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Dependence of biopolymer activity on pH and their influence on soil moisture behavior

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Abstract. The study presents the treatment of soil with chitosan and xanthan gum, examines the influence of the pH of base solutions on the solubility and activity of these biopolymers, and investigates the changes in soil properties resulting from their application. The first stage of the study is devoted to the peculiarities of preparing soil reinforcement with biopolymers and their mixing process. The obtained samples were analyzed for their texture, which allowed identifying the optimal conditions for maximum solubility. The second stage of the study is devoted to evaluating the modified soil's behavior under wetting conditions. The moisture level of the soil directly affects its physical and mechanical properties. Understanding these changes makes it possible to predict the behavior of the soil under different service conditions. The study considered 10 soil samples prepared with base solutions of different acidity (pH 4, pH 7, pH 9), among which one sample serves as a control sample without modification with biopolymers. This makes it possible to evaluate the effect of modification on soil properties and to identify optimal conditions for its use. The analysis showed that the solutions' moisture level and acidity significantly affect the samples' structural characteristics. At the same time modified soils show improved performance compared to the control sample, the sample reinforced with chitosan increased density by 16 %. These data are important for the development of effective solutions in geotechnical and construction engineering.
Keywords: soil properties, biopolymer, pH, moisture, mixing process, soaking time.

1. Introduction

Using new biopolymers for soil improvement is a significant step in sustainable construction practices [1]. Biopolymers are increasingly applied in geotechnical engineering due to their unique properties and environmental safety. Biopolymers are natural polymers formed in living organisms and are categorized into three main groups: polynucleotides, polypeptides, and polysaccharides. They are sustainable, low-carbon, and renewable resources because they originate in nature. Polysaccharides such as xanthan, gellan, guar gum, alginate, and agar are known for their properties that contribute to soil quality. The constant discovery of different biopolymers provides engineers with a wide range of options, allowing them to find more customized solutions to meet specific project requirements. Thus, in the study [2], the modification efficiency of xanthan gum increases when combined with utilizing alkaline Class-F fly ash (FA). Improvement of mechanical strength and compressibility of acidic soils containing xanthan gum (XG) can be caused by crosslinking of XG molecular filaments and weakening of XG hydrogels hydrolysis under the action of FA. Based on the results obtained, it was proposed to use FA in combination with XG for the treatment of acidic soils and to use only XG for the treatment of neutral soils. In [3] the silty sand from Waynad, Kerala was treated with agar biopolymer, providing significant liquefaction resistance as a noteworthy reduction in excess pore pressure was observed. A series of cyclic triaxial tests showed that shear modulus increased with an increase in biopolymer content, curing period, and over-consolidation ratio.

Chitosan is a biopolymer derived from chitin, which is found in the exoskeletons of crustaceans and the cell walls of fungi [4]. It has high strength and biocompatibility, which makes it a promising material in geotechnical engineering. Chitosan has antimicrobial properties, which can reduce the risk of pathogens in the soil. Due to its adhesive properties, it binds soil particles, preventing soil leaching and erosion. Xanthan gum is a polysaccharide derived from the fermentation of sugars involving bacteria such as Xanthomonas campestris. It is known for its gel-forming properties and high viscosity. This biopolymer forms gels that help bind soil particles, due to its biocompatible properties, it is safe for the environment and non-toxic to plants and microorganisms [5]. The authors [6] in the paper note that stable strength parameters under all curing conditions in unconfined compressive strength (UCS) tests were demonstrated by specimens treated with Stabilized soil composites incorporating Cr3+-crosslinked xanthan gum (CrXG) with a clay-sand mixture (CSM) containing 15% fines. CSM15 also retains a 90% durability index after eight dry-to-wet cycles and a dry UCS of 300 kPa after 130 days of atmospheric weathering. The microscopic analysis confirmed the stable agglomeration of the CrXG-clay matrix between sand grains. The results of this study indicate that these composites can be applied as a sustainable surface protection strategy for earth structures such as dams and road slopes. The study of the effect of gum stabilization has been presented in many research [7], [8]. The investigation into the characteristics of soil stabilized with biopolymeric materials—specifically xanthan gum and guar gum—conducted by [6], [7], [8], [9], confirms their effectiveness, demonstrating that the strength of the soil increases with the addition of these biopolymers.

In another study [10], different concentrations of biopolymer were used and tested before and after soil curing. At the same time, mixing parameters were measured in both wet and dry soil conditions. Thus, a relationship between the way biopolymers are mixed with soil and their further utilization has been established.

The importance of soil pH in biopolymer activity is noted in a study [11]. The effect of pH on the activity of biopolymers is due to changes in the structure and function of these molecules depending on the acidity or alkalinity of the medium. For example, at low pH, biopolymers can denature, that is lose their spatial structure and functionality due to disruption of hydrogen bonds and ionic interactions between amino acids or other elements of the molecule. Moreover, at high pH, changes in the structure of biopolymers may also occur, which affects their ability to interact with other molecules and participate in biological processes in the soil [12]. Thus, optimal soil pH can help to maintain the activity of biopolymers and their role in soil fertility and plant growth. Liming techniques or the addition of organic fertilizers are often used to maintain appropriate soil pH levels to compensate for changes caused by anthropogenic influences or natural soil processes [13].

The interaction of chitosan and xanthan gum with soil depends on their properties and the pH of the medium [14]. Chitosan is a positively charged biopolymer that has good adhesion to soil particles due to electrostatic attractions. At a low pH value, chitosan has a high solubility in water, which favors its interaction with soil. However, at higher pH values, chitosan can deprotonate, lose its positive charge, and become less adhesive to soil particles. Xanthan gum has a high viscosity and good stability in solution. Its interaction with soil depends on the pH of the medium. At low pH values, xanthan gum can form gels with soil particles and improve their adhesion. However, at high pH values, it is possible to form gravitational suspensions, which may result in reduced adhesion to the soil. Thus, it is important to consider the pH of the medium when chitosan and xanthan gum interact with soil to optimize their solubility and adhesion to soil particles. Also, the physical properties of biopolymers can vary significantly depending on their type and composition [15]. The main objective of this study is to investigate the effect of different pH values on the interaction of biopolymers (xanthan gum and chitosan) with soil, which may influence their solubility and interaction with soil particles, and to evaluate the behaviour of modified soils under moisture conditions. Humidity is a critical factor affecting soil behaviour as it can significantly alter the soil structure. When moistened, the soil begins to absorb water, which can lead to a change in its volume and a reduction in strength, especially if insufficiently resistant materials are used. Moisture resistance also affects the durability of structures, so such assessments are key to evaluating the risk of failure.

2. Methods

The investigations were conducted in the “ENU-Lab” laboratory of L.N. Gumilyov Eurasian National University, Astana, Republic of Kazakhstan. The experiment’s technical process consisted of the following main procedures:

1. Test setup and equipment calibration.
2. Determination of physical and mechanical properties of soil.
3. Preparing solutions with different pH.
4. Preparing modified soil.
4. Measurement of the pH level of soil and the biopolymer soil.
5. Evaluation of the behavior of modified soil samples under humid conditions.
6. Scanning electron microscopy analyses of soil and the biopolymer soil.
7. Analysis exploring the interrelationship between received results.

Sand with fine friction (Astana, Kazakhstan) was employed for the experiment. Sieve, hydrometer, liquid, and plastic limit analyses were conducted to classify the soil. The liquid and plastic limit analyses assessed the soil's consistency and plasticity characteristics [16]. These tests allowed for a comprehensive understanding of the soil's texture and behavior, essential for evaluating its suitability for reinforcement.

The study used pre-dissolution of chitosan and xanthan gum, which were pre-dissolved in water before their application to the soil. One of the main advantages of this procedure is the improved interaction of the components, which promotes a more homogeneous distribution in the soil. This procedure also reduces the likelihood of clumping, which is important for achieving a homogeneous mixture texture, and allows easier control of the moisture level in the soil, which is particularly useful when preparing samples for experiments. It also avoids the loss of active ingredients that can occur with mixing [10]. The preparation of base solutions included the preparation of solutions with different pH values tested with litmus paper. The pH values were 4, 7, and 9 (Figure 1). The choice of pH levels 4, 7, and 9 is because they represent three different values on the pH scale, reflecting acidic, neutral, and alkaline conditions respectively.

A pH level of 4 corresponds to acidic conditions, which may be caused, for example, by the presence of acidic precipitation in the environment or the use of acidic solutions in construction. Acidic conditions can lead to corrosion of metal structures and damage to concrete surfaces. A pH level of 7 corresponds to neutral conditions, which are the most favorable for most building materials and structures. A neutral pH provides stability and preservation of materials over long periods. A pH level of 9 corresponds to alkaline conditions, which can be caused by the use of alkaline solutions or highly alkaline soil conditions. Alkaline conditions can also lead to corrosion of metal structures and changes in the properties of building materials.

Thus, selecting pH levels of 4, 7, and 9 allows the effects of different conditions on building materials and structures to be assessed and precautions to be taken for their protection and durability.

a) pH 4 b) pH 7 c) pH 9

Figure 1 – Preparation of solution with different pH

The ratio of biopolymer to soil was 2g:100g respectively. Soil samples were prepared with the addition of different concentrations of chitosan and xanthan gum at different pH levels, and one control sample without the addition of biopolymer. Mixing of the soil was carried out gradually to avoid the formation of lumps and to obtain a homogeneous consistency (Figure 2). An important step after mixing the biopolymer with the soil is to ensure its stabilization. This process allows the biopolymers to interact with the soil particles, forming stronger bonds, which in turn increases resistance to external loads and moisture. The finished modified soil was evaluated for pH levels.

a) mixing with chitosan at the beginning of the process

b) mixing with chitosan at the end of the process

c) mixing with xanthan gum at the beginning of the process

d) mixing with xanthan gum at the end of the process

Figure 2 – Process of soil mixing with biopolymers

When chitosan is mixed with water, the homogeneity of the mixture is quickly achieved. Chitosan dissolves easily, does not stick to gloves, and is then effectively combined with the soil. In the case of mixing the soil with gum, it is necessary to mix the gum with water thoroughly beforehand to obtain a homogeneous mass. When gum comes into contact with water, a thick gel is formed, which requires additional thorough mixing when adding the soil to ensure homogeneity of the entire mixture. Gum, in turn, being a complex polysaccharide upon initial reaction with water leads to the formation of heterogeneous areas in the mixture. The evaluation of the behavior of the modified specimens under moisture conditions involved the preparation of specimens of the same size and weight to ensure comparability (Figure 3).

Figure 3 – Modified samples

After the samples were subjected to humidification. Instrumental and visual inspection were used during the testing process. The initial dimensions of the specimens were recorded and the dimensions after wetting were measured at fixed intervals using a caliper. The control interval was every 20 minutes for the first hour and 3, 5, 9, 13, 17, 21, and 24 hours thereafter. One of the parameters monitored was also the change in weight of the samples.

Changes in color, texture, and cracking were recorded during visual inspection. A rating scale from 1 to 5 was applied to assess the shape preservation, in which: 1 - destruction: the specimen is destroyed, and has lost structural integrity; 2 - significant destruction: the specimen has severe cracks, deformations, or destroyed areas; 3 - moderate failure: the specimen shows some signs of failure, such as minor cracks or deformations; 4 - minor degradation: the specimen is generally intact, with minor surface damage or cracks; 5 - perfect condition: the specimen is in perfect condition, with no visible damage or changes.

The water absorption coefficient and soil density were calculated by equation 1,2 [17]:

$$W = \frac{\mathrm{m_{wet}} - \mathrm{m_{dry}}}{\mathrm{m_{dry}}} \cdot 100\%, \quad (1)$$

where: m_{wet} – mass of moistened soil sample, g.; m_{dry}– mass of dry soil sample, g.

$$\rho = \frac{\mathrm{m}}{\mathrm{V}}, \quad (2)$$

where: m – soil weight, g.; V– the volume of the wet sample, cm^3.

3. Results and Discussion

Table 1 presents the soil's physical characteristics obtained in laboratory tests. The soil composition contains 60.794 % sand, 19.193 % silt and 15.609 % clay. The particle size distribution curve for soil is shown in Figure 4.

Table 1 – Physical characteristics of the soil

Soil characteristic	Value
Specific gravity, g/cm3	2.538
Maximum dry density, g/cm3	2.031
Optimum water content, %	10.194
Sand-sized fraction (75 µm–2 mm), %	60.794
Silt-sized fraction (5–75 µm), %	19.193
Clay sized fraction (<5 µm), %	15.607
Liquid limit, LL, %	23.251
Plastic limit, PL, %	1.190
Plasticity Index, PI, %	22.061

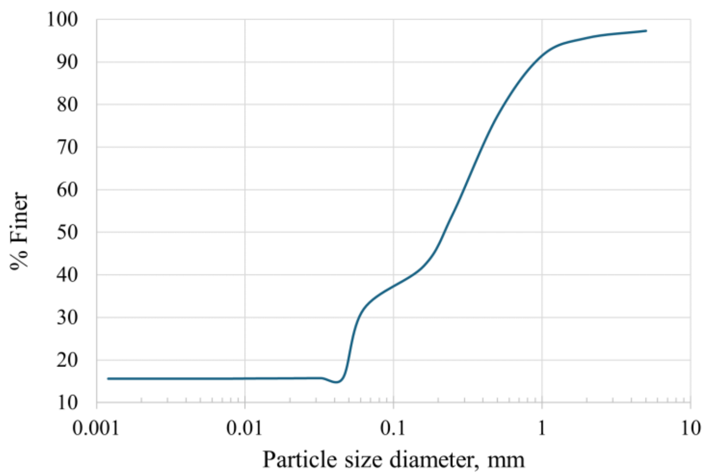


Figure 4 – Particle size distribution curve

The modified soils' pH results corresponded to the prepared solutions' pH values. Table 2 presents the changes in parameters for chitosan – and xanthan gum-modified soil samples.

Table 2 – Weight of moistened samples

Time, hour	Soil sample without modification	Soil sample modified by chitosan			Soil sample modified by xanthan gum		
	Weight of moistened sample, g.						
		pH 4	pH 7	pH 9	pH 4	pH 7	pH 9
0	105	105	105	105	105	105	105
0.3	110	111	112.3	115.5	111.5	111	112
0.7	111	114	117.6	121	111.9	111.3	112.2
1	114	116.3	120.5	128.3	114	116	116.3
3	115	124.2	131.4	136.2	117	119	120.8
5	123	128.6	135	140.1	124	127.3	128
9	126	131.4	139.1	144.3	126.2	128.1	129.8
13	114	135.5	142.3	147.7	129	130.1	131.5
17	110	137	144.1	150.1	129.1	131	133
21	107	134.3	144.1	145.2	128.5	129.6	131
24	103	131.2	140.2	145	127.2	128.4	130.6

According to the data obtained, the weight of the control soil sample changed from 105 grams to 103 grams when moistened. Moistening caused a change in the soil's structure, leading to its loosening. This factor affects the bearing capacity of the soil. The chitosan-modified soil sample showed significant performance when alkaline base solution was used, the weight increase was from 105 grams to 145 grams, indicating an increase in moisture-holding capacity caused by the biopolymer. This may be because chitosan improves the soil structure by increasing porosity and water retention capacity.

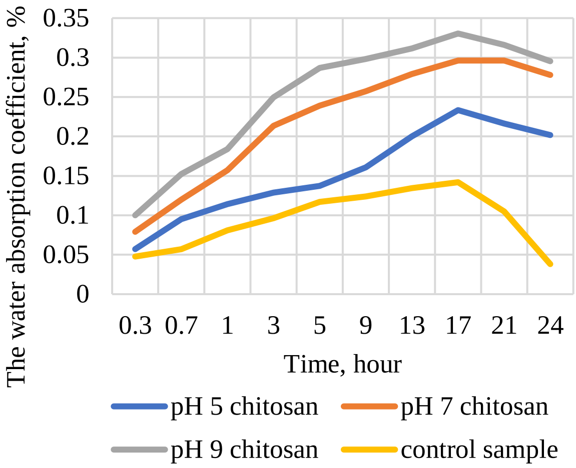
A significant performance improvement was observed in experiments with chitosan-modified soil, especially when an alkaline base solution was used, as previously stated in the study [14].

The modification with xanthan gum increased the weight from 105 grams to 130.6 grams, indicating that the soil increased its moisture retention capacity and improved its structural characteristics. This weight increase indicates that xanthan gum promotes the formation of gels that fill the pores and improve the soil's water retention properties.

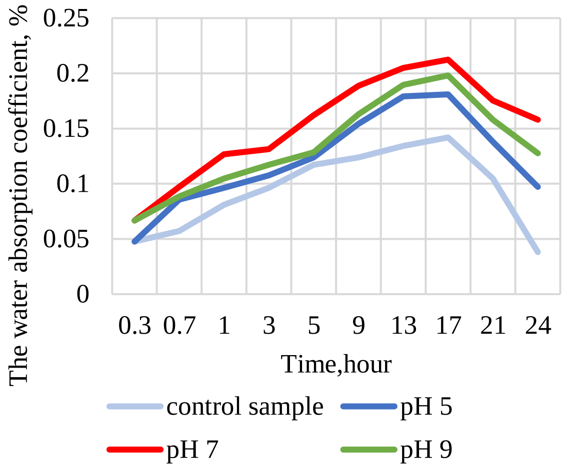
Samples of soil modified with biopolymers in the process of moistening are presented in Figure 5.

Figure 5 – Samples during the process of moistening

Figures 6-7 present the values of the modified specimens' water absorption coefficient and soil density.



a) W, soil modified by chitosan



b) W, soil modified by xanthan gum

Figure 6 – Graphs of water absorption coefficient

The error of each measurement was reduced by using weight instruments and accurately accounting for the biopolymers added. The total error consists of measurement error and test error and ranges from 0.01-0.1%.

The results showed that with increasing soil acidity, the use of xanthan gum leads to an improvement in the geotechnical performance of soils which is also established in the study [2]. This improvement can be attributed to cross-linking of the biopolymer molecular strands and attenuation of hydrolysis of soil particles under acid exposure. It is suggested to use xanthan gum in combination with acids for the treatment of acidic soils or separately for neutral soils. Along with this, when the studied soil was modified with xanthan gum, the soil behavior showed a stable result in terms of establishing the dependence of water absorption on the amount of biopolymer used, the results of which are presented in Table 2.

The water absorption coefficient shows how much water the soil absorbs about its original mass. The data presented in Figure 6 show that soil modified with chitosan absorbs more water than soil modified with gum. However, when modified with gum, the behavior of the soil is more stable, and there are no large variations in the data. The results of determining soil density as a characteristic that determines the mass of soil per unit volume showed variation depending on the biopolymer used for modification. Figure 7 shows the density values for each soil modification. The maximum density value was demonstrated by the soil modified with chitosan under an alkaline environment in relation to the density of the control soil sample.

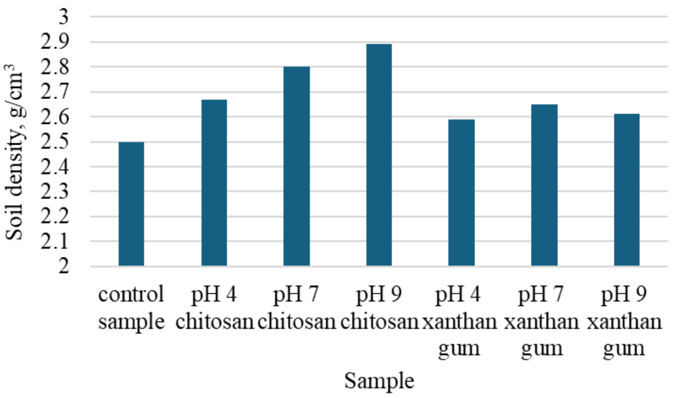


Figure 7 – Soil density values

Many studies [2], [3] do not provide information on the density of biopolymer-modified soil, which is an important aspect of evaluating its physical and mechanical characteristics. However, this study considered the density of biopolymer-modified soil at different pH values, which allows a more accurate assessment of the effect of changing the acidity of the medium on its structure and properties. Consideration of density in such studies is important because it directly affects characteristics such as water absorption and strength properties of soils.

After modifying the soil with chitosan, there was a 16 percent increase in density and a 6 percent increase in gum density. Visual observation of the behavior of the soil samples modified with biopolymers under different media of the base solution showed that the soil with chitosan retained its original shape, did not collapse, and absorbed moisture well. In contrast, the soil with gum under alkaline and acidic environments was quickly susceptible to drying out, and small cracks formed on the top surface of the molds, first small cracks and then larger cracks. However, the gum-modified soil samples were less susceptible to cracking and failure than the control soil sample.

According to the five-point scale evaluation of the behavior of the modified soil during wetting, presented in Figure 8, it is revealed that over time the soil samples lose their shape.

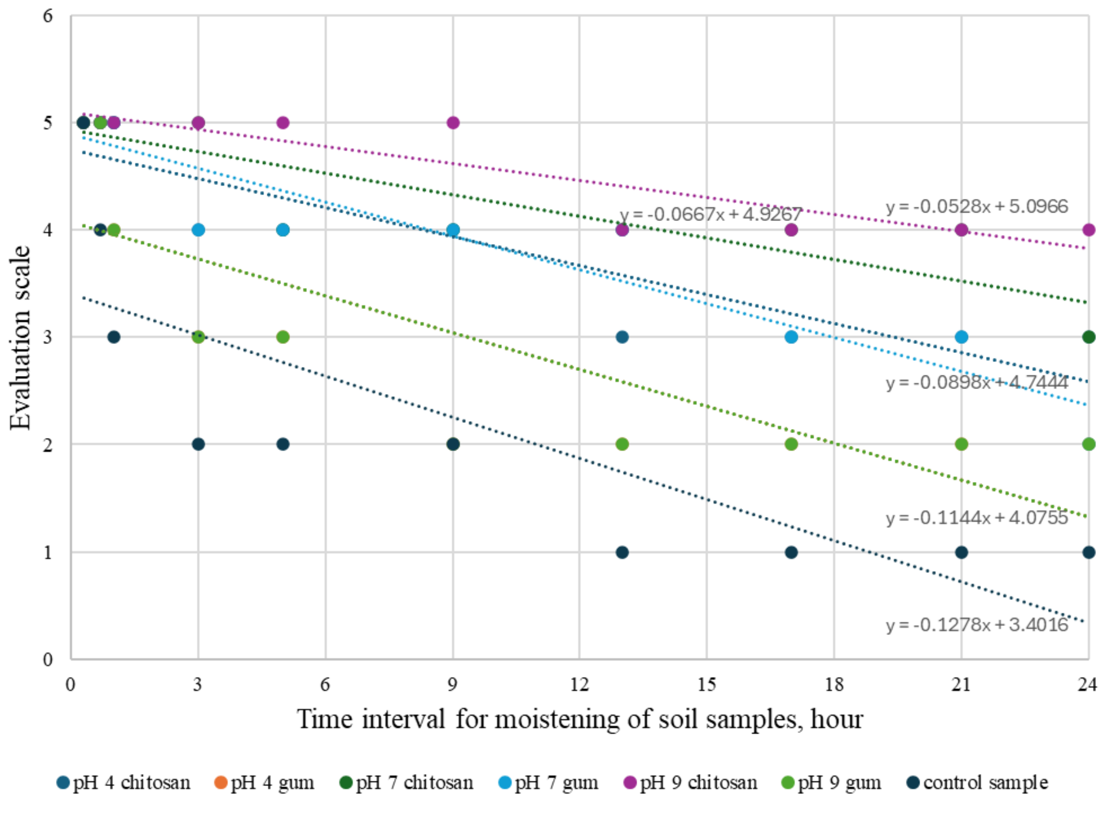


Figure 8 – Correlation of visual assessment data

However, a comparative analysis of the control sample with the biopolymer-modified samples shows that the modification favors soil strengthening. In particular, the biopolymer-treated samples show significantly less susceptibility to deformation and failure, indicating improved resistance to moisture. This is due to improved soil structure, increased cohesion, and soil density.

4. Conclusions

The applications of biopolymers for soil stabilization are extensive and each can be used according to their properties. Some biopolymers can improve the properties of drainage systems by promoting more efficient water drainage, while others are used to stabilize slopes and prevent slumping. The conducted study showed that:

1. The biopolymers showed good compatibility with the soil, and the wet mixing method allowed for a homogeneous structure.

2. The treated soil showed the best water absorption results in the following sequence using biopolymers: chitosan with alkaline medium base solution, chitosan with neutral medium, chitosan with acidic medium, gum with neutral medium, gum with alkaline medium, and gum with acidic. medium.

3. The density of the soil increased in the following ratio compared to the control soil sample: chitosan with alkaline medium 16 %, chitosan with neutral medium 12 %, chitosan with acidic medium 7 %, gum with neutral medium 6 %, gum with alkaline medium 4 % and gum with acidic medium 3 %.

4. Visual inspection showed that the soil sample reinforced with xanthan gum in solution with pH 4 is most susceptible to shape change and destruction.

To improve the physicochemical properties of soil in engineering practices, it is recommended to carry out preliminary site-specific tests to determine the optimum dose and type of biopolymer, and for this purpose, it is necessary to investigate the required composition of the base solution to dissolve with the biopolymer.

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Iliyas Zhumadilov – methodology, material.
Gulshat Tleulenova – editing, funding acquisition.

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