

Effects of oil palm bunches and coal fly ash on the cation exchange capacity of reclaimed mining soil

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ABSTRACT

Cation exchangeable capacity (CEC) is a significant soil chemical property influencing the availability and exchange of cation nutrients in soils. This study aims to quantify the alterations in CEC of reclaimed mining soil (RMS) treated with oil palm bunches (OPB) and coal fly ash (CFA). The experiment was carried out by adding 3 levels of OPB (0, 20, and 40 Mg ha⁻¹) and CFA (0, 50, and 100 Mg ha⁻¹) were counted to RMS. After 15 days of incubation, CEC with other soil chemical characteristics were measured. The results indicated that the application of 40 Mg ha⁻¹ of OPB increased soil CEC from 20.4 cmol kg⁻¹ to 35.6 cmol kg⁻¹, and 100 Mg ha⁻¹ of CFA caused a 25% decrease. These changes in CEC were associated to the changes in number of functional groups due to the addition of OPB and CFA. The results suggested that adding organic matter may offset the decrease in CEC caused by the presence of multivalent cations from ash, thereby increasing net soil CEC.

Keywords: dissolution, pH-dependent charge, hydrolysis, dissociation, carboxylic groups.

INTRODUCTION

Coal production in Indonesia is experiencing a significant increase reaching 833.69 million tonnes in 2024, with 83% rise compared to 2016 (Ministry of Energy and Mineral Resources of the Republic of Indonesia, 2024). Although the increase can enhance government revenue, it poses environmental challenges regarding the expansion of RMS consisting of various materials. These include topsoil, subsoil, and overburden, which are byproducts of the open-pit mining process. Additionally, coal mining is often carried out in the country using open-pit system, which includes stripping away soil and rock layers above the mineral deposit. The objective of forming RMS is to rehabilitate the mined lands by creating soil profile capable of supporting vegetation growth (Worlanyo and Jiangfeng, 2021).

Regarding previous reports, vegetation growth on RMS often shows sub-optimal performance compared to natural soil (Vidal-Macua et al., 2020; Honscha et al., 2021).

The sub-optimal performance of RMS is due to low level of soil fertility, organic C contents, acidic pH, and CEC (Ahirwal et al., 2017; Kumar et al., 2018; Lwin et al., 2018). CEC is a significant chemical property of soil affecting the ability to retain and exchange nutrient cations. It also influences the adsorption and desorption of pollutant cations, for example heavy metals (Defo et al., 2017; Derakhshan Nejad et al., 2021). However, low level of CEC in RMS limits nutrient retention and exchange capacity which affects the ability to manage pollutant cations. This causes high environmental risks related to heavy metal contamination. CEC is the amount of negative charge present in soil, where higher negative charge

correlates with greater CEC value. This negative charge can originate from the isomorphous substitution reaction, such as the replacement of Al^{3+} in the octahedral sheet by lower valency cations like Ca^{2+} or Mg^{2+} , including iron (Fe) and aluminum (Al) oxide-hydroxides in soil (Huang et al., 2024). These oxide-hydroxides including soil organic matter also increase negative charge in soil and enhance CEC (Costa et al., 2020). Prior investigation conveyed that a rise in soil organic matter led to a higher CEC (Ramos et al., 2018). Consequently, adding soil organic substances with Al and Fe oxide-hydroxides may significantly influence CEC level, soil fertility, and the sorption-desorption processes of heavy metals.

CFA is a residue of coal processing in power plants containing high amounts of Al and Fe oxides-hydroxides (Saidy et al., 2021). Additionally, OPB can be utilized to improve soil quality (Formaglio et al., 2021; Adu et al., 2022). The incorporation of ameliorants containing Al and Fe oxides-hydroxides with organic matter into soil has proven to increase CEC (Ramos et al., 2018; Durn et al., 2019). However, previous studies only examined the effects of adding Al and Fe oxides-hydroxides with organic matter separately. This shows the need for co-applying CFA and OPB on changes in soil CEC in RMS to enhance the planning of using industrial and agricultural waste to improve soil properties. This study aimed to measure the changes in CEC in RMS given CFA and OPB.

MATERIALS AND METHODS

Study locations and sample collection

Soil samples were taken from a coal mine reclamation area in South Kalimantan Province, precisely in Mulia Village, Satui District, Tanah Bumbu Regency, Indonesia. Sampling was performed at a depth of 0–30 cm from multiple locations, homogenized into one soil sample, as well as air-dried. Some of the samples were applied to determine soil characteristics and others were kept at 4 °C until used for incubation study in the laboratory. Table 1 presents the characteristics of the utilized soil.

CFA was gathered from the waste site of Asam Asam Power Plant (PLTU) located in Tanah Laut Regency, Jorong Sub-district, Asam Asam Village, South Kalimantan, Indonesia. Subsequently, sampled CFA was air-dried, sieved via a 2 mm

filter, kept at 4 °C for further use, and partly used for CFA characterization, with its properties detailed in Table 1.

OPB were sourced from oil palm factory in Ambungan Village, Pelaihari Sub-district, Tanah Laut Regency, South Kalimantan, Indonesia. The samples underwent oven drying at 60 °C for 72 hours and finely ground to a size of 0.5 mm. Portions of these samples were stored at 4 °C for incubation studies, whereas others were analyzed using standardized laboratory procedures. The OPB characteristics utilized are presented in Table 1.

Incubation experiment

A two-factorial completely randomized design was employed in this study. The first aspect was the application of CFA at rates of 0, 100, and 200 Mg ha⁻¹. Meanwhile, the second aspect was the application of OPB at rates of 0, 20, and 40 Mg ha⁻¹. Each treatment as well as combination of treatments had three replications. According to the treatment plan, CFA and OPB were applied to 5 kg of post-mining soil in experimental pots, followed by adding distilled water to achieve 70% of the field capacity water content. Experimental pots were incubated in a greenhouse for 30 days, with soil water content maintained at 70% of field capacity throughout the incubation period. Soil samples of 200 g were collected after incubation to determine various chemical properties.

Changes in chemical properties were observed following the application of CFA and OPB including soil pH (McLean, 1982), exchangeable (K) potassium (Knudsen and Peterson, 1982), exchangeable (Ca) calcium, as well as exchangeable (Mg) magnesium (Lanyon and Heald, 1982). Based on observations, changes in CEC were quantified following the method by Rhoades (1982). The number of carboxylic groups in treated soil was quantified using exchange of carboxyl groups by barium chloride-triethanolamine method (Schafer, 1984). Meanwhile, total functional groups were assessed according to Kim and Park (2016), and organic carbon content was quantified using the Walkley-Black method (Nelson and Sommers, 1996).

Data analysis

Observation data were analyzed to analysis of variance (ANOVA) to evaluate the influence of treatments on the changes in soil CEC. Prior

to ANOVA, data showing a normal distribution and homogeneous variance were assessed using the Shapiro-Wilk and Bartlett tests, respectively. When ANOVA showed a significant treatment effect, a LSD (Least Significant Difference) test at $p < 0.05$ was used for mean comparisons. All statistical analyses were executed using GenStat 11th Edition.

RESULTS AND DISCUSSION

Soil, CFA, and OPB characteristics

In this study, soil showed a clay texture with a bulk density of 1.58 kg m^{-3} and an acidic

reaction, having a pH of 4.79 (Table 1). The organic (C) carbon and total (N) nitrogen contents were classified as low, while the cation contents of sodium (Na), K, Ca, and Mg ranged from medium to high. Soil also contained relatively high levels of Al and Fe, with significant concentrations of heavy metals like chromium (Cr), lead (Pb), cobalt (Co), and manganese (Mn). Cation exchangeable capacity (CEC) of the soil used in this research is 24 cmol kg^{-1} (Table 1). These characteristics, including clay texture, high bulk density, low organic C content, and the presence of various heavy metals, are typical of soils found in post-mining lands (Iskandar et al., 2022; Rosa et al., 2022).

Table 1. The characteristics of soil, CFA, and OPB. The numbers after \pm are the standard deviation of the mean (n=3)

Characteristics	Soil	Coal fly ash	Oil palm bunches
Soil texture ^a			
Sand (%)	26.54 \pm 4.56	-	
Silt (%)	24.87 \pm 3.89	-	
Clay (%)	48.59 \pm 5.23	-	
Bulk density (kg m^{-3}) ^b	1.58 \pm 0.09	1.93 \pm 0.12	-
Particle density (kg m^{-3}) ^c	1.45 \pm 0.08	2.45 \pm 0.15	-
Soil pH (H_2O) ^d	4.79 \pm 0.08	7.87 \pm 0.23	-
Organic C (g kg^{-1}) ^e	10.75 \pm 0.65	6.73 \pm 0.76	432.67 \pm 9.78
Total N (g kg^{-1}) ^f	0.47 \pm 0.07	0.41 \pm 0.08	20.67 \pm 1.38
P (g kg^{-1}) ^g	9.65 \pm 1.23	4.87 \pm 0.87	18.65 \pm 1.56
Na (mg kg^{-1}) ^h	1.98 \pm 0.08	165.65 \pm 9.23	-
K (mg kg^{-1}) ^h	4.34 \pm 0.76	298.67 \pm 4.89	-
Ca (mg kg^{-1}) ^h	6.78 \pm 1.12	896.45 \pm 9.45	-
Mg (mg kg^{-1}) ^h	4.78 \pm 0.78	799.34 \pm 8.56	-
Al (g kg^{-1}) ⁱ	32.65 \pm 0.34	49.32 \pm 1.87	
Fe (g kg^{-1}) ⁱ	16.24 \pm 0.87	29.36 \pm 2.45	
Cr (mg kg^{-1}) ^j	113.56 \pm 3.56	187.45 \pm 7.56	
Pb (mg kg^{-1}) ^j	13.65 \pm 0.45	98.36 \pm 4.41	
Co (mg kg^{-1}) ^j	136.76 \pm 9.67	197.78 \pm 8.45	
Mn (mg kg^{-1}) ^j	89.56 \pm 2.65	165.32 \pm 6.23	
CEC (cmol kg^{-1}) ^j	24.54 \pm 1.34	-	-
Lignin (g kg^{-1}) ^k	-	-	87.32 \pm 0.98
Carbohydrates (g kg^{-1}) ^l	-	-	32.67 \pm 0.54

Note: The methods used to determine soil characteristics, CFA, and OPB include: ^ahydrometer (Gee and Bauder, 1979); ^bsoil ring sampler (Blake and Hartge, 1986a); ^cvolumetric flask method (Blake and Hartge, 1986b); ^delectrode glass (McLean, 1982); ^eWalkley-Black (Nelson and Sommers, 1996); ^fKjeldahl (Bremer and Mulvaney, 1982); ^gdigestion of soil, CFA, and OPB using 60% HClO_4 followed by calculation at 660 nm with a spectrophotometer (Olsen and Sommers, 1982); ^hdigestion of soil and CFA with a mixture of HNO_3 and HClO_4 , and analysis of the extracted solution examined by an AAS (Knudsen and Peterson, 1982; Lanyon and Heald, 1982); ⁱwashing of soil as well as CFA, digestion of the ash with a mixture of HClO_4 and HNO_3 , and subsequent measurement of the digested solution using AAS (Baker and Amacher, 1982; Barnhisel and Bertsch, 1982; Burau, 1982; Olson and Ellis, 1982); ^jammonium acetate pH 7.0 (Rhoades, 1982); ^ksodium hydroxide (Chesson, 1981); lanthrone-sulfuric acid (Grandy et al., 2000).

Coal ash used had a high bulk density (1.93 kg m^{-3}), alkaline pH, and very low C-organic and N-total contents (Table 1). Basic cations (Ca, Na, K, and Mg) in coal ash were found in quite high amounts, varying from 166 to 897 mg kg^{-1} . Various heavy metals, such as Pb, Cr, Co, and Mn with concentrations ranging from 98–197 mg kg^{-1} were also found in coal ash used for the study.

The C/N ratio of OPB used was relatively high, namely 20.93 (Table 1). This is attributed to the high organic C content and low total N content of OPB. Additionally, OPB contained a higher proportion of C compounds resistant to microbial decomposition, such as lignin, compared to easily decomposable C compounds like carbohydrates. Table 1 provides further details on the OPB characteristics.

Changes in CEC of RMS

ANOVA showed that the application of CFA or OPB significantly affected CEC, the total of carboxylate groups, and the total functional groups ($p < 0.05$). However, the interaction between CFA and OPB applications did not significantly impact these soil properties ($p > 0.05$). Table 2 provides a detailed account of the changes in CEC, the number of carboxylate groups, and the total functional groups in soil resulting from the application of CFA or OPB.

The application of OPB significantly enhanced CEC, the number of carboxylate groups, and the total functional groups in soil. In comparison, the application of coal ash reduces these soil characteristics. Specifically, applying OPB at rates of 20–40 Mg ha^{-1} increases soil CEC by 37–76% (Table 1). This increase in soil CEC is associated with a rise in carboxylate groups as

well as total functional groups, which contribute to the enhancement of negative soil charge. The application of OPB at 20–40 Mg ha^{-1} causes an increase in carboxylate groups from 0.2 mmol g^{-1} to 1.3–2.2 mmol g^{-1} and total functional groups from 0.9 mmol g^{-1} to 4.8–8.6 mmol g^{-1} (Table 2). Both functional and carboxylate groups in soil experience decarboxylation and dissociation, thereby increasing the negative charge (Strawn et al., 2015). This analysis suggested a highly significant correlation between soil CEC and carboxylic groups ($r = 0.95$; $P < 0.001$) and total functional groups ($r = 0.95$; $P < 0.001$), as shown in Figure 1.

Several studies have indicated the significant role of organic matter in regulating soil CEC levels (Hailegnaw et al., 2019; Bi et al., 2023). Ramos et al. (2018) found a very strong correlation ($r = 0.92$; $p < 0.01$) between organic matter content and CEC. The results showed that at soil depth of 20 cm, an organic C content of 1.8 kg C m^{-2} caused a 25% increase in CEC. Solly et al. (2020) also reported that at depth of less than 30 cm, organic matter contributed 35–50% to CEC of forest soil in Switzerland. According to He et al. (2021), higher negative charge was observed in soil fertilized with manure over 17 years compared NPK + straw, NPK, and control. This increase was linked to the higher content of organic matter, particularly from aromatic-C functional groups. These results showed the organic matter role in enhancing the negative charge, thereby increasing CEC.

In comparison, the application of CFA on RMS decreased soil CEC, carboxylic groups, and total functional groups. Specifically, carboxylic and total functional groups decreased from 1.6 mmol g^{-1} to $0.9\text{--}1.2 \text{ mmol g}^{-1}$ and 6.0 mmol g^{-1} to $3.5\text{--}4.9 \text{ mmol g}^{-1}$, respectively, with the

Table 2. Changes in CEC, total functional groups, and carboxyl groups as influenced by CFA and OPB treatments. Numbers in parentheses indicate the standard deviation of the average ($n=9$). Parameters sharing the identical letters signify no significant difference in treatment effects, as determined by LSD test at $p < 0.05$

Treatments	CEC (cmol kg^{-1})	Total functional groups (mmol g^{-1})	Carboxylic groups (mmol g^{-1})
Oil palm bunches (Mg ha^{-1})			
0	20.26 (4.67) a	0.92 (0.09) a	0.23 (0.07) a
20	27.80 (7.43) b	4.83 (0.45) b	1.31 (0.12) b
40	35.56 (2.56) c	8.56 (0.88) c	2.16 (0.11) c
Coal fly ash (Mg ha^{-1})			
0	32.03 (1.45) c	5.97 (1.23) c	1.58 (0.12) c
50	27.70 (2.12) b	4.90 (0.98) b	1.24 (0.14) b
100	23.98 (2.56) a	3.45 (0.34) a	0.87 (0.07) a

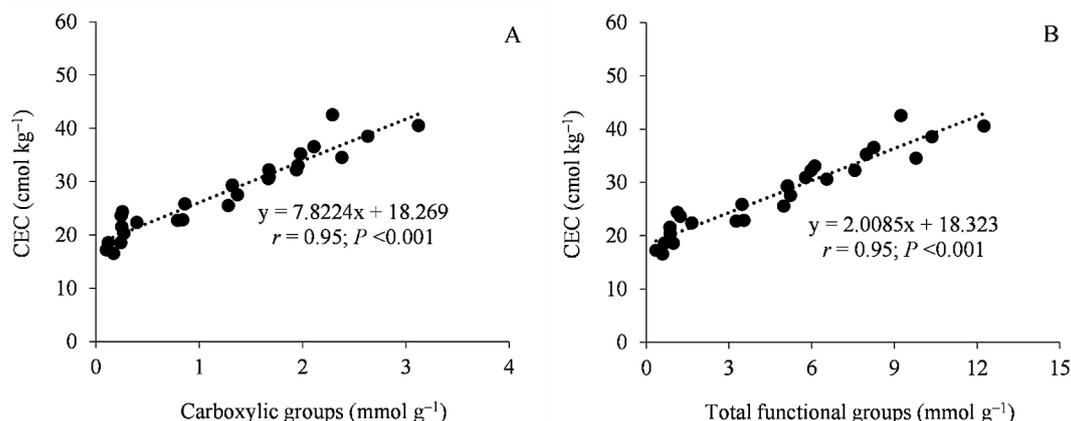


Figure 1. Correlation between carboxylic groups (A) and total functional groups (B) and CEC of RMS

application of CFA at 50–100 Mg ha⁻¹ (Table 2). This reduction in carboxylic and total functional groups led to a decrease in soil CEC by 13.5–25.1%. The decrease in soil CEC is closely related to the ionic reactions between the negative charges in soil and the positively charged cations from CFA. As presented in Table 1, high cation content in CFA showed the potential to react with the negative charge in organic matter and soil. This reaction reduced the number of negative charges in soil and CEC levels. The findings proposed that applying CFA to RMS could alter soil chemical properties by reducing the number of negative charges available for cation exchange, thereby reducing capacity to store and exchange essential nutrients for plants.

Reduction in soil CEC with CFA application followed in this study was in line with prior reports showing negative impact on soil characteristics. For example, Hale et al. (2020) conducted field trials with corn plants over 5 planting seasons, showing a reduction in soil CEC during the 3rd, 4th, and 5th seasons after CFA application. Jambhulkar et al. (2018) reviewed multiple studies on using CFA for soil improvement and reported a decrease in soil CEC. These studies suggested the important of carefully considering the long-term use of CFA as soil amendment, due to the potential to reduce CEC essential for soil fertility and plant productivity.

ANOVA results indicated that soil pH was significantly affected by the application of CFA and OPB ($p < 0.05$). The application of CFA and OPB raised soil pH from 4.3 in the control to a range between 4.66 and 6.16, depending on the amount applied (Figure 2A). The rise in soil pH with CFA application is attributed to the high content of alkaline components such as MgO and

CaO in CFA (Table 1). Ca and Mg oxides contribute to the production of OH⁻ ions through dissolution and hydrolysis reactions hydrolysis (Iyer, 2002), which neutralizes H⁺ ions, ultimately raising soil pH. Similarly, Ahmad et al. (2021) indicated an increase in soil pH from 6.8 to 8.2–8.5 with the application of 30–50% CFA. According to Hamanaka et al. (2022), soil pH increased from 3.1–3.7 in the control to 7.9–11.2 using 5–50% CFA. The role of CFA in increasing soil pH has also been documented by (Tsadilas et al., 2018; Varshney et al., 2022), showing potential as an effective ameliorant.

OPB increased soil pH because of the ability of organic materials to bind cations, thereby contributing to soil acidity, such as aluminum (Al) as well as iron (Fe). Fe and Al cations contribute to soil acidity by releasing H⁺ ions through hydrolysis reactions that transform Al³⁺ to Al(OH)²⁺ or Fe³⁺ to Fe(OH)²⁺ (Strawn et al., 2015; Yerima et al., 2020). The decomposition of OPB generates carboxylate and phenolic, which bind or adsorb Al and Fe, thereby causing inactiveness. This process prevents hydrolysis reactions and increases soil pH (Jiang et al., 2018; Wang et al., 2019).

Based on the results, the co-application of CFA and OPB significantly influenced the exchangeable base levels (Ca, K, and Mg) in soil. Specifically, the exchangeable Mg content increased by 77–148%, 138–264%, and 186–446% with the application of 20–40 Mg ha⁻¹ OPB, 50–100 Mg ha⁻¹ CFA, and their combination, respectively. The addition of OPB increased the exchangeable Ca content from 1.4 cmol kg⁻¹ in the control to 3.42 ± 1.4 cmol kg⁻¹ with 40 Mg ha⁻¹ of OPB, and 5.9 cmol kg⁻¹ with 100 Mg ha⁻¹ of CFA (Figure 2C). When 100 Mg ha⁻¹ of CFA

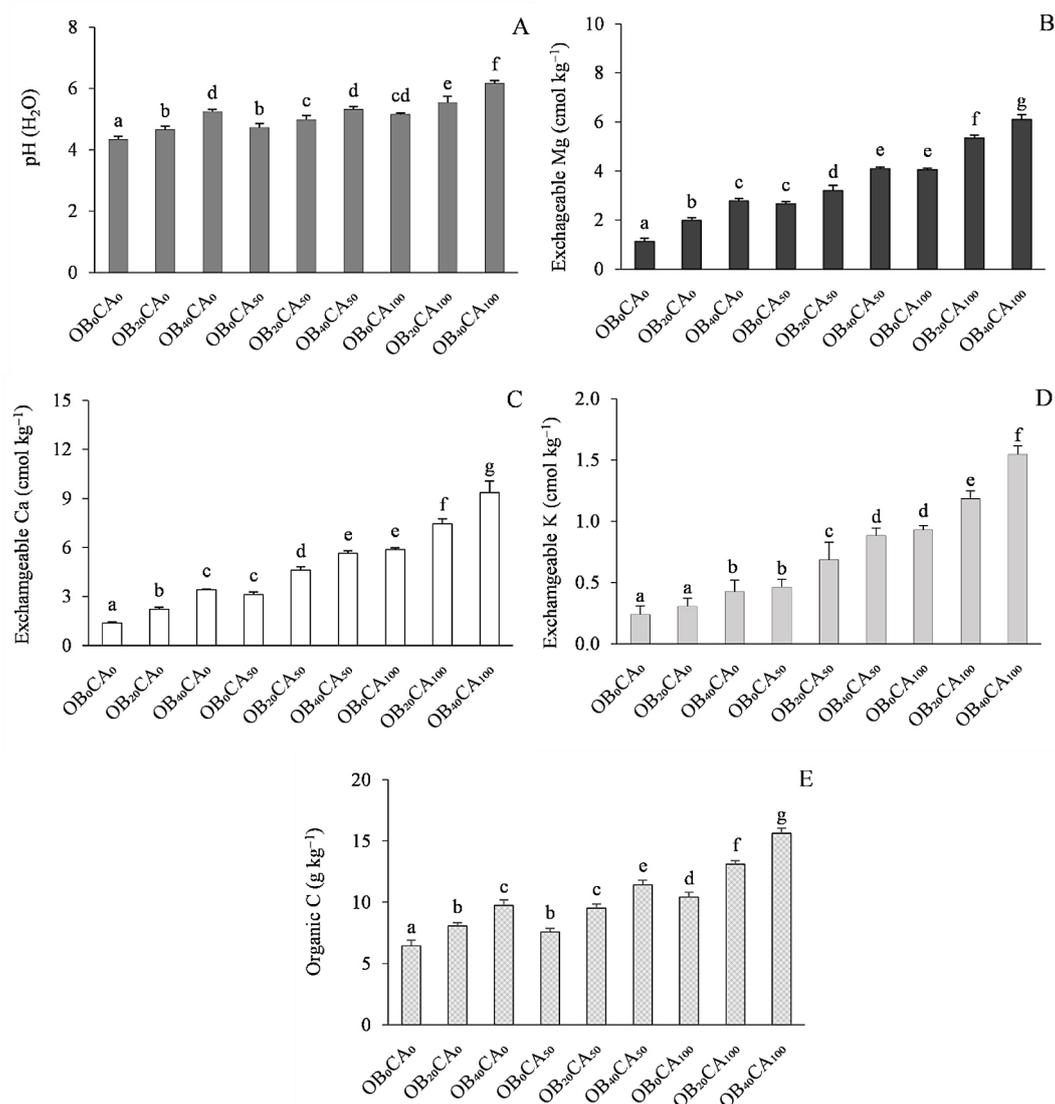


Figure 2. Variations in soil pH (A), exchangeable Mg (B), exchangeable Ca (C), exchangeable K (D), and the contents of organic carbon (E) were observed following the application of OPB and CFA. The line above each bar denotes the standard deviation of the mean (n=3). Identical letters above the lines signify no significant difference in treatment effects, as determined by LSD test at $p < 0.05$

and 40 Mg ha⁻¹ of OPB were applied together, the exchangeable Ca content increased by 576% compared to the control (Figure 2C). A comparable synergistic effect was noted for exchangeable K (Figure 2D).

Several previous studies have reported increases in exchangeable bases in soil with the application of organic matter and ash (Shi et al., 2017; Rowley et al., 2018). Paramisparam et al. (2021) stated that applying ash from biomass combustion combined with biochar increased exchangeable K in soil. Additionally, exchangeable Ca and Mg increased when ash from coniferous plants was used at a rate of 3–9 Mg ha⁻¹ (Hansen et al., 2017). As shown in Table 1, CFA contains

a high number of base cations with potential as an ameliorant, which increases the base exchange cations in soil. Organic matter enhances the negative charge of soil, thereby improving capacity to retain exchangeable cations. These results showed the synergistic effect of CFA and OPB in enhancing soil CEC.

ANOVA results revealed that the organic carbon (C) content in soils was influenced by the combined application of CFA and OPB. In soils without CFA, applying OPB at rates of 20 and 40 Mg ha⁻¹ increased organic C content from 6.4 g kg⁻¹ to between 8.1 and 9.7 g kg⁻¹ (Figure 2E). When OPB was applied at the same rates alongside 50 and 100 Mg ha⁻¹ of CFA, organic

C content increased from 7.6 g kg⁻¹ to 9.5–11.4 g kg⁻¹, and from 10.4 g kg⁻¹ to 13.1–15.6 g kg⁻¹, respectively (Figure 2E). These findings highlight the significant role of CFA in enhancing organic C content in soils.

OPB is known to contain relatively high levels of organic carbon (Table 1), which suggests that its application to soils enhance organic C content. Although CFA contains low organic C, its combination with OPB has been shown to significantly boost organic C levels in soils (Figure 2E). This suggests that mechanisms beyond the direct contribution of organic C from CFA are at play when CFA is used alongside OPB in the reclamation of mining soils. CFA is rich in multivalent cations such as Ca²⁺, Mg²⁺, Al³⁺, and Fe³⁺ (Table 1), and these cations may act as bridging agents between the negatively charged soil particles and organic matter (Barreto et al., 2021; Galicia-Andrés et al., 2021). This cation bridging facilitates the formation of strong bonds between organic matter and soil, thereby reducing microbial decomposition and increasing organic C content (Xing et al., 2023). Solly et al. (2020) found a strong correlation between effective cation exchange capacity (CEC_{eff}) – a measure of how well metal cations are retained in soils – and organic C content across various forest soils, highlighting the significant role of metal cations such as Ca, Fe, and Al in enhancing organic C levels. Several studies have also demonstrated the role of cation bridging in stabilizing and increasing organic C content in soils (Wang et al., 2021; Feng et al., 2023).

CONCLUSIONS

This investigation demonstrated that the application of CFA and OPB had varying impacts on soil CEC. The decomposition of OPB increased the number of carboxylate and total functional groups, which enhanced negative charge and soil CEC. However, CFA caused a decrease in CEC due to the ionic reaction between the positively charged cations from the ash and the negative charges in soil. Compared to CEC, the amount of exchangeable bases (Ca, Mg, and K) in soil was notably affected by the combined application of CFA and OPB. These results showed that the co-application of CFA and OPB optimized soil quality by balancing CEC and the availability of exchangeable bases.

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