

The Stability of pH and the Concentrations of Iron and Manganese in Acid Mine Drainage Following Coal Fly Ash and Empty Fruit Bunch of Oil Palm Treatments

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ABSTRACT

AMD (acid mine drainage) with low pH and high content of heavy metals is a serious environmental problem in mining activities. Proper AMD management is crucial to ensure compliance with the standards of environmental quality before allowing the flow to the public water system. The objective of this study was to assess the efficacy of increasing pH and decreasing Fe alongside the concentrations of Mn in AMD with the addition of coal fly ash (CFA) and empty fruit bunch of oil palm (EFBOP). A total of four treatments, namely: (1) control (soil without treatment), (2) soil + EFBOP, (3) soil + CFA, and (4) soil + EFBOP + CFA were tested for the ability to improve AMD quality in a batch reactor experiment for 90 days. Weekly observations were carried out for pH, Fe, and Mn concentrations during the experiment, where part of AMD in the reactor was drained and replaced with fresh ones. The results showed that single treatment of EFBOP or CFA caused a pH increase at 2.8 to 5.1–5.4 and 6.3–6.8, respectively. Furthermore, a greater increase occurred from 2.8 to 7.0–7.8 when EFBOP was combined with CFA application. This combination also showed a greater reduction in the concentrations of Fe and Mn compared to the single treatment of EFBOP or CFA. The increase in pH and decrease in Fe alongside the Mn concentrations began in the 3rd week, and this effect was stable during the 90 days of the experiment. The results underscore the potential of EFBOP and CFA as agricultural and industrial wastes in long-term AMD management.

Keywords: carboxyl groups; dissociation; remediation; sorption; sulphuric compounds

INTRODUCTION

Mining activities are often associated with AMD (acid mine drainage) formation, a phenomenon triggered when the sulfide minerals found in rocks and soils are exposed to air and water (Tabelin et al., 2022; Jiao et al., 2023). This exposure results in the production of sulfuric acid,

which then dissolves other minerals in the rocks, releasing heavy metals, including iron (Fe), aluminum (Al), and manganese (Mn) (Trifi et al., 2022). Consequently, AMD becomes highly acidic and contains high concentrations of these toxic metals (Zheng et al., 2023). The AMD effect towards aquatic ecosystems is profound, including the disruption of fish and benthic invertebrate

survival and reproduction (Núñez-Gómez et al., 2019; Lebepe et al., 2020). Rice grown on the agricultural soils previously exposed to AMD for 22–25 years has also resulted in concentrations of total chromium and Mn above the WHO/FAO limit (Senoro et al., 2020). Furthermore, the AMD discharge to agricultural soils reportedly caused a 62% rice production reduction (Choudhury et al., 2017). The studies mentioned underscored the importance of preventing the release of AMD into agricultural soils and implementing remediation measures to mitigate the detrimental effects on the environment.

Active treatments, such as lime application, are user-friendly and efficient approaches in AMD remediation (Elghali et al., 2021; Daraz et al., 2023), but this method is frequently considered expensive and uneconomical. Passive treatment is also often applied to decrease the destructive AMD effects toward the environment. This method implements some biochemical processes, including precipitation, adsorption, ion exchange, sedimentation, and complexation in reducing acidity and the concentrations of toxic metals (Sheoran and Sheoran, 2006; Vasquez et al., 2022). Passive treatment is considered a cheaper, less operational, and higher energy energy-efficient method compared to active treatment (Rambabu et al., 2020). Several studies also showed that passive treatments had high effectiveness in raising pH and decreasing the AMD heavy metal concentrations (Chen et al., 2020; Singh and Chakraborty, 2020). The effectiveness of passive treatments in remediating AMD is determined by the natural processes to counterbalance the acidity as well as to oxidize, decrease, and precipitate toxic metals (Sheoran and Sheoran, 2006; Ben-Ali et al., 2019). Therefore, the existence of substances capable of lowering or adsorbing H^+ ions or toxic metals has an essential function in the effectiveness of this system (Neff et al., 2021).

Coal fly ash (CFA) found in coal power plants typically has a high cation-oxides content (Laxmidhar and Subhakanta, 2020; Zimar et al., 2022), making CFA a potent candidate for neutralizing H^+ ions and increasing AMD pH. Several previous studies reported the role of CFA in AMD remediation (Kalombe et al., 2020; Weinberg et al., 2022). Moreover, empty fruit bunch of oil palm (EFBOP) produced by oil palm processing factory has a high organic carbon (C) content (Noirot et al., 2022), capable of binding metals in soils and water. Modified EFBOP has been applied as adsorbent materials for adsorbing pollutants

from wastewater (Elias et al., 2021; Zubaidah et al., 2021). These studies highlighted the potential of CFA and EFBOP as industrial and agricultural wastes in suppressing the detrimental effect of AMD on the environment.

The usage of various organic materials (OM) and different materials in remediating AMD often leads to varying longevity in improvement. Furthermore, Noor et al. (2020) stated that the mixture of EFBOP and reclaimed mine soil improved AMD pH from below 4.0 to 7.0 during a 15-day treatment. Moreover, Vasquez et al. (2016) found that the different organic and inorganic materials resulted in increased pH as well as decreased concentrations of Fe and Mn during a 45-day batch experiment. Furthermore, the application of CFA containing high CaO and MgO led to the cationic element removal, including Mn, Fe, and Al from AMD during short-term (24 h) and long-term (up to 5 weeks) based on the lab-scale experiments. The findings showed that the effect of CFA and other materials on improving the quality of AMD occurred at different time durations. Despite the numerous studies on agricultural and industrial waste utilization, information on the longevity of changes in AMD characteristics following EFBOP and CFA application remains very limited. Hence, the objective of this study was to quantify the impact of EFBOP and CFA application toward the stability of pH, as well as the Fe and Mn concentrations in AMD. Observations were carried out for 90 days to assess the impact of treatment on the duration of changes in AMD characteristics.

MATERIALS AND METHODS

Sampling and characterization of soil, coal fly ash, EFBOP, and acid mine drainage

A sample was taken from reclaimed mining soil in Desa Tiung, Banjar Regency, South Kalimantan, Indonesia. This reclaimed mining soil was previously coal mining land that had been planted with rubber plants for 7 years. The soil sample was taken at a depth of 0–30 cm from several points, and homogenized after being cleaned of roots and plant litter. Subsequently, it was carried to the laboratory to be air-dried and ground to a 2.0 mm size, kept until further use, and some parts were used to determine soil characteristics. CFA was collected from the coal power plant disposal site at Desa Jorong, Tanah Laut Regency, while EFBOP was

obtained from oil palm factory situated at Desa Ambungan, Pulau Laut Regency, South Kalimantan, Indonesia. CFA and EFBOP were transported to the laboratory and then air-dried for several days. Air-dried CFA was filtered to obtain a size of ≤ 2.0 mm, while EFBOP was ground to a 2.0 mm size. Furthermore, both materials were stored until further use, and some were used for characterization. AMD was collected from abandoned voids of a coal mine located in Desa Tiung, Banjar Regency, South Kalimantan, Indonesia.

Characterization of soil and CFA carried out included the determination of bulk density utilizing the ring sampler technique (Blake and Hartge, 1986), pH through the electrode glass method (McLean, 1982), organic C by Walkley-Black method (Nelson and Sommers, 1996), and total nitrogen (N) utilizing Kjeldahl technique (Bremer and Mulvaney, 1982). Soil and CFA were digested using HClO_4 60% and the total phosphorous content was quantified at 660 nm with a spectrophotometer (Olsen and Sommers, 1982). The contents of Mg, Ca, Al, and Fe were determined through the soil and CFA digestion utilizing the of HNO_3 and HClO_4 mixture, as well as quantification of the digested solution utilizing an atomic absorption spectrophotometer (Barnhisel and Bertsch, 1982; Knudsen and Peterson, 1982; Lanyon and Heald, 1982; Olson and Ellis, 1982). Meanwhile, soil texture and exchangeable cation were assessed with sieving-sedimentation method (Gee and Bander, 1986) and ammonium acetate at pH 7.0 (Rhoades, 1982), respectively.

Characterization of EFBOP included the determination of organic C content using the Walkley-Black technique (Nelson and Sommers, 1996) and total N content utilizing the Kjeldahl technique (Bremer and Mulvaney, 1982). Total P content was specified with the procedure of HClO_4 60% digestion (Olsen and Sommers, 1982). The contents of carbohydrates and lignin were quantified utilizing the anthrone-sulfuric acid method (Grandy et al., 2000), and sodium hydroxide method (Chesson, 1981), respectively.

Batch experiment

The effect of CFA and EFBOP application on the stability of pH and the concentrations of Fe and Mn in AMD was determined using a batch experimentation. The treatments tested in this study were: (1) control (soil without treatment), (2) soil + EFBOP, (3) soil + CFA, and (4) soil + EFBOP +

CFA. All treatments had 6 replicates, totaling 24 experimental units. About 2000 g soil was placed in an acrylic reactor with dimensions of 30 cm in length, 15 cm in width, and 10 cm in height, and EFBOP as well as CFA were added and homogenized to soil in accordance to the treatments. The amount added was equal to the field at 100 Mg ha^{-1} and 200 Mg ha^{-1} , respectively. Aquadest was incorporated into the mixture of soil-EFBOP/CFA to obtain 70% of water holding capacity, hence the incubation of mixtures were carried out at a constant temperature within 2 weeks. In line with the incubation period completion, 200 g of soil was sub-sampled from each reactor for the measurement of several soil characteristics. The pH and CEC were determined with a similar method used to characterize untreated soils. Meanwhile, total functional groups of organic matter and specific surface areas of soil were determined by using the technique based on Kim and Park (2016) as well as Sepaskhah et al. (2010), respectively.

AMD was flooded gradually to each reactor until the height reached 3 cm from soil surface, while the differences in pH and the metal (Fe and Mn) concentration were observed every 7 days during a 90-day observation period. Furthermore, the measurement of pH was conducted utilizing a portable pH meter (Hanna HI98190), and the concentrations of Fe alongside Mn were measured by accumulating treated AMD at 50 mL from every reactor. The sample filter were carried out through a 0.45 syringe filter (MF-Millipore® Membrane Filter), and quantified with atomic absorption spectrophotometry. After measuring pH and the concentrations of metals every week, AMD in each reactor was drained up to the surface, and then fresh ones were slowly added until the height reached 3 cm from the soil surface. The cycle of drainage and fresh AMD addition to the reactor was repeated weekly.

Data analysis

The EFBOP and CFA effect on the stability of pH, Fe and Mn concentrations in treated AMD was determined by analysis of variance (ANOVA). All collected data were quantified through the Barlett and Shapiro-Wilk tests to ensure homogeneous variance and normal distribution, respectively. In addition, the mean comparison of the treatments with a significant effect on the observed variables was carried out using least significant difference (LSD) test at $P < 0.05$. The

software package of GenStat 12th Edition was used for the entire statistical analysis.

RESULTS AND DISCUSSION

Characteristics of soil, coal fly ash, and empty fruit bunch of oil palm

This study utilized the soil characterized by the texture of clay, an increased bulk density, and an acid soil reaction (pH H₂O = 4.1 and pH KCl = 3.7). The organic C and total N contents were also low, reaching 12.7 g kg⁻¹ and 1.1 g kg⁻¹ (Table 1). Furthermore, the Al and Fe contents were relatively low, with soil CEC reaching 24 cmol kg⁻¹ (Table 1). The results were consistent with previous studies stating that clay soil texture, high bulk density, low pH, and low organic C, and total N were characteristics of reclaimed mining soil (Liu et al., 2017; Kumari and Maiti, 2022).

The CFA used in this study showed a high bulk density at 1.7 kg m⁻³ with an alkaline pH (pH H₂O = 7.9, pH KCl 1.0 N = 6.9). The organic C, N, and P content were relatively low, while the Ca and Mg levels were high. The Al and Fe contents also reached 376 mg kg⁻¹ and 213 mg kg⁻¹, respectively, as shown in Table 1. Meanwhile, EFBOP contained a high organic C content (412 g kg⁻¹), low total N content (22 g kg⁻¹), along with higher carbohydrates than lignin.

Changes in pH of AMD influenced by CFA and EFBOP applications

The study indicated that pH in the control (soil without treatment) of AMD remained relatively unchanged for 90 days, ranging from 2.8–3.7 (Figure 1a). Meanwhile, the application of CFA and EFBOP either individually or in combination increased pH. In EFBOP treatment, pH increased from 2.8 to 5.1–5.4 in the 2nd and 3rd weeks, then remained relatively unchanged until day 90 (Figure 2a). The application of CFA also increased pH, and this change was relatively stable for 90 days, ranging from 6.3–6.8. The combined application of EFBOP and CFA showed similar results with a pH range of 7.1–7.8 (Figure 2a). Observation of changes on day 90 demonstrated that the combination of EFBOP, and CFA application showed the highest enhancement in pH compared to other treatments (Figure 2b). The treated AMD pH increased from 2.8 to 5.3 with EFBOP, and 6.7 with the CFA, while in the combination treatment, the value was 7.7.

The pH increase could be related to the neutralization reaction between positively charged H⁺ ions of AMD and negatively charged functional groups of OM originating from the decomposition of added EFBOP. This process led to a reduction in H⁺ ions in AMD, followed by an increase in pH. A previous study showed that the addition of OM to reclaimed-mined soil raised the total functional

Table 1. Characteristics of soil, CFA, and EFBOP. Numbers following the plus-minus sign (\pm) represent the standard deviation of mean ($n = 3$)

Characteristics		Soil	Coal fly ash	Empty fruit bunch of oil palm
Texture:	Sand (%)	32.34 \pm 4.23	-	-
	Silt (%)	23.87 \pm 3.76	-	-
	Clay (%)	43.79 \pm 7.54	-	-
Bulk density (kg m ⁻³)		1.87 \pm 0.84	1.76 \pm 0.09	-
pH (H ₂ O)		4.12 \pm 0.87	7.98 \pm 0.89	-
pH (KCl 1.0 N)		3.65 \pm 0.34	6.87 \pm 0.45	-
Organic C (g kg ⁻¹)		12.56 \pm 5.43	4.56 \pm 0.87	412.45 \pm 9.76
Total N (g kg ⁻¹)		1.13 \pm 0.76	0.41 \pm 0.07	21.56 \pm 2.45
Total P (g kg ⁻¹)		14.65 \pm 3.45	4.65 \pm 0.12	14.67 \pm 1.12
Magnesium (mg kg ⁻¹)		5.43 \pm 0.56	476.45 \pm 9.65	-
Calcium (mg kg ⁻¹)		7.54 \pm 0.87	687.23 \pm 8.67	-
Iron (mg kg ⁻¹)		4.23 \pm 0.56	213.45 \pm 7.84	-
Aluminium (mg kg ⁻¹)		3.65 \pm 0.32	376.34 \pm 8.43	-
CEC (cmol kg ⁻¹)		23.65 \pm 3.23	-	-
Carbohydrates (g kg ⁻¹)		-	-	41.56 \pm 0.67
Lignin (g kg ⁻¹)		-	-	78.89 \pm 0.98

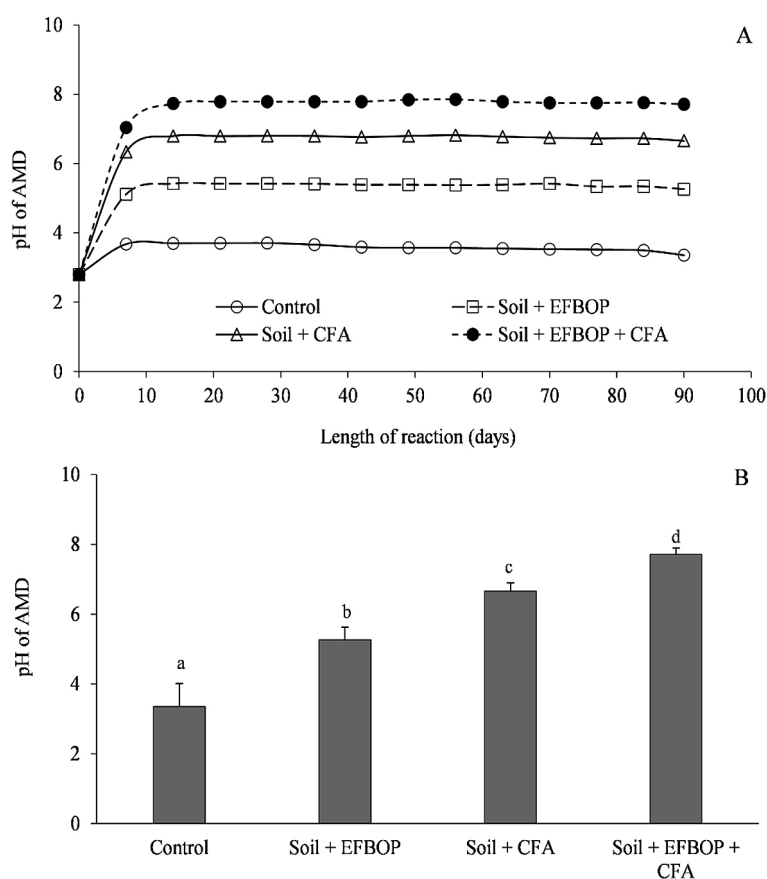


Figure 1. Differences in pH of AMD influenced by CFA and EFBOP applications during a 90-day observation (a) and pH observed on the 90th day (b). The lines above the bar indicate the standard deviation of the mean ($n = 6$). Identical letters above the lines show the comparable effects of the treatments as per the LSD test at $P \leq 0.05$

groups of organic matter at 365–696%, based on the type and amount applied (Saidy et al., 2021a). In another study, Hamoud (2010) found that the application of rice straw compost raised the number of carboxylic and phenolic groups in soil. The results underscored the importance of functional groups from the organic material decomposition in AMD remediation.

CFA caused a rise in pH because Ca and Mg oxides were subjected to a dissolution reaction to produce OH^- ions which then reacted with the H^+ ions from AMD (Gitari et al., 2008; Jones and Cetin, 2017). Dissolution of MgO and CaO oxides produced the pH of CFA-AMD mixture in the range of 6.20–6.80 (Gitari et al., 2018). According to a study, the sulfur content of CFA determines the ability to increase the pH of AMD (Plank and Martens, 1974). Acid ($\text{pH} < 7.0$) and alkaline CFA generally originate from coal with a high (anthracite) (Furr et al., 1977) and low sulfur content (Page et al., 1979), respectively. Furthermore, Qureshi et al. (2016) stated that the ability to neutralize acidity varied from 20 kg CaCO_3

Mg^{-1} in CFA originating from lignite coal to 25 kg $\text{CaCO}_3 \text{Mg}^{-1}$ in coal ash from bituminous coal.

The pH increase with the CFA addition was in accordance with several previous studies. For example, Mungazi and Gwenzi (2019) observed changes in pH in coal mine minerals combined with CFA using a column experiment, and reported an expansion from very acidic ($\text{pH} 2.9$) to alkaline ($\text{pH} 8.0$). Furthermore, Nasir et al. (2016) recorded a rise in AMD pH with column experiments containing CFA. Because of high CaO and MgO contents, CFA can be utilized as an ameliorant material in waste-based AMD management (Keller et al., 2020; Yang et al., 2020).

Changes in the concentration of iron and manganese of AMD influenced by CFA and EFBOP applications

The study stated that CFA and EFBOP reduced the Fe concentration in AMD. During a 90 day period, the Fe concentration in the sample without treatment (control) ranged from 6.5–7.1

mg L⁻¹ (Figure 2a). The addition of EFBOP to soil resulted in a decrease to 4.7 mg L⁻¹ in the 1st week, 4.3 mg L⁻¹ in the 2nd week, and then stabilized to 4.0 mg L⁻¹ in the 13th week. The Fe concentration in AMD with CFA addition treatment also decreased from 7.1 mg L⁻¹ to 3.2 mg L⁻¹ in the 2nd week and remained relatively unchanged at 2.9 mg L⁻¹ in the 13th week. In the combination treatment, Fe decreased from 7.1 mg L⁻¹ to a range of 0.9–1.1 mg L⁻¹ in the 3rd to 13th week. On the basis of the results, the Fe concentration in all treatments from week 3 to week 13 relatively did not change. Furthermore, the application of EFBOP and CFA caused a reduction by 39% and 55%, respectively. The level also decreased significantly by 85% when CFA was applied in combination with EFBOP (Figure 2B).

Similar to the Fe concentration, the CFA and EFBOP treatments also led to the stability of Mn during a period of 3–13 weeks after incorporation of AMD into the reactors. The concentration in the control was in the range of 19.1–20.0 mg L⁻¹ during 13 weeks (Figure 3a). The application of EFBOP resulted in a decrease from 19.1 mg L⁻¹

in the control to 8.52 mg L⁻¹ in the 3rd week and remained stable until the 13th week. Furthermore, the Mn concentration in the CFA treatment decreased from 19.1 mg L⁻¹ to 8.5 mg L⁻¹ in the 3rd week and did not change until the 13th week. In the combination treatment, a reduction was evaluated from 19.1 mg L⁻¹ to 4.06 mg L⁻¹ and remained unchanged until the 13th week (Figure 3a). At week 13, the Mn concentrations decreased by 55% with the addition of EFBOP, 70% with CFA application, and 80% in the combination treatment (Figure 3b).

The decrease in the Fe, and Mn concentrations was attributed to increasing adsorption of the metals in the presence of EFBOP. According to previous reports, the organic matter decomposition process produces functional groups, which in turn increase the negative charges of soils (Choppala et al., 2018; Cooper et al., 2020). Total functional groups including carboxyl, phenolic, and hydroxyl in this study, increased from 1.4 mmol g⁻¹ in the control to 9.2–11.5 mmol g⁻¹ in the EFBOP treatment (Table 2). An increase in negative soil charges was also shown by a rise

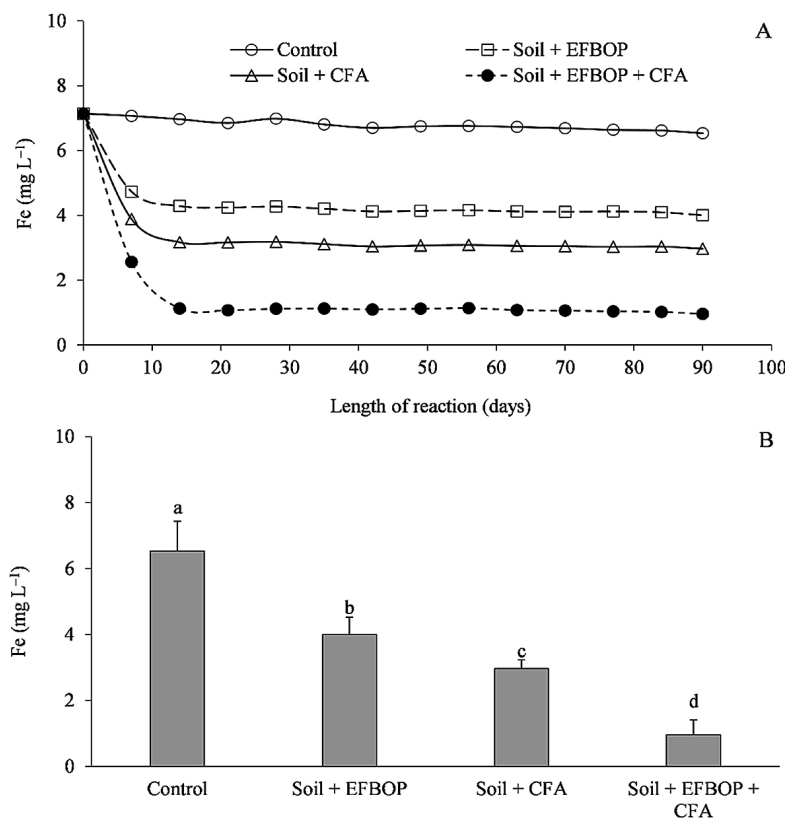


Figure 2. Changes in the Fe concentration of AMD influenced by CFA and EFBOP applications during the 13-week observation period (A) and the Fe concentration observed on the 13th week (B). The lines above the bar indicate the standard deviation of the mean (n = 6). Identical letters above the lines show the comparable effects of the treatments as per the LSD test at $P \leq 0.05$

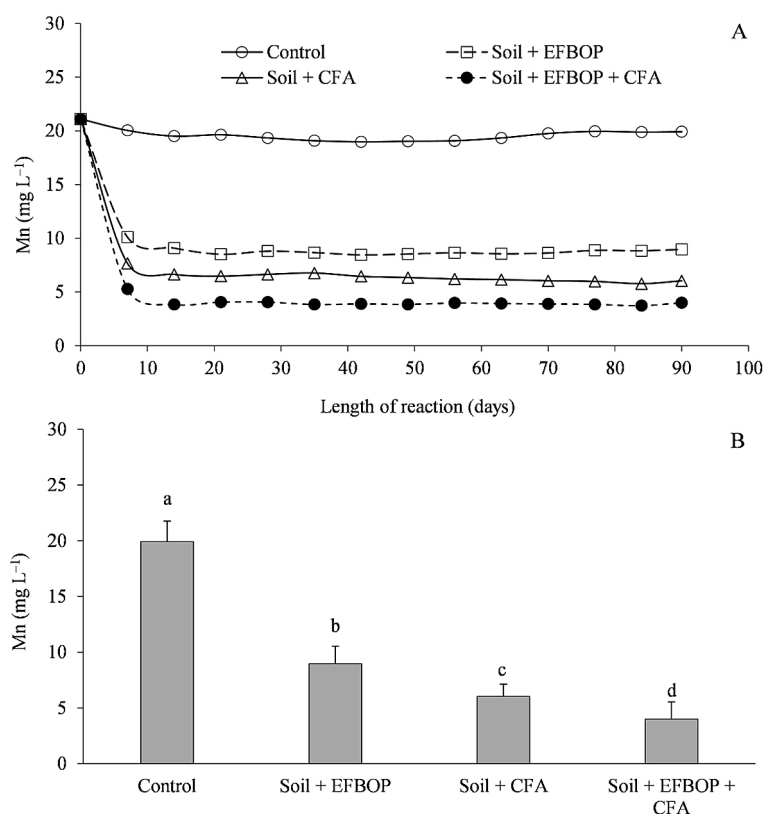


Figure 3. Changes in the Mn concentration of AMD influenced by the CFA and EFBOP applications during the 13-week observation (A) and the Mn concentration observed on the 13th week (B). The lines above the bar indicate the standard deviation of the mean (n = 6). Identical letters above the lines show the comparable effects of the treatments as per the LSD test at $P \leq 0.05$

in cation exchangeable capacity (CEC). Furthermore, the presence of EFBOP resulted in a rise in CEC from 23.5 cmol kg⁻¹ in the control to 29.8–30.7 cmol kg⁻¹ (Table 2). Furthermore, an increase in negative charges shown by a rise in soil CEC with OM application was found in several previous examinations (Abu-Bakar et al., 2011; Neswati et al., 2022).

According to previous studies, negative charges serve as an essential factor in control of the amount of metals adsorbed onto mineral surfaces (Li et al., 2017; Choppala et al., 2018). An

increase in negative charges facilitated improved interactions on metals with positive charges in AMD, and OM with negative charges, ultimately increasing the amount of metals absorbed to the mineral surface. This result corroborated the study of Arce et al. (2017) which reported an increase in the AMD metal reduction using the aggregation of metal-OM complexes with the addition of OM. In another study, Lazareva et al. (2019) found a decrease in metal concentrations in AMD through an absorption process in the presence of OM. The decrease in metal AMD

Table 2. Effect of CFA and EFBOP application on changes in soil pH, cation exchangeable capacity (ECE), total functional groups, and specific surface areas. Numbers after \pm represent the standard deviation (n = 6)

Treatments	Soil pH	Soil CEC (cmol kg ⁻¹)	Functional groups (mmol g ⁻¹)	Surface areas (m ² g ⁻¹)
Control	4. 4.16 \pm 0.13 a*	23.47 \pm 1.36 a	1.43 \pm 0.96 a	10.22 \pm 1.37 a
Soil + EFBOP	5.26 \pm 0.12 b	30.65 \pm 1.98 c	9.23 \pm 2.12 b	10.88 \pm 2.43 a
Soil + CFA	6.04 \pm 0.13 c	21.21 \pm 3.23 b	2.56 \pm 0.98 a	17.96 \pm 3.54 b
Soil + EFBOP + CFA	7.10 \pm 0.25 d	29.78 \pm 2.56 c	11.54 \pm 2.46 b	18.60 \pm 3.21 b

Note: *similar letters in each column show insignificant effects of the treatments for each soil/control based on the LSD test at $P < 0.05$.

concentration was attributed to the increase in specific surface areas (SSA) of soil with the CFA addition. On the basis of the results, the application of CFA increased SSA from $10.2 \text{ m}^2 \text{ g}^{-1}$ in the control to $17.9\text{--}18.6 \text{ m}^2 \text{ g}^{-1}$ in the treatment sample (Table 2). The existence of hydro(oxides) of Al and Fe in CFA may increase SSA through the enhancement of sites given by the high density of reactive surface functional groups related to the oxides (Saidy et al., 2020). This increase in sorption sites facilitated a rise in the amount of Fe and Mn adsorbed onto mineral surfaces, while also decreasing the concentrations in AMD. Similarly, several previous studies reported an increase in the metal cation removal from contaminated soil and AMD with CFA application (Mujtaba-Munir et al., 2020; Shirin et al., 2021). The presence of Na^+ , Ca^{2+} , and Mg^{2+} in CFA has an essential function in the sorption of Cd(II) into mineral surfaces through cation exchange and electrostatic interaction mechanisms (Mokgehle et al., 2019). Kalombe et al. (2020) using a 1500 L reactor showed a reduction in the Fe and Al concentrations of AMD by one to four orders of magnitude with CFA application. The result suggests an enhancement in the sorption processes of metals onto mineral surfaces with reactive site addition of soil minerals through CFA application, consequently reducing the concentration of metals in AMD. This implies the potential use of this industrial waste use in AMD remediation.

CONCLUSIONS

In conclusion, this study indicated that the combination of CFA and EFBOP positively affects increasing the pH levels and reducing the heavy metal content AMD. This effect was more significant compared to the single treatments of CFA or EFBOP application, with the stability lasting up to 8 weeks. Specifically, the combination treatment consistently increased pH levels and decreased the heavy metal content from the 3rd week until the final of the experiment. The results underscored the potential of using industrial and agricultural wastes, such as CFA and EFBOP, in the long-term remediation of AMD. By effectively increasing pH and reducing the heavy metal content, the waste materials contribute to the restoration of contaminated environments and the prevention of further degradation.

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