.1M BaCl₂ or 0.1M CsCl) to measure ion adsorption. Pre-treatment shaking had a significant effect on ion adsorption for both biochars. Ion adsorption for the green waste biochar was significantly increased with pre-treatment shaking, whereas it decreased for the cow manure biochar. Compulsive exchange of cations to determine the ability of a substrate to retain positively charged ions on its surface may not be an appropriate method for biochar.

Key Words

Biochar, cation exchange capacity, surface charge, electrostatic forces

Introduction

The summation of values from the compulsive exchange of cations (isomorphic substitution of calcium, sodium, potassium, and magnesium) is often used as a quantitative method for determining the ability of a substrate to retain positively charged ions on its surface (cation exchange capacity, CEC). This value can then give an indication of the surface charge of the substrate, depending on pH and the size of the exchanging ions. While some substrates can also have positive surface charge, and the net surface charge is the difference between these two charges, many soils favour a net negative charge. The two substrate properties that account for ion adsorption and retention are particle surface area and surface charge. Colloid surfaces within the substrate are the major sites of this isomorphic substitution and the ionisation of functional groups, resulting in the development of charge. Charge in soils can be both permanent and pH-dependant (Bohn *et al.*, 2001). The surface charge of substrates can also be determined by the difference between pH_{KCl} and pH_{H₂O} (Black and Waring, 1976; Kingston *et al.*, 1972). Hence a net negative number would suggest a negative surface charge, and vice versa.

Substrates must maintain electrical neutrality, and so this is often maintained by H⁺ and OH⁻ from (soil) water. Some substrates may have low exchangeable cations adsorbed to their surface, relying on H⁺ to fulfil charge neutrality. So a measure of exchangeable cations for these substrates will produce low values. The measures of exchangeable cations for a cow manure and greenwaste biochar (obtained from Pacific Pyrolysis Pty. Ltd.) for this project were significantly different (45.6 vs 4.23 Cmol/kg). The relatively low value for the greenwaste biochar would imply little negative charge on its particle surface. However the pH difference for this biochar was -2.04, suggesting the potential for a substantial cation adsorption capacity. Biochar particles may also possess both positive and negative charge on their surfaces. These zwitterion-like properties may be due to inherent biochar charge, or it may occur through the adsorption of other zwitterions such as amino acids onto their surface.

It was hypothesised that ion adsorption of the two biochars in this project may vary according to particle surface charge. It was also hypothesised that the ion adsorption may be increased through the loss of ions from differing pre-treatment shaking times.

Materials and Methods

All shaking was performed in a temperature-controlled laboratory (20.1°C).

Experiment A: Pre-treatment of Biochars

- 100 ml of distilled water was added to 5g samples of 2 unground biochars and shaken end over end for 6 shake times (2, 8, 16, 32, 64, 120 hours; 6 replicates per time treatment).
- All samples were filtered with Advantec 5C filter papers (pore size 5 µm), with the leachate kept for analysis and the solid biochar material and filter papers kept for Ba/Cs treatments.
- A control of distilled water was filtered as above with the leachate kept for analysis and the filter papers kept for Ba/Cs treatments.
- Leachates were analysed using an ICP AES (Varian, Liberty 2, Environmental and Analytical Laboratory, Charles Sturt University, Wagga Wagga). Initially 2 samples from each biochar were qualitatively analysed by examining intensities across the full spectrum, to determine what elements may be present in the solutions.
- Standards were then made, and the identified elements quantitatively analysed.
- Leachate samples were also analysed through a UV VIS spectrometer for phosphate, and a segmented flow analyser for mineral nitrogen.

Experiment B: BaCl₂/CsCl Saturations

- 25 ml of 0.1 M BaCl₂ was added to biochar samples and filter papers retained from experiment A (pre-treatments) and shaken end over end for 2 hours (3 replicates/biochar).
- 25 ml of 0.1 M CsCl was added to biochar samples and filter papers retained from previous experiment (pre-treatments) and shaken end over end for 2 hours (3 replicates/biochar).
- 25 ml of 0.1 M BaCl₂ or 0.1 M CsCl was added to 5g samples of both biochars that had NOT undergone pre-treatment (3 replicates/biochar/solution).
- All samples were filtered with Advantec 5C filter papers (pore size 5 µm), with the leachate kept for analysis.
- Leachates were analysed for proportion of cation (Ba or Cs) remaining using ICP AES.
- Leachates were analysed for proportion of anion (Cl) remaining using an Ion Chromatograph (Dionex 1CS-2000, Environmental and Analytical Laboratory, Charles Sturt University, Wagga Wagga).

Results

Analysis of Pre-treatments

There was an increase in calcium desorption with increasing shake times for the green waste biochar, and the loss was significantly larger than the calcium desorption of the cow manure biochar. The loss of magnesium significantly increased with increasing shake times for both biochars, and this was significantly larger for the cow manure biochar compared to the green waste biochar.

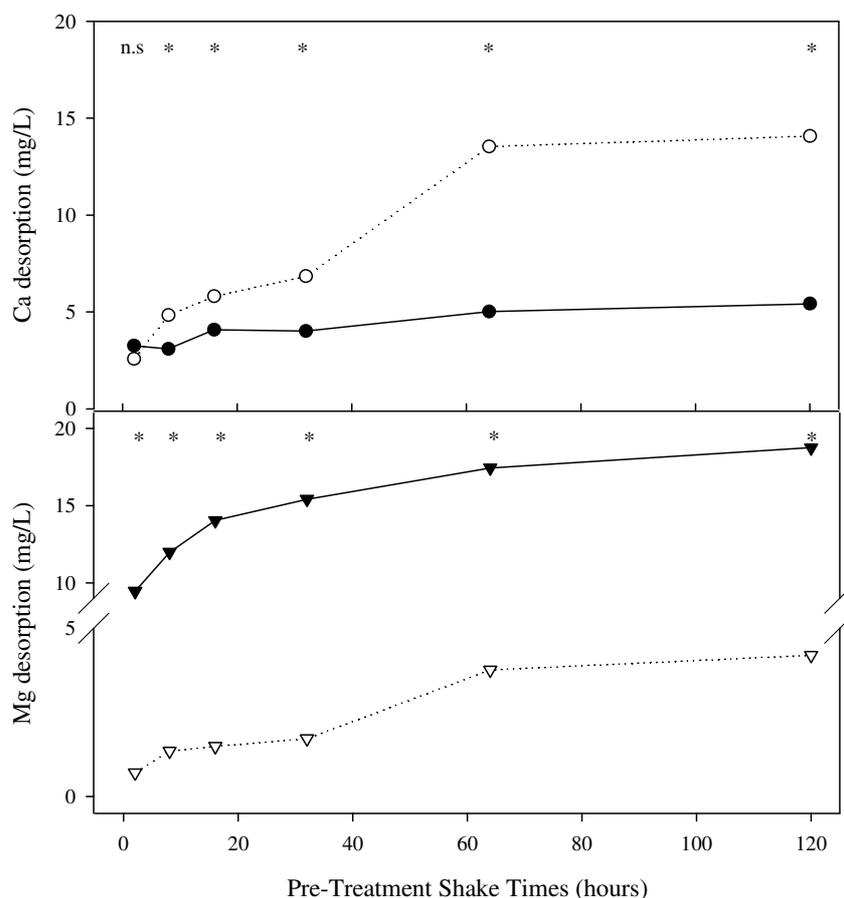


Figure 1. Amount of Calcium (○ and ●) and Magnesium (▽ and ▼) desorption for a cow manure biochar (solid lines) and green waste biochar (dashed lines) with different pre-treatment shake times (* indicate significant difference ($p < 0.05$) between biochars, n.s. = not significant).

Analysis of $BaCl_2/CsCl$ Saturations – Cations

The sorption of barium in the cow manure biochar was significantly greater for all pre-treatment shake times than in the green waste biochar. However, the sorption of barium in the cow manure biochar significantly decreased with the effect of pre-treatment shaking compared to no pre-treatment shaking, whereas the barium sorption in the green waste biochar significantly increased with pre-treatment shaking. There were similar trends for the cesium sorption in both biochars, with no significant difference between biochars at the 16 hour pre-treatment shake time.

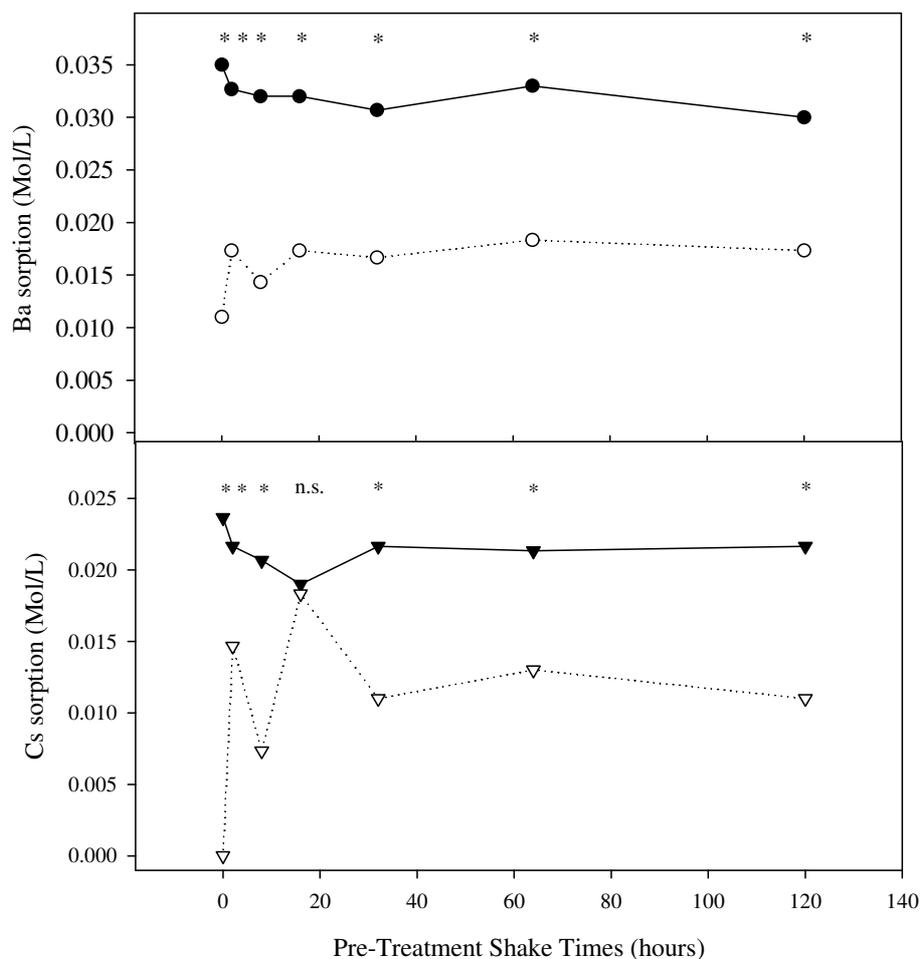


Figure 2. Amount of barium (○ and ●) and cesium (▽ and ▼) adsorption for a cow manure biochar (solid lines) and green waste biochar (dashed lines) with different pre-treatment shake times (* indicate significant difference ($p < 0.05$) between biochars, n.s. = not significant).

Conclusion

The simple measure of compulsive exchange of ions may not be an appropriate method for the determination of the ion exchange capacity of biochar. The pre-treatment of biochars through shaking in water over differing times has manipulated the biochar particle-ion structure, thereby changing the potential for the biochar particle to adsorb ions.

References

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