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Amelioration with Nano-Sulfur Suspensions Mitigates Calcium Carbonate of Calcareous Sandy Soil

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TUSE of nano-sulfur (NS) as a suspension to mitigate calcium carbonate ($CaCO_3$) of calcareous sandy soil is a new strategy and has not yet been tested. In a pot experiment, this study evaluated four NS suspensions containing 15, 30, 60, and 90 kg NS ha^{-1}, plus the control (distilled water only, 0 NS). Pots were incubated under laboratory conditions for two months. Then, total, active, and active/total $CaCO_3$, as well as the $CaCO_3$-related properties were estimated. The suspension containing 90 kg NS ha^{-1} was superior, while that containing 30 kg NS ha^{-1} was optimum. However, from an economic perspective, the suspension containing 15 kg NS ha^{-1} was preferred. With the optimum suspension, active, total, and active/total $CaCO_3$ reduced by about 24%, 40%, and 22% compared to the control, respectively. Furthermore, the $CaCO_3$-related properties, such as pH decreased by 0.48 unit and sodium adsorption (Na-adsorption) ratio by 18%, while soluble Ca^{2+}, K^+, SO_4^{2-}, water stable aggregate index, and macro- to micro-pores ratio increased by about 100%, 44%, 19%, 33%, and 60% compared to the control, respectively. In general, the optimal active $CaCO_3$ for better soil properties improvement is less than 10%. The NS suspension has a high corrective power on $CaCO_3$ and its related properties in the short term (60 days). However, regular application is recommended to continue pH reduction and neutralize $CaCO_3$. Therefore, NS suspension may be an effective option when an immediate reaction from the amendment is needed, especially at critical stages of growth.

Keywords: sodium adsorption ratio; macro to micro pores ratio; liquid nano-sulfur; nanotechnology.

1. Introduction

The desert accounts for approximately 96% of Egypt's total area. The government has recently given priority to the conversion of desert lands to agriculturally productive ones. Calcareous soils are widely present in the desert areas of Egypt. The amelioration and cultivation of these soils have become an essential necessity to increase our agricultural production in order to meet the ever-growing food demand (Abou Hussien et al. 2019; Yassin et al. 2023).

Calcareous soils are those with a high content of CaCO3 (≥ 15%; FAO 2023; Nada and Elbaalawy 2023), which causes some side chemical and physical problems, i.e., high pH, imbalances between nutritional elements, and changes the pore size distribution (Abou Hussien et al. 2019; Goossens et al. 2014; Hafshejani and Jafari 2017**;** Alghamdi et

al., 2023; Abou Hussien et al., 2021). Increased $CaCO_3$ has a significant impact on soil fertility status, leading to a reduction in crop yields (Ingole et al. 2018; Yassin et al. 2023). Moreover, it leads to decrease pore area and increase the total number of pores in soil, which results in decreased soil water-holding capacity, and thus hardening upon drying, forming, surface crusts (Chen et al. 2020; Abou Hussien et al., 2023 ; Nada and Elbaalawy 2023). In general, the optimal total and active/total $CaCO_3$ for better aggregate stability is between 20 to 48% (Umer et al. 2020).

It's known that elemental sulfur (ES) application has a long-lasting effect on neutralizing $CaCO_3$ in the soil, where it needs to a year or more for causes only a slight pH reduction in application zone (Wiedenfeld 2011; Derafshi et al., 2023). ES, as a soil acidifier, undergoes a microbial oxidation process which depends on a number of soil-related

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factors, including temperature, aeration, texture, and organic matter content (Germida and Janzen 1993; Soaud et al. 2011; Al-Mayahi et al., 2023). The particle size is the main factor that determines the oxidation rate, where small particles with a large total surface area are more reactive, so the finer the particles are, the faster the oxidation process (Sholeh et al. 1997; El-Kholy et al. 2013; López-Mosquera et al. 2015; Zhao et al. 2016; Al-Mayahi et al., 2023). This, in turn, could lead to lowering soil pH, improving nutrient availability (Brownrigg et al. 2022; Derafshi et al., 2023 ; Al-Mayahi et al., 2023), and affecting pore size distribution (Umer et al. 2020). The application of ES can ameliorate the Na hazard effect through decrease the Na:K ratio (Abdelhamid et al. 2013; Al-Mayahi et al., 2023). The application of ES in fine size (50 μm) increased the corrective power of CaCO3, resulting in a 35-day correction period. Furthermore, it decreased the pH value and increased the ions of SO_4^{2-} and K^+ in the calcareous sandy soil (AbdEl-Azeem and Ramadan 2018; El-Kholy et al. 2013). The treatment of calcareous soils with low concentrations of sulphuric acid (SA) resulted in some physical changes, such as a decrease in $CaCO_3$ content and bulk density. In addition, there was a decrease in soil pH and an increase in infiltration rate (Al balawna and Abu-Abdoun 2021). The chemigation use of micron-sulphur in drip systems rapidly reduced soil pH and has proven to be a useful short-term remedy to high pH problems (Almutairi et al. 2017). Application of nano-sulphur (NS) powder at a rate of 36 kg ha^{-1} in saline soils decreased pH and increased the availability of macro and micro nutrients (Esmaeil et al. 2020). Application of NS powder at a rate of 40 kg ha^{-1} together with organic fertilizer on calcareous soil released large amounts of sulfur (S) over the 60-day incubation period (Yazhini et al. 2023).

S compounds are used as soil Acidifiers to neutralize $CaCO_3$ in four forms. The first one is solid, e.g., ES (Brownrigg et al. 2022) and sulphur compost (Abou Hussien et al. 2020); the second is an aqueous solution, e.g., SA (Derafshi et al. 2023) and compost tea enriched by sulphur (Nada et al. 2023); the third is a suspension, e.g., Micron S (Almutairi et al. 2017); and the fourth is a solid NS (Esmaeil et al. 2020; Yazhini et al 2023). However, the use of NS as a suspension is a new strategy and has not yet been tested. Therefore, this study aims to (1) evaluate NS as a soil Acidifier to neutralize $CaCO_3$, and (2) determine the optimal dose of NS that should be added to mitigate the adverse effects of high $CaCO_3$ in calcareous sandy soils.

2. Materials and methods

2.1. Study soil
A bulk soil sample was collected from surface layer (0-20 cm) for a field in El-Hamam area (Latitude 30.81 and longitude 29.37) in Matrouh governorate province, Egypt. Then it was air-dried and sieved (2 mm sieve) before being analyzed for their physical and chemical properties.

The soil's texture is sandy (88.37% sand, 6.8% silt, and 4.83% clay). Soil pH (1:2.5 extract) is 8.44. Soil EC (soil paste extract) is 0.43 dS m^{-1}. Soil contains of 49% total CaCO3 (T-CaCO3), 10% active CaCO3 (A-CaCO3), 30.10 mg kg^{-1} soil Ca^{2+}, 42.90 mg kg^{-1} soil K^+, 16.44 mg kg^{-1} soil SO_4^{2-}, and 0.41% organic matter. Sodium adsorption ratio (SAR) is 1.89. Water stable aggregate index (SAI) is 33%. Total soil porosity (T-porosity; ww^{-1}) is 34.09%.

2.2. Preparation of NS suspensions

NS suspensions were prepared in two steps. First, a potassium polysulfide (K-poly) solution was prepared by dissolving ES (12 g of S) in potassium hydroxide (1N; 400 ml) with stirring at a temperature of 250°C. Second, four aqueous solutions of K-poly were prepared by diluting 0.5, 1, 2, and 3 ml of K-poly with 500 ml of distilled water. Next they were equilibrated with SA (dropwise) to form NS particles. Finally, distilled water was added to bring the volume to 1 liter. The endpoint of the reaction was the formation of a white suspension. The transmission electron microscopy showed that S-particles are spherical and poly-dispersed with diameter <30 nm (Figure 1). The particles with diameter <100 nm is known as nanoparticles (Tripathi et al. 2018). The four suspensions prepared contained 15, 30, 60, and 90 mg NS l^{-1}, which is equivalent to 15, 30, 60, and 90 kg NS ha^{-1}, respectively, calculated based on bulk density for soil surface layer (0.20 m) is 1750 kg m^{-3} and the air-dry weight of soil used to fill each pot is 3.5 kg.

2.3. Experimental design and treatments

The soils (< 2 mm, 3.4 kg dry weight) were weighed and packed in plastic pots (25 cm high, 15 cm internal diameter). A completely randomized design (RCD) was utilized in the statistical analysis of the experiment. Four treatments consisting of four NS suspensions at a rate of 15, 30, 60, and 90 mg l^{-1} pot^{-1}, which is equivalent to 15, 30, 60, and 90 kg NS ha^{-1}, which is equivalent to 15, 30, 60, and 90 kg NS ha^{-1}, respectively, plus control (distilled water; 0 kg NS ha^{-1}); giving five treatments × four replications = 20 pots. The first time of watering, the

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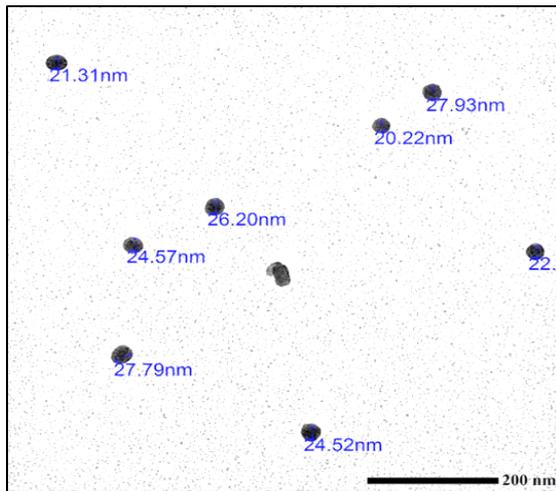NS suspensions (one liter per pot) were added to obtain the soil moisture content at saturation.

Fig. 1. The transmission electron microscopy test for the NS particle.

2.4. Incubation of the pots

At a laboratory temperature of 29 ± 2℃ and a relative humidity of $65 \pm 5\%$, the pots were incubated for two months. The pots were periodically watered with distilled water at field capacity (FC, 24% ww^{-1}) depending on their weight.

2.5. Soil chemical and hydro-physical analysis

After the incubation period, soil samples from each pot were taken to determine total CaCO₃ by the volumetric calcimeter method (FAO 2020) and active CaCO₃ by the back-titration method using potassium permanganate after shaking the soil with 0.2 *N* ammonium oxalate solution as described by (Bashour and Sayegh 2007).

Total pores, i.e., total porosity (%) were calculated using the following equation:

$$\text{Total pores} = [1 - (\rho_b|\rho_s)] \times 100 \qquad (1)$$

where: ρ_b, is the soil bulk density (g cm^{-3}) after incubation period; ρ_s, is the soil real density, taken as 2.65 g cm^{-3}.

According to the method described by (Estefan et al. 2013); soil pH was measured by the pH-meter (HI2211 PH/ORP Meter, HANNA Company) in a soil-to-water ratio of 1:2.5; In soil paste extract, soluble Ca^{2+} and Mg^{2+} were determined by EDTA titration method; soluble Na$^+$ and K$^+$ were measured by flame photometer (PFP7 Flame photometer, JENWAY Company) method; and soluble SO₄$^{2-}$ was determined by the BaCl₂ turbidity method.

Sodium adsorption ratio (SAR) was calculated using the following equation (Sundha et al. 2020):

$$\text{SAR} = \text{Na}^+ / \sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+})/2} \qquad (2)$$

where: cations values used in the equation were expressed as meq l^{-1}.

The wet sieving method was used to determine soil aggregates in water (unstable fraction) and dispersing solution (stable fraction), following that, the water stable aggregate index (SAI) was calculated using the following equation (Saygin et al. 2017):

$$\text{SAI}_{\text{water}} = \text{MDS}/(\text{MDS} + \text{M}_{\text{water}}) \qquad (3)$$

where: SAI, is the water stable aggregates index; MDS, is the weight of the stable aggregates (g); M$_{\text{water}}$, is the weight of unstable aggregates (g).

The soil water retention curve (pF-curve) was determined by the pressure plate apparatus (Soil Moisture Equipment Corp., Santa Barbara, CA, USA) (Estefan et al. 2013). Then the pore diameter was calculated using the following equation:

$$d = (4\,\sigma\,\cos\theta)/(h\rho g) \qquad (4)$$

where: d is pore diameter (m), σ is the surface tension of water (N m^{-1}), θ is the contact angle (°, assumed as zero for wetted surface), ρ is the water density (kg m^{-1}), g is the gravitational acceleration (m s^{-2}), and h is the matric potential (m). Pore space is classified to, (1) macro-pores (Mac-pores; non-capillary pores) with diameter < 29.73 μm, and (2) micro-pores (Mic- pores; capillary pores) or soil matrix with diameter > 29.73 μm (Abd El-Halim and Kumlung 2015). The present study has chosen h = -10 kPa as the limit between macro- and micro-pores (Amer 2012).

2.6. Statistical analysis

The statistical program SPSS v. 13.0 for Windows (Inc. Chicago, IL, USA) was used to test differences between the means using one-way analysis of variance (ANOVA), followed by Tukey honestly significant difference (HSD) test when a significant difference was detected ($P < 0.05$).

3. Results

3.1. Total, active, and active/total CaCO₃

Application of NS suspensions changed the total, active, active/total CaCO₃ of calcareous sandy soil significantly ($P < 0.001$) compared to the control (Table 1). The HSD of the arithmetic mean of all

characteristics showed that application NS at a rate of more than 30 kg ha^{-1} did not result in any significant differences. As a result, it can be concluded that the optimal NS rate was 30 kg ha^{-1}. However, the application of NS at a rate of 15 kg ha^{-1} and 30 kg ha^{-1} had also no significant difference; this suggests that it was sufficient to neutralize carbonates, and from an economic perspective, the preferred NS rate is 15 kg ha^{-1}. On the other hand, the superior NS rate, which decreased the the total, active, and active/total CaCO$_3$ more than other rates, was 90 kg ha^{-1}. total, active, and active/total CaCO$_3$ decreased with the superior NS rate of about 24%, 40%, and 22%; while they decreased by about 24%, 40%, and 22% with the optimum NS rate; whereas they decreased by about 20%, 20%, and 9% with the preferred NS rate; compared to the control, respectively.

Table 1. Impacts of nano-sulfur (NS) suspensions at different rates on total CaCO$_3$% (T), active CaCO$_3$% (A), and A/T CaCO$_3$% of the soil after 2 months of incubation

NS rate	CaCO$_3$		
	T	A	A/T
kg ha^{-1}		%	
0	49.83a	10.00a	20.08a
15	40.00b	8.33ab	18.33ab
30	38.00b	6.00bc	15.77ab
60	37.33b	5.00c	13.40bc
90	36.49b	3.33c	9.04c
P-value	<0.001	<0.001	<0.001
SEM	0.78	0.62	1.21
HSD	3.62	2.86	5.64

Means of column under each subheading followed by different upercase letters (a-c) are significantly different at Tukey's Honestly Significant Differences (HSD) test ($p \leq 0.05$; otherwise statistically at par); SEM is the standard error of the mean; $p <$ 0.001 means strongly significant.

3.2. Soil pH, Ca^{2+}, K$^+$, SO$_4^{2-}$, SAR, and SAI

The pH, Ca^{2+}, K$^+$, SO$_4^{2-}$, SAR, and SAI of the soil was significantly ($P <$ 0.001) altered by the application of NS suspensions compared to the control (Table 2). The reduction of total active , and active/total CaCO$_3$ to a range between 20-27%, 17-67%, and 9-55%, respectively, had a positive impact on improving soil pH, increasing soluble K$^+$ and Ca^{2+}, increasing soluble SO$_4^{2-}$, reducing Na$^+$ hazard (SAR), and increasing SAI (Table 2). This indicates that there is an optimum range for active and active/total CaCO$_3$ in soil to increase oxidation of NS and solubility of nutritional elements, this range between 3% to 8% for active CaCO$_3$ and 9% to 18%

for active/total CaCO$_3$. The reduction in soil pH resulted in an increase in soluble Ca^{2+}, K$^+$, and SO$_4^{2-}$ which contributed to an increase in SAI, while decreasing SAR. In general, the optimum active CaCO$_3$ for better aggregate stability may not exceed 10%. The pH and SAR, compared to the control, decreased with the superior NS rate by about 0.56 unit and 25%, respectively; while soluble Ca^{2+}, K$^+$, and SO$_4^{2-}$ increased by about 116%, 40%, and 80%, respectively, whereas the SAI increased by about 43%. In the same line, the pH and SAR, compared to the control, decreased with the optimum NS rate by about 0.48 units and 18%, respectively; while soluble Ca^{2+}, K$^+$, and SO$_4^{2-}$ increased by about 100%, 44%, and 19%, respectively, whereas the SAI increased by about 33%. In the same trend, the pH and SAR, compared to the control, decreased with the preferred NS rate by about 0.55 units and 20%, respectively; while soluble Ca^{2+}, K$^+$, and SO$_4^{2-}$ increased by about 100%, 24%, and 9%, respectively, whereas the SAI increased by about 20%.

1.1 Total, macro, micro, and macro/micro pores ratio

The addition of NS suspensions to the calcareous sandy soil improved the aggregate stability and thus the overall porosity, especially the Mac-pores. The total, macro, micro, and macro/micro pores ratio of the soil was significantly ($P < 0.001$) altered by the application of NS suspensions compared to the control (Figure 2). The pore size distribution positively correlated with the increase of NS rate in the applied suspensions, where the total pores and macro pores increased while micro-pores decreased, as a result, the macro/micro pores ration increased. The total pores, macro pores, and macro/micro pores ratio, compared to the control, increased with the superior NS rate by about 8%, 53% and 64%, respectively, while micro pores decreased by about 7%. In the same trend, the total pores, macro pores, and macro/micro pores ratio, compared to the control, increased with the optimum NS rate by about 8%, 70% and 98%, respectively, while micro pores decreased by about 12%. By the same method, the total pores, macro pores, and macro/micro pores ratio, compared to the control, increased with the preferred NS rate by about 11%, 64% and 73%, respectively, while micro pores decreased by about 6%.

Table 2. Impacts of nano-sulfur (NS) suspensions at different rates on soil reaction (pH), soluble calcium (Ca^{2+}), soluble potassium (K$^+$), soluble sulfate (SO$_4^{2-}$), sodium adsorption ratio (SAR), and water stable aggregate index (SAI) of the soil after 2 months of incubation.

NS rate kg ha^{-1}	pH unit	Ca^{2+}	K$^+$	SO$_4^{2-}$	SAR	SAI %
			mg kg^{-1} of soil			
0	8.44	30.10c	42.90c	15.76d	1.94a	30b
15	7.89	60.10a	53.21b	17.13cd	1.55b	36ab
30	7.96b	60.10a	61.92ab	18.73c	1.60b	40a
60	7.98	50.10b	64.93a	22.15b	1.71ab	41a
90	7.88	65.10a	59.91ab	28.43a	1.46b	43a
P-value	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
SEM	0.02	1.29	2.08	0.61	0.07	1.56
HSD	0.09	6.01	9.68	2.84	0.30	7.25

Means of column under each subheading followed by different upercase letters (a-c) are significantly different at Tukey's Honestly Significant Differences (HSD) test ($p \leq 0.05$; otherwise statistically at par); SEM is the standard error of the mean; $p < 0.001$ means strongly significant.
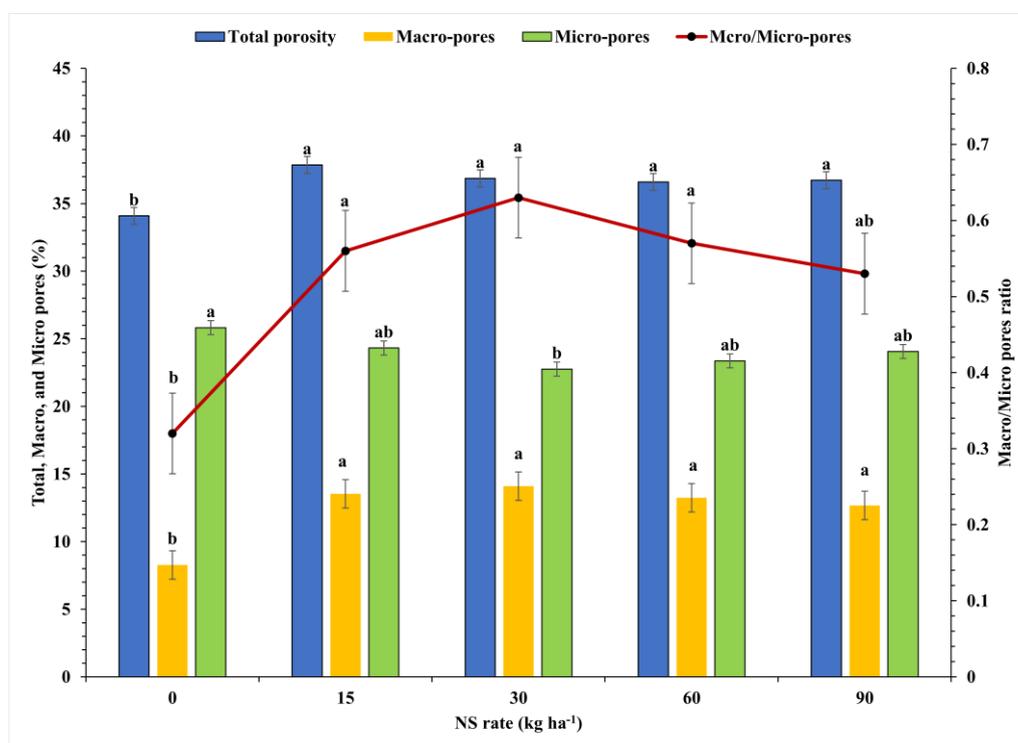

Fig. 2. Impacts of nano-sulfur (NS) suspensions at different rates on percentage of Total-pores, Macro-pores, Micro-pores, and Macro/Micro-pores ratio of the soil after 2 months of incubation; Means of column followed by different letters (a-b) are significantly different at Tukey's HSD test ($p \leq 0.05$; otherwise statistically at par); Error bars represent the standard error of the mean.

4. Discussion

Application of NS suspensions to calcareous sandy soil with high CaCO₃ had a positive impact to reduce total and active CaCO₃, consequently reduce the ratio of active/total CaCO₃. The reason for this is the positive effect of NS in the dissolution of excess CaCO₃ (Abou Hussien et al. 2020; Dawood 1989; Neilsen et al. 1993). The sulfuric acid generated from NS oxidation is responsible for the dissolution of excess CaCO₃, which is considered one of the most important factors (Al balawna and Abu-Abdoun 2021). The sulphuric acid reacts with CaCO₃ releasing CO₂ into the atmosphere, thereby reducing native lime content of calcareous sandy soil (Derafshi et al. 2023; Soaud et al. 2011; Yang et al. 2010). Active, reactive CaCO₃ is the most significant property of CaCO₃ that has a significant impact on all soil processes that occur within chemical, pedogenic, and rhizosphere levels (García-Montero

et al. 2007). Reducing active $CaCO_3$ to less than 8% improved the chemical and hydro-physical properties of calcareous sandy soil (Carter 1981; Farrag and Bakr 2021; Wassif and Wassif 2021). However, the soil's inherited chemical properties are more affected by active/total $CaCO_3$ than total $CaCO_3$ and active $CaCO_3$ alone, because it represented the actual active portion of $CaCO_3$, which governs and affects most chemical properties. In general, the optimum active/total $CaCO_3$ for micro-aggregate formation and its stability may not exceed 18% (Umer et al 2020).

The pH change induced by the application of NS suspension could be also due to NS oxidation process. The NS particles are rapidly oxidized by S-oxidizing bacteria to hydrogen ions and sulphuric acid within a few weeks under optimal conditions (Shakoor et al. 2023; Yazhini et al 2023). The hydrogen ions and sulphuric acid's action causes the relatively high pH value of calcareous sandy soil to be reduced (Akay et al. 2019; Amin and Mihoub 2021). The particle size plays a key role in the accelerating NS oxidation process (El-Kholy et al. 2013; López-Mosquera et al. 2015; Sholeh and Blair 1997; Scherer et al. 2012). The high oxidation rate of nanoparticles is a result of their large total surface area and higher reactivity (Degryse et al. 2016; Zhao et al. 2016). It can be concluded, therefore, that due to rapid oxidation, NS suspension had a markedly short-term effect on soil pH (AbdEl-Azeem and Ramadan 2018; Al balawna and Abu-Abdoun 2021; Almutairi et al. 2017; El-Kholy et al. 2013; Esmaeil et al. 2020; Yazhini et al 2023).

The sulphuric acid's action causes an increase the availability of nutrients like calcium, magnesium, potassium, and sulphate (Amin and Muhammed 2015). The released Ca^{2+} would react with SO_4^{2-} to form gypsum ($CaSO_4$). However, $CaSO_4$ formation is largely controlled because of the NS rapid oxidation (Reda and Modaihsh 1990; Yazhini et al 2023). Regardless of pH, $CaSO_4$ is a good Ca^{2+} additive when Ca^{2+} is needed. $CaCO_3$ can also provide Ca^{2+}, but $CaSO_4$ is 150-200 times more soluble than it (Aramrak et al. 2021). The clay particles in soils were either coated or cemented by carbonate. In calcareous soils, carbonate has a coating and cementing effect that is 80% of its total effect (Al-Saedy et al. 2003). As an effective cement material, carbonates can aggregate many clay particles so that they appear as larger units, like silt or sand particles (Pihlap et al. 2021; Zhang and Norton 2002). Then, after carbonate removal and aggregate is breakdown, the amount of silt and sand

particles decreases, and the clay content increases (Francis and Aguilar 1994). Ca^{2+} is known to play an important role in increasing the quantity and quality of aggregates and the attraction energy (interaction forces) between clay particles (Hu et al. 2018; Liu et al. 2023; Moghal et al. 2020; Pihlap et al. 2021; Safar and Whalen 2023). On the one hand, high divalent cations like Ca^{2+} in the soil solution, due to the fast dissolution of $CaSO_4$, are the main mediators of clay-to-clay bonding, responsible for the formation of large (macro-aggregates) stabilized aggregates (Pihlap et al. 2021). In other words, the presence of high-content carbonates and bivalent Ca^{2+} cations can flocculate clay particles and these particles then act as larger particles (macro-aggregates) in soils, which are not easily disturbed, thus increasing soil structural stability (Safar and Whalen 2023). On the other hand, increasing monovalent K^+ in the soil solution increases the attractive energy between clay particles, i.e., it increases clay-to-clay bonds, where K^+ is a good flocculant (Aramrak et al. 2021; Arienzo et al. 2012). Increasing the interaction force between soil particles is an important factor influencing the enhancement of soil structural stability (Hu et al. 2018; Liu et al. 2023). Therefore, the high stabilizing power of Ca^{2+} and K^+ might be the reason for increasing soil aggregate stability index (SAI) caused by application NS suspensions. A decline in SAR, an indirect indicator of soil structural stability, supports this finding (Khaled and Ahmed 2023; Table 2).

There are two types of pore space are commonly distinguished in the literature for bare soil with low organic matter content, such the soil of this study, that is the structural porosity and the textural porosity (Dexter and Richard 2009). Structural porosity, also known as inter-aggregate pores (macro-pores), is pores between aggregates, whereas, textural porosity, also known as intra-aggregate pores (micro-pores), is formed between primary soil particles, which depends on the intra-aggregate arrangement and particle type (clay, oxides) (Dlapa et al. 2020). The ratio of macro/micro pores ratio has an increasing trend with increasing NS rate and this trend suggests that with an increasing NS rate, the relative increase in the macro-pores is higher compared to that of micro-pores. The reason is likely due to the increased content of inter-connected structural pores. This is due to the fact that $CaCO_3$ is removed and more clay particles are released, redistributed, and stabilized by the highly attractive energies of Ca^{2+} and K^+ ions, formation of large stable groups or aggregates, effectively behaving like silt-sized particles (Al

balawna and Abu-Abdoun 2021). In this case, the pore spacing between these large stable groups is considered part of the structural porosity (macro-pores) (Al-Saedy et al. 2003). The high increase in pores with diameter of > 30 μm (macro-pores) in calcareous soil was also indicated due to the addition of chemical conditioners (Mohamed 2014). The increase in the aggregate size can cause a remarkable increase in the total pores, i.e., total porosity (Figure 2). In addition, aggregate size has a considerable effect on the fractal dimension of the micro-pore structure (He et al. 2021).

The study's findings revealed that the optimal NS rate of the investigated soil was 30 kg ha^{-1} and the best incubation period for NS oxidation was 60 days. However, the application of NS at a rate of 15 kg ha^{-1} was sufficient to neutralize carbonates, and from an economic perspective, is preferred. Applied NS to calcareous soil at a rate of 40 kg ha^{-1} with organic manure showed a high release of S during a 60-day incubation period (Yazhini et al 2023). Also, applied NS to groundnut at a rate of 30 kg ha^{-1} was sufficient to attain a higher S-use efficiency with a reduction of S-fertilizer to the tune of 25% besides augmenting the soil S reserve without harming the environment (Thirunavukkarasu et al. 2018). Furthermore, the application of NS at a rate of 15 kg ha^{-1} on the saline soil was the best in reducing pH, EC, bulk density, hydraulic conductivity, and total porosity, while soil available macro- and micro-nutrients increased (Esmaeil et al. 2020). In addition, during an incubation period of 60 days, the application of NS-enriched bio-organic phosphate composites on the calcareous soil at a rate of 50 kg ha^{-1} rendered the high K and S concentrations due to lower soil pH (Shakoor et al. 2023).

5. Conclusion

In calcareous sandy soil, NS suspension is capable of changing soil pH in a relatively short-term period of 60 days, and consequently, it has high corrective power for CaCO$_3$ and its related properties. These improvements were most probably related to the large surface area, which helped NS to rapidly oxidize, resulting in a fast improvement in the soil pH, and consequently a reduction in active CaCO$_3$ %, and also release more soluble cations and anions (Ca^{2+}, K$^+$, and SO$_4^{2-}$). Hence, these cations can attract soil particles and form very stable structural units by the coalescence of micro-aggregates and preventing clay dispersion leading to decreased SAR and increased SAI and macro-pores. NS suspension is an excellent source of acidity to be used under

certain circumstances such as correction of a high soil pH condition after a crop is planted; a rapid change in soil pH if acidifying is delayed to just before planting a crop; for maintaining pH in the optimal range for plant growth and yield.

Conflicts of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Author contributions

Smaa A. EL-Madah contributed with resources, conceptualization, methodology, formal analysis, and writing—original draft preparation; Mahmoud M. Ibrahim contributed with supervision and validation; and Abd El-Halim A. Abd El-Halim contributed with conceptualization, methodology, formal analysis, investigation, data curation, writing—review and editing, supervision, and project administration.

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