



Influence of Chitin Nanofiber and Rice Husk Ash on Properties and Bearing Resistance of Soft Clay Soils

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P A P E R I N F O

Paper history:

Received 14 December 2018

Received in revised form 30 January 2019

Accepted 07 March 2019

Keywords:

Soft Clay Soils

Chitin Nanofiber

Rice Husk Ash

Bearing Resistance

Atterberg Limit

A B S T R A C T

Use of soft clay soils in construction activities has faced many problems. Some improvement, stabilization, and reinforcement methods is required to use these soils in body of roads, sub-foundations and embankments. In this research, the effect of chitin nanofiber and rice husk ash as additives on the behavioral properties and bearing resistance of soft clay soils by considering the processing time of 7, 28, 42 and 90 days was investigated. The suitability of chitin nanofiber to be used as an additive was evaluated by FTIR, XRD and SEM analysis. Different percentages of additives (1, 2, 4, 6 and 8%) with variations in chitin nanofiber and rice husk ash ratio were added to soil containing 6% lime. Maximum reduction on liquid limit and plastic index was obtained by addition of 2% additives to the soil containing 6% lime in which the percentage of chitin nanofiber was more than rice husk ash. Using examined additives in clay soil resulted in to a significant increase in bearing resistance, specifically at higher percentages of additives and curing times (days). As a whole, obtained results confirmed the potential use of chitin nanofiber and rice husk ash as additives for the improvement of soft clay soils.

doi: 10.5829/ije.2019.32.03c.04

1. INTRODUCTION

Soft clay soils are one of the problematic types of soils which have led to significant damages in the operation of structures constructed on these soils [1]. The problem of soft clays include damages such as cracking, displacement, tilting, rising, or even the destruction of structures due to pressure generation and deformation. Literature reviews showed that the problem and damages associated with soft clays are more than total natural disasters such as earthquakes and floods [2]. Swelling phenomenon in soft clays entirely depends on the type of clay minerals, type and amount of absorbing cations, and molecular bond between them [3, 4] which leads to various types of complications. Among the damages caused by soil, the diametric cracks in the wall, separation of wall from the structure floor, stuck doors, cracks in the floor coating, rise of the floor slab, and arched walls can be mentioned [2].

Various typical techniques such as pre-soaking, soil replacement of project site, chemical stabilization of soil (by lime, Portland cement, bitumen and fly ash as traditional stabilizers, enzymes and resin as nontraditional stabilizers), electrochemical method, and moisture barrier have been widely used for soft clay modification as previously reported in literature [5–7]. Researches confirm that adding lime to clay leads to increase in resistance and significantly reduces the dough properties and swelling potential. However, some soils do not react with lime due to lack of silicates and aluminates in the soil. In these cases, the combined lime with a pozzolanic material such as fly ash or microsilica can be used [8–10]. Cement is another material which can be used in stabilization of various types of soils, such as clay. Nevertheless, in contrast to lime, cement is poorly suggested to be used for stabilizing the fine-grained soils [11]. Another problem caused by various additives is the issue of environmental pollution; though, using

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biodegradable additives such as agricultural waste which are environmentally compatible may have desirable effect on reduction of environmental pollutants [12]. As mentioned, sometimes traditional stabilizers are not suitable for improvement of the soft clays properties due to long curing time and significant usage volume of additives. Therefore, search on new additives are always interests of researchers. Today, due to the recognition of the beneficial effects of nanotechnology in various areas of the environment, materials, energy, and national security, the tendency to study on nanoadditives in this area is increasing because of their technically, commercially and economically potentials [13–15].

Concerning that problematic clay soil is one of the problems of stabilizing soils for large scale projects, especially the construction ones in Iran, the engineering properties of this type of soil can be changed using the nanoscale stabilizers. So, nanopolymer materials can be used because they reduce the water adsorption in clay soil.

Chitin is the most abundant biopolymer in nature after cellulose and is found in the structure of organisms such as shrimp, crabs, insects, and turtles. Chitin is a semi-crystalline polymer like cellulose and starch; can be hydrolyzed by using acidic hydrolysis or other methods. The amorphous regions of this biopolymer can be decomposed to obtain chitin nanocrystal. So far, the successful production of chitin nanowhiskers from crab shells and shrimp waste has been reported [15]. The relatively high annual production of rice in Iran gathers large quantities of rice husk which has led to study on rice husk for extracting silica as an inexpensive alternative source for the production of silicon-based materials with the aim of technological and industrial uses [16]. In this regard, some researcheres have investigated the effect of using rice husk on stabilization and unconfined compressive strength of soil [17].

In this research, the influence of addition of different percentages of rice husk ash and chitin nanofiber on behavior properties of soft clay containing 6% lime is evaluated. As a matter of fact, rice husk is utilized for several reasons: first it is a natural by-product self-renewable which grown over a wide range of northern parts of Iran. Second, this material, rice husk, is very cheap and easily available. Chitin nanofiber has been also selected as an additive due to considerable properties such as biodegradability, reduction in water adsorption and smaller usage volume of additives. Another objective of this study is to monitor the variation of bearing resistance versus processing times.

2. MATERIALS AND METHODS

2. 1. Materials The clay used in this research was prepared as kaolinite ZMK2 in 50kg packages from Iran

China Clay Industries Co. The physical and chemical properties of clay are summarized in Table 1. Chitin nanofiber was purchase from Nanonovin Co. Lime was supplied in 40kg packages from PARS Chemical Industries and stored in the nylon bags to prevent the reaction with carbon dioxide of the air. Rice husk ash (white powder) was obtained by burning the rice husk in furnace at temperature of 700°C for 3 h. The chemical properties of lime and rice husk ash are depicted in Table 2. The required identification experiments were also performed based on ASTM standard method which is presented in Table 3.

2. 2. Atterberg Test Fine-grained soils have different shapes with an increase in for the amount of absorbed water. As water increases, the thickness of the water layer surrounding to the seeds growths and the slip of seeds on each other becomes easier. Therefore, the soil behavior actually depends on the level of water inside the

TABLE 1. Physical and chemical properties of clay

Chemical Analysis		Mineralogical Analysis		Particle Size Distribution%	
Element	Weight percent (%)	Element	Weight percent (%)	Description	
L.O.I	6±1	Kaolinite	41±2	<5	>150 μ
SiO ₂	74±1	Quartz	52±2	35±2	>40 μ
Al ₂ O ₃	15±1	Calcite	3±0.5	53±2	>20 μ
Fe ₂ O ₃	0.45±0.05	Total Feldspar	-	20±2	>2 μ
TiO ₂	0.04±0.01	Others	4±1		
CaO	1.5±0.2				
MgO	0.4±0.05				
Na ₂ O	0.35±0.05				
K ₂ O	0.3±0.05				
SO ₄	-				

TABLE 2. Chemical properties of lime and rice husk ash

Element	Weight percent (%)	
	Lime	Rice husk
CaO	89.26	0.67
CaCO ₃	4.36	-
Al ₂ O ₃	0.91	0.46
Fe ₂ O ₃	0.88	0.67
MgO	2.74	0.44
SiO ₂	0.93	88.32
Sodium oxide and potassium	-	3.13

TABLE 3. Experiments conducted in this research

Description of experiment	ASTM Standard
Atterberg's limits [18]	
Liquid limit	ASTMD4318
Plastic limit	ASTMD4318
Plastic index	ASTM D4318
Bearing resistance [19]	D 216613
Chemical tests	
* XRD	D1031-96
** XRF	E1031-96

* X-Ray Diffraction; ** X-Ray Fluorescence

complex. The fine-grained soil can be classified based on the moisture content in one of the solid states as semi-solid, plastic, and liquid. The specifications of Atterberg test for these states are defined in Table 4.

The liquid limit was determined using Casagrande Apparatus which is a mechanical device with a brass cup, internal diameter of 54 mm, thickness of 2 mm, and weight of 200 g. The cup is hinged on the back by a pin on two pillars, which is located on a platform made of hard plastic. The cup spins on the hinge and rises by rotating a handle. Then, it falls and hits the floor. The height of the cup fall can be adjusted to the standard level. Along with this device, a bar is embedded for creating a standard gap in the soil sample in the cup. The liquid limit of some clay minerals is mentioned in Table 5.

TABLE 4. Specifications for Atterberg test

Soil moisture content	Mechanical mode (Kneaded)	Degree of difficulty (Kneaded)
	Liquid	Very loose
	Sluggish (plastic state start)	loose
PI=LL-PL	plastic	medium
LL-Liquid limit	Semi-solid state start	-
PL-plastic limit		
SL-shrinkage limit	Semi solid	stiff
	Solid state start	-
	Solid	Very stiff
	Solid	Hard

TABLE 5. Liquid limit of some clay minerals

Mineral clay	Liquid limit
Kaolinite	35-100
Illite	55-120
Montmorillonite	100-860

2. 3. Preparing and Processing the Samples This research aims to investigate and compare the effect of addition of different percentages of rice husk ash and chitin nanofiber as stabilizers on the behavior properties and bearing resistance of soft clay containing 6% lime.

First, the experiments were conducted on initial soil sample to determine the plastic and liquid limits. After preparing the clay sample, dry powdered lime (6% w/w) was added to it. For performing experiments, different percentages of additives (1, 2, 4, 6 and 8%) which were the mixture of rice husk ash and chitin nanofiber were added to the clay samples containing 6% lime. The ratio of each additive in any samples were shown as (N100P0), (N75P25), (N50P50), (N25P75), and (N0P100). In all experiments, two samples were selected as the control samples. These samples contained pure clay (C) and clay containing 6% lime (C-L). In addition, N and P refers to chitin nanofiber and rice husk ash, respectively. For instance, N75P25 means that 75% of any percentages of addition is chitin nanofiber and 25 % of it is made of rice husk ash.

2. 4. Unconfined Compressive Strength Test

Unconfined compressive strength test, a small amount of clay soil was taken and sieved by sieve no. 4. The sieved clay soil was poured into a container and a small amount of water was added to it using pipette to become wet for properly mixing. After mixing, the wet clay was poured in sampling framework (Figure 1) as three layers. Each layer was compacted properly by the bouncing rod. Then, after compacting the last layer and filling the framework, the surface of the framework is properly smoothed and polished by the spatula. The cylindrical samples were slowly removed from the framework without any variation or damaging. The obtained samples were preserved in the special place of treatment samples to maintain their moisture for performing desired measurement at the required time intervals of 7, 28, 42, and 90 days. Then, the samples consisting of 6 wt% lime and initial clay soil as well as the samples containing chitin nanofiber and rice husk ash additives were



Figure 1. Cylindrical container for single axial compressive test

prepared at known percentages similar to the samples prepared in the plastic limit test. Based on the curing days, the samples were placed under unconfined compressive strength device. After placing the samples under the jack, the indicator clocks were manually set on zero and, then, the sample was loaded. After the first force was applied to the sample by the device, reading begun and, for each unit of the applied force, the number shown by the indicator clock hand was read and recorded. These readings were continued until the force became negative. The obtained results from the device were shown in the related figures, the diagram of the test process was plotted and the results were analyzed and compared.

3. RESULTS AND DISCUSSIONS

The main goal of the present work is to improve the properties of clay inflation associated with simultaneous reinforce and increase of the bearing resistance of the clay soils. In previous studies, various materials were developed to reduce the properties of the inflation in the clay soils. However, simultaneous combination of reinforce with stabilization method has not been used. Considering the significant role of lime and rice husk ash in improving the inflation properties of clay soils, we have done experiment to determine which material has potential to increase the bearing resistance and simultaneous reinforces and stabilization of clay soils containing lime and rice husk ash.

3. 1. Chemical Tests For confirming the proper interaction between the chitin nanofiber and clay soil, Fourier-transform infrared spectroscopy (FTIR), XRD (X-Ray diffraction) and Scanning electron microscope (SEM) analysis were performed on chitin nanofiber/clay composite. The FTIR spectrum of chitin nanofiber (Figure 2(a)) shows the vibration bands at 3623 cm^{-1} for O-H stretching, 3129 cm^{-1} due to interlayer and intra-layer H-bonded O-H stretching, 2917 cm^{-1} for aliphatic C-H stretching, 1654 cm^{-1} for C=O group of R-CO-NH₂, 1548 cm^{-1} for N-H bending and 1437 and 1035 cm^{-1} for C-O stretching. The spectrum of chitin nanofiber/clay (Figure 2(b)) showed that all chitin nanofiber messages appeared on the soil; due to interactions with groups and elements of soil, the intensity of the messages was reduced to lower frequencies. These results indicated that chitin nanofiber was present in soil components.

Figure 3 illustrate the XRD patterns of chitin nanofiber/clay nanocomposite. The XRD pattern of clay shows a reflection peak at about $2\theta = 26^\circ$, corresponding to a basal spacing of 3.32 \AA . The XRD pattern of chitin nanofiber/clay shows the characteristic crystalline peaks at around $2\theta = 24^\circ, 39^\circ, 42^\circ, 49^\circ$ and 54° , characteristic to chitin nanofiber. The shift of the basal reflection of clay

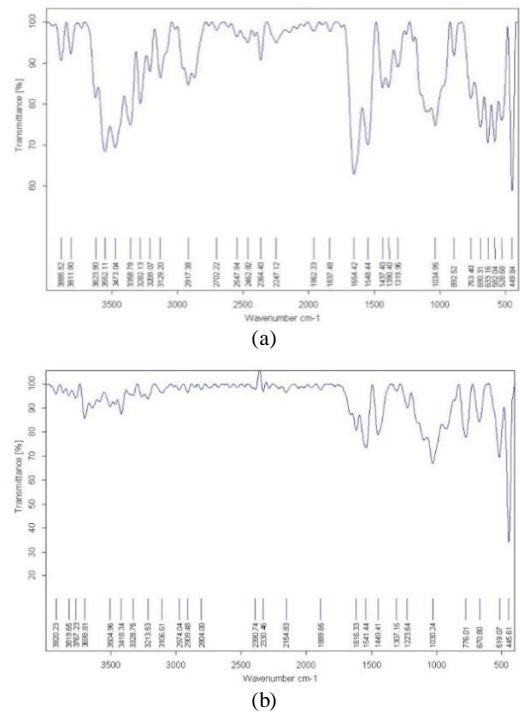


Figure 2. FTIR spectrum of (a) chitin nanofiber, (b) chitin nanofiber/clay

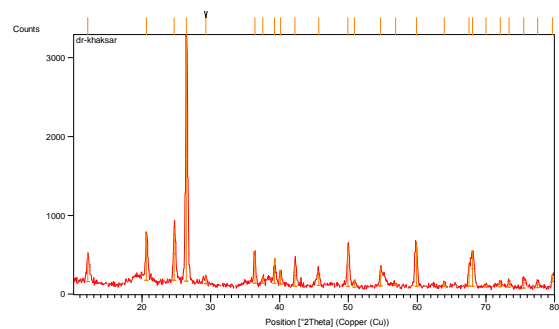


Figure 3. XRD patterns of chitin nanofiber/clay

to lower angle indicates the presence of chitin nanofiber in clay. In addition, the intensity of the other messages mentioned above is reduced, which indicates the structure is immersed or the layer is chitin nanofiber/clay layer.

SEM result is presented in Figure 4, which were placed in a layered layer, and chitin nanoparticles in the sizes of 20 to 30 nm on clay particles are distributed uniformly with a little irregularity. As the image shows, the dark points are related to clay particles and chitin nanoparticles as white points. Chitin has amino and hydroxyl groups, which can lead to strong interaction between the matrix and silicate layers by forming hydrogen bond with the hydroxide silicate edges. The result of analysis shows the presence of chitin nanofiber in clay.

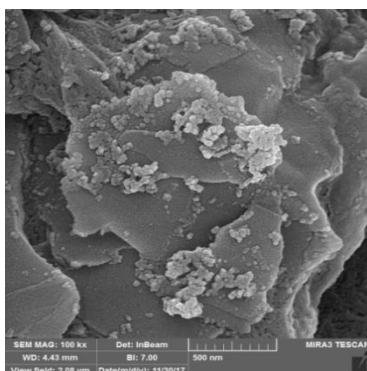


Figure 4. SEM of chitin nanofiber/clay nanocomposite

3.2. Unconfined Compressive Strength Test The results of Unconfined compressive strength test on initial soil (c) and soil containing 6% lime (C-L) at various processing time are shown in Table 6.

3.3. Behavior Properties Influence of the addition of various percentages of chitin nanofiber and rice husk ash to clay containing 6% lime on the liquid limit, plastic limit and plastic index are shown in Figures 5a to 5c, respectively. Figure 5(a) shows that changes in liquid limit resulted in by addition of various percentages of additives is approximately identical and linear, and the maximum change obtained by addition of 2% additives to the soil containing 6% lime (100% chitin nanofiber without any rice husk ash). By combining the initial soil sample with soil containing 6% lime, the liquid limit increased two-fold and after that by adding additives, a reduction trend was observed.

By addition of 6% lime to the initial clay soil, the plastic limit decreased from 33.87 to 23.38 which showed 31% reduction. Thereafter, with the beginning of adding different percentages of chitin nanofiber and rice husk ash, the reduction rate became very slow and variations were identical, in such a way that the maximum change occurred by addition of 2 and 6% additives. However, the decreasing trend had a slight slope. The lowest plastic

limit was 20.51 (in condition of 2% additives contained 50% chitin nanofiber and 50% rice husk ash). It was 39% and 12% lower than plastic limit of initial soil sample and soil sample containing 6% lime, respectively. However, the decreasing rate of plastic limit was observed in all soil samples.

A decrease in plastic index is favorable because it has resulted in to a reduction in consolidation properties of the problematic and consolidated soil sample. The reduction of 84% was achieved in plastic index by addition of 2% additives (100% chitin nanofiber without ash rice husk ash) to the initial soil in which the plastic index decreased from 30.64 to 4.79. An average reduction of about 50 -85% was obtained in plastic index for all samples by addition of additives showing an effectiveness and appropriate performance of examined additives. Results also showed that the influence of addition of chitin nanofiber to the soil samples on reduction of plastic index was more than addition of rice husk ash. Although, adding 6% lime to the initial soil samples efficiently reduced the plastic index; but, addition of different percentages of chitin nanofiber and rice husk ash caused significantly higher reduction in plastic index and improvement of plastic properties of problematic soils.

3.4. Unconfined Compressive Strength Results showed that by passing time from the preparation and production of the samples, the normal stress and bearing resistance increased with steep and ascending slope, and the improvement in stress and initial resistance was well expressed and desirable. It should be noted that, on the early days, unconfined compressive strength test results of the clay with low percentages of chitin nanofiber and rice husk ash additives had about 20-30% decline in compared with the preliminary soil clay and clay composed of 6% lime. With an increase in processing time and additive percentages in samples, the decline was highly reduced. In addition, the larger amount of chitin nanofiber in the samples resulted to the higher increase in stress and strength of the samples.

TABLE 6. Results of Unconfined compressive strength test on initial soil (c) and soil containing 6% lime (C-L) at various processing time

	Days of test	H ₀ (cm)	d ₀ (cm)	w (%)	G _s	□ _d (gr/cm ³)	e ₀	S _r	q _u (kg/cm ²)
C	-	8.00	3.80	15	2.56	1.65	0.81	0.47	1.23
	7	8.00	3.80	11	2.56	1.65	0.55	0.19	2.11
C-L	28	8.00	3.80	7	2.56	1.63	0.57	0.09	3.08
	42	8.00	3.80	5	2.56	1.58	0.62	0.08	3.55
	90	8.00	3.80	4	2.56	1.50	0.71	0.07	4.12

h₀: height; d₀: diameter; W: humidity; G_s: specific gravity of soil; □_d: dry soil specific gravity; e₀: porosity ratio; S_r: degree of saturation; q_u: pressure resistance

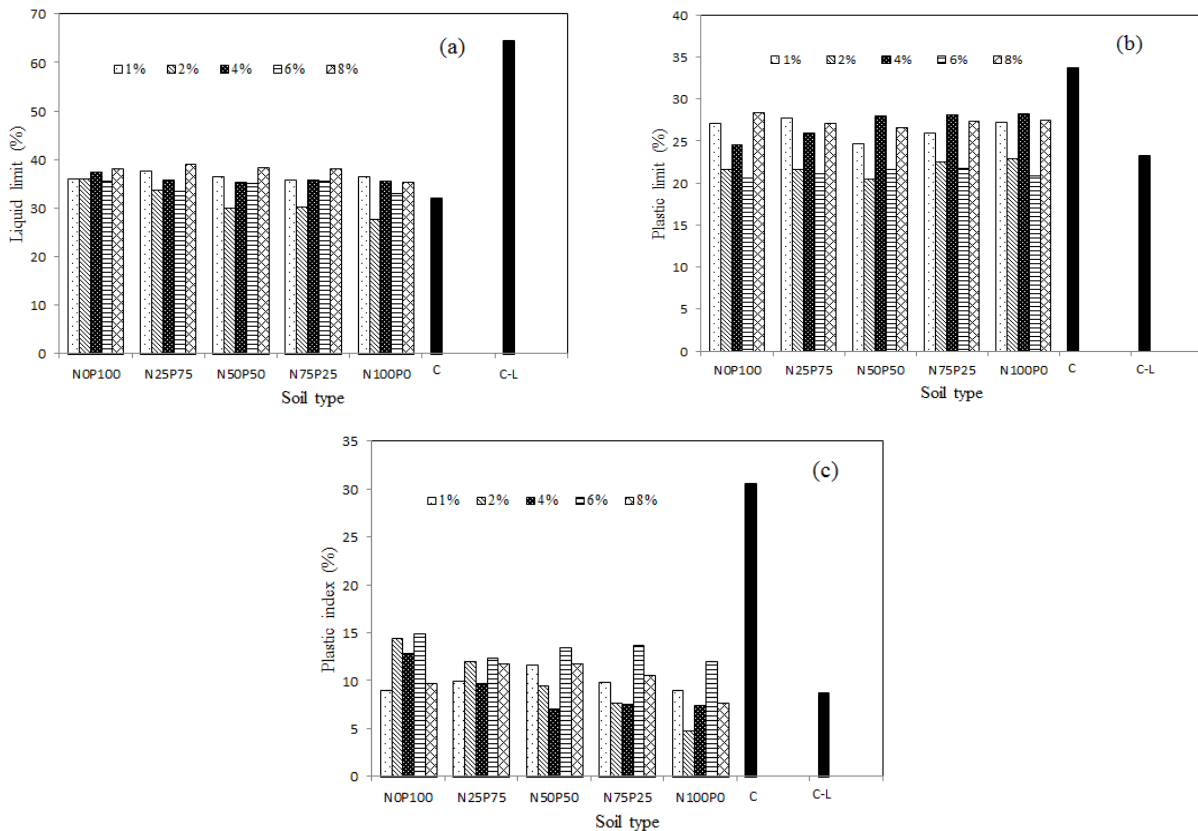


Figure 5: Effect of the addition of various percentages of chitin nanofiber and rice husk to clay containing 6% lime on (a) liquid limit (b) plastic limit, and (c) plastic index of soil samples

Variation of bearing resistance versus processing times for addition of various chitin nanofiber and rice husk ash percentage to clay containing 6% lime is shown in Figure 6 (a-e).

With 100% contribution of rice husk ash in the compounds based on the processing time, the trend of changes in the normal stress and bearing resistance was increased. This enhancement was within the range of 10 to 235% during the processing period of 7 to 90 days, compared to the initial compressive strength of the soil samples which was 1.23 kg/cm². With 6% addition of additives while all of them was rice husk ash, the normal stress was reached to its maximum value of 4.116 kg/cm². However, comparing the strength results of 100% ash contribution with the strength results of clay soil containing 6% lime and initial soil sample showed a slight decrease in the range of 2 to 35%. The highest reductions occurred in 1-2% addition of compounds. With an increase in additives percentages, the decline decreased and in 42- and 90-day periods, this trend continued.

An increase in chitin nanofiber percentages in the formulation of soil samples caused an enhancement in increasing trend of normal stress and bearing resistance.

This increasing trend was associated with more severe slope during the processing time at 42 and 90-day periods. In comparison with the strength value of initial soil sample from 7 and 90 days, an increase was within the range of 20 and 268%. The highest enhancement in strength number (4.51 kg/cm²) were obtained by addition of 6% additive (268% increase compared to the initial value). The desirable increasing trend of resistance and stress was maintained in all additional percentages to the initial soil sample in which chitin nanofiber and rice husk ash had 75 and 25% contribution, respectively. The longer the processing time, the more improvement in the resistance and stress would be. Results showed the desirable effects of two additives, especially chitin nanofiber on the normal stress and bearing resistance. The increasing trend in stress and bearing resistance is quite obvious by using 100% chitin nanofiber in soil samples. While the processing time increased, the bearing resistance was increased to about 3.5 folds more than its initial value (5.44 kg/cm²). Results also showed that addition of chitin nanofiber and rice husk ash to the soil containing 6% lime caused considerable increase in bearing resistance, especially at higher processing time and additives percentages.

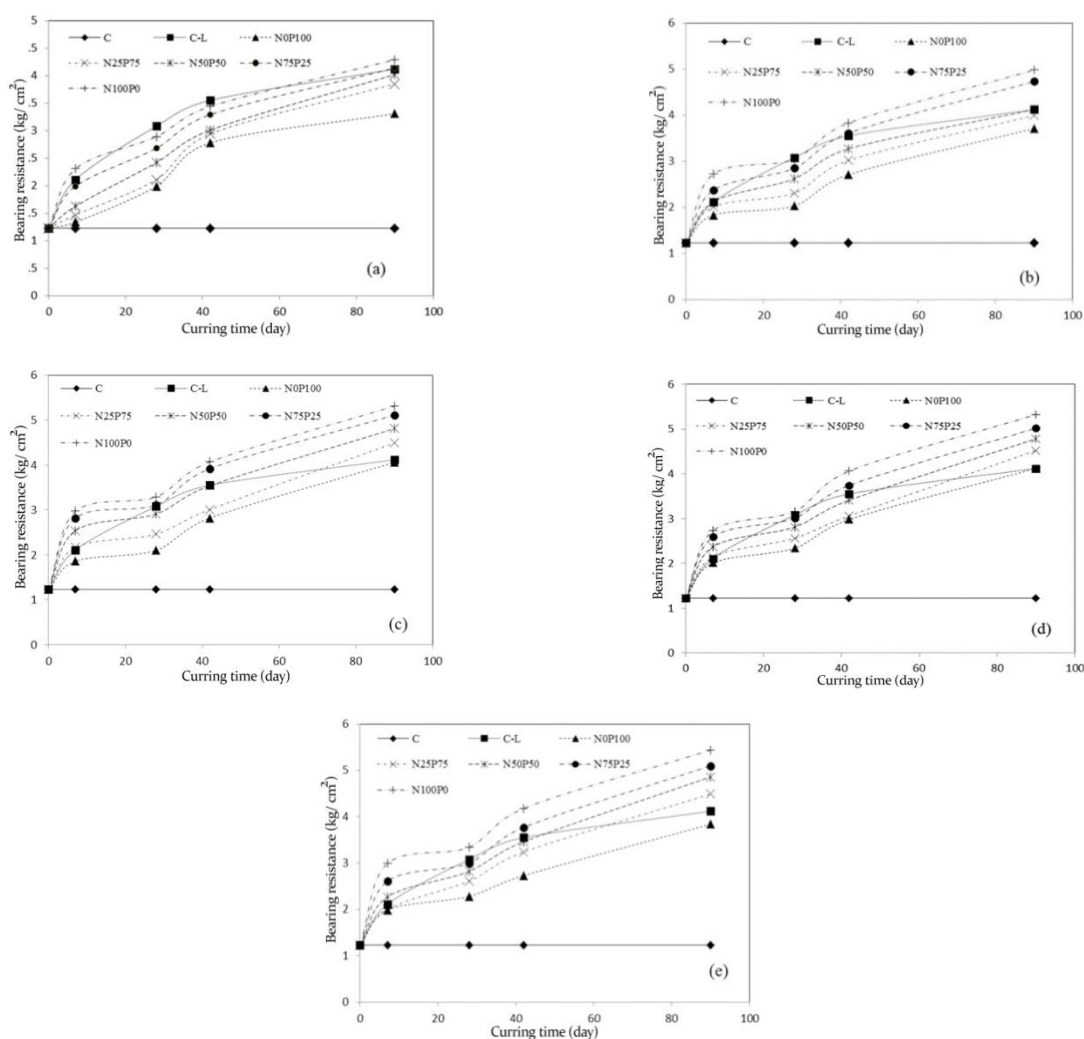


Figure 6. Variation of bearing resistance versus processing times for addition of various chitin nanofiber and rice husk ash percentage to clay containing 6 % lime: (a) 1%; (b) 2%; (c) 4%; (d) 6%; and (e) 8% additives

4. CONCLUSIONS

Due to many problems in the constructional structures on soft clay beds, particularly the consolidated soils, or the possibility of using these types of soils in soil structures, there was a need for the improvement and stabilization of these soils.

In this research, two additives namely chitin nanofiber and rice husk ash were added to the clay soil at different percentages, and the plastic properties and bearing resistance were studied.

- Results showed favorable chemical bond between chitin nanofiber and soil clay which confirmed chitin nanofiber potential to be used as an additive in soil stabilization study.
- In all samples, addition of chitin nanofiber and rice husk ash led to a significant reduction in the plastic properties of clay soil sample.

- The maximum effect of additives on reducing the temporal plastic index can be observed, where the addition percentage of chitin nanofiber was larger than rice husk ash.
- The maximum effect of additives on reducing the plastic limit was when the percentage of rice husk ash was higher in the additives.
- Addition of chitin nanofiber and rice husk ash to the soil containing 6% lime resulted to a significant increase in bearing resistance, specifically at higher additives percentages and curing time.

5. ACKNOWLEDGEMENTS

Special thank is to Dr. Samad Khaksar, faculty member of Ayatollah Amoli branch, Islamic Azad University, Amol, Iran for his contribution in this research.

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P A P E R I N F O

چکیده

Paper history:

Received 14 December 2018

Received in revised form 30 January 2019

Accepted 07 March 2019

Keywords:

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Bearing Resistance

Atterberg Limit

استفاده از خاک‌های رسی نرم در فعالیت‌های ساختمانی با مشکلات فراوانی مواجه شده است. برخی از روش‌های بهبود، تثبیت و تسلیحات برای استفاده از این خاک‌ها در جاده‌ها، زیر پایه‌ها و کف زمین مورد نیاز است. در این تحقیق، تأثیر نانوفیبر کیتین و خاکستر پوسته برنج به عنوان مواد افزودنی روی خواص رفتاری و مقاومت فشاری خاک رس نرم با توجه به زمان پردازش ۰.۷، ۲.۸، ۴.۲ و ۹.۰ روز بررسی شده است. مناسب بودن نانوفیبر کیتین به عنوان یک افزودنی توسط آنالیزهای FTIR، XRD و SEM ارزیابی شده است. درصد‌های مختلفی از افزودنی‌ها (۱، ۲، ۴، ۶ و ۸ درصد) با تغییرات در نسبت نانوفیبر کیتین و نسبت خاکستر پوسته برنج به خاک حاوی ۶ درصد آهک اضافه شده است. حداکثر کاهش در حد خمیری و شاخص پلاستیکی با افزودن ۲٪ مواد افزودنی به خاک حاوی آهک ۶٪ که درصد نانوفیبر کیتین بیشتر از خاکستر پوسته برنج بود، بدست آمد. استفاده از مواد افزودنی مورد بررسی در خاک رس باعث افزایش قابل توجهی در مقاومت فشاری، به ویژه در درصد‌های بالاتر از مواد افزودنی و زمان‌های پردازش شده است. به طور کلی، نتایج به دست آمده، استفاده بالقوه از نانوفیبر کیتین و خاکستر پوسته برنج را به عنوان مواد افزودنی برای بهبود خاک‌های رسی رسوبی تأیید کرده است.

doi: 10.5829/ije.2019.32.03c.04