

Research Article

The sorption and desorption of organic carbon onto tropical reclaimed-mining soils with coal fly-ash application

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Abstract: Coal fly ash, resulted from coal combustion in power plants, with relatively high amounts of aluminium, iron, calcium, and magnesium oxides may modify the sorption capacity of soils. A batch experiment was conducted to examine the capacity of reclaimed mining soils (RMS) to adsorb organic carbon (OC) in response to coal fly ash application. Extraction of dissolved OC was carried out from dried albizia shoot residue and reacted with the RMS at dissolved OC concentrations varying from 0 to 175 mg C L⁻¹ at pH 5.5. The results showed that the sorption capacity of the RMS for OC increased significantly with coal fly ash application, which may relate to increasing the contents exchangeable Ca and Mg, dithionite- and oxalate-extractable aluminium and iron, and surface areas of soils. Desorption experiment indicated that only 5–23% of the OC initially sorbed onto soil-coal fly ash interactions was freed using a single extraction step, suggesting that most of the OC is strongly sorbed to the mineral surfaces. Results of the study indicate an important role of fly ash in increasing OC sorption capacity of soils and reducing the percentage of OC sorption from the RMS-coal fly ash association.

Keywords: *mineralization, retention, sequestration, sorption, stabilization*

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Introduction

Coal surface mining in tropical areas has disturbed thousands of hectares of soils. Surface mining activities result in significant changes in physical, chemical and biological characteristics of soils (Ussiri et al., 2006; Pardo et al., 2014; Yuan et al., 2018; Feng et al., 2019). Mining operations such as land clearing and removal of top soil layers result in a decrease in soil organic carbon (SOC) contents (Shrestha and Lal, 2011; Liu et al., 2017; Kumar et al., 2018). Observations on the coal-mined soils which has been reclaimed by planting forest tree for 22–25 years showed that OC content reached 4.7 to 41.6 g C kg⁻¹ soil (Yuan et al., 2017). Ahirwal and Maiti (2017) reported that the SOC content of the RMS was equivalent to that of the undisturbed site after 14 years of revegetation. The RMS is potentially

utilized for sequestration of carbon as indicated by considerable quantities of carbon are stored following the restoration of mined-soil (Tripathi et al., 2016). The SOC contents of the RMS was positively correlated with clay contents (Shrestha and Lal, 2011; Zhang et al., 2019). These results suggest that the RMS experiencing relatively high contents of clays has a high capacity for carbon sequestration.

The sorption of OC onto soil mineral surfaces performs a significant function in a variety of natural environments. Biodegradation of mineral-bound organic carbon, available nutrients and bioavailability of contaminants in soils are influenced by the OC sorption (Adhikari et al., 2019; Bento et al., 2019; Martz et al., 2019; Verbeeck et al., 2019). Only a portion of the OC sorbed to mineral surfaces could be released back to soils (Saidy et al., 2013; Nguyen and

Marschner, 2016), indicating high stability of mineral-bound OC. Moreover, the mineral bound-OC mineralize in a slower rate and to smaller magnitude than OC either in soil solution or not protected by soil minerals (Saidy et al., 2015; Adhikari et al., 2019; Fujii et al., 2019; Singh et al., 2019). Lately, Sleutel et al. (2010) showed experimental data that the microbial decomposition of OC in soils had a negative correlation with the amount of OC sorbed to minerals. Results of this study imply that the sorption of OC onto surface minerals control the deposition and the stabilization of OC in the soil environment. The significance of mineral-protected OC in controlling the contents of soil OC is found in several studies (e.g. Kalbitz et al., 2005; Oren and Chefetz, 2012; Giannetta et al., 2019; Nguyen et al., 2019).

Clay minerals and hydrous-oxides controls soil OC–mineral surface interaction. The sorption and the stabilization of OC in soil have been found to be influenced by the different types of phyllosilicate clays (Nguyen and Marschner, 2016; Singh et al., 2016) and soil clay contents (Roychand and Marschner, 2014; Hayakawa et al., 2018). Sites for OC sorption onto soil minerals are also provided by iron and aluminium hydrous–oxides; therefore, the presence of these hydrous–oxides in soils influence the mineral–OC associations. Several studies showed that the presence of oxalate-extractable and dithionite-extractable of iron and aluminium in soils increased the amounts and the strength of OC–mineral association (Oren and Chefetz, 2012; Saidy et al., 2013; Kutzner et al., 2018), thereby improved the stability of the mineral bound–OC against microbial decomposition (Hayakawa et al., 2018; Fujii et al., 2019; Singh et al., 2019). This suggests that the importance of phyllosilicate clays and hydrous–oxides of aluminium and iron in the increasing soil OC contents through soil OC stabilization.

Coal fly-ash that resulted from coal combustion in power plants contains high amounts of oxides of aluminium, iron, calcium, and magnesium (Pandey and Singh, 2010; Ram and Masto, 2014). Thus, coal fly-ash is frequently added to soils for soil property improvement. Many studies show the improvement of soil pH, soil available phosphorus, micronutrient contents, and soil microbial activities following coal fly ash application (Nayak et al., 2015; He et al., 2017; Ribeiro et al., 2018; Schönegger et al., 2018). Many studies were conducted recently on the influence of phyllosilicate clays and iron–aluminium hydrous–oxides on the preservation of OC in soils, while only a few

studies looked at the utilization of unused materials such as coal fly ash to improve the sorption of OC onto mineral surface for OC stabilization. The aim of this study was to examine the sorption of OC onto the RMS in response to coal fly ash application. For this aim, this study shows the influence of coal fly ash addition on (i) the changes in physical-chemical characteristics of the RMS, (ii) changes in the sorption isotherms derived from the Langmuir equation and (iii) desorption of OC bound to the surface of the RMS.

Materials and Methods

Sampling of soil and coal fly ash

The research site was located in the Kecamatan Satui, District of Tanah Bumbu, Province of South Kalimantan, Indonesia. The site is a surface mine of coal and was reclaimed by the application of topsoil, and then revegetated with *albizia chinensis*. This research site has an annual rainfall in the range of 1157–4459 mm, with nearly 75% rainfall occurs in the period of March–July. The mean annual rainfall and temperature are 3001 mm and 27.5 °C, respectively. Mean minimum temperature is 22.7 °C occurring in June, while the mean maximum temperature is 31.9 °C occurring in November.

Two reclaimed mining soils experiencing different ages: Gatokaca (reclaimed in 2014) and Sadewa (reclaimed in 1997) were chosen for this research. The soils were sampled from a depth of 0–30 cm using a cylindrical core (5 cm in diameter) at several different points. After cleaning for litter and plant roots, soil samples were placed on a rack in a closed room for air-drying, sieved to obtain soil samples with a size of < 2.0 mm, and kept in polyvinyl chloride (PVC) containers at 4 °C for soil characterization and incubation experiment. Coal fly ash was collected from the Coal Power Plant of Asam Asam, the District of Tanah Laut, Province of Kalimantan Selatan, Indonesia. Samples of coal fly ash were transferred to the laboratory, air-dried for several days, then sieved to obtain coal fly ash with a diameter of <2.0 mm prior to being used for the experiments. Coal fly ash properties for this research have been reported by Saidy et al. (2020).

Incubation experiment

An amount of air-dried soils (≈ 29 g) was mixed homogeneously with coal ash fly corresponding to field application of 0, 20, 40, 60 and 80 Mg ha⁻¹ in PVC tubes ($\varnothing=1.95$ cm). The mixtures of coal fly ash–soils were compressed to obtain a thickness

of 20 cm and a soil bulk density (BD) as determined in the field. Distilled water was then added carefully to the mixtures to obtain 70% water-filled pore space (WFPS), and then incubated at a constant temperature for 15 days. Addition of distilled water to the PVC tubes was conducted periodically to compensate for the loss of water through evaporation and to guarantee steady water contents during the incubation time. At the end of incubation, the soil mixtures were then sub-sampled for determining selected soil chemical properties.

Characterization of soils and coal fly ash-amended soils

Soil texture of reclaimed-mining soils was measured using the sieving and sedimentation method (Gee and Bander, 1986), and BD of soils was determined using the cylindrical metal ring sampler (Blake and Hartge, 1986). The measurement of the organic C and total N contents in the soils was carried out using a LECO CNS2000 (LECO Corporation, MI, USA). Soil pH was measured using the electrode glass method (1:5 = mass: volume) (McLean, 1982). Measurement of total P in soils was carried out by soil digestion using 60% HClO₄, then the amount of total P in the digested soils was quantified spectrophotometrically (Olsen and Sommers, 1982). Exchangeable cations of reclaimed-mining soils (Na, K, Ca and Mg) were obtained using 1.0 M NH₄OAc at pH 7.0, and the concentration of exchangeable cations in the extract was measured using atomic absorption spectrophotometry (Shimadzu AA6300G). Cation exchangeable capacity (CEC) of soils was quantified using the 1.0 M NH₄OAc method (Rhoades, 1982).

Selected soil chemical characteristics were measured at the end of the incubation experiment. Exchangeable Ca, Mg and CEC of coal fly ash-amended soils were quantified using the methods explained formerly. Extraction and determination of aluminium and iron by oxalate (Al_O and Fe_O) and dithionite (Fe_D) solutions were conducted using the method described by Blakemore et al. (1987). Adsorption and desorption of nitrogen at 77 K using an autosorb apparatus (Nova 4200 Analyser, Boynton Beach, USA) was applied to coal fly ash-amended soils to quantify the specific surface areas (SSA).

Preparation of dissolved organic carbon

Dissolved OC was acquired by the extraction of an oven-dried albizia (*Albizia chinensis*) shoot residue by combining 1000 mL of distilled water to 100 g of ground albizia (<2.0 mm) in 2000 mL of beaker glass, then swirled slowly for 15 minutes. After settling for 48 h, the filtrate was

separated from residues using a 0.45 µm cellulose membrane filter (Merck Chemicals and Life Science, Germany). This solution contains 17.8 g C L⁻¹ (determined using the wet digestion method (Heanes 1984)). Ten dissolved OC solutions ranging from 0 to 175 mg C L⁻¹ were made by diluting the filtrate of OC with a mixture solution of 1.4×10⁻⁴ M K₂SO₄, 1.4×10⁻⁴ M CaCl₂·2H₂O and 1.7×10⁻⁴ M NaCl, then the pH of the diluted OC solutions was corrected to 5.5 by HCl or NaOH addition.

Sorption and desorption experiments

The batch equilibrium method was employed to carry out the sorption experiments by adding of 30 mL of dissolved OC solution at pH 5.5 to 0.03 mg soils in centrifuge tubes. The mixture of dissolved OC-soils were stirred for 12 hours at room temperature, and the suspensions were centrifuged at 2000 g for 20 minutes, and the supernatants were filtered through 0.45-µm nylon syringe filters. The amounts of dissolved OC in the filtrate was quantified by the modified method of Walkley and Black (Heanes, 1984), and the amounts of sorbed dissolved OC onto soils was measured as differences between the concentration of OC in the initial and final solutions. The data of sorbed OC onto soils were then fitted to the Langmuir equation by the non-linear curve fitting method (de Levie, 2001).

Desorption experiments were conducted by exposing the soil-dissolved OC association with the greatest OC loading to 20 mL desorption solution, shaken for 12 hours at room temperature, centrifuged at 2000 g for 10 minutes, then a 0.45-µm nylon syringe filter was used to filter the supernatant. Desorption solution was a mixture solution of 1.4×10⁻⁴ M K₂SO₄, 1.4×10⁻⁴ M CaCl₂·2H₂O and 1.7×10⁻⁴ M NaCl, and the pH of the desorption solution was corrected to 5.5 by HCl or NaOH addition. Prior shaking, 20 mL desorption solution was combined to the settled soil-dissolved OC associations, centrifuged at 2000 g for 10 minutes, decanted cautiously to remove OC that did not sorb to the soils. The filtrate was kept at 4 °C before the amounts of OC in the desorption solution was quantified using by the modified method of Walkley and Black (Heanes, 1984). The amounts of desorbed OC were normalised to dried-weight of soils, and the % desorption was quantified as,

$$q_{des}/q_{sor} \times 100\%,$$

where q_{des} is the quantity of desorbed OC (mg C g⁻¹) and q_{sor} is the quantity of sorbed OC (mg C g⁻¹) at the greatest OC loading (data from the sorption experiment).

Statistical analysis

The effect of treatments on the Langmuir parameters and the chemical properties of coal fly ash amended soils were tested by the analysis of variance (ANOVA). Prior to the ANOVA test, the Shapiro-Wilk and Bartlett tests were conducted to validate the normality and homogeneity of data, respectively. The least significant difference (LSD) test at $P < 0.05$ was used to quantify differences in the effect of the treatments on the Langmuir parameters and the chemical properties of coal fly ash amended soils. The package of GenStat (Payne, 2008) was applied for all statistical analyses.

Results and Discussion

Properties of coal fly ash-amended soils

Gatokaca soil had a higher clay content than Sadewa soil, so that the soil texture in Gatokaca was clay, while Sadewa soil had a loam clay texture. Bulk density of Gatokaca soil also had bulk density was slightly higher compared to that of Sadewa soil. However, the organic content of C and total N was higher in Sadewa soil than in Gatokaca soil. Exchangeable cations and CEC in both soils were comparable (Table 1). Differences in soil physical and chemical characteristics between both soils were attributed to the difference in the duration of reclamation and revegetation. Sadewa soil had a longer duration of land reclamation and revegetation than Gatokaca soil so that the contribution of biomass from the vegetation resulted in the improvement of soil properties in Sadewa soil. Several previous

studies have also shown improvements in the properties of reclaimed mining soils after revegetation and land reclamation. Yuan et al. (2018) reported decreasing soil BD after 30 years of reclamation and revegetation. Organic carbon, total nitrogen and total phosphorus increased with increasing reclamation period (Xie et al., 2017). Mukhopadhyay et al. (2014) found that based on the mine soil quality index (MSQI), it will require at least 17 years for the recovery of mining soils to have adequate nutritional and microbial properties such as soils that have not been mined. Regardless of coal fly ash application, Sadewa soil had higher exchangeable Ca and Mg contents, CEC, contents of Fe_D , Al_O , Fe_O and SSA than Gatokaca soil (Table 2). Coal fly ash application to both soils increased the contents of exchangeable Ca and Mg, Fe_D , Fe_O , and Al_O , in which these increases were in line with the amounts of added coal fly ash (Table 2). Coal fly ash encompassed quite high amounts of Ca, Mg, Al and Fe (Saidy et al., 2020); thus, the addition of coal fly ash raised the amounts of exchangeable Ca and Mg, Fe_D , Fe_O , and Al_O of the amended soils. Results of this study are in agreement with the previous studies that reported the improvement of soil chemical characteristics following coal fly ash application (Pandey and Singh, 2010; Riehl et al., 2010). Contrast to other soil chemical characteristics, CEC reduced when coal fly ash was applied to the soils (Table 2). This reduction may be attributed to decreasing the number of negative charges of soils through the electrostatic interactions between the negative charges of soils and positive charges of cations contained in the coal fly-ash.

Table 1. Characteristics of soil used in the experiment. Numbers in the parenthesis showed the standard deviation (n=3).

Soil Characteristics	Gatokaca	Sadewa
Texture		
Sand (%)	18.49 (3.45)	30.64 (6.87)
Silt (%)	30.47 (9.34)	30.18 (8.34)
Clay (%)	51.04 (7.43)	39.18 (4.32)
pH (H ₂ O)	3.03 (0.53)	4.32 (0.76)
Bulk density (kg m ⁻³)	1.54 (0.10)	1.42 (0.09)
Organic C (g kg ⁻¹)	4.25 (0.98)	16.69 (2.67)
N (g kg ⁻¹)	0.62 (0.04)	1.60 (0.09)
P (g kg ⁻¹)	0.98 (0.06)	1.89 (0.08)
Exchangeable Ca (cmol kg ⁻¹)	0.83 (0.02)	1.18 (0.09)
Exchangeable Mg (cmol kg ⁻¹)	1.27 (0.06)	1.12 (0.09)
Exchangeable K (cmol kg ⁻¹)	0.85 (0.05)	1.54 (0.12)
Exchangeable Na (cmol kg ⁻¹)	0.23 (0.40)	0.34 (0.03)
Exchangeable Al (cmol kg ⁻¹)	4.34 (0.21)	3.65 (0.43)
CEC (cmol kg ⁻¹)	21.89 (1.23)	26.89 (2.12)

Table 2. Characteristics of the tropical reclaimed-mining soils applied with different amounts of coal fly-ash. Numbers in parenthesis showed the standard deviation (n=3).

Amount of coal fly-ash (Mg ha ⁻¹)	Ca* (cmol kg ⁻¹)	Mg (cmol kg ⁻¹)	CEC (cmol kg ⁻¹)	Fe _D (g kg ⁻¹)	Fe _o (g kg ⁻¹)	Al _o (g kg ⁻¹)	SSA (g kg ⁻¹)
Gatotkaca							
0	0.80 (0.10)	1.27 (0.03)	22.36 (0.55)	2.15 (0.19)	1.22 (0.20)	0.78 (0.12)	15.25 (0.99)
20	2.99 (0.07)	1.80 (0.10)	19.29 (0.86)	2.95 (0.19)	3.00 (0.12)	1.70 (0.17)	21.10 (1.95)
40	3.61 (0.08)	2.52 (0.12)	17.51 (0.25)	3.45 (0.07)	3.22 (0.05)	2.23 (0.11)	24.00 (0.39)
60	4.96 (0.13)	3.07 (0.18)	16.23 (0.22)	3.91 (0.06)	3.70 (0.16)	2.80 (0.22)	25.41 (1.09)
80	5.51 (0.03)	4.20 (0.14)	15.09 (0.81)	4.30 (0.23)	4.37 (0.17)	3.06 (0.07)	28.15 (1.44)
Sadewa							
0	1.16 (0.14)	1.01 (0.22)	26.88 (1.10)	4.12 (0.14)	2.25 (0.09)	1.55 (0.33)	19.87 (1.35)
20	3.44 (0.60)	3.03 (0.09)	23.17 (0.33)	5.32 (0.30)	3.71 (0.36)	2.48 (0.18)	26.22 (1.90)
40	4.59 (0.08)	3.58 (0.12)	20.84 (0.47)	5.92 (0.08)	4.56 (0.22)	2.99 (0.12)	27.47 (1.12)
60	6.06 (0.06)	4.53 (0.25)	18.73 (0.66)	6.12 (0.14)	5.19 (0.25)	3.35 (0.18)	30.24 (1.81)
80	7.42 (0.51)	5.37 (0.59)	17.03 (0.24)	6.51 (0.29)	5.80 (0.17)	3.49 (0.22)	31.10 (2.05)

*Ca = exchangeable calcium; Mg = exchangeable magnesium; CEC = cation exchangeable capacity; Fe_D = dithionite-extractable iron; Fe_o = oxalate-extractable iron; Al_o = oxalate-extractable aluminium; SSA = specific surface areas.

Results of our previous study showed that the coating of oxide-hydroxides of Fe and Al to phyllosilicate clays resulted in a reduction in CEC of the clays due to ionic bonding between negative charges of phyllosilicate clays and positive charges of oxide-hydroxides of Fe and Al (Saidy et al., 2013).

Organic carbon sorption to reclaimed-mining soils with coal fly-ash addition

The sorption isotherms of dissolved OC to reclaimed-mining soils applied with the different amounts of coal fly-ash are displayed in Figure 1. All of these isotherms can be defined as type L isotherms, which could be modelled satisfactorily using the Langmuir equation (Figure 1), with *r*² values were in the range of 0.97 to 0.99 (Table 3). Increases in the *Q*_{max} values of both Gatotkaca and Sadewa soils were observed with increasing the amounts of applied coal fly-ash (Table 3). Increasing these *Q*_{max} values may relate to increasing SSA of soils. The addition of 20–80 Mg ha⁻¹ coal fly ash resulted in increases in SSA from 15 to 28 m² g⁻¹ and from 20 to 31 m² g⁻¹ for Gatotkaca and Sadewa soils, respectively (Table 2). Surface areas of soils, as measured by the adsorption of dinitrogen gas, could be used to estimate the external surface area of minerals that is possibly accessible for OC sorption. Relationship between SSA and the sorption of OC has been found in the previous studies. Saidy et al. (2013) reported that coating of clay minerals with iron oxide led to increases in the SSA, and eventually resulted in a higher OC sorption capacity than clay minerals without iron oxide coating.

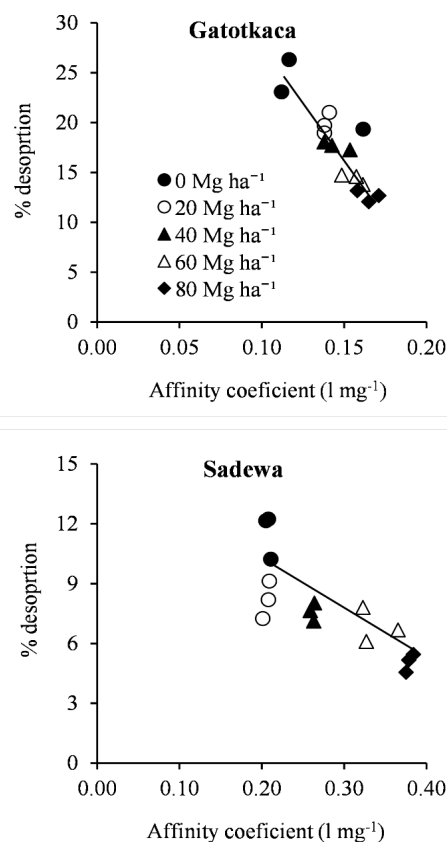


Figure 1. Sorption isotherms of dissolved OC onto two reclaimed-mining soils applied with different amounts of coal fly-ash. Symbols indicated experimental data while the lines represented the Langmuir equation fitted to the experimental data.

Table 3. Parameters of the Langmuir equation fits to the sorption of dissolved OC onto two reclaimed-mining soils applied with different amounts of coal fly-ash. Numbers in parenthesis showed the standard deviation (n=3).

Amount of fly-ash (Mg ha ⁻¹)	Q _{max} (mg kg ⁻¹)	k (L mg ⁻¹)	r ²
Gatotkaca			
0	1424.04 (38.42) a*)	0.130 (0.016)	0.99
20	1595.07 (13.96) b	0.139 (0.001)	0.97
40	2270.56 (12.81) c	0.145 (0.005)	0.99
60	2768.92 (10.37) d	0.156 (0.004)	0.99
80	3124.29 (9.30) e	0.165 (0.004)	0.99
Sadewa			
0	3452.77 (2.52) a	0.208 (0.002)	0.99
20	3645.23 (10.61) b	0.206 (0.003)	0.99
40	3820.36 (16.58) c	0.262 (0.002)	0.99
60	4031.32 (7.07) d	0.338 (0.014)	0.99
80	4216.99 (1.21) e	0.381 (0.005)	0.99

*) Similar letters in each column indicated no statistical difference between treatments based on the LSD test at P<0.05.

Significant positive relationships between SSA and the sorption of OC were reported in other studies (Kahle et al., 2004; Rakhsh et al., 2020). The higher SSA of soils observed with the larger amount of added fly-ash have been suggested to favour more adsorption sites provided by fly-ash for OC–soil interactions and thereby facilitate higher the OC sorption capacity.

Increasing Q_{max} values of soils with coal fly ash application may also be ascribed to increasing the contents of exchangeable Ca and Mg. Increasing exchangeable Ca and Mg with coal fly ash application (Table 2) was coincident with increasing Q_{max} values of amended soils (Table 3). Polyvalent cations such as Ca and Mg increase OC sorption onto soils through their function as bridging between negatively charges of soils and negatively charges of OC (Feng et al., 2005; Sowers et al., 2018).

Result of this result is in agreement with other studies (e.g. Mavi et al., 2012; Saïdy et al., 2013; Singh et al., 2018) who observed increasing OC sorption onto soils through cation bridging with the presence of exchangeable Ca and Mg. Increasing contents of Fe_o, Fe_D and Al_o due to coal fly ash application also contributes to increasing the Q_{max} values of reclaimed-mining soils. It is well documented that reactive sites provided by iron oxides (Fe_{ox}) and aluminium oxides (Al_{ox}) and amorphous aluminosilicate phases control the amounts of OC sorption onto soils (Eusterhues et al., 2005). Kothawala et al. (2009) reported a positive and significant correlation between the amounts of Fe and Al oxides and the Q_{max} values observed for 52 soil samples. Removal of sesquioxides (Fe/Al oxides) from soil clay fractions by extraction resulted in

lower OC sorption compared to those without sesquioxide removal (Singh et al., 2016). Under such the experimental settings, we observed that the application of 20–80 Mg coal fly-ash ha⁻¹ to Gatotkaca soil led to 12–119% increases in the Q_{max} values, while the values increased only 6–22% in Sadewa soil (Table 3). More responsive Q_{max} values to coal fly ash application in Gatotkaca soil than in Sadewa soil may attribute to larger changes in the amounts of Fe_D, Fe_o, and Al_o in Gatotkaca soil than in Sadewa soil. The amounts of Fe_D, Fe_o, and Al_o in Gatotkaca soil increased 37–100%, 146–258%, and 119–294% with 20–80 Mg coal fly ash ha⁻¹, respectively, while only 29–58%, 65–158%, and 59–125% increases in iron- and aluminium-oxides were observed in Sadewa soil (Table 3). Results of this research indicate the profound effect on iron- and aluminium-oxides on the sorption of OC onto soils.

Desorption of organic carbon to soils with coal fly-ash application

Not all OC sorbed onto soils could be removed using a single extraction. Result of variance analysis revealed that the proportion of OC desorbable from Gatotkaca and Sadewa soils was substantially affected by the coal fly ash addition (P<0.05). The amounts of desorbable OC from both soils reduced with coal fly-ash addition, in which desorption of OC was higher in Gatotkaca soil compared to that in Sadewa soil (Table 4). Coal fly-ash application to Gatotkaca soil caused a reduction in desorbable OC from 23% to 13–20%, while reduction from 12% to 5–8% in the amount of desorbed OC was observed from Sadewa soil (Table 4). The amount of desorbed

OC (%) in the current study was lower than stated by Singh et al. (2016) who found that 6–55% of sorbed OC onto soil clay fractions varying in mineralogy was released by a single extraction. Kahle et al. (2004) found 17–50% OC desorption from different phyllosilicate clays and soil clays fraction. A similar result was also reported by Mikutta et al. (2007) who found 2–35% desorption of OC originally sorbed to pyrophyllite, goethite and vermiculite. However, results obtained in this study were in line with results of our previous study that reported only 6–14% desorption of OC originally sorbed to illite and smectite coated with

oxy-hydroxides of iron (Saidy et al., 2013). The addition of coal fly ash improved the contents of Fe_D, Fe_O and Al_O in soils (Table 2), which in turn affected the desorption of OC from soils. A smaller proportion of OC desorption was noticed with larger coal fly ash application may attribute to the stronger OC–iron oxide associations (Kahle et al., 2004; Singh et al., 2016). Results of this study confirmed that strong chemisorptive bonding of OC–iron oxides controls the amounts of released OC originally sorbed onto iron oxides and soil samples (Kaiser and Guggenberger, 2000).

Table 4. Desorption of OC observed at the maximum sorption onto two reclaimed-mining soils applied with different amounts of coal fly ash. Numbers in parenthesis showed the standard deviation (n=3).

Amount of coal fly-ash (Mg ha ⁻¹)	Adsorption (mg kg ⁻¹)	Desorption (mg kg ⁻¹)	% desorption
Gatatkaca			
0	1335.31 (58.45)	243.96 (13.40)	22.91 (2.03) d*
20	1581.50 (17.25)	227.04 (14.44)	19.90 (0.60) c
40	2103.91 (3.42)	238.87 (7.63)	17.68 (0.23) b
60	2605.39 (6.05)	213.50 (11.13)	13.47 (0.29) a
80	2977.87 (13.52)	197.36 (15.35)	12.64 (0.32) a
Sadewa			
0	3231.75 (7.26)	372.94 (21.50)	11.54 (0.66) c
20	3462.21 (13.22)	283.53 (18.39)	8.19 (0.55) b
40	3655.37 (13.48)	277.61 (9.09)	7.60 (0.27) b
60	3927.29 (9.19)	269.70 (20.36)	6.86 (0.50) b
80	4139.42 (16.76)	209.34 (11.67)	5.06 (0.27) a

*) Similar letters indicated no statistical difference between treatments based on the LSD test at P<0.05.

The increasing affinity of OC sorbed to soils with coal fly ash application may also contribute to decreasing OC desorption. The affinity coefficient derived from the Langmuir equation had a negative and significant correlation with the proportion of desorbed OC ($r = -0.87$; $P < 0.01$ for Gatatkaca soil, and $r = -0.80$; $P < 0.01$ for Sadewa soil Figure 2). This result is in line with the concept that strong OC sorption onto the mineral surface led to the small proportion of OC desorption (Henrichs, 1995). Results of this study are also consistent with previous studies that found OC desorption decreased with increasing the affinity of OC derived from the Langmuir equation (Mikutta et al., 2007; Saidy et al., 2013).

Conclusion

This study revealed that, under the experimental settings, coal fly ash application caused changes in the properties of reclaimed-mining soils.

Increasing the amounts of applied coal fly ash lead to increasing exchangeable magnesium, calcium, oxalate and dithionite extractable iron and aluminium and specific surface areas of reclaimed-mining soils. As a consequence, the maximum sorption capacity of reclaimed-mined soils for organic carbon sorption increased with coal fly ash application.

Results of this study demonstrate that the capability of reclaimed mining soils to adsorb organic carbon could be controlled by interactions with coal fly ash; which in turn multivalent cations and oxide hydrous iron and aluminium present in the coal fly ash seem to modify the sorption capacity of the soils. Not all organic carbon initially sorbed onto reclaimed-mining soils (5–23%) was freed using a single extraction step, suggesting strong sorption of organic carbon onto the mineral surfaces. Fly ash application reduced desorption of organic carbon, in which a higher amount of applied coal fly ash led to a

lower proportion of desorbable organic carbon from soil-coal fly ash association.

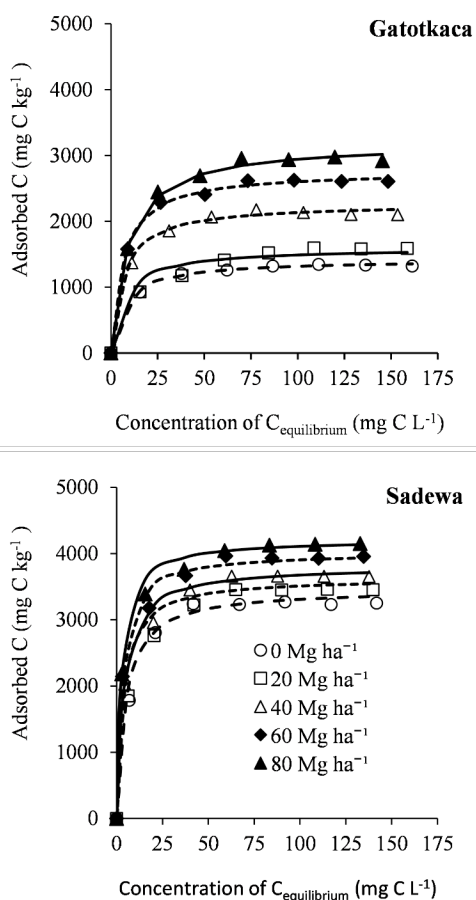


Figure 2. Relationship between the affinity coefficient (k) derived from the Langmuir equation and OC desorption of two reclaimed-mining soils applied with different amount of coal fly-ash.

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