

Research Article

Collapsibility of Gypseous Soil Treated with Pectin-Biopolymer through Leaching

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Gypsum reinforcement in dry soil provides activity resistance. It quickly becomes a source of danger in the conditions of partial and complete soaking of gypsum soil as a result of the dissolution of gypsum, which poses a great danger to the structures built on this soil. The danger increases when water flows through it and works to leach the soil, which leads to the loss of its mass by leaching gypsum. The soil is chemically and mechanically improved to enhance its geotechnical properties, but despite its great advantages in strengthening, it has significant negative effects on the ecosystem, so the use of environmentally friendly materials is essential. Pectin was selected as an improved biopolymer and added at three different contents (0.5, 1, and 2%) to create a soil mixture and at four different gypsum contents (10, 20, 40, and 62%) to evaluate the chemical and mechanical properties of the improved mixture. Develop an engineering model to leach the soil and pectin mixture. The results showed a significant decrease in CH and C_p values due to biogel encapsulation of soil particles and pore filling properties. The percentage decrease in the values of (CH) reaches (0.67, 73, 75, and 68%) for soils 1, 2, 3, and 4, respectively. After soil (1, 2, 3, and 4), C_p values decreased in percent (0.63, 0.63, 0.65, and 0.7%). TDS decreased at a biopolymer content of 2% from 1050, 1200, 2200, and 2500 mg/ml to 320, 540, 468, and 570 mg/ml of soils 1, 2, 3, and 4, respectively.

1. Introduction

Gypsum soil is regarded as one of the most challenging unsaturated soils to work with while constructing roads and structures. The presence of gypsum (hydrated calcium sulfate, $(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$) in the soil alters its mechanical and physical qualities, as well as making it more susceptible to water [1, 2]. In civil engineering, soil is classified as “gypsum soil” based on the quantity of gypsum content in it, independent of soil color or form. Some scholars suggested that a particular percentage of gypsum should exist, such as 3%, 4%, or 6% as a lower limit [3]. These gypsum rates have a significant impact on the physical and mechanical properties of soil, and this impact varies depending on the quantity of gypsum present.

Effective gypsum cementation made gypseous soils are often resistant to dry climates. However, when soil is partially or completely coated, soluble compounds dissolve,

leading to a significant loss of resistance [4]. This problem gets more problematic when water movement in the soil causes soil mass loss due to gypsum leaching. Leaching is a phenomenon in which soluble materials are dissolved and removed as a result of the natural or artificial movement of fluids in soil. This is critical to investigate since the safety and behavior of structures like embankments and dams are largely reliant on changes in the chemical and mechanical characteristics of these soils [5].

Collapsible soils include gypseous soils. When dry, gypsum offers an apparent cementation, but water infiltration causes breakdown and softening of the soil, which can lead to partial or full collapse of buildings [6]. Temperature, the amount of water in contact with the gypsum substrates, applied pressure, water velocity, and grain size are all natural elements that might influence gypsum dissolving [7, 8]. Long-term dissolution is a major regulating

element in modifying the geotechnical parameters of gypseous soils. Their findings also suggested that extremely tiny nongypsum particles, such as clay, can be lost, causing changes in the general particle size distribution in the soil [9].

[4, 10] discovered that gypseous soils can develop enormous void spaces following breakdown, significantly reducing substrate strength [11]. Leaching appeared to have an impact on the geotechnical parameters, increasing the sand percentage, void ratio, and coefficient of permeability. It was discovered that soaking gypseous soils in brine doubles the collapse potential compared to pure water that the permeability coefficient of the oedometer shows lower results than the modified leaching, and the permeability coefficient of the modified permeability test is more believable results than the permeability test of the oedometer [12]. The elimination of soluble salts and dissolved materials alters the soil's physicochemical and mechanical qualities. The procedure happens by diffusion or a hydraulic gradient. Gypseous soils experience a number of changes in their features as a result of their ongoing mass loss, as well as changes in the constituent materials' properties brought on by leaching and the elimination of bond strength connecting sand grains [12].

Al-Badran et al. used the oedometer permeability leaching test to examine leaching behavior on gypseous soil with various OCR ratios. They came to the conclusion that the leaching strain is greater than $OCR > 1$ when $OCR = 1$. Additionally, they came to the conclusion that when $OCR > 1$, the strain was unaffected because the void ratio rose [13, 14]. They demonstrated that consolidation tests and typical interpretation methods are ineffective for gypseous soils and developed a novel type of stress-strain relationship for these soils [15] found that increasing the gypsum content results in a reduced angle of internal friction as well as lower expansion indices and greater cohesiveness. They also said that compressibility reduces with decreasing salt concentration and increases with sand addition to gypsum. In their study, [16] aimed to increase the bearing capacity of collapsible soils during wetness by partially replacing the soil with dune sand. Geogrids and geotextiles have been shown to improve bearing capacity and reduce settling values.

The bulk dissolving of gypsum, as well as the elimination of gypsum connections between soil particles, alters the chemical composition of the soil and lowers its compressibility and strength characteristics. As a result, structures erected in this location are at high risk of subsidence and foundation collapse; appropriate steps should be taken before construction to enhance soil quality [4]. Problem soils are treated to improve their engineering qualities. Traditional chemical and mechanical stabilizers are used to improve soil characteristics. Lime, cement, chemical plaster, epoxy, phenoplast, polyurethane, and acrylamide are among these stabilizers with the improvements and reinforcement supplied by these technologies. However, these additives have a substantial detrimental influence on the ecosystem [17–20].

The manufacturing of the most commonly used stabilizers, such as lime and cement, results in large carbon dioxide and nitrogen oxide emissions. It can induce

desertification because of its low, deteriorating character, in addition to disrupting the environment by modifying and raising the acidity of the soil. Aside from chemical pathogens that have been documented to be poisonous and/or harmful, with the exception of sodium silicate [21]. Because of these drawbacks, it is critical to stabilize unstable soils with ecologically benign, nontoxic alternative stabilizers. Researchers' (Mitchell and Carlos Santamarina [22–24]) current biotechnological efforts to stabilize soils for geotechnical applications presented novel soil stabilizers and key achievements using biopolymers of biological origin. Agar, xanthan, chitosan, guar, and other biopolymers have been used to prepare hydrogen bonds that form the branching structure of polymeric chains inside the soil structure and produce a water-insoluble gel supplied by organisms such as algae, bacteria, and fungus [20, 21].

Biopolymers have been employed by a few researchers to improve the shear strength and hydraulic conductivity of degraded soils and sandy clays [21, 25], which shows effective employed biopolymers of agar, gellan, and beta-glucan to enhance the Cheonan sandy soil and the strength of the remaining Korean clay soil. The durability of gypsum soils, however, has not been investigated using a biopolymer combination. Gypsum soils provide major challenges for geotechnical construction due to excessive collapse and shrinkage caused by gypsum salt dissolving. Furthermore, when water saturation increases, shear strength falls [26, 27]. Agar offers a dense covering and coating that surrounds the soil particles produced by the formation of a dense gel web, resulting in decreased biodegradability [26]. In the above-mentioned scholarly literature, we observe a dearth of research on the difficulties of gypsum soils in the field of biopolymer processing.

Despite the possibility that leaching-based changes in the chemical composition and engineering properties of these soils have been studied, no study on gypsum soil has yet addressed this problem. Studies on gypsum soil lack studies on the effect of biological stabilizers on gypsum soil, and if any, they lack studies on the effect of washing, that is, the passage of water through gypsum soil and the changes that result. The research aims to study some geotechnical properties of soils with different gypsum contents during leaching and the possibility of improving them by adding pectin biopolymer and reducing the damage resulting from the dissolution of gypsum salts during the leaching process.

2. Materials and Methods

2.1. Soil. Samples of soil were taken at a depth of one meter from places southwest of Lake Tharthar, north of Ramadi city in Iraq, between $N43^{\circ}15'E32'33''$, in Anbar, Iraq. Four gypsum contents were used for soil, which are 10, 20, 40, and 62%, which were designated with 1, 2, 3, and 4 soils, respectively. All soils were classified as graded poor sandy (SP) according to the standard soil system (ASTM D2487-17e1). The chemical composition of gypsum soil was analyzed, as shown in Table 1. A modified Proctor test was performed to determine the maximum dry density (MDD) and the ideal moisture content (OMC) as shown in Table 2. Modified

TABLE 1: Chemical properties of soil.

Properties	Soil 1	Soil 2	Soil 3	Soil 4
Gypsum content (%)	9	20	40	62
Total soluble salts (T.S.S) (%)	28	37.13	52.34	64.28
Organic matters (O.M) (%)	0.45	0.38	0.28	0.13
pH value	8.06	7.8	8.1	8.07

Proctor chose to obtain higher compaction energy and reduce the percentage of voids in gypsum soil because it has weak points for gypsum soil and passages for water penetration that work on gypsum melting and bonding dissolution of gypsum soil mass particles. Uniformity and curvature coefficients found after drawing the distribution curves are as shown in Figure 1. Atterberg Limits for each soil type according to ASTM D4318, where values for (L.L) were obtained no values were obtained for (PL) because the soil is sandy Table 2.

2.2. Pectin Biopolymer. Pectin is a high-molecular-weight heteropolysaccharide found in plant cell walls that helps firm up and form the vegetal tissue. It is commercially manufactured as a white to light brown powder derived mostly from citrus fruits, and it is used in cuisine as a gelling ingredient, notably in jams and jellies. It is also utilized as a stabilizer in fruit juices and milk drinks, as well as a source of nutritional fiber in dessert fillings, medications, and sweets. Pectin is a frequently utilized food component due to its capacity to add texture and hardness to food items (hydrogels), while new fascinating applications are also connected to other pectin features, such as interfacial activity [28]. Figure 2 shows pectin powder use in this study.

Prepare a pectin solution with optimum moisture content by adding (0.5, 1, and 2%) by weight of the soil with proper mixing in the magnetic device. Mix with soil to make a soil-treated pectin mixture. The mixture is transferred and reformed in five layers in a metal cylinder with a diameter of 75 mm and a height of 200 mm for the diagram of the leaching test engineering model shown in Figure 3(a) and stored for 14 days for treatment, after which the water is passed through it to conduct the washing process and take the target measurements. All samples were prepared at optimum moisture content and maximum soil dry density. In order to choose the time period needed to reach the highest possible strengthening of the soil mixture and biopolymer, the soil was molded with a ratio of 40% gypsum, and pectin was added at a rate of 1% of the weight of the soil for this purpose and in three different ways to add pectin, namely: (1-making a pectin solution with the optimum moisture content (OMC). 2-adding dry pectin powder to the soil and mixing them, then adding the optimum moisture content and mixing them again. 3-a pectin solution with five times the OMC to make a soil-pectin mixture). The result of this methodology showed that the best treatment period is 14 days, and the best way to add it is the biopolymer solution method. Figures 4 and 5 show the relationship between the internal friction angle and the cohesion during the residence time after re-molding.

3. Leachate Water Samples

The standard of the innovative model (leaching test) to carry out the leaching process shown in Figure 3 according to the standard (ASTM D5333, 2003) in terms of the principle of loading, but as a sample size, the constant head device cell was used to check the hydraulic conductivity. Each sample was remolded into a perforated cell measuring 75 mm in diameter and 210 mm in length for leaching before being linked to water storage with a constant head of 900 mm. Filter sheets were put on the top and bottom of the cell to prevent leaking, and the drain was kept closed for 24 hours to allow the samples to get saturated. The tap was then turned on, allowing the water (distilled water) to flow through the samples. Figure 3(a) shows the cell used for soil leaching. For each sample, every 200 ml of the leachate was gathered and used to determine TDS, CH, and pH. Between each water collection stage, the drain tap was kept closed for 1 to 2 hours to let the salt concentration balance [11].

Leaching was then continued until the TDS and CH of the leachate reached a constant value. At the same time, the deformation of the soil resulting from the leaching process of the soil sample was observed under a constant normal load of 200 kPa. Figure 3(b) shows the engineering model used to perform the leaching process. After loads were gradually added at 50 kPa every 24 hours until reaching a load of 200 kPa and the deformation that occurred after each load was recorded, the water tap was opened, the sample was allowed to saturate, and the deformation was recorded, then the leaching process began as mentioned above. To find the values of TDS and CH, use the model YL-TDS2-A, which works by dipping the electrodes in leachate water at a depth of 3–5 cm to get the correct reading. Determine the collapse potential (C_p) of the soil according to ASTM D5333, 2003. The term “collapse potential” is used to classify the hazards’ state of collapsibility. The collapse potential, abbreviated as C_p , is defined as follows:

$$\begin{aligned}
 CP(\%) &= \Delta\varepsilon \\
 &= \frac{\Delta He}{H_o} \\
 &= \frac{\Delta e}{1 + e_o} * 100,
 \end{aligned} \tag{1}$$

where $\Delta\varepsilon$ is the vertical strain, ΔHe is the change in height of soil resulting from wetting, H_o is the initial height of the soil, Δe is the change within the void ratio of the sample resulting from wetting, and e_o is the natural void ratio. That was (0.761, 0.762, 0.771, and 0.795) for soils 1, 2, 3, and 4, respectively.

4. Results and Discussion

4.1. Chemical Test

4.1.1. Soil. The results of chemical analysis for all untreated soil samples are shown in Figures 6(a), 6(b), and Table 3, which show the total dissolved solids (TDS), calcium

TABLE 2: Physical properties of soil.

Soil types	Grain size distributions (ASTM D422, 2007)			Atterberg limits (ASTM D4318)		Compaction test (ASTM D1557)		
	USCS	Cu	Cc	LL (%)	PL (%)	γ_{feild} (kN/m ³)	γ_{dmax} (kN/m ³)	OMC (%)
1	SP	6.3	0.64	35	N.P	14.3	17.3	11
2	SP	7.8	0.55	34	N.P	13.5	16.7	12
3	SP	6	0.58	29	N.P	14.8	15.8	11
4	SP	7	0.78	27	N.P	13.2	15.5	12

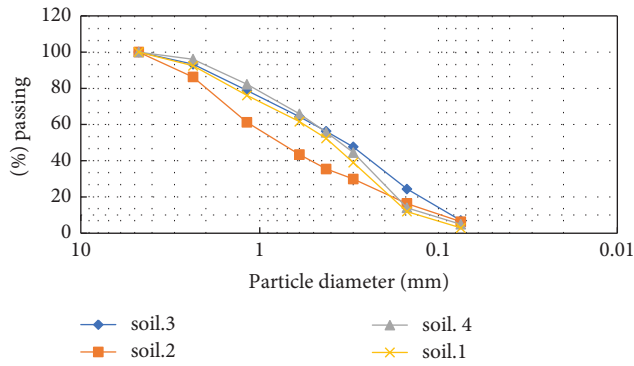


FIGURE 1: The grain-size distribution curve of the soil samples corresponds to four types of soil.

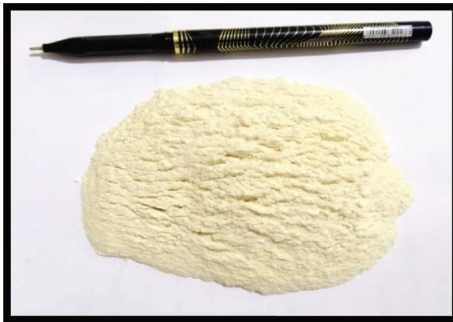


FIGURE 2: Commercially produced powder of pectin, extracted from citrus fruits.

hardness (CH), and pH, where the curves of total dissolved salts (TDS) and calcium hardness (CH) with the volume of water passing through the leaching process were plotted. As the table and graphs show, in the early stages of the leaching, the samples had large amounts of gypsum, the TDS was at its maximum, and the CH was increasing. As leaching continued, these parameters decreased and tended to a constant value. According to the findings of the researchers [2, 4].

4.1.2. Soil-Pectin Mixture. The results of the chemical analysis of four types of gypsum soil treated with biopolymer are shown in Figure 7, which shows the change in TDS with volume of leaching water for different pectin contents. Through these figures, the results showed a decrease in the values of TDS with an increase in the percentage of biopolymer added for all samples of treated soils; this corresponds to Asghari et al. [4]. The decrease was more visible in

soil 3 and soil 4 samples with high gypsum content (Figures 7(c) and 7(d)). The value of TDS decreased at 2% biopolymer content from 1050, 1200, 2200, and 2500 to 680, 1050, 1440, and 1235 for the maximum values of soils 1, 2, 3, and 4, respectively (Figures 7(a)–7(d)). After that, the decrease continued to 320, 540, 468, and 570 for the values; the minimum order is the same as in Table 4. This decrease is due to the fact that the biopolymer hydrogel enhances the agglomeration of the particles by covering their surfaces with a bio-coating that prevents them from being affected by water and thus reduces the solubility of calcium carbonate and the dissolution of bonds between those particles, thereby resulting in a decrease in TDS. It also reduces the exposure of soil particles to leaching.

Upon reaching these minimum values of TDS, we notice that the curves begin to rise until they reach constant values. This rise results from the separation of the monomers on the outer surface of the main gel body after saturation with water, which leads to a rise in TDS values, and this is confirmed by the results of calcium hardness CH shown in Figure 8, where we note: The remaining values of CH decreased to constant values, and this indicates that the calcium carbonate that was coated in the biogel was not affected by the washing water and that the reason for the increase in TDS is the separation of the surface monomers of the main gel body.

The calcium hardness measurement results in Figure 8 show a significant difference between the curves of the biopolymer-treated and untreated models. The curves of the untreated models show a significant increase in CH values in the first period of the washing process until they begin to decrease in the last period and reach almost constant values. In contrast, the curves of the models treated with biopolymer show a decrease since the first period of the washing process. Table 4 shows the different values of CH during the process leaching of the samples before and after the treatment with biopolymer; the results showed that the samples with the highest gypsum content had the highest values of CH in Figures 8(c) and 8(d) for soils 3 and 4, respectively.

4.2. Mechanical Test

4.2.1. Soil. To evaluate the effect of the leaching process on the deformation of gypsum soil, a collapse test was performed using the geometric model mentioned in the third chapter. The soil sample was remolded in the cylindrical cell with dimensions of 210 mm in height and 75 mm in diameter, and the cumulative loads were shed to reach the load of 200 kPa in the dry state, taking the

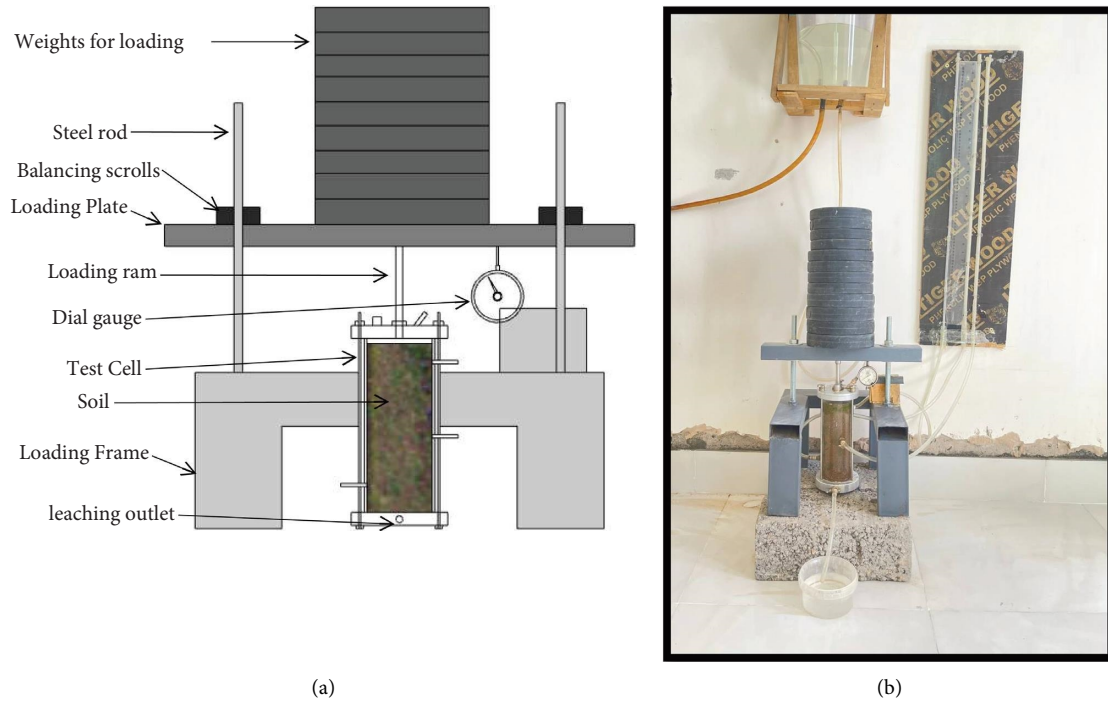


FIGURE 3: Engineering model of the leaching process: (a) schematic diagram and (b) apparatus for loading and leaching.

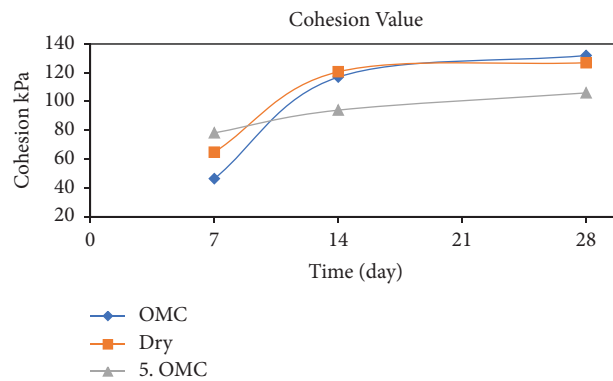


FIGURE 4: Relationship between the cohesion and the curing time after remolding.

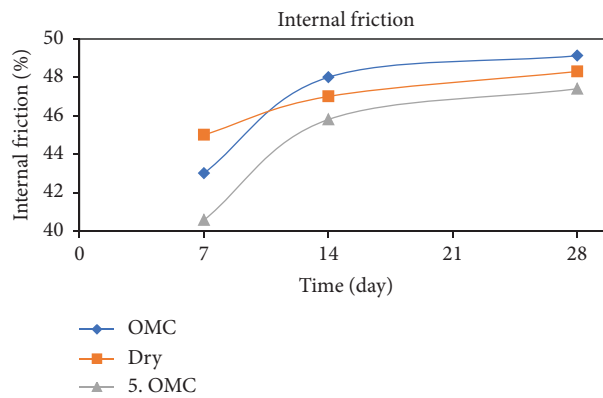


FIGURE 5: Relationship between the internal friction and the curing time after remolding.

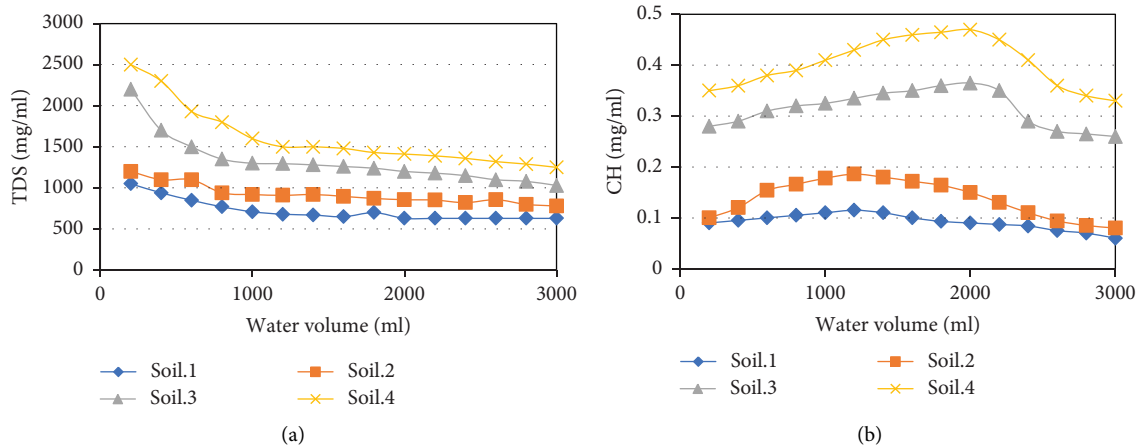


FIGURE 6: Relationship of the water leaching volume of untreated soil with (a) TDS and (b) calcium hardness (CH).

TABLE 3: Results of chemical analysis of leachate from untreated soil samples.

Soil types	TDS (mg/ml)		CH (mg/ml)		pH	
	Max	Min	Max	Min	Max	Min
1	1050	630	0.115	0.073	7.6	7.1
2	1200	780	0.186	0.08	7.4	8.2
3	2200	1030	0.365	0.26	7.3	7.8
4	2500	1250	0.217	0.33	7.2	8.4

reading after 24 hours at each load. Then we allow the water to pass into the sample, and the outlet tap is closed for 24 hours to allow the soil sample to saturate. The reading Take it after 24 hours of saturation. The water outlet tap is then opened to allow 200 ml of leach water to be collected and the deformation meter reading to be taken after 24 hours. The process continues until the collapse values are established for the first 3000 ml of the total volume of water passing through the soil. The curves shown in Figure 9 show the relationship between the potential collapse and the water volume of the leaching. The potential for collapse continues to increase with larger leaching water volumes under a constant load of 200 kPa. This is consistent with what the researcher (Al-Badran) reached [13]. In terms of the result with the gypsum content away from the loading conditions that were not included in the researcher's study. The increase continued in soil 4 and soil 3 to a volume of water of 2600 mL, or until day 13, after which the collapse value was taken to reach the steady state.

Samples with high gypsum content gave the highest collapse values because the gypsum content is dominant over the collapse values as a result of the dissolution of calcium carbonate during the saturation process and exposure to the leaching process. The values of the collapse at the first day of saturation and before starting the leaching process were (7.72) for soil 4, but after starting the leaching process and allowing water to pass through the soil structure, we notice that the value of the collapse increased and reached a nearly constant value (9.6) after 13 days from the start of the leaching process. As for the soil 3, the collapse was (5.42) on the first day of

the leaching process, and it was (6.94) after a period of 13 days. As for the collapse values of soil samples 1 and 2 for the first day of the washing process, they were 1.77 and 3.29, respectively, and after 7 days, the values became 1.94 and 3.87 for the first day of the washing process, they were 1.77 and 3.29, respectively, and after 7 days, the values became 1.94 and 3.87. So, soil samples with higher gypsum levels pose a greater danger when exposed to water soaking and the leaching process, as this leads to the dissolution of gypsum and its exit during the leaching process, thus generating gaps and cavities and a loss of connection between the soil particles, changing the soil structure, which increases the collapse values.

4.2.2. Leaching of Soil with Pectin. Figure 10 shows the relationship between the collapse values and the volume of leaching water for soil samples and for pectin contents of 0.5, 1, and 2%. The results of the leaching process indicate a decrease in the collapse of the treated soil samples, regardless of the gypsum content. The results of the collapse before and after the soil treatment during the leaching process are shown in Table 5.

The results in Table 5 show a significant decrease in the collapse and the time period for the leaching process to reach a steady state for all soil samples. Where the difference in collapse between the lowest and maximum value decreased from 1.88 to 0.36 times, that is, at the beginning and stability of the collapse value, respectively, during the leaching process of soil (Figure 10(d)). For soil 3, the difference was 1.52 times at the start of the leaching process and 0.16 times at the end of the leaching process (Figure 10(c)), and for soils

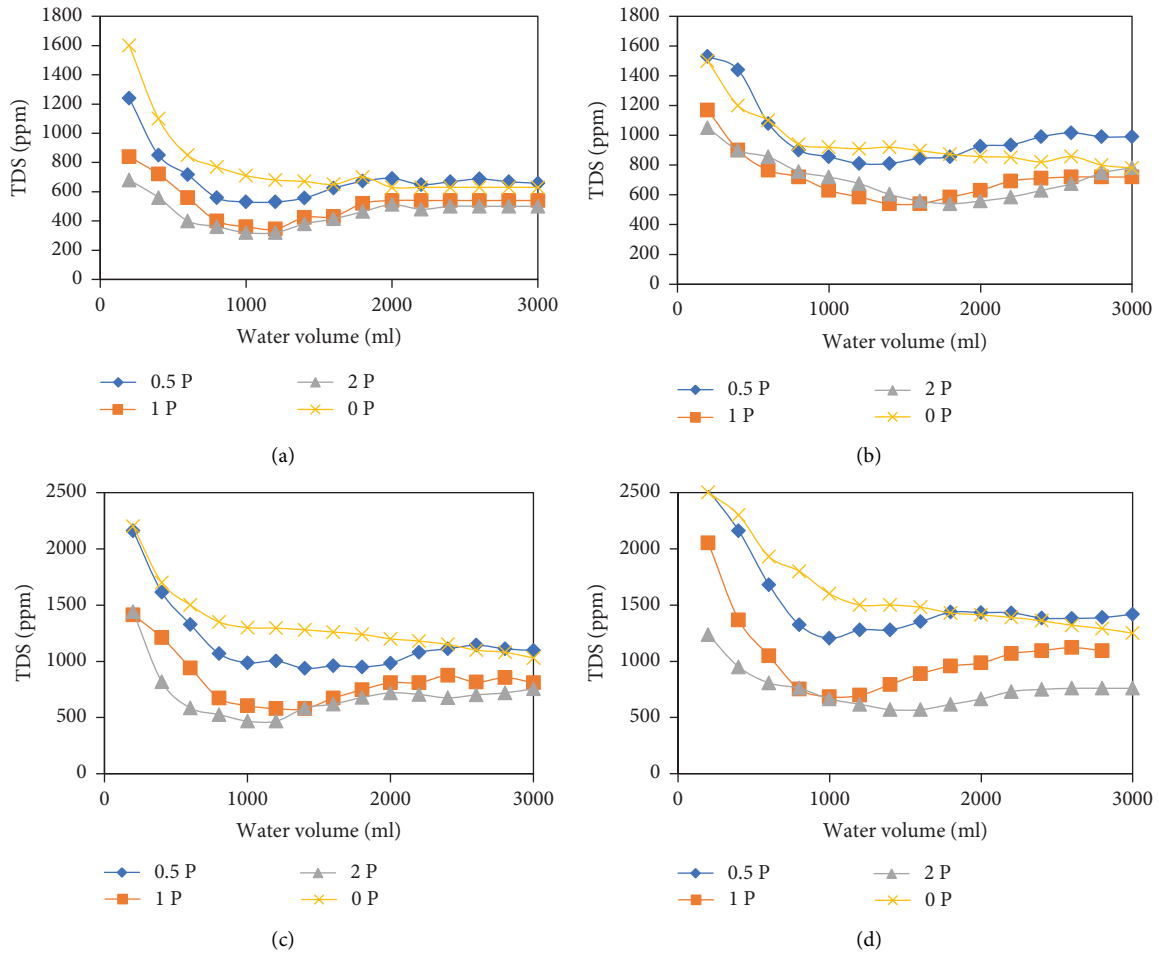


FIGURE 7: TDS-leachate water change of pectin-treated soil samples (a) soil 1, (b) soil 2, (c) soil 3, and (d) soil 4.

TABLE 4: The chemical composition of soil before and after treatment.

Soil type	Pectin (%)	TDS (mg/ml)		CH (mg/ml)	
		Max	Min	Max	Min
1	0	1050	630	0.115	0.073
	0.5	920	529	0.092	0.065
	1	840	344	0.087	0.038
	2	680	320	0.08	0.025
2	0	1200	780	0.186	0.08
	0.5	1130	810	0.12	0.071
	1	1170	540	0.103	0.056
	2	1050	540	0.098	0.05
3	0	2200	1030	0.365	0.26
	0.5	2160	936	0.26	0.16
	1	1412	578	0.18	0.12
	2	1440	468	0.2	0.093
4	0	2500	1250	0.47	0.33
	0.5	2520	1229	0.33	0.26
	1	2052	684	0.34	0.2
	2	1235	570	0.31	0.15

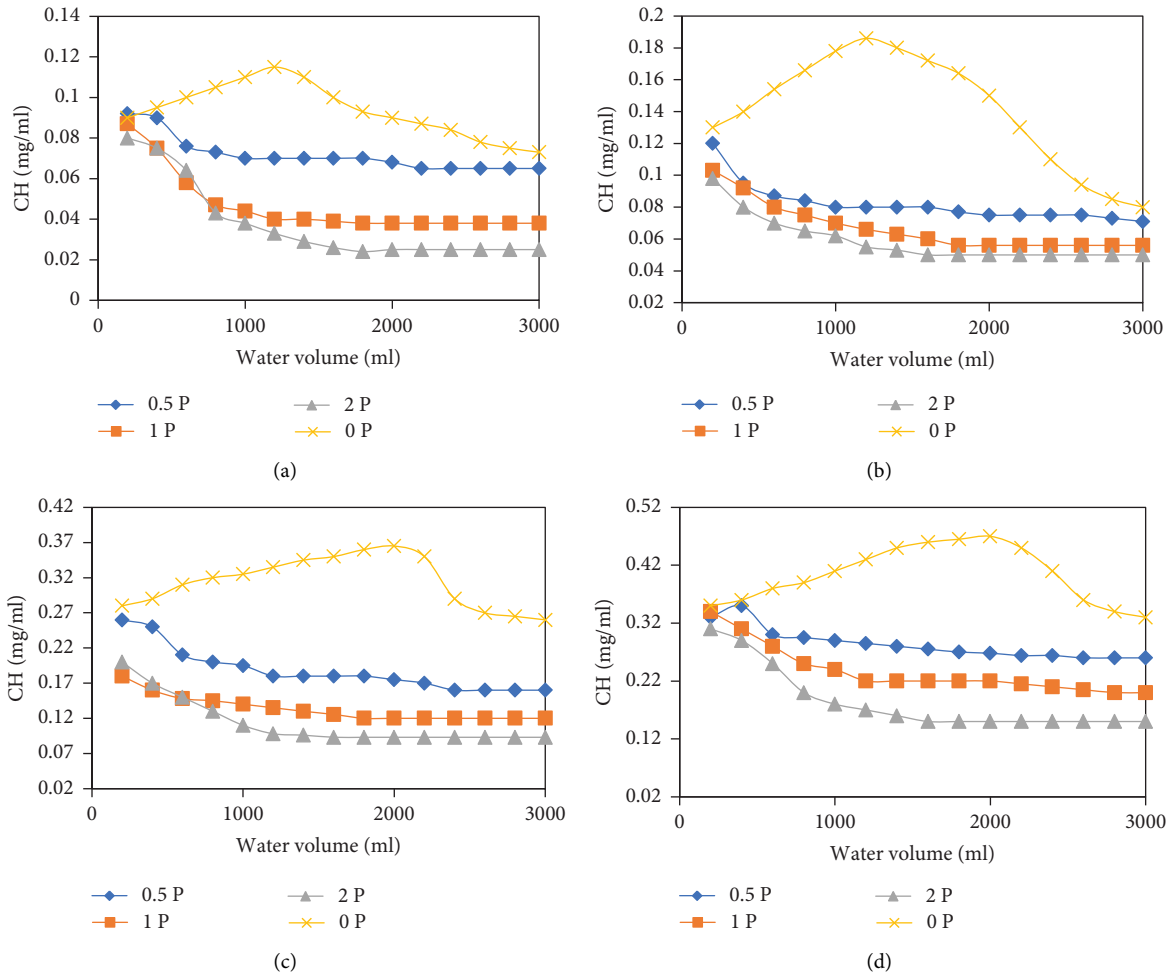


FIGURE 8: CH-leachate water change of soil samples with pectin for (a) soil 1, (b) soil 2, (c) soil 3, and (d) soil 4.

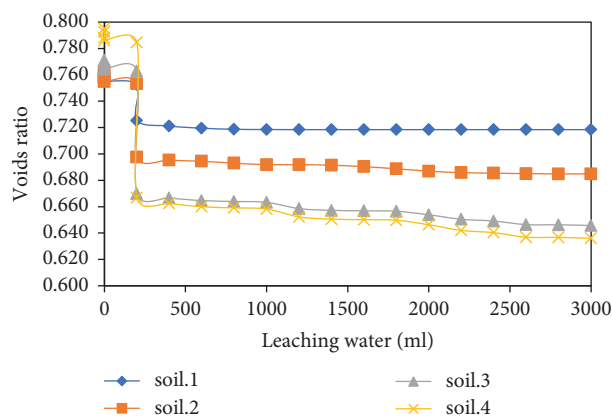


FIGURE 9: The voids ratio with leachate water relationship for untreated soil samples.

2 and 1, the difference was 0.58 times, 0.25 times, and 0.17–0.095 times between the start and end of the washing process for samples treated with 2% pectin content (Figures 10(a) and 10(b), respectively).

The results indicate that increasing the added pectin content reduces the time to reach a steady state. The biofilms of pectin increase the bridging and cohesion of the soil structure while filling the pores. The increased content of the

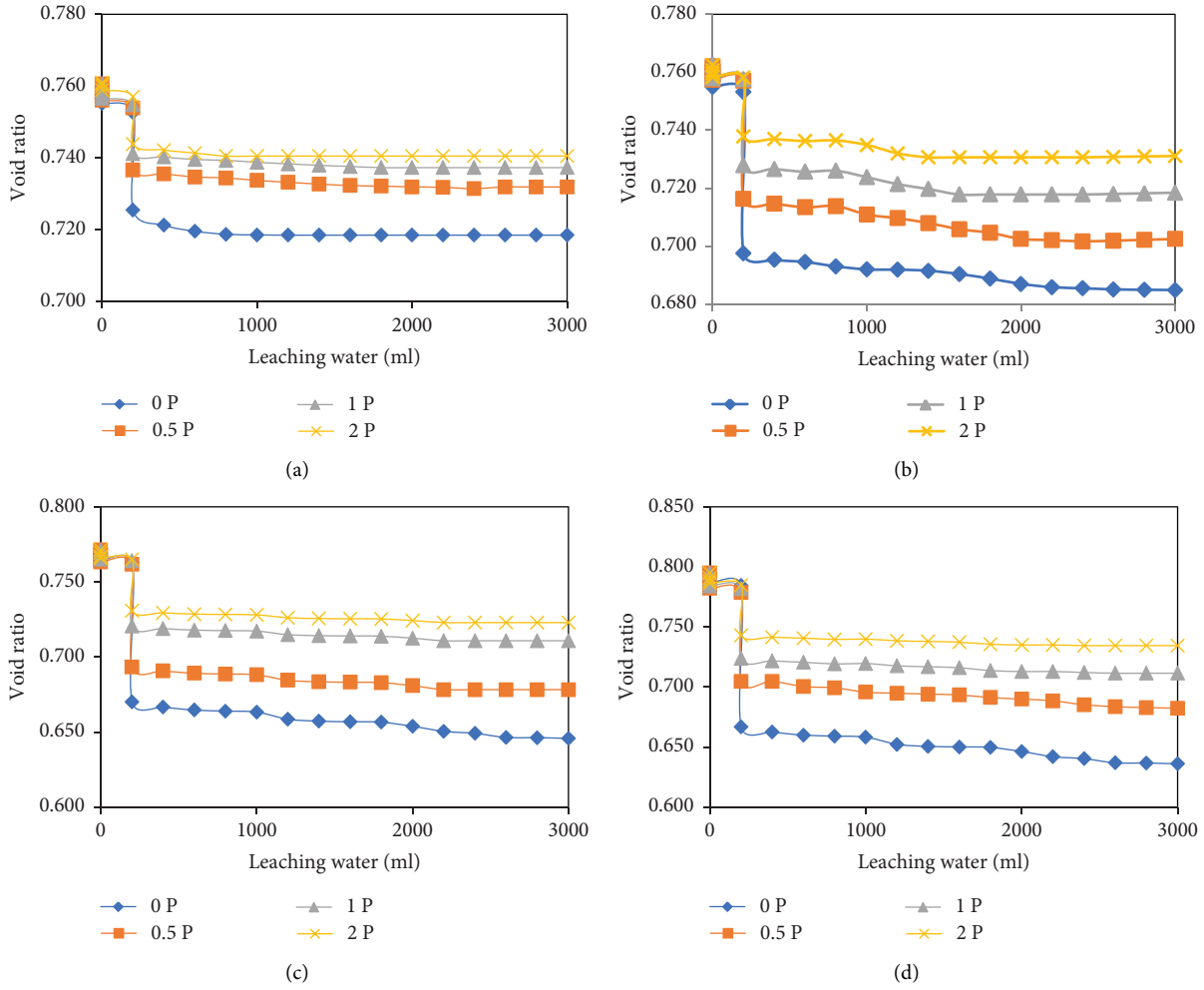


FIGURE 10: The relationship between void ratio and leachate water for pectin-treated soil samples (a) soil 1, (b) soil 2, (c) soil 3, and (d) soil 4.

TABLE 5: The collapse potential of samples before and after pectin treatment during the leaching process.

Pectin (%)	Collapse potential (C_p %)							
	Soil 1		Soil 2		Soil 3		Soil 4	
	Min	Max	Min	Max	Min	Max	Min	Max
0	1.77	1.94	3.29	3.87	5.42	6.94	7.72	9.6
0.5	1.04	1.24	2.41	3.14	3.99	4.87	4.31	5.6
1	0.77	0.94	1.7	2.1	2.63	3.11	3.51	4.11
2	0.665	0.76	1.2	1.45	2.06	2.44	2.57	2.93

treated pectin worked on the condensation of the hydrogels that filled the pores and the condensation of the pectin biofilms, which enhanced particle agglomeration by coating the surface and creating bridges between the gypsum soil grains, reducing or preventing calcium carbonate dissolve in gypsum soils and generating an encapsulated agglomerate structure that is resistant to the effect of water soaking.

5. Conclusions

After leaching the soil samples with different gypsum contents, the following can be concluded:

- (i) The results of the leaching process of the biopolymer-improved soil samples showed a significant decrease in the calcium (CH) values due to the biopolymers that encapsulate the soil particles and fill the pores.
- (ii) After a period of leaching, the TDS values increased slightly, which is a result of the saturation of the hydrogels and the beginning of the separation of the outer monomers of the main gel body.
- (iii) Soil samples with higher gypsum levels pose a greater risk of collapse when exposed to water soaking and the leaching process, as this leads to the dissolution of gypsum and its exit during the leaching process, thus generating gaps and cavities and a loss of connection between the soil particles, changing the soil structure and increasing the collapse values.
- (iv) Increasing the added pectin content reduces the time to reach the steady state. Pectin biofilms further seal the cohesive soil structure and fill in pores. The increase in the treated pectin content led to thickening of the hydrogels filling the pores and

thickening of the pectin biofilms, which promoted agglomeration of particles by coating the surface and creating bridges between the grains of the gypsum soil, thereby reducing or preventing the dissolution of calcium carbonate in the gypsum soil, leading to the formation of an encapsulated agglomerate structure and resistant to the effect of soaking in water.

- (v) The potential for collapse continues to increase with larger leaching water volumes under a constant load of 200 kPa. The increase continued in soil 4 and soil 3 to a volume of water of 2600 mL, or until day 13, after which the collapse value was taken to reach the steady state.

Data Availability

The data is in Excel files and is part of an extensive study for the doctoral thesis, which is still under study and preparation.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

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