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A multi-scale experimental investigation of Sulfur-Free Lignin as novel soil stabilizer

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Abstract

With the rapid process of urbanization, more and more infrastructures are inevitably built on problematic soils, which require improvement and reinforcement. In this study, a novel material Sulfur-Free Lignin (SFL), which is a by-product of bioethanol industry, was used to improve the soil's geotechnical behavior as a sustainable, nontoxic and eco-friendly stabilizer. To systematically investigate the geotechnical properties of SFL-stabilized soil, the natural soil was modified by adding five different contents (3, 7, 10, 12 and 15%) and then a series of geotechnical experiments including unconfined compressive strength (UCS), Atterberg limits tests, electrical resistivity and pH were carried out after 1, 7, 28, 60-days curing. In addition, to preliminary investigate the stabilization mechanism, the mineral composition, function group and microstructure characteristic were also studied through X-Ray Diffraction (XRD), Fourier Transform

Infrared Spectroscopy (FTIR), Mercury Intrusion Porosity (MIP) and Scanning Electron Microscopy (SEM) tests. The test results demonstrate that with increasing SFL content, the electrical resistivity gradually decrease, on the contrary, the Atterberg limits show a slightly increase. However, the pH values are unchanged indicating the SFL would not lead to pH contamination risk which is usually caused by traditional chemical stabilizer. Furthermore, the 10% SFL-stabilized soil after 60 days of curing shows the greatest strength, which increases about 600% compared to the natural soil. Furthermore, the relationship between E_{50} and UCS is generally proportional. According to the results of MIP and SEM, the strength improvement could contribute to a smaller total volume of pores, reduction in the mean size of the pores and stronger bonds former by SFL between isolated grains. In addition, the results of XRD and FTIR test reveal there is no new mineral and function group generated after adding SFL. Above all, the natural soil stabilized by SFL shows a satisfactory engineering performance and it would be a win-win solution to utilize SFL as a soil stabilizer for soil improvement in civil engineering and waste elimination in bioethanol industry.

Key words: Sulfur-Free Lignin, soil stabilization, curing time, eco-friendly and sustainable stabilizer, multi-scale investigation

1 Introduction

With the expanding process of urbanization, more and more civil engineering structures, such as rail/road subgrade, foundations and embankments, are inevitably constructed above problematic soils, which could cause safety and reliability problems for the structure if the soil properties are not improved or stabilized. Stabilization of problematic soils has traditionally been achieved by mixing grout or other chemical agents to increase soil shear strength, decrease its compressibility and alter other undesirable engineering properties, such as high permeability (Karim et al., 2013; Jafer et al., 2018; Wang et al., 2019a). At present, the traditional chemical cementitious agents involving Ordinary Portland Cement (OPC) and lime have been used as preferred binder materials to enhance the engineering properties of weak soils and achieve good results (Chen and Wang, 2006; Modarres and Nosoudy, 2015; Liu et al., 2019b). However, these cementitious agents are associated with some considerable problems: (i) to produce them, huge amounts of energy are consumed and large CO₂ emission occur in the clinker production process. For example, the typical manufacturing of 1 t OPC consumes 5000 MJ and releases about 0.95 t CO₂ and overall this accounts for 4 - 5 % of global CO₂ emissions (Thives and Ghisi, 2017; Zhang et al., 2017b). (ii) the soils stabilized with these materials show a remarkable increasing trend in pH values, which may pose a risk of environmental contamination (Sreekrishnavilasam et al.,

2007; Jiangying et al., 2008). (iii) the performance of treated soil is barely satisfactory under dynamic cyclic loads, due to excessively brittle properties. The above problems push to find innovative soil stabilizers to improve the geotechnical properties of weak soils, while meeting the requirements of being eco-friendly, low-carbon and energy-efficient. Therefore, various alternative agents (such as lignin, fly ash, reactive MgO, rice husk ash and wastepaper sludge ash) based on industrial by-products or waste materials have been tested in the attempt to replace OPC in the process of soil stabilization (Tingle et al., 2007; Rahmat and Ismail, 2011; Lee and Shang, 2014; Liu et al., 2019a; Wang et al., 2019b).

In recent years, lignin begins to draw more and more attention from researchers as a potential soil stabilizer due to its use as a renewable biomass. In the past industrial processes, massive lignin amounts were obtained in the form of lignosulfonate (LS) from paper pulping industry (Chio et al., 2019). Due to the increasingly grim energy safety problems caused by massive consumption of non-renewable fossil fuels, bio-based energy production has flourished under the support of advancing technology. The second-generation ethanol production especially overcomes the concerns regarding food security by utilizing readily available lignocellulosic biomasses (such as corncob, maize straw and tree leaves) instead of crops to produce bioethanol and shows a huge potential to replace petroleum-based resources (Yano et al., 2009; Pourhashem et al.,

2016; Wang and Cheng, 2018). However, a large amount of lignin is left as a by-product or waste material in the process of generating bioethanol. This kind of lignin based on bioethanol production is different from lignosulfonate from pulping industry, as it is sulfur free and contains more lignin (about 50 - 75%) with moderate macromolecular size making it more similar to native lignin.

Currently, considerable research has been conducted to investigate the performance of lignosulfonate (LS) from pulping industry as an innovative reinforcement geomaterials. Tingle and Santoni treated clay soils and silty sands with different LS quantities and tested the load-bearing capacity of the stabilized soils (Santoni et al., 2002; Tingle and Santoni, 2003). The results showed all stabilized soils had a significant strength improvement. They also preliminarily discussed the possible stabilization mechanism of LS (Tingle et al., 2007). Surdahl et al. investigated the performance of lignosulfonate-stabilized soils for dust control, rutting, raveling and washboarding over a 24-month period through a field test in south central Arizona, America (Surdahl et al., 2007). The physical monitoring results showed the LS stabilized have a satisfactory improvement overall. Indraratna, Vinod et. al (2008; 2010) and Alazigha et al. (2018) used LS to stabilize dispersive and expansive soil respectively and evaluated the behavior of erosion resistance and swelling resistance. Vakaili et. al (2018) also studied the internal erosional behavior of dispersive clay stabilized

with LS and similarly to Indraratna et al. the LS-stabilized soil showed a significant reduction in soil dispersivity. In addition, Zhang et al. (2015; 2017a, 2018a) comprehensively assessed the engineering performance of LS-stabilized silty soil as pavement subgrade through a series of laboratory and field tests, employing shear-wave velocity and thermal resistivity as fast and nondestructive methods to evaluate the strength performance for LS-stabilized soils. However, scarce research has been conducted to study the engineering performance of bioethanol-derived sulfur-free lignin as a geotechnical stabilizer, even if sulfur-free lignin has advantages over LS and its production is increasing rapidly along with the flourishing bioethanol industry.

In view of the above, the purpose of this study is to investigate the feasibility of using Sulfur-Free Lignin (SFL) based on a bioethanol industry by-product to stabilize soil, improving its geotechnical properties of soil, while reducing product energy consumption and CO₂ emissions by using a waste. A series of laboratory experiments were conducted including Atterberg limits, Unconfined Compressive Strength (UCS), pH, electrical conductivity, X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Mercury Intrusion Porosimetry (MIP) and Scanning Electron Microscopy (SEM). Based on the analysis of the experiments, the effects of different SFL contents and different curing times were obtained. In addition, the stabilization mechanism of Sulfur-Free Lignin is also

preliminary analyzed in this paper.

2 Materials and methods

2.1 Soil samples

The soil samples used in this study were extracted from about 40 cm depth below ground level in Qian'an city that is located in the western of Jilin Province, China [N45° 02'25.490", E123° 47'1.148"]. The particle size distribution (measured by Laser Diffraction Particle Analyser) of the soil used in this study is shown in Fig.1. The main geotechnical properties of the soil are summaries in Table.1 along with the results of total dissolved solids, pH and organic matter content. The chemical elemental components of the soil were determined by X-ray Fluorescence and the result are listed in Table. 2. As shown in Fig.2, the X-ray Diffraction quantitative analysis indicates that the main mineral components include Quartz, clay minerals and Plagioclase, accounting for 38.7, 22.9 and 16.4% respectively. Moreover, the main clay minerals are the by Illite/Smectite mixer layer and Illite, which are the most common crystalline minerals (Budhu, 2008).

Fig. 1. Grain size distribution of the natural soil.

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Table 1
Geotechnical properties of the tested soil

Property	Values
Soil natural density(g/cm ³)	1.909
Natural water content w (%)	21.58
Sand % (2-.075 mm)	18.5
Silt % (0.075-0.005 mm)	53.4
Clay % (<0.005 mm)	29.1
liquid limit (%)	34.85
plasticity limit (%)	18.47
plasticity index PI	16.49
Optimum moisture content (%)	15.6
Maximum dry unit weight(γ_{dmax}) (kN/m ³)	1.781
Total dissolved solids (mmol/kg)	43.92
Organic matter (%)	0.40
pH	8.7

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Table 2**The chemical composition of the tested soil based on the XRF**

Composition	percentage (%)
Silicon oxide (SiO_2)	66.27
Aluminum oxide (Al_2O_3)	11.55
Iron oxide (Fe_2O_3)	2.51
Ferric oxide (FeO)	0.40
Calcium oxide (CaO)	5.04
Magnesium oxide (MgO)	1.69
Potassium oxide (K_2O)	2.88
Sodium oxide (Na_2O)	2.57
Titanium oxide (TiO_2)	0.50
Phosphorus oxide (P_2O_5)	0.07
Manganese oxide (MnO)	0.07
Loss on ignition (LOI) ^a	6.33
Other	0.10

Note: LOI means value of loss on 950°C ignition.

Fig. 2. Mineral composition of the natural soil.

2.2 Sulfur-Free lignin

The Sulfur-Free Lignin (SFL) used in this study was supplied by a corn-based bioethanol corporation in Shandong Province, China. The main components according to the supplier are 91.2% lignin, 0.12% residual cellulose/hemicellulose, and 0.67% ash content. The low ash content indicates the high purity levels of SFL as obtained in the processing of bioethanol. The SFL used in this study is a light-brown powder with wood fragrance odour that is slightly soluble having neutral pH.

Fig. 3. FTIR spectra of the sulfur-free lignin.

The functional groups of SFL were determined through Fourier Transform Infrared Spectroscopy (FTIR). The wavenumbers and the important band identification for SFL are present in Fig. 4. It is evident

from Fig. 4 that the SFL contains different function groups such as C-O stretching for methoxyl groups (1221 cm^{-1}), deformation of aromatic ring and C-H ($1032, 1463$ and 1513 cm^{-1}), unconjugated C=O and carbonyl/carboxyl ($1703, 1602\text{ cm}^{-1}$), CH stretching vibrations ($2937, 2850\text{ cm}^{-1}$) and OH (3420 cm^{-1}).

2.3 Sample preparation

The natural soil collected from the site was left to air-dry for several days (not less than 3 days) rather than oven dried to avoid altering the mineral composition. Then the soil lumps were pulverized with a rubber hammer and passed through a 2 mm sieve. Six different SFL amounts - 0, 3, 7, 10, 12 and 15%- were added as a percentage of the soil dry weight. Before adding distilled water, the mixture of SFL and natural soil was mixed for approximately 5 minutes to ensure homogenisation. The same operation was also carried out after mixing a predetermined amount of distilled water. Afterwards, the mixture was tightly sealed in a metal bucket for 24 h until the moisture was distributed homogeneously. It should be noted that the amount of water employed for the moisture content in all specimens was the optimum moisture content of the natural soil. Subsequently, the mixture was placed into a steel cylindrical mould with specific dimensions (39.1 mm inner diameter and 80 mm height) and statically compacted to a density equal to 95% the maximum density of the

natural soil. Finally, the demoulded specimens were wrapped with cling film, labelled and sealed with waterproof bags, then stored in a curing room with $20^{\circ} \pm 2^{\circ} \text{C}$ and relative humidity $92 \pm 3\%$ for either 1, 7, 28 and 60 days.

2.4 Testing methods

In this study, the two-electrode probe method was adopted to determine the electrical resistivity of the SFL-stabilized soil using the Anbai AT810A Precision LCR Meter instrument (Fig.4). Two-electrode probes were used to make full contact with the specimens and measure the voltage and current. According to Ohm's law, the electrical resistivity of SFL-stabilized soil, ρ (Ωm), was calculated based on the following equation:

$$\rho = \frac{\Delta U}{I} \frac{A}{L} \quad (1)$$

Where ΔU is the applied voltage (V), I is the applied electrical current (A), A is the cross-sectional area of the samples (m^2) and L is the height of the samples (m). In this experiment, the voltage and electric frequency of the instrument were set to 2 V and 10 Hz, respectively, and in order to avoid temperature effects, the electrical resistivity tests were performed in a constant room temperature (25°C). The pH tests were performed using a PB-10 probe (Sartorius Crop. Germany) according to ASTM D4972 (ASTM, 2007). The Atterberg limits for the natural and stabilized samples were measured by fall cone test as per ASTM D4318 (ASTM, 2010). To

207 characterize the strength of the SFL-stabilized soil, Unconfined
 208 Compressive Strength tests (UCS) were carried out in accordance to ASTM
 209 D4219 (ASTM, 2002). A fixed loading rate equal to 2 mm/min was used
 210 and the peak normal stress in the stress-strain curve was selected as the
 211 compressive strength.

Fig. 4. Schematic diagram of the two-electrode probe method.

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 213 To investigate the function groups, elemental and mineral composition
 214 of SFL-stabilized soil, the Fourier Transform Infrared (FT-IR) Spectra, X-
 215 ray diffraction and X-ray fluorescence tests were conducted. The FT-IR
 216 spectrum was measured and recorded in the mid-IR region of 475-4000
 217 cm^{-1} by a Thermo Scientific Nicolet iS10 Fourier transform infrared
 218 spectrometer (America). An X-ray diffractometer (D/MAX-2500, Rigaku,
 219 Japan) with a $\text{Cu-K}\alpha$ radiation source at a voltage of 30kV was used to
 220 conduct mineral pattern testing. The setting scanning angle ranged from
 221 2.6° to 45° with a scanning speed of $6^\circ(2\theta)/\text{min}$. In order to perform
 222 quantitative analysis of the mineralogical composition, the “K-value”
 223 method described in SY/T 5163-2010 (China, 2010a) was adopted. The

elemental composition for all samples were measured and analyzed by a tube-above wavelength dispersive X-ray fluorescence spectrometer (ZSX primus II, Rigaku, Japan) and EZ-scan software according to GB/T 14506 Standard (China, 2010b).

The pore size characteristics were investigated by Mercury Intrusion Porosimetry tests (MIP), using an AUTO-PORE 9500 device (Micromeritics Instrument Corp. America), which can reach a maximum pressure of 228 MPa. As suggested by Delage (1984), the tested specimens were subsampled into 1 cm³ cubes and were then completely dehydrated by freeze-drying, which involves rapid freezing in liquid nitrogen (boiling point -196°C) followed by sublimation in a true vacuum. Scanning Electron Microscopic analysis (SEM) has also been used to identify the microstructure of natural and SFL stabilized soils after being exposed for to different curing periods. A Phenom ProX Desktop scanning electron microscope (Thermo Fisher Scientific, America) was used with an accelerating voltage of 10 kV. The pretreatment process for SEM tests was almost the same as for MIP tests, however, the specimens were sputter-coated with a thin layer of gold prior to the SEM testing to improve the image quality and avoid electrical charging.

3 Results and discussion

3.1 Electrical resistivity and pH

Fig. 5(a) shows the electrical resistivity of the stabilized soil as a function of Sulfur-Free Lignin content. It can be found that the natural soil has the maximum electrical resistivity, on average equal to 102.43 ($\Omega \cdot m$), and the electrical resistivity decreases with increasing SFL content. In previous studies, some researchers (McCarter, 1984; Samouëlian et al., 2005; Cai et al., 2013) reported that two main factors control the electrical resistivity: (1) the degree of water saturation (water content) and (2) the electrical resistivity of pore fluid (solute concentration). The water content is not relevant in this case since this is the same for all samples (17.5%). Thus, the results may be due to the SFL powder mixing with some of the soluble salts used in the production process. In the process of corn-based bioethanol production, the lignocellulose structure of corncobs and corn stover are pretreated by high-pressure steam to break bonds between polymeric components. The SFL is then separated from the steam solution through delignification reactions (adding alkaline compounds to sediment the lignin and acids to neutralize the pH) (Rocha et al., 2012). As a result, the solute ion concentration in the pore fluid increases with SFL, resulting in a decrease in the electrical resistivity.

Fig. 5. Electrical resistivity for samples in terms of (a) sulfur-free lignin and (b) curing time.

Fig 5(b) shows the relationship between the electrical resistivity of SFL-stabilized soil and curing time. The electrical resistivity of the stabilized soil shows a slight decreasing trend with increasing number of curing days. This may be because the ions in the pore fluid diffuse more

with time. This result is not consistent with the research by Void et al. (2012) who did not observe any clear change in the electrical conductivity with curing time, which may be due to a different measuring method.

Fig. 6 presents the variation of pH for the stabilized soil with different SFL contents. The pH values decrease from 8.7 to 8.2, showing a very slight reducing trend with SFL content up to 15%. This means that utilizing SFL to stabilize soil would not lead to pH contamination risk as usually caused by traditional chemical stabilizer (Chew et al., 2004; Sharma et al., 2012) although the ion concentration in the pore fluid increases according to the electrical resistivity result.

Fig. 6. Variation of pH values for different sulfur-free lignin content.

3.2 Atterberg limits

The Atterberg limits are a basic measurement of key water contents for a fine-grained soil, which include shrinkage limit, plastic limit and liquid limit. The plastic limit (w_P) defines the water content at which a soil transitions from a semi-solid to a plastic state, while the liquid limit (w_L) defines the water content at which the soil behavior changes from plastic to liquid. The variation in liquid limit (w_L), plastic limit (w_P) and plastic index ($I_P = w_L - w_P$) of the stabilized soil variation with increasing SFL content after 28-days curing is plotted in Fig. 7. It can be seen from Fig. 7(a) that both w_L and w_P increase with SFL content, but w_L shows a more significant growth reaching about 18% more compared to the natural soil, which leads to I_P increasing by 24% when adding 15% SFL, resulting in the stabilized soils change from medium plastic ($7 < I_P < 17$) to highly plastic ($I_P > 17$). A similar result was reported by Zhang et al. (2018b) who used lignosulfonate from pulping industry to improve silt soils. The increase in Atterberg limits may be primarily because the fine soil particles are coated and bonded to coarse particles by the lignin fibers and the soil structure becomes more stable, resulting in more water being required to achieve the state transitions. Another reason may be the low solubility of SFL, which leads to strong water holding capacity in the stabilized soil.

With respect to influence of the curing time on I_P , as shown in Fig. 7(b), there is no clear trend as the SFL content increases.

Fig. 7 (a) Variations of Atterberg limits for different sulfur-free lignin contents after 28-days curing and (b) Variations of plasticity index for different sulfur-free lignin after different curing days.

3.3 Stress-strain behavior and strength characteristics

Fig.8 shows the stress-strain behavior of natural and the SFL stabilized soils after 60-day curing time, as obtained from Unconfined Compressive

306 Strength tests (UCS). The stress-strain behavior of all samples shows
 307 strain-hardening where the stress gradually increases with strain until an
 308 approximately constant value is reached at failure. This stress-strain
 309 behavior is entirely different from that of Ordinary Portland Cement (OPC)
 310 or lime stabilized soil (Nalbantoglu, 2006; Farouk and Shahien, 2013; Önal,
 311 2015) and the SFL stabilized soil shows more ductile properties. Based on
 312 the stress-strain curve, the UCS strength (σ_c) and deformation modulus (E_{50})
 313 can be determined.

Fig. 8. Stress -strain curves of Sulfur-free lignin stabilized soil curing 60 days.

314
 315 Fig.9 (a) shows the relationship between σ_c and SFL content. It can be
 316 observed that the maximum UCS is found at 10% SFL content, reaching
 317 1165 kPa after 60-days curing time. This value is approximately 600%
 318 compared to the natural soil (about 214 kPa). This means SFL is extremely

Fig. 9. Unconfined compressive strength for samples in terms of (a) different sulfur-free lignin content and (b) curing time.

stabilized soil has a distinct strength improvement when SFL content exceeds 7%.

The deformation modulus E_{50} as a function of σ_c is shown in Fig.10. The relationship between E_{50} and σ_c is generally proportional ($UCS=9.07E_{50}$, $R^2 = 0.959$). As the deformation modulus E_{50} of the SFL stabilized soil increases, so does σ_c . In other words, both strength and stiffness increase when adding SFL.

Fig. 10. Relationship between deformation modulus E_{50} and unconfined compressive strength.

3.4 X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) analysis

The powder diffraction patterns obtained from the XRD testing of the natural soil, 10% and 15% SFL-stabilized soil are presented in Fig.11.

Fig. 11. XRD diffraction spectra of the natural soil ,10% and 15% SFL stabilized soil after 28-days curing.

Comparing the diffraction peak pattern of the natural soil with those of SFL-stabilized soil, there is no obvious difference between them. This means there are no new compounds generated that affect the soil mineralogy. However, it also can be seen that some peak intensities (such as 26° , 35° and 36.6°) become “weaker” or even disappear. This phenomenon may be principally attributed to the amorphous properties of lignin which restrict the diffraction of mineral atomic planes. In Fig. 11 the main minerals are identified in the diffraction patterns of all samples according to the Chinese standard (China, 2010a). For example, the dominant peak intensity found at 26.6° is caused by the overlap diffraction of Quartz, Illite and Illite/Smectite mixed layer; The diffraction peaks of Quartz are identified at 20.84° , 36.52° and 39.56 to 40.28° In addition, the

crystalline structure of Potassium and Calcite are found at around 19.76° and 25.48° . Therefore, the SFL does not generate new minerals through chemical reaction to stabilize soil unlike lime or OPC.

The FTIR spectra for the natural and SFL stabilized soil in the middle-infrared region ($4000 - 475 \text{ cm}^{-1}$) are presented in Fig.12. In general, the spectra of the three samples are very similar, which indicates that SFL does not cause huge changes in the functional groups of the soil structural components. The broad band centered around 3416 cm^{-1} corresponds to the OH stretching vibration of inner-surface hydroxyl groups (Madejova and Komadel, 2001). The presence of IR absorption peaks at 2520 cm^{-1} is attributed to the C=O stretch vibration and this band indicates that calcite is present in the samples. The sharp peaks at around 1617 and 1460 cm^{-1} may be related to aromatic C=C stretching and aliphatic C-H, respectively (Madari et al., 2006). Furthermore, the absorption band at 1027 cm^{-1} is widely accepted to be due to the Si-OH of alumino-silicate lattice associated with clay minerals (illite/smectite) (Tinti et al., 2015). This is also consistent with the XRD results. At lower frequency, the peaks at around 778 and 693 cm^{-1} could be ascribed to the Si-O symmetrical bending vibrations which identifies the presence of Quartz, while the band at around 513 cm^{-1} results from Si-O-Al bending (Eisazadeh et al., 2012; Latifi et al., 2017).

However, there still are few noticeable changes in Fig. 12, for instance,

the absorption band intensities show an increasing trend with SFL content at around 2928 and 2851, 1512 as well as 1125 cm^{-1} . Combined with the already described FTIR spectra of SFL, these changes contribute to the function group from sulfur-free lignin including aliphatic methylene groups, deformation of aromatic ring and dialkyl ether linkages (Smidt et al., 2002; Grube et al., 2006; Lisperguer et al., 2009).

Fig. 12. FTIR spectra of the natural soil and 10%, 15% SFL stabilized soil after 28-day curing.

3.5

3.5 Micropore structure analysis

Fig. 13 (a) shows the variations of pore size distribution for the natural soil and 10% SFL-stabilized soil after 28-days curing, including cumulative pore volume and differential pore radius distribution. Compared to the natural soil, the total mercury intrusion of the stabilized soil reduces around 0.13 ml/g , from 0.162 to 0.148 ml/g . Moreover, the

amount of macropores (4 - 40 μm) obviously decreases corresponding to an increase of the mesopores (0.4 – 4 μm), as a result of SFL macropores into filling macropores to reduce the pore space. At the same time, according to the differential distribution curve, a typical bimodal and unimodal pore size distributions can be seen for the natural soil and the 10% SFL-stabilized soil respectively. The natural soil has a double porosity fabric that contains two pores population which distribute around 0.02 – 0.04 μm diameter and 5 -7 μm diameter, respectively. However, for the stabilized soil, the two population pores as observed in the natural soil specimens are no longer apparent and most of them are transformed to mesopores with diameter between 1 and 3 μm .

Fig. 13(b) illustrates the variations in pore size distribution for the 10% SFL-stabilized soil with different curing times. The curve of total mercury intrusion volume is similar for the 7-days and 28-days curing time (*i.e.* 0.05 ml/g difference). With respect to the differential pore distribution, both the 7-days and 28-days curing specimens show a unimodal distribution with noticeable differences in the mesopore scale. The families of mesopores shift slightly towards the left from 4 μm to 2 μm as the curing time increases from 7 to 28 days, indicating a reduction in the mean size of the mesopores as the curing time increases.

Fig. 13. (a) Mercury intrusion porosimetry results for the natural soil and 10% SFL-stabilized soil after 28-days curing; (b) Mercury intrusion porosimetry results for the 10% SFL-stabilized soil after 7-days and 28-days curing.

3.6 Scanning electron microscopic (SEM) analysis

The photomicrographs of the natural and SFL-stabilized soil at different curing times are shown in Fig. 15, which contains a series of SEM

images magnified by 800 and 1000 times. Fig. 15 (a) shows that the particles of the natural soil are distinctly separated with clear boundaries and the particles mainly connect with each other by point-point or point-surface contacts. Furthermore, it can be seen that there are more voids in the matrix of the natural soil, which results in a looser structure. Fig. 15 (b) indicates that the separated soil particles are coated and bonded with adhesive material like natural polymer when adding SFL. A few filamentous cellulose fibres impurity can also be recognized in the SFL-stabilized soil. From Fig. 15 (c) and (d), it can be observed more clearly under 1000 times magnification that when the SFL content increases to 15%, most intergranular voids are filled and the soil particles are more tightly packed through adhesive material formed by SFL, which improves the soil structure to be more stable.

These observations are consistent with the results of UCS and MIP discussed above. In addition, based on the results of XRD and XRF, it can be deduced that the SFL reinforces the soil by filling intergranular pores and forming cementing materials that physically bonds soil particles together. Tingle et al. (2007), Vinold et al. (2010) and Alazigha et al. (2018) thought that cementing could arise from electrostatic attraction between lignin and soil minerals.

Fig. 15 Scanning electron microscopy images of the natural soil and the SFL-stabilized soil with different magnification: (a) natural soil (800 $\times$); (b) 10% SFL stabilized soil after 7-day curing (800 $\times$); (c) 15% SFL stabilized soil after 7-day curing (1000 $\times$); (d) 15% SFL stabilized soil after 28-day curing (1000 $\times$).

4 Conclusions

This paper systematically investigates utilizing Sulfur-Free Lignin (SFL) which is a sustainable, nontoxic and eco-friendly by-product from bioethanol industry, to stabilize soil for geotechnical applications from the viewpoint of engineering properties, micro-characteristic, mineral

composition and function group. According to the present results, specific conclusions can be drawn as follows:

1. The electrical resistivity of SFL-stabilized soil shows a reducing trend with increasing SFL content. This is mainly because SFL powders are mixed with an amount of soluble salts in the pretreatment process for producing bioethanol, which increase solute ion concentration in the pore fluid. However, the pH of stabilized soil does not show significant changes, meaning SFL would not lead to pH contamination risk usually caused by traditional chemical stabilizer. In addition, different curing times do not show obvious effects on the electrical resistivity.
2. The stress-strain curve of SFL-stabilized soil shows strain-hardening behavior indicating better ductile properties. The unconfined compressive strength (σ_c) of stabilized soils improved significantly from 214 kPa for the natural soil to 1165 kPa for the 10% SFL-stabilized soil after 60-days curing. This improvement is approximately 6 times σ_c for the remoulded natural soil. Moreover, the stabilized soil strength increased mainly in the first 28-day curing. The E_{50} and σ_c of SFL-stabilized soil show a proportional relationship with a fitting equation of $\sigma_c = 9.07E_{50}$ ($R^2 = 0.959$).
3. The results of Atterberg limits test illustrate that the liquid limit (w_L) and plastic limit (w_P) of the stabilized soil increase with SFL, but

the w_L shows a more significant growth, which leads to I_P increasing by 24% when adding 15% SFL. As a consequence, the stabilized soils change from medium plastic ($7 < I_P < 17$) to highly plastic ($I_P > 17$). Just like the results of electrical resistivity, the curing time does not show any apparent influence on I_P .

4. The XRD patterns of the SFL-stabilized soil are similar with that of the natural soil over curing time, indicating that there is no new mineral generated after adding SFL. Furthermore, compared with the natural soil, some specific IR absorption peaks of SFL (2928, 2851, 1512 and 1125 cm^{-1}) were also overserved in the FTIR spectrum for SFL-stabilized soil. But all these characteristic bands (functional group) are inherent of the materials rather than formed by chemical reaction.

5. The pore size distribution of the stabilized soil has an obvious change in that the small pores ($< 0.04 \mu\text{m}$) and macropores ($> 5 \mu\text{m}$) are gradually diminishing, resulting in a lower cumulative pore volume, as a result the porosity fabric changes from bimodal to unimodal. Through the different magnified SEM images, it can be clearly observed that the SFL coats and bonds isolated soil particles and fills the intergranular pores after 28-days curing which leads to a more stable fabric structure. These observations also explain well the test results of Atterberg limits, UCS and MIP.

6. Based on the data obtained from XRD and FTIR tests, no apparent chemical change in mineralogy and function group are observed, but the formation of physical bonds between soil particles are visualized in SEM images. It may be concluded that the mechanism of SFL mixtures are more by physical rather than chemical means.

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