Eco-friendly Improvement of Water Erosion Resistance of Unstable Soils with Biodegradable Polymers

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Abstract. The improvement of water erosion resistance of soils is gaining the attention of the scientific community. Erosion represents a threat to agricultural productivity because of the loss of valuable superficial soil and nutrients. Cultivation soils erosion is one of the main contributors to the desertification process, which is, itself, a global problem. Recently, polysaccharides have been tested as additives to improve earth construction materials with respect to their mechanical properties and water erosion resistance. This paper studies the use of biodegradable polymers to improve soil stabilization with respect to erosion by water. Aqueous solutions of the polysaccharides chitosan and carrageenan were used to improve wettability and runoff resistance of sandy and loose soils. Chitosan becomes positively charged when dissolved in dilute acidic solutions, while carrageenan becomes negatively charged. Their capacity to form polyelectrolytes in aqueous solutions may be a contributor in retaining cohesiveness in loose soils.

1. Introduction
The soil has been an important component in human development, both for its use as a construction material and because of its fundamental role in agriculture. Some of the problematics concerning these two areas are related to its erosion. The propensity to erosion is originated by the presence of weakly-bonded small particles in the surface of the material [1]. Erosion occurs when an external agent such as wind, flowing water or mechanical friction grounds down particles causing the loosening of the already weak bonds, affecting the integrity of the material. As a consequence, erosion facilitates the loss of soil components either in the form of fugitive dust, as a result of loose particles being blown off and suspended in the air, or as sediments being carried away. Dust suspension is one of the causes of air pollution and can have negative effects: blocking sunlight affecting vegetation and crops development, altering near water bodies’ characteristics such as pH and turbidity [2], and creating potential respiration health issues. On the other hand, loose soil particles displacement menaces the agricultural productivity due to the loss of valuable surface soil and its nutrients [3], which is one of the causes of desertification [4].

Synthetic and natural chemical products have been used as additives to modify loose soil properties and improve its strength and stability, which improves the resistance to water and wind erosion [4] through techniques like cementation, chemical linkage and waterproofing [5]. The effects of numerous synthetic additives, like a mixture of sulfonate-urea-melamine-formaldehyde resins and poly(vinyl alcohol) [1] and polyacrylamides, xanthates and cellulose charged microfibrils [3], over runoff resistance tests have been studied.
Biodegradable polymers have also been used as additives, carrageenan and chitosan have been studied as an additive in adobe, evaluating their water erosion resistance through drip tests [5, 6]. Biodegradable additives have the advantage of avoiding both soil pollution by chemical accumulation and the formation of toxic intermediates during their degradation process [3]. Therefore, application of these additives can help fight soil erosion for vegetation growth and control fugitive dust generated in gravel and dirt roads.

2. Experimental part
For this study, biodegradable polymers were used as additives, specifically carrageenan and chitosan, spraying their aqueous solutions over sand and soil surfaces. Three tests were conducted to evaluate impermeability and water-erosion resistance of treated soils: Measurement of the contact angle of a sessile water-drop and drip resistance test of treated sand and soil; and water runoff resistance over a sand surface.

2.1. Preparation of the additives and loose soil samples
Carrageenan was extracted from algae Chondracanthus chamissoi while chitosan was purchased from Aldrich. Additives consisted of solutions of carrageenan in deionized water and chitosan in a 1% (v/v) aqueous acetic acid solution. For contact angle measurements and drip tests, solutions of 0.5 % (w/v) were used, while for the runoff tests 0.5 % (w/v) as well as 0.2 % (w/v) solutions were used. For each test, a reference sample (control) consisting of the material without additive was also evaluated. The soil was sieved in order to remove gravel and larger particles. Both the soil and sand were slightly compacted by manual pressure for contact angle and drip tests.

2.2. Contact angle of a sessile water-drop
Two sets, one for sand and the other for soil, of five samples each were prepared: A petri dish (6 cm of diameter) was filled with the respective material, sand or soil. Samples were weighed before and immediately after spraying the additive solution. Table 1 shows the additives and quantities used to cover each sample, as well as the average contact angles measured.

| Sample*                 | Additive quantity** (mg·cm⁻²) | Contact angle (°) |
|-------------------------|-------------------------------|-------------------|
|                         | Carrageenan          | Chitosan          |                     |
| Control-Sand            | 0                         | 0                 | n.m.               |
| Sand-Car                | 0.503                    | 0                 | n.m.               |
| Sand-Chi                | 0                         | 0.220             | 140.7 ± 5.5        |
| Sand-Car/Chi            | 0.0503                   | 0.470             | 131.0 ± 12.2       |
| Sand-Chi/Car            | 0.0370                   | 0.220             | 140.3 ± 46.0       |
| Control-Soil            | 0                         | 0                 | n.m.               |
| Soil-Car                | 0.816                    | 0                 | n.m.               |
| Soil-Chi                | 0                        | 0.644             | 106.8 ± 5.9        |
| Soil-Car/Chi            | 0.715                    | 0.513             | 133.7 ± 4.1        |
| Soil-Chi/Car            | 0.323                    | 0.724             | 138.6 ± 3.8        |

* Car/Chi = First layer of carrageenan, second (top) layer of chitosan.
** Additive quantity corresponds to dry polymer added.
 n.m. = Could not be measured (water drop was immediately absorbed).

Samples were left to dry at room temperature for 1 day after additive application. Once dry, 20 µL deionized water drops were deposited gently on their surface with a microsyringe. For each sample, five
drops were randomly distributed and their contact angles were measured. Ten measurements were performed for each type of sample, when possible.

2.3. Water drip resistance test
For this test, four sets, two of sand and two of soil (each consisting of 3 samples) were prepared. Samples were similar to the ones used for contact angle measurements, a petri dish filled with sand or soil with a section of the container's wall cut and replaced by a filter to avoid water stagnation. Table 2 shows the additives and their amount. Control samples were evaluated but omitted from the table since they contained no additive.

Water erosion was evaluated by adaptation of a Spanish standard test for compressed soil blocks [7]. According to this test, water drops were allowed to fall vertically from a height of 1 meter at a flow rate of 50 mL·min⁻¹ directly over the sample, placed at a slope of 27° in relation to the horizontal. Erosion damage was evaluated at 1 minute and changes were registered by video and photos. The test was continued for the samples that showed no damage after 1 minute of dripping until significant erosion was observed.

Table 2. Samples and drip resistance test results.

| Sample         | Additive quantity* (mg·cm⁻²) | Time of damage observed (s) |
|----------------|------------------------------|-----------------------------|
|                | Carrageenan                  | Chitosan                    |                             |
| Control-Sand-1 | 0                            | 0                           | 0                           |
| Sand-Chi/Car-1 | 0.636                        | 0.596                       | 15                          |
| Sand-Car/Chi-1 | 0.665                        | 0.569                       | 600                         |
| Control-Sand-2 | 0                            | 0                           | 0                           |
| Sand-Chi/Car-2 | 0.594                        | 0.523                       | 10                          |
| Sand-Car/Chi-2 | 0.607                        | 0.542                       | 300                         |
| Control-Soil-1 | 0                            | 0                           | 0                           |
| Soil-Chi/Car-1 | 0.640                        | 0.922                       | 13                          |
| Soil-Car/Chi-1 | 0.858                        | 0.587                       | 220                         |
| Control-Soil-2 | 0                            | 0                           | 0                           |
| Soil-Chi/Car-2 | 0.527                        | 0.697                       | 12                          |
| Soil-Car/Chi-2 | 0.779                        | 0.498                       | 170                         |

* Additive quantity corresponds to dry polymer added.

2.4. Water runoff resistance test
A tray of dimensions 36.5 x 23.4 x 0.8 cm (length, width and depth), was filled with sand. This tray was tilted 15° from the horizontal. A continuous stream of water (234 mL·min⁻¹ flow rate) fell from a height of 5 cm and, after impact, it flowed over the sand surface for 1.5 minutes. Two tests were performed, in the first one, half of the sample's surface was sprayed with a chitosan 0.5% solution, while the remaining half was left without additive (control). In the second test, half was coated with carrageenan 0.5% as a bottom layer and chitosan 0.5% on top, while the other half of the surface was coated with the same additives (same order of application) but with a concentration of 0.2% each. Videos and pictures were taken.

3. Results and Discussion
3.1. Contact angle of a sessile water-drop
Water drops were not formed in control samples nor in the ones treated with carrageenan only, water applied was immediately absorbed. In contrast, water drops formed in samples Sand-Chi, Sand-Car/Chi and Sand-Chi/Car and their soil homologs, as shown in figures 1 and 2. Angles were obtuse, as table 1
shows, which reveal a hydrophobic surface and suggests improvement in the impermeability of the material. On sand, all angles fall within a range. Angles for soil samples showed similar values as the additives used were the same, except for the sample Soil-Chi, which shows a lower value. An important difference between soil and sand is that water drops on sand samples (Sand-Chi, Sand-Car/Chi and Sand-Chi/Car) remained on the surface for more than one day, while the ones formed on top of the soil were absorbed more rapidly. In the case of Soil-Chi, the drop was absorbed in about 3 seconds. For Soil-Chi/Car, the drop lasted around 128 seconds, while for Soil-Car/Chi sample, the absorption time was 67 seconds. The difference in contact angle results may be due not only to soil and sand chemical composition but also to their particle size, porosity and affinity to water. Even more, surface texture is also important when evaluating contact angles, in this respect, the lotus effect is explained by surface rugosity at the micro and nanoscale. On the other hand, the viscosity of the polymer solution might affect its deposition and distribution with soil or sand particles on the surface, carrageenan forms more viscous solutions than chitosan. And finally, once samples are dry, chitosan's insolvability in neutral water (from sessile water-drop) should form a less permeable film than carrageenan, which is water soluble.

![Figure 1. Water drops formed on samples a) Sand-Chi, b) Sand-Car/Chi and c) Sand-Chi/Car.](image)

![Figure 2. Water drops formed on samples a) Soil-Chi, b) Soil-Car/Chi and c) Soil-Chi/Car.](image)

### 3.2. Water drip resistance test

Results for sand and soil samples after 1 minute of drip test were similar and are shown in figure 3. Control samples of both materials showed instant erosion from dripping and after 30 s, a wide and deep hole was formed. Samples covered by a layer of chitosan and a top layer of carrageenan revealed the formation of a narrow hole after 10-15 seconds, exactly where the drop impacted the surface. The best resistance to water drop erosion was exhibited by samples covered by a layer of carrageenan and a top layer of chitosan in both samples, soil and sand, showed no damage at all after 1 minute. The time at which these samples showed damaged differed and can be observed in table 2.
3.3. Water runoff test
Sand with no additives was completely carried away by the flow of water as figure 4(B) illustrates. In comparison, all the samples treated with chitosan or a combination of carrageenan and chitosan solutions, as shown in figures 4(A), 4(C) and 4(D), resisted water erosion and avoided sand sliding, and water came out clear at the end of the tray after flowing over them. Lower concentrations of additives were also observed to successfully protect the samples.

![Figure 3. Pictures of drip test results for soil and sand samples, after 1 minute.](image)

![Figure 4. Water runoff tests over sand: (A)-Chitosan 0.5 % against (B)-Control; (C)-Carrageenan 0.5 % and chitosan 0.5 % (top) against (D)-Carrageenan 0.2 % and chitosan 0.2 % (top).](image)

Results and observations of all the tests suggest that chitosan was effective in changing the properties of the surface of loose soil and sand. Chitosan efficacy can be due to its cationic nature in solution (polycation) which can bind strongly to soil and sand particles, which are known to hold negatively charged surfaces [8]. On the other hand, carrageenan itself could not protect loose soil nor sand against water erosion, which may be due to its solubility in water. However, electrostatic interactions between carrageenan and chitosan (polyelectrolytes of opposite charges) may help stabilize the particles even more. Moreover, the higher viscosity of polymer solutions, which allows the formation of 3-dimensional bridges between the polymeric solution and the particles [8], together with their capacity to form films when the solvent is eliminated, may also contribute to hold particles attached to each other and in place.
4. Conclusions

Improvement of water erosion resistance and impermeability of soil and sand surfaces by application of biopolymers chitosan and carrageenan was demonstrated. As contact angle measurements of water drops suggest, waterproofing was achieved for all samples in which chitosan was applied (only momentarily in the case of soil), either as a sole additive or as part of a mixture, and also, when carrageenan was applied on top of a chitosan layer. Drip test's results revealed that a combination of layers of chitosan and carrageenan improved water erosion resistance, being the sample with chitosan on top the one that showed the best performance. A combination of 0.2% chitosan solution on top and 0.2% carrageenan on the bottom was also able to avoid sand from being carried away by water flow, as the runoff test results evidenced. Altogether, an additive consisting of chitosan on top of a carrageenan layer seems to be an effective means of soil and sand stabilization.

5. References

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