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Amendment with A Composite of Bentonite Based Nanosulfur and Humate Reduces the High Carbonate Levels in Calcareous Soils



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IGH pH values and high calcium carbonate content in calcareous soils are the major chemical IGH pH values and high calcium carbonate content in calculated and high calcium carbonate content in calculated and solid fertility declines. phosphorus, nitrogen and micronutrients. Due to the increasing population and soil fertility declines, there is currently a large gap between agricultural production and food demand. Therefore, it is necessary to address the limitations of calcium carbonate-rich soils for crop production by developing a new strategy. In this work, a calcareous soil conditioner for reducing high carbonate content based on a composite material consisting of bentonite clay impregnated with humate-capped nanosulfur was synthesized using the Raffo process. The innovative composite material with uneven surface and numerous embedded smooth nanosulfur spheres and a high number of active sites can be used efficiently as a calcareous soil conditioner. This soil conditioner effectively improves soil health and quality and maintains it by reducing high levels of calcium carbonate. The optimal amount was 500 kg ha⁻¹ composite, which reduced the soil pH by 0.59 units and the active carbonate content by 57%. Fourier transform infrared spectra of treated soil with the optimal amount showed that the intensity of the absorption bands corresponding to the active carbonate groups and calcite mineral was reduced. Interestingly, powder X-ray diffractometer matching phase analysis revealed that a new peak appeared due to the new formation of sulfate-carbonate coprecipitates or the so-called rapidcreekite mineral, which forms under limited conditions with high levels of dissolved sulfate compared to carbonate. Although the composite optimal rate provided more favourable soil conditions, the study recommends that the synthesis composite be further evaluated in future field trials with different calcareous soil conditions and crops.

Keywords: Organic-mineral, XRD analysis, FT-IR analysis, Complex, Humic acid, Soil amendment.

1. Introduction

The term "calcareous soil" refers to a soil that contains either calcium carbonate or a calcium and magnesium carbonate content of over 15% and possibly up to 95% and can be in various forms such as crusts, nodules or powder (Abou Hussien et al., 2021; Bolna et al., 2023). These soils are characterized by a calcareous horizon with high CaCO₃ or other carbonate content and a high pH (7 to 8.5), but the presence of NaCO₃ causes the pH to rise above nine (Bolna et al., 2023; Taalab et al., 2019). Theses soil found in arid and semi-arid regions and occupy >30% of the earth's surface (Taalab et al., 2019). The total area of Egypt covers approximately 25–30% of these soils (Abou Hussien et al., 2021). The majority of these soils are located on the Mediterranean coast of northern Egypt, as well as other areas in the Western and Eastern Desert and Sinai (Wahba et al., 2019). Crust formation in newly cultivated calcareous soils is one of the most significant physical problems that prevent seedling emergence, even when other factors such as moisture availability, oxygen, soil temperature and planting depth are not limiting (El-Saied et al., 2016). In addition, CaCO₃ can accumulate in soil layers, forming a very hard layer that is impermeable to water and plant roots (Bolna et al., 2023; Singare et al., 2022; Yassin et al., 2023). Cultivating calcareous soils is challenging due to many obstacles, such as: high infiltration rate, weak structure, low water holding capacity, low clay content (Aboukila et al., 2018; Krouma 2023). In addition, high pH values and high CaCO₃ content in calcareous soils are the major chemical problems (Alghamdi et al., 2023), which have a significant impact on the availability of nutrients, especially phosphorus (P), nitrogen (N) and micronutrients (Alghamdi et al., 2023; Bolna et al., 2023). Due to the increasing population and soil fertility declines, there is currently a large gap between agricultural production and food demand. Therefore, it is necessary to address the limitations of calcium carbonate-rich soils for crop production by developing a new strategy.

Organic and/or mineral conditioners can mitigate the side effects of high CaCO₃ levels in calcareous soils (Ampong et al., 2022; Ma et al., 2022; Nada et al., 2023; Sakin and Yanardag, 2023). Organic conditioners such as humic acid (HA) or humate are dark brown to black humic substances and a bioproduct from the decomposition of organic substances. It is characterized by a pH value in the range of 7 to 9, which makes it soluble in alkali but insoluble in acid or water (de Melo et al., 2016; Duary, 2020; Vikram et al., 2022). Its molecular structure is divided into hydrophilic (contains OH groups) and hydrophobic (aliphatic chains and aromatic rings) regions. In addition, HA contains functional groups such as carboxylic acid, phenol, quinone, enol and ether, but can also contain peptides and sugars (de Melo et al., 2016; Duary, 2020; Ampong et al., 2022; Vikram et al., 2022). It can lower the pH of the soil (Ampong et al., 2022; Bhatt and Singh, 2022). On the other hand, mineral conditioners such as calcium bentonite clay (BC) are widely used in many arid areas of the world (Zhang et al., 2020). BC is an aluminum silicate material, a type of clay mineral (2:1) that consists almost entirely of the smectite minerals, mostly montmorillonite, usually beige or light gray, but can also be reddish or green and have a fine texture (Ibrahim et al., 2017; Zhang et al., 2020). It is found in large quantities worldwide, is easy to mine and process and is therefore relatively inexpensive (Adane et al., 2022; Abulimiti et al., 2023). It helps to improve the soil physical, chemical and microbiological properties, which increases crop yield and the efficiency of fertilizer application (Zhang et al., 2020; Liu et al., 2023). In addition, the application of elemental sulfur (ES) as a soil acidulant is known to have a long-lasting effect on neutralizing $CaCO_3$ in soil, taking a year or longer to achieve a small pH reduction. As a soil acidifier, ES undergoes a microbial oxidation process that depends on several soil-related factors, including temperature, aeration, texture, and organic matter content. Due to the large particle size, enormous volume consumption, non-quick action and the need for a longer incubation period to improve soil, an alternative had to be found. The use of nanosulfur (S-Nano) to reduce the application rate and increase efficiency in soil improvement met with great interest (EL-Madah et al., 2024). Particle size is the main factor determining the oxidation rate, with small particles with a large total surface area being more reactive. The finer the particles are, the faster the oxidation process occurs (Khan et al., 2019).

Nanotechnology is a promising technology that has contributed to the development of agriculture by increasing the fertility of soils characterized by problems that limit their productivity, such as calcareous soils. The only solution to such problems is to mitigate the high carbonate content. The main option is to use organic or mineral additives or both together. The organic nano-mineral composite is a new innovative strategy that could address this challenge (Ma et al., 2022). However, the use of soil conditioners as a nano-form organic-mineral composite has not been widely investigated. Therefore, the main objective of this study is to (1) synthesize a bentonite-clay composite impregnated with humate-capped nanosulfur, (2) investigate its properties and characterization, and then (3) evaluate its effect in reducing high carbonate concentrations finally (4) determine the optimal application rate for calcareous soil.

2. Materials and Methods

2.1. Synthesis composite

The modified Raffo method (acidification method) was used to obtain S_{-Nano} (Mérai et al., 2020; Tarekegn et al., 2022). Briefly, at a temperature of 250 °C with stirring, 5 g of pure elemental sulfur (ES, 99.9%) powder (Kafr El Zayat Pesticides and Chemicals-KZ, Egypt) was dissolved in 150 ml of 1 <u>N</u> aqueous KOH solution to obtain potassium polysulfide (KS_{-Poly}). Then, at a temperature of 30° C ± 2 °C with gentle stirring, 150 ml of 1 <u>N</u> H₂SO₄ solution was added dropwise to the KS_{-Poly} solution until it became cloudy, i.e., the color of the solution became milky white. The H₂SO₄ time consumed was 20 minutes, and the pH of the solution was between 3 and 4 during the formation and precipitation of sulfur nanoparticles. For capping with potassium humate or humic acid (HA), 3 g of HA (Shenyang Humate Technology Co., LTD, China) was dissolved in 50 ml of deionized water. It was then added to the S_{-nano} suspension under magnetic stirring to make the streaming potential positive (Tarekegn et al., 2022). The S_{-nano} capped with HA suspension was stirred for an additional 30 minutes and the pH was corrected to 6 to 7 with 1 <u>N</u> KOH solution. To synthesize a bentonite-clay composite impregnated with humate-capped nano-sulfur, 92 g of calcium bentonite clay (BC, ICMI, International Company for Mining and Investment, Egypt) were thoroughly mixed with the previous suspension under mechanical stirring to obtain a

completely homogenized slurry, the pH remained between 6 and 7 to support complete adsorption of HA-capped S_{-Nano} on the surface of BC (Suseno and Warisaura, 2022). The slurry was finally oven dried at a temperature of 60 °C and then milled to produce aggregates with a diameter of <0.5 mm. Therefore, the BC impregnated with HA-capped S_{-Nano} aggregates prepared in this study were referred to as "composite". The BC: HA: S_{-nano} ratio was 92:3:5 (wt %) to produce 100 g of the composite.

2.2. Characterization of composite

The crystalline phase and crystalline size were identified using a powder X-Ray Diffractometer (XRD, GNR, APD 2000 PRO, Italy) equipped with Ni-filtered Cu-Ka radiation ($\lambda = 1.541$ Å, accelerating voltage = 35 kV, applied current voltage = 25 mA) at 20 1° min⁻¹ goniometer speed. Profiles were measured in the range 5° < 20 $< 80^{\circ}$ with a step of $0.03^{\circ}/2$ s, a divergence gap of 0.5 mm and a reception gap of 0.3 mm. Mineralogical analysis and semi-quantitative determination of minerals present in the samples were done with the program Match! using the reference intensity ratio method (RIR) with mineral reference diffraction data taken from the Crystallography Open Database (COD) and the PDF cards of the International Centre for Diffraction Data (ICDD) (Karadag et al., 2022). The surface functional group, available molecules and compounds were determined using the KBr method of Fourier transform infrared spectroscopy (FT-IR) spectra analysis (BRUKER TENSOR 27, Germany) with the recorded infrared spectra in the range of $5000-200 \text{ cm}^{-1}$ a resolution of 4 cm⁻¹. An average of 24 scans were performed for each sample. To obtain each KBr carrier wafer, 1 mg of sample was mixed with 20 mg of potassium bromide (KBr) and pressed into a pellet using the minimum required pressure. The sample pellet was placed in a quartz cell with KBr windows and treated in a vacuum desiccator (residual pressure <10⁻³ mbar) at room temperature. The morphology and particle size were characterized by field emission scanning electron microscopy (SEM; FEI Nova NanoSEM 450, Hillsboro, OR, USA) at a voltage of 20 kV and magnifications ranging from \times 200 to \times 10,000. The particle size distribution of S-nano was estimated using NICOMP 380 DLS and the particle size distribution analysis system (Windows CW388-V1.71 Software\Cw388.tbl, Santa Barbara California, USA) under the following conditions: at a wavelength of 632.8 nm, running time 2 min 9 seconds, count rate 20 KHz, scattering angle 90°, water refractive index 1.33 and intensity setpoint 300 KHz. To measure the particle size, a volume of 0.1 ml of the S.nano solution in 2 ml of deionized water was placed in a polystyrene cuvette and measured at 23°C. The particle size of S-nano was determined using transmission electron microscopy (TEM; JEM-1400 Plus, JEOL Ltd. USA) at a voltage of 34 kV and a magnification of ×40,000. The TEM samples were prepared as follows: a small amount of the photocatalyst was dispersed in ethanol and the suspension was sonicated for 10 min. A single drop of the suspension was then placed on a carbon-coated grid and allowed to dry at ambient temperature. Selected area electron diffraction patterns were analyzed using ImageJ software (LOCI, Madison, WI, USA).

2.3. Study soil, experimental design , treatments, incubation period and chemical analysis

A calcareous soil sample was collected from the surface layer (0-20 cm) of an uncultivated field in the El-Hamam area (latitude 30.811N and longitude 29.372E) from Matrouh Governorate, Egypt. It was then air dried, sieved (2 mm sieve) and analyzed for some physical and chemical properties. Physicochemical characteristics of the studied soil are shown in Table 1. The soil samples (< 2 mm, 3.5 kg dry weight) were weighed and mixed with different amounts of the composite and then packed in plastic pots (25 cm high, 15 cm inner diameter). A completely randomized design (RCD) was used in the statistical analysis of the experiment. Four treatments consisting of four composites of 200, 500, 1,000 and 2,000 kg ha⁻¹, respectively, plus control (without composite), five treatments × four replicates = 20 pots. The pots were incubated for two months at a laboratory temperature of 29 ± 2 °C and a relative humidity of $65 \pm 5\%$ and watered regularly with distilled water at field capacity (FC, 24% ww⁻¹) depending on weight. After the incubation period, soil samples were taken from each pot to determine T_{-CaCO3} by the volumetric calcimeter method (FAO, 2020) and A_{-CaCO3} by the back titration method using potassium permanganate after shaking the soil with 0.2 <u>N</u> ammonium oxalate solution (Estefan et al., 2016). The pH value was measured with the pH meter (HI2211 PH/ORP Meter, HANNA Company) (Estefan et al., 2016).

Soil characteristics	Measurement unit	Value
pH (saturated soil past)		8.44
Electrical conductivity	dS m ⁻¹	0.43
Organic matter	g kg ⁻¹	4.10
Sand	g kg ⁻¹	883.70
Silt	g kg ⁻¹	68.00
Clay	g kg ⁻¹	48.30
Total CaCO ₃	%	49.83
Active CaCO ₃	%	10.00
Dissolved cations and anions		
Na^+	meq L-1	2.11
\mathbf{K}^+	meq L-1	1.10
Ca ²⁺	meq L-1	1.50
Mg^{2+}	meq L-1	1.00
CO ₃ ⁻²	meq L-1	0.00
HCO ₃ ⁻¹	meq L-1	2.00
Cl-1	meq L-1	1.50
Sulphates	meq L-1	0.33

	Table 1. Physi	icochemical	characteristics	of	the	studied	soil
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2.4. Statistical analysis

The statistics program SPSS v. 13.0 for Windows (Inc. Chicago, IL, USA) was used to test differences between means using one-way analysis of variance (ANOVA). Tukey's Honestly Significant Difference (HSD) test was used when a significant difference was found (P < 0.05) (Verma, 2013).

3. Results

3.1. S_{-Nano} characterization by SEM, DLS, and TEM

Figures 1a shows the shape and size of S_{-Nano} measured by scattering electron microscopy (SEM) analysis. They show the presence of S_{-Nano} in a spherical shape, characterized by irregular agglomerates with smooth surfaces in a cluster shape and a diameter <831.6 nm. The DLS image (Figure 1b) from S_{-Nano} shows that the average diameter measured by intensity was 122.9 nm. However, transmission electron microscopy (TEM) analysis (Figure 1c) shows that the nano-sulfur particles have a spherical shape and polydispersity with an average diameter of 25 nm.



Fig. 1. Scattering electron microscopy (SEM) analysis (a) for the shape of nanosulfur particles, transmission electron microscopy (TEM) analysis (b) for the size of nanosulfur particles, and (c) dynamic light scattering (NICOMP distribution) analysis for the mean diameter of solid nanosulfur particles by intensity, number and volume.

3.2. SEM analysis of bentonite and composite

Figure 2b shows the bentonite clay particles had a folded and wrinkled morphology characterized by high surface roughness and pores, whereas the composite show underwent further changes, evolving into a more folded and highly wrinkled material (Figure 2a and 2d) with numerous smooth S-nanospheres (Figure 2c) were buried throughout the surface.



Fig. 2. Scattering electron microscopy (SEM) analysis of the structure of the synthesized composites (a) and (d), the bentonite clay (b) and the nano-sulfur particles (c), Collision interaction (green circle) and collapse interaction (blue circle).

3.3. FT-IR analysis of bentonite, humic acid, and composite

The infrared spectrum of the synthesized composite shows absorption peaks that are somewhat different from those of the bentonite clay (Figure 3). In bentonite clay, the stretch and bend bands of 3,696.53 cm⁻¹ typical of the octahedral layer (Al-Al-OH) disappeared. Moreover, the bands measuring 2924.71 cm⁻¹ typical of silicon or quartz impurities were absent. The bands 1424.01 cm⁻¹ and 1823.33 cm⁻¹ typical of carbonate impurities have also disappeared. In addition, the bands 4523.67 cm⁻¹, 3419.55 cm⁻¹ and 1635.58 cm⁻¹ associated with water and hydroxide groups have been greatly degraded and have disappeared. Conversely, the absorption bands of 1031.95 cm⁻¹, 914.41 cm⁻¹ and 791.65 cm⁻¹ shifted to a lower intensity due to the formation of organic siloxane (Si-O-C) and of alumina (Al-O-C). Absorption bands 692.04 cm⁻¹, 532.11 cm⁻¹ and 425.91 cm⁻¹ were also shifted to a lower intensity by formation of thiosulfates (v S–O), aryl thioethers (v Φ –S), disulfites (v C–S), polysulfites (v S–S), and v S–S in the presence of the S₈ molecule. Figure 3 also shows the presence of the humic.

3.4. XRD of bentonite, humic acid, and composite

The XRD of bentonite clay and the synthesized composite (Figure 4) show that montmorillonite is the predominant mineral phase and quartz being the major impurity with traces of Kaolinite. Moreover, it shows that they have identical peaks of approximately the same composition. However, the results of the synthesized composite showed a greater increase in 2-theta spacing and a decrease in basal spacing (7.58 Å).



Fig. 3. Fourier transform infrared (FT-IR) of bentonite, humic acid, and composite.



Fig. 4. X-ray diffractometer (XRD) of bentonite, humic acid, and composite.

3.5. Soil reaction (pH), Total, active, and active/total CaCO3

Data in Table 2 showed a highly significant decrease in soil pH. Compared to the control treatment (0 kg composite ha⁻¹), the pH value decreased by 0.58, 0.59, 0.49 and 0.56 units at the rates of 200, 500, 1000 and 2000 kg ha⁻¹, respectively. Reducing soil pH affected T_{CaCO3} , A_{CaCO3} and A_{CaCO3}/T_{CaCO3} . Compared to the control treatment, the amounts of 200, 500, 1000 and 2000 kg ha⁻¹ decreased T_{CaCO3} by 15.4%, 23%, 24% and 22.4%, while A_{CaCO3} decreased by 37%, 57%, 57% and 57%, respectively. Furthermore, A_{CaCO3}/T_{CaCO3} decreased by 25.2%, 44%, 43% and 44.2%, respectively (Table 2). Tukey's Honestly Significant Difference (HSD) of the arithmetic mean of soil reaction (pH), active CaCO₃ (A_{CaCO3}), total CaCO₃ (T_{CaCO3}), and active to total CaCO₃ (A_{CaCO3}/T_{CaCO3}) showed that amounts above 500 kg ha⁻¹ did not lead to significant differences (Table 2). Therefore, the optimal amount of synthesized composite is 500 kg ha⁻¹. This is enough to neutralize carbonates and reduce pH. The optimal amount reduced the pH value by 0.59 units and A_{CaCO3} content by 57%.

$(A_{CaCO3}/1_{CaCO3})$.				
Composite amount	рН	T _{CaCO3}	A _{CaCO3}	A_{CaCO3}/T_{CaCO3}
(kg ha ⁻¹)	(Unit)	(%)	(%)	(%)
0.00	8.44 ^a	49.83 ^a	10.00^{a}	20.08 ^a
200	7.86 ^b	42.16 ^b	6.33 ^b	15.02 ^b
500	7.85 ^b	38.44 ^c	4.33°	11.27 ^b
1000	7.95 ^b	37.89 ^c	4.33 ^c	11.44 ^b
2000	7.88 ^b	38.67 ^c	4.33 ^c	11.21 ^b
P-value	< 0.001	< 0.001	< 0.001	< 0.001
S.E.M	0.022	0.459	0.394	0.930
HSD	0.100	2.135	1.836	4.328

Table 2. Influence of different amounts of synthesized composite on soil reaction (pH), total calcium carbonate (T_{CaCO3}), active calcium carbonate (A_{CaCO3}), and active/total calcium carbonate (A_{CaCO3}/T_{CaCO3}).

3.6. FT-IR analysis of untreated and treated soil with recommended amount of Composite

Figure 5 shows the forms and effective functional groups according to FT-IR spectra of untreated and treated soil with the optimal amount of composite (500 kg ha⁻¹). The infrared spectra of the treated soil provide absorption peaks that are somewhat small shifting from the infrared spectra of untreated soil (Figure 5). The broad band at 3428.34 cm⁻¹ with the shoulder at 3695.64 cm⁻¹ is attributed to the N-H bond and vibration of layered silicates (Si-O-H). The small sharp band at 2921.94 cm⁻¹ with the very small shoulder at 2856.29 cm⁻¹ and the small broad band at 2519.56 cm⁻¹ became lower intensities and characterize the v_s C–H₂, v_{as} C–H₂, and ambient CO₂, respectively. The sharp bands at 1443.96 cm⁻¹ with two very small sharp shoulders at 1620.68 cm⁻¹ and 1797.32 cm⁻¹ are attributed to the carboxylate group (COO⁻), the v C=O or N-H bend and attributed to the dominance of calcite or carbonate (CO⁻³) group. The broad sharp band at 1034.13 cm⁻¹ corresponds to organic siloxane (Si–O– C). The strong sharp bands at 788.64 cm⁻¹ and 1823.33 cm⁻¹ correspond to vs Si–O–Si. Furthermore, the strong sharp bands at 792.28 cm⁻¹ and 874.23 cm⁻¹ correspond to out-of-plane nonaromatic δ C–H and aromatic δ C–H and polyaromatic, respectively. On the other hand, the strong sharp bands at 468.52 cm⁻¹, 523.74 cm⁻¹ and 712.80 cm⁻¹ are attributed to aryl disulfides (v S–S), disulfides (v S–S) and aryl thioethers (v Φ –S) or v C–S. The strong sharp band at 323.43 cm⁻¹ corresponds to v Fe–O (iron oxide). Apparently, there is a decrease in the absorption intensity bands corresponding to the active carbonate groups (CO_3^{2}) and calcite mineral, the bands between 2150 cm⁻¹ and 3150 cm⁻¹, yellow selected area (Figure 5).



Fig. 5. Fourier transform infrared (FT-IR) of untreated and treated soil with the optimal amount of synthesized composite (500 kg ha⁻¹).

3.7. XRD of untreated and treated soil with recommended amount of Composite

Matching phase analysis of the XRD patterns (Figure 6) showed that the untreated and treated soil with the optimal composite amount has quartz as the predominant mineral phase (89.7% in the untreated soil and 81% in the treated soil) and as the second most important mineral calcite (10.3% in untreated soil and 10.8% in treated

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soil), but the treated soil contained only significant amounts of potassium hydrogen sulfide (23.4%). The XRD patterns of untreated and treated soil showed the same peaks with almost the same composition, but the 20 value shifted from 21.15° to 18.77° and the d-spacing (d_{001}) shifted from 4.19 Å to 4.72 Å for untreated and treated soil, respectively. The 20 positions for removed or volatile $CO_3^{2^-}$ were as follows: 30.92°, 43.25°, 47.63°, 48.59°, 60.77°, 63.23°, 64.76° and 73.64°. The sulfate-CaCO₃ coprecipitate had 20 positions of 36.08°, 43.25°, 56.66°, 57.53°, and 69.02°. The 20 positions for substituted $SO_4^{2^-}$ were 26.63°, 45.8°, 50.57° and 68.04°. The 20 positions for SO₄²⁻ formation were 27.50°, 41.78° and 60.14°. Interestingly, a new peak appeared in the XRD pattern of the treated soil with a d-spacing of 4.72 Å and a 20 of 18.77°, which could be due to the new formation of sulfate-CaCO₃ co-precipitate.



Fig. 6. X-Ray Diffractometer (XRD) of untreated and treated soil with the optimal amount of synthesized composite (500 kg ha⁻¹), as well as removed CO_3^{-2} and substitution SO_4^{-2} .

4. Discussion

4.1. S.-Nano characterization by SEM, DLS, and TEM

The presence of S_{-Nano} in a spherical shape, characterized by irregular agglomerates with smooth surfaces in a cluster shape and diameter <831.6 nm can be attributed to the rapid agglomeration and coarsening of hydrophilic nano-S8 (polysulfide) rings, which were formed as colloidal suspensions using the sol technique in this study. The agglomeration or coarsening process involved a combination of flocculation, classical nucleation, and/or Ostwald ripening. The Ostwald ripening process is described as the exchange of volume by the mechanisms of collision and particle collapse. The confirmation of the Ostwald ripening process was further supported by the observation of various collision shapes (green circle) and particle collapse (blue circle), as depicted in Figure 2c. These findings align with the research conducted by Garcia and Druschel (Garcia and Druschel, 2014), as well as by Steudel (Steudel, 1996). The coarsening of the S.-Nano sol likely occurs either as Ostwald ripening or as aggregation after an initial stage in which critical nuclei would form. In DLS analysis, the initial stages escape this coarsening because the speed of these initial steps is much faster than DLS techniques can capture under these conditions (Steudel, 1996; Garcia and Druschel, 2014). Therefore, the DLS image (Figure 1b) from S. Nano shows that the average diameter measured by intensity was 122.9 nm. However, transmission electron microscopy (TEM) analysis (Figure 1c) shows that the nano-sulfur particles have a spherical shape and polydispersity with an average diameter of 25 nm. This confirms that the agglomerate spheres formed by the Ostwald ripening process consisted of individual sulfur nanoparticles stuck together but are easily dispersed (Mol et al., 2021). The nanoparticles are those with a diameter <100 nm (Yazhini et al., 2023).

4.2. SEM analysis of bentonite and composite

When the composite was synthesized, the bentonite clay underwent further changes, evolving into a more compact and highly wrinkled material with several smooth S_{-nano} spheres buried throughout the surface, indicating improved surface orientation of the active sites by increasing the number of sites. These changes may be due to acidic conditions during the synthesis process, which increased the ability to remove several metal ions such as iron and impurities such as calcium and silica and caused a greater void in the surface of the product, resulting in a structural collapse (Usman et al., 2012; Pluangklang and Rangsriwatanan, 2021). The collapse of the interlayer sites is likely to have contributed to the formation of a tight-knit structure that facilitated the adsorption of humate and the fixation of the S_{-Nano} molecules on the composite surface (Adane et al., 2022).

4.3. FT-IR analysis of bentonite, humic, and composite

The absence of the bands typical of an octahedral layer and the absence of silicate impurities indicate that the sulphuric acid used in the synthesis of S-Nano dissolved the octahedral cations, such as Al³⁺ and Mg²⁺, from the bentonite clay structure, which is the cause of the collapse. In addition, the active groups silanol (-Si-OH) and almanol (-Al-OH) have been strengthened in the synthesis composite structure by dissolution of silicate (Usman et al., 2012; Pluangklang and Rangsriwatananon, 2021). In addition, degrading and disappearing of the bands that are associated with the presence of water and hydroxyl groups in synthesized composite due to the dehydroxylation process that caused the decomposition of bentonite clay structure and reduced the distance between layers (Timofeeva et al., 2017; Perez et al., 2022). This is confirmed by the SEM analysis and explained in the previous section. Moreover, formation of organic alkoxysilane groups (C-S, S-O, S-S and -SH) in addition to silanol groups (-Si-OH) under acidic conditions in the presence of carboxyl groups (-COOH), methylene groups, aromatic ethers, aromatic rings and alcohol from humate led to silylation and loss of crystallinity of bentonite clay (Abd-Elshafi et al., 2022; Crucho 2023; Hennecke et al., 2023). Silylation is a direct condensation reaction between silanol groups (-Si-OH) of bentonite clay and the organic alkoxysilane groups of the humate and S-Nano molecules (grafting agent). The silvlation reactions are considered unique because they involve an irreversible covalent cross-linking step that involves the formation of Si-O bonds with the surface hydroxyl groups but also with the silicon atom in the neighboring chains (Jadhav 2011). In this reaction, the hydrolysable methoxy groups (-OCH₃) act as a link between the silicon atom and the alkoxysilane group during the coupling reactions (Crucho, 2023; Herzer et al., 2010). These results confirm that bentonite clay has been successfully functionalized by the $S_{\text{-Nano}}$ molecules.

4.4. XRD of bentonite, humic, and composite

The larger increase in 2-theta spacing and the decrease in basal spacing of the synthesized composite suggest that it was shrunk more. This could be due to K^+ ions originating from the potassium polysulfide (KS_{-Poly}) successfully penetrated the intermediate layer of the bentonite clay and replaced Ca²⁺ during the composite synthesis process. K⁺ ions are smaller than Ca²⁺ ions and therefore have a smaller hydration sphere and consequently a lower hydration capacity, making the composite hydrophobic and thereby reducing the interlayer distance (Timofeeva et al., 2017; Perez et al., 2022). The montmorillonite crystallinity index, which is a good parameter to represent the montmorillonite structural disorder, was determined using the method of Full Width at Half Maximum (FWHM) (001) (Amigo et al., 1994). The XRD analysis showed that the FWHM (001) for montmorillonite in bentonite clay and synthesized composite was 1.3 and 4.1, respectively. These results suggested that montmorillonite in bentonite clay had better crystallinity than in synthesized composite. This is evidence that montmorillonite in the bentonite clay lost its crystallinity structure during the synthesis of the composite through a dehydration process, resulting in the collapse of the interlayers. This result is confirmed by the results of the FT-IR analysis. Also, this is evidence that humate-coated S-Nano did not penetrate the bentonite clay interlayer and was mainly associated with the edges as well as the outer surfaces and therefore did not increase the interlayer distance (Osman et al., 2017). The humate adsorbs, and the S-Nano molecules are fixed on the surface of the bentonite clay particles through electrostatic interactions. As the content of adsorbed humate and fixed S_{-Nano} molecules increased, the wetting and structural properties of the synthesized composite changed from hydrophilic to hydrophobic, which prevented the penetration of water molecules between the layers and led to a decrease in the distance between them (Timofeeva et al., 2017). Most researchers believe that montmorillonite has low swelling capacity and high hydrophilicity when montmorillonite layers contain cations with weak hydration ability such as potassium (Morodome and Kawamura, 2011; Shapley et al., 2013; Xu et al., 2017). KS-_{Poly} typically relies on the penetration of K⁺ ions into the clay lattice, altering the clay structure by reducing water holding capacity (Shapley et al., 2013). Smectite clay such as montmorillonite, which swells greatly when treated with K⁺ ions, exhibits less swelling because K⁺ ions penetrate the clay lattice and make it less active (Zhou et al., 2014; Al-Bazali et al., 2021). The decrease in swelling capacity of montmorillonite is due to the collapse of some interlayers after aluminum release and calcium substitution by potassium in the octahedral layer, producing a non-swelling mineral such as Illite (Figure 4) (Ayari et al., 2005; Mosser-Ruck et al., 2010).

4.5. Soil reaction (pH), total, active, and active/total CaCO₃

The pH change could be due to the S_{-Nano} particles are quickly oxidized to H^+ and H_2SO_4 by S-oxidizing bacteria within a few weeks (Shakoor et al., 2023). The reason for these results is the positive effect of S-Nano and humate in dissolving excess CaCO₃ (Ali and Mindari, 2016; EL-Madah et al., 2024; Shakoor et al., 2023; Yazhini et al., 2023). The H₂SO₄ produced during S_{-Nano} oxidation is responsible for dissolving excess CaCO₃, which is considered one of the most important factors (Al balawna and Abu-Abdoun, 2021). The H₂SO₄ reacts with CaCO₃ and releases CO₂ into the atmosphere, reducing the native lime content of sandy calcareous soils (Soaud et al., 2011; Derafshi et al., 2023). Also, the addition of humate resulted in a decrease in soil pH, thereby reducing the CaCO₃ content of sandy calcareous soils (Ali and Mindari, 2016). The addition of organic compounds such as humate supports the proliferation of heterotrophic sulfur-oxidizing bacteria, which promotes S_{-Nano} oxidation in alkaline soils (Yazhini et al., 2023). The effect of H^+ and H_2SO_4 lowers the relatively high pH of sandy calcareous soils (Akay et al., 2019; Amin and Mihoub, 2021). Particle size plays a key role in the accelerated S.Nano oxidation process (El-Kholy et al., 2013; López-Mosquera et al., 2015). The high oxidation rate of S_{-Nano} particles is due to their large total surface area and higher reactivity (Salem et al., 2015; Degryse et al., 2016; Zhao et al., 2016). Moreover, the pH changes decrease as the concentration of organic matter and clay increases. Therefore, the effect of human being was effective in the investigated soil because it was sandy and had low clay and organic matter content (Ali and Mindari, 2016). It can be concluded that S-Nano had a significant short-term effect on soil pH due to rapid oxidation (Abd El-Azeem and Ramadan, 2018; Esmaeil et al., 2020; Yazhini et al., 2023).

4.6. FT-IR analysis of untreated and treated soil with recommended amount of composite

The large decrease in the absorption intensity bands corresponding to the active carbonate groups (CO_3^{2-}) and calcite minerals suggest that the addition of the composite to the soil caused more carbonate to volatilize into CO_2 , resulting in a lower amount of active calcium carbonate. This is confirmed by the estimated decrease in A_{CaCO3} in the treated soil (Table 2). The increase in absorption intensity bands corresponding to Si-O, Si-O-Si bridging and Si-O-Al could be due to the silylation process. In addition to the carboxyl, methylene, aromatic ether and ring groups as well as the alcohol from HA, the organic alkoxysilane groups are responsible for the formation of organoalkoxysilane compounds (Esmaeil et al., 2020; Abd-Elshafi et al., 2022; Crucho et al., 2023). These compounds can absorb more infrared spectra, thereby shifting the spectral bands, resulting in an increase in absorption intensity. The absorption peak at wave number 1034.13 cm⁻¹ was shifted to the lower wave number, followed by broadening of the peak width, indicating that the composite caused an increase in the interlayer space of the soil minerals and showed a decrease in the crystallinity of the soil. This is confirmed by the decrease in quartz content from 89.5% to 81% after treatment with the composite (Figure 6).

4.7. XRD of untreated and treated soil with recommended amount of composite

The untreated and treated soil showed the same XRD peaks with almost the same composition, but with a shift in 2-theta value and the d-spacing. This could be due to volatile CO_3^{2-} , sulfate-CaCO₃ coprecipitate, and substituted SO_4^{2-} and SO_4^{2-} formation. However, the formation of sulfate-CaCO₃ co-precipitates and substituted SO_4^{2-} is largely controlled due to the rapid S_{-Nano} oxidation (Reda and Modaihsh, 1990; Yazhini et al., 2023). On the other

hand, the new peak appeared in the XRD pattern of the treated soil could be due to the new formation of sulfate-CaCO₃ co-precipitate, which is called Rapidcreekite. The structure of Rapidcreekite is related to the structure of gypsum by twinning of the gypsum structure along alternate rows of (SO₄) groups coupled with incorporation of (CO₃) groups along each twin plane. This is a rare, hydrate sulfate carbonate mineral with formula Ca₂ (SO₄) (CO₃).4H₂O. Rapidcreekite has only been identified in a limited number of locations worldwide and is thought to form under restricted conditions with high levels of dissolved sulfate compared to carbonate (Lau et al., 2017). Rapidcreekite occurs as a secondary phase on extended articular surface sand beds in a blocky, quartz-rich bed in the Sideritic Iron formation. This is confirmed by the appearance of a strong sharp band at 323.43 cm⁻¹, corresponding to Iron oxide (Figure 5), as well as the increase in Iron (Fe) content from 0.3% to 8.2% after treatment with the composite material (Figure 6).

5. Conclusions

Based on the results, the following conclusions can be drawn: 1) Farmers can effectively use the synthesized composite as a calcareous soil conditioner; 2) 500 kg ha⁻¹ synthesized composite was the optimal amount; 3) Optimum amount improves and maintains soil health and quality by reducing high calcium carbonate levels; 4) The optimal rate reduced the active carbonate content by 57% and created an acidic state due to the high solubility of nanosulfate ions, resulting in a decrease in soil pH by 0.59 units and the volatile release of carbonate ions in the form of carbon dioxide released into the atmosphere increased; 5) The optimal rate provided more favorable soil conditions due to the more soluble sulfates compared to carbonate ions and these led to the formation of a new sulfate-CaCO₃ coprecipitate or a so-called rapidcreecite mineral. The study therefore recommends that the synthesized composite be further evaluated through further future field studies under different calcareous soil conditions with different crops.

List of abbreviations:

BC: Bentonite clay HA: Potassium humate or Humic acid ES: Elemental sulfur S_{-Nano}: Nanosulfur XRD: X-Ray Diffractometer FT-IR: Fourier transform infrared spectroscopy SEM: Scanning electron microscopy TEM: Transmission electron microscopy DLS: Dynamic light scattering T_{-CaCO3}: Total CaCO₃ A_{-CaCO3}: Active CaCO₃

Declarations

Ethics approval and consent to participate

Consent for publication: The authors declaire that the article contains no such material that may be unlawful, defamatory, or which would, if published, in any way whatsoever, violate the terms and conditions as laid down in the agreement.

Availability of data and material: Data is provided within the manuscript file. A.A. Abd El-Halim should be contacted if someone wants to request the data from this study.

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