



Determining the true cation exchange capacity of biochar

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Abstract

Determining the cation exchange capacity (CEC) of biochar is needed to evaluate its potential to improve soil fertility and nutrient retention. However, standard soil CEC methods applied to biochar can give inflated values because soluble salts and carbonates dissolve during extraction. This study measured the CEC of five biochars: coffee husk (CH), coconut shell (CS), wood chips (WC), high-temperature Meva Energy biochar (ME), and seed waste (SW). Two methods were used: the ammonium acetate base cation summation method (CEC_{sum}) and the Na^+ index cation displacement method (CEC_{Na}), applied at pH 4.8 and pH 7 on both acid-washed (AW) and non-acid-washed (NAW) samples. An ion exchange resin (IER) and sea sand were included as positive and negative controls.

Acid washing significantly reduced CEC_{sum} across all five biochars at both pH 4.8 and pH 7, with reductions ranging from approximately 30% in coconut shell to approximately 85% in wood chip biochar. The magnitude of the reduction scaled with the acid neutralising capacity of each biochar, confirming that soluble salts and carbonates dominate apparent CEC in non-acid-washed samples. In coffee husk and seed waste, K^+ accounted for nearly all the removed fraction, with acid washing reducing K^+ by 94% and 87% respectively. In wood chip and Meva Energy biochars, Ca^{2+} and Mg^{2+} were the dominant fractions removed. CEC_{Na} was 0 $\text{cmol}_\text{c} \text{ kg}^{-1}$ for WC, ME and SW in both NAW and AW samples at both pH values, confirmed by supplementary CaCl_2 extraction, indicating that these freshly produced biochars lack Na^+ -accessible surface exchange capacity. For coffee husk and coconut shell, elevated CEC_{Na} values measured at pH 7 are best interpreted as experimental artefacts arising from colloidal biochar particle migration during NaOAc saturation rather than as measurements of true exchange capacity. The IER reference confirmed that the underlying displacement procedure functioned as expected, with CEC_{sum} at pH 7 within 3% of the calculated reference value.

These findings show that non-acid-washed CEC values overestimate the true surface exchange capacity of biochars, and that the divergence between CEC_{sum} and CEC_{Na} exceeds an order of magnitude for the low-ash biochars. Acid washing followed by index cation measurement is recommended for reliable biochar CEC determination, with quantification of colloidal particle losses incorporated as a standard quality control step in future studies more especially when percolation tube procedure is employed.

Keywords: True Cation Exchange Capacity, exchangeable cations, index cation, ash, coffee husk biochar, coconut shell biochar, wood biochar, high meva energy biochar, seed waste biochar.

Popular Science

Biochar is a charcoal-like material made by heating organic biomass such as crop residues, food-processing by-products, or wood under low-oxygen conditions. When added to agricultural soil, it can help retain nutrients that would otherwise wash away with rainwater. This property is called cation exchange capacity, or CEC. A higher CEC means the material can hold more positively charged nutrient ions such as calcium, potassium, and magnesium, keeping them available for plants instead of losing them through leaching.

Measuring the true CEC of biochar is not straightforward. Standard laboratory methods for measuring CEC in soils do not work reliably for biochar, because biochar often contains soluble mineral salts and carbonates that dissolve during the measurement. This makes the CEC appear higher than it actually is. It is like weighing a wet sponge and concluding it is heavier than a dry one. The water inflates the measurement but is not part of the sponge itself. If researchers or farmers rely on these inflated values when deciding how much biochar to apply to a field, they may overestimate the benefit to the soil.

This study tested five biochars made from different raw materials: coffee husk, coconut shell, wood chips, a high-temperature industrial biochar produced at over 1000°C, and seed waste. Each biochar was tested with two measurement methods at two pH values. Importantly, each was tested both with and without a pre-treatment step in which the biochar was washed with dilute acid (0.1 M HCl) to remove soluble salts and carbonates before measurement.

The acid washing step made a clear difference. For coffee husk and seed waste biochars, the measured CEC fell by about 47% and 75% after acid washing. Most of the removed fraction was potassium that had been in soluble salt form rather than on the biochar surface. For wood chip and Meva Energy biochars, the inflated fraction was mainly calcium and magnesium from carbonate minerals. After acid washing, wood chip, Meva Energy, and seed waste biochars showed almost no measurable exchange capacity by the index cation method at either pH value, which was confirmed by an additional verification step. Coffee husk and coconut shell appeared to show higher exchange capacity at the higher pH value, but further investigation showed this was a measurement artefact: fine biochar particles from these two biochars were carried out of the test column along with the measurement solution and counted as if they were dissolved exchange cation. This effect was visible as a yellow-brown discolouration of the percolate.

These findings have practical implications for using biochar as a soil amendment. Measuring biochar CEC without prior acid washing can give values that are several times higher than the true surface exchange capacity, especially for biochars made from agricultural residues rich in potassium and calcium. This study recommends that future biochar characterisation should include acid washing before CEC measurement, and that measurements should be done at pH 7 rather than at the more acidic pH values often used in soil laboratories. It also recommends that researchers measuring biochar CEC by index cation displacement through a percolation tube procedure should monitor for fine particle loss from the column, as this can inflate apparent exchange capacity values. These steps give a more reliable picture of what a given biochar can actually contribute to nutrient retention in the soil.

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Abbreviations

Abbreviation	Description
AEC	Anion Exchange Capacity
ANC	Acid Neutralising Capacity
AW	Acid Washed
BC	Biochar
CEC	Cation Exchange Capacity
CEC _{Na}	CEC determined by Na ⁺ index cation displacement method
CEC _{sum}	CEC determined by base cation summation method
CH	Coffee Husk biochar
CS	Coconut Shell biochar
DOC	Dissolved Organic Carbon
EC	Electrical Conductivity
HTT	Highest Treatment Temperature
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IE	Ion Exchange resin (positive control)
ME	Meva Energy biochar
NAW	Non-Acid Washed
NH ₄ OAc	Ammonium Acetate
NaOAc	Sodium Acetate
SLU	Swedish University of Agricultural Sciences
SW	Seed Waste biochar
WC	Wood Chip biochar

1. Introduction

Biochar is a carbon-rich material produced by the thermal decomposition of organic feedstocks under conditions of limited or absent oxygen, a process known as pyrolysis (Ahmad et al. 2014 ; Lehmann & Joseph 2015; Racek et al. 2020). Over the past two decades it has attracted considerable scientific interest as a soil amendment capable of improving soil fertility, sequestering atmospheric carbon, and remediating metal-contaminated soils (Ahmad et al. 2014; Lehmann & Joseph 2015). Among the many soil properties that biochar can influence, cation exchange capacity (CEC) is of agronomic and environmental importance. Cation exchange capacity governs the ability of a soil or amendment to retain nutrient cations against leaching whilst keeping them available for plant uptake and is therefore one of the most widely used indicators of soil fertility (Sumner & Miller 1996; Brady & Weil 2008). Despite a growing body of research on biochar application, the accurate and reproducible determination of its true CEC remains a persistent methodological challenge. Unlike mineral soils, biochar has a heterogeneous surface chemistry, variable and pH-dependent charge characteristics, and a microporous structure that complicates the direct application of conventional soil CEC methods (Munera-Echeverri et al. 2018). A clear understanding of the surface chemistry that gives rise to CEC, the methods available for measuring it, and the practical limitation of each approach is therefore essential before biochar can be reliably characterised for use in agricultural or environmental settings.

1.1 Biochar and its role in soil fertility

The pyrolysis process involves the thermal decomposition of biomass, during which volatile compounds including hydrogen, oxygen, phenolic compounds, and volatile fatty acids are driven off, leaving behind a recalcitrant carbon-rich residue composed predominantly of aromatic organic molecules alongside mineral ash components (Chen et al. 2014; Wei et al. 2022). Variations in pyrolysis conditions, particularly the highest treatment temperature (HTT), residence time, heating rate, and feedstock composition, influence the physical and chemical properties of the resulting biochar (Mukherjee et al. 2011; Budai et al. 2014; Ghorbani et al. 2024). At lower pyrolysis temperatures, biochars retain a greater proportion of aliphatic and oxygenated functional groups, whilst at higher temperatures the carbon structure becomes increasingly aromatic and graphitic in character, with a corresponding decline in surface functional group density and pH-dependent charge (Keiluweit et al. 2010, as cited in Mukherjee et al. 2011; Peiris et al. 2019; Tusar et al. 2023)

The addition of biochar to agricultural soils has been demonstrated to produce a range of beneficial effects, including improvements in water holding capacity, enhancement of soil structure, provision of habitat for soil microorganisms, and increases in nutrient retention through elevated CEC (Lehmann and Joseph, 2015; Hazrati et al. 2021; Tusar et al. 2023). These effects are, however, strongly dependent on both biochar and soil properties, and the direction and magnitude of CEC change following biochar application can vary considerably across soil types (Hailegnaw et al. 2019). Domingues et al. (2020) demonstrated that high-ash biochars derived from coffee husk pyrolysed at 350°C were effective at increasing the CEC of weathered oxisols in Brazil, with feedstock type, pyrolysis temperature, and application rate all identified as key controlling factors. Similarly, Antonangelo et al. (2024) found that poultry litter-derived-biochar with an ash content of 45.9% significantly increased soil CEC by up to 91%, whilst switchgrass-derived biochar with an ash content of 4.4% reduced CEC by 27% on average, reflecting the important role of feedstock physiochemical characteristics in determining the agronomic outcome of biochar application. A meta-analysis by Ghorbani et al. (2024) further confirmed that straw and herbaceous feedstocks consistently yield higher CEC responses than wood-based feedstocks, and that biochars produced at lower pyrolysis temperatures below 400°C produce the greatest increases in CEC following acid washing, attributable to the greater density of oxygenated surface functional groups retained at lower charring temperatures. Beyond fertility improvement, biochar has also demonstrated considerable promise for the immobilisation of heavy metals such as copper, with Teng et al. (2024) reporting that biochars with a specific surface area of 50 to 100 m²g⁻¹ enhanced CEC by 183% or more, thereby reducing copper mobility in contaminated soils through mechanisms including ion exchange, surface complexation, and precipitation.

1.2 Cation exchange in soils and biochar

Cation exchange is the reversible electrostatic attraction of positively charged ions principally Ca²⁺, Mg²⁺, K⁺, Na⁺, NH₄⁺, and Al³⁺ to negatively charged surfaces on soil colloids and organic matter (Brady & Weil 2008). The total quantity of cations a material can hold at a given pH, expressed in centimoles of positive charge per kilogram (cmol_c kg⁻¹), defines its CEC. Materials with higher CEC values are generally better able to retain nutrients against leaching and to supply them to plants on demand, making CEC one of the most widely cited indicators of soil fertility and amendment quality (Sumner & Miller 1996).

Negative charges on soil and biochar surfaces arise from two fundamentally different sources. Permanent charges result from isomorphic substitution within phyllosilicate mineral lattices, for example, the replacement of Si⁴⁺ by Al³⁺ in tetrahedral sheets creating a charge deficit that is fixed and independent of pH

(Helling et al. 1964). Variable or pH-dependent charges arise from the dissociation of protons from hydroxyl groups on mineral surfaces, and from carboxylic ($-\text{COOH}$) and phenolic ($-\text{OH}$) functional groups in organic matter. Because proton dissociation increases with rising pH, the variable charge component of CEC, and therefore total CEC, increases as pH increases. This pH-dependence has direct practical consequences for CEC measurement: the value obtained reflects only the charge that is active at the pH of measurement, and comparisons between materials measured at different pH values are not straightforward (Munera-Echeverri et al. 2018).

The affinity of exchange sites for different cations is not uniform. Higher-valence cations with smaller hydrated ionic radii are preferentially retained, following the lyotropic series: $\text{Al}^{3+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ \approx \text{NH}_4^+ > \text{Na}^+$ (Steiner 2018). This hierarchy has direct practical implications for CEC measurement, because the saturating cation used in the index cation method must be capable of displacing all native cations from exchange sites whilst itself being readily and completely displaced in a subsequent step.

1.3 Surface charges and surface properties of biochar

The surface chemistry of biochar is considerably more complex than that of most mineral soil components. Biochar surfaces carry both negative and positive charges, the balance of which depends on pyrolysis conditions, feedstock composition, and the degree of post-production weathering or ageing (Mukherjee et al. 2011). Zeta potential measurements confirm that biochar surfaces are predominantly negatively charged under most environmentally relevant conditions: Mukherjee et al. (2011) reported zeta potentials of -9 to -4 mV at neutral pH for biochars from oak, pine, and grass feedstocks, with an isoelectric point near pH 2 to 3. Yang et al. (2016) compiled data across a wider range of feedstocks and production temperatures and reported that biochar colloids typically carry zeta potentials of -20 to -50 mV at pH 4 to 9, again with an isoelectric point consistently near pH 2 to 3 regardless of feedstock treatment temperature. The progressive shift in zeta potential with increasing pH reflects the ionisation of surface functional groups, principally carboxylic groups with pK_a values of approximately 3 to 5.

The primary sources of negative charge on biochar surfaces are oxygen-containing functional groups, most importantly carboxyl ($-\text{COOH}$), lactone, and phenolic ($-\text{OH}$) groups, all of which can donate protons and become negatively charged above their respective pK_a values. Carboxyl groups become charged at relatively low pH ($\text{pK}_a \approx 3$ to 5), whilst phenolic groups contribute charge predominantly at higher pH ($\text{pK}_a \approx 8$ to 10), making the pH at measurement a critical variable in CEC determination (Lehmann & Joseph 2015). The density of these surface functional groups is itself dependent on pyrolysis conditions. Yuan

et al. (2011) demonstrated that in crop-residue biochars produced at 300°C, alkalinity is carried primarily by organic functional groups including carboxyl and phenolic groups, but as charring temperature increases these functional groups are progressively destroyed. Budai et al. (2014) similarly found that CEC peaked at lower pyrolysis temperatures for both corncob and *Miscanthus* biochars and declined above approximately 400 to 500°C. Fidel et al. (2017) distinguished four categories of biochar alkalinity, of which two low- pK_a structural functional groups (pK_a 5 to 6.4) directly bonded to the condensed aromatic carbon matrix, and higher- pK_a organic surface groups contribute to long-term surface exchange capacity and are the principal sources of true biochar CEC.

In addition to the pH-dependent negative charge arising from acidic functional groups, biochar surfaces also carry positive charge, giving rise to anion exchange capacity (AEC). Lawrinenko & Laird (2015) measured AEC values of 0.6 to 27.8 $\text{cmol}_c \text{ kg}^{-1}$ for biochars produced from four feedstocks at 500 and 700°C, and demonstrated that AEC increased significantly with decreasing pH, averaging 2.5, 7.4, and 18.0 $\text{cmol}_c \text{ kg}^{-1}$ at pH 8, 6, and 4 respectively. Two principal sources of AEC were identified: pyridinic nitrogen heterocycles, which are protonated and carry a positive charge below their pK_a (approximately 5.2), contributing pH-dependent AEC; and oxonium oxygen heterocycles, which carry a permanent pH-independent positive charge and can therefore contribute AEC even at pH 8 where pyridinic groups are expected to be deprotonated (Lawrinenko & Laird 2015). The existence of AEC is directly relevant to CEC measurement: at low pH values such as pH 4.8, active AEC sites may compete with cation exchange, contributing to underestimation of true CEC when index cation methods are applied under acidic conditions. This effect would be expected to be most pronounced in high temperature biochars with condensed aromatic carbon structures, where oxonium heterocycles are most likely to persist.

Beyond functional group chemistry, the pore structure of biochar plays an important role in determining the effective surface area available for cation exchange. Micropores generated during pyrolysis substantially increase total surface area in biochars produced at lower temperatures, whereas at higher temperatures the condensation of aromatic carbon structures creates larger macropores (Budai et al. 2014). In high-ash biochars, clogging of pores by mineral ash can reduce effective pore volume, although acid washing can partially restore accessibility by dissolving soluble and acid-labile mineral phases (Hazrati et al. 2021). Biochar surfaces also evolve with time: pristine biochars are predominantly hydrophobic, but oxidative ageing in soil progressively introduces carboxylic and phenolic groups, shifting the surface towards hydrophilic character and increasing the density of charge-bearing sites (Yang et al. 2016). This ageing-induced development of low- pK_a structural functional groups is particularly significant, because these groups contribute not only to short-term acid

neutralisation but also to long-term soil CEC and pH-buffering capacity. As a result, the exchange capacity of freshly produced biochar is likely to underestimate its long-term agronomic contribution to soil nutrient retention.

1.4 Methods for measuring CEC in soils and biochar

Several methods have been developed for measuring CEC in soils and adapted for use with biochar. However, because biochar has pronounced variable-charge character, soluble-salt content, and sensitivity to the pH and ionic strength of the extractant, the direct application of soil CEC methods to biochar introduces significant potential for error (Munera-Echeverri et al. 2018). The two most widely used approaches are the base cation summation method and the displacement method using an index cation, both of which are employed in the present study.

1.4.1 Summation of exchangeable base cations

The summation method determines CEC by extracting all exchangeable cations with a displacing solution and measuring the concentrations of each cation individually typically Ca^{2+} , Mg^{2+} , K^{+} , Na^{+} , and Mn^{2+} by ICP-OES, then summing their contributions to total charge. Antonangelo et al. (2024) demonstrated that this approach provides a nuanced picture of individual cation contributions to total exchange capacity and found that cation ratios, particularly the $[\text{Ca}+\text{Mg}]/\text{K}$ ratio, were more informative predictors of plant growth responses than CEC alone. A key limitation of the summation method when applied to non-acid-washed biochars is that soluble salts present in the biochar matrix dissolve during extraction and contribute to measured cation concentrations, thereby inflating the apparent CEC (Munera-Echeverri et al. 2018). This artefact is particularly pronounced in high-ash biochars rich in soluble K and Ca, such as those derived from coffee husk or seed waste (Domingues et al. 2020). Acid washing prior to extraction substantially reduces this interference by removing soluble and acid-labile mineral phases, although it may also alter the surface chemistry of the biochar.

1.4.2 Displacement Method Using an Index Cation

The index cation method is regarded as the most analytically rigorous approach to CEC determination. In this method, all exchange sites in the sample are saturated with a single, chosen cation (the index cation) at a defined pH; excess index cation is removed by washing; and the retained index cation is then displaced by a competing cation and quantified in the resulting extract (Chapman 1965). Because the amount of index cation displaced corresponds directly to the number of exchange sites occupied at the saturation pH, the method provides a direct

measure of CEC without the need to sum individual cation contributions or correct for differences in affinity among competing ions (Chapman 1965; Page 1982).

The choice of index cation significantly influences the measured CEC. An ideal index cation should be monovalent, present at negligible background concentrations in the material being tested, capable of displacing all native cations from exchange sites, and readily quantifiable by standard analytical techniques (Page 1982; Steiner 2018). Ammonium (NH_4^+), used as 1 M ammonium acetate (NH_4OAc) buffered at pH 7, is the most widely adopted index cation in routine soil analysis and remains the basis of the standard ISRIC reference method (Chapman, 1965; Van Reeuwijk, 2002). Barium (Ba^{2+}), applied as barium chloride–triethanolamine buffered at pH 8.2, was developed specifically for calcareous soils where NH_4OAc is unreliable owing to carbonate dissolution; however, its divalent nature introduces selectivity effects that can cause systematic deviations from monovalent index cation estimates (Mehlich 1953; Rhoades 1982). Potassium (K^+) has been used for biochar CEC determination by (Mukherjee et al. 2011 and Munera-Echeverri et al. 2018) but carries the risk of underestimating exchange site saturation in K-rich feedstock biochars due to native K^+ contributions. In this study, Na^+ was selected as the index cation lowering the risk of native Na with a belief that most biochar feedstocks have low Na content.

1.4.3 Effect of acid washing on measured CEC

The presence of soluble salts and mineral phases in non-acid-washed biochars poses one of the most significant methodological challenges in CEC determination. Acid washing prior to measurement removes water-soluble and acid-soluble mineral phases including carbonates, sulphates, and readily soluble K and Ca salts that would otherwise dissolve during extraction and inflate apparent CEC values (Munera-Echeverri et al. 2018). Yuan et al. (2011) demonstrated that carbonates are the dominant alkaline component in biochars produced at 500 and 700°C from crop residues, and that these carbonate alkalis are directly responsible for the strong buffer plateau observed on acid–base titration curves; their dissolution during CEC extraction would therefore release Ca^{2+} , Mg^{2+} , and other base cations into the percolate, indistinguishable from genuinely exchangeable cations. Fidel et al. (2017) corroborated this, showing that inorganic alkalis, principally carbonates but also phosphates, sulfates, and iron and aluminium hydroxides, consistently constituted the majority of total alkalinity in lignocellulosic biochars (55 to 95%), and that this inorganic fraction was effectively removed by washing with 0.05 M HCl. Fidel et al. (2017) also showed that total alkalinity was strongly correlated with acid-soluble base cation concentration ($r^2 = 0.84$), meaning that the magnitude of CEC inflation in non-

acid-washed samples is predictable from the base cation content of the biochar. This effect is especially pronounced in high-ash biochars derived from agricultural residues such as coffee husk, seed waste, and sugarcane bagasse (Domingues et al. 2020), all of which are rich in soluble K and Ca associated with carbonate and other mineral phases.

The difference in measured CEC between acid-washed and non-acid-washed samples therefore serves as a practical indicator of the soluble salt contribution to apparent exchange capacity and helps to separate true surface-exchangeable cations from artefactual dissolution products (Munera-Echeverri et al., 2018).

1.5 Reported CEC values for biochar

Published CEC values for biochar shows a wide range from near zero to several hundred $\text{cmol}_\text{c} \text{ kg}^{-1}$ reflecting the diversity of feedstocks, pyrolysis conditions, and measurement methods used across the literature. Munera-Echeverri et al. (2018) compiled a comprehensive review of reported values and found that the highest CEC estimates, typically exceeding 200 $\text{cmol}_\text{c} \text{ kg}^{-1}$, were associated with low-temperature biochars from nutrient-rich agricultural residues measured at pH 7 using buffered ammonium acetate without prior acid washing, making it likely that soluble salts contributed substantially to those values. Mukherjee et al. (2011) reported CEC values of approximately 10 $\text{cmol}_\text{c} \text{ kg}^{-1}$ for biochars produced at 400 and 650°C, with no measurable pH dependency, consistent with the dominance of permanent charge at high pyrolysis temperatures. By contrast, biochars produced at 250°C showed strongly pH-dependent CEC values rising to as much as 70 $\text{cmol}_\text{c} \text{ kg}^{-1}$ at pH 7, reflecting the large number of weakly acidic carboxyl and phenolic groups retained at low HTT. Budai et al. (2014) confirmed that CEC peaked at lower pyrolysis temperatures for biochars from both corncob and miscanthus, declining above 400 to 500°C.

Collectively, the literature makes clear that the measured CEC of a biochar is highly sensitive to feedstock type, pyrolysis temperature, acid washing status, extraction pH, and the choice of index cation. Without careful standardisation of these variables, published CEC values are difficult to compare and may not reflect the true surface exchange capacity of the material. Graber et al. (2014) identified methodological inconsistency as the most urgent challenge in biochar CEC research and called for standardisation of pretreatment, pH control, biochar-to-solution ratio, equilibration time, and washing procedures. The present study responds to this call by applying two complementary methods at two pH values on both acid-washed and non-acid-washed variants of five contrasting biochars, providing a systematic assessment of how each of these variables influences the measured CEC.

1.6 Objectives and hypotheses

The overall aim of this study was to determine the true cation exchange capacity of a range of biochars produced from the contrasting feedstocks: coffee husk (CH), coconut shell (CS), wood chips (WC), high-temperature Meva Energy biochar (ME), and seed waste (SW) using two complementary analytical methods. An ion exchange resin (IER) was included as a positive control of known CEC, and sea sand as a negative control to correct for background contributions. Both the ammonium acetate base cation summation method and the Na^+ index cation displacement method were applied at two extraction pH values (pH 4.8 and pH 7) in separate experiments, and each biochar was tested in both acid-washed (AW) and non-acid-washed (NAW) form, enabling a systematic evaluation of the influence of soluble salt content, extraction pH, and method choice on measured CEC. The choice of pH 4.8 as the lower extraction pH was not arbitrary, both the ammonium acetate and sodium acetate solutions were adjusted to this value by addition of acetic acid, which has a pK_a of approximately 4.8, meaning the buffer operates at maximum capacity at this pH and provides stable pH control throughout the extraction.

The following hypotheses were tested:

Hypothesis 1

Non-acid-washed biochars will show significantly higher apparent CEC_{sum} values than acid-washed biochars, and this difference will increase proportionally with the ash content of the biochar.

Hypothesis 2

The difference in CEC_{sum} (i.e. between pH 4.8 and 7.0) would be smaller in non-acid washed biochars than for acid-washed biochars. This is because the ash fraction in non-acid-washed biochars buffers the pH 4.8 extractant solution upwards, reducing the effective pH difference between the two experiments and therefore compressing the apparent difference in CEC_{sum} between pH 4.8 and pH 7.0.

Hypothesis 3

In acid-washed biochars, CEC_{sum} measured at pH 7.0 will be significantly higher than CEC measured at pH 4.8, indicating a substantial contribution of pH-dependent charge to total CEC

2. Materials and methods

This chapter describes the experimental design, materials, pretreatment procedures, and analytical methods used to determine the CEC of five biochar types by two complementary approaches: the ammonium acetate base cation summation method and the sodium index cation displacement method. Both methods were applied at pH 4.8 (experiment 1) and pH 7 (experiment 2), and each biochar was tested in both acid-washed (AW) and non-acid-washed (NAW) form. The soil percolation tube procedure was adopted as the basis for both experiments, adapted for biochar following the recommendations of (Munera-Echeverri et al. 2018) and the ISRIC soil analysis protocol 2002. All glassware and apparatus were soaked overnight in dilute nitric acid, rinsed thoroughly with deionised water (resistivity $\geq 18.2 \text{ M}\Omega\cdot\text{cm}$), and oven-dried at 105°C prior to use. Sea sand and glass wool were acid-washed, rinsed over a $150 \mu\text{m}$ sieve, and oven-dried overnight at 105°C .

2.1 Biochar materials

Five biochar types were selected to represent a range of feedstocks and pyrolysis conditions: coffee husk biochar (CH), coconut shell biochar (CS), wood chips biochar (WC), high-temperature Meva Energy biochar produced above 1000°C (ME), and seed waste biochar (SW). A synthetic ion exchange resin (IER) was included as a positive control of known CEC ($220 \text{ cmol}_\text{c} \text{ kg}^{-1}$), and sea sand was used as a negative control to correct for background cation contributions from the column matrix. Each biochar was tested in both AW and NAW form, giving twelve biochar treatments in total. All treatments were replicated twice. Table 1 summarises the materials and column masses while table 2 shows the physicochemical properties of the five biochars.

Table 1. Summary of biochar materials, controls, column masses, and replication used in both experiments. AW = acid washed; NAW = non-acid washed. Coffee husk mass reduced to 1.8 g owing to material losses during rinsing

Biochar / Control	Code	Acid-washed?	Mass used (g)	Replicates
Coffee husk biochar	CH	AW and NAW	1.8	2
Coconut shell biochar	CS	AW and NAW	2.0	2
Wood chips biochar	WC	AW and NAW	2.0	2
Meva Energy biochar (>1000°C)	ME	AW and NAW	2.0	2
Seed waste biochar	SW	AW and NAW	2.0	2
Ion exchange resin (positive control)	IE	None	0.5	2
Sea sand (negative control)	—	None	2.0	2

2.2 Extract solution preparation

All extract solutions were prepared in 5 L volumetric flasks. The 1 M NH_4OAc solution was prepared by dissolving 385.4 g of ammonium acetate ($\text{CH}_3\text{COONH}_4$, MW = 77.08 g/mol) in approximately 3.0-3.5 L of deionised water with magnetic stirring, then making up to the 5.00 L mark. Two pH variants were prepared: for the pH 4.8 solution, the pH was adjusted by the gradual addition of glacial acetic acid (CH_3COOH , 99–100%), allowing the solution to equilibrate for one hour after each addition until the pH stabilised at 4.8 ± 0.02 ; for the pH 7.0 solution, no pH adjustment was required, as 1 M NH_4OAc is approximately neutral at this concentration.

The 1 M NaOAc solution was prepared by dissolving 410.2 g of sodium acetate (CH_3COONa , MW = 82.03 g/mol) in approximately 3.0-3.5 L of deionised water, then making up to 5.00 L. Two pH variants were prepared using the same approach as for NH_4OAc : one adjusted to pH 4.8 by addition of glacial acetic acid, and one adjusted to pH 7.0 by addition of approximately 2 mL of glacial acetic acid to bring the initial pH of 9.05 to the target value. The NaOAc solution served as the Na^+ index cation solution throughout both experiments.

2.3 Biochar pretreatment

Approximately 25 g of each biochar was gently crushed using a pestle and mortar and sieved to 0.5 mm (500 μm) to obtain a uniform and representative particle size fraction. The sieved material was then divided into two portions: one retained as the non-acid-washed (NAW) fraction and one subjected to acid washing (AW) to remove soluble salts and carbonates that would otherwise inflate measured CEC values.

The NAW fraction (approximately 15 g) was oven-dried at 105°C and stored in a desiccator until use without further treatment.

For the AW fraction (approximately 10 g), the sieved biochar was immersed in deionised water in a 1 L beaker and 0.1 M HCl was added gradually under continuous stirring until the suspension pH reached 5.5. The suspension was left overnight, the pH rechecked, and further additions of HCl made if necessary until the pH remained stable around pH 5.6, to ensure removal of carbonate and other alkaline ash components. For each biochar, the pH, electrical conductivity (EC), and volume of HCl added were recorded, from which the acid neutralising capacity (ANC) of each biochar was calculated. The acid-washed biochar was then rinsed three times with deionised water to remove residual acid, using vacuum filtration through a 3 μm membrane filter on a Büchner funnel connected to a vacuum pump. The rinsed biochar was oven-dried and stored in a desiccator.

Coffee husk biochar could not be processed by vacuum filtration owing to its fine particle size, which caused rapid clogging of the membrane filter. Dialysis was used instead: the acid-washed biochar was placed in a dialysis membrane tube, submerged in deionised water, and the surrounding water changed repeatedly over three days, with the EC monitored at each change. Washing continued until the EC of the surrounding water approached that of deionised water (approx. 5 $\mu\text{S}/\text{cm}$), indicating that residual acid and soluble ions had been sufficiently removed.



Figure 1. Shows vacuum filtration setup (Büchner funnel, 3 μm membrane, Alcatel vacuum pump) used for rinsing acid-washed biochars with deionised water, the beaker contains the biochar-water suspension being filtered.



Figure 2. Shows dialysis membrane tubes immersed in a beaker full of deionised water used for rinsing acid-washed coffee husk biochar.

2.4 Preparation of percolation columns

Percolation tubes of 3.5 cm inner diameter and approximately 12.5 cm length, fitted with a Hoffmann clip outlet, were used throughout both experiments. Each column was assembled from bottom to top in the following sequence: approximately 1 g of glass wool as a basal plug; approximately 25 g of ignited, acid-washed sea sand as a lower support layer; a filter paper; the biochar-sand mixture; a second filter paper; approximately 25 g of sea sand as an upper support layer; and approximately 1 g of glass wool at the top. For most biochars, 2 g of each biochar was thoroughly mixed with 12 g of sea sand to promote uniform packing and even solution flow. For coffee husk, only 1.8 g was used due to losses during rinsing. For the ion exchange resin control, 0.5 g IER was mixed with 12 g of sea sand, and for the sand-only negative control, 2 g of sea sand was used in place of biochar, mixed with 12 g of additional sea sand in the same manner for consistency.

For each biochar, eight columns were assembled in total: two replicates of the AW fraction at pH 4.8 (experiment 1), two replicates of the AW fraction at pH 7 (experiment 2), two replicates of the NAW fraction at pH 4.8, and two replicates of the NAW fraction at pH 7, giving a total of 24 columns per experiment including the controls.



Figure 3. Experimental setup showing percolation columns filled with glass wool, sand and biochar–sand mixture and collecting beakers containing percolates.

2.5 Analytical procedure

The analytical procedure comprised five sequential stages designed to: (i) displace native cations from the biochar with NH_4^+ ; (ii) remove excess NH_4^+ from the column; (iii) saturate exchange sites with Na^+ as the index cation; (iv) remove excess Na^+ ; and (v) displace retained Na^+ with NH_4^+ for quantification. A conceptual overview of the procedure is presented in figure 4. All percolation steps were conducted at a flow rate of approximately 10 drops per minute. After each solution addition, the column was allowed to stand for two hours before the outlet was opened, permitting equilibration within the biochar pore system. This equilibration period is critical for biochar, which possesses internal pore structures that slow ion diffusion relative to mineral soils and can lead to incomplete exchange if concentration gradients between the particle interior and exterior are not allowed to dissipate (Munera-Echeverri et al., 2018). All solutions were matched to the pH of the experiment: pH 4.8 solutions were used throughout experiment 1 and pH 7 solutions throughout experiment 2.

2.5.1 Displacement of exchangeable base cations with 1 M NH_4OAc (Stage 1)

A 200 mL collection beaker was placed beneath the outlet of each column and the Hoffmann clip open. A 100 mL volumetric flask containing 1 M NH_4OAc at the appropriate pH was inverted into the top of the column to maintain a continuous head of solution; any entrapped air was removed by gentle tapping. When the first solution appeared at the outlet of the column the clip was closed. After the two-hour equilibration period, the clip was opened and the solution allowed to percolate at approximately 10 drops per minute. Once the first 100 mL had percolated completely, the procedure was repeated with a further 100 mL of NH_4OAc to ensure complete displacement of all exchangeable cations. The two percolates were combined, and a 100 mL aliquot was collected into a labelled bottle and retained for ICP-OES analysis of displaced Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and Mn^{2+} . The cation concentrations in this percolate provided the base cation summation data from which CEC_{sum} was subsequently calculated.

2.5.2 Removal of excess NH_4^+ with deionised water (Stage 2)

Excess NH_4^+ remaining in the free solution and pore space of the biochar was removed by three successive washes with 100 mL of deionised water. For each wash, the water was added to the column, allowed to equilibrate for two hours, and then percolated through at a moderate rate. The percolate was discarded. This step ensures that only NH_4^+ adsorbed on exchange sites remains in the column prior to Stage 3, so that free NH_4^+ in solution does not displace Na^+ from exchange sites during the subsequent NaOAc saturation.

2.5.3 Saturation of exchange sites with 1 M NaOAc (Stage 3)

Following removal of excess NH_4^+ , exchange sites were saturated with Na^+ by percolating 1 M NaOAc solution at the same pH as Stage 1, using the same procedure described in Section 2.5.1. The first 100 mL percolate was discarded. A second 100 mL pass was then performed to ensure complete saturation of all exchange sites; this percolate was also discarded.

2.5.4 Removal of excess Na^+ with deionised water (Stage 4)

Excess NaOAc remaining in the free solution within the column was removed by successive washes with 100 mL of deionised water using the same procedure as Stage 2. Removal of free Na^+ is critical: any Na^+ remaining in solution at this stage would be collected in the Stage 5 percolate and cause overestimation of CEC_{Na} . The EC of each wash percolate was measured and compared to that of deionised water as a guide to the completeness of removal. In experiment 1 (pH 4.8), four water washes were performed; following inspection of the stage 5 results from experiment 1, the number of washes was increased to eleven in experiment 2 (pH 7) to achieve more complete EC reduction and minimise residual free Na^+ . All wash percolates were discarded.

2.5.5 Displacement of retained Na^+ with 1 M NH_4OAc (Stage 5)

Na^+ retained on the biochar exchange sites was displaced by NH_4^+ using 1 M NH_4OAc at the same pH as the preceding stages, following the same procedure as stage 1. The collected percolate was labelled (Na^+ -pH 4.8 or Na^+ -pH 7) and retained for ICP-OES analysis of Na^+ concentration, from which CEC_{Na} was calculated.

2.5.6 CEC analysis

All percolates collected in stages 1 and 5 were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). Stage 1 percolates were analysed for Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and Mn^{2+} , providing the data for the CEC_{sum} calculation. Stage 5 percolates were analysed for Na^+ , providing the data for the CEC_{Na} calculation. Percolates from the sand-only control columns were analysed alongside all biochar percolates and used to apply background corrections to each measured cation concentration. Percolates from the IER columns were analysed to validate the procedure against a material of known CEC.

2.5.7 Supplementary CaCl_2 extraction

A CaCl_2 displacement check was performed at pH 7 on acid-washed WC, ME, and SW, the three biochars that returned near-zero CEC_{Na} values in experiment 2

to determine whether these low values reflected a genuine absence of exchange sites or incomplete displacement of Na^+ from within micropores during the standard percolation procedure. The same biochar samples used in the full experiment (approximately 2 g of each biochar) was placed in a 50-mL centrifuge tube, saturated with 40 mL of 0.01 M CaCl_2 , and placed on an orbital shaker overnight to allow equilibration and facilitate diffusion of the index cation into the biochar pore network. The resulting extracts were analysed by ICP-OES for Na^+ . A near-zero Na^+ concentration in this extract, independent of the percolation procedure, would confirm that the low CEC_{Na} values obtained in both experiments represent a true absence of accessible exchange sites in these biochars rather than a methodological artefact.

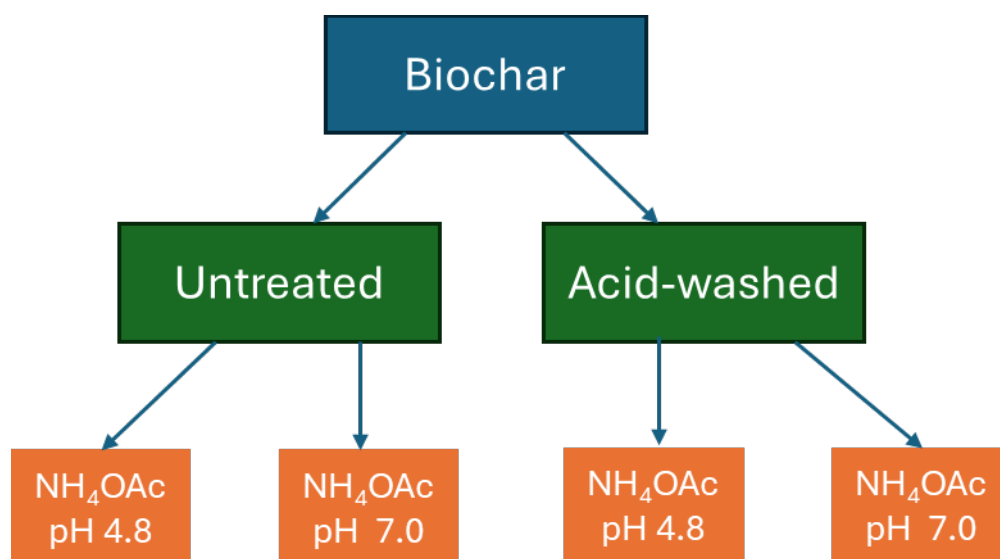


Figure 4. Conceptual figure providing an overview of the method of this study.

2.6 Statistical analysis

All statistical analyses were performed using R software (version 4.5.3). Pearson correlation coefficients (r) were calculated to assess the relationship between acid neutralising capacity (ANC) and individual base cation concentrations extracted during the first NH_4OAc displacement, with statistical significance set at $p < 0.05$. A paired t-test was used to determine whether acid washing significantly reduced CEC_{sum} across the five biochars, with both replicates per treatment included as paired observations ($n = 10$ pairs per experiment). The test was applied separately for experiment 1 (pH 4.8) and experiment 2 (pH 7), with a one-sided alternative hypothesis that NAW CEC_{sum} exceeded AW CEC_{sum} . Prior to the paired t-test, normality of the differences between NAW and AW values was confirmed using the Shapiro-Wilk test, indicating that the parametric test was appropriate. All figures were produced in R, using the ggplot2 package, and in Excel.

3. Results

3.1 Observation on yellow-amber discolouration

A visible yellow-amber discolouration of the column percolate was observed during NaOAc saturation of CH and CS columns at both pH 4.8 (figure 5, top) and pH 7 (figure 5, bottom) and was most pronounced in the CH columns and at pH 7. No discolouration was observed in the WC, ME or SW columns at either pH. This observation is relevant for the interpretation of the CEC_{Na} results for CH and CS, which are reported in section 3.8.

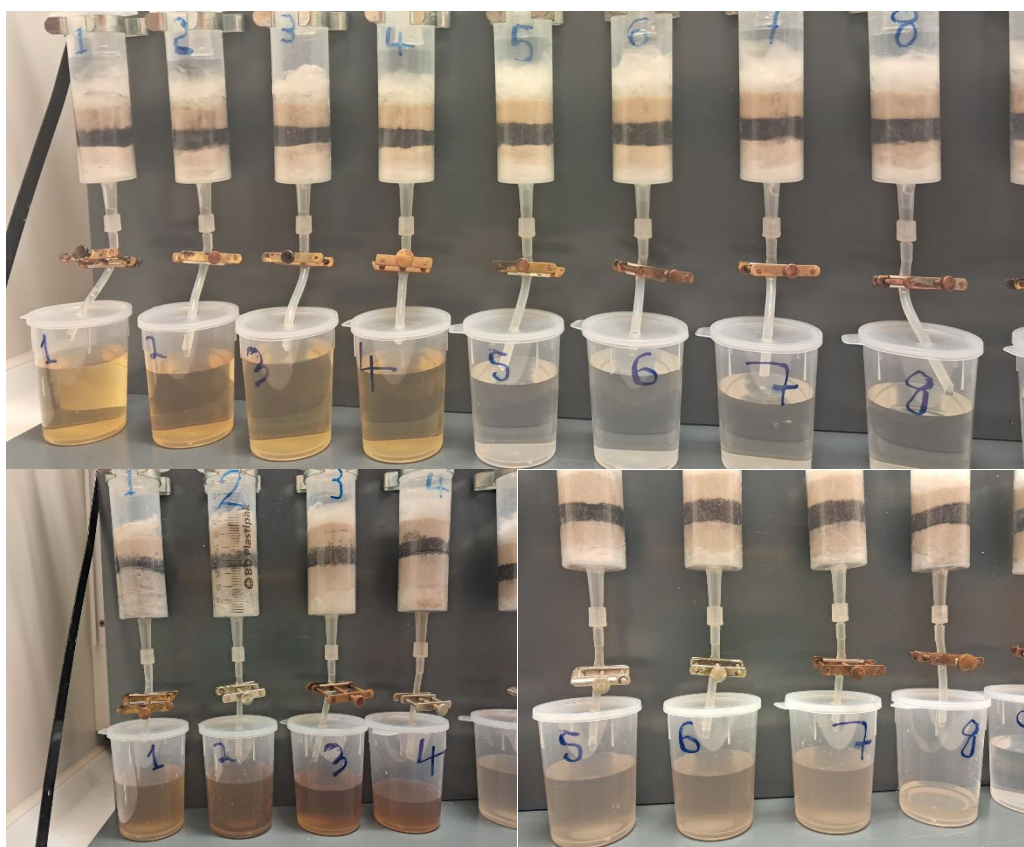


Figure 5. Yellow-amber discolouration of the column percolate observed during NaOAc saturation of CH and CS columns. Top: Experiment 1 (pH 4.8), beakers 1–4 = CH, beakers 5–8 = CS. Bottom left: Experiment 2 (pH 7), beakers 1–4 = CH. Bottom right: Experiment 2 (pH 7), beakers 5–8 = CS. No discolouration was observed in the WC, ME or SW columns at either pH.

3.2 Biochar physicochemical properties

The physicochemical property data of the five biochars used in this study are presented in Table 2. The ash content varied across the biochars, with CH and SW at 27.4% and 18.4%, ME at 7.2%, and CS and WC at similar values of 2.8% and 2.2% respectively. The total carbon content followed the opposite trend, with WC and ME at 91.2% and 84.6%, CS at 63.1%, and SW and CH at 52.7% and 46.9%. Nitrogen content was similar in CH and SW at 2.97% and 2.32%, whereas ME, WC and CS were all below 1%. The pH (CaCl₂) values were determined only for WC and SW, at 8.83 and 9.57 respectively.

Regarding element concentrations, CH and SW had similar Si content at 38.05 and 38.70 g kg⁻¹ and similar K content at 32.54 and 30.85 g kg⁻¹, while CH additionally had higher Al and Fe contents of 39.32 and 20.70 g kg⁻¹. ME had a higher Ca content of 25.00 g kg⁻¹, while CH and SW were similar at approximately 11 g kg⁻¹. Magnesium content was higher in SW at 5.66 g kg⁻¹, with ME and CH at 3.20 and 2.73 g kg⁻¹ and lower values in WC and CS. Sodium content was similar in CH and SW at 1.36 and 1.19 g kg⁻¹, while the other biochars had values below 0.5 g kg⁻¹. SW had a higher P content of 13.49 g kg⁻¹, whereas the other biochars had values below 2 g kg⁻¹. CS and WC generally had lower concentrations across all measured elements.

Table 2. Physicochemical properties of the five biochars used in this study. CH = coffee husk; CS = coconut shell; WC = wood chips; ME = Meva Energy; SW = seed waste. n.d. = not determined. Element concentrations data on a dry mass basis. Total solids and ash content expressed in percentages.

Parameter	CH	CS	WC	ME	SW
<i>General properties</i>					
Ash content (%)	27.4	2.8	2.2	7.2	18.4
Carbon, C (%)	46.9	63.1	91.2	84.6	52.7
Nitrogen, N (%)	2.97	0.18	0.47	0.59	2.32
pH (CaCl ₂)	n.d.	n.d.	8.83	n.d.	9.57
<i>Element concentration (g kg⁻¹ dry mass)</i>					
Si	38.05	7.81	0.40	2.30	38.70
Al	39.32	1.05	n.d.	0.48	n.d.
Ca	11.29	1.04	4.87	25.00	11.18
Fe	20.70	1.50	0.45	0.90	1.93
K	32.54	2.29	2.79	9.90	30.85
Mg	2.73	0.25	0.66	3.20	5.66
Na	1.36	0.47	0.09	0.25	1.19
P	1.95	0.12	0.18	1.30	13.49

3.3 Removal of ash fraction

The volume of HCl required to bring each biochar suspension to pH 5.5 ± 0.3 was largest for CH at 57 mL, followed by SW at 38 mL and ME at 20 mL (Figure 6). WC and CS required relatively small volumes of 14.5 and 1 mL, although CS had a slightly higher ash content than WC (2.8% vs 2.2%). The HCl volume correlated linearly with the ash content of the biochars ($R^2 = 0.937$).

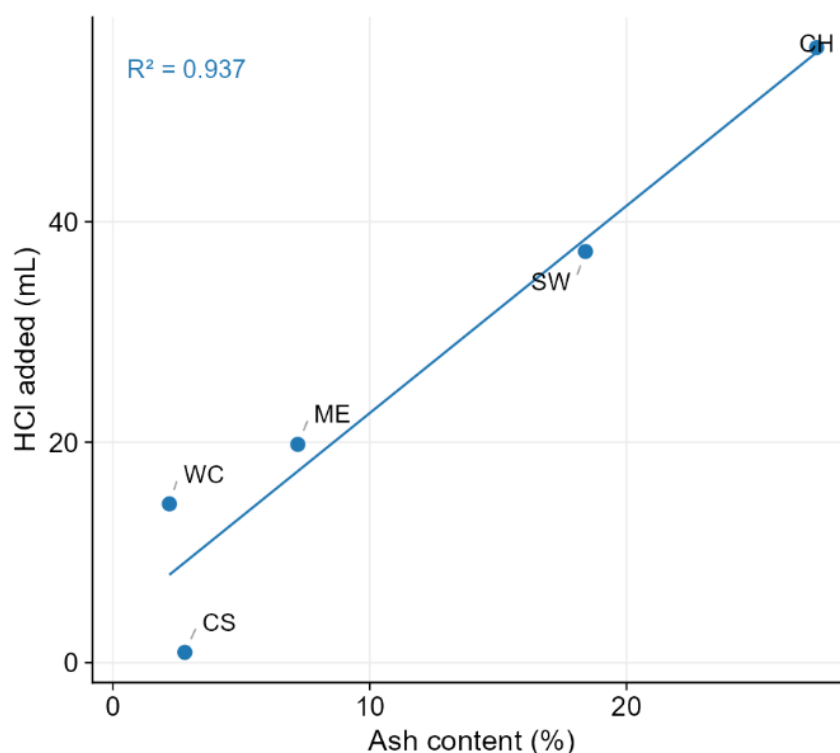


Figure 6. Volume of 0.1 M HCl required to bring each biochar suspension to pH 5.5 ± 0.3 plotted against the ash content of the biochar. Each point represents one biochar (CH = coffee husk; SW = seed waste; ME = Meva Energy; WC = wood chip; CS = coconut shell). The line shows the linear regression fit ($R^2 = 0.937$).

3.4 Effect of acid washing on CEC_{sum}

3.4.1 Experiment 1 (pH 4.8)

The CEC_{sum} at pH 4.8 of the NAW biochars correlated linearly with the ash content of the biochars ($R^2 = 0.995$), ranging from $12.2 \text{ cmol}_c \text{ kg}^{-1}$ in CS to $120.1 \text{ cmol}_c \text{ kg}^{-1}$ in CH (figure 7). After acid washing, the CEC_{sum} was reduced in all biochars, although the relationship with ash content remained linear with a slightly lower R^2 of 0.853. The largest reductions were observed in SW, from 81.8 to $20.3 \text{ cmol}_c \text{ kg}^{-1}$, and in CH, from 120.1 to $63.6 \text{ cmol}_c \text{ kg}^{-1}$. ME and WC showed reductions from 29.4 to 7.1 and from 16.6 to $2.5 \text{ cmol}_c \text{ kg}^{-1}$ respectively, while CS showed a small reduction from 12.2 to $8.4 \text{ cmol}_c \text{ kg}^{-1}$. A paired t-test confirmed that the reduction in CEC_{sum} at pH 4.8 was statistically significant ($t = 4.01$, $df = 9$, $p = 0.002$).

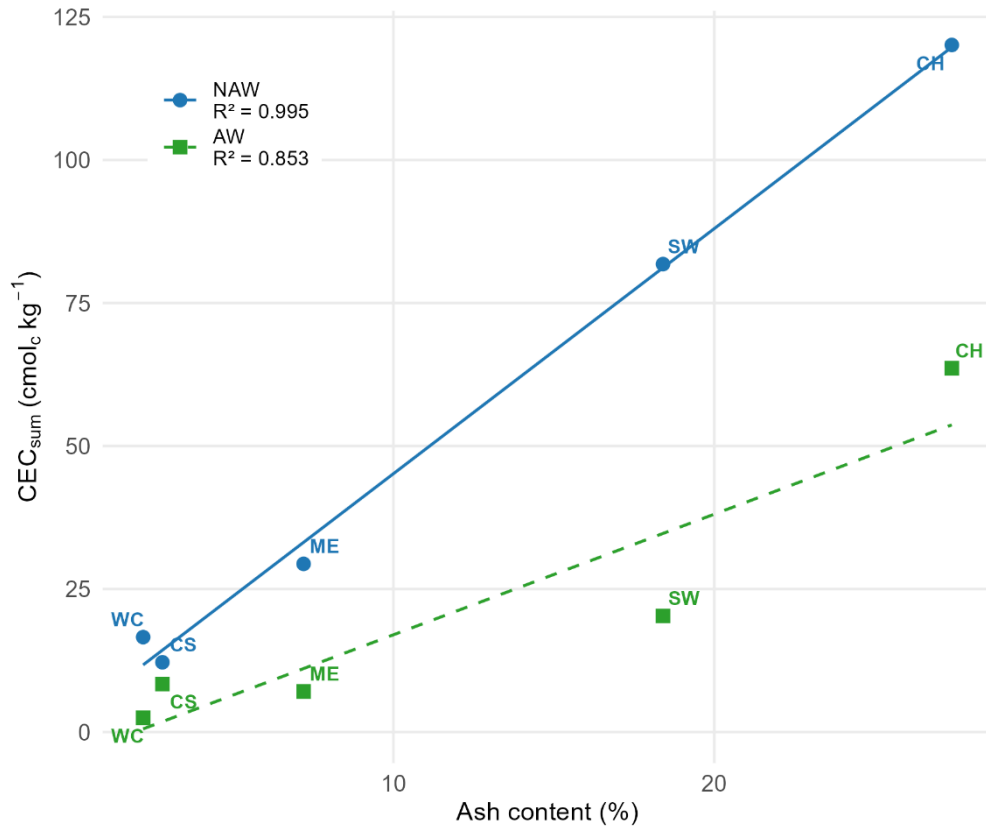


Figure 7. CEC_{sum} ($Na^+ + Mg^{2+} + Mn^{2+} + Ca^{2+} + K^+$) at pH 4.8 plotted against the ash content of the biochars, for NAW (blue circles) and AW (green squares) samples. Each point represents the mean of two replicates. CH = coffee husk; SW = seed waste; ME = Meva Energy; WC = wood chip; CS = coconut shell. The solid and dashed lines show the linear regression fits for NAW ($R^2 = 0.995$) and AW ($R^2 = 0.853$) respectively.

3.4.2 Experiment 2 (pH 7)

The results of the CEC_{sum} at pH 7 of the NAW biochars presented in figure 8 also correlated linearly with the ash content of the biochars ($R^2 = 0.996$), ranging from 14.2 $cmol_c kg^{-1}$ in CS to 106.7 $cmol_c kg^{-1}$ in CH. After acid washing, the CEC_{sum} was reduced in all biochars, with the relationship between CEC_{sum} and ash content showing a lower R^2 of 0.799. Similarly with experiment 1 (pH 4.8), the largest reductions were also observed in SW, from 71.5 to 17.0 $cmol_c kg^{-1}$, and in CH, from 106.7 to 62.0 $cmol_c kg^{-1}$. ME and WC showed reductions from 29.3 to 6.7 and from 17.5 to 3.7 $cmol_c kg^{-1}$ respectively, while CS showed a small reduction from 14.2 to 9.9 $cmol_c kg^{-1}$. A paired t-test confirmed that the reduction in CEC_{sum} at pH 7 was statistically significant ($t = 4.46$, $df = 9$, $p < 0.001$).

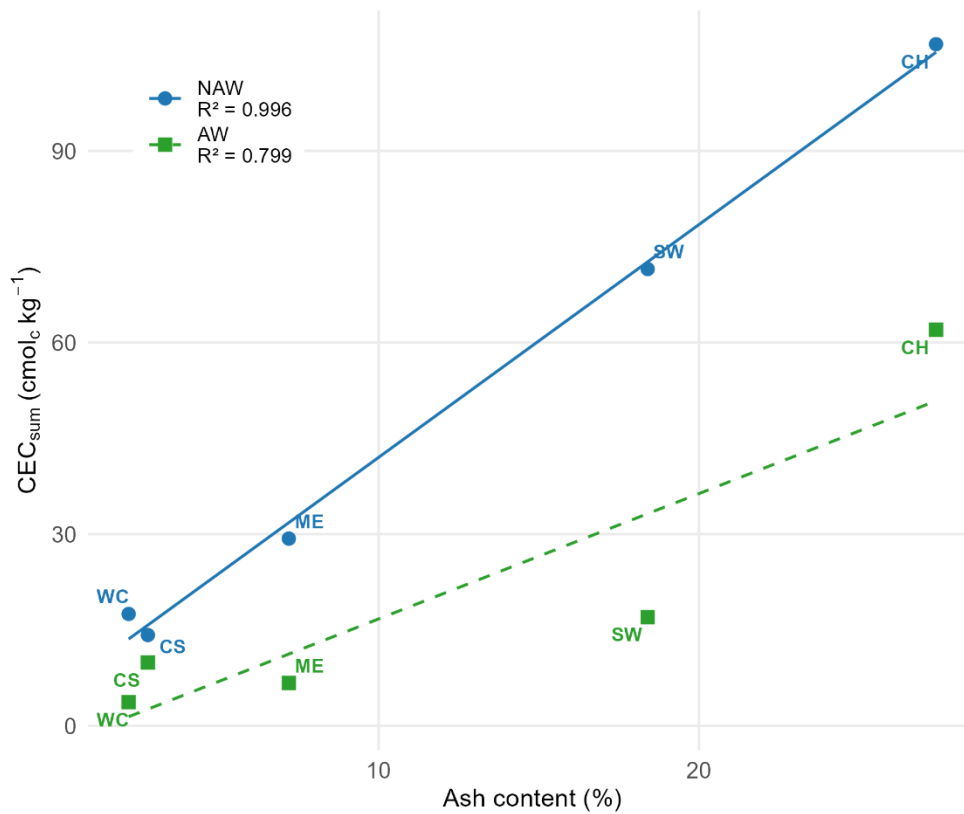


Figure 8. $CEC_{sum}(Na^+ + Mg^{2+} + Mn^{2+} + Ca^{2+} + K^+)$ at pH 7 against the ash content of the biochars, for NAW (blue circles) and AW (green squares) samples. Each point represents the mean of two replicates. CH = coffee husk; SW = seed waste; ME = Meva Energy; WC = wood chip; CS = coconut shell. The solid and dashed lines show the linear regression fits for NAW ($R^2 = 0.996$) and AW ($R^2 = 0.799$) respectively.

3.5 Combined effects of pH and acid washing on CEC_{sum}

The reduction in CEC_{sum} caused by acid washing correlated linearly with the ANC of the biochars at both extraction pH levels, with a higher R^2 at pH 4.8 (0.853) than at pH 7 (0.784) (figure 9). The results show that biochars with higher ANC, which also contained more ash, lost more of their CEC_{sum} during AW. In addition, the reductions in CEC_{sum} were generally larger at pH 4.8 than at pH 7, with the largest difference between the two pH values observed in CH (56.5 at pH 4.8 vs 44.7 $cmol_c kg^{-1}$ at pH 7) and in SW (61.5 vs 54.5 $cmol_c kg^{-1}$). For ME, WC and CS, the reductions at the two pH values were within 2 $cmol_c kg^{-1}$ of each other, indicating that for these biochars the AW effect was largely independent of the extraction pH.

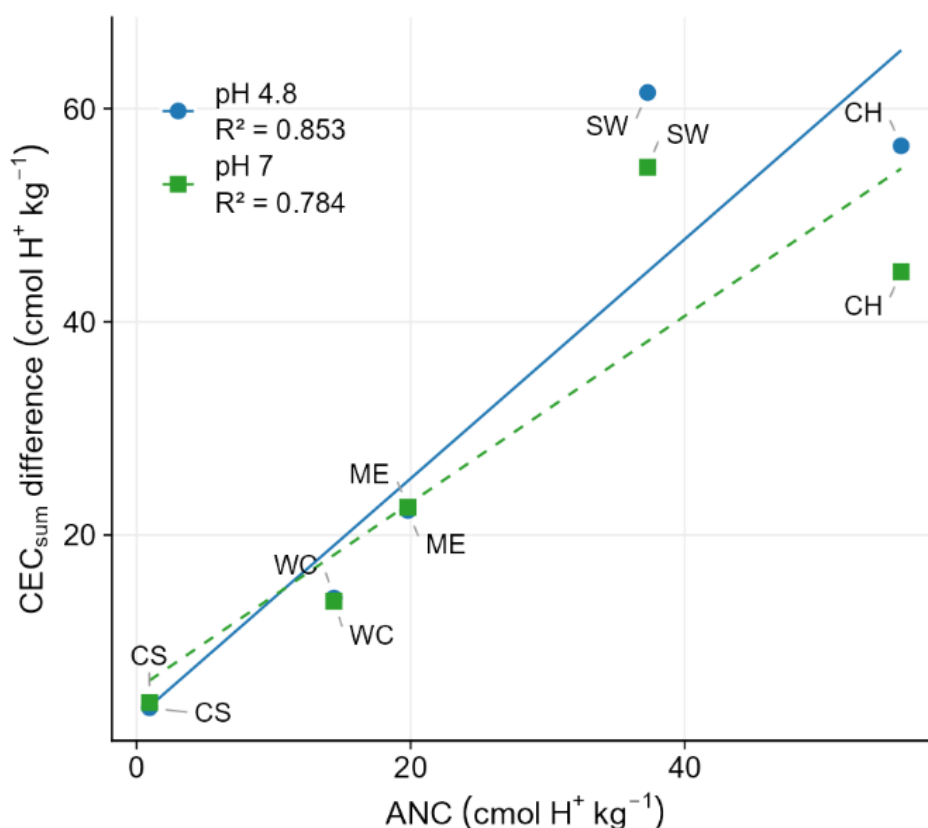


Figure 9. Reduction in CEC_{sum} caused by acid washing ($CEC_{sum} NAW - CEC_{sum} AW$) plotted against the ANC of the biochars, at extraction pH 4.8 (blue circles) and pH 7 (green squares). Each point represents the mean of two replicates. CH = coffee husk; SW = seed waste; ME = Meva Energy; WC = wood chip; CS = coconut shell. The solid and dashed lines show the linear regression fits at pH 4.8 ($R^2 = 0.853$) and pH 7 ($R^2 = 0.784$) respectively.

3.6 Individual cation contribution to CEC_{sum}

3.6.1 Experiment 1 (pH 4.8)

The cation contributions to CEC_{sum} at pH 4.8 are presented in figure 10a. K^+ was the dominant cation in CH-NAW, CS-NAW and SW-NAW, contributing 47.2%, 58.6% and 58.2% respectively, while Ca^{2+} was dominant in WC-NAW and ME-NAW at 58.6% and 66.0%. After acid washing, the contribution of K^+ dropped to 5.5% in CH-AW and to 26.9% in SW-AW, while Ca^{2+} rose to 70.7% and 52.2% respectively. In CS, WC and ME the shifts were smaller, with K^+ remaining dominant in CS-AW at 52.1% and Ca^{2+} remaining dominant in WC-AW and ME-AW at 49.9% and 58.1%. Mg^{2+} contributions ranged from 7.7% to 20.9% across all biochars, and Na^+ contributions were highest in CS-NAW and CS-AW at 14.3% and 12.4% respectively, while Mn^{2+} remained a minor contributor in all biochars.

3.6.2 Experiment 2 (pH 7)

The cation contributions to CEC_{sum} at pH 7 are presented in Figure 10b and showed similar patterns to those observed at pH 4.8. K^+ was the dominant cation in CH-NAW, CS-NAW and SW-NAW, contributing 49.2%, 59.5% and 69.0% respectively, while Ca^{2+} was dominant in WC-NAW and ME-NAW at 58.7% and 60.7%. Acid washing reduced K^+ in CH-AW and SW-AW to 5.5% and 43.2%, while Ca^{2+} rose to 68.9% and 38.2%. K^+ remained dominant in CS-AW at 52.9%, and Ca^{2+} remained dominant in WC-AW and ME-AW at 52.6% and 56.5%. Mg^{2+} contributions ranged from 4.7% to 21.0%, and Na^+ contributions were again highest in CS at 14.9% (NAW) and 13.4% (AW).

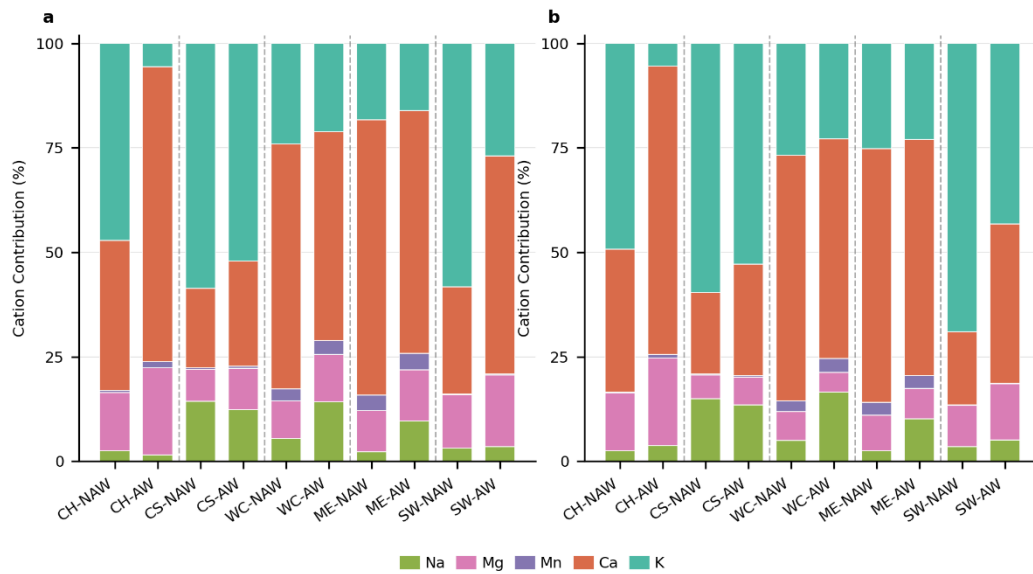


Figure 10. Cation contributions (%) to CEC_{sum} in NAW and AW biochars at (a) pH 4.8 and (b) pH 7. Each bar represents the mean of two replicates. CH = coffee husk; CS = coconut shell; WC = wood chip; ME = Meva Energy; SW = seed waste.

3.7 Comparison between CEC_{sum} and CEC_{Na}

The CEC_{Na} values for all biochars at pH 4.8 and pH 7 are presented in Figure 11. At pH 4.8, CEC_{Na} was 0 $cmolc\ kg^{-1}$ for WC, ME and SW in both AW and NAW treatments. CH-AW and CH-NAW recorded values of 10.7 and 11.3 $cmolc\ kg^{-1}$ respectively, and CS-AW and CS-NAW recorded 1.6 and 1.2 $cmolc\ kg^{-1}$. At pH 7, CEC_{Na} for WC, ME and SW remained 0 $cmolc\ kg^{-1}$, while the values for CH-AW and CH-NAW increased to 71.0 and 78.8 $cmolc\ kg^{-1}$, and CS-AW and CS-NAW to 36.2 and 35.3 $cmolc\ kg^{-1}$. The IE reference returned 340.5 $cmolc\ kg^{-1}$ at pH 4.8 and 259.6 $cmolc\ kg^{-1}$ at pH 7.

Compared with the corresponding CEC_{sum} values, CEC_{Na} at pH 4.8 was lower across all biochars, with CH-NAW returning 11.3 vs a CEC_{sum} of 120.1 $cmolc\ kg^{-1}$ and SW-NAW 0 vs a CEC_{sum} of 81.8 $cmolc\ kg^{-1}$. At pH 7, CEC_{Na} for CH

and CS approached or exceeded their corresponding CEC_{sum} values: CH-AW returned 71.0 vs a CEC_{sum} of 62.0, CS-AW 36.2 vs 9.9, and CS-NAW 35.3 vs 14.2 $cmol_c\ kg^{-1}$, while WC, ME and SW continued to show CEC_{Na} of 0 $cmol_c\ kg^{-1}$ against CEC_{sum} values of 3.7 to 71.5 $cmol_c\ kg^{-1}$.

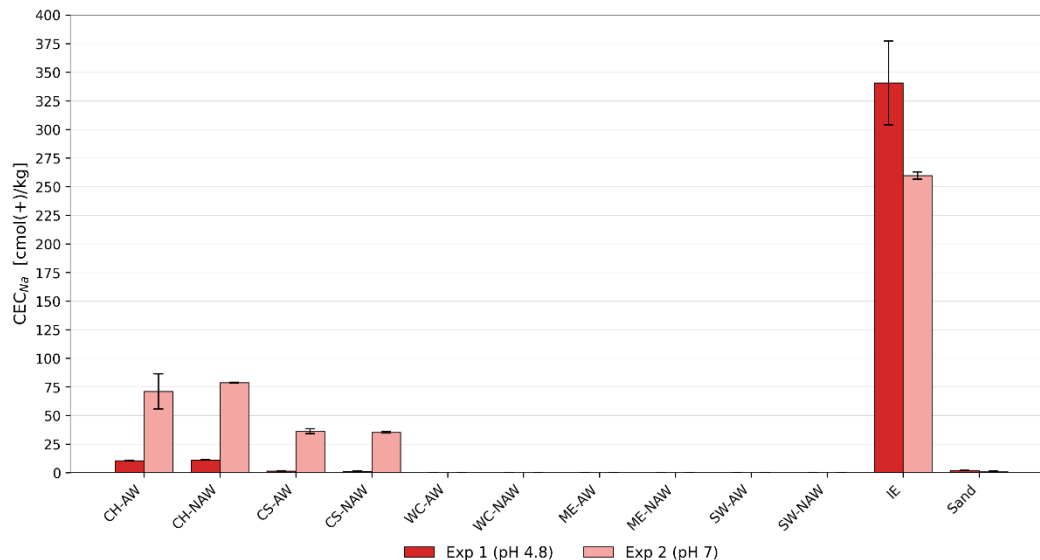


Figure 11. CEC_{Na} ($cmol(+)/kg$) determined by Na^+ index cation displacement for all samples across experiment 1 (pH 4.8, dark red) and experiment 2 (pH 7, light red). Error bars denote ± 1 SD ($n = 2$ replicates). Note the marked increase in CEC_{Na} between pH 4.8 and pH 7 for CH and CS, the persistent near-zero values for WC, ME, and SW at both pH values, and the high IE values confirming method validity at both pH values.

3.8 Verification of low CEC_{Na} values

To verify that the near-zero CEC_{Na} values obtained for WC-AW, ME-AW and SW-AW in experiment 2 were not the result of Na^+ remaining within the biochar pore network after the NH_4OAc percolation, a second extraction was carried out on the same biochars using 0.01 M $CaCl_2$. The biochars were saturated with $CaCl_2$ overnight on an orbital shaker.

The Na^+ recovered by the $CaCl_2$ extraction ranged from $0.079 \pm 0.013\ cmol_c\ kg^{-1}$ in WC-AW to $0.228 \pm 0.023\ cmol_c\ kg^{-1}$ in SW-AW, with ME-AW at $0.105\ cmol_c\ kg^{-1}$. All values remained below $0.25\ cmol_c\ kg^{-1}$, indicating that only trace amounts of Na^+ remained on the biochars after the NH_4OAc step. This supports the conclusion that the near-zero CEC_{Na} values reported in Section 3.7 reflect a genuine absence of accessible Na^+ -exchange capacity in these biochars rather than incomplete displacement of Na^+ during the standard percolation procedure.

4. Discussion

4.1 Effect of acid washing to CEC_{sum}

The five biochars used in this study differed substantially in their ash content and in their base cation profiles. CH and SW, both crop residues, were the high-ash biochars and were also enriched in K and Ca. ME, produced above 1000°C, was the principal exception among the lower-ash biochars, with a high Ca concentration. WC and CS, both with low ash contents, contained limited concentrations of base cations across all measured elements. These compositional differences predicted that acid washing should have differential effects on apparent CEC, with the largest reductions expected in biochars containing the most carbonate and soluble salt phases.

The ANC of the biochars followed the same ranking as their ash content, and the HCl volume required to bring each biochar suspension to pH 5.5 correlated linearly with ash content. This pattern was consistent with the natural pH values measured for each biochar prior to acid washing, which ranged from 6.2 for CS to 10.22 for SW, with CH (9.3), WC (9.7), and ME (8.7) falling between these extremes. These observations confirm that the ANC measured here reflects the carbonate and soluble mineral salt fraction of the biochar ash rather than the density of surface functional groups. Fidel et al. (2017) reported that inorganic alkalis, principally carbonates, sulphates, phosphates and Fe/Al hydroxides, constitute 55 to 95% of total alkalinity in lignocellulosic biochars and are effectively removed by mild HCl washing. Yuan et al. (2011) further demonstrated that in crop residue biochars, alkalinity transitions from organic functional groups at 300°C to carbonates at 500 to 700°C, helping to explain why CH and SW showed the largest ANC values. The ANC therefore served as a pre-screening indicator of the magnitude of soluble salt and base cation contribution from the ash fraction to apparent CEC measurements before acid washing.

Acid washing reduced CEC_{sum} across all five biochars at both pH values, and the reduction was statistically significant in both experiments. The magnitude of the reduction was associated with the ANC of each biochar, scaling with the ash content of the feedstock as anticipated from the compositional data. NAW biochars therefore showed substantially higher apparent CEC_{sum} values than AW biochars, with the magnitude of the difference reflecting the size of the soluble salt and carbonate pool in each feedstock. Munera-Echeverri et al. (2018) identified soluble K and Ca salts as the primary source of apparent CEC inflation in non-acid-washed high-ash biochars, and Wei et al. (2022) quantified this effect in a high-ash biomass biochar, reporting that mild HCl washing removed close to 95% of K, 88% of Ca and 85% of Mg. Ghorbani et al. (2024), in a meta-analysis of 83 biochar studies, identified feedstock composition and ash content as

important determinants of biochar CEC and showed that crop- and straw-derived biochars generally exhibit larger increases in CEC than woody feedstocks following modification.

The dominant soluble salt fraction differed between feedstocks. In CH and SW, K^+ accounted for nearly the entire removed cation pool, indicating that most of the K^+ in these biochars was held in soluble phases such as K_2CO_3 or KCl rather than on exchange sites. This is consistent with the high K concentrations measured in the parent feedstocks and with the higher mineral and ash contents commonly observed in crop-derived biochars, which contribute to soluble salt pools and can inflate apparent CEC measurements prior to acid washing (Ghorbani et al. 2024). In WC and ME, by contrast, the cation pool removed by acid washing was dominated by Ca^{2+} and Mg^{2+} . The substantial reductions in these cations suggest that a major proportion of the Ca^{2+} and Mg^{2+} in WC and ME was associated with acid-soluble mineral phases, including carbonates, rather than solely occupying exchange sites. This interpretation is consistent with Yuan et al. (2011), who identified carbonates as major alkaline constituents of crop-residue biochars, particularly at higher pyrolysis temperatures.

The behaviour of Ca^{2+} in CH was distinctive in this dataset. Unlike all other biochars and cations, CH showed higher Ca^{2+} extraction in AW than in NAW samples at both extraction pH values. The most likely explanation is the migration of fine colloidal biochar particles through the column during the NH_4OAc displacement step. Any colloidal particles entrained in the percolate would be measured even if the Ca^{2+} was still sitting on the particles. Acid washing may have predisposed CH to greater particle dispersion by dissolving the mineral phases that previously held the carbon matrix together, releasing fine particles into the percolate during NH_4OAc displacement and inflating the apparent CEC_{Ca} of AW relative to NAW. The elevated Ca^{2+} extraction in CH-AW is therefore best interpreted as an experimental artefact of particle carry-over rather than as evidence of additional exchange capacity exposed by acid washing.

4.2 Comparison of CEC_{sum} and CEC_{Na} and the pH effect

A visible yellow-amber discolouration of the percolate was observed during $NaOAc$ saturation of CH and CS columns at both pH values, and was most pronounced in the CH columns and in experiment 2 (pH 7). No discolouration was observed in WC, ME or SW columns. The discolouration most likely reflects the mobilisation of fine biochar-derived colloidal particles during $NaOAc$ saturation. If the elevated CEC_{Na} values measured for CH and CS at pH 7 had reflected residual Na^+ remaining in the columns, the additional rinsing applied in experiment 2 would have suppressed them. The contrary pattern observed instead indicates greater colloidal mobility of these biochars at higher pH, where the

increased negative surface charge of their particle surfaces would render them more hydrophilic and therefore more readily dispersed and transported through the column. Any colloidal particles carried into the Stage 5 percolate would be measured even if the Na^+ was still sitting on the particles. The pH 7 CEC_{Na} values for CH and CS must therefore be treated as experimental artefacts arising from particle carry-over rather than as measurements of true Na^+ -accessible exchange capacity. A similar concern applies to the IER CEC_{Na} value at pH 4.8 ($340.5 \text{ cmol}_c \text{ kg}^{-1}$), which substantially exceeds the calculated reference CEC of $220 \text{ cmol}_c \text{ kg}^{-1}$ for the resin and is most likely inflated by incomplete rinsing of free Na^+ from the IER column during stage 4. Experiment 1 used four water washes at this step compared to eleven washes in experiment 2. The pH 7 IER CEC_{Na} value of $259.6 \text{ cmol}_c \text{ kg}^{-1}$ is closer to the reference but remains approximately 18% above it, suggesting that even the additional washes in experiment 2 did not fully remove residual free Na^+ from the column. The IER CEC_{sum} at pH 7 ($215 \text{ cmol}_c \text{ kg}^{-1}$) was within 3% of the reference value, confirming that the underlying NH_4OAc displacement step functioned as expected in experiment 2 and supporting the interpretation that the inflated CEC_{Na} values for IER arise from carry-over rather than from a failure of the displacement procedure itself.

For WC, ME and SW, CEC_{Na} was $0 \text{ cmol}_c \text{ kg}^{-1}$ in both NAW and AW samples at both pH values. The supplementary CaCl_2 extraction recovered less than $0.25 \text{ cmol}_c \text{ kg}^{-1}$ of Na^+ from these biochars, ruling out incomplete Na^+ displacement during the NH_4OAc step as the cause of the near-zero readings. An alternative explanation for the near-zero CEC_{Na} values is that exchange sites may have been partially occupied by NH_4^+ from Stage 1; however, the CaCl_2 extraction recovered negligible Na^+ from these biochars, suggesting that Na^+ was not retained on exchange sites in measurable quantities. This indicates that the near-zero CEC_{Na} values more plausibly reflect a genuine absence of Na^+ -accessible exchange sites. This interpretation is consistent with the high pyrolysis temperatures of these feedstocks (above 500°C for SW, above 700°C for WC, and above 1000°C for ME). Mukherjee et al. (2011) reported a strong decline in CEC with increasing pyrolysis temperature due to loss of oxygen-containing functional groups, while Budai et al. (2014) observed that CEC peaks at intermediate temperatures (350 to 475°C) and decreases sharply above 500°C . This trend is further supported by Ghorbani et al. (2024), who confirmed a general inverse relationship between pyrolysis temperature and biochar CEC across a large number of studies.

The divergence between CEC_{sum} and CEC_{Na} for WC, ME, and SW is the most informative observation of this part of the study. After acid washing, CEC_{sum} for WC, ME and SW remained between 2.5 and $20.3 \text{ cmol}_c \text{ kg}^{-1}$ at pH 4.8 and between 3.7 and $17.0 \text{ cmol}_c \text{ kg}^{-1}$ at pH 7, while CEC_{Na} was $0 \text{ cmol}_c \text{ kg}^{-1}$ for all three. This divergence implies that the CEC_{sum} method, even when applied to acid-washed samples, captures cation contributions beyond what genuine surface

exchange sites can hold. A likely source is residual mineral phases that the mild HCl wash at pH 5.5 did not fully remove but that the NH_4OAc extractant could dissolve, particularly at pH 4.8 where the buffered acetate is acidic enough to attack acid-soluble phases such as carbonate and phosphate residues. Yuan et al. (2011) demonstrated that carbonates are the dominant alkaline phase in biochars produced above 500°C , and Wei et al. (2022) showed that even 0.1 M acid washing leaves residual inorganics in biochar matrices. The Na^+ index cation method, by contrast, measures only the cations bound to exchange sites at the saturation pH and is therefore the more conservative estimate of true exchange capacity for these biochars. The choice of method therefore matters considerably for high-temperature, low-ash biochars, with CEC_{sum} approximately one order of magnitude above CEC_{Na} for ME and WC.

The dissociation of carboxyl and phenolic surface functional groups above their pK_a values would be expected to produce higher CEC at pH 7 than at pH 4.8 in AW biochars, where soluble salt and carbonate contributions have been removed. The CEC_{sum} AW data did not show this pattern: values at the two pH levels were within $4 \text{ cmol}_c \text{ kg}^{-1}$ of each other across all five biochars, with SW and ME returning slightly lower values at pH 7 than at pH 4.8. From the CEC_{Na} measurements the same prediction can be tested directly only for the three biochars not affected by colloidal leaching (WC, ME and SW); for these, the pH 7 values were not higher than the pH 4.8 values and both were $0 \text{ cmol}_c \text{ kg}^{-1}$. These results point to an absence of pH-active surface functional groups in the high-temperature feedstocks studied rather than a methodological failure to detect them. The same mechanistic explanation applies to the larger pH-dependent variability seen in NAW samples than in AW samples for CH and SW (Section 4.1): in these biochars, the pH-dependent change in apparent CEC is dominated by the differential dissolution of carbonate and soluble salt phases at the two extractant pH values rather than by the deprotonation of surface functional groups.

4.3 Agronomic implications

The substantial inflation of apparent CEC measured on NAW samples relative to AW samples indicates that nutrient retention estimates based on unwashed CEC values overstate the contribution of true surface exchange sites. For the high-ash biochars CH and SW, where the effect was largest, between 41% and 76% of the apparent NAW CEC disappeared after acid washing. Much of this cation pool consists of soluble K and Ca salts that would be subject to leaching from the soil profile rather than retained against displacement by competing cations. Hailegnaw et al. (2019) demonstrated that the effect of biochar on soil CEC depends on the interaction between biochar CEC and the existing exchangeable cation pool of the soil, with the same biochar increasing CEC in soils of lower exchangeable Ca^{2+}

but decreasing CEC in soils of higher exchangeable Ca^{2+} . Agronomic decisions based on unwashed CEC values therefore risk overestimating the nutrient retention potential of high-ash biochars and misjudging their compatibility with specific soil chemistries.

The biochars used in this study were freshly produced. Oxidative ageing in soil progressively develops carboxyl and phenolic functional groups on biochar surfaces (Yang et al. 2016; Munera-Echeverri et al. 2018), and the near-zero CEC_{Na} values reported here for WC, ME and SW therefore likely underestimate the long-term exchange capacity these biochars would develop following extended field exposure. Ghorbani et al. (2024) reported that high-pyrolysis-temperature biochars show the largest CEC gains following modification or ageing, suggesting that the agronomic value of high-temperature biochars may lie more in their potential for ageing-induced CEC development than in their immediate freshly produced exchange capacity.

4.4 Limitations and future directions

Several limitations of this study should be acknowledged. Each treatment was replicated only twice ($n = 2$), which limits the statistical power of within-biochar comparisons and the reliability of standard deviation estimates. Future studies should include a minimum of three replicates per treatment to allow more robust statistical testing of differences between biochar types and between methods.

The colloidal particle leaching observed in CH and CS columns during NaOAc saturation was not quantified. Fine biochar-derived colloidal particles mobilised during stage 3 may have been carried into the Stage 5 displacement percolate, contributing surface-bound Na^+ to the measured concentration and inflating apparent CEC_{Na} for these two biochars. Quantification of colloidal losses, for example through turbidity measurement of the percolate or filtration through a sub-micron membrane prior to ICP-OES analysis, is therefore recommended as a standard quality control step in future biochar CEC determinations, to allow the colloidal contribution to be separated from genuine Na^+ displacement. Lago et al. (2021) noted that comparisons of CEC values across studies are complicated by differences in pre-washing, index cation, displacement cation, and solution pH, reinforcing the need for standardised protocols in which potential artefacts such as colloidal particle leaching are systematically controlled and reported.

The mild acid washing procedure used in this study where the pH was not allowed to get substantially lower than pH 5.5 may not have removed all acid-soluble mineral phases from high-ash biochars, particularly those occluded within the carbon matrix. Wei et al. (2022) showed that even a more concentrated acid wash left residual mineral phases in high-ash biochar, and that water washing alone was insufficient to address Ca and Mg phases, suggesting that the HCl

procedure used here may have left a fraction of the mineral salt artefact intact in CH and SW.

The different number of deionised water washing steps applied at Stage 4: four in experiment 1 and eleven in experiment 2 may have contributed to differences in CEC_{Na} between the two experiments, as residual free Na^+ remaining after fewer washes would be collected in the stage 5 percolate and inflate the apparent index cation CEC. A standardised washing protocol, verified by electrical conductivity monitoring to a consistent threshold value, is required to ensure comparable results across future experiments.

5. Conclusion

Five biochars coffee husk (CH), coconut shell (CS), wood chips (WC), Meva Energy (ME), and seed waste (SW) were analysed for their true cation exchange capacity using the base cation summation method (CEC_{sum}) and the Na^+ index cation displacement method (CEC_{Na}) at pH 4.8 and pH 7 on both acid-washed (AW) and non-acid-washed (NAW) variants, with the aim of separating true surface exchange capacity from methodological artefacts.

Hypothesis 1, which predicted that non-acid-washed biochars would show significantly higher apparent CEC values than acid-washed biochars and that the difference would scale proportionally with ash content, cannot be rejected. Acid washing significantly reduced CEC_{sum} across all five biochars at both pH 4.8 and pH 7, and the magnitude of the reduction scaled with the acid neutralising capacity of each biochar. The dominant soluble salt fraction differed between feedstocks: K^+ was the principal artefact in CH and SW, while Ca^{2+} and Mg^{2+} dominated in WC and ME. NAW CEC values overestimate true surface exchange capacity in high-ash biochars and should not be used as indicators of nutrient retention potential.

Hypothesis 2, which predicted that the pH-dependent difference in CEC between pH 4.8 and pH 7 would be smaller in non-acid-washed biochars than in acid-washed biochars, is rejected. The opposite pattern was observed for CH and SW: the pH-dependent difference in CEC_{sum} was larger in NAW than in AW samples. This reflects the pH-dependent dissolution of carbonate and soluble salt phases at the two extractant pH values, which contributes a substantial pH-sensitive component to NAW CEC_{sum} independent of any deprotonation of surface functional groups.

Hypothesis 3, which predicted that in acid-washed biochars CEC at pH 7 would be significantly higher than at pH 4.8 due to a substantial contribution of pH-dependent charge, is rejected. AW CEC_{sum} was not significantly higher at pH 7 than at pH 4.8 for any of the five biochars, and AW CEC_{Na} for WC, ME and SW remained at zero at both pH values, confirmed by a supplementary CaCl_2 extraction. These results indicate a genuine absence of pH-active surface functional groups in the high-temperature feedstocks studied. For CH and CS, the elevated pH 7 CEC_{Na} values are experimental artefacts arising from colloidal particle migration during NaOAc saturation and cannot be interpreted as a substantial pH-dependent contribution to CEC, although the greater colloidal mobility of CH and CS particles at pH 7 (Section 4.2) suggests that these biochars retain some pH-sensitive surface chemistry that is not visible in the CEC_{sum} or CEC_{Na} measurements.

CEC_{Na} gave consistently lower and more conservative estimates than CEC_{sum} , particularly for WC, ME, and SW where CEC_{sum} remained between 2.5 and 20.3

cmolc kg⁻¹ after acid washing while CEC_{Na} was effectively zero, showing that even acid-washed CEC_{sum} captures residual mineral dissolution rather than true exchange sites. Acid washing combined with index cation measurement at pH 7 is therefore recommended for reliable biochar CEC determination. The near-zero CEC_{Na} values for WC, ME, and SW reflect freshly produced materials, and their exchange capacity is expected to increase with oxidative ageing in soil.

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