Research Article

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Nano titanium oxide for modifying water physical property and acid-resistance of alluvial soil in Yangtze River estuary

https://doi.org/10.1515/secm-2021-0016
received October 26, 2020; accepted March 15, 2021

Abstract: This study aims to investigate the role of nano TiO_2 in modifying the characteristics of Shanghai clayey silt – alluvial soil in Yangtze river estuary. The Shanghai clayey silt is first mixed with nano TiO_2 with different size group and content before it is made to undergo liquid and plastic limit tests, standard Proctor compaction tests, and acid-resistant tests. The results show that nano TiO_2 can substantially increase the liquid limit and plastic limit of TiO_2-treated clayey silt, but can decrease the plasticity index of it to some degree. The result from standard Proctor compaction tests shows that the maximum dry bulk density (MBD) decreases and the optimum water content (OWC) increases compared with untreated samples. Acid-resistance of sample is significantly increased after being treated by nano titanium dioxide. The data provided by this study can be used for not only the soil and water conservation, but also for soil improvement, diversity of vegetables and animals, amelioration of crop land, as well as sustainable development.

Keywords: nano TiO_2, alluvial clayey silt, consistency, standard proctor compaction, acid-resistance

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1 Introduction

Shanghai, the largest city for commerce and industry, is located in the due east of China, where Yangtze River meets with east China sea, with deep alluvial deposit. It is low in strength, bad in permeability, and easy to deform [1]. Most of civil engineering projects cannot proceed before the foundations of them are processed [2]. Therefore, a lot of soil amendments have been used to improve the ground to make it suitable for special engineering demands, such as cement, lime, fly ash, construction waste, among others. However, most of above traditional soil admixtures either pollute environment in use or are detrimental to surroundings in the course of production [3].

In addition, there are part of agricultural, horticulture land and shoaly land, such as east shoaly land in Chongming island of Shanghai, which are badly in need of improvement to satisfy their expected purposes [4]. Some of soil amendments have been effectively used to realize the above goal, for example, rice-husk ash [5], diatomite [6], silica fume and lime [7–9], and nanomaterials [10]. These soil amendments have been employed either for amelioration in ground structure, aerating and draining, increasing soil water holding capacity and decreasing soil compaction, or better workability range with spurring root development and increasing yield. This modification on soil performance would be substantially helpful to not only improve ecological biota and multiformity of plants and animals, and increasing of agricultural production, but also promote sustainable development of society and economy, environmental protection, and even serving as a new powerful way resisting against climate changes.

Nano TiO_2 is a new type of geo-material additive that has a particle size less than 100 nm, with a high specific surface area [11]. Nano TiO_2 is also a type of inorganic substance that has many structural forms. One of the common forms is anatase. The octahedron of the anatase type TiO_2 has obvious oblique crystal type distortion, and the distance of the Ti–O bond is very small and the length of the Ti–O bond is heterogeneous. This heterogeneity makes the TiO_2 molecule have strong polarity, which makes the surface of the TiO_2 easy to adsorb water molecules that are polarized to form carboxy group so as to have the super-hydrophilicity of the surface [12].

The study on nano TiO_2 as a new amendment material for soil is a hot research direction attracting many researchers from international geotechnical engineering circle. However, currently most of the researches on nano TiO_2 as an additive are centered on industries such as electronics, textiles, construction materials, cosmetics, food, biomedicine, and aerospace [13–19]. In civil engineering construction, a majority of investigations on nano TiO_2 as an additive are predominantly focused on cement-based materials. Bending fatigue and acid-resistance properties of concrete can be effectively improved if proper quantity of nano TiO_2 is added to concrete [20]. Abrasive resistance of concrete pavement will not be affected by adding nano TiO_2 through load tire tester test (LWT) and rotary wear test (RA) [21]. Anticorrosive quality can be obviously improved if appropriate fraction of nano TiO_2 is added to cement [22,23]. The adding of nano TiO_2 to set cement can increase its ratio of shrinkage [24]. There is positive effect of nano TiO_2 on improving the anti-permeability of self-compact concrete [25]. However, different types of nanomaterials have been used to modify the physical, water physical, and mechanical characteristics of clayey soil, silt, etc. so far in recent decade, with not including mostly the nano-TiO_2. The most used nanomaterials in improving the characteristics of soil include nano-clay [26–36], nano-SiO_2 [36–45], nano-CuO [26,27,35,36,46–50], nano-MgO [27,48,35,36, 51,52], nano-Al_2O_3 [26,46,48,51], nano-Kaolin [53], nano-chemical [54,55], nano-bentonite [56,57], Carbon nanotube [58,59], and nano-zeolite [60]. Of course, some of the researches have used TiO_2 as an additive to improve the performance of geo-materials [61–76].

In this study, the nano TiO_2 will be used as an additive of Shanghai alluvial clayey silt to modify its water-related performance. This research is a useful exploration because much few researches have previously been focused on the investigation of the effect of nano TiO_2 on physical and water physical properties of Shanghai clayey silt. Nano TiO_2 creates nontoxic and non-environmental pollution, and the cost of production of nano TiO_2 is relatively cheap that makes large scale of manufacturing available. It is expected to be a promising alternative to traditional additives. In this study, consistency tests, standard Proctor compaction tests, and acid-resistant tests have been carried out to assess the effects of nano TiO_2 on water physical properties of Shanghai alluvial clayey silt. The data provided by this study can be used as a beneficial reference to better development of all stockholder industries.

2 Materials and methods

2.1 Materials

2.1.1 Shanghai clayey silt

Shanghai alluvial clayey silt has been obtained from 0 to 30 cm beneath the surface in a vegetable land of Zhangjiang hi-tech park in Pudong new area, east of Shanghai. The soil is allowed to pass through 2 mm seive after air-dried and crushed by rubber hammer on rubber sheet to remove a few of organic debris and other bigger gravels for further processing. Table 1 shows the basic physical and water physical properties of Shanghai clayey silt. Figure 1 shows particle size distribution curve of Shanghai clayey silt.

2.1.2 Nano TiO_2

The nano TiO_2 used in this test is type anatase, commercially obtained from Hefei Ge En hi-tech company, which falls into 3 particle group: 5–10, 20–30, 90–110 nm. Table 2 shows the basic properties of anatase.

2.2 Methods

2.2.1 Samples preparation

The nano TiO_2 (anatase) with different particle size group and content is manually mixed with dried soil until the homogeneous appearance takes place. Then, the proper

Table 1: Physical and chemical properties of Shanghai clayey silt

Optimum water content (W_{opt}/%)	Liquid limit (W_L/%)	Plastic limit (W_p/%)	Plastic index (I_p)	Clay content (%)	Silt content (%)	Sand content (%)	Maximum dry density (ρ_{dmax}/kg m^{-3})	Specific gravity (G_s)	Uniformity coefficient (C_u)
18	34	24	10	9	57	34	1,620	2.72	4.33

Coefficient of curvature (C_c)	pH[a]	EC[a] (mS cm^{-1})	CEC (cmol$_{(+)}$ kg^{-1})	$CaCO_3$ (%)	Organic matter (%)	Bulk density (g cm^{-3})	Soil classification
1.97	8.1	0.12	15.00	7.00	1.59	1.26	Clayey silt

[a]Determined in 1:2.5 (soil:water) extract. EC: electric conductivity. CEC: cation exchange capacity. Determined based on US Soil Classification Standard Keys to Soil Taxonomy.

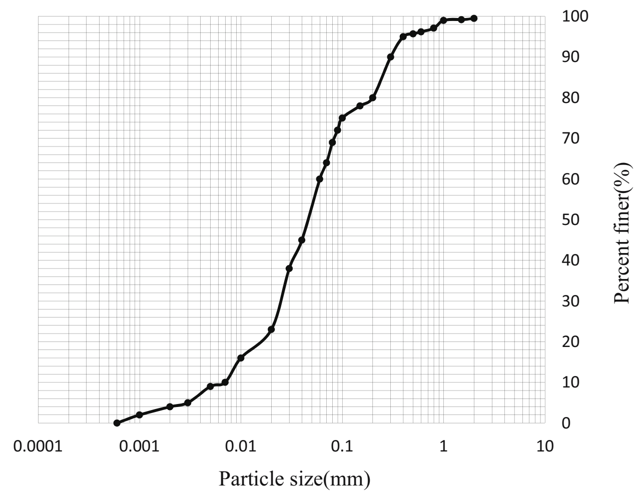

Figure 1: Particle size distribution curve of Shanghai clayey silt.

amount of distilled water is slowly added to the mixture, while keeping mixing so that the mixture becomes paste. The paste then is wrapped in the plastic bags for curing 24 h, being prepared for subsequent tests.

2.2.2 Consistency tests

The liquid and plastic limits tests are carried out based on ASTM D4318-10 [77]. Each test is repeated three times for reproducible goal with their average being used. The liquid and plastic limits of samples with different particle group and content of nano TiO_2 can be obtained through this consistency tests.

2.2.3 Standard proctor compaction tests

The Proctor compaction tests are executed based on ASTM D 698-00a [78]. Every test is repeated three times for reproducible goal. The range of water content is selected around the plastic limit with change step of 3%.

2.2.4 Acid-resistant tests

The soil mixture after 24 h curing is used to prepare samples for acid-resistant tests. The soil mixture is first spread out in a large tray to make its water content at amount calculated for optimum water content (OWC) through regulating by air drying or adding fresh water. Then the stabilized clay mixes were compacted in standard cylindrical steel molds to produce specimens with dimensions of 80 mm in height × 39 mm in diameter for

Table 2: Basic properties of anatase

Crystal form	Appearance	Content (%)	Grain size (nm)	Specific area ($m^2 g^{-1}$)	pH value	Character of surface	Bulk density ($g cm^{-3}$)
Anatase	White powder	99.8	5–110	80–200	6.5–8.5	hydrophily	0.35

acid-resistant tests. Every test will be repeated three times for reproducible goal. Accelerated deterioration testing is applied in acid rain simulation experiments. Submerging and spraying are two major methods to accelerate the deteriorations caused by acid rain in the laboratory. Based on the study of [79] and specific condition of this test, the spraying method (once every 2 h automatically) is selected to accelerate nano TiO_2-treated samples' deterioration caused by acid rain. Because H_2SO_4 is generally more aggressive than HNO_3 solution [80], the relatively mild HNO_3 solution is selected to simulate the acid rain. The acid rain solution was prepared by dropping dilute nitric acid (HNO_3) into distilled water.

A corrosion-resistant rectangular tank, shown in Figure 2, is used for the experiment. After 7 days' nano TiO_2-treatment and 48 h oven drying, the nano TiO_2-treated samples were divided into four scenarios denoted by G0, G1, G2, and G3 group as shown in Table 3. G0 is used as the control scenario, which has 0% of TiO_2 content. G1 through G3 are meant for treated samples with TiO_2 whose particle size group ranging between 5–10, 20–30, and 90–110 nm, respectively. The content of TiO_2 in G1 through G3 is 6% and spraying time is 15 days. G0 through G3 all expose pure water of pH = 7.0 and HNO_3 solution of pH = 3.5. The spraying time of G0 is also 15 days.

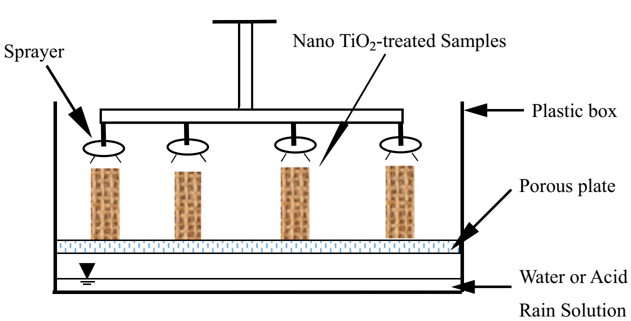

Figure 2: Acid-resistant rectangular tank.

The spraying is applied at interval of 2 h with pH value of 7.0 and 3.5, respectively. After being intermittently sprayed for 15 days, the control and three nano TiO_2-treated samples as one batch are taken out for later testing as shown in Table 3. The control and nano TiO_2-treated samples are oven-dried for 48 h, followed by weighing. The TiO_2 content of 6% is selected according to [81], which shows that the strength of treated samples is maximized as nano particle content is 6%.

3 Results and discussion

3.1 Results

3.1.1 Results of consistence tests

Three size groups of nano TiO_2 application significantly ($p < 0.05$) increase LL and PL values of treated Shanghai clayey silt (Table 4), due to the potential activity of nano TiO_2. LL and PL values increase with content of nano TiO_2 in all three particle size groups of nano TiO_2. The highest values of LL and PL are obtained from the maximum content of nano TiO_2 for every group. However, the increase in LL and PL in G1 is more obvious than that in G2 and G3 with the same content. Generally, the smaller the particle size, the higher the increase in LL and PL; the more the content of nano TiO_2, the higher the value of LL and PL. Figure 3 intuitively shows the development trend of LL and PL with particle size and content of nano TiO_2, which may possibly be closely related to the high activity of the extremely fine particle size of nano TiO_2 because the finer

Table 3: Testing details of acid rain simulation

Designation	TiO_2 content (%)	Repeated times	Spraying time (days)	Exposing condition	Solution acidity
G0	0	3	15	Pure water, HNO_3	pH = 7.0, 3.5
G1	6	3	15	Pure water, HNO_3	pH = 7.0, 3.5
G2	6	3	15	Pure water, HNO_3	pH = 7.0, 3.5
G3	6	3	15	Pure water, HNO_3	pH = 7.0, 3.5

Table 4: Effect of nano TiO_2 application on liquid limit (LL), plastic limit (PL), and plasticity index (PI) of soil (Mean ± SD[a])

Designation	Nano TiO_2 (nm)	Application rate (m/m)	LL (%)	PL (%)	PI (%)
G1	5–10	0 (Control)	34.2 ± 0.5	23.8 ± 0.3	10.4 ± 0.1
		3	40.0 ± 0.3	34.0 ± 0.4	6.0 ± 0.2
		6	46.2 ± 0.4	41.3 ± 0.3	4.9 ± 0.3
		10	52.3 ± 0.6	48.6 ± 0.3	3.7 ± 0.2
G2	20–30	0 (Control)	34.2 ± 0.5	23.8 ± 0.3	10.4 ± 0.1
		3	38.4 ± 0.3	32.7 ± 0.4	5.7 ± 0.1
		6	43.0 ± 0.3	38.6 ± 0.5	4.4 ± 0.2
		10	49.2 ± 0.2	46.0 ± 0.5	3.2 ± 0.1
G3	90–110	0 (Control)	34.2 ± 0.5	23.8 ± 0.3	10.4 ± 0.1
		3	35.4 ± 0.3	30.0 ± 0.1	5.4 ± 0.2
		6	36.9 ± 0.2	32.5 ± 0.4	4.4 ± 0.1
		10	43.1 ± 0.3	39.6 ± 0.3	3.5 ± 0.2
General		0 (Control)	34.2 ± 0.5	23.8 ± 0.3	10.4 ± 0.1
		3	37.9 ± 1.0	32.2 ± 1.6	5.7 ± 0.2
		6	42.0 ± 0.5	37.5 ± 1.2	4.5 ± 0.1
		10	48.2 ± 1.2	44.7 ± 0.8	3.5 ± 0.2

[a] SD means standard deviation of three parallel tests.

particle size generally means higher specific surface area and nano TiO_2 has strong polarity.

However, the changing trend of plastic index (PI) is contrary to those of LL and PL. As content of nano TiO_2 increases, the PI decreases for all particle size groups. This is due to the fact that the increasing rate of plastic limit is higher than that of liquid limit at the same content of nano TiO_2 for each particle size group. This is important because high PI means high plasticity, which can lead to more shrinkage and cracks of soil when drying.

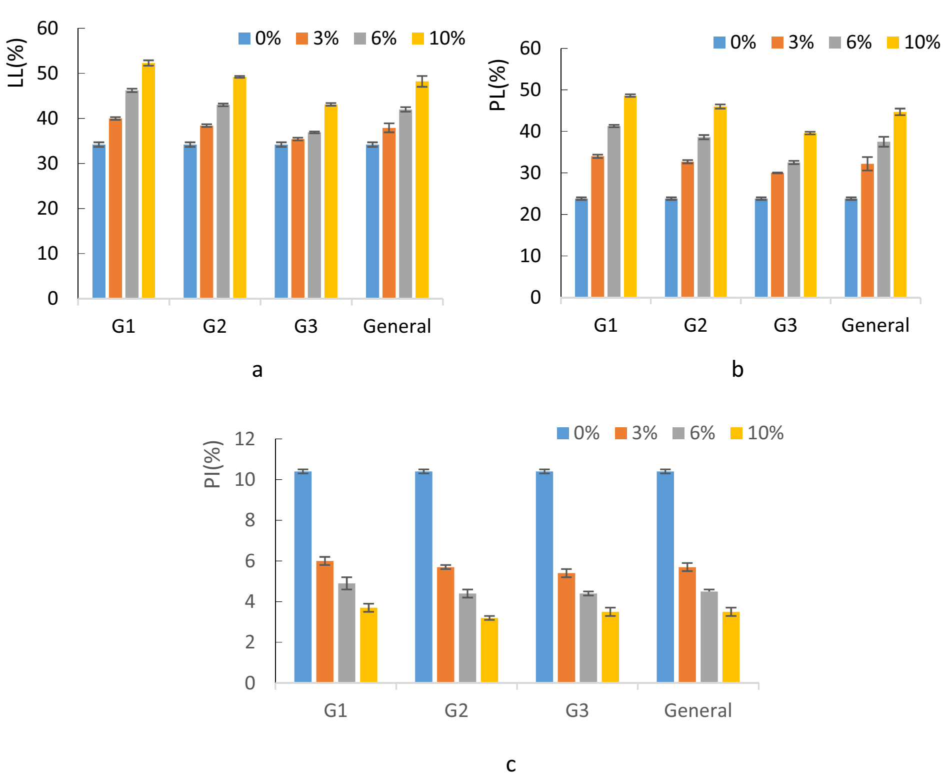

Figure 3: Variation of LL (a), PL (b), and PI (c) with particle size and content of nano TiO_2.

They are usually prevented as much as possible in geotechnical engineering. The above result can be basically explained from two perspectives. First, it resides in the characteristics of nanomaterials itself. As the particle size is small enough and can be compared to molecular scale, there will be a substantial change in chemical and physical characteristics, which cause the property change in nanomaterial-treated soil, such as its enhanced activity. Second, it is the characteristics of TiO_2 itself; such as extremely strong polarity and hydrophily etc., which can cause the consistency state to substantially change for TiO_2-treated clayey silt. The octahedron of the anatase type TiO_2 possesses distinct oblique crystal type distortion, and the gap between Ti–O bond is extremely short and heterogeneous. This causes the surface of the TiO_2 to easily adsorb water molecules that are polarized to form carboxy group forming the super-hydrophilicity of the surface [12].

3.1.2 Results of standard proctor compaction tests

Table 5 and Figure 4 show the relationship between water content and dry bulk density of the soil at different level of content and particle size of nano TiO_2 with standard Proctor test. The result clearly suggests that inclusion of nano TiO_2 to the clayey silt can extend the OWC, but lower the maximum dry bulk density (MBD). In all of the same application rate of nano TiO_2, the largest OWC and lowest MBD are obtained from G1, which has the finest particle size (5–10 nm), while the lowest OWC and the highest MBD are obtained from G3, which has the coarsest particle size (90–110). The condition for G2 is between G1 and G3.

For 3, 6, and 10% of application, the OWC increases with the increase of nano TiO_2 content, while the MBD decreases with the increase of nano TiO_2 content. For G1, the maximum increase in OWC and maximum drop in MBD are obtained when the content of nano TiO_2 is about 10%. The maximum increase in OWC is approximately 61% compared with the control sample. The maximum drop in MBD is approximately 25%.

For G3, the maximum increase in OWC and maximum drop in MBD are also obtained when the content of nano TiO_2 is about 10%. However, the maximum increase in OWC is approximately 38% compared with the control sample. The maximum drop in MBD is approximately 21%. This means the particle size of nano TiO_2 has significant influence on the performance of treated samples. It seems to be that the finer the particle size of nano TiO_2, the more the influence on the performance of nano TiO_2-modified clayey silt. This may be closely related to the high activity of extremely fine particle size of nano TiO_2 and the extremely strong hydrophillicity, which also increase the activity of modified clayey silt. The finer the particle size group of nano TiO_2, the higher the PI seems to confirm above argument.

It is important to understand the action mechanism of nano TiO_2 on performance of soil because the increase in liquid limit, plastic limit, and OWC can increase field

Table 5: Effect of nano TiO_2 on maximum dry bulk density (MBD) and optimum water content (OWC) (Mean ± SD[a])

Designation	Nano TiO_2 (nm)	Application rate (m/m)	MBD (g cm^{-3})	OWC (5%)
G1	5–10	0 (Control)	1.62 ± 0.01	18.4 ± 0.1
		3	1.50 ± 0.01	21.1 ± 0.1
		6	1.38 ± 0.15	23.9 ± 0.3
		10	1.21 ± 0.05	29.6 ± 1.0
G2	20–30	0 (Control)	1.62 ± 0.01	18.4 ± 0.1
		3	1.53 ± 0.03	20.7 ± 0.3
		6	1.41 ± 0.01	23.4 ± 0.3
		10	1.23 ± 0.02	29.0 ± 0.2
G3	90–110	0 (Control)	1.62 ± 0.01	18.4 ± 0.1
		3	1.59 ± 0.02	19.4 ± 0,3
		6	1.46 ± 0.03	22.0 ± 0.3
		10	1.28 ± 0.02	25.4 ± 0.2
General		0 (Control)	1.62 ± 0.01	18.4 ± 0.1
		3	1.54 ± 0.01	20.1 ± 0.6
		6	1.42 ± 0.01	23.1 ± 0.4
		10	1.24 ± 0.01	28.0 ± 0.7

[a] SD means standard deviation of three parallel tests.

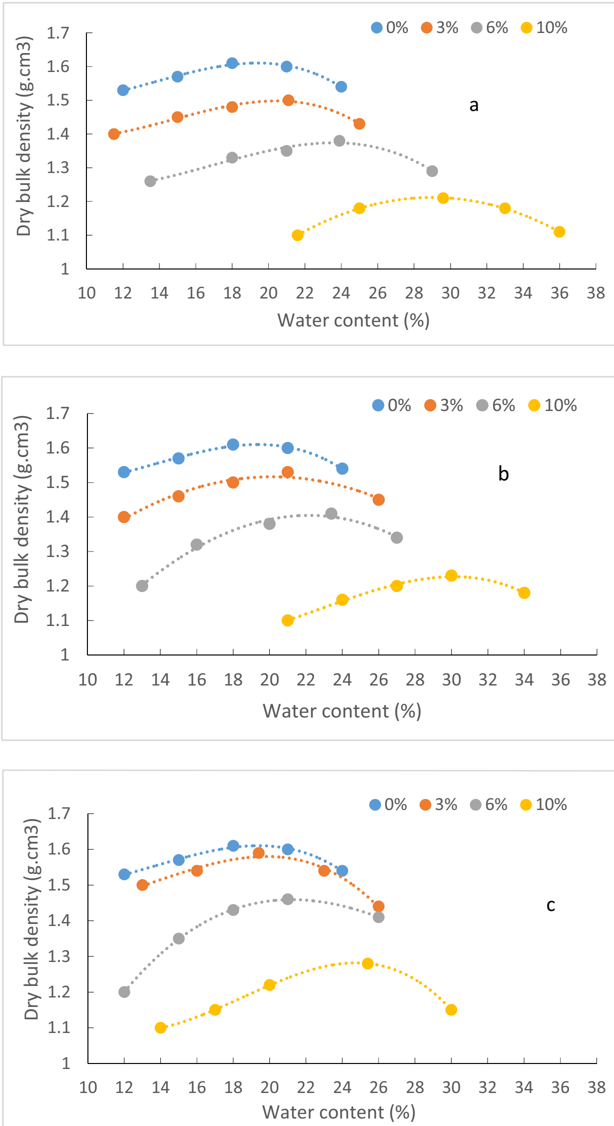

Figure 4: Proctor compaction test curves of the nano TiO_2-treated soil studied. (a) 5–10 nm, (b) 20–30 nm, (c) 90–110 nm.

water capacity, which is helpful to vegetable growth, crop production, diversity of vegetable and animal, and even resistance against drought possibly caused by climate change.

3.1.3 Results of acid-resistant tests

Samples modified with particle size groups of 5–10, 20–30, 90–110 nm of nano TiO_2 are selected to research the influence of nano TiO_2 on acid-resistance of treated samples. For the sake of saving space and simplicity, 6% content of nano TiO_2 is selected based on the research from [80], which shows that the content of 6% is optimal for strength.

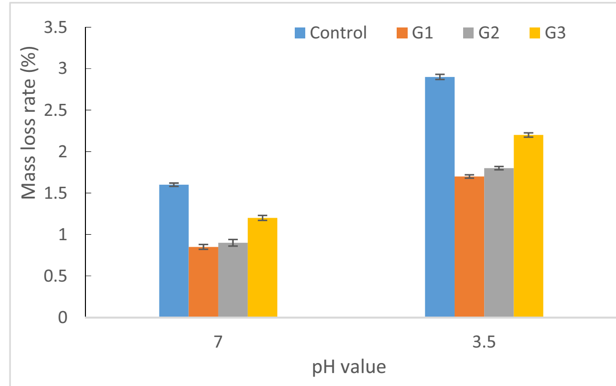

Figure 5: Relationship of mass loss rate with pH value and different particle size groups of nano TiO_2 under spraying of pure water and acid rain solution for 15 days.

The 15 days of spraying time is selected and solution acidity is selected as pH = 7.0 and 3.5 according to [79]. The mass of samples is tested before and after environmental condition to determine the mass loss rate, which is defined as Mass loss rate = $(m_i - m_n)/m_i$. Where m_i is mass of sample before environmental condition, and m_n is mass of sample after environmental condition.

Figure 5 shows variation of mass loss rate with pH value and different particle size groups of nano TiO_2 under spraying of pure water and acid rain solution for 15 days, intermittently and automatically. As shown in Figure 5, the mass loss rate increases with decreases of pH value from 7 to 3.5. Whether the pH = 7.0 or 3.5, the samples without admixture of nano TiO_2 show the highest mass loss rate, which suggests that the nano TiO_2 possesses anti-acid capability. For pH = 3.5, the mass loss rate for G1 is decreased by 41% compared with that of control samples. At the same time, it can also be seen that for the same acidity, the finer the nano TiO_2 particle size group, the better the acid-resistance, because of G1 < G2 < G3 with regard to mass loss rate whether pH = 7 or 3.5. Generally, nano TiO_2 shows stronger acid-resistance against environmental corruption than without nano TiO_2.

The reason of above results may reside in that the finer the particle size, the larger the specific surface area that is higher in activity. In addition, nano TiO_2 itself possesses inherent property of pollution cleaning and disinfecting. Therefore, it can be arguably expected that nano TiO_2 being advisable admixture not only used for improving stabilization of soil, but also restoring polluted farmland or something like this. TiO_2 is snowy white powder, with extremely strong adsorption capacity, not susceptible to chemical change, and has a capacity to clean pollution, anti-sunburn. Actually, it has been widely used in every field due to its natural characteristics. The exerting of TiO_2 to clayey silt to modify its physical and water physical properties will open up a new field of application.

3.2 Discussion

It is said that the cost of nano TiO_2 is relatively too high to be applied in improving the performance of soil, but at least two reasons justify the application of it to modifying soil. The first is that the cost of nano TiO_2 is expected to be considerably decreased in the near future with large-scale industrial production. Second, the prospect of nano TiO_2 used in not only improving the strength property of soil, but also in modifying and restoring the industrially polluted soil may make its potential benefit exceed its cost. Therefore, our research is worthy.

Because of the limited time, microstructure of nano TiO_2-treated samples was not studied, which may be useful in well understanding the internal action between particles of nano TiO_2 and soil, especially, the research of their action mechanism that is expected to be special in view of high specific area and hydrophilicity.

Consistency test and acid-resistant test have been carried out in this study. The result shows there is a significant increase in liquid and plastic limit, which may be important for amelioration of vegetable land in resistance action caused by tillage and against drought caused by climate changes. In addition, the field water holding capacity can also be improved which is helpful to the growth of plants and animals.

Results for Standard proctor compaction test show that nano TiO_2-modified soil has higher OWC and lower MBD, and the finer the particle size of nano TiO_2, the more the improvement, which is helpful to tilling and farming of crop land, because the land can bear more mechanical loading without land harden. Therefore, the research on the effect of nano TiO_2 on soil is meaningful to eco-environmental protection and sustainable development of human society not only in economy, but also in healthy living condition. As to many concerns for experts of cost of nano TiO_2, there is no need to worry so much because the large-scale production is now available due to the fast development of industrial manufacturing technology.

In addition, the nano TiO_2-modified clayey soil has stronger ability fighting against acid corruption, so this is meaningful in areas where acid rain occurs or there is heavy industry that may cause serious acid rain pollution.

3.3 Mechanism analysis

The effect of nano TiO_2 on water physical performance of clayey soil may come from a root cause, namely, the extremely fine particle size (0–100 nm). Specifically, it can be covered as follows.

First, super-hydrophilicity. The octahedron of the anatase type TiO_2 and obvious oblique crystal type distortion make the TiO_2 molecule have strong polarity, which makes the surface of the TiO_2 easy to adsorb water molecules that are polarized to form carboxy group so as to have the super-hydrophilicity of the surface. This mechanism may be used to explain why LL and PL are increased with samples-modified nano TiO_2, and the finer the particle size, the higher the LL and PL, because the finer particle size is more active and has higher specific surface.

Second, the size and diffusion of nano TiO_2 may function in Standard proctor compaction test that coacted with strong polarization and super-hydrophilicity leading to the increase of OWC and decrease of MBD.

Third, the addition of nano TiO_2 may change the microstructure of soil that leads to the exchange between Ca^+ in soil and H^+ in acid solution, which improves the acid-resistant ability. This is just what happens in the acid rain test [23].

4 Conclusions and recommendations

In this study, liquid and plastic limit, Standard proctor compaction, and acid-resistant tests on nano TiO_2-modified soil under different particle size and content of nano TiO_2 have been carried out. Conclusions obtained from above tests are as follows.

The liquid and plastic limits significantly increase. The finer the particle size of nano TiO_2, the more the increase in LL and PL; the more the content of nano TiO_2, the more the increase in LL and PL, but inversely PI decreases.

In the Standard proctor compaction test, the OWC increases and MBD decreases with the increase of content and decrease in particle size of nano TiO_2.

Acid-resistant capacity of nano TiO_2- modified soil is improved substantially as per mass loss rate after exposing to the simulating acid rain environment (regular spraying).

The exploration of effect of nano TiO_2 under different particle size and content on water physical property of alluvial clayey soil has been tried. But because of limited time, many microstructure analyses have failed to be completed which are supposed to be very important for a perfect study, such as scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). Therefore, the future study should be centered on microscopic analysis of modification mechanism by the help of microscopic tools.

Acknowledgments: The authors thank Shanghai municipal government for financial support (No. 57-19-119-002).

Funding information: The authors are grateful to the financial support from Shanghai municipal government (No. 57-19-119-002).

Conflict of interest: No potential conflict of interest was reported by the authors.

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