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ORIGINAL PAPER

A novel clean biopolymer-based additive to improve mechanical and microstructural properties of clayey soil

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Abstract

Conventional soil additives can cause serious environmental problems due to the greenhouse gas emission, consumption of huge amounts energy in their production process and threatening plant cover and underground water quality. To eliminate these destroying effects, environmentally friendly additives have gained great consideration. Although polysaccharides are considered as powerful biocompatible soil additives in recent studies, the effect of their crosslinked hydrogel with elevated rheological and adhesive properties has been very rarely investigated. In this paper, calcium chloride was used as ionic crosslinker to enhance recently proposed Persian gum biopolymer. A group of macro and micro scale tests including unconfined compressive strength, direct shear test, freeze thaw durability, scanning electron microscopy, stereo zoom microscopy, Brunauer, Emmett and Teller and x-ray diffraction were conducted. The tests were also performed on soil treated with xanthan gum as a common hydrocolloid of soil stabilization. Combination of 2% Persian gum and 2 molar ionic crosslinker was determined as optimum additive content. The superior compressive strength improvement of crosslinked hydrogel (about 201.1%) than xanthan gum (83.5%) shows its powerful strengthening performance. In terms of durability, crosslinked hydrogel has reduced mass loss of pure Persian gum treated soil from 19.1 to 10.25% that is comparable with xanthan gum. Consumption of lower amounts of Persian gum at presence of crosslinker can make stabilization projects economical efficient. Microscale tests also confirmed the powerful impact of optimum modified hydrogel on soil interstructure by filling the pores, agglomeration of soil particles and formation of new cementitious compounds.

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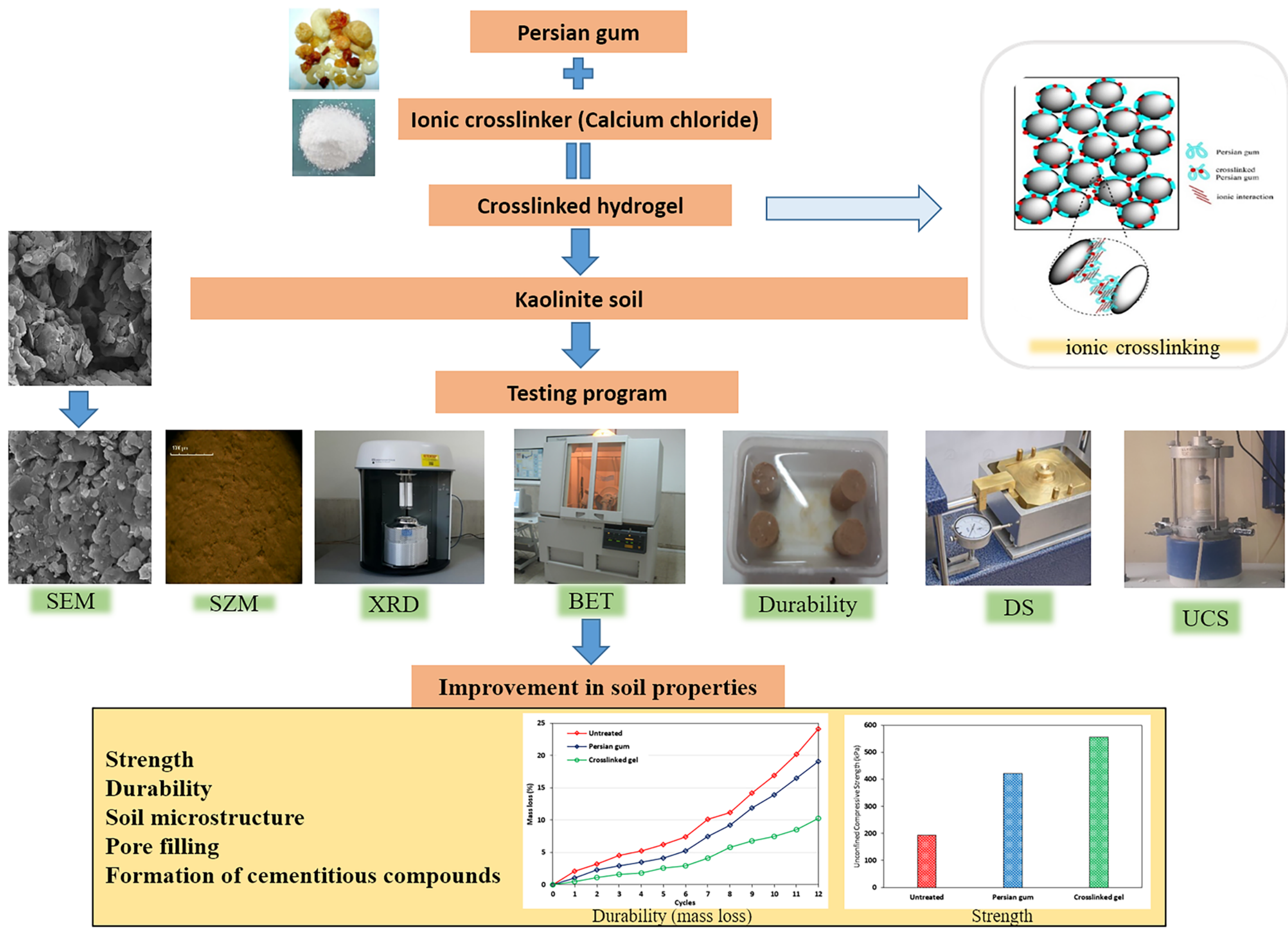
Graphical abstract



Keywords Persian gum · Xanthan gum · Soil stabilization · Ionic crosslinker · Calcium chloride solution

Introduction

Utilization of traditional additives such as bituminous materials, cement, gypsum, lime and fly ash in soil stabilization is accompanied with some environmental concerns. Energy and natural resources consumption, increase of soil pH after stabilization, destruction of plant cover and deterioration of groundwater quality are examples of these detrimental effects (Arab et al. 2019). In addition, high greenhouse gas emission in the production procedure of these additives is a major problem. Total CO_2 emissions caused by production process of conventional cement and lime additives can rise to about 66 and 110 kg for one cubic meter of treated soil, respectively (Ahmadi et al. 2021). To mitigate detrimental effects of conventional additives, non-traditional ones like Resins (Ghasemzadeh et al. 2020), polymers (Mehrpajouh et al. 2021) and nanomaterials (Changizi et al. 2021) were utilized. The alternation of these additives with cement caused lower energy consumption and CO_2 emission. In this way, by-products of various industries such as calcium carbide residue, rice husk ash and ground furnace slag as non-traditional ones attracted lots of attention in recent researches. Lignosulfonate as an organic polymer is also the by-product of paper industries that has found great consideration in stabilization of different kinds of soil (Ghasemzadeh and Tabaiyan 2017). With the increasing attention to the environmental issues and in order to eliminate any stress on the environment, some biocompatible and biodegradable additives obtained from living organisms were introduced to the soil investigations. For instance, some biopolymers such as protein based casein and sodium caseinate provided from milk were used to satisfy stabilization goals (Fatehi et al. 2018) considering different variables such as biopolymer and fat milk content, curing temperature and curing time. Chitosan obtained from Shrimp shell is the other kind of biopolymer that improves soil strength through the increase of interactions between soil particles (Hataf et al. 2018). Natural gums, also called Hydrocolloids, with considerable thickening, film forming, viscosity enhancement and adhesive properties constitute the main biopolymers used for soil improvement. Xanthan with microbial source and guar gum with plant origin are mostly investigated natural gums in soil stabilization (Dehghan et al. 2019). Their positive effect on compaction properties, compressive strength, shear parameters, compressibility and swelling, hydraulic conductivity, erosion, durability and collapse potential of the various expansive and cohesive problematic soils using a very tiny percentage of these gums (about 1.5% of dry soil weight) is proven (Cabalar et al. 2018). The influencing factors in the treatment process including curing time, mixing method and drying condition were also investigated in the conducted studies. Sodium alginate as the other kind of biopolymers, categorized as sea weed gums, was investigated for enhancement of weak subgrades including silty and clayey soil against heavy traffic loads (Arab et al. 2019). The thermal treatment of some natural gums such as Agar and Gellan gums gives them so powerful potential in soil strength and durability improvement (Chang et al. 2015). The effectiveness of these thermos-gelation biopolymers were examined on both clay and sandy soil. The enhanced mechanical and physical properties of the soil caused by hydrocolloids on one hand and the increasing global need for renewable and green materials on the other hand have encouraged investigators to seek new sources of hydrocolloids as soil stabilizers.

Persian gum is a novel source of hydrocolloid biopolymers categorized as plant exudates gums and obtained from branches of wild almond (Amygdalus scoparia) plants in arid and semi-arid regions of Zagros forest in Fars province, Iran (Dabestani and Yeganehzad 2019). Since Persian gum is a plant gum that is obtained from wild Almond trees, its mass production requires cultivation of so many trees that is advantageous for the environment. This polysaccharide has found wide applications in various industries such as food, pharmacy and textile (Abbasi and Rahimi 2015; Chahibakhsh et al. 2019) due to its comparable effects with commonly used hydrocolloids (Dabestani et al. 2018; Raoufi et al. 2019). In a recent paper, Ghasemzadeh and Modiri (2020) introduced Persian gum as a novel kind of hydrocolloid soil stabilizers. The study proved comparable soil strengthening capabilities of this gum to well-known xanthan and guar gums at their optimum contents. However, improving properties of Persian gum through modification methods can be a major step forward to make it a more enhanced soil stabilizer.

Modification of polysaccharides is changing their molecular structure by strengthening bonds and interactions between polymer chains to obtain networks with more enhanced viscosity, solubility and rheological properties (Akhtar and Ding 2017). Typically, the modification methods are categorized into chemical and physical crosslinking (Patil and Jadge 2008). In physical crosslinking, physical interactions between polymer chains are formed. However, in chemical crosslinking, covalent bonds between different polymer chains are induced. Among modification methods, physical ones with less chemical contamination risk (due to the absence of crosslinking agent) have been preferred by many researchers (Ullah and Chen 2020). Ionic crosslinking as a way of physical modification methods involves entanglement of ionic moiety with polymer chains through non-covalent interactions. There are conducted studies on ionic crosslinking of natural gums hydrogels that demonstrate the positive effect of ionic crosslinking on physiochemical and rheological properties of them (Petri 2015). However, application of crosslinked hydrogels of natural gums in soil environment has been mostly restricted to water maintenance and purification purposes (Masoumi and Ghaemy 2014). To the best of the authors' knowledge, the only study on ionic crosslinking of polysaccharides for mechanical improvement of soil is carried out on sodium alginate which showed the effectiveness of Ca-alginate as an ionic crosslinked polysaccharide (Wen et al. 2019). Persian gum with numerous functional groups (Dabestani and Yeganehzad 2019), can easily interact and crosslink with other materials (Samari-Khalaj and Abbasi 2017). On the other hand, calcium chloride is a practical and inexpensive ionic crosslinker that has the ability to connect polymer chains via Ca^{2+} ionic moiety (Khalesi et al. 2012). Therefore, it can be an appropriate candidate for crosslinking Persian gum hydrogels.

This paper is an attempt to enhance recently proposed Persian gum for soil stabilization. The powerful performance of Persian gum in soil strength and microstructure improvement was proved in the previous study (Ghasemzadeh and Modiri 2020). However, the higher content of Persian gum at its optimum state in comparison to other common gums was a weak point. In this paper, crosslinking was applied as an effective method to reduce Persian gum concentration and improve viscosity and rheological properties of hydrogels. For this purpose, calcium chloride solution was used as ionic crosslinker to make Persian gum a more effective soil stabilizer. The introduced hydrogel was applied to stabilize low-plasticity clay, as a kind of problematic soil. To understand how elevated properties of crosslinked Persian gum affect stabilization goals, compressive and shear strengths and freeze thaw durability were used as soil improvement indicators. Also, some micro-scale tests including scanning electron microscopy (SEM), stereo zoom microscopy (SZM), Brunauer, Emmett, and Teller (N2-BET) test and x-ray diffraction (XRD) analysis were conducted to provide insight into underlying mechanism of soil strengthening before and after stabilization at micro level. The tests were also conducted on soil stabilized with well-known xanthan gum to evaluate its effectiveness in comparison to investigated polysaccharides of soil stabilization.

Materials

Soil

The used soil is white kaolinite, sourced from Sahand region of Azerbaijan province, Iran. It was provided from Khak-Chini Company in 35 kg bags in white powder form. The used cohesive fine-grained soil has liquid and plastic limit of 45 and 25.7, respectively and is classified as low-plasticity clay (CL) according to the Unified Soil Classification. Compaction characteristics of the used kaolinite include maximum dry density of 1.925gr/cm^3 and optimum moisture content of 25% (ASTM D1557 2012). The kaolinite soil with the presented properties (Table 1) was chosen considering its importance as a kind of commonly used problematic soil.

Xanthan gum

Xanthan gum is a high molecular weight hydrocolloid that can be produced from fermentation of carbohydrates by a bacteria called X. campestris (Palaniraj and Jayaraman 2011). The chemical structure of this microbial sourced gum is composed of hexose units including D-glucose, D-mannose, and also D-glucuronic and pyruvic acids. The main chains of β-D-glucose is repeatedly connected to the side chains of trisaccharides (α-D-mannose, β-D-glucuronic acid and β-D-mannose that contains an acetyl group) to form a helical structure. β-D-glucose is (1 → 4) linked to α-D-mannose in the backbone. Also β-D-mannose is (1 → 4) linked to β-D-glucuronic acid and β-D-glucuronic acid is (1 → 2) linked to the α-D-mannose in the side chain. pyruvate and acetyl groups are attached to the terminal β-D-mannose at C6 (Petri 2015) (Fig. 1). The pyruvic units and glucuronic acids are responsible for negative charge of Xanthan. This anionic nature gives some desired characteristics to the gum such as high hydration and water solubility. Xanthan gum, even at low concentrations, can considerably increase the viscosity of liquids and its viscous gel is stable under different pH values and temperatures (Sworn 2009).

Table 1 Soil properties

Soil properties	Standard	Values
Unified soil classification system	ASTM D2487	CL
Fine percentage, P#200 (%)	ASTM D854	82
Plasticity index (%)	ASTM D4318	19.3
Liquid limit (%)	ASTM D4318	45
Plastic limit (%)	ASTM D4318	25.7
Maximum dry density (gr/cm3)	ASTM D1557	1.925
Optimum moisture content (%)	ASTM D1557	25
Specific gravity (S_G)		2.66
Chemical compounds (%)	ASTM D8064	
SiO_2		63
Al_2O_3		24
Fe_2O_3		0.55
TiO_2		0.04
CaO		1.2
Na_2O		0.33

Persian gum

Persian gum, also known as Zedo, Shirazi, Farsi and Angum gum, is a complex polysaccharide classified as plant exudate gums. The backbone of Persian gum includes galactose (1 → 3 linked β-D-Glap) and rhamnose and side chains contain (1 → 6) linked β-D-Glap and (1 → 3) linked α-L-Araf residues (Abbasi and Rahimi 2015; Molaei and Jahanbin 2018) (Fig. 1). Persian gum has 30% soluble part which solves in cold water and 70% insoluble part that solves partially in hot water. According to the GC/MS chromatographic method, the main monosaccharides of PG are arabinose and galactose units with 2:1 ratio (Dabestani et al. 2018). FTIR analysis of this novel gum (Dabestani et al. 2018) revealed presence of –CH_2, –CH_3, O–H, C–H, C–O, C–C, C=O, –COO–, C–OH, alcohol and amide groups. These functional groups, along with considerable molecular weight and branched structural shape of PG, cause high tendency of it to interact with other materials. There are some conducted studies about the feasibility of interactions between Persian gum and other hydrocolloids (Khodaei et al. 2020). The used Persian gum was purchased from a mucilage and gum provider company named Reihan Gum Parsian in white powder form. According to the manufacturer, it contains 91.3% carbohydrate, 2.16% total ash, 1.2% protein and 0.2% fat. The physiochemical properties of used biopolymers including xanthan and Persian gum are summarized in Table 2.

Calcium chloride solution

To provide Calcium chloride Persian gum (Ca-PG) hydrogel, Persian gum should be dissolved in calcium chloride ($CaCl_2$) solution. $CaCl_2$ solutions were prepared by mixing the required amount of $CaCl_2$ powder with distilled water at room temperature. $CaCl_2$ powder was purchased from a local supplier with properties mentioned in Table 3.

Sample preparation and testing program

First, the gravel and large particles were removed from the soil by passing it through a 2 mm sieve. The maximum dry density (MDD) and optimum moisture content (OMC) were

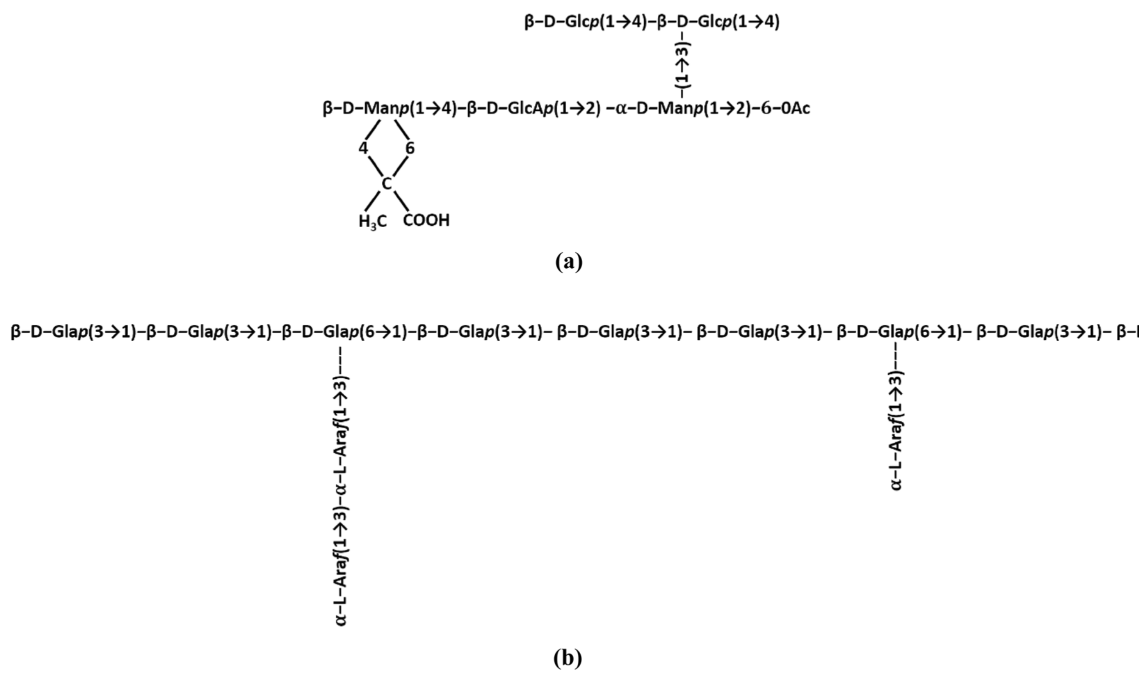


Fig. 1 Chemical structure of used biopolymers, **a** xanthan gum (Sworn 2009) **b** Persian gum (Abbasi and Rahimi 2015)

Table 2 Physiochemical properties of used biopolymers, xanthan and Persian gum

property	Persian gum	Xanthan gum
Appearance	White powder	White powder
Category	Plant exudate	Microbial
Water solubility	30%	100%
Molecular weight (Da)	4.6×10^6	5.0×10^6
Viscosity for 1% solution (mPa.s)	48	1100
Charge	Negative	Negative
Ash (%)	2.19	3.5
Protein (%)	1.2	5
Carbohydrate (%)	91.3	82
Moisture (%)	5.14	9.4

Table 3 Physiochemical properties of calcium chloride

Property	Values
Appearance	A white odorless granule
Soluble/insoluble in water	100% soluble
Density (gr/cm^3)	2.15
Molar mass (gr/mol)	110.98
pH	8
Calcium (%)	38
Chloride (%)	59.4
NaCl (%)	1.6
$MgCl_2$ (%)	0.09
Other impurities (%)	0.91

calculated from the results of standard proctor test (ASTM D1557 2012). Mixing is an important part of sample preparation that affects the results. There are two mixing methods including wet and dry. In the wet method, the biopolymer powder is dissolved in water and then the obtained solution is added to the soil. However, in dry method, the biopolymer powder is mixed with the soil and then the required water is added. Since the findings of the previous studies revealed the superior performance of wet mixing method for strength results of biopolymer treated soil (Ayeldeen et al. 2017; Arab et al. 2019; Ghasemzadeh and Modiri 2020), this method was applied to prepare the samples. Biopolymer contents of 1, 1.5, 2, 2.5 and 3% by weight of dry soil were dissolved in the required water or $CaCl_2$ solutions of 0.5, 1, 1.5, 2 and 2.5 molarities to reach optimum moisture content. Then the obtained solutions were mixed with dry soil. Curing time and curing condition, measurement errors and accuracy of balance are also the influencing factors that can affect the testing results of this paper.

For UCS test, the mixtures were compacted in cylindrical molds of 38 diameter and 76 mm height using a hydraulic jack based on ASTM D2166 (2016) to achieve maximum dry density and optimum moisture content. The obtained samples were extruded using a hydraulic specimen extruder, trimmed and cured in a controlled room of about 22 °C for 7 days. The samples were put in an automated compression machine equipped with a data acquisition system and UCS test was conducted according to the ASTM D2166 (ASTM D2166 2016). To conduct DS test, the mixtures were placed in steel cubic-shaped molds of 60 × 60 × 20 mm and compacted using static pressure approach. The extruded samples were then air dried in a controlled room of about 22 °C for 7, 14 and 28 days and placed in the shear box. The strain rate of 0.8 mm/min was applied until the samples failed or experienced maximum horizontal displacement of 10 mm (Latifi et al. 2015). Three normal stresses of 100, 200 and 300 kPa were applied and Cohesion and friction angle of each specimen were estimated considering obtained failure envelopes. For durability test, the samples were constructed in accordance with ASTM D558 test method (ASTM 2011) for soil material passing a No. 4 sieve. The soil, additive and water mixture were compacted in a mold with an internal diameter of 101.6 mm and volume of 944 cm^3 to reach maximum dry density. After removing the molds, obtained specimens were trimmed with knife and cured at the room temperature of 22 °C for 28 days. Then they were exposed to freeze thaw cycles according to the ASTM D560 (Standard 2016). Each freeze thaw cycle includes placing the samples in a freezing cabinet (having a temperature of − 23 °C) for 24 h and then storing them into a moist room with 23 °C temperature and relative humidity of 100% for 23 h. The procedure was continued for 12 cycles. The mass and moisture loss at the end of each cycle were recorded.

Small pieces of crushed specimens at the end of UCS test were used to conduct further microscale analysis using SEM, SZM, BET and XRD. Since being dried is the requirement for microscale tests, they were dried in the oven before conducting tests. A very tiny piece of specimen was coated with gold cover before being set into the SEM device. SZM images were taken from cross section of dried UCS specimens. The samples were placed at Motic SZM-140–143-FBGG Stereo Zoom Microscope with considerable zoom property that enables it to prepare high quality images.

The tiny pieces of specimens were powdered to conduct BET and XRD tests. To degas the specimens as the prerequisite of BET test, the samples were exposed to the nitrogen gas injection in a glass cell with high vacuum temperature of 130 °C for 3 h. Considering gas adsorption model and adopting BET equation, surface area of particles can be estimated. Pore volume is also recognized considering the volume of the adsorbed nitrogen gas at 77°K and 1 atm. The XRD tests were conducted using X'pert pro MPD diffractometer made by Malvern Panalytical. Radiation of Cu-Kα at 2θ range of 0.945° to 99.953° with λ = 1.54A° and loading step size and time of 0.026° and 2 s was employed. XRD data analysis was conducted through Eva valuation software of Bruker company using its comprehensive database of known compounds.

The designated labeling to identify specimens has five parts: The abbreviation of K is used as the first part to represent kaolinite soil. The second part includes UNT for pure soil and hydrocolloid name for treated samples: PG for Persian gum and XG for xanthan gum. The third part demonstrates PG content. The fourth part, C, shows the $CaCl_2$ crosslinking agent and the fifth part is related to its molar concentration. For example, KPG2C2 is related to a kaolinite specimen stabilized with Ca-PG hydrogel, in which 2% PG by weight of dry soil is dissolved in 2 molar $CaCl_2$ solution.

Results and discussion

Unconfined compressive strength test

The UCS values of untreated and treated soil specimens with xanthan gum, Persian gum and crosslinked Persian gum are shown in Fig. 2. The biopolymer contents of 1, 1.5, 2, 2.5 and 3% by weight of dry soil were used to treat the soil. For crosslinked specimens, the aforementioned contents of PG were dissolved in $CaCl_2$ solutions of 0.5, 1, 1.5 and 2 molarities. The goal is to determine the proper combination of Ca^{2+} ions and PG to improve viscosity and rheological properties of formed hydrogels. As it can be seen, for each specified $CaCl_2$ molarity, an increasing and decreasing trend is

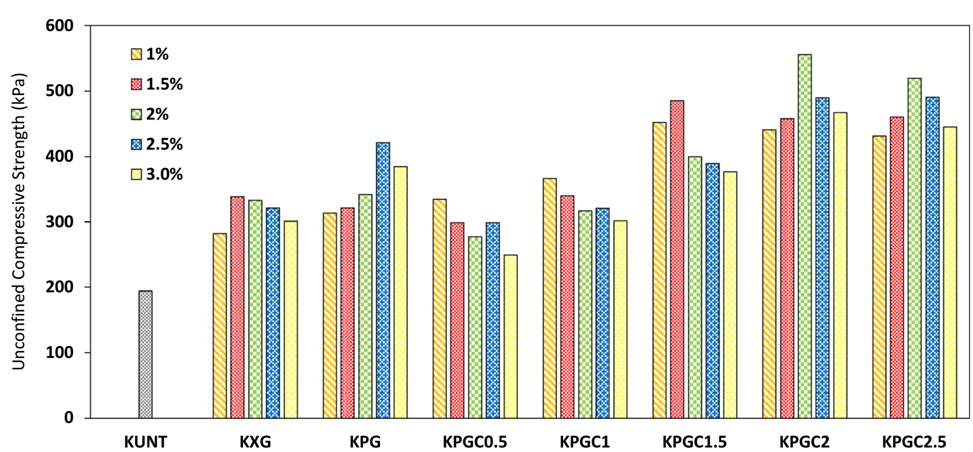


Fig. 2 UCS test results for different biopolymer content (1, 1.5, 2, 2.5 and 3 by weight of dry soil) and $CaCl_2$ solution concentration of **a** 0.0 **b** 0.5 **c** 1.0 **d** 1.5 **e** 2.0 **f** 2.5 molar

observable in UCS results as PG content grows. The amount of additive that causes maximum compressive strength is known as its optimum content. The obtained optimum additive contents are 1.5% for xanthan gum, 2.5% for pure PG treated specimen and 1, 1, 1.5, 2 and 2 for Ca-PG treated ones in the presence of 0.5, 1, 1.5, 2 and 2.5 molarities of $CaCl_2$, respectively. As the results show, the UCS values of xanthan and pure PG treated soil at their optimum content have been increased to 83.5 and 128.3% in comparison to the untreated soil, while for KPG1C0.5, KPG1C1, KPG1.5C1.5, KPG2C2 and KPG2C2.5 specimens, the increase values are 81.3, 98.6, 163, 201.1 and 181.6%, respectively. As can be seen, the most elevated strength result is obtained for the specimen with 2% PG and 2 molar $CaCl_2$. The reason is related to proper content of PG and calcium chloride that causes effective ionic crosslinking between polymer chains. The branched structure and functional groups of PG such as C–H, $–CH_2$, $–CH_3$, C–C, –COO–, C=O, C–O, O–H, C–C and –COOH (Dabestani et al. 2018), also enable it to interact with other materials easily. In addition to polymer chains, Ca^{2+} free stabilizer ions interact with Si and Al of the soil and form improved textural characteristics. However, the low content of Ca^{2+} has no crosslinking role for higher PG contents and causes less contracted interchain reactions which conversely weaken the viscosity of formed hydrogels and mechanical strength results. For instance, the presence of 0.5 molar calcium chloride causes the strength results of 1.5, 2, 2.5 and 3% PG to be reduced and 1 molar $CaCl_2$ has decreasing effect on the strength of 2, 2.5 and 3% PG. To explain this, one should consider that viscosity of hydrogel as the substantial factor in strength results is highly affected by the content of adding salt due to the exudates gums' polyelectrolyte property. According to the previous studies, when the ratio between crosslinker molarity and gum concentration is very low (less that about 0.5), the least contraction of macromolecules results in reduction of viscosity and binding property of gels (Koocheki et al. 2009), and less UCS results are expected. However, these low concentration of $CaCl_2$ (0.5 molar) effectively promotes UCS of low PG content (1%) treated sample. Therefore, the relation between ionic solution and PG content is the influential factor that determines whether crosslinking has been occurred or not. Crosslinking has also positive effects on the strain results. The stress–strain curves of optimum crosslinked specimens show more ductility in comparison to xanthan and pure Persian gum at their optimum state.

Reduction in gum concentration using crosslinker agent, is one of the considerable advantages of the crosslinked hydrogels. As it can be seen in Fig. 2, the strength improvement caused by 1.5% xanthan gum can be achieved using 1% of PG at presence of 1.5 and 1 molar calcium chloride. Also, the required pure PG content to achieve maximum UCS can be reduced from 2.5% to less than 1.5% (the optimum content of xanthan gum) in the presence of 1 molar $CaCl_2$ solution. Since the preparation process of the gums to make them applicable in industry is sometimes complicated and expensive, the restricted consumption of them in the soil projects can make them economically efficient. Therefore, substitution of some content of PG with $CaCl_2$ solution as an inexpensive and simple crosslinker that is also environmentally friendly with no dependency to cement industries is recommended.

Direct shear test

Shear performance of treated specimens with optimum additive contents, obtained from UCS test results, including KXG1.5, KPG2.5, KPG1C0.5, KPG1C1, KPG1.5C1.5, KPG2C2 and KPG2C2.5 were evaluated through direct shear test. The samples were air-dried at 22 °C room temperature for curing times of 7, 14 and 28 days. The obtained shear parameters have been shown in Fig. 3. As it can be seen, cohesion of 28 days treated KXG1.5, KPG2.5, KPG1C0.5, KPG1C1, KPG1.5C1.5, KPG2C2 and KPG2C2.5 specimens has been improved to about 142.9, 133.3, 110.8, 120.8, 153.3, 170.8 and 125.8% in comparison to the untreated soil, respectively. The reason is related to the formed agglomerated particles that counteract lots of transitional and rotational stresses in grain scale and improve shear resistance in macro scale. Similar to UCS test results, combination of 2% PG and of 2 molar $CaCl_2$ solution is the optimum ratio of these two additives that causes the most enhanced shear performance by creation of some extra bonds between polymer chains. These new bonds have made interstructure of PG hydrogels powerful networks that resist against shear forces. Xanthan and pure PG treated specimens have shown close strength results after 7, 14 and 28 days curing. However, the cohesion parameter of Ca-PG samples has indicated considerable growth over time. This is related to the formation of more bonds in the interstructure of crosslinked hydrogels that are being completed over time. Remarkable strength growth of Ca-PG specimens over time can make them desirable for long term strength achievement objectives. The reduced cohesion parameter for 7 days Ca-PG treated samples in comparison to pure optimum PG treated ones is related to the moisture maintenance property of Ca-PG hydrogels that postpones evaporation of trapped water existed in the hydrogel networks. According to the gel features (Chen et al. 2019), this trapped water prevents the real adhesive properties of gel to be appeared.

As discussed in the previous section, the interesting point about using Ca-PG treated samples is the possibility of PG content reduction to achieve the same strength results. For instance, cohesion parameter of 14 days treated KPG2.5 and KPG1.5C1.5 specimens are approximately the same. The variations of friction angle as the

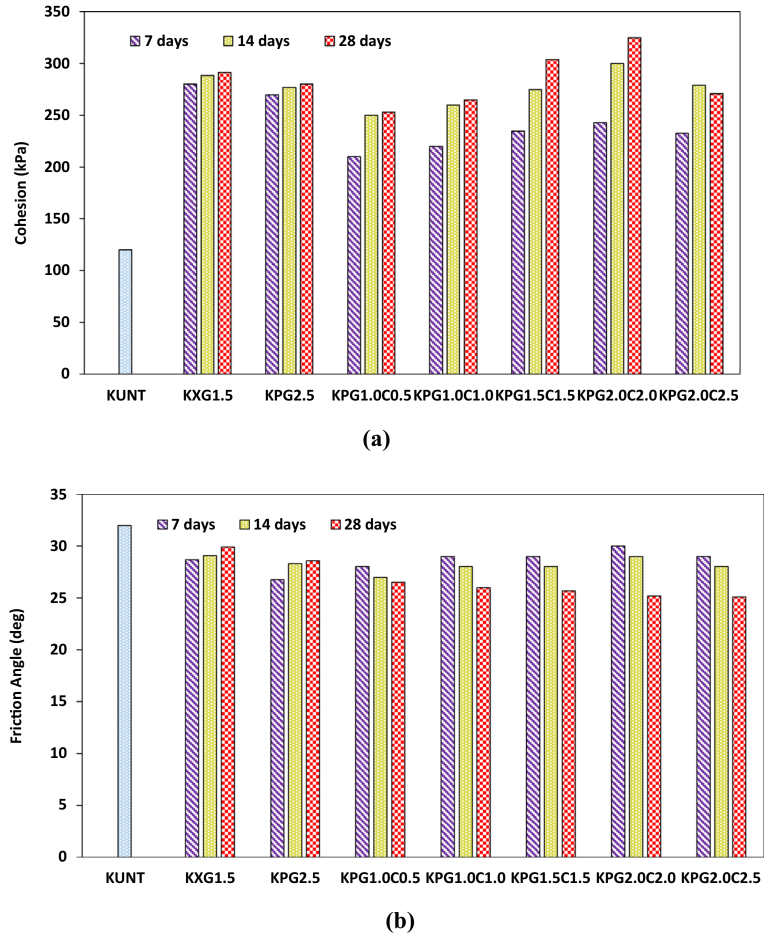


Fig. 3 DS test results for untreated and treated specimens using xanthan, pure and calcium chloride Persian gum treated specimens at their optimum additive contents: **a** Cohesion **b** Friction angle

other shear parameter have been shown in Fig. 3b. In fact, formed hydrogels play as lubricant in soil biopolymer medium and cause soil particles to move more smoothly on each other. This has led to reduction of internal friction angle due to the stabilizing agent. Similar to the cohesion results, the friction angle value of pure PG treated specimens has no significant variation for curing times of 7, 14 and 28. However, for Ca-PG treated samples, the value of this parameter has shown observable decreasing trend as time passes. The samples with 2% PG and 2 molar calcium chloride showed a friction angle of 25.2° and cohesion of 325 kPa at the end of 28 days curing that resulted in shear resistance of 372.05 kPa under normal stress of 100 kPa, while the pure clay with friction angle of 32° and cohesion parameter of 120 kPa represented 182.5 kPa shear strength under the same normal stress. The growth of shear stress (about 104%) for KPG2C2 specimens is more considerable than the strength increase induced by optimum xanthan gum treated specimens (91%). Therefore, optimum content of crosslinked PG indicates more elevated shear performance in comparison to well-known xanthan gum.

Durability tests

Weathering condition was studied by applying freeze thaw cycles on untreated and treated soil specimens to evaluate their durability. According to the previous studies (Ahmadi et al. 2020), the optimum content of additives leads to the increase in freeze thaw durability performance of fine grained soils. Therefore, KUNT, KXG1.5, KPG2.5 and KPG2C2 specimens were chosen to be tested. The 28 days cured specimens were retained in a moist room for 7 days and then subjected to the freeze thaw cycles according to ASTM D560 (Standard 2016). The mass and moisture loss of the specimens at the end of each cycle were presented in Fig. 4. As the results show, the amount of mass loss after 12 freeze thaw cycles is 24.1% for untreated specimen, while for the xanthan, pure and crosslinked PG specimens, the mass loss values are 8.28, 19.1 and 10.25%, respectively. The enhancement of soil durability in term of mass loss reduction for treated soils can be explained by the sticky nature of formed hydrogels between soil particles, that binds them together and forms agglomerated particles with enhanced

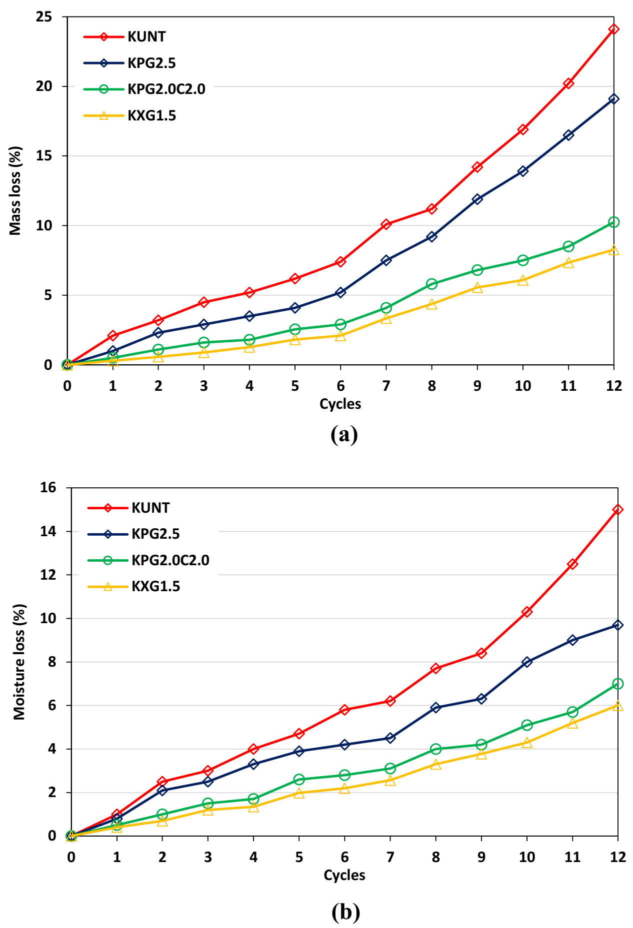


Fig. 4 Durability test results for untreated and treated specimens using optimum xanthan gum (KXG1.5), pure Persian gum (KPG2.5) and crosslinked Persian gum (KPG2C2): **a** mass loss **b** moisture loss

freeze thaw resistance. Xanthan gum with powerful gel formation property shows the most powerful performance in durability improvement of the soil. The higher mass loss of PG treated soil in comparison to xanthan treated one can be illustrated by the fact that some extent of PG does not contribute in gel formation process due to its insoluble part (Abbasi 2017). Therefore, the gel network of PG is not as strong as xanthan gum in terms of durability improvement. However, the mass loss values of crosslinked specimens are more remarkable than the pure PG treated sample. This shows the success of crosslinking in durability improvement of PG treated samples to reach the mass loss values of xanthan gum treated specimens. The reason is related to the certain amounts of Ca^{2+} ions that improve viscosity and rheological properties of PG hydrogels by crosslinking polymer chains together.

The same trend has been observed for moisture loss of the specimens during freeze thaw cycles (Fig. 4b). The amount of moisture loss after 12 freeze thaw cycles for KUNT, KXG1.5, KPG2.5 and KPG2C2 specimens is 15, 6 and 9.7 and 7%. As represented, the similar durability results of xanthan gum treated soil are accessible using crosslinked hydrogels of PG. The amount of moisture loss for Ca-PG specimens is much lower than pure PG treated soil samples. This is related to the moisture maintenance property of crosslinked hydrogels due to their three dimensional network structure. The decreasing rates of mass and moisture loss at higher cycles for both treated soils demonstrate positive effect of treatment on the durability of soil specimens. The reduction of slope at higher cycles is more obvious for KXG1.5 and KPG2C2 that shows powerful durability performance of xanthan and modified PG treated sample in comparison to pure PG treated one.

Microscale test results

SEM and SZM tests

The microstructures of optimum pure and crosslinked PG treated specimens were compared to the untreated soil in order to discover how $CaCl_2$ solution affects interparticle interactions at microscale. For this purpose, SEM and SZM microscopic images of KUNT, KPG2.5 and KPG2C2 are shown in Fig. 5. As it can be seen, optimum Ca-PG solution has made the soil interstructure more enhanced and uniform in comparison to optimum pure PG solution and has powerful performance in pore filling of the pure clay. The proper quantity of Ca and PG in KPG2C2 specimens required for powerful crosslinking of polymer chains is the reason for such an enhanced microstructure. The compact microstructure of KPG2C2 verifies the results of UCS tests that represent its superior strength performance. To more quantitatively investigate the effect of pore filling of the crosslinked specimens, image processing was carried out on the SEM images. To separate pores from the soil particles, thresholding was employed using the Huang and Wang (Huang and Wang 1995) method. After segmentation of Pores and soil particles, their areas were calculated. Figure 6 shows the schematic diagram of the employed image processing method. In this figure, pores and soil particles are shown in black and white colors, respectively. According to the segmentation results (Table 4), the treated specimens have shown less void ratio in comparison to the pure soil. KPG2C2 has shown the most reduction (about 33%) in void area.

Brunauer, Emmett and Teller (N2-BET) tests

Nitrogen-based Brunauer, Emmett and Teller test as a powerful method for determination of specific surface area and pore diameter, volume and distribution was used. Calculation method of Barret, Joyner and Hallenda (BJH) was used for determination of pore diameters. The

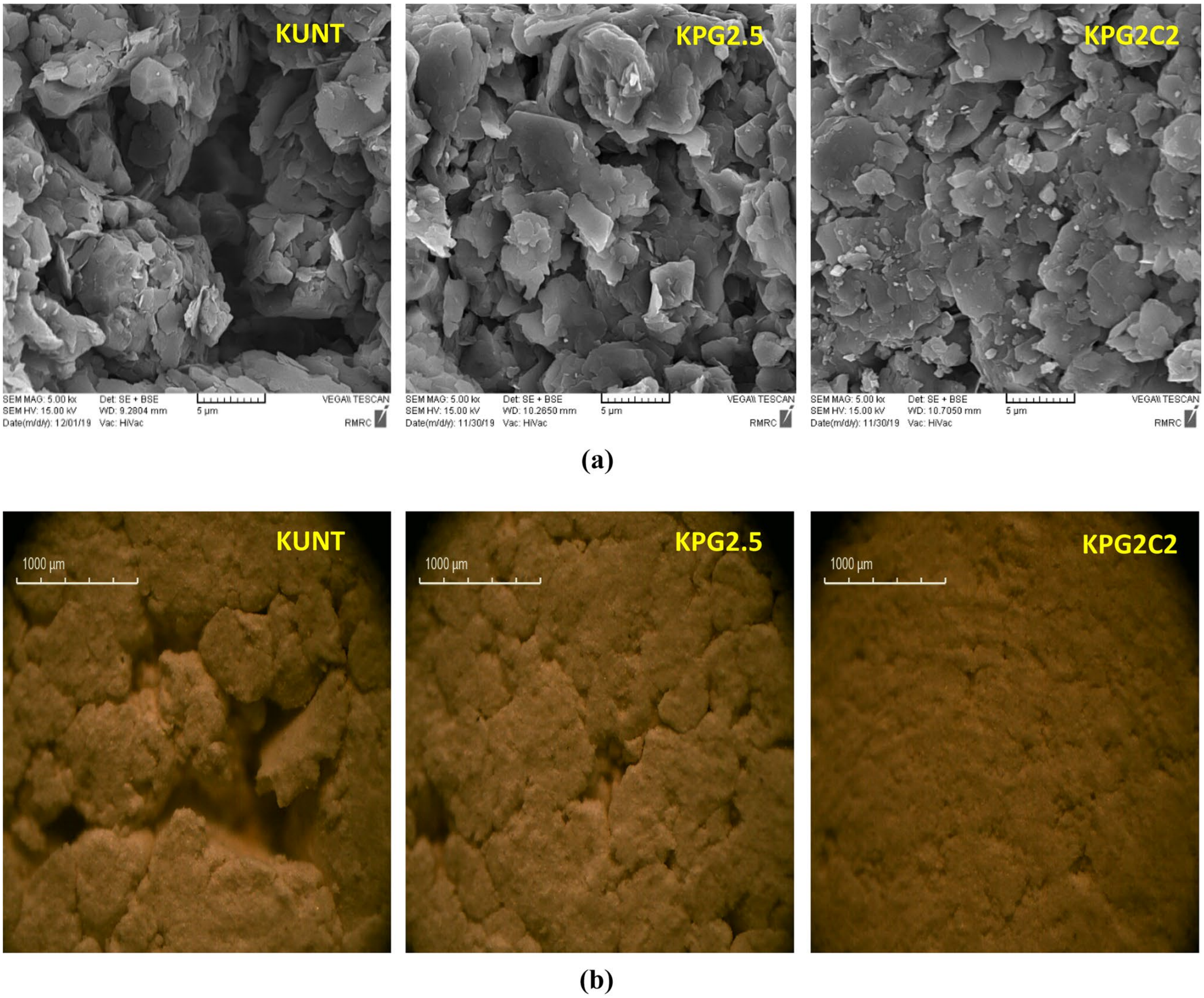


Fig. 5 Microscopic images: **a** SEM **b** SZM for pure kaolinite and treated specimens by optimum pure and crosslinked Persian gum including KPG2.5 and KPG2C2

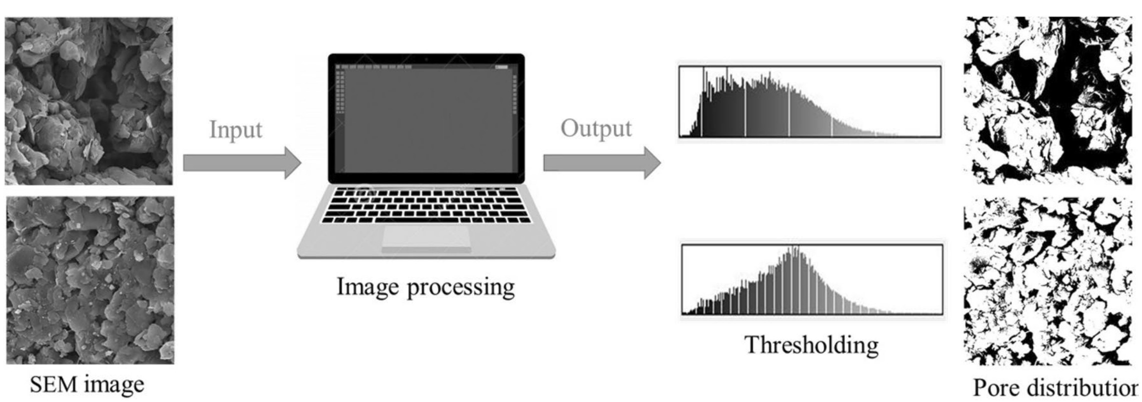


Fig. 6 Schematic diagram of image processing

Table 4 Image processing results of SEM images

	KUNT	KPG2.5	KPG2C2
Soil area (μm^2)	28,168	38,228	45,957
Void area (μm^2)	52,740	42,681	34,952
Void ratio (%)	65.2	52.8	43.2

Table 5 BET test results of pure kaolinite (KUNT) and treated ones by optimum xanthan gum (KXG1.5), Persian gum (KPG2.5) and crosslinked Persian gum (KPG2C2)

Sample name	BET surface area (m^2/gr)	BJH pore volume (cm^3/gr)	BJH average pore diameter (nm)
KUNT	8.17	0.054	26.45
KXG1.5	4.8	0.047	28.41
KPG2.5	4.64	0.042	31.52
KPG2C2	3.95	0.031	33.43

tested specimens are pure soil and treated samples at their optimum state. The obtained parameters including BET surface area, BJH average pore diameter and BJH pore volume are represented in Table 5. As the results show, the specific surface area was reduced from 8.17 m^2/gr for pure soil to 4.8, 4.64 and 3.95 m^2/gr for KXG1.5, KPG2.5 and KPG2C2 specimens. The reduction in specific surface area of the soil particles after stabilization is related to their agglomeration that results in formation of larger particles with reduced specific surface area. Among the treated specimens, the one stabilized with 2 molar $CaCl_2$ and 2% PG content has superior performance in reduction of specific surface area and particle accumulation. This feature makes it beneficial for soil improvement goals. Pore volume distribution plots of treated and untreated specimens are shown via BJH pore volume diagram at the range of 1–95 nm pore diameter (Fig. 7). The decreasing effect of treatment on pore volume confirms formation of larger particles that fill the pores. As the results show, the optimum content of PG has elevated performance in pore filling of the soil in comparison to optimum xanthan gum. This is related to the higher amount of biopolymer in the optimum state of PG treated specimens (2.5%) in comparison to xanthan gum treated ones (1.5%). Also, combination of 2 molar $CaCl_2$ and 2% PG caused the most considerable reduction in pore volume of the soil. This confirms formation of more hydrogels and ionic bonds in the interstructure of the crosslinked hydrogel treated soil in comparison to other kinds of treated samples. In addition to strength improvement objectives, the compact interstructure of this kind of soil also makes it a more attractive alternative for permeability reduction purposes.

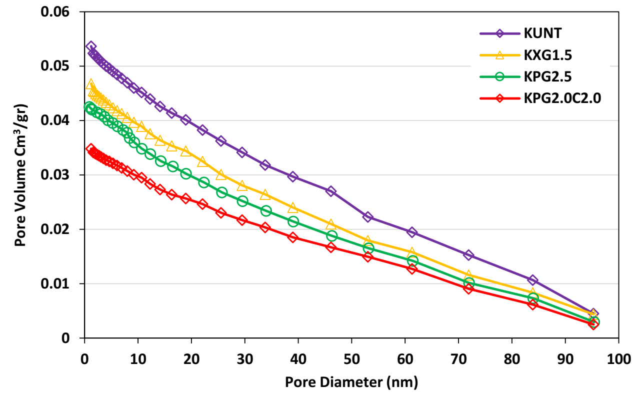


Fig. 7 BET test results: pore distribution of pure kaolinite (KUNT) and treated ones by optimum xanthan (KXG1.5), Persian gum (KPG2.5) and crosslinked Persian gum (KPG2C2)

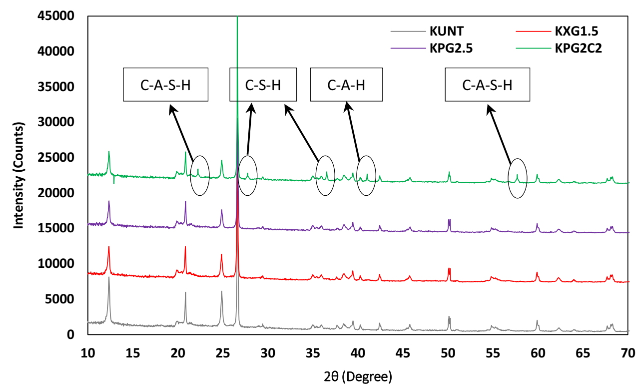


Fig. 8 XRD results of pure (KUNT) and optimum xanthan gum, pure and crosslinked Persian gum treated specimens (KXG1.5, KPG2.5, KPG2C2)

X-ray diffraction

To realize how stabilizing agent alters the mineralogical structure of the soil, XRD tests were applied on pure and treated soils with optimum additive contents. The XRD patterns of tested samples including KUNT, KXG1.5, KPG2.5 and KPG2C2 are shown in Fig. 8. Pure soil has shown kaolinite peaks at 2θ of 12, 20, 25, 38.5 and 62°, Quartz diffraction lines at 2θ angles of 21, 26.5, 50 and 60° and very tiny trace of calcite and montmorillonite at about 29.5°. In the stabilization process using xanthan and Persian gum, no new peaks can be observed due to the organic nature and very low content of additives that make incomplete reactions with alumina and silica of the soil. However, for KPG2C2 specimens some noticeable peaks were appeared in the XRD spectrum and a slight reduction in some peaks of pure soil was observed. The new peaks of crosslinked PG treated soil were developed at 2θ of 27–28° and 37–38.5°, which are related to calcium silicate hydrate (CSH) (Latifi et al. 2016; Yong et al. 2019), 2θ of 41°, representing the formation of calcium aluminum hydrate (CAH) (Yong et al. 2019), and 2θ of around 23–24° and 57°, which shows the existence of crystalline calcium aluminum silicate hydrate (CASH) (Sukmak et al. 2019). The abundance of Ca, Al, Si and O in the mixture of Ca-PG specimens prepares the ground for formation of cementitious CAH, CSH and CASH gels. These pozzolanic products are the results of reaction between alumina and silica ions of soil and calcium ions from $CaCl_2$ solution and PG structure (Abbasi 2017). The new compounds form a hard skeleton that resist against axial and shear forces properly. The reduced peak intensities of kaolinite and quartz compared to the original soil can be the result of Si dissolution in the process of formation of new cementitious products including CSH, CASH and CAH.

Conclusion

In this paper, a comprehensive set of macro and microscale tests were used to evaluate the effectiveness of the ionic crosslinked hydrogels of PG and compare the stabilizing effect of it with well-known xanthan gum. The results proved its effectiveness in terms of mechanical strength and durability improvement, pore filling and compacting interstructure of soil in comparison to pure PG treated soil. From the mechanical strength test results, combination of 2% PG and 2 molar $CaCl_2$ solution was determined as the optimum additive content. The increase of strength for optimum Ca-PG specimens with the maximum strength of 555.6 kPa (2.86 times the untreated soil) is more remarkable than the strength growth induced by optimum xanthan gum (1.74 times the pure soil). The results of direct shear test also represented more strength growth for Ca-PG treated specimens (104%) in comparison to xanthan treated specimens (91%) at the end of 28 days drying. The considerable cohesion growth of Ca-PG treated samples over time can make Ca-PG hydrogels favorable for long term strength achievement objectives. Furthermore, substitution of some extent of PG with $CaCl_2$ to achieve the same strength results, is economically efficient considering the difficulties in PG preparation process. In terms of durability characteristics, the improved durability of Ca-PG treated samples in comparison to pure PG treated soil is due to the more cation bonds in the soil-biopolymer mixture that help to resist against water and mass loss. The compacted interstructure, reduced pore volume and specific surface area for optimum Ca-PG specimens, observed from SEM, SZM and BET results, verified capability of these kinds of specimens to achieve maximum compressive strengths. Also, formation of new cementitious crystalline compounds, shown in the XRD pattern of optimum Ca-PG treated soil, is the other reason for enhanced performance of this green stabilizer.

Due to the novelty of the introduced additive, some important aspects of soil stabilization such as consolidation, collapse potential, erosion control and durability against wet dry cycles and also dynamic and large scale behavior of it have not been investigated yet. Using newly developed crosslinking methods of robust and smart hydrogels with more elevated characteristics can be the other useful advancement in this area. Also, the purification and water maintenance properties of crosslinked hydrogel of PG for contaminated and agricultural applications needs further investigation.

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Declarations

Conflicts of interest The authors declare that they have no conflict of interest.

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