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Investigation on geoengineering properties of organic silt soil treated with chitosan nanoparticle additive

Govindarajan Kannan[1], Evangelin Ramani Sujatha[2]✉ & Brendan C. O'Kelly[3]

Organic soil deposits are often unsuitable for safely bearing structural loads without proper soil stabilization measures. Sustainable methods of soil stabilization are gaining attention, with nano-additives showing promising effects owing to their high reactivity and better soil interaction. The present study attempts to investigate the feasibility of treating a low-plasticity organic silt soil using chitosan nanoparticle (CNP) additive, a crustacean polysaccharide. The modifications in the soil plasticity index (PI), compaction, unconfined compressive strength (UCS), permeability and consolidation properties were studied for 0.5 to 2.5% CNP addition, considering the curing period durations of between 0 and 90 days. Results showed that 1% CNP addition produced a better outcome in terms of geoengineering properties. For instance, compared to the untreated soil, the compacted 1% CNP-treated soil achieved a 146% UCS gain and 69% permeability coefficient reduction for 90-day curing, with negligible change in the coefficient of consolidation. Whereas 2.5% CNP-treated soil exhibited a comparatively smaller UCS gain (of 100%), along with a 59% permeability coefficient reduction for 90-day curing. SEM analysis indicated that the CNP additive enhanced the geomechanical properties by forming a fibrous network in the soil matrix. Finally, a critical discussion has been presented on the aspects of necessity of nano-based soil stabilization, cost analysis and material degradation effects to understand the suitability of the technique for practical applications.

Keywords Biopolymer, Nano-chitosan, Organic silt, Compaction, UCS, Permeability

Cement and lime are conventional choices for additive-based soil stabilization. However, organic matter content present in the soil could inhibit the formation of calcium-silicate-hydrate (CSH), and hinder the strength improvement achieved for lime stabilization[1]. Another important concern with employing traditional cement and lime additives for soil stabilization purposes is the high carbon emission rate occurring during their production. According to the 17th Global Carbon Budget (2022), 4% of total carbon emissions arise from cement production[2]. In addition, it reported a 1% increase in the emission rate results from the combustion of fossil fuels and cement manufacturing. Although lime production was 90% less than cement production in 2022, the average carbon emission from lime production was 74% higher than for cement production. Although research is ongoing to partially replace cement with supplementary cementitious materials like calcinated shale[3,4], the growing environmental concerns encourage researchers to identify new methods and techniques, as alternatives to traditional additives for soil stabilization. Biopolymer stabilization is a trending method of ground improvement, where the geoengineering behavior/properties of the treated soil are enhanced through sustainable additives[5].

Chitosan is a crustacean-based biopolymer obtained from the exoskeletons of crab, shrimp and prawns. Chitosan has been used for a variety of civil engineering applications, e.g., wind erosion control for surficial soil layer[6], and as a flocculating agent and adsorbent in water treatment[7]. In recent times, researchers have also started testing the potential of using chitosan as a strength-enhancing agent. Hataf et al.[8] treated low-plasticity clay with chitosan hydrogel biopolymer, and found that the formation of fibrous threads and ionic bonding caused an improvement in the soil strength. Kannan and Sujatha[9] showed that 2.5% chitosan powder additive produced a 103% enhancement in the soil strength for 28-day curing. The bond between the soil solids and chitosan

[1]Department of Civil Engineering, Mepco Schlenk Engineering College, Sivakasi, Tamil Nadu 626005, India. [2]Centre for Advanced Research in Environment, School of Civil Engineering, SASTRA Deemed University, Thanjavur, Tamil Nadu 613401, India. [3]Department of Civil, Structural and Environmental Engineering, Trinity College Dublin, Dublin D02PN40, Ireland. ✉email: r.evangelin@gmail.com; sujatha@civil.sastra.edu

additive, and the fibrous threads formed by the additive, enhanced the treated soil's geomechanical properties. Furthermore, several researchers proved that, in its nanoform, chitosan exhibited enhanced performance for use in various engineering applications. For instance, Kahalili et al.[10] showed that, due to their smaller particle size and lower viscosity, chitosan nanoparticles (CNP) performed better as a water-based electrolyte in liquid dye-sensitized solar cells. Civil engineering is one such field that has potential for employing CNP as an additive for soil stabilization purposes. In fact, the application of nano-additives for soil stabilization is a well-received technique, since the quantity of nano-additive required is significantly less compared to conventional chemical stabilizers; nano-additives processing considerably higher specific surface area (SSA) for better interaction, and exhibit superior performance for substantially lower dosage compared to micro-sized additives[11]. For instance, Majeed et al.[12] stabilized organic clay, achieving approximately 7.13-, 7.0- and 3.55-fold strength improvements employing 0.7% nano-copper, 0.2% nano-clay and 0.3% nano-magnesium additives, respectively. They reported that the nanoparticles filled the soil pore-voids and increased the soil strength, but excess additive present led to strength reduction due to the aggregation effect. Similarly, Rafiei et al.[13] showed that 2% nano-cement can improve the strength of clayey soil by up to 7 fold for 28-day curing. In fact, such nano additives are more effective even when added in combination with other chemical additives, like cement[14], or with physical reinforcement, like fibers[15].

For stabilization of organic soil, Ghadr et al.[16] attempted to stabilize peat with 5% colloidal nano-silica (NS), reporting a 3.76-fold increase in 28-day strength. The silica globules coagulated in the soil matrix, resulting in strength improvement. Kannan and Sujatha[17] treated organic silt with 0.6% NS. The formation of CSH between the soil minerals and NS produced a 2.21-fold strength improvement for 180-day curing. Kannan et al.[18] stabilized organic silt with 0.4% nano-calcium-carbonate (NCC), which produced a 3.04-fold UCS improvement for 180-day curing. The NCC reacted with the clay minerals to form a viscous CSH that binds the soil solids. Hence, it is inferred that nano-additives are more compatible with strengthening organic soils at significantly lower dosage compared to conventional soil stabilizers.

A review of the literature reveals that studies on the application of chitosan for the stabilization of organic soil are limited, despite its potential to improve the geotechnical behavior/properties. Moreover, the few reports available regarding chitosan-based soil stabilization are limited to micro-sized varieties and solution forms of chitosan. As such, the performance of environmentally friendly, biocompatible and biodegradable CNP in the field of soil improvement/stabilization remains largely unexplored. The present study investigates the potential of incorporating CNP to treat a low-plasticity organic silt, investigating the modifications in various geoengineering properties. Soil treated with between 0.5% and 2.5% CNP additive is tested for its plasticity, compaction, age-based strength, permeability and consolidation properties. Additionally, the microstructural modification responsible for the strength improvement is investigated using scanning electron microscope (SEM), Fourier-transform infrared (FTIR) spectroscopy and X-ray diffractometer (XRD) analyses.

Materials

Soil

The investigated organic soil was sourced from a depth of 1.5 m in the agricultural fields of Ariyalur, Tamil Nadu, India. The same soil material was previously employed by the authors in investigating the stabilization performance achieved for a different nano-additive, specifically NS and NCC, as reported in Sujatha and Kannan[17] and Kannan et al.[18]. Table 1 lists some pertinent geotechnical engineering properties of the test soil, which was black in color, indicative of its 13.6% organic matter content. The latter was determined by completely burning 50 g of the oven-dried soil (110 °C) in a muffle furnace at (440 °C), as per ASTM D2974[19].

Property	Value
Specific gravity of solids	2.33
Organic matter content	13.6%
Percentage of gravel	2%
Percentage of sand	25%
Percentage of silt	52%
Percentage of clay	21%
Differential free-swell index	35%
Liquid limit	48.8%
Plastic limit	26.3%
Plasticity index	22.5%
Optimum water content for compaction	17.5%
Maximum dry unit weight (MDUW)	16.8 kN/m^3
Unconfined compression strength at MDUW	172.4 kPa
Coefficient of permeability	8.8×10^{-8} cm/s
Coefficient of consolidation	0.12 m^2/year

Table 1. Index and engineering properties of test soil[17,18].

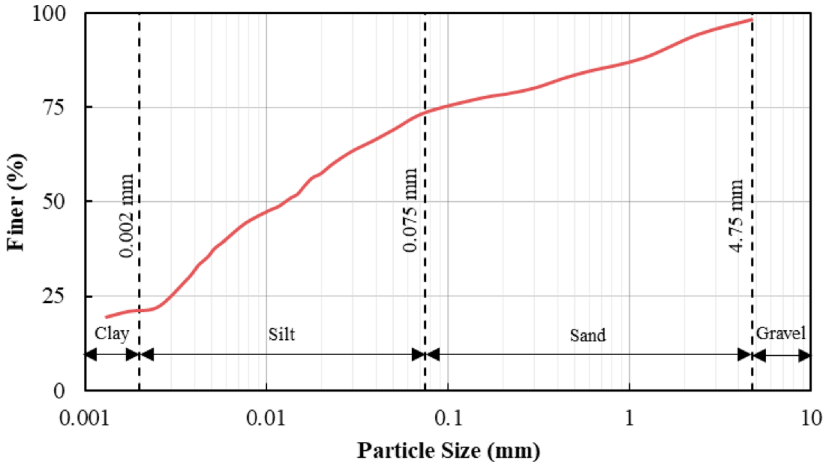

Fig. 1. Particle-size distribution of the test soil[17,18].

Compound	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	MgO	K_2O	P_2O_5	MnO_2	Others
Proportion (%)	58.05	16.37	15.09	4.28	2.07	1.75	0.59	0.57	0.29	0.04

Table 2. Chemical composition of the test soil.

Property	Value
Molecular formula	$(C_6H_{11}NO_4)_n$
Molecular weight (g/mol)	161
Degree of deacetylation (%)	70–85
Average particle size (nm)	30–50
Specific gravity of solids	1.4
pH (1% solution)	5.97
Water solubility	Nil
Purity (%)	>99

Table 3. CNP material properties.

Figure 1 shows the particle-size distribution plot obtained for the dry pulverized soil material, as determined from dry sieving and hydrometer analyses[20,21], with constituent gravel (> 4.75 mm), sand (75 μm to 4.75 mm), silt (2 μm to 75 μm) and clay (< 2 μm) sized fractions of 2%, 25%, 52% and 21%, respectively. Based on the particle-size distribution results, measured liquid limit of 48.8%, plasticity index of 22.5%[22], and organic matter content of 13.6%, this natural soil material was classified in accordance with the Unified Soil Classification System (USCS)[23] as "low-plasticity silt with organic content", with Group Symbol OL. Finally, Table 2 lists the chemical constituents of the tested soil material, as determined from X-ray fluorescence analysis.

Chitosan nanoparticles

Chitosan is a linear cationic polysaccharide, obtained by the deacetylation of chitin by demineralizing and deproteinizing the cleaned shells of crustaceans[8]. Chitosan has good adsorption capacity, and is more effective as nano-sized particles, having more adsorption surfaces and increased functional groups[24]. It is insoluble in water, but dissolves in dilute aqueous acids.

The CNP additive used in the present study was a nano-sized variety of chitosan material prepared from shrimp shell waste (procured from Nano Research Laboratories, Jharkhand, India). The general production procedure, as shared by the supplier, was that the shrimp shells were sun-dried, followed by a demineralization process in diluted hydrochloric acid to remove the calcium carbonate. Then the samples were neutralized by washing in distilled water, followed by soaking in sodium hydroxide solution for deproteinization. The deproteinized flakes were neutralized and dried to obtain an intermediate product called chitin. The chitin was then deacetylated with a strong base (sodium hydroxide) to obtain chitosan. Finally, the chitosan material was converted to nano-size to obtain the CNP additive. The manufacturer specifications given to the authors for the CNP material are listed in Table 3. It has a middle degree of deacetylation (DDA); the degradation of CNP

depending on the DDA, i.e., chitosan produced with a greater DDA lasts longer compared to chitosan material with lower DDA[25].

Experimental method

Additive dosage fixation

The dosage range for this study was fixed based on preliminary unconfined compression strength (UCS) tests conducted after 7 days of curing, as the main objective of the study is to investigate the potential strength improvement. Initially soil specimens treated with 0.2, 0.4 and 0.6% of CNP additive (dry soil mass basis) were tested for their strength gains, but there was no appreciable variation in their strengths. Hence, the dosage increment was increased (i.e., from 0.2 to 0.5%), investigating 0.5, 1, 1.5, 2 and 2.5% of CNP additive.

Additive mixing

The study adopted the dry mixing sample preparation approach. The quantity of soil required for each experiment was oven dried and divided into ten equal parts. Similarly, the required quantity of the CNP additive was also proportioned into ten equal parts and added to each split. These were then separately hand-mixed for 5 min and finally blended together to achieve a homogeneous dry soil–CNP sample. Subsequently, the required quantity of water was sprayed onto the sample, followed by further mixing. Prior to performing any tests, the prepared samples were stored in moisture-lock airtight bags for a 2-h period to ensure uniform water distribution and to promote chemical reactions, if any. The sample preparation process is summarized in Fig. 2.

Experimental investigation

Liquid and plastic limit tests

Liquid limit (LL) and plastic limit (PL) tests were conducted, as per ASTM D4318[22], to investigate the plasticity properties of the untreated and CNP-treated soil. For these tests, the dry soil sample was mixed with 10% of water and stored in airtight bags for a 2-h period, as mentioned in Sect. 3.2. Then the LL tests were conducted using Casagrande's (percussion-cup) method, based on which the water content corresponding to 25 number of blows is regarded as the LL. The PL was determined using the thread-rolling method, in which the water content that the prepared soil thread crumbles at a diameter equivalent to 3 mm is regarded as the PL. For both tests, three number of trials were performed at each CNP dosage to ensure uniformity in the results.

Compaction test

Standard Proctor-compaction testing was performed, as per ASTM D698[26], to determine the optimum water content (OMC) for compaction and the maximum dry unit weight (MDUW) achieved. Like the sample preparation employed for the LL and PL tests, 10% of water was initially added to the dry-mixed soil, followed by a 2-h maturing period. For the compaction tests, the prepared samples were compacted in three equal-height layers with 25 rammer blows applied in each layer. Subsequent trials were conducted investigating 2% increments in the water content.

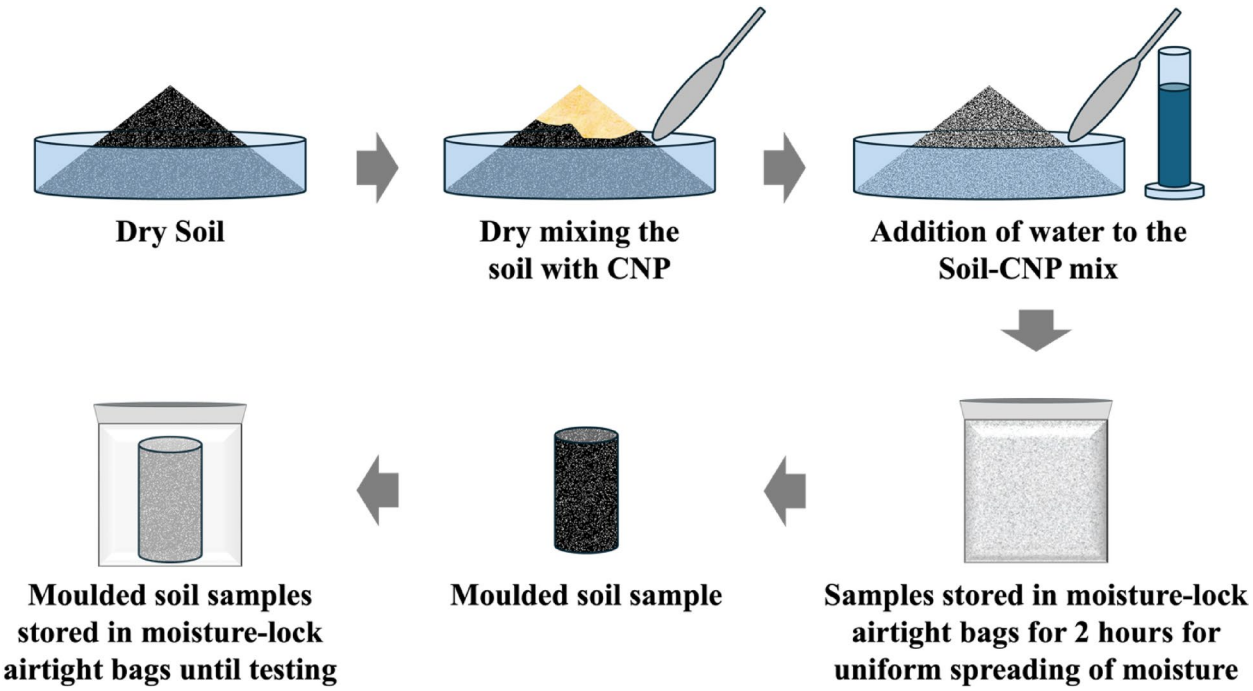

Fig. 2. Soil–CNP mixture preparation method.

UCS tests

UCS testing was conducted following ASTM D2166[27] guidelines to study the strength improvement of the CNP-treated soil. 38-mm diameter by 76-mm high UCS test-specimens were prepared at their MDUW, for which the dry soil–CNP mixtures were added with the water content corresponding to their OMC. These UCS specimens were allowed to cure in airlock bags for periods of 0, 7, 14, 28, 56 and 90 days before performing the strength tests, employing an axial strain rate of 1.25 mm/min.

Permeability tests

Falling-head permeability testing was conducted, per the guidelines of ASTM D5856[28] and IS2720(Part 17)[29], to assess any change in the drainage behavior of the CNP-treated soil samples, monitored over a 90-day period. Initially the samples (each 100-mm diameter by 127-mm high) were molded at their MDUW in the permeameter, sandwiched between a filter paper and porous stone at both top and bottom ends. Then the samples were allowed to achieve full saturation, followed by permeability testing. The water levels in the permeameter standpipes were monitored daily, and on the days of testing (i.e., 0, 7, 14, 28, 56 and 90 days after saturation) three separate readings were taken to ensure that the deviation between the results is less.

Consolidation test

The untreated soil and 0.5%, 1% and 1.5% CNP-treated soil were tested to assess their one-dimensional (1D) consolidation behaviors, as per ASTM D2435[30]. After applying a seating load of 0.05 kg/cm^2 for 24 h, the test specimens were subjected to vertical sequential loading of 0.1, 0.2, 0.4, 0.8, 1.6 and 3.2 kg/cm^2, each load stage applied for 24 h, followed by sequential unloading.

Microstructural and material property investigations

Microstructural investigations were performed for the untreated and 1% CNP-treated soil using a TESCAN Vega-3 SEM apparatus for three different magnifications (of 5,000x, 10,000x and 15,000x) whereas the field emission SEM was done using Zeiss Gemini 300 instrument. The functional group variation was analyzed using a Perkin Elmer FTIR spectrophotometer between a wavenumber from 350 cm to 1 and 3950 cm^{-1}. The chemical compounds were analyzed using a Bruker XRD apparatus for a 2θ range of 20 to 80° with copper anode.

Results and discussion

Plasticity properties

Plastic behavior indicates the soil's ability to deform under loading without experiencing cracking or crumbling. Figure 3 shows the LL, PL and plasticity index (PI) properties of the untreated and CNP-treated soil, with the plasticity index determined as PI = LL – PL. Referring to Fig. 3, CNP addition produced an increase in the LL, from LL = 48.8% for the untreated soil, to 57.0% measured for 2.5% CNP-treated soil (i.e., the highest CNP dosage investigated). In terms of the soil's classification, the increase of LL for the CNP-treated soil beyond the 50% threshold (as defined in the USCS[23] renders it as likely to exhibit highly compressible behavior.

Whereas the CNP treatment had a negligible influence on the PL; the untreated and 2.5% CNP-treated soil having PLs of 26.3% and 27.4%, respectively. Furthermore, the results in Fig. 3 show that both the untreated and CNP-treated soil had high plasticity (i.e., PI > 17), with the PI value monotonically increasing for greater CNP addition.

Fatehi et al.[31] reported that most biopolymers impart a marginal increase in the LL and PL of treated soil. CNP being hydrophilic in nature, causes water adsorption in the soil–CNP matrix, thus producing marginal

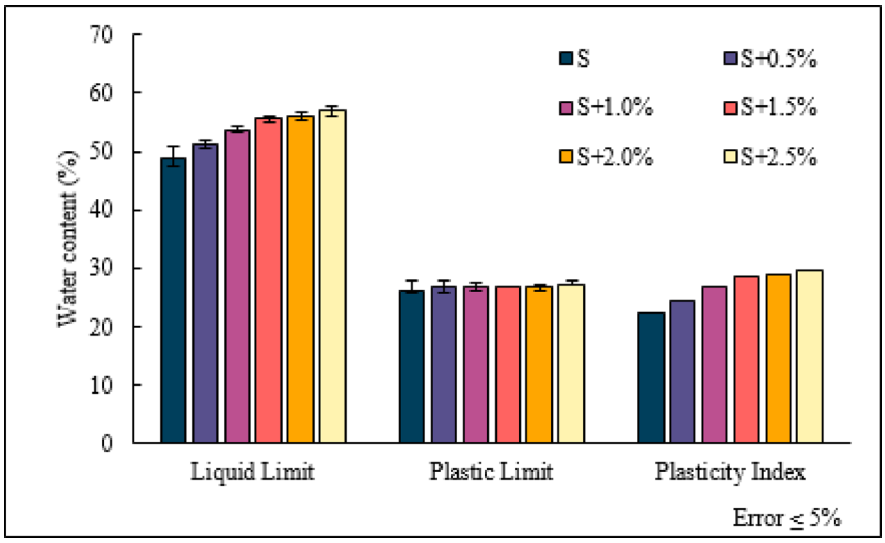

Fig. 3. Index properties of the untreated and CNP-treated soil.

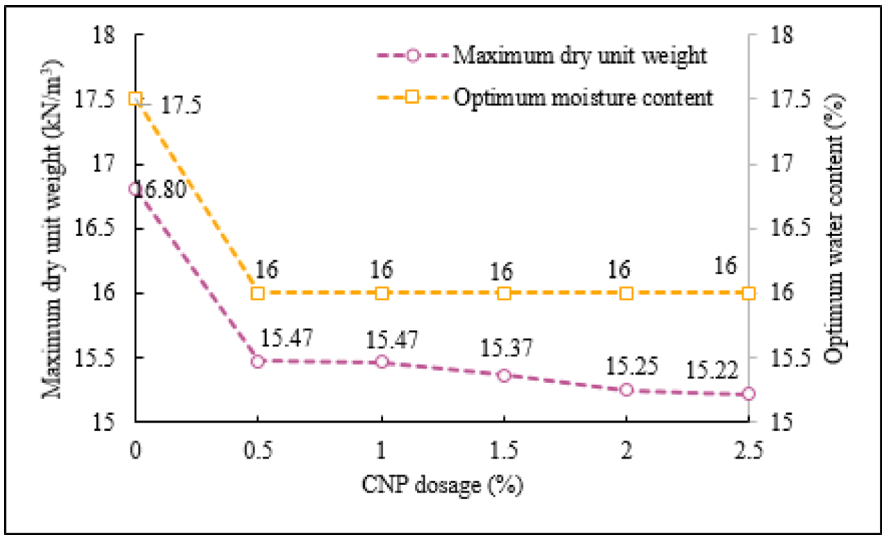

Fig. 4. Variation in MDUW for standard compaction of the soil–CNP mixtures at their OMC.

CNP dosage (%)	Failure strain (%) for curing periods of:					
	0 day	7 day	14 day	28 day	56 day	90 day
0	4.61	–	–	–	–	–
0.5	4.61	4.61	3.62	3.62	3.62	3.62
1	4.61	4.28	3.62	3.29	3.29	3.29
1.5	4.61	4.28	3.29	3.29	2.96	2.96
2	4.28	3.95	3.29	3.29	2.96	2.96
2.5	3.95	3.95	3.29	3.29	2.96	2.96

Table 4. Failure strain of untreated and CNP-treated soil UCS-tested after different curing periods.

increases in the LL and PL for the CNP-treated soil. Additionally, the CNP material has an SSA substantially greater than that of the soil solids, such that the CNP addition increases the LL of the treated soil.

Compaction behavior

The untreated soil had an MDUW of 16.8 kN/m^3, achieved for an OMC of 17.5%. CNP addition marginally decreased both the OMC and MDUW (see Fig. 4), with the OMC reducing to 16.0% for 0.5–2.5% CNP and the MDUW reducing to 15.47 kN/m^3 for 0.5% CNP and then to 15.22 kN/m^3 for 2.5% CNP addition.

The MDUW reduction is explained by the CNP additive promoting soil aggregation on account of (i) chitosan, being cationic, attracting the negatively-charged clay particles present in the soil mass[8], and (ii) the higher SSA of the CNP material offering more regions for soil–CNP interaction. On the other hand, the filling of the soil pore-voids by the CNP and the aggregation effect prevented further interaction of pore water with the soil, such that the OMC value remained steady for increasing CNP dosage from 0.5% to 2.5%. This is a typical behavioral response observed by the authors in previous investigations of this soil treated with NS and NCC additives[17,18]. Another reason for the MDUW reduction is that the unit weight of the CNP material is lower than for the soil solids, such that the presence of more CNP additive in the treated soil resulted in the lesser MDUW than for the untreated soil[9].

Strength characteristics

Failure strain

The failure strain is an indirect indicator of the shear deformation experienced by the UCS test-specimens on reaching ultimate failure. In all unconfined compression tests, the CNP-treated specimens experienced partial shear failure, accompanied by vertical cracks. The measured failure strains for the untreated and CNP-treated soil specimens are listed in Table 4. For instance, the untreated soil specimen failed at an axial strain of 4.6%, while the 90-day cured 2.5% CNP-treated soil specimen failed at 3.0% axial strain. Referring to Fig. 5, the presented stress–strain behaviors indicate that the test-specimens experienced a plastic-type deformation response, i.e., a gradual reduction in stress evident post-failure for up to 14-day curing, which modifies to a mild brittle nature for longer curing periods.

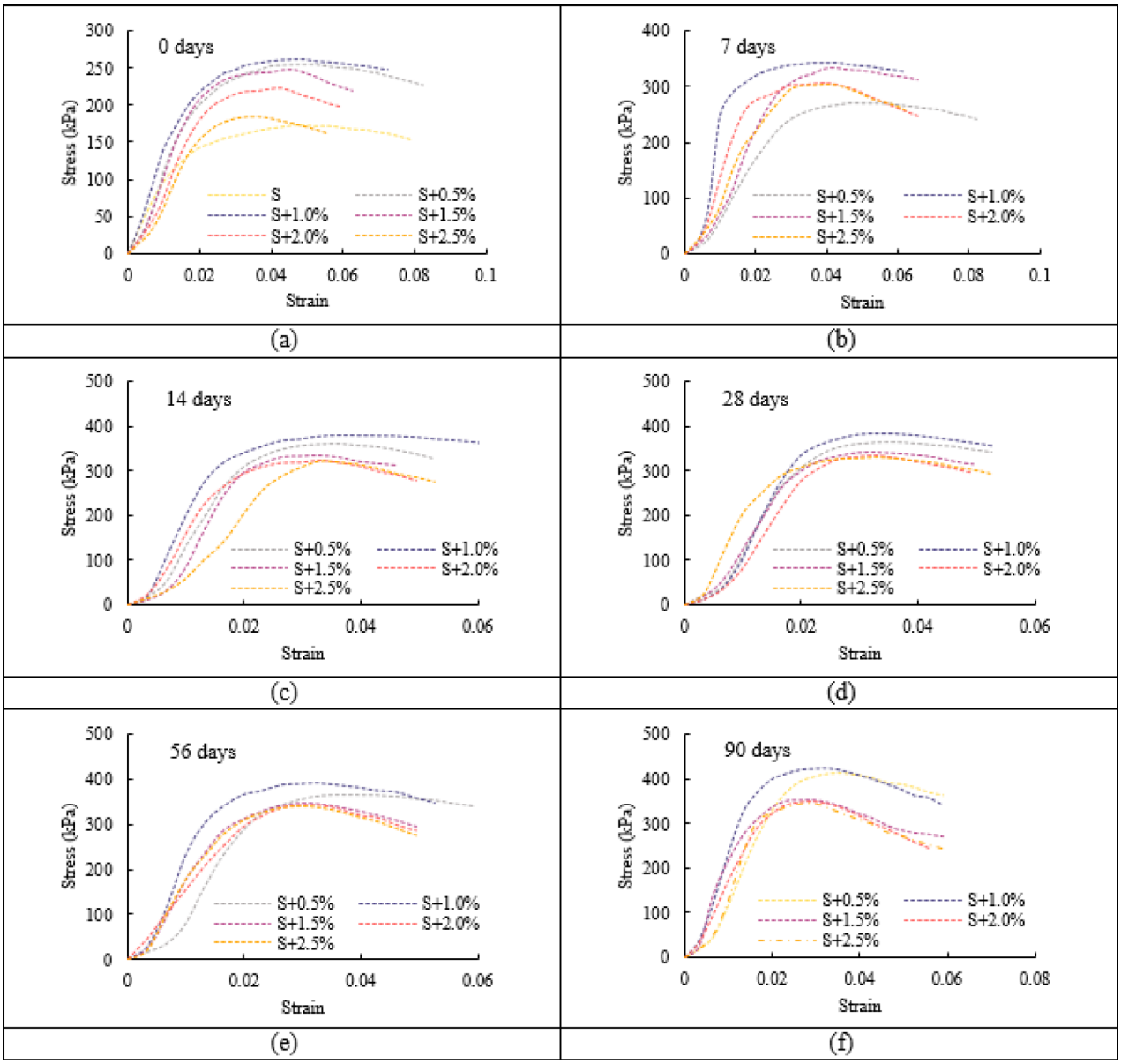

Fig. 5. Stress–strain responses of untreated and CNP-treated soil in unconfined compression tests for curing periods of (**a**) 0, (**b**) 7, (**c**) 14, (**d**) 28, (**e**) 56 and (**f**) 90 days.

UCS

The untreated soil, compacted at its MDUW, mobilized a UCS of 172.4 kPa. Referring to Fig. 6, CNP addition generally increased the UCS for all investigated dosages and curing periods. Initial testing performed for fresh (uncured) specimens indicated that compared to the untreated soil, the UCS of 1% CNP-treated soil was improved by 52%, although higher CNP dosages were found to produce smaller UCS gains. Referring to Fig. 6, a similar trend is observed for increasing curing periods, indicating that the optimum CNP dosage in terms of UCS gain was achieved for 1% CNP addition, i.e. enhancing the UCS by 99%, 121%, 123%, 128% and 146% for 7-, 14-, 28-, 56- and 90-day curing periods, respectively. The reduction in the UCS improvement for greater than 1% CNP addition is explained by the excess of non-gellable CNP hindering the natural cohesion of the soil. Furthermore, it can be observed from Fig. 6 that after 14-day curing, soil treated with a given CNP dosage showed only marginal increases in UCS, suggesting that a nominal 14-day curing period should be sufficient prior to further construction activities on deposits of this CNP-treated soil.

Failure modulus

The secant modulus at failure (i.e., failure modulus) is computed as the ratio of the mobilized UCS to failure strain, and provides an indirect measure of the test-specimen's resistance to failure. Referring to the values listed in Table 5, the untreated soil had a failure modulus of 3.74 MPa. This was found to increase in value for up to 1% CNP addition and then decreased for higher CNP dosages, i.e., following a similar trend to that observed for the

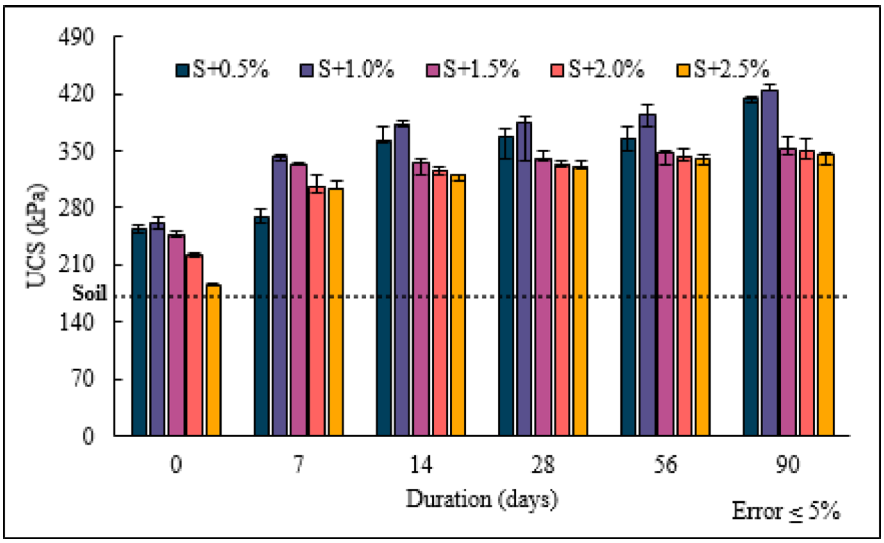

Fig. 6. Variation in UCS of CNP-treated soil with curing period.

CNP dosage (%)	Failure Modulus (MPa) for curing periods of:					
	0 day	7-day	14-day	28-day	56-day	90-day
0.5	5.53	5.85	10.01	10.13	10.08	11.44
1	5.68	8.03	10.55	11. 70	11.95	12.90
1.5	5.37	7.80	10.19	10.37	11.71	11.88
2	5.19	7.74	9.88	10.10	11.59	11.82
2.5	5.14	7.70	9.73	10.03	11.50	11.65

Table 5. Failure modulus of CNP-treated soil UCS-tested after different curing periods.

Fig. 7. Failed test-specimens of untreated and 1% CNP-treated soil.

UCS. Furthermore, the increase in the failure modulus with curing period indicates that the test specimens are getting stiffer with ageing. For instance, 1% CNP-treated soil UCS tested after 90-day curing achieved the highest failure modulus value of 12.9 MPa, indicating that it experienced less deformation and sustained more load at failure compared to any of the other test-specimens investigated. The failed specimens of untreated soil and 1% CNP-treated soil for 28-day curing are shown in Fig. 7. Untreated soil shows a bulging-type failure, characteristic of its ductile stress–strain curve presented in Fig. 5(a). Whereas the 1% CNP-treated soil showed a minimal bulging, with distinct vertical cracking, indicative of combined ductile and brittle failure, and which produced the change in the stress–strain response evident in Fig. 5(d), i.e., it got stiffer with ageing.

Reaction mechanism

The results in Fig. 6; Tables 4 and 5 clearly show that CNP addition has a positive effect on the UCS of the treated soil in its present study state.

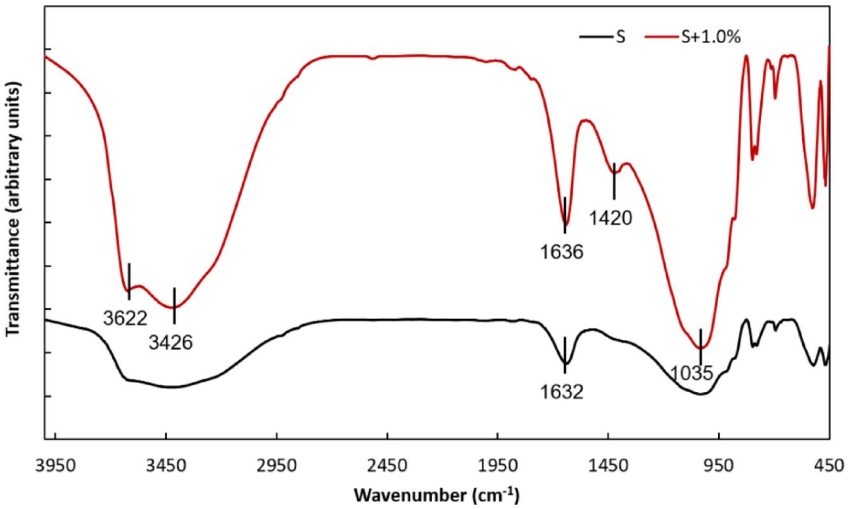

Fig. 8. FTIR spectra for untreated and 1% CNP-treated soil.

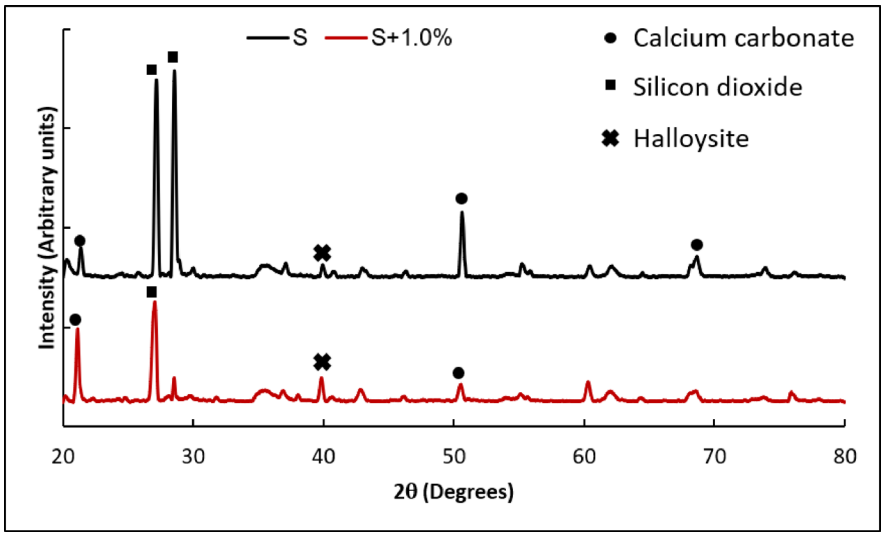

Fig. 9. XRD spectra of untreated and 1% CNP-treated soil.

Figure 8 shows the FTIR spectra for the untreated and 1% CNP-treated soil, giving an indication of the clay minerals, the water absorption and the presence of nano-bioadditives. Referring to this figure, the wavenumber variation around 1035 cm^{-1} for the untreated and treated soil suggests the presence of the alumino-silicate lattice of clay minerals, like kaolinite, smectite and/or illite[32]. This result augments the presence of saponite; a clay mineral belonging to the smectite group. The peak around the wavenumber of 3426 cm^{-1} indicates the OH stretching of water molecules due to absorption, and the peaks around 1632 and 1636 cm^{-1} denote the OH bending of water molecules[32]. The deeper trough between 3200 cm^{-1} and 3500 cm^{-1}, and the stronger absorption around 1600 cm^{-1} in the treated soil, indicate the presence of CNP.

However, the FTIR spectra do not give any indication of the chemical new substances formed. Accordingly, XRD analysis was conducted to investigate the formation of new chemical compounds. The XRD spectra presented in Fig. 9 show that both the untreated and 1% CNP-treated soil exhibited similar peaks, which only varied in their intensities, confirming that no new chemical compounds had been formed following the 1% CNP addition. The distinct peaks evident in Fig. 9 indicate the presence of silicon dioxide, calcium carbonate and halloysite clay mineral. A similar behavior of potential ionic bonding, without formation of new chemical compounds, was reported by Kannan and Sujatha[9] for chitosan-treated organic silt.

Morphological variations for the untreated and 1% CNP-treated soil were studied from comparisons of SEM images obtained at 5,000x, 10,000x and 15,000x magnifications for 7-day cured samples (Fig. 10). The untreated soil had a dispersed structure, whereas 1% CNP addition resulted in the development of fibrous threads that bridged the soil matrix. This bridging effect strengthened with increased curing period, and the fibers tended to aggregate the soil matrix, resulting in higher UCS mobilization. Another possible reason could be that the

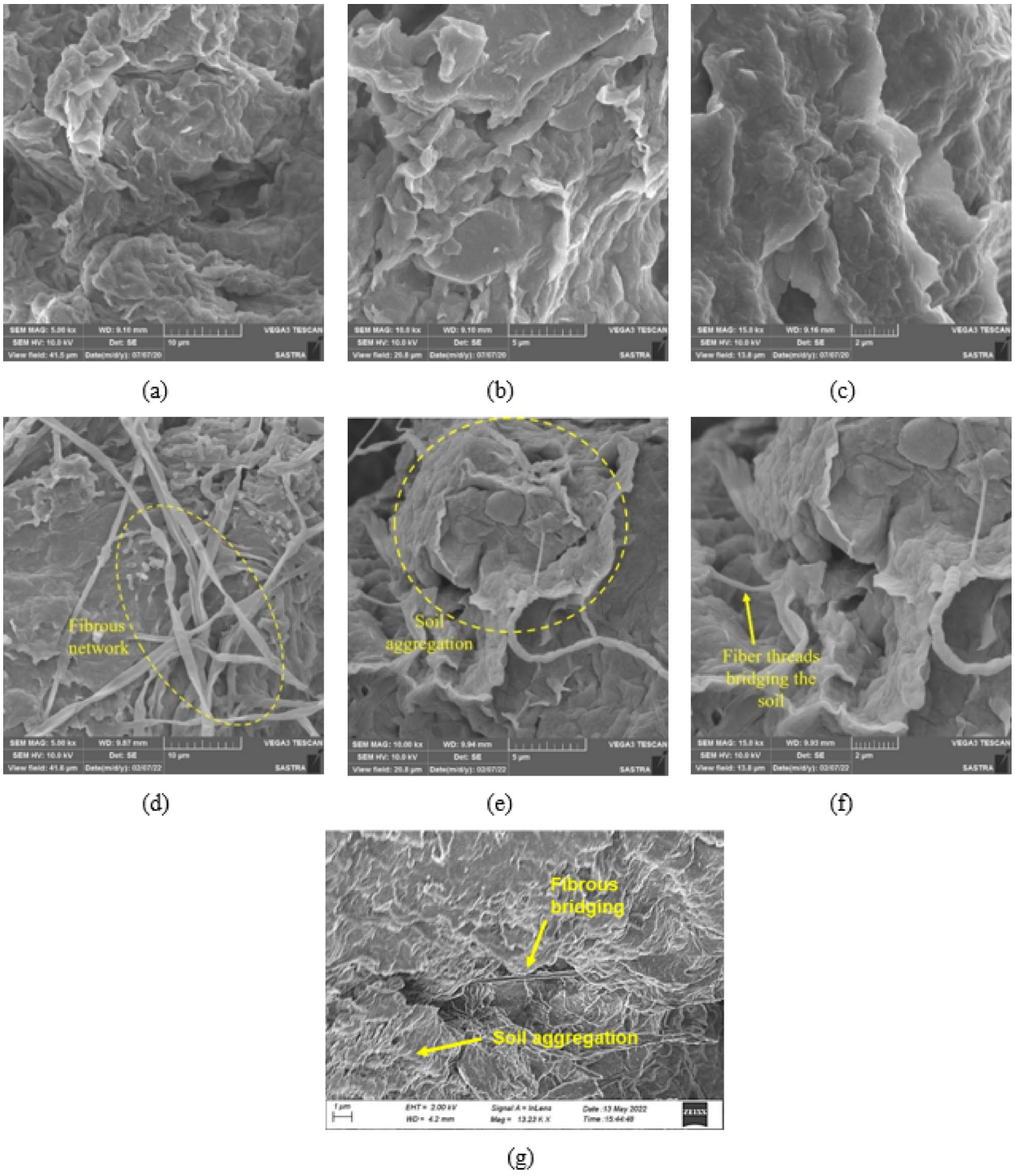

Fig. 10. SEM images of untreated soil at (**a**) 5,000, (**b**) 10,000 and (**c**) 15,000 magnifications, and 1% CNP-treated soil at (**d**) 5,000, (**e**) 10,000 and (**f**) 15,000 magnifications; (**g**) field emission SEM image of 1% CNP-treated soil showing fiber bridging[33].

cationic nature of the CNPs makes them readily adhere to the negatively charged clay particle surfaces, forming ionic bonds, as reported by Hataf et al.[8]. Although FTIR analysis cannot prove ionic bond formations, broadening and mild shifting of band around regions of 3600 cm^{-1} to 3200 cm^{-1}, the increase in intensity around 1420 cm^{-1}, the increased intensity and mild peak intensity around 900 cm^{-1} to 1100 cm^{-1}, as well as high intensity peaks in the low wavenumber regions hints the presence of ionic linkages. Additionally, Hataf et al.[8] observed that the diffused double layer (DDL) water around the clay mineral particles and the presence of cationic CNPs creates

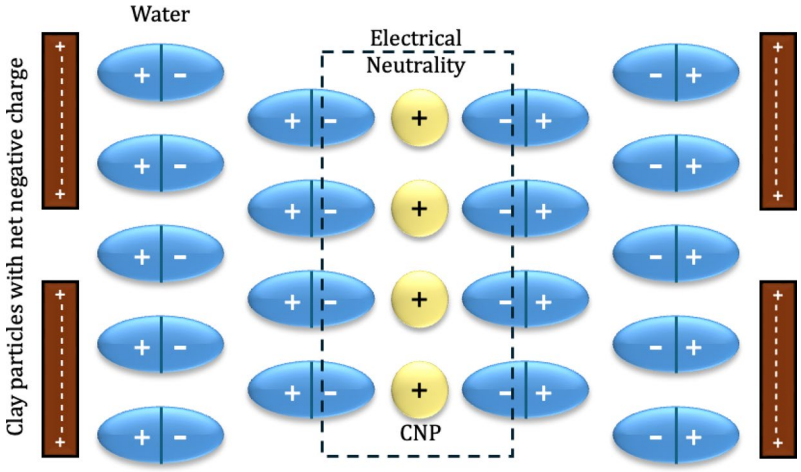

Fig. 11. Concept of electrical neutrality in CNP-treated soil.

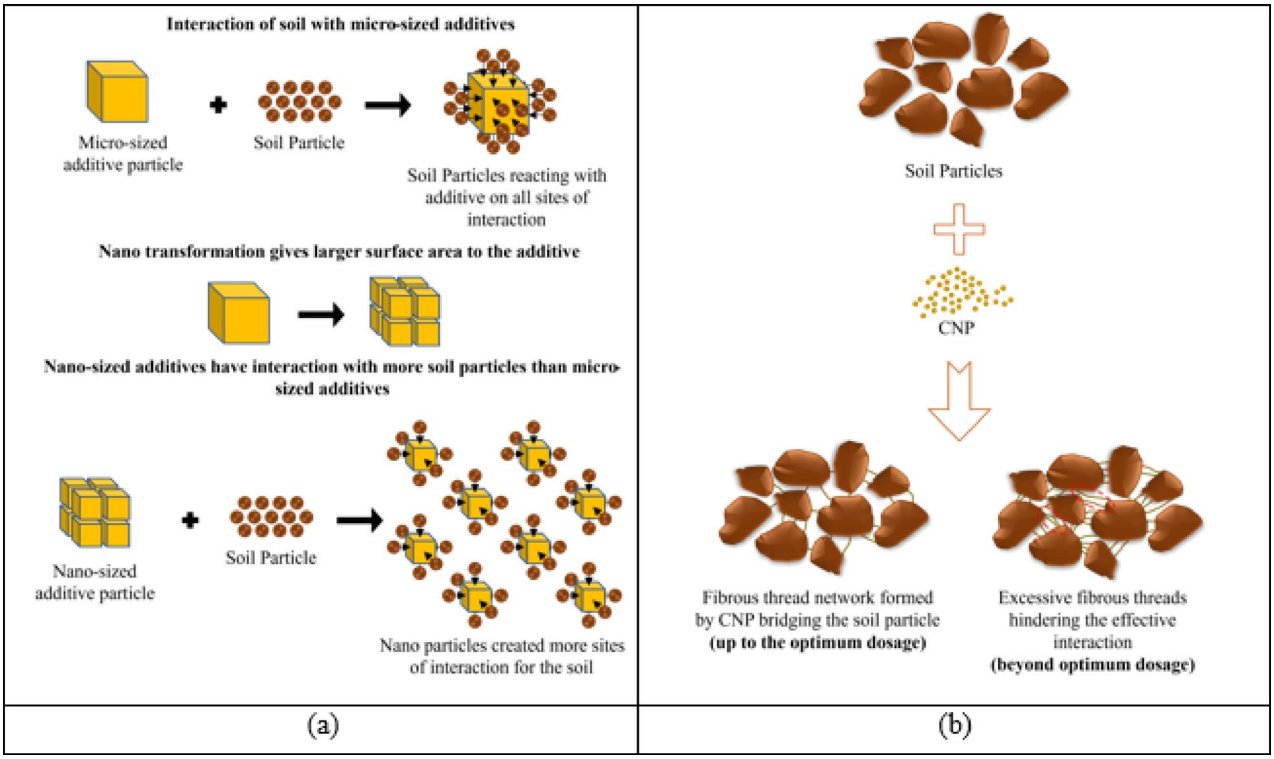

Fig. 12. Concepts of (**a**) reactivity of nano-additives on fine-grained soil, and (**b**) fibrous thread formation between soil–CNP.

an electrical neutrality, as conceptually shown in Fig. 11, thereby improving the geomechanical behavior of the CNP-treated soil[8,9].

Furthermore, as depicted in Fig. 12(a), compared to conventional micro-sized additives (e.g., of lime and cement), the nano-size of the CNPs (i.e., with their larger SSA) provides more reactive sites for soil–CNP interactions to occur. This causes additional soil (clay) particles to interact on all the newly exposed sides of the smaller CNP particles[34]. Beyond the optimum additive dosage (of 1% CNP), the higher content of CNP per unit volume of the soil and bundling of excessive fibers affect the cohesive force developed in the soil mass, leading to a progressive UCS reduction considering a given curing period duration (Fig. 12(b)).

Permeability behavior

The untreated soil, compacted at its MDUW, had a permeability coefficient of 8.8×10^{-8} cm/s. Biopolymers generally have a tendency to reduce the soil permeability[31]. This was the case for CNP treatment, which produced

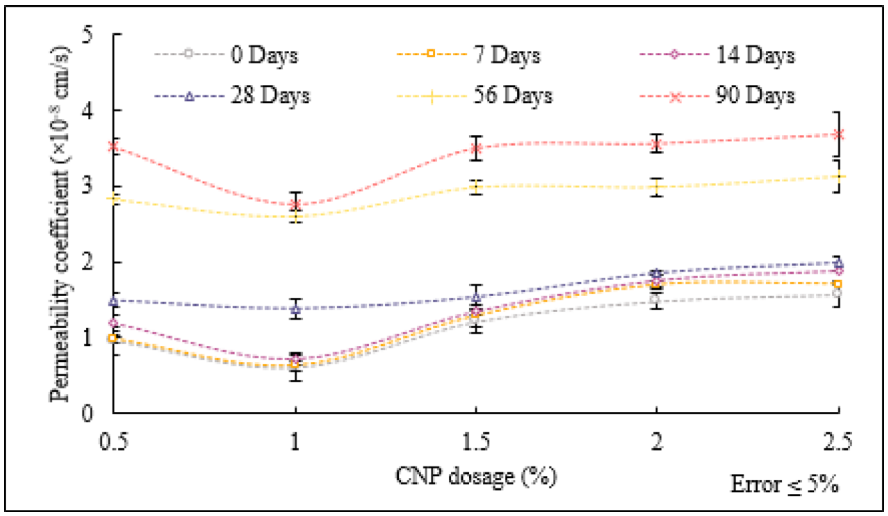

Fig. 13. Variation in permeability coefficient for CNP-treated soil.

Parameter	Soil	CNP dosage for treated soil		
		0.5%	1%	1.5%
c_v (m²/year)	0.12	0.12	0.12	0.10
C_c (no units)	0.97	0.61	0.59	0.59
C_s (no units)	0.05	0.05	0.05	0.05

Table 6. 1D consolidation results for untreated and CNP-treated soil.

marginal permeability reductions for the test soil at all CNP dosages and curing periods investigated (see Fig. 13). Like the optimum CNP dosage for maximum UCS gain, the greatest permeability reduction was also achieved for 1% CNP addition. For instance, relative to the untreated soil, a permeability coefficient reduction of ~0.92 order of magnitude was observed for the 1% CNP-treated soil specimens with 0 to 14 days of curing. The permeability coefficient reductions were caused by the presence of cationic CNPs in the soil pore-voids and the possible electrical neutrality produced in the DDL (refer to Fig. 11), which inhibit the water flow[8].

With an increase in curing period, the fiber bridging effect tends to increase soil aggregation, resulting in an increase in the pore-void volume and hence in the permeability coefficient value[35]. For instance, relative to the untreated soil, permeability coefficient reductions of ~0.84, 0.70 and 0.69 orders of magnitude were observed for the 1% CNP-treated soil at 28, 56 and 90-day curing, respectively. Previous studies[18] showed that the same soil treated with 0.6% NS or 0.4% NCC produced increases in the permeability coefficient (to 68.2×10^{-8} and 85.0×10^{-8} cm/s, respectively, with 90-day curing), which is very much higher than that measured for the untreated soil. Both NS and NCC additives showed signs of hydration product formation which caused very high aggregation of the soil particles, producing larger pores and resulting in higher permeability.

Consolidation behavior

The 1D consolidation behavior of the untreated and CNP-treated soil, compacted at its MDUW, was assessed in terms of the coefficient of consolidation (c_v), the compression index (C_c) and the swell index (C_s) parameters (see Table 6). Note, C_c and C_s represent the change in void ratio per log cycle change in the vertical stress applied for the loading (compression) and unloading (swelling) conditions, respectively (see Fig. 14). While the c_v parameter, determined in the present study using Taylor's square-root-of-time method, gives a measure of the rate of primary consolidation settlement.

The untreated soil exhibited a c_v of 0.12 m²/year, with the c_v value remaining largely unchanged for 0.5–1.5% CNP additions, i.e., only marginally decreasing to 0.10 m²/year for 1.5% CNP additive. Whereas the compressibility of the 0.5–1.5% CNP-treated soil was ~38% lower than for the untreated soil — the fiber bridging mechanism of CNP suppressing the compression. This tendency to resist compression makes the CNP-treated soil more suitable as a load bearing medium for foundations and structural loading applications, i.e., the resulting settlements will be relatively lesser for the treated soil. When compared to the performance of other nano additives at their optimum dosages in the same soil, the C_c (of 0.59) for 1% CNP is smaller than that for 0.6% NS treated soil (C_c = 1.66)[17], but slightly higher compared to 0.4% NCC-treated soil (C_c = 0.57)[18]. In other words, with 1% CNP addition, the resistance to consolidation deformation would be superior compared to the NS-treated soil, but inferior to the NCC-treated soil. The constant C_s value of 0.05 measured for the untreated and CNP-treated soil suggests that the CNP treatment has no significant influence on the swelling behavior.

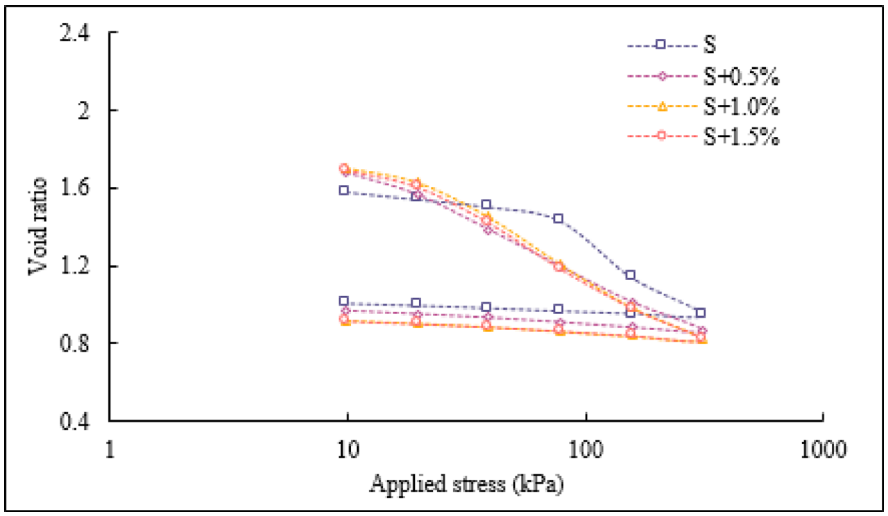

Fig. 14. Void ratio against applied stress curves for untreated and CNP-treated soil tested in 1D compression.

Curing period (day)	UCS for 2.5% MCP	UCS for 1% CNP	Superior performance of CNP (%)
0	245	261	6.7
7	280	344	22.7
14	308	382	24.1
28	350	385	9.9

Table 7. Comparison between UCS mobilized for CNP- and MCP-treated low-plasticity organic silt soil tested at different curing periods.

Feasibility and limitations for soil stabilization applications

The results presented above indicate that CNP addition has marginally modified soil properties, especially in enhancing the UCS. However, it is also necessary to critically analyze whether the choice of CNP material is essential. The following are some important focus points to be addressed in future studies.

Strength comparison with soil stabilized using micro-sized Chitosan powder

In an earlier work[9], the authors studied the UCS improvement achieved for the same low-plasticity organic silt soil treated with micro-sized chitosan powder (MCP) having particle sizes of less than 425 µm. Although the chitosan materials for this earlier study and the present investigation were obtained from different sources, nevertheless, a comparison of their experimental findings would essentially give an idea of their relative UCS improvements. In contrast to the optimum CNP dosage (of 1%), the optimum MCP dosage was 2.5%, with the MCP tests only investigating curing periods of up to 28 days. Table 7 compares the UCS values mobilized for the 1% CNP-treated soil and 2.5% MCP-treated soil for curing periods of 0 to 28 days. The results indicate the 1% CNP additive produces higher UCS compared to 2.5% MCP additive.

However, it should be noted that the relative UCS improvements achieved for the CNP-treated soil were more effective for 7- and 14-day curing periods, with the rate of UCS improvement reduced for 28-day curing. It is not conclusive whether the comparative trend in the UCS results for these two additives would proceed in a similar way, as the UCS results for the MCP-treated soil presented in Kannan and Sujatha[9] were limited to 28-day curing.

Material degradation

A crucial factor to consider is the degradability of the CNP additive. Both studies mentioned in Sect. 4.6.1 were conducted at bench scale in a controlled laboratory environment, and no visible material degradation was noticed. However, considering the fact that soil deposits stabilized with such additives may support heavy structures, it is essential to investigate their degradation mechanism in open/external environments, and its effect on the long-term soil properties/behavior before employing these novel additives in soil stabilization applications. Although few studies directly report the degradation rate of CNP in soils, many studies report on chitosan and modified varieties degradation as thin films. For instance, Vikhoreva et al.[36] reported that untreated chitosan film degrades within 5 to 7 days, whereas if the pH and salt concentration of the solution medium is weakly basic and stable, then the degradation will be delayed to months. They also indicated that increasing the cross-linking agent content further enhances the degradation resistance. So future studies should be focused on cross-linking and delayed degradation.

Additive				Stabilizing one cubic meter of soil			
Type	Dosage (% dry soil mass)	Cost per kg (Rupee)	kg of CO_2 produced per kg of additive	Cost# (Rupee)	kg of CO_2 emissions	Carbon emission tax (Rupee)	Total cost (Rupee)
Lime*	6	9.0	1.50	936	155.9	318	1254
Cement*	9	8.8	0.99	1372	154.4	315	1687
CNP	1	3000.0	0.98	47,309	15.4	31	47,340

Table 8. Cost analysis of soil treatment with lime, cement and CNP additives. *The dosage and MDUW of cement and lime are based on practical experience. #Calculated based on the MDUW of the additive-treated soil at optimum dosage.

Cost analysis

Based on the material prices reported in the online market 'Indiamart'[37], Table 6 compares the costs of stabilizing one cubic meter of soil using lime, cement and CNP additives. All three additives would be incorporated into the soil matrix using a similar dry-mixing method, such that the associated mixing and labor costs are excluded from this analysis. Many countries have levied a tax on carbon emissions to control such emissions. For ease of comparison, the Indian rupee equivalent of the carbon emission tax is adopted for this analysis; the tax ranging from as low as 9 rupees per tonne of CO_2 emissions for Poland, to a maximum of 13,921 rupees per tonne of CO_2 emissions for Uruguay[38]. The tax discussed in Table 8 is based on a nominal tax rate of 2038 rupees per tonne of CO_2 emissions charged in the United Kingdom[38].

Even with the inclusion of carbon tax, the cost associated with the nanomaterial soil stabilization is substantially higher compared to lime and cement stabilization. Another interesting fact to note in Table 6 is that the CO_2 emissions associated with cement and CNP production are nearly equivalent. However, the required dosage is much lower in the case of CNP treatment. Nevertheless, despite its effective geoengineering performance for much smaller dosage, the cost of the CNP material presently represents a substantial drawback for such a technically promising soil additive. This higher material cost arises because most commercially available nanomaterials are of laboratory or pharmaceutical grade, such that they cost a great amount due to their limited production. In other words, the commercialization of this nano market has not been effectively established, for instance regarding soil stabilization with nanomaterials, as the technology transfer has not successfully happened for most of the nano-based research[39].

Challenges in field application

An important concern with the use of novel additives is the challenges that might be encountered during field applications, since the new materials may not be as versatile as the established techniques. Especially when nano materials are used, ensuring homogeneity is a crucial challenge, without which the mere purpose of the nano additive inclusion is lost. Furthermore, compared to the laboratory experiments, the in-situ soil deposit may not be homogeneous, such that variations in the soil type would have some impact on the geoengineering performance. Also, as a sensitive material to moisture, which would influence the CNP's degradation, the effect of fluctuating moisture in the field conditions has to be studied in detail for a better understanding.

Summary and conclusions

This study attempted a novel approach of using eco-friendly CNP material as a potential additive to treat a high plasticity organic silt by observing the modifications in its geoengineering behavior/properties. The PI, compaction, UCS, permeability and consolidation properties of the untreated and 0.5–2.5% CNP-treated soil were investigated for curing periods of up to 90 days, supplemented with SEM, FTIR and XRD analyses. The following inferences were made:

- The PI showed a consistent increase from 22.5% (for untreated soil) to a maximum of 29.6% (for 2.5% CNP-treated soil), attributed to the hydrophilic nature of the CNP additive.
- The MDUW reduced marginally from 15.47 kN/m^3 to 15.22 kN/m^3 for an increase in the CNP dosage from 0.5% to 2.5% for an almost constant OMC for compaction of 16%.
- For the investigated CNP range (of 0.5–2.5%), 1% CNP addition was found to produce the greatest UCS gain for all curing periods studied, with a maximum UCS of 424 kPa mobilized for 90-day curing. XRD analysis confirmed that no new chemical compounds were formed, while the SEM analysis showed that fibrous bridges developed in the soil matrix would have contributed to the UCS improvement. Test-specimens cured for up to 14 days experienced plastic (bulging) failure, whereas mild brittle cracks accompanied with bulging occurred for longer curing periods.
- For the 1% CNP additive, the permeability coefficient was found to increase from 0.6×10^{-8} cm/s to 2.76×10^{-8} cm/s over a 90-day curing period; these values were lower than that of the untreated soil (at 8.8×10^{-8} cm/s).
- The coefficient of consolidation and the swell index of the compacted soil did not change with 1% CNP addition; however, the compression index reduced from 0.97 to 0.59.

Despite the above-mentioned technical improvements, the synthesis of nano-biomaterials, like CNP, is still an expensive process that requires further research aimed at their cost-effective production, considering their growing demand in the various industries. Furthermore, as a relatively new investigated biopolymer and recent technology, extended studies on the behavior of the CNP material when incorporated with various soil types and

considering different site conditions are necessary before transferring the proposed soil stabilization approach to field applications. Although the possibility of ionic bonding is hinted by indirect observations, the XRD did not show any new mineral formation explicitly; hence a detailed study on the microstructural analysis is needed to fully understand the behavioral modifications. More importantly, biopolymers, like chitosan, are biodegradable; hence, a better understanding of their degradation behavior under extreme environmental conditions (e.g., of soil pH range and temperatures) as well as ways to subside them is necessary before exploring the possibility of field applications.

Data availability

All data generated or analyzed during this study are included in this published article.

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Author contributions
Govindarajan Kannan – Methodology, Investigation, Writing—Original DraftEvangelin Ramani Sujatha – Conceptualization, Methodology, Validation, Writing—Review & EditingBrendan C. O'Kelly – Visualization, Writing—Review & Editing.

Declarations

Competing interests
The authors declare no competing interests.

Additional information
Correspondence and requests for materials should be addressed to E.R.S.

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