

Modification of Surface Charges on Ex-Gold Mining Soil Ameliorated with Activation of Sub-Bituminous Coal - NaOH

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Abstract—The high mercury contamination in the ex-gold mining soil is the impetus for the development of soil remediation with amelioration technology that utilizes sub-bituminous coal activated with 10% NaOH (SC-NaOH) to modify the soil surface charge by affecting the chemical properties of the ex-gold mining soil. This research aimed to determine and study the modified surface charge of ex-gold mining soil ameliorated with SC - NaOH. The experimental design used in this study was a Completely Randomized Design with three replications. The treatment was implemented in a pot with equivalent dose: A = 0 (0.0g); B = 10 (0.5g); C = 20 (1.0g); D = 30 (1.5g), and (E) 40 t ha⁻¹ (2g 100g⁻¹ soil). The results showed amelioration technology with SC - NaOH, at the application of 40 t ha⁻¹ on ex-gold mining soils, can modification of soil surface charge through changes in chemical characteristics by increasing the pH H₂O EC, CEC, and SOM, respectively of 5.77; 4.33 dS m⁻¹; 2.41 cmol(+) kg⁻¹ and 17.15% compared to the control. Soil surface charge supported by soil minerals [Quartz (SiO₂), Graphite (C), and Periclase (MgO)] and also happening decreases transmittance in the OH group (0.18%), which causes an increased adsorption capacity of the soil to Hg, which causes a decrease in total Hg of 2.84 mg kg⁻¹ compared to the control. The correlation between total Hg and soil chemical properties in ex-gold mining soil ameliorated with SC - NaOH (Total Hg with SOM > ΔpH > EC > pH H₂O > CEC).

Keywords—Activation; amelioration technology; ex-gold mining soil; NaOH; soil surface charge; sub-bituminous coal.

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I. INTRODUCTION

Gold mines may be discovered in the Dharmasraya Regency near the Batanghari River and its tributaries. Panning for gold is used in mining activities. The problem frequently seen in historic gold mines is the highest heavy metal level of > 0.3 ppm (polluted). This can contaminate the mining region's ecosystem, reducing soil production. Soil contamination arises as a result of heavy metals in historic gold mines. Heavy metals in the soil can carry out ion exchange and adsorption processes in tiny particles with broad surfaces and opposing charge groups [1].

Ex-mining land includes a high concentration of heavy metals, particularly mercury, which causes harm and endangers the health of the soil, plants, and humans. Mercury (Hg) is a heavy metal that is highly harmful since it may pollute the environment. The typical limit for heavy metal Hg in the soil is 0.3 ppm [2]. One of the reasons for the high mercury level is that it is so close to gold mining, namely the

amalgamation process. High levels of mercury (Hg) in the soil can cause plants to absorb a large amount of Hg. Because it is a toxic accumulation, Hg that is translocated into plants can accumulate in the plant body and stay a long time. This becomes important for selecting the correct remediation method to use; one of the novelty techniques being developed is amelioration technology. Amelioration technology is one of the technologies that can increase soil fertility and will indirectly increase the soil's surface charge in absorbing organic or inorganic pollutants [3]. Increasing the negative charge of the soil can be done by increasing the cation exchange capacity (CEC) and soil organic matter (SOM) and analyzing the soil pH PZC (point of zero charges).

Increasing soil pH and CEC are essential indications of surface charge activity in the soil, also known as pH PZC. pH PZC or pH₀ is the pH value of the soil solution where the positive and negative charges on the soil colloids are equal or when the charge on the soil colloids is equal to zero [4], [5]. The size of the burden on the soil colloid system at a given

pH is reflected by pH PZC, or the magnitude of the colloid load is defined by the connection between pH H₂O and pH PZC. If the pH PZC value is close to or greater than the pH H₂O value of the soil, the colloid surface is positively charged, and if it is smaller, then the colloid surface is negatively charged. pH PZC is an essential indication in the soil management system because it is directly related to the availability of nutrients and the absorption of organic or inorganic pollution in the soil. This phenomenon can be modified through amelioration technology, affecting the concentration level of pH, EC, CEC, SOM, and minerals. One of the ameliorant materials used is Sub-bituminous coal activated with 10% NaOH.

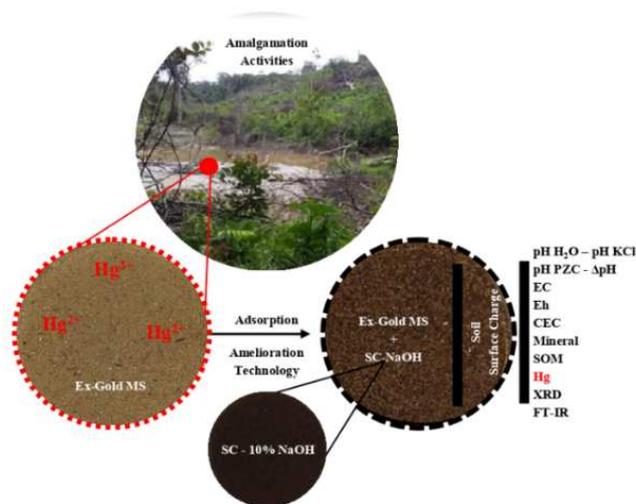


Fig. 1 Modification of surface charges of ex-gold mining soil with Sub-bituminous coal activated with 10% NaOH.

The use of sub-bituminous coal Indonesian (SC) as a soil enhancer begins with its potential as the highest humic substance (HS) source compared to other organic materials such as peat and compost. SC as HS has been used on marginal lands such as *Ultisols* and *Oxisols* [6]–[11]. Optimization of SC utilization was also developed through a chemical activation process using alkaline materials such as NaOH and chemical fertilizers such as *Urea*, *KCl*, and *NaCl*. Based on various studies that have been carried out, it has been proven to increase soil pH, CEC, and SOM, and NaOH is the best alkaline material in the SC activation process as a soil ameliorant.

Activation of SC with 10% NaOH (SC-NaOH) can increase the chemical properties of SC, such as pH (5.34 to 12.65 units) and CEC (24.39 to 148.20 cmol(+) kg⁻¹). There is an increase in the number of functional groups O-H, C=O, and CH₃ and can also increase the chemical properties of Ultisol soils such as pH H₂O, CEC, organic C, available P, and total N respectively 1.49 units, 28.08 cmol(+) kg⁻¹, 1.63% C, 2.37 ppm P, 0.06% N, and reduced Al-dd by 1.17 cmol(+) kg⁻¹ and Sodium Adsorption Ratio (SAR) by 0.03% and Exchangeable Sodium Percentage (ESP) of 0.82%, compared to control [12]. The potential and utilization of SC - NaOH that has been carried out, but in the context of controlling heavy metals with high mobility, such as Hg, have not yet been applied to modify soil surface charge. This research aims to determine and study the modified surface charge of ex-gold mining soil amelioration with SC - NaOH.

II. MATERIALS AND METHODS

This research was conducted at the Laboratory of Soil Chemistry and Fertility, Faculty of Agriculture, University of Andalas (UNAND), Padang, from May to July 2022. Analysis of XRD and FT-IR spectrum at the Laboratory of Chemical and Physic, Faculty of Mathematics and Natural Science, State Padang University (UNP).

A. Experimental Design

The experimental design used in this study was a Completely Randomized Design (CRD) with three replications. The treatment was implemented in a pot with equivalent dose: (A) 0 [0g 100g⁻¹ soil], (B) 10 [0.5g 100g⁻¹ soil], (C) 20 [1g 100g⁻¹ soil], (D) 30 [1.5g 100g⁻¹ soil], and (E) 40 t ha⁻¹ [2g 100g⁻¹ soil].

B. Activation of Sub-Bituminous Coal with NaOH and Soil Sampling

SC was taken from the Bonjol Pasaman, West Sumatra, at a depth of 1-2 meters from the ground soil [13], then cleaned, smoothed with Disc Mill model FFC 23, and sieved with a sieve of 500µm Electromagnetic Sieve Shaker EMS-8 for 10 minutes, after SC is obtained. The SC is weighed based on the dosage and percentage of the formulation used (sample weight). Activation is carried out by giving 10% NaOH as the activating agent dissolved with H₂O based on the field capacity of SC, and the calculations are shown in Formula 1.

$$\text{NaOH (g)} = 10 / 100 * \text{Sample Weight} \quad (\text{F.1})$$

Furthermore, the composition is stirred evenly, allowed to stand for 1*24 hours in a 250 mL beaker, and covered with plastic wrapping. The results of SC (SC - NaOH) are dried using an oven at a temperature of 70°C for 1*24 hours to homogenize the water content in the ameliorant. Ex-gold mining soil (Ex-Gold MS) samples were taken in a composite at 0 - 20 cm depth from Dharmasraya Regency West Sumatra. SC - NaOH was dried, ground, sieved with a 2 mm sieve, homogenized, and put into the experiment pot. SC - NaOH that has been weighed as much as treatment is then incubated into the soil (100g) for one week, and soil samples were taken to analyze changes in soil chemical properties after incubation.

C. Analysis of Soil and Statistical Analysis

Soil analysis includes pH H₂O (pH-active), pH KCl (pH-potential), pH PZC [(2*pH KCl) - pH H₂O], and ΔpH (pH H₂O - pH KCl), electrical conductivity (EC) and potential redox (Eh) [1:1] by the Electrometric method, CEC, by the leaching of NH₄OAc pH seven method, Mineral, and SOM by the dry-ashing method. Ex-gold mining soil and Ex-gold mining soil ameliorated with selected SC - NaOH dose were x-rays diffracted using a Bruker D8 Advance with Davinci X-ray Diffractometer with a Cu radiation source in the range 200 to 900, with a step size of 0.020. Whereas FT-IR spectra were measured in the 600 to 4000 cm⁻¹ range using an ABB instrument MB-3000 Series FTIR Spectrometer with Internal Reflection Element (IRE) of diamond in absorbance mode [14] [15] [16].

The statistical analysis has carried the software SPSS 16.0, Statistics 8, and Microsoft Excel 2016 to analyze soil. Bivariate correlations using a Pearson correlation coefficient

and a two-sided significance test were used; the coefficient R^2 and p-values [$**$ = Correlation is significant at the 0.01 level (2-tailed); $*$. Correlation is significant at the 0.05 level (2-tailed)].

III. RESULTS AND DISCUSSION

A. Chemical Characteristics of Ex-Gold Mining Soil Ameliorated with Sub-Bituminous Coal - NaOH

The results of the chemical characteristics of the ex-gold mining soil ameliorated with SC-NaOH can be seen in Table 1. The ex-gold mining soil's pH value is described through H_2O (active) and 1M KCl (potential). The presence of H^+ charge in soil solution and soil colloids, where the average pH values of H_2O and KCl of the ex-gold mining soil ameliorated with SC-NaOH were 8.19 and 5.92, respectively. The pH value with the KCl solution is lower than with the H_2O solution. In Figure 2A, the application of SC-NaOH significantly increased the pH of H_2O and KCl while keeping the pH value of the KCl solution smaller than H_2O . Also, increasing the pH and the application dose at a dose of 40 t ha^{-1} SC - NaOH was the best in increasing the pH H_2O by 5.77 and pH KCl of ex-gold mining soil by 2.63 and 2.53 at a dose of 30 and 40 t ha^{-1} SC - NaOH, respectively, compared to the control. Application of Sub-bituminous coal activated with 10% NaOH can increase soil pH value because it has COOH and OH functional groups. The HS from SC - NaOH comprises hydroxyl and carboxyl functional groups that may bind Hg soluble, which indicates that consuming H^+ ions are soluble in the soil solution, resulting in lowered and raised soil pH [17].

TABLE I

DESCRIPTIVE STATISTICS OF CHEMICAL CHARACTERISTICS OF EX-GOLD MINING SOIL AMELIORATED WITH SUB-BITUMINOUS COAL - NaOH

Analysis	Unit	N	Min	Max	Mean	SE	SD
pH H_2O	unit	15	4.20	10.10	8.19	0.56	2.18
pH KCl			4.10	6.90	5.96	0.26	1.02
EC	dSm $^{-1}$		0.05	0.70	0.35	0.06	0.23
Eh	volt		0.08	0.28	0.14	0.02	0.07
CEC	cmol(+) kg^{-1}		2.41	5.22	3.61	0.25	0.97
Mineral	%		83.90	98.41	89.87	1.34	5.17
SOM			1.62	19.19	11.61	1.61	6.22
a pH PZC	unit		3.30	4.00	3.73	0.05	0.19
b Δ pH		0.20	6.60	4.47	0.59	2.32	
Total Hg	mg kg^{-1}		3.85	6.98	5.29	0.27	1.04

Remarks: EC = Electrical conductivity; Eh = Potential redox; CEC = Cation exchange capacity; SOM = Soil organic matter; N = Number of observation values; SE = Std. Error and SD = Std. Deviation

Formula : a pH PZC = ($2 \times$ pH KCl) - pH H_2O ; b Δ pH = pH H_2O - pH KCl

Table 1 shows the average EC and Eh on ex-gold mining soil ameliorated with SC - NaOH of 0.35 dS m^{-1} and 0.14 Volts, respectively. In Figure 2B, the EC value increases with the increase in the application dose of SC - NaOH. The effect of SC - NaOH was significant on EC on ex-gold mining soil with the best dose on 40 t ha^{-1} with an increase of 0.64 dS m^{-1} compared to the control. The study of humic solutions by conductometric means is possible because the dissolved humates carry a negative charge, primarily due to dissociated carboxyl moieties, and therefore move in an external electric

field [18]. The motion of a singly charged ion is determined by a simple force balance involving the electric field and the viscous resistance of the solution. However, it looks different from the potential redox value in the ex-gold mining soil, where the Eh value decreases along with the increase in the SC - NaOH application dose. It significantly affects Eh in the ex-gold mining soil with a decrease of 0.19 at a dose of 40 t ha^{-1} compared to controls. The electron transfer rate commonly limits reduction reactions under anaerobic conditions, which redox mediators can accelerate with specific reactions. HS contain redox-active functional groups such as quinones and can transfer electrons and donate them to minerals, thus accelerating the reduction [19].

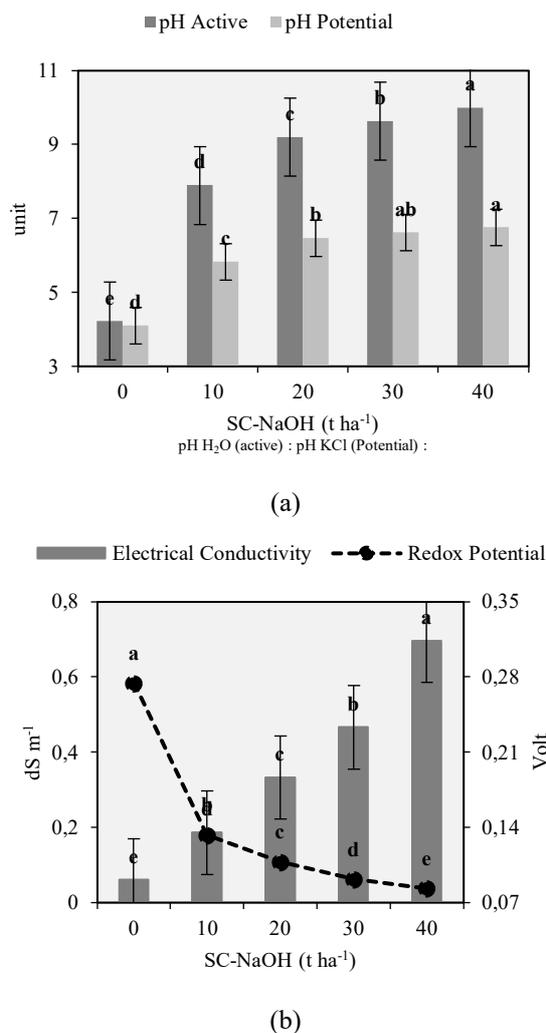


Fig. 2 pH H_2O (CV = 1.61; DNMRT Test = $**$; SE = 0.11); pH KCl (CV = 1.89; DNMRT Test = $**$; SE = 0.09) (a); EC (CV = 5.64; DNMRT Test = $**$; SE = 0.02) and Eh (CV = 1.80; DNMRT Test = $**$; SE = 0.002) (b) on ex-gold mining soil ameliorated with sub-bituminous coal - NaOH.

The motion of single-charged ions is determined by a simple balance of forces involving the electric field and the viscous resistance of the solution. The exchangeable sodium percentage (ESP), cation exchange capacity (CEC), soil specific surface area (S), soil surface charge density (δ_0), soil surface potential (ϕ_0), and soil surface electric field strength is the most important soil surface electrochemical parameters (E_0) [20] [21]. The electron transfer rate generally limits the reduction reaction under anaerobic conditions, which can be

accelerated by redox mediators with certain reactions. HS contains redox-active functional groups such as quinones and can transfer electrons and donate them to minerals, thereby accelerating reduction [22].

The average CEC on ex-gold mining soil ameliorated with SC - NaOH is 3.61 cmol(+) kg⁻¹ (Table 1). application of SC - NaOH, the CEC value increased along with the increase in the applied dose and significantly affected the CEC of the ex-gold mining soil. The 40 t ha⁻¹ dose is the best in increasing the CEC of ex-gold mining soil by 2.41 cmol(+) kg⁻¹ compared to the control.

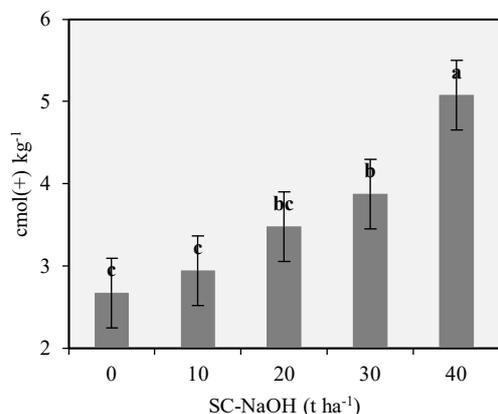


Fig. 3 CEC (CV = 13.76; DNMRT Test = **; SE = 0.41) on ex-gold mining soil ameliorated with sub-bituminous coal - NaOH.

The ability of HS with activation of SC - NaOH to adsorb cations follows the lipotropic sequence eg. Al³⁺ = (H⁺) > Fe³⁺ > Fe²⁺ > Ca²⁺ > Mg²⁺ > K⁺ = NH₄⁺ > Na⁺. The Sorption of NH₄⁺ is similar to Na⁺. The exchange of cations in solution or that adsorbed by clay-HS from SC - NaOH occurs during cation adsorption by humic acid. The cations are easily absorbed by the roots, increasing micronutrient transfer to the plant circulatory system and thus changing the cation balance. Adsorption of cations or metals by HS from SC - NaOH can be through as follows:

- Direct adsorption.
- Complexation or outer-sphere interactions for hydrated.
- Serving as a cation bridge (outer-sphere complex) through direct or indirect chelation.
- Interaction with Hg - HS HS from SC - NaOH aggregates or with amine groups.

Interaction of clay with HS from SC - NaOH has a solid affinity for weak acids containing phenolic hydroxyl and carboxyl groups. Changes in the electrochemical properties of clays are closely related to the number of Al-hydroxy complexes incorporated in the clays and their chemical composition and charge properties [23]. The effect of the amount of interlayer on the cation exchange capacity of the clay affects the zero charge point [24].

Table 1 shows the average Mineral and SOM content value in ex-gold mining soil ameliorated with SC - NaOH of 89.87% and 11.61%, respectively. In Figure 4, the application of SC - NaOH decreases the mineral content and increases the SOM content along with the increase in the given application dose (0 - 40 t ha⁻¹) where the application of SC - NaOH is significant to the mineral and SOM content. On ex-gold

mining land. The decrease in mineral content in the application of 40 t ha⁻¹ SC - NaOH was 14.22%, compared to the control, and also seen the best dose in increasing SOM was 40 t ha⁻¹ by 17.15%, compared to the control. Sub-bituminous coal has an ash content of around 34.90% - 46.30% and a C content of around 33.68% - 44.28% [25]. A typical HS from SC - NaOH molecule polymer structure may consist of a six-carbon aromatic ring containing di- or trihydroxy phenols connected by -O-, -NH-, -N-, -S-, and group-OH and quinone (O- C₆H₄-O-). HS is a cyclic organic molecule with a high molecular weight, a long chain, and an active carboxyl group (-COOH) and phenolic group (-OH), which function as importers and binders of cations/anions at specific pH levels (pH-dependent charge) [26]. Carboxylate is released from certain carboxyl groups below pH 6, increasing the negative charge on the functional groups [27]. H⁺ dissociation from amide (=NH) can also enhance the negative charge. Protonated groups such as R-OH₂ and R-NH₃ can produce a positive charge, but the overall humus is negatively charged [28].

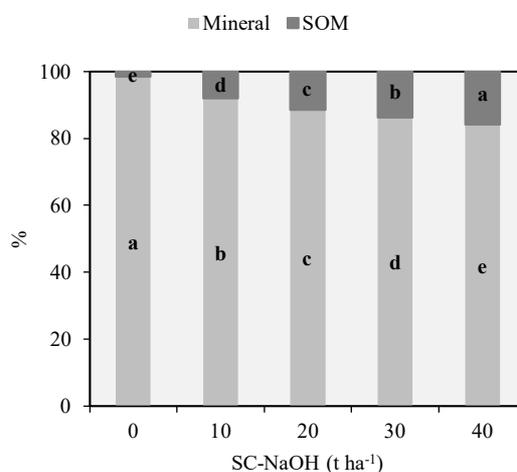


Fig. 4 Mineral (CV = 0.35; DNMRT Test = **; SE = 0.26) and SOM (CV = 3.54; DNMRT Test = **; SE = 0.35) on ex-gold mining soil ameliorated with sub-bituminous coal - NaOH.

An increase in pH, EC, CEC, and SOM will indirectly increase the activity of the negative charge of the soil. This modification is essential to increase the availability of nutrients and the absorption of pollutants (organic and inorganic), especially in ex-gold mining soil. The use of SC - NaOH in amelioration technology increased the range of negative charge on the surface charge of the soil colloid. When SC - NaOH was applied to ex-gold mining soils, the average pH PZC and pH were 3.73 and 4.47, respectively. The kind of charge in ex-gold mining soil following SC - NaOH treatment. The zero-charge point is often included in the surface charge characteristics and the acidity/alkalinity properties of the soil surface (PZC). The hydroxyl functional sites are proton adsorption sites and inorganic and organic pollutant adsorption sites. PZC is a state in which positive and negative charges are equal. The important indices in determining the buffering properties of soil [29].

In Figure 5, the pH PZC decreased with increasing application dose, where the application of SC - NaOH was significant for pH PZC, while ΔpH increased with increasing dose. However, the 40 t ha⁻¹ dose was still the best in

increasing ΔpH by 6.25, compared to the control. The pH of PZC is lower than the pH of H_2O , so the net surface charge is negative in the soil. The ex-gold mining soil with amelioration of 40 t ha^{-1} SC - NaOH has a longer negative charge range (ΔpH) on the colloidal soil surface than the control. The negative charge activity will be higher and expected to overcome pollution by Hg in ex-gold mining soil. The description of surface charge usually consists of permanent and variable charges, two types of surface charge in the soil [30]. Through isomorphous substitution effects in clay minerals, permanent loads are formed during soil formation or weathering processes [31]. The variable charge arises from surface functional groups' protonation/ deprotonation process. The soil is mainly found in clay minerals and metal oxides [32].

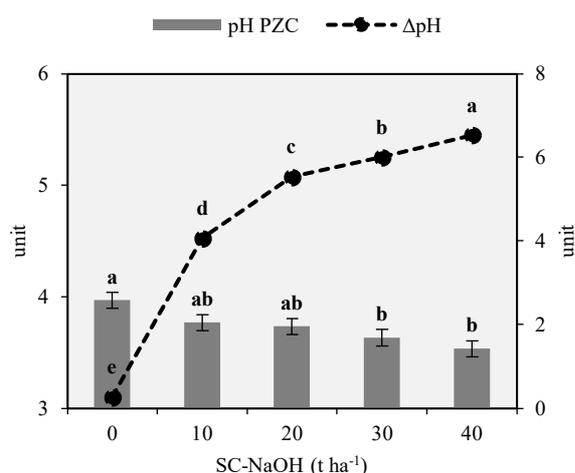


Fig. 5 pH PZC (CV = 3.92; DNMRT Test = *; SE = 0.12) and ΔpH (CV = 3.66; DNMRT Test = **; SE = 0.13) on ex-gold mining soil ameliorated with sub-bituminous coal - NaOH.

B. Characteristics of XRD and FT-IR on Ex-Gold Mining Soil Ameliorated with Sub-Bituminous Coal - NaOH

The mineral composition of ex-gold mining and ex-gold mine soil with amelioration of SC - NaOH was determined using X-ray diffraction (XRD). Table 2 and Figure 4 show the mineral composition's descriptive and XRD diffractogram. The results of the XRD analysis showed a decrease in d-spacing (\AA) from 3.34 to 3.33 after applying 40 t ha^{-1} SC - NaOH, with results indicating the identification of Quartz, Graphite, and Periclase minerals.

TABLE II
CHARACTERISTICS MINERAL ASSIGNMENTS OF EX-GOLD MINING SOIL AMELIORATED WITH SUB-BITUMINOUS COAL-NAOH

Soil	Pos. [$^{\circ}2\theta$.]	d-spacing [\AA]	Description of Minerals*
			Pattern List (Score - Mineral - Scale Fac.) : Chemical Formula
Ex-Gold MS	26.69	3.34	(79-Quartz-0.733) : SiO_2
Ex-Gold MS + SC - NaOH	26.77	3.33	(74-Quartz-0.733) : SiO_2 (26-Graphite-0.059) : C (19-Periclase-0.016) : MgO

Remarks: Ex-GM = Ex-gold mining soil; Ex-GM + SC-NaOH = Ex-gold mining soil ameliorated with 40 t ha^{-1} sub-bituminous coal-NaOH.

Quartz is a mineral with the chemical formula SiO_2 that occurs naturally in two forms, as evidenced in both types of minerals detected in ex-gold mining soil and after applying 40 t ha^{-1} SC - NaOH. The trigonal variety, low-temperature alpha-quartz, which is stable on the surface, can experience the most frequent and substantial modifications. The alpha-quartz crystal structure is a three-dimensional network of $[\text{SiO}_4]$ 4-tetrahedra connected by oxygen atoms and organized in helical chains (c) along to form structural channels (Fig. 7A). The quartz structures correspond to the right or left crystal morphology, which may be determined by the relative placement of trapezoidal face (x) to the positive main rhombohedron face (r). The c axis in trigonal symmetry is similar to the optical axis; quartz has an alpha-optic uniaxial characteristic. [33].

The silicon atoms in the quartz structure are on the double axis, whereas all oxygen atoms are in the exact location. Quartz is one of the purest minerals in the earth's crust in terms of chemical contaminants expressed as trace element concentrations. Due to ion charge and radius constraints, only a few ions may replace Si^{4+} in the crystal lattice or integrate with the interstitial region [34]. As a result, most elements are present at less than one ppm concentration in quartz. Monovalent and divalent ions can occupy interstitial lattice sites at low quantities, as can charge-compensated trivalent substitution ions [35].

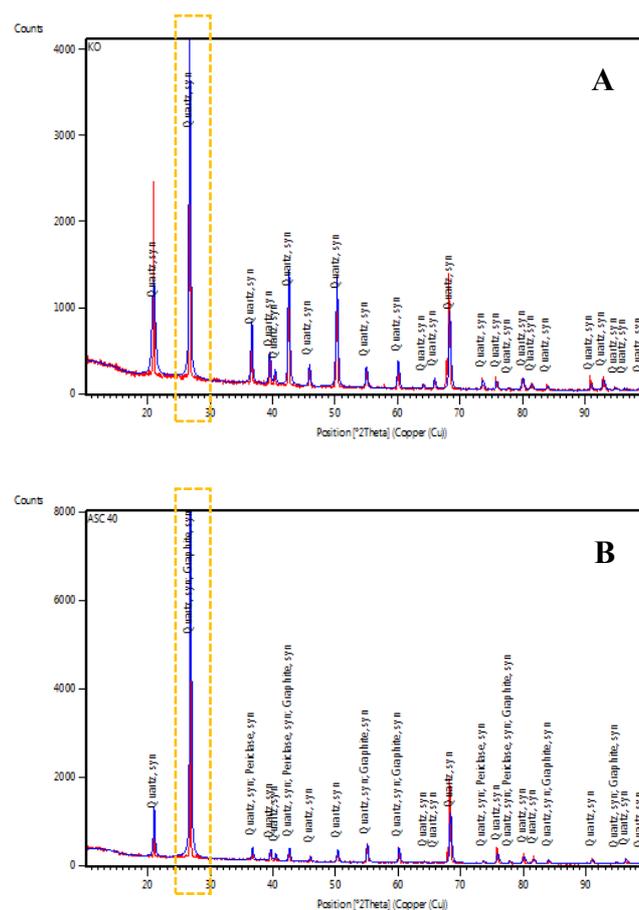


Fig. 6 XRD on ex-gold mining soil (A) and ex-gold mining soil ameliorated with 40 t ha^{-1} sub-bituminous coal-NaOH (B).

Graphite is made up of layers of graphene, which is a two-dimensional conductive structure. It has a large surface area

due to its layered structure (Fig. 7B), making it excellent for intercalation or adsorption. This Mineral formed due to the application of 40 t ha⁻¹ SC - NaOH. Graphite, like diamond and fullerenes, is crystalline carbon [36]. Graphite is an anisotropic material having high electrical and thermal conductivity within layers but low electrical and thermal conductivity between layers (due to metallic bonding in the plane) (due to weak van der Waals forces) [37]. Graphite is a unique mineral in a wide range of applications and is a substance made up of hexagonally organized sheets of carbon atoms [38]. Graphite possesses outstanding properties such as strong electrical conductivity, thermal conductivity, and a high boiling point [39]. Periclase (MgO) is cubic and has a perfect cleavage of 001. This Mineral emerged only after applying 40 t ha⁻¹ SC - NaOH. The fundamental components of this Mineral are derived from metamorphosed limestone. The structure of periclase is identical to that of halite and NaCl, with magnesium and oxygen ions filling the sodium and chlorine positions, respectively (Fig. 7C) [40] [41].

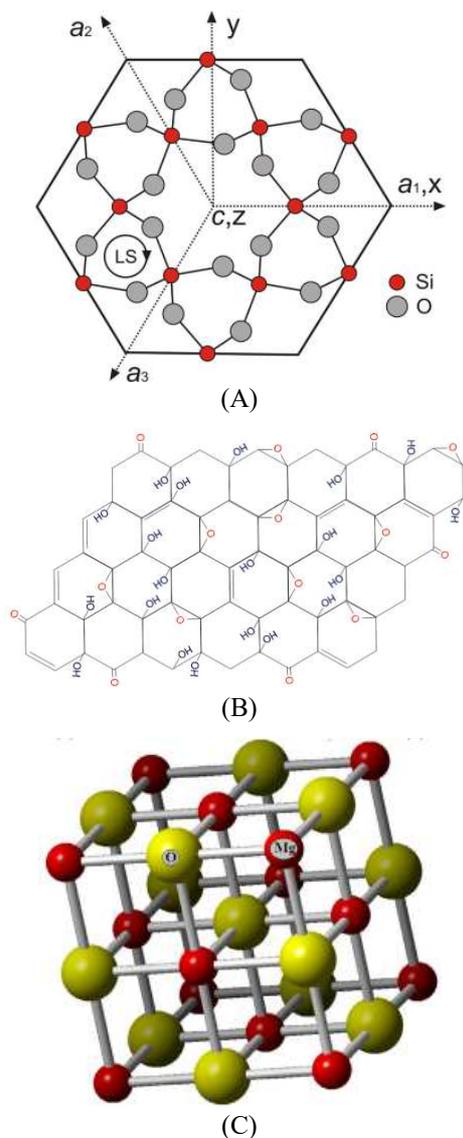


Fig. 7 The crystal structure of quartz (A), graphite (B), and periclase (C).

The FT-IR study determines variations in functional groups and chemical bonds of ex-mining soil before and after treatment with amelioration of SC - NaOH. According to the

chemical characteristics (Table 1 and Fig. 2, 3, 4, and 5), the application of 40 t ha⁻¹ SC - NaOH is the best dose for increasing the surface charge characteristics (pH PZC, CEC, and ΔpH) of ex-gold mining soil and increasing the adsorption capacity of the soil to Hg (Fig. 9) as well as the mineral composition of the soil formed to support the surface charge characteristics (Table 2 and Fig. 6).

Table 3 and Figure 8 depict the changes in the soil functional groups and chemical bonds, with the first occurring at a wavelength and transmittance of 3746.17 cm⁻¹/ 97.51% to 3619.39 cm⁻¹/ 97.33%, notably O-H bonds; N-H.

TABLE III
CHARACTERISTICS SPECTRAL BAND ASSIGNMENTS OF EX-GOLD MINING SOIL AMELIORATED WITH SUB-BITUMINOUS COAL-NAOH

Ex-GM Wavenumbers / Transmittance (cm ⁻¹ / %)	Ex-GM + SC - NaOH	Assignment
3746.17/ 97.51	3619.39/ 97.33	v(OH) from non-hydrogen bonded O-H groups
1029.75/ 73.07	1009.87/ 80.83	v(Si-O) from clay minerals associated with SC-NaOH
779.50/ 80.29	777.34/ 86.05	O-H bending peaks: trio- quatro
689.70/ 85.71	-	Mineral e.g. MgO
535.10/ 72.92	539.32/ 77.16	

Remarks: Ex-GM = Ex-gold mining soil; Ex-GM + SC-NaOH = Ex-gold mining soil ameliorated with Sub-bituminous coal - NaOH

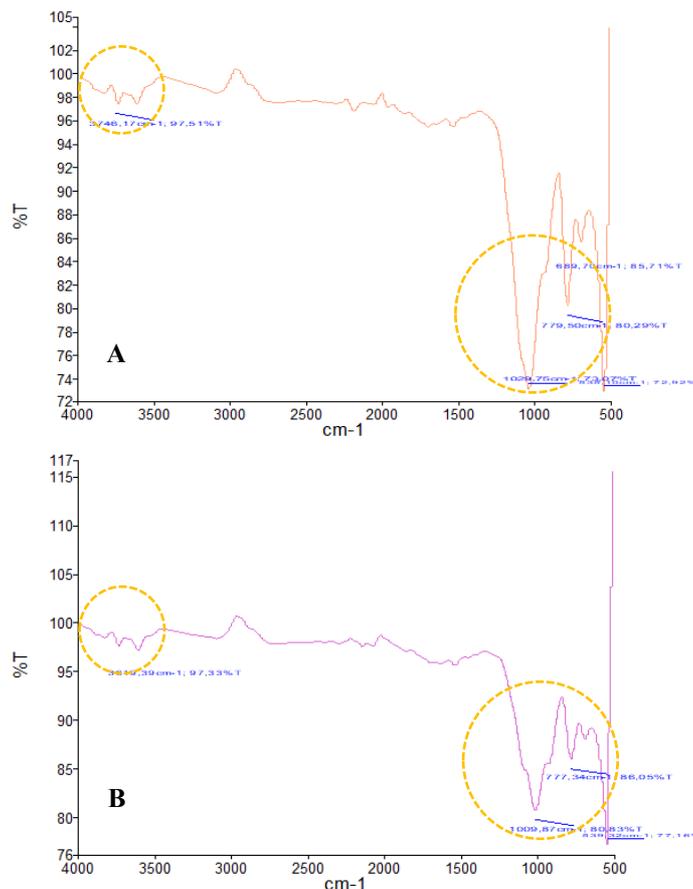


Fig. 8 FT-IR spectrum on ex-gold mining soil (A) and ex-gold mining soil ameliorated with 40 t ha⁻¹ sub-bituminous coal - NaOH (B).

It can be seen that the wavelength and transmittance decrease, causing the OH group adsorption power to rise. The inclusion of OH groups in SC - NaOH structure and the addition of H₂O during the activation process. According to

Herviyanti et al., [11] O-H vibrations occur in two ways: structural OH and H₂O. The mineral identification findings revealed that graphite minerals are a contributor to the OH group in the ex-gold mine soil ameliorated with SC - NaOH.

TABLE IV
CORRELATION OF MERCURY WITH CHEMICAL CHARACTERISTICS OF EX-GOLD MINING SOIL AMELIORATED WITH SUB-BITUMINOUS COAL - NAOH

Correlations	pH H ₂ O	pH KCl	EC	Eh	CEC	Mineral	SOM	pH PZC	ΔpH	Total Hg
pH H ₂ O (unit)	1	0.998**	0.844**	-0.992**	0.694**	-0.973**	0.962**	-0.717**	0.998**	-0.933**
pH KCl (unit)		1	0.832**	-0.990**	0.698**	-0.964**	0.951**	-0.670**	0.992**	-0.916**
EC (ds m ⁻¹)			1	-0.804**	0.896**	-0.937**	0.951**	-0.721**	0.853**	-0.939**
Eh (Volt)				1	-0.654**	0.953**	-0.938**	0.707**	-0.990**	0.898**
CEC (cmol kg ⁻¹)					1	-0.785**	0.801**	-0.440	0.688**	-0.741**
Mineral (%)						1	-0.999**	0.775**	-0.978**	0.972**
SOM (%)							1	-0.779**	0.968**	-0.974**
pH PZC (unit)								1	-0.757**	0.825**
ΔpH (unit)									1	-0.945**
Total Hg (mg kg ⁻¹)										1

Remarks: EC = Electrical conductivity; Eh = potential Redox; CEC = Cation exchange capacity; SOM = Soil organic matter; **. Correlation is significant at the 0.01 level (2-tailed); *. Correlation is significant at the 0.05 level (2-tailed); n = 15.

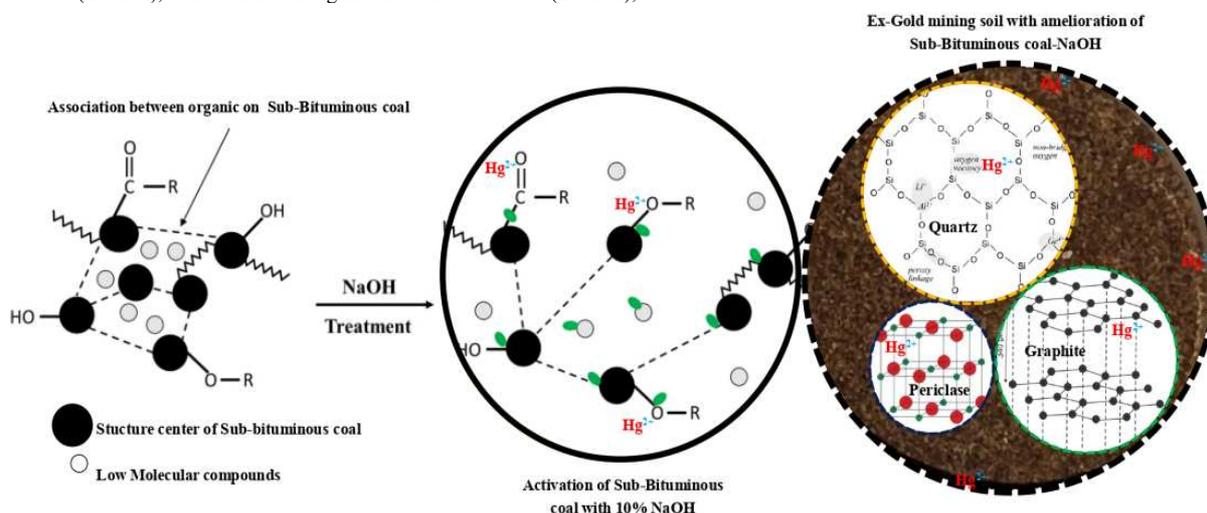


Fig. 9 Prediction of surface charge mechanism on ex-gold mining soil ameliorated with activation of sub-bituminous coal with 10% NaOH to Hg

The wavelength and transmittance of 1029.75 cm⁻¹/ 73.07% to 1009.87 cm⁻¹/ 80.83%, namely the ν(Si-O) from clay minerals associated with SC - NaOH, changed the greatest. The wavelength drops as the transmittance rises. According to mineral identification, this group is dominated by quartz minerals in the ex-gold mining soil with amelioration of SC - NaOH. Regarding wavelength and transmittance, peak bend O-H: trio-Quatro and minerals such as MgO are 779.50 cm⁻¹/ 80.29%; 689.70 cm⁻¹/ 85.71%, and 535.10 cm⁻¹/ 72.92% to 777.34 cm⁻¹/ 86.05% and 539.32 cm⁻¹/ 77.16%. The ex-gold mining soil was ameliorated with 40 t ha⁻¹ SC - NaOH identified periclase (MgO) minerals. This is evident from the FT-IR identification at wavelengths of 600 - 500 cm⁻¹. Still, there was also an increase in transmittance.

C. Characteristics and Correlation of Total Hg between Chemical Properties of Ex-Gold Mining Soil Ameliorated with Sub-Bituminous Coal - NaOH

Table 1 shows the average value of total Hg in ex-gold mining soil ameliorated with SC - NaOH of 5.29 mg kg⁻¹. Figure 10 shows a decrease in the total Hg of ex-gold mining

soil along with the increase in the application of SC - NaOH, where the effect of the application is significant for total Hg soil. The best decrease in total Hg was seen in the application of 40 t ha⁻¹ SC - NaOH of 2.84 mg kg⁻¹ compared to the control. Changes in the electrochemical properties of clays are closely related to the number of Hg complexes incorporated in the clays and their chemical composition and charge properties. Table 4 shows the correlation between Hg and the chemical characteristics of the ex-gold mining soil with amelioration of SC - NaOH, where the chemical characteristics of the ex-gold mine soil are significantly correlated with Hg.

The results show a positive correlation (total Hg with redox potential, Mineral, and pH PZC) and a negative (total Hg with pH H₂O; pH KCl, EC, CEC, SOM, and ΔpH). The positive correlation of total Hg with redox potential, Mineral, and pH PZC in the ex-gold mining soils ameliorated with SC - NaOH was r = 0.898, 0.972, and 0.825, respectively. The correlation of total Hg with Mineral is higher than total Hg with redox potential and pH PZC (total Hg with Mineral > Eh > pH PZC).

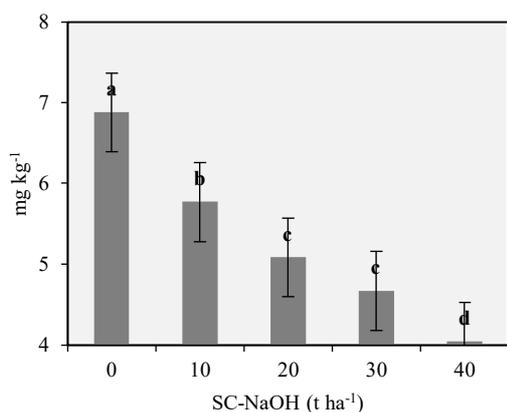


Fig. 10 Total Hg (CV = 5.35; DNMRT Test = **; SE = 0.23) on ex-gold mining soil with amelioration of sub-bituminous coal-NaOH.

The decrease in total Hg is determined by the mineral content of the ex-gold mine soil repaired with SC - NaOH. The distribution patterns of clay, silt, and sand are comparable to those of mercury, indicating that grain size is the primary factor influencing mercury levels in the soil [42]. Compared to loam and sand, clay has the best capacity for mercury adsorption, showing that a smaller grain size is better for mercury enrichment. Hg is bound to surface matrix minerals and SOM by forming organometal Hg complexes so that they simultaneously exist in different forms [43].

The negative correlation of total Hg with pH H₂O; EC, CEC, SOM, and ΔpH on soils ex-gold mining soil with ameliorated SC - NaOH of $r = 0.933; 0.916; 0.939; 0.741; 0.974$ and 0.945 . This shows that the order of correlation is total Hg with $SOM > \Delta pH > EC > pH H_2O > CEC$. The SOM content in the ex-gold mining soil ameliorated SC - NaOH determines the decrease in total Hg. SOM is the highest correlation ($r = 0.974$) compared to other chemical parameters. SOM is critical for improving metal binding capacity and influencing mercury dispersion behavior in soil. Similar study findings have been found to support the SOM-Hg association [44].

The predicted mechanism is depicted in Figure 9, where SC - NaOH shows that there is depolymerization (polymer breakdown) from the degradation of the SC molecules to become more open and form more negative charges. The ex-gold mining soil increased OH groups in the soil with a decrease in the percentage transmittance of OH groups in the soil (Fig. 2 and 8). This confirms an increase in soil surface charge (Figs. 3 and 5) supported by minerals and SOM (Fig. 4). Thus, the complex bonding process of Hg was higher in the ex-gold mining soil ameliorated with SC - NaOH, which causes the total Hg in the soil to decrease (Fig. 10).

IV. CONCLUSION

Amelioration technology with SC - NaOH, at the application of 40 t ha^{-1} on ex-gold mining soils, can modification of soil surface charge through changes in chemical characteristics by increasing the pH H₂O, EC, CEC, and SOM, respectively of $5.77; 4.33 \text{ dS m}^{-1}; 2.41 \text{ cmol}(+) \text{ kg}^{-1}$ and 17.15% compared to the control. Soil surface charge supported by soil minerals [Quartz (SiO₂), Graphite (C), and Periclase (MgO)] and also happening decreases transmittance

in the OH group (0.18%), which causes an adsorption capacity of the soil to total Hg increasing with a decrease of 2.84 mg kg^{-1} compared to the control. The correlation between Hg and soil chemical properties in ex-gold mining soil ameliorated with SC - NaOH (Total Hg with $SOM > \Delta pH > EC > pH H_2O > CEC$).

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