An Eco-Sustainable Stabilization of Clayey Road Subgrades by Lignin Treatment: An Overview and a Comparative Experimental Investigation

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Abstract: Subgrade conditions significantly affect functionality of the road pavement during its service life. Among the different stabilization techniques for upgrading poorly performing in-situ soil subgrades, an economically attractive example involves the use of waste materials, such as lignin. A deep bibliographic analysis of previous studies is carried out in the first section of this paper. The literature review suggests that use of lignin as a stabilizing agent of road subgrade soils is not completely consolidated. In addition, this study reports an investigation on the strength and performance characteristics of a lignin-treated clayey soil. Several experimental tests were carried out on both the untreated and lignin-treated soils in order to shed some light on different aspects with limited knowledge available, such as the behaviour of the stabilised soil in specific conditions (e.g., the presence of water). Finally, the test results are discussed and compared with those obtained when the same soil is treated with lime, which is more widely used. The most relevant finding is the poor ability of lignin to upgrade the bearing capacity of the soil in wet conditions compared to lime; on the contrary, the presence of lignin helped in controlling the swelling potential of this type of soil.

Keywords: soil stabilization; lignin; clay soil; road subgrades; road construction; lime stabilization; pavement engineering; waste reuse; sustainable development; recycled materials

1. Introduction

Road pavement functionality is strictly related to the properties and conditions of several intrinsic and extrinsic factors. Among all the variables affecting functionality of the pavement structure during its service life, the stability of the subgrade significantly affects its performance in the long term. The subgrade, as well as each layer of the pavement system, must satisfy specified structural quality standards in order to prevent permanent deformations, resist shear and fatigue, and safeguard the integrity of the overlying layers. Locally available materials often do not meet these requirements as they lack performance properties to answer both traffic and environmental demands [1,2]. Subgrade conditions dramatically impact the pavement life, the initial cost of the pavement, as well as its maintenance costs [3].

Stabilization is an effective solution to upgrade the poor native properties of in-situ soil subgrades. Specific engineering properties such as strength, permeability, volume stability, and freeze–thaw durability can be improved in order to obtain a material of required or desired specifications [4].

Although the main engineering advantage of stabilization is to improve the strength and durability of the soil that is unsuitable for use in the pavement structure, this practice can also be used to reduce dust generation, control volume changes, and improve workability [5].

The most widely applied methods for the stabilization of the road subgrades are typically grouped into three categories: mechanical stabilization, chemical admixture stabilization, and reinforcement with geosynthetics [6,7].

Over the years, several researchers have obtained noticeable results in the implementation of alternative practices and materials [8]. From the sustainability point of view, the aim was to optimize the use of "marginal materials", namely, materials that do not meet the quality requirements established by the standards currently in force [9,10]. Moreover, the additional purpose was to seek cost-effective alternatives that could contribute to the decrease of energy consumption and greenhouse gas emission [11,12].

Several suitable techniques for stabilizing the pavement subgrade currently involve the use of waste materials such as agricultural waste, wood waste, and construction waste materials or by-products obtained from industries [13,14]. In the sphere of road construction, an economically attractive example is the application of lignin-based by-products as stabilizing agents of rejected or marginal locally available soils.

Together with cellulose and hemicellulose, lignin is one of the main components of lignocellulosic materials; its basic function is to lend rigidity and strength to the structure of cell walls [15].

Commercially, lignin is a waste product, traditionally obtained from the paper and pulp industry. The global production of lignin is estimated to be about 100 million tonnes/year; almost all of this quantity (about 98%) is destined for low-value uses or energy sources such as the generation of fuels, heat, and electricity [16].

A deep bibliographic analysis of previous studies is carried out in the first section of this paper. The application of lignin as a stabilizing agent of poorly performing subgrade soils is not completely consolidated. Among all additives, lime is probably the most widely used concerning subgrade soil stabilisation [17].

Furthermore, the study reports an investigation on the strength and performance characteristics of a lignin-treated clayey soil. In particular, the clayey soil (A-6) used in this investigation was obtained as a laboratory mix of two soils with different properties: a fine sand S1—(A-3) and a pure clayey soil S2—(A-7-6), respectively. The main aim of the mixing of S1 and S2 was to obtain a resultant mixed soil (S12) which can be used as road subgrade but it has poor performance given the presence of the clay matrix (about 50%); therefore, the use of stabilizing agents is required to improve their performance. Several experimental investigations were carried out on both the untreated and lignin-treated soils, such as Atterberg limits, CBR (California bearing ratio), UCS (unconfined compressive strength), and ITS (indirect tensile strength) tests. In addition, test results were discussed and compared with those obtained when the same soil was treated with lime. The purpose of this analysis was to highlight the benefits and limits of lignin and its effectiveness as a non-traditional stabilizing agent of clayey soil subgrades. In particular, the study aimed to shed some light on several aspects with limited knowledge available, such as the engineering behaviour of the stabilised soil in specific conditions (e.g., the presence of water).

2. Literature Review

In contrast to rigid pavements, the sequence of thicknesses in flexible pavements aims at supporting and distributing the imposed loads through each sublayer; the purpose of this structural logic is to contribute to the attenuation of the stresses generated by traffic on the underlying soil [18]. Although stresses decrease with depth, the unbound soil thicknesses contribute to the overall structural capacity of flexible pavements by more than 50% [19].

Subgrade properties are of considerable importance for the design and rehabilitation of pavements. The procedure aimed at the determination of the pavement structure translates into one of the most significant implementations of soil mechanics knowledge in the field of road engineering. Several theoretical and empirical methods base the calculation of thickness of pavement layers on the strength of the soil foundation [20].

A direct relationship can be determined between the quality of a soil layer, its intrinsic bearing capacity, and the thickness of the layers; in fact, a higher ability of a layer to distribute the traffic load over a greater area is generally linked to the increased quality rate of that soil layer [21]. A reduction in the required thickness of the overlying pavement layers may be permitted as a consequence of the increased strength of the subgrade. Such improvement positively affects pavement life, too [3].

As a general example, the AASHTO Pavement Design Guide [22], an internationally consolidated design method, among several important items such as pavement performance, traffic, and features of the materials includes also consideration of the subgrade soil in defining the method of flexible pavement design.

The pavement system must be designed to adequately protect the subgrade from excessive stress and in every operating condition; characterizing soil is a key factor for design purposes [23,24].

The design of the pavement structure defined by the AASHTO guidelines [22] takes into account the properties of the subgrade soil by the average value of the resilient modulus (M_R). Special attention is required for the assessment of the specific conditions of the roadbed soil: concerning the soil types and conditions, some particular situations are pointed out, such as the presence of excessively expansive soils and frost-susceptible or highly organic soils.

The high water content, high compressibility, low strength, high swelling/shrinkage, and poor workability pose some restrictions to the potential of local soils to be used in road construction [25–27].

Petry and Little [28] laid emphasis on the problems of expansive clay subgrades; in this type of soil, noticeable changes in volume rely on the variation of the moisture content. Edil et al. [29] focused on soft subgrades with poor properties for highway construction, evaluating different methods as stabilizers, including five types of geosynthetics.

Zhu and Liu [30] carried out a series of laboratory tests to verify the potential of the stabilized silty soil to meet the construction standards as a highway subgrade.

Bheemasetti et al. [31] investigated the suitability of a controlled low-strength material (CLSM) as a pavement subgrade of high-traffic volume roads. In their experimental study, they used a local soil classified as high-plasticity clay.

At the stage of construction, issues related to underlying soil stability may result in time delays and additional costs [29,32]. In a recent study, Ardah et al. [33] examined the aspects related to locally weak subgrade soils and suggested specific stabilization treatments to support both the construction and pavement loading.

Replacement of the existing in-situ soil with higher-quality soil to achieve the required bearing capacity of the subgrade increases the cost and time of the operations [13].

In-situ soil use is generally a viable and effective alternative as it minimizes the environmental impacts and contributes to a substantial decrease in project costs [31,34].

A substantial difference must be highlighted between two mechanisms that occur in the overall process commonly known as "stabilization". The first phase includes the improvement of soil strength achieved in the short term; this mechanism is defined as "modification" and is mainly characterised by the reduction in soil plasticity. At this stage, an advantage is an improvement in workability. The stabilization mechanism implies long-term reactions and significant changes in the mechanical behaviour of the treated soil. By comparing the strength of the stabilized soil with the strength of the untreated soil, an increase in strength of 350 kPa can be linked to a process of stabilization [1,35].

Modification/stabilization of the existing in-situ materials can be achieved in many ways, such as chemical, mechanical, thermal, and electrical methods. Selection of the stabilizing method type is a function of several factors. Among the parameters governing the choice of the stabilizing process, the most important are the type of in-situ soil (e.g., gradation and plastic index), the environment (e.g., the climate), the characteristics of the areas requiring stabilization, availability, and costs of admixture [4,36].

The most widely used mechanical stabilization technique involves compacting the in-situ soil [35].

The compaction mechanism is based on the basic assumption that a long-lasting condition of stability of the subgrade depends on a higher level of soil compaction. A soil properly and thoroughly compacted is less permeable and less compressible, increases its density, and potentially improves its property to carry a higher load [4,37].

Chemical stabilization involves mixing the soil with chemicals and emulsions. Traditional chemical stabilizers are cement, lime, fly ash, and bitumen.

Non-traditional soil stabilization additives are typically grouped into the following categories: ionic, enzymes, lignosulfonates, salts, petroleum resins, polymers, and tree resins [38].

Chemical agents may result in a higher compaction level of the soil, contribute to dust control, water erosion control, and development of a stronger composite material [35,39]. As summarised by Das [39], the introduction of chemicals into subgrades improves their durability, strength, and compaction level.

The combination of both chemical and mechanical mechanisms is probably the most common practice of treating soils [4]. The subgrade stabilization process includes the following macro-activities: soil preparation, application of the stabilizing agent, mixing, compaction, and curing [5].

In the field of soil stabilization, the term "lignosulfonates" refers to one of the seven categories in which non-traditional stabilizers are typically grouped. This macro-category includes lignosulfonates, lignin, lignin sulphate, and lignin sulphides [35].

Besides the use as a stabilizing agent for road subgrades, previous studies focused on the advantages and disadvantages related to a different application of lignin-based products in the road industry. The use of lignin covers many applications to achieve the following main purposes:

- dust suppression;
- unpaved roads stabilization;
- erosion resistance improvement (e.g., for road embankments);
- asphalt substitution as an environmentally friendly alternative to asphalt binders.

The cementitious features of lignosulfonates allow the loose material to be bonded together; the reduction in particle loss translates into the inclusion of these materials in road surface dust suppression solutions [40].

Lignosulfonates are commonly applied by a sprayed-on method on the dirt road surface previously scarified to allow a quicker and more uniform penetration into the surface material [41]. Usually, the application at low rates concerns an unbound thickness of 25 mm of the top surface [6].

For lignosulfonate-treated roads, the dust could be reduced by more than 50%, according to some researchers [41]. Moreover, the use of lignosulfonates as dust suppressants provides some environmental benefits as they are typically non-toxic, biodegradable, and non-corrosive, as well as more efficient than other chemical alternatives [42].

Lignosulfonates can be used as soil stabilizers and dust suppressants in different soil conditions. In terms of cost benefits, their implementation is more effective for soils characterised by a plasticity index greater than 8 and a percentage of fines in the range of 8–30%; moreover, some restrictions are defined depending on factors such as traffic, climate, and weather conditions [41].

A long-term disadvantage of the use of lignosulfonates in the field of roadway surfacing is related to their poor water resistance; therefore, their use is not recommended in wet conditions and high precipitation areas [41]. Some studies investigated the decrease in sulphur content as a solution for the reduction in the soluble property of lignosulfonates [15,42].

A study by Bolander [43] aimed at finding a cost-effective solution for road stabilization and maintenance of unpaved roads in order to minimize dust generation, erosion phenomena, and surface wear. An experimental analysis was carried out to investigate the

performance of various additives including lignin sulfonate. The results showed that lignin sulfonate contributed to increasing the compacted dry density; however, in specific weather conditions (wet environments, rainwater, melting snow), the additive tended to leach out of the material. For this reason, the author suggested taking into account the climate together with traffic and road surface geometry in selecting and applying the additive.

Another research in this field [44] suggests that lignosulfonate and other wood products and by-products can be a suitable alternative to gravel as stabilizing materials of unpaved low-volume roads.

A lignin-based emulsion was used to improve the stability of a low-volume forest road in Alabama [45]. Field CBR values showed an increase in surface and subgrade strength characteristics.

A blend of emulsified bitumen and lignosulphonate was used for a series of road construction projects for a total length of 115 km. The results reported that the stabilizer method improved the load-bearing capacity of the roads and provided an increased rate of compaction [36,46]. Furthermore, Indraratna et al. [47] stated that lignosulfonates are an effective treatment in the mitigation/elimination of the possibility of soil erosion for silty sand.

Several studies investigated the potential of lignin as an asphalt substitute in order to develop an environmentally friendly alternative to asphalt binders [48].

Sundstrom et al. [49], in their research on lignin-modified asphalts, found that a higher lignin content increased the viscosity and decreased the ductility of the binders. Similar results were found by Wang and Derewecki [50] in their analysis of the rheological characteristics of two types of asphalt binder modified with different lignin contents. Furthermore, Wang and Derewecki found that the presence of lignin improves the performance of the asphalt binder at high temperatures in terms of rutting resistance.

2.1. Lignin Utilization for Road Subgrades Stabilisation

Among the variables that affect the stability of a lignin-based stabilized soil, the main contributing parameters are the following [51]:

- soil,
- lignin,
- mixing,
- curing and compaction.

As concerns lignin, the most significant contributory factors to be highlighted are related to the material properties and the additive content mixed with the soil.

The type of extraction process and the source of lignin are the main factors impacting the structure and properties of the material. The most common classification of lignin is based on the sulphur content: kraft lignin, lignosulfonates, and hydrolysed lignin are some types of sulphur-containing lignin [16].

Table 1 shows a review of field and laboratory studies concerning the application of lignin as a stabilizing agent for soil subgrade in road construction. The main properties of lignin and the amount mixed with the soil are reported for each study. The additive content (%) is calculated by dry weight of the soil. For some studies, the optimum percentage addition of lignin is specified. In most cases, lignin is a by-product of paper and biomass processing production. The studies were grouped according to the AASHTO soil classification [52]. When the group classification was not explicitly defined in the study, it was obtained based on the liquid limit and plasticity index values. The A-4, A-6, and A-7 groups include silty and clayey soils typically rated as "fair and poor" for highway subgrade purposes [52].

Table 1. A review of studies concerning the application of lignin as a stabilizing agent for soil subgrade in road construction.

AASHTO Soil Classification	Maximum Dry Unit Weight ($\gamma_{d, max}$) (kg/m^3)	Main Properties of the Stabilizing Agent	Additive Content (%)	References
A-2	2260	Lignosulfonate; powder	2.9, 5 (*), 8	[53]
	–	Lignin; by-product of a paper mill; powder	3, 6 (*), 9, 12, 15	[54]
A-4	1631–1839	5% lignin + 50% hemicellulose + 20% cellulose + 25% other components; by-product of ethanol production (corn)	12	[55]
	1720	80% lignin + 10% cellulose + impurities; by-product of the paper manufacturing industry; powder	2, 5, 8, 12 (*), 15	[56]
	1720	60–70% lignin + water + other components; by-product of commercial biomass conversion; powder	2, 5, 8, 12 (*), 15	[57]
	1720	Lignin; by-product from a paper mill; powder	8, 12 (*)	[58]
	1631	5% lignin + 25% water + 5–10% gases + 4% char + 35–41% aldehydes; by-product of commercial biomass conversion; liquid	12	[59]
	1631	5% lignin + 50% hemicellulose + 20% cellulose + other components; by-product of ethanol production (corn); powder	12	
	1631	40% lignin-derived phenolic oligomers + 20% water + 40% other components; liquid	12	
	1720	Lignin; by-product of the the paper manufacturing industry; powder	2, 5, 8, 12 (*), 15	[60]
	1720	Lignin; by-product of the paper manufacturing industry; powder	2, 5, 8, 12	[61]
	–	Lignosulfonate; co-product of the paper pulp industry; liquid	2.5	[62]
A-6	1691	25% lignin + 25% water; by-product of commercial biomass conversion (agricultural residues); liquid	12	[63]
	1691	5% lignin + 50% hemicellulose + 20% cellulose + other components; by-product of ethanol production (corn); powder	12	
	1693	25% lignin + 25% water + 5–10% gases + 4% char + 35–41% aldehydes; by-product of commercial biomass conversion (forest and agricultural residues); liquid	1, 3, 6, 12 (*), 15	[64]
	1858	Lignosulfonate; powder	3.37, 5 (*), 8	[65]
A-7	1100–1400	Lignin; by-product from a paper mill; liquid	1, 2, 3, 4, 5	[66]
	1420–1690	Lignosulfonate; powder	0.5, 1, 2, 4	[67]

(*) Optimum percentage addition of lignin.

Zhang et al. [58] carried out a field trial analysis to examine the performance of a highway subgrade low-plasticity silty soil (ML). The soil stabilized with two different lignin contents (8% and 12%) was submitted to a series of field tests to obtain information on its mechanical properties. In particular, the CBR results showed that higher CBR values can be linked to:

- higher lignin content,

- an increase in curing time.

Therefore, the highest CBR value was recorded at 15 days of curing for the 12% lignin stabilized silt (CBR = 124.0%). The same authors [60] underlined that CBR values depend on the degree of compaction, too. In particular, higher CBR values can be observed increasing the degree of compaction from 94% to 96%. The analysis of the CBR values as a function of the additive content showed that the highest value can be recorded for a 12% stabilized soil at 28 days of curing and 96% degree of compaction, whereas lower values are measured for an additive dosage of 15%.

Aschuri and Yamin [66] compared two different types of soil and observed that the highest values of CBR were measured for the soil with the smaller plasticity index; therefore, they concluded that lignin application is more effective for soils with lower PI.

For a low liquid limit silt (A-4/ML), Cai e al. [57] observed that an increase in lignin content produced an increase in both the liquid limit and plastic limit but a reduction in the plasticity index.

Uzer [55], in his study, investigated the performance of four different soils (A-6 and A-4 types) stabilized by a 12% bio-based energy co-product containing lignin. The results showed that the Atterberg limits were higher for all the treated soil types compared to the untreated soils. However, the change in lignin content may not always show a change in the Atterberg limits, given the dependency on soil gradation and the chemical properties of lignin [61,66]. Alazigha et al. [68] indicated that for expansive soils, the decrease in the plastic index is mainly attributed to aggregation between soil particles and the consequent decrease in clay size particles.

Figure 1 depicts a comparison between previous works (see Table 1). Liquid limit (LL) and plasticity index (PI) are reported for the untreated soil (US) and optimum lignin-treated soil (OLTS), respectively. In the second case, values refer to lignin-stabilised soil with the optimum additive quantity defined in each study. Data on optimum lignin content is reported in Table 1. It can be noted that in most cases there is not a significant variation in both Atterberg limits between untreated and lignin-treated soil.
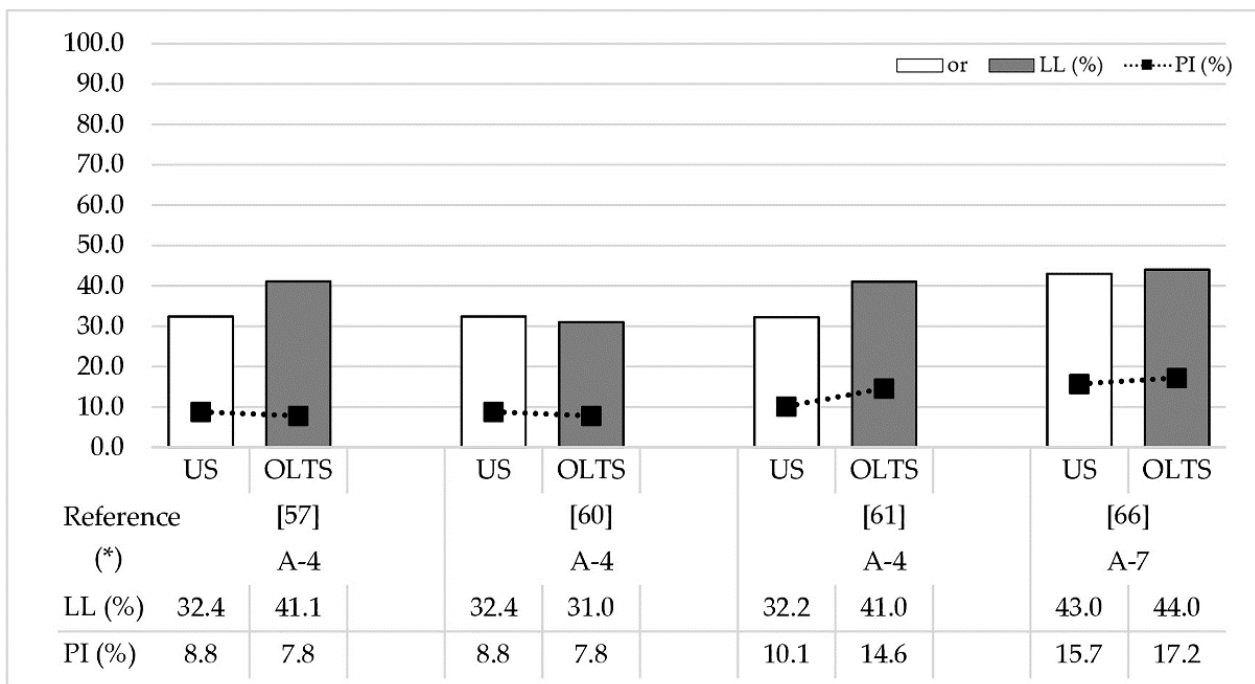

	US	OLTS		US	OLTS		US	OLTS		US	OLTS
Reference		[57]			[60]			[61]			[66]
(*)		A-4			A-4			A-4			A-7
LL (%)	32.4	41.1		32.4	31.0		32.2	41.0		43.0	44.0
PI (%)	8.8	7.8		8.8	7.8		10.1	14.6		15.7	17.2

Figure 1. Comparison between Atterberg Limits. (*) AASHTO soil classification.

Several research studies carried out a series of tests in order to investigate the stabilization mechanism and mechanical features at the particle level such as X-ray diffraction

(XRD), scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP), and Fourier transform infrared resonance spectroscopy (FTIR). An important result showed that the addition of lignin to silty soil caused an increase in the particle size after a period of curing [57]. The stronger microstructure in the lignin stabilized soil compared to that of the untreated soil is strictly related to the cementitious feature of lignin which allows the material to occupy the interparticle pores and facilitate the bonding of soil particles [60]. Cementation is the main effect characterizing the lignosulfonate stabilization mechanism [69].

For untreated silty soils, the high number of particles that are originally detached are bonded together; this phenomenon helps to develop a high-density structure; the structure becomes denser as a consequence of the increase in the lignin content [61].

The increase in the percentage of lignin significantly reduces the volume and the mean diameter of the pores thus the structure of the treated soil is more stable [56].

Similar results were reported by Chavali and Reshmarani [67] in their study on an expansive clayey soil treated by lignosulfonates. SEM images showed the formation of polymeric chains in the microstructure of the lignosulfonate soil.

In a recent study, Zhu et al. [54] investigated the microstructure of silt sand treated with lignin. The SEM analysis carried out after a freeze–thaw cycle showed that the soil structure remained compacted at the particle level and almost all the pores were filled with cementitious material which bonded together the soil particles. In addition, the same authors in a before–after analysis observed that the mixture of lignin and silt sand does not create new chemical elements or new mineral components.

Kim et al. [63] investigated the moisture susceptibility of a subgrade soil classified as AASHTO A-6(8). They concluded that coproducts containing sulphur-free lignin can be used as an effective soil stabilizing agent; in fact, it has been observed that these products have excellent properties in contrasting moisture degradation. Furthermore, Tingle and Santoni [65] reported high resistance to moisture for lignosulfonate treated clay soils. In addition, they observed that the optimum additive dosage of about 5% provided a noticeable improvement in strength thus making lignosulfonates suitable for treating poor-quality soils for use in low-volume road subgrades (both clayey and silty soils) [53].

Li et al. [62] carried out a field investigation to monitor the strength and durability of a gravel road subgrade (the soil is classified as A-4) stabilized by lignosulfonate. They noticed variability in the subgrade strength mainly due to the traffic load and the climate; moreover, freeze–thaw durability was compromised. In contrast, Yang et al. [59] observed an improvement in the freeze–thaw durability of a soil classified as A-4(2) treated with a biofuel co-product containing sulphur-free lignin.

3. Materials and Methods

3.1. Materials

The first step of the experimental plan was the definition and characterization of the soil. The soil used in this investigation is the mix of two different types of soil, S1 and S2, respectively.

Table 2 shows the particle size distribution according to the designation of gravel, sand, and silt clay stated in the AASHTO classification system (AASHTO M 145) [52] and the Atterberg limits (LL—liquid limit, PL—plastic limit, PI—plastic index) for each soil. Furthermore, the maximum dry density and the optimum moisture content obtained from the standard Proctor compaction test are reported for Soil 1.

Table 2. Properties of soils used for the investigation.

	S1	Soil 1	S2	Clayey Soil	Resultant Soil Mix S1 + S2 = S12
Particle size distribution (%)			
Gravel (2–75 mm)	48.6	-	28.2
Coarse sand (0.425–2 mm)	22.5	-	13.1
Fine sand (0.075–0.425 mm)	14.5	-	8.4
Silt and clay (<0.075 mm)	14.4	100	50.3
Atterberg limits (%)			
Liquid limit (LL)	-	52	38
Plasticity limit (PL)	-	22	20
Plasticity index (PI)	NP *	30	18
Proctor compaction test			
Optimum water content (w_{opt}) (%)	6.02	-	13.4
Maximum dry unit weight ($\gamma_{d,max}$) (kg/m^3)	2290	-	1910
AASHTO soil classification	A-3	A-7-6	A-6

NP * = non-plastic.

Soil 1 includes limited amounts of silty and clayey materials; it was classified as A-3 (fine sand); thus, it has good natural properties to be used as road subgrade [52]. This soil is non plastic (clay particles are not reactive in the presence of water); thus, it does not allow investigating the performance linked to the stabilisation mechanism in specific situations such as wet conditions.

The second soil (S2) can be classified as A-7, clayey soil; more specifically, it can be included in the subgroup A-7-6 as the plasticity index is greater than the difference LL-30. Its plasticity characteristics are reported in Table 2.

The study of the mineralogical properties and the elemental composition of the clayey soil S2 was carried out by EDS/TEM analysis (energy-dispersive X-ray spectroscopy and transmission electron microscopy, JEM-1400) [70]. The analysis showed the presence of elements such as Si, Al, K, Mg, and Ca (see Figure 2) highlighting that the clay mineral consists of mixed layers of illite and montmorillonite. The presence of oxygen is associated with the hydroxyl group contained in most phyllosilicates and with the presence of water in the sample [71].

Soils S1 and S2 (Figure 3) were mixed as a function of the fraction passing the No. 200 ASTM sieve. A mix design procedure was carried out to estimate the percentages of S1 and S2 to mix in order to obtain about 50 percent of the mass of the resultant mix smaller than 0.075 mm. This objective was achieved by mixing 58% of S1 and 42% of S2.

The resultant mix S12 can be classified as A-6 (clayey soil) given the values of Atterberg limits and the material passing through the 0.075 mm (No. 200) sieve (50.3%). For stabilization purposes, if the fraction passing the No. 200 sieve is greater than 25%, the soil can be classified as subgrade soil [1].

The main aim of the mixing of S1 and S2 was to obtain a resultant mixed soil S12 which has poor performance to be used as subgrade soil given the significant presence of the clay matrix (about 50%). In fact, clayey soils are traditionally considered to be problematic materials in the road construction field; therefore, the use of stabilizing agents is required to improve their performance as subgrade soils [65]. Moreover, as reported in [1], the level of reactivity of the stabilizing agent depends on the type and amount of clay minerals in the soil. In this study, the use of soil obtained as a laboratory mix allows fixing the amount of clay (50% of the mass of the resultant mix) as well as the control of its mineralogical properties and elemental composition.
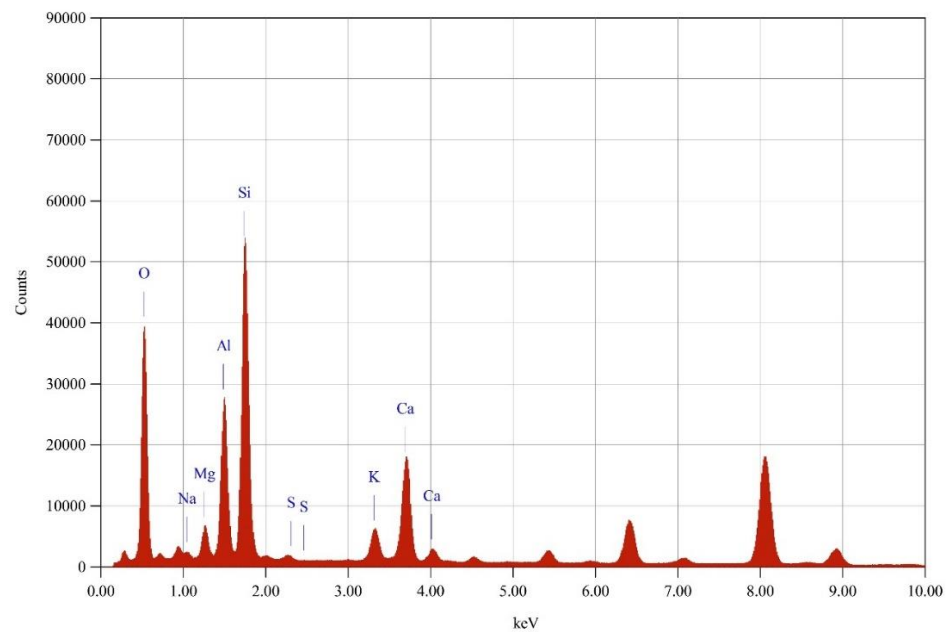
Figure 2. Energy-dispersive X-ray spectroscopy (EDS) spectrum obtained by TEM. The graph highlights the main chemical elements.

(**a**)

(**b**)

Figure 3. (**a**) Soil S1 selected for size and (**b**) clayey Soil S2 used in the experiment.

Lignin used in this study as a stabilizer is obtained by cooking red spruce with a calcium bisulphite solution; it is a dark brown liquid. The sulphur content is about 6%. Lignin was characterised as follows [72]. The lignin sample was dissolved in methanol (1:1000, *v:v*) and directly analysed by mass spectrometry. LDI-MS (laser desorption/ionization mass spectrometry) experiments were performed using a 5800 MALDI TOF–TOF Analyzer (AB SCIEX) equipped with a neodymium−yttrium−aluminium−garnet laser (laser wavelength, 349 nm) in the reflection-positive ion mode. At least 2500 laser shots were accumulated in the MS mode, with a laser pulse rate of 400 Hz. The spectra were elaborated using Data Explorer version 4.0.

LDI-MS experiments indicated that the presence of specific peaks, the way in which the peaks were grouped, and the global shape of the spectrum reflected the global structure of lignin oligomers [73]. LDI-MS analysis revealed a wide mass distribution of lignin oligomers [74,75]. However, the experimental conditions allowed the analysis of monocharged species with low fragmentation. The MS spectrum (Figure 4) showed resolved signals of protonated lignin oligomers $[M + H]^+$ over mass range of 300–1000 m/z.
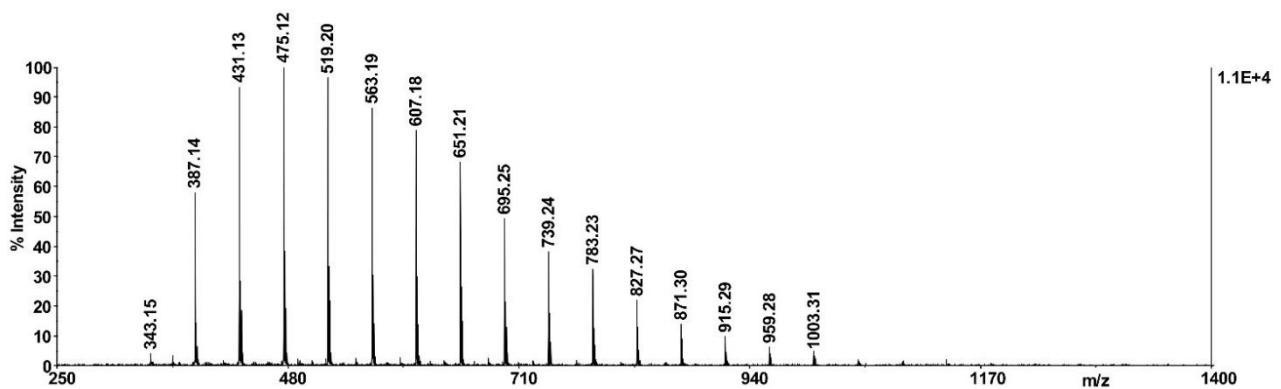
Figure 4. LDI-MS of protonated lignin oligomers.

In particular, the groups of signals at *m/z* 343, 387 and 431 represent dimeric products, probably of the phenylcoumaran type, the resinol type, and the dimeric species of sinapyl alcohol (S), respectively. All the other signals can be ascribed to the superior homologue species (trimer, tetramer, pentamer, and hexamer) derived from oligomerization of monolignol coniferyl alcohol (G).

3.2. Tests and Methods

In this study, three different lignin contents were selected based on the quantities suggested by the supplier; 0.25%, 0.40%, and 0.55% of lignin were added to the clayey soil (resultant mix S12 = S1 + S2) as a percentage of the optimum water content determined before (see Table 2). The type of lignin used in the experiment required dilution before mixing as it was in a concentrated condition. Part of the required optimum water content was used to ensure uniform mixing. The optimum content of lignin was selected based on the additive quantity that allowed recording both the maximum dry unit weight and the highest California bearing ratio (CBR) value.

For the preparation of specimens, the soil was mixed with lignin at specific percentages and optimum water content. The mixture was allowed to cure for 12 h to ensure better interaction between water, lignin, and soil materials. The samples for testing were prepared using the standard Proctor compaction test. Each test was carried out on three compacted specimens in accordance with the European Standard (EN 13286-47:2012) [76]. As reported above, these test findings allowed defining the optimum lignin content. The lignin content which optimises CBR values tested after 0 days was 0.40% by optimum moisture content.

The sequence of planned tests was carried out on the soil mixture treated with this additive rate.

The mechanical performance of the 0.40% lignin-treated soil was assessed by the California bearing ratio (CBR). Two different conditioning procedures were adopted before the CBR test was performed. The air drying curing time was set at 7 days for both procedures, but the second test implied a wet test procedure: the specimens were completely immersed in a water bath for additional 4 days.

Water sensitivity ratio (WSR$_{ar}$) is defined as follows:

$$\text{WSR}_{ar} \, [\%] = \frac{(\text{CBR}_{ad+s})_{ar}}{(\text{CBR}_{ad})_{ar}} \tag{1}$$

where CBR refers to different curing periods: CBR$_{ad+s}$ is the CBR value obtained after a curing period involving both dry and wet conditioning (7 days of air drying and 4 additional days of soaking in this study); CBR$_{ad}$ refers to the test results obtained after only dry conditioning (7 days). The subscript "ar" after "WSR" indicates the specific additive rate of the tested soil specimens. This index allows a mechanical evaluation of the potential loss of bearing of the soil due to moisture conditions.

The full saturation test allowed recording useful information about the swelling behaviour of the lignin-treated soil as established by the reference standard EN 13286-47:2012 [76].

The swelling strain ε (%) was estimated as follows [77]:

$$\varepsilon = \frac{100\Delta h}{h_1} \tag{2}$$

where Δh is the change in specimen height due to absorption of water (mm) and h_1 is the initial specimen height (mm).

Unconfined compressive strength (UCS) (EN 13286-41:2006) [78] and indirect tensile strength tests (ITS) (EN 13286-42:2006) [79] were carried out to measure the effects of lignin on the compressive and tensile strength of the clayey soil. The specimen dimensions were 10.00 cm in diameter and 11.66 cm in height and they were compacted by the standard Proctor compaction method for both UCS and ITS tests. Three specimens were prepared for each test and the average was obtained. The curing time was fixed at 7 days for both tests.

The indirect tensile strength is calculated as follows [79]:

$$ITS = \frac{2P}{\pi DH} \tag{3}$$

where P is the peak load (daN), D and H are the diameter (cm) and the height (cm) of the specimen, respectively.

Atterberg limits (EN ISO 17892-12:2018) [80] were examined for the treated soil and the results were compared with the values obtained for the untreated soil.

All the tests were carried out on untreated and lignin-treated specimens. In addition, the tests were carried out on the same soil improved by the addition of lime for comparison purposes. The clayey soil (resultant mix) was treated with lime by the addition of the optimum content of 2.5%. More specifically, the soil was treated with three different additive contents: 2%, 2.5%, and 3%. The optimum lime content was selected based on the value maximizing the CBR test results.

To obtain a quantitative evaluation of the comparison between the treated soil and the untreated one in terms of bearing capacity, the following indicator was defined:

$$CII_{T-U} = 1 - \frac{CBR_U}{CBR_T} \tag{4}$$

where CII_{T-U} is the CBR increase index (%) and CBR_U is the CBR of the untreated soil (U). CBR_T refers to the treated soil (T): lignin (Lg) or lime (Lm).

For the comparison procedure between the treatments, ΔCII was also estimated as follows:

$$\Delta CII_{Ti-Tj} = CII_{Ti-U} - CII_{Tj-U} \tag{5}$$

where Ti and Tj are the treatments compared in the analysis (lignin or lime).

In this study,

$$\Delta CII_{Lg-Lm} = CII_{Lm-U} - CII_{Lg-U} \tag{6}$$

where $CII_{Lg-U} = 1 - (CBR_U/CBR_{Lg})$ and $CII_{Lm-U} = 1 - (CBR_U/CBR_{Lm})$.

A comparison procedure was carried out for data obtained by swelling, ITS, and UCS tests.

A comprehensive summary of the experiment design, methodology, and organization of all the activities on the materials used in this study is reported in Figure 5.
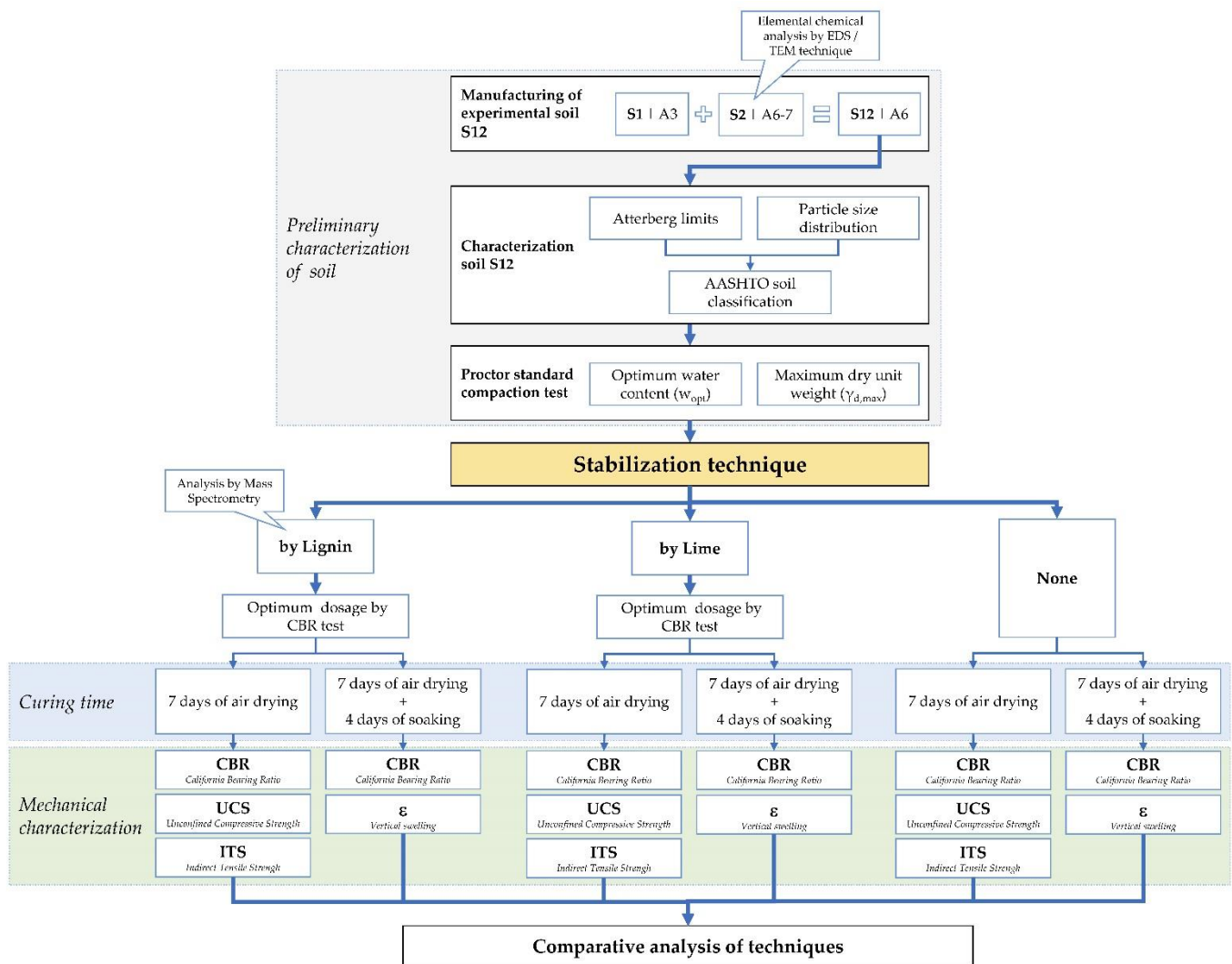
**Figure 5.** Summary of the experiment design and main activities.

4. Results and Discussion

4.1. Effects of Lignin on Soil Mix S12

4.1.1. California Bearing Ratio (CBR) Test with Dry and Wet Conditioning

As discussed in the previous section, CBR was first assessed without storage conditions between manufacturing and testing of the specimens. The test results reported in Figure 6 allow assessing how different lignin contents affect soil strength. Each bar in the graph indicates the CBR value (%) obtained by the mean of the values of two specimens prepared with the same additive dosage. The horizontal axis indicates the corresponding percentage of lignin content (0%, 0.25%, 0.40%, and 0.55%). Comparing the treated soil with the untreated soil, it is evident that the lignin addition increased the CBR value by more than 70%. Moreover, the findings highlight that the highest value of CBR tested immediately could be recorded for the 0.40% lignin-treated soil. An increase in the amount of the additive (0.55%) translated into a decrease in mechanical properties. For this reason, the additive rate of 0.40% was selected as the optimum in this study.
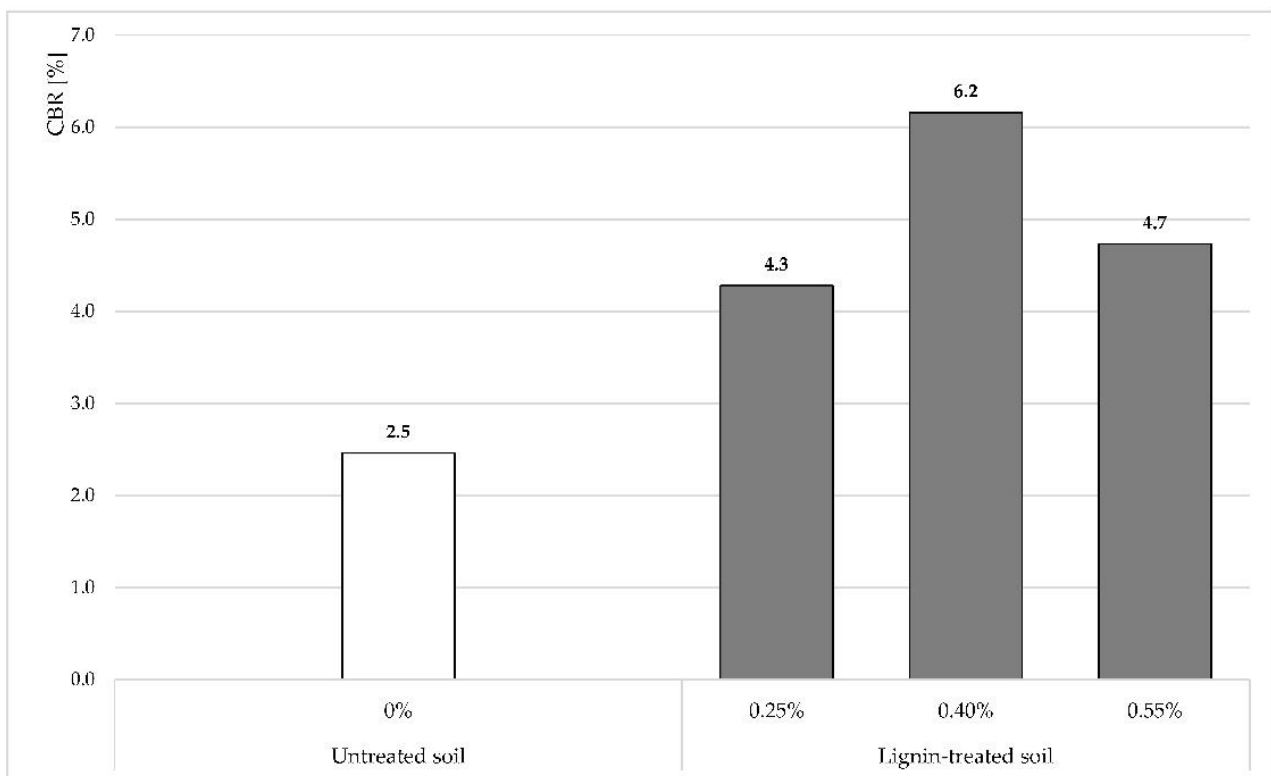
Figure 6. CBR values recorded for the untreated soil and the lignin-treated soil, respectively.

In addition, CBR was tested after air-drying the material for 7 days to investigate the effects of the curing time on mechanical performance. CBR data were collected for specimens tested after dry and wet conditioning. Table 3 reports CBR values for dry and wet tests, respectively. The wet test refers to values obtained for specimens submerged in water for 4 days at the end of the seventh air drying day and before testing.

Table 3. Effect of curing time on CBR values for the untreated soil and the lignin-treated soil, respectively.

| Lignin Content (%) | CBR (%) | | Water Sensitivity Ratio (%) |
| | Curing Time | | |
	7 Days of Air Drying	7 Days of Air Drying + 4 Days of Soaking	
0% (untreated soil)	18.2	2.2	12.1
0.40%	25.1	3.4	13.5

It can be seen from Table 3 that the highest CBR value was recorded for the lignin-treated soil after 7 days of curing; this implies that the addition of 0.40% lignin contributed to upgrading the mechanical performance of the soil. Compared to the untreated soil, the presence of a stabilizing agent allowed obtaining an increase of about 38% in the average value of CBR after 7 days of curing. Moreover, the increase in CBR values is noticeable comparing the results obtained after curing for 7 days with the above-discussed CBR values. These results confirm the literature findings [58,60].

When the curing time includes a soaking period of additional 4 days, the CBR values of the treated soil and untreated soil are approximately comparable. This last result suggests that 4 days after soaking, the stabilised soil lost the effect of lignin on its mechanical properties; thus, the CBR values drastically decreased.

The values of the water sensitivity ratio suggest that, for the specific case study, the untreated soil and the lignin-treated soil had similar moisture susceptibility (water sensitivity ratio was about 12–13% for both conditions).

This result confirms the inadequate contribution in terms of bearing provided by lignin in wet conditions.

4.1.2. Swelling Behaviour of the Stabilised Soil

One of the most negative aspects of A-6 soils is their tendency to have high-volume change between wet and dry states [52].

The immersion in water as part of the curing of the samples for the CBR test allows the determination of vertical swelling of the specimens. The increase in thickness of the soil specimen caused by wetting was monitored at 24 h intervals for 4 days.

Figure 7 shows swelling data relating to the untreated soil and the 0.40% lignin-treated soil, respectively. The graph shows that the presence of lignin helps in controlling the swelling potential of this type of soil.
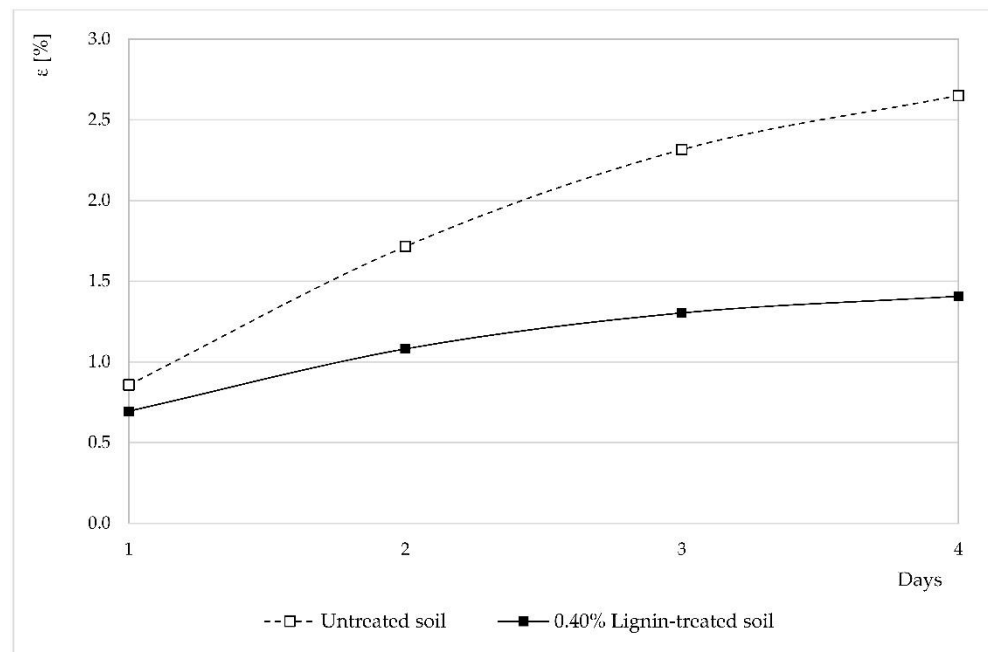

Figure 7. Time–swelling curve for the untreated soil and the 0.40% lignin-treated soil.

4.1.3. Unconfined Compressive Strength and Indirect Tensile Strength Tests

Unconfined compressive strength and indirect tensile strength tests allowed obtaining information on the variation of the compressive and tensile strength as a function of lignin content.

As can be seen in Table 4, the indirect tensile strength obtained for the lignin-treated soil was slightly higher than the ITS obtained for the untreated clay. The studies analysed in Section 2.1 do not include an ITS test.

Table 4. Effect of lignin content on ITS and UCS values.

	Tests	
Lignin Content (%)	**Curing Time: 7 Days of Air Drying**	
	ITS (daN/cm^2)	**UCS (N/mm^2)**
0% (untreated soil)	1.1	1.4
0.40%	1.2	1.6

Table 4 shows that lignin provided a slight increase in the UCS of the treated soil when compared with the natural soil.

The increase in strength for lignin-treated soil compared to natural soil was reported in several previous studies [56,57,65]. The strength of lignin-stabilised soil may be higher than that of untreated soil in wet conditions [63]. Overall, the mechanical properties of lignin-treated soil increase with lignin content and the curing period [56,57]. In some cases, the excessive lignin content causes a decrease in the strength of lignin-treated soil [56,57]. Strength loss is attributable to the formation of weak spots due to the excessive content of the additive [56].

However, Tingle et al. [65] concluded that lignin-treated clay soils allow recording the highest increase in both the dry and wet UCS compared to other soils stabilised with non-traditional additives.

4.1.4. Effects on Atterberg Limits

Atterberg limits were examined for the 0.40% lignin-treated soil. As can be seen from Table 5, the presence of additional lignin does not significantly affect Atterberg limits. In particular, the lignin-treated soil allowed recording slightly higher values of both the liquid limit and of the plasticity index. This result is in good agreement with some previous studies [61,66].

Table 5. Atterberg limits recorded for the untreated soil and the 0.40% lignin-treated soil.

Lignin Content (%)	Atterberg Limits		
	Liquid Limit (LL)	Plastic Limit (PL)	Plasticity Index (PI)
0% (untreated soil)	38	20	18
0.40%	41	21	20

As discussed in the literature review, the effects of lignin on Atterberg limits cannot be generalised. Results may depend on the specific characteristics of the materials (both soil and lignin). However, the slight increasing trend in both LL and PI, confirmed by several past studies (see Figure 1), may be related to residual moisture within the intra-aggregate pores of the stabilized soil [61].

4.2. Comparison between the Lignin-Treated Soil and the Lime-Treated Soil

In this section, the results of tests carried out on the lignin-treated soil are compared with those obtained when the same soil was treated with lime. Table 6 shows the data relating to CBR values obtained for each different type of stabilisation treatment. Comparing the lignin-treated soil with the natural soil, as noted in Section 4.1, the lignin treatment allowed recording an improvement in bearing characteristics in every type of curing conditions. However, when lignin effects on bearing are compared with those recorded for the lime treatment, the highest values of CBR were observed for the 2.5% lime-treated soil; the measures were significant for CBR tested after 7 days of air drying (CBR = 39.1%). Water immersion caused a reduction in the bearing capacity for both treated soils, but the lime treatment allowed recording the lowest decrease. This result is confirmed by the WSR_{ar} values: $WSR_{2.5\%} = 57.5\%$ for the 2.5% lime-treated soil whereas $WSR_{0.4\%} = 13.5\%$ for the 0.4% lignin-treated soil; this result translated in the significantly lower water sensitivity of the lime-stabilised soil compared to the lignin-stabilised soil.

Table 6. Comparison between the results of the CBR test carried out on the untreated soil, the lignin-treated soil, and the soil treated with lime.

Stabilizing Agent Content (%) and Type	CBR (%)	CII (%)	
0 days of curing			
0% (untreated soil)	2.5	-	
0.4% lignin-treated soil	6.2	$CII_{Lg-U} = +60$	$\Delta CII = +23\%$
2.5% lime-treated soil	14.2	$CII_{Lm-U} = +82$	
7 days of air drying + 4 days of soaking			
0% (untreated soil)	2.2	-	
0.4% lignin-treated soil	3.4	$CII_{Lg-U} = +35$	$\Delta CII = +55\%$
2.5% lime-treated soil	22.5	$CII_{Lm-U} = +90$	

Considerations on the CII and ΔCII values must be shown for each set of results in relative terms, taking into account the particular conditions determined by different curing procedures. Table 6 reports the CBR, CII, and ΔCII values related to two confined cases. In terms of moisture content, the first case (0 days of curing) refers to the optimum moisture content (w_{opt}); CII values obtained for this case suggest that both lignin and lime contributed to the increase in bearing capacity of the untreated soil in a measure of about 60% and 80%, respectively. The difference in the CBR increase between the lime effect and the lignin effect was about 20%.

Comparing the first case with the second one (7 days of air drying + 4 days of soaking), the second case was considered to be the worst condition. Water absorption rate depends on the type of clay. For the case study soil, illite, the predominant clay mineral, is characterised by a water absorption rate that ranges between 70% and 150% [81]. As a consequence, full saturation may represent an issue in clayey soil road subgrades.

Analysis of the CII values recorded for the cured and soaked specimens suggested that lime addition continued to strongly impact the load-bearing capacity of the soil: CII increased from 82% to 90%. CII obtained for the cured and soaked lignin-treated soil specimens was about two times lower than CII obtained for the first case: these findings underline that when lignin-treated clayey soil is exposed to wet conditions, its effect on increasing the bearing capacity dramatically decreases. In the second case, the value of ΔCII, which was more than 50%, reflected the poor ability of lignin to upgrade the bearing capacity of the soil in wet conditions compared to lime.

Furthermore, the values of the swelling strain ε show that lignin seems to be the most adequate stabilizing agent for the control of volume changes of the investigated soil. The ε value recorded for the soil treated with lime on the fourth day was 1.6% against the value of 1.4% observed for the lignin-treated specimens.

Finally, for a comprehensive analysis, Figure 8 reports the comparison between each different soil treatment for ITS and UCS tests. It is easy to note that the values were comparable for both tests and for each type of treatment.
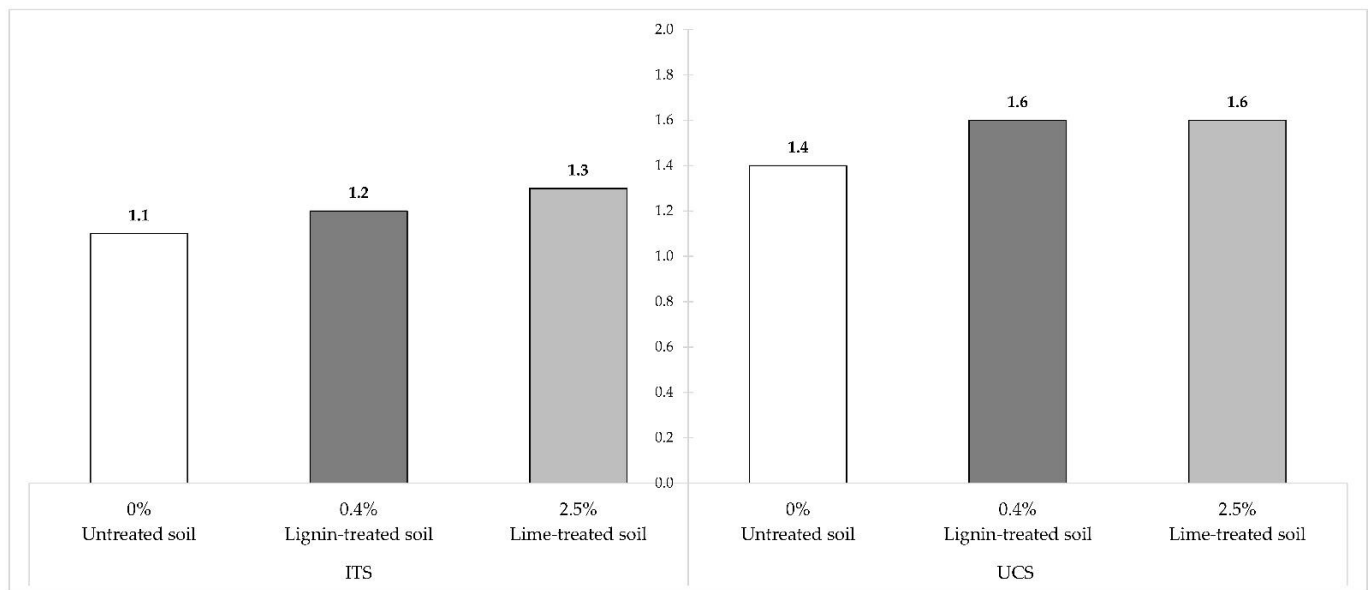
Figure 8. Comparison between the results of the ITS (daN/cm^2) and UCS (N/mm^2) tests carried out on the untreated soil, the lignin-treated soil, and the soil treated with lime.

5. Conclusions

In this study, a series of laboratory tests were carried out on untreated and lignin-treated specimens in order to obtain information on the potential improvement of the performance of the stabilised clayey soil. It is necessary to underline that the soil used in this investigation was obtained as a laboratory mix of two soils with different properties: a fine sand (A-3) and a clayey soil (A-7-6), respectively. The resultant mix was classified as A-6 (clayey soil).

For the physical and mechanical characterization of both the natural and lignin-treated soils, a series of tests such as Atterberg limits, swelling behaviour, CBR, UCS, and ITS tests were carried out according to the standards. The test results were discussed and compared with previous studies. Furthermore, tests were carried out on the same clayey soil improved by the addition of lime, for comparison purposes.

The comprehensive analysis of the various tests findings allowed us to draw the following main conclusions:

- CBR tests carried out on specimens with three different types of curing showed that the addition of lignin improved the bearing capacity of the case study soil. In particular, after 7 days of air drying, the lignin-treated soil allowed recording an increase in the bearing of about 38% compared to the untreated soil. When the curing time included a soaking period of additional 4 days, the CBR values of the treated soil and untreated soil were approximately comparable. This latest result suggested that moisture conditions had an impact on the mechanical properties of the stabilised soil which lost the effect of lignin; thus, CBR values drastically decreased.

- The comparison between lignin-treated soil and lime-treated soil highlighted that the highest values of CBR were observed for the 2.5% lime-treated soil; water immersion caused a reduction in bearing capacity for both treated soils but the lime treatment allowed recording the lowest decrease. This result translated into the significantly lower water sensitivity of the lime-stabilised soil compared to the lignin-stabilised soil.

- The analysis of CII values recorded for the cured and soaked specimens suggested that lime addition continued to strongly impact the bearing capacity of the soil. The value of ΔCII, which was more than 50%, reflected the poor ability of lignin to upgrade the bearing capacity of the soil in wet conditions compared to lime. For this reason, the use of lignin must be carefully considered when wet soil conditions are present

(e.g., in the presence of an aquifer, water infiltration into the pavement structure, wet environments).

- The immersion in water as part of the curing of the samples for the CBR test allowed investigating the swelling behaviour of the stabilised soil. The test showed that the presence of lignin helped in controlling the swelling potential of this type of soil. In particular, the values of the swelling strain were lower than the values recorded for the lime-treated soil.

For a comprehensive analysis, Atterberg limits, ITS, and UCS test results are reported, too.

The approach proposed in this study contributes to highlighting the limits and effectiveness of the use of lignin as a non-traditional stabilizing agent of clayey soil road subgrades. These findings underline that the selection of a stabilizing agent and treatment cannot be generalised, given the dependency on site-specific conditions. For this reason, in future research, attention will be focused on:

- the application of lignin with different types of extraction processes and sources;
- the application of clayey soils with different properties;
- other types of tests for the characterization of the stabilised soil.

These approaches could benefit both researchers and practitioners in the identification of more reliable and wider ways for the incorporation of lignin into soil stabilization in the field of road construction.

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