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Water-Retaining Efficiency of Starch-Based Hydrogel in Clay and Sandy Soils Under Different Administration Conditions

Eficiência de Retenção de Água do Hidrogel a Base de Amido em Solos Argilosos e Arenosos Sob Diferentes Condições de Administração

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Abstract

Water retention in the soil is crucial for maintaining soil structure and nutrient availability, thus ensuring productivity. However, clayey and sandy soils exhibit varying water retention capacities, which can limit agricultural output, particularly in sandy soils. This study assessed the efficacy of starch-based hydrogel (HG) as a water-retaining polymer for both sandy and clay soils. Results revealed a quantity-dependent water-retaining capacity in sandy soil, with up to 62 mL of water retention per gram of HG, while no such dependence was observed in clay soil. Dry HG incorporation into the soil resulted in enhanced water retention, whereas application in a swollen or sandwich form proved less effective due to mechanical issues and increased water loss via osmosis. The ability of HG to absorb water was influenced by ionic strength, with up to 5 times more absorption observed under conditions of low ionic strength compared to high ionic strength, attributed to the ionic nature of the HG matrix. Furthermore, HG showed consistent effectiveness across different matrices at both pH 5 and pH 7, suggesting its potential as a water-retaining agent and nutrient retainer. These findings lay the groundwork for the development of novel agricultural technologies tailored especially to sandy soil conditions.

Keywords: Starch-Based Hydrogel. Agricultural Productivity. Soil Water Retention. Sandy Soil Productivity.

Resumo

A retenção de água no solo é crucial para manter a estrutura do solo e a disponibilidade de nutrientes, garantindo assim a produtividade. Contudo, os solos argilosos e arenosos apresentam diferentes capacidades de retenção de água, o que pode limitar a produção agrícola, particularmente em solos arenosos. Este estudo avaliou a eficácia do hidrogel à base de amido (HG) como polímero retentor de água para solos arenosos e argilosos. Os resultados revelaram uma capacidade de retenção de água dependente da quantidade em solo arenoso, com até 62 mL de retenção de água por grama de HG, enquanto tal dependência não foi observada em solo argiloso. A incorporação seca de HG no solo resultou em maior retenção de água, enquanto a aplicação na forma inchada ou em sanduíche mostrou-se menos eficaz devido a problemas mecânicos e aumento da perda de água por osmose. A capacidade do HG de absorver água foi influenciada pela força iônica, com até 5 vezes mais absorção observada sob condições de baixa força iônica em comparação com alta força iônica, atribuída à natureza iônica da matriz de HG. Além disso, o HG apresentou eficácia consistente em diferentes matrizes tanto em pH 5 quanto em pH 7, sugerindo seu potencial como agente de retenção de água e retentor de nutrientes. Estas descobertas estabelecem as bases para o desenvolvimento de novas tecnologias agrícolas adaptadas especialmente às condições de solo arenoso.

Palavras-chave: *Hidrogel a Base de Amido. Produtividade Agrícola. Retenção de Água no Solo. Produtividade do Solo Arenoso.*

1 Introduction

Drought is a climate factor that directly affects the productivity of various cultures (Leite; Federizzi; Bergamaschi, 2012). The reduction of agricultural productivity is more intense in regions with sandy soil, as in the case of some northwester areas of Paraná, Brazil. In these regions, water retention capacity is extremely reduced (Suzuki *et al*., 2007). The sandy soil has high porosity, which means high hydraulic conductivity and low water storage capacity (Huang; Hartemink, 2020)these soils are increasingly used to provide food, feed, fiber, energy, and other services to our society. In this paper, we summarize some recent studies on sandy soils and review the main soil and environmental issues related to the understanding, use, and management. We classify the soil issues into three categories: 1. Therefore, cultures in this soil type suffer from constant water stress (Letey, 1958). Sandy soils do not retain nutrients easily due to the easiness of water infiltration, thus requiring great attention to fertilization, liming, and gypsum of this soil (Nolla; Minosso; Castaldo, 2023). Clay soils, on the other hand, present higher plasticity and agglutination capacity, becoming both more efficient in retaining nutrients and maintaining soil moisture for longer (Letey, 1958).

In periods of severe drought, regardless of their unique characteristics, both soils (sandy and clay) may suffer a reduction in productivity (Naorem *et al*., 2023; Saha; Sekharan; Manna, 2020). In this context, the search for alternatives that promote the absorption and retention of water in the soil, especially in regions of rainwater scarcity and water irrigation scarcity, is well-known to the scientific community (Liu *et al*., 2020; Liu *et al*., 2022; Patra *et al*., 2022;water availability is one of the principal ecological constraints that hinder agriculture's sustainability. The super absorbent polymer (agricultural Rizwan *et al*., 2021). Many studies have been carried out to discover ways for increasing water retention in soil (Eden; Gerke; Houot, 2017it lowers soil fertility that directly impairs agricultural crop production and affects a number of other soil properties like water retention capacity, aggregation and structure formation, soil mechanical strength or compactibility. Scarcity in plant available water poses a risk to agriculture, especially in drought-prone areas. However, the increase of organic waste recycling in agriculture may also lead to an increase in soil organic matter contents and to changes in related soil properties. Here, we review 17 long-term field experiments (≥9 years; Oladoseu *et al*., 2022; resulting in an acute water shortage. Presently, the agricultural sector consumes more than 70% of freshwater in most regions of the world, putting more pressure on water scarcity. Hydrogels are superabsorbent polymers that can hold plant nutrients and water when the soil around plant roots starts to dry out. Research evidence has revealed that water stored by hydrogel slowly returns to the soil, thereby increasing the volumetric water content of the soil. Hydrogel increases water use efficiency and irrigation intervals, decreases irrigation costs, and provides plants with the required nutrients and moisture. Numerous properties of hydrogels, including moderate water retention and high swelling, make them ideal as a safe delivery mechanism in agriculture for soil conditioners and agents for the controlled release of fertilizers. Numerous research publications on hydrogel polymer synthesis and its characteristics have been published. However, the current review emphasizes the critical role of superabsorbent hydrogels in an integrated approach for the balanced protection of seeds, plants, and soil to conserve the ecosystem. Wesseling; Ritsema, 2010). Certain organic residues can absorb and retain water up to 20 times its weight (Reicosky; Wilts, 2005). These residues tend to reduce the surface temperature and the penetration of wind in the soil, which contributes greatly to water evaporation. The problem with organic residues is the high amount necessary to achieve significance (Reicosky; Wilts, 2005).

Material Science represents a remarkable aid regarding agricultural developments. For example, its water-retaining polymers have already shown their efficiency under in vivo conditions. Hydrogels are three-dimensional (3D) materials formed by physical or chemical crosslinking of synthetic, natural, or artificial polymers, or by a mixture of them (Guilherme *et al*., 2005; Kathi *et al*., 2021)water scarcity and nutrient availability are major constraints for food production. Excess fertilization to make up for the limited nutrient availability in dry soils leads to nitrogen runoff and groundwater contamination. Reducing nitrogen leaching into surface water while providing adequate nutrition remains a major challenge. Superabsorbent polymers (SAPs. The 3D characteristic of these materials allows the absorption of water and nutrients, which enables their gradual delivery according to crop needs (Ullah *et al*., 2015; Rodrigues *et al*., 2023). Their water absorption might go from just a few times (≈ 1.1 g g^{-1}) (Pellá *et al*., 2023) up to more than 1500 times their initial mass (Ghobashy, 2018), all depending on the polymers forming the matrix and on the arrangement assumed by them during polymerization. Hydrogels with high water absorption capacity are called superabsorbents (Guilherme *et al*., 2005; Ramli, 2019).

Hydrogels based on natural polymers such as starch are often preferred for agricultural purposes due to their lower toxicity. However, these hydrogels are more prone to having their performance impaired due to mechanical stresses (Pellá *et al.,* 2023). It disrupts their 3D structure and might affect the efficiency of absorbing and retaining water in the soil (Li *et al.,* 2009). Blend formation is a viable alternative to overcome the limitations inherent in natural polymers (Pellá *et al*., 2023).

Although the use of hydrogels in agriculture is consolidated, the literature still does not have enough studies assessing the forms of administration and ideal dosages (Neto *et al*., 2017) studies of methids that minimize water use water are essential. As a result, agricultural hydrogels have been extensively tested in as a means of promoting agriculture improvements because of their water- and nutriente-retention characteristics. However, even though hydrogels are used in several sectors of Brazilian agriculture, there are still very few studies on their applications, the best methods and the quantities to be used. Consequently, there is a need for research into the applicability of this technology in Brazil, so that future research needs can be identified and appropriate decisions made at the production level. Therefore, the aim of this study was to collate currently available information on the applicability of agricultural hydrogels in Brazilian agriculture. Over the last decade, forestry is the sector in Brazil that has most studied and used hydrogels, but others such as fruit- and coffeegrowing have also been involved. The method of applying the polymer in granules directly mixed-in with growth substrates is the most used in the production of seedlings. However, use of hydrated gel at planting sites has also been explored. While synthetic hydrogels are most commonly used, those made of natural materials have great potential due to the low preparation costs and their in-soil biodegradability. The quantities of hydrogel used vary according to the target species, application method and objective. (LOPES MONTEIRO NETO et al., 2017. This lack of information may cause disagreements regarding the best administration form and the amount of hydrogel that must be added to the soil to achieve high levels of efficiency. Using the wrong hydrogel application protocol and dosage may lead to ineffective results (Flannery; Busscher, 1982; hydrophylic substance Permabsorb (1.6, 3.2, and 6.4 gm/1Mendonça *et al.,* 2013; Monteiro *et al.,* 2016)como o Cerrado, uma vez que o hidrogel possui a capacidade de aumentar a retenção de água no solo e fornece-la lentamente às plantas. Assim, o presente trabalho visa avaliar o efeito do hidrogel em plantio de recuperação em área degradada pela exploração de areia no bioma Cerrado. O delineamento experimental utilizado foi inteiramente casualizado, composto por 12 parcelas de 1.000 m² cada uma. Em metade das parcelas foi aplicado o tratamento com hidrogel (400 mL.

It should be reinforced that the efficiency of a hydrogel depends not only on the type of soil (Narjary *et al.,* 2012; Saha; Sekharan; Manna, 2020) but also on the physical-chemical characteristics of the hydrogel matrix itself. Thus, this work aimed to evaluate the water absorption and retention capacity in sandy and clay soils containing a starchy water-retaining hydrogel (HG; starch-g-poly (2-propenamide-co-2-propenoic acid) potassium salt). Both the hydrogel and the soils were characterized. Besides the amount of hydrogel added to the soils, this work also assessed the effect of adding the hydrogels in dry and swollen states, administrated as a layer (sandwiched between two soil layers), or mixed in the soil.

2 Material and Methods

2.1 Materials

Experiments were performed using clay and sandy soil dried in an oven at 105 °C for 24 h. The clay soil was collected in Maringá while the sandy soil was collected in Umuarama. Both cities are located in the state of Parana, in the South region of Brazil. The hydrogel chosen is the commercially one known as UPDT, which 88% of its composition consists of starch-g-poly (2-propenamide-co-2-propenoic acid) potassium salt. It is produced by the company United Phosphorus Limited (UPL), and here is generally mentioned as HG. Sodium chloride (NaCl) and sodium hydroxide (NaOH) were acquired from Sigma-Aldrich. Hydrochloric acid (HCl; 37%), sodium dihydrogen phosphate (NaH_2PO_4), and dibasic sodium hydrogen phosphate (Na_2HPO_4) were acquired from Synth. All the reactants were used as received.

2.2 Characterization of HG

Since the HG is commercially available, it was only characterized using a Fourier Transform Infrared Spectroscopy (FTIR) equipment from Thermo Scientific Nicolet iZ10 equipped with Attenuated Total Reflectance apparatus (ATR; iS10 Smart iTR equipment). The scans were performed from 4000 to 650 cm^{-1}, at a resolution of 4 cm^{-1}. The obtained spectrum is the mean of 128 scans. The obtained data were processed in data processing software regarding baseline subtraction and data normalization. The results are expressed by arbitrary units (a.u.).

The swelling capacity of hydrogels was evaluated in two different pH and two different ionic strengths. The pH responsiveness was assessed by placing known amounts of dry HG in beakers containing 50 mL of phosphate buffer solution (PBS) at pH 5 and pH 7 (adjusted using 0.1 mol L^{-1} NaOH or 0.1 mol L^{-1} HCl). The ionic-strength responsiveness was assessed by placing known amounts of dry HG in beakers containing 50 mL of NaCl solutions of concentrations equal to 1x10^{-5} or 0.1 mol L^{-1}. For both conditions, the samples were kept at room temperature (T ≈ 25 °C), and no stirring (magnetic, mechanical, or orbital) was employed.

The samples were weighed until sustaining the same value for three consecutive measures. This stable weight indicated that the samples had reached the swelling equilibrium, it is, they had swelled all the amount of water they could in that given experimental condition. This constant weight was used to calculate the degree of swelling (DS; g g^{-1}) using Eq. (1), in which W_d refers to the weight of the dry hydrogel and W_t to the weight of the sample swollen for time t.

$$DS = \frac{W_t - W_d}{W_d}$$

The swelling capacity analysis was performed in duplicate for each condition, and the results are expressed by mean ± standard deviation (SD; mean ± SD).

2.3 Physical and chemical characterization of the soils

The decanting method was used for the physical analysis (granulometry). In the chemical analysis, the pH was determined using a calcium chloride solution ($CaCl_2$). An extracting 1 mol L^{-1} KCl solution was used for the determination of exchangeable aluminum (Al^{3+}). The adsorbed Al^{3+} was then analyzed by volumetry using a diluted NaOH solution. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined by complexometry using EDTA as a standard solution. Potassium (K^+) and phosphorus (P) were determined using Mehlic's extracting solution (Teixeira *et al.,* 2017).

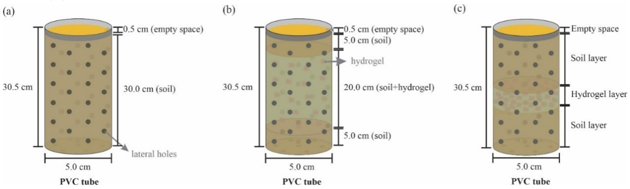
2.4 Experimental apparatus

The efficiency of the HG as a water-retaining system was assessed for two different soils, following the methods described in the literature (Narjary *et al.*, 2012; Mazen; Radwan; Ahmed, 2015), with adaptations in both cases.

Initially, PVC tubes were cut into smaller pieces (height = 30.5 cm; diameter = 5.0 cm). The cut PVC tubes were randomly punctured to form holes (diameter = 0.6 mm) throughout their entire structure to mimic horizontal water losses observed in in vivo conditions. The bottom of the tubes was sealed with TNT fabric (scotch-taped onto the tube's bottom part) to prevent soil losses throughout the experiment. The tubes were exposed to environmental conditions, during summer and fall. However, to prevent interferences from potential precipitations, they were placed under a plastic cover (1.85 cm in width, 1.75 cm in depth, and 0.55 cm in height).

Subsequently, the tubes were filled with soil (sandy or clay) in amounts that allowed mimicking their natural densities (1.10 g cm^{-3} for clay soil and 1.30 g cm^{-3} for sandy soil) (Rai; Singh; Upadhyay, 2017). Figure 1 provides a schematic representation of the setting used for each experimental condition. The control group (Figure 1(a)) consisted of 30.0 cm of the respective soil. Hydrogel (HG) was incorporated into the tubes in two sets: mixed with the soil in a layer covered by 5 cm of soil on each side (Figure 1(b)) or sandwiched between two soil layers (Figure 1(c)). The thickness of the HG layer depended on the amount added to each PVC tube. Both conditions containing HG were evaluated using four different amounts of the hydrogel: 0.00 g (control group), 0.50, 1.00, or 1.50 g.

Figure 1 - Schematic representation of the PVC tubes, the respective dimensions, and the distribution of soil and hydrogel in the tubes: (a) control group (no addition of HG), (b) HG mixed, and (c) HG sandwiched in the soil



Source: the authors.

Besides varying the experimental set, the hydration state of the HG was also evaluated. The respective amounts of HG (0.00, 0.50, 1.00, or 1.50 g) were added to the sets presented in Figure 1 (b) and (c) in the dry and swollen state. The dry state consisted of using the HG with no previous water exposure. Meanwhile, the respective amount of HG administrated in the swollen state was initially swollen in 10.0 mL of distilled water.

2.5 Water-retaining efficiency

The water-retaining efficiency was assessed by measuring mass variations between water additions. Hence, after preparing the tubes, the procedure started with the addition of 78.5 mL of water in each PVC tube to theoretically simulate regular rainfall (50 mm). The tubes were weighed (initial mass) immediately after this first water addition and subsequently placed under the plastic cover.

The weight of the tubes was registered every day for a period of 148 days (from February 23, 2022, to July 21, 2022), comprising the seasons of summer (45 days) and fall (103 days). New water additions were performed every 15 days. During summer, the volume of water added to the tubes was 78.5 mL (a total of three water additions). However, when the season changed to fall, the soil saturated quickly. Therefore, the analysis continued with the addition of 25 mm of distilled water every 15 days.

All experimental conditions were assessed in triplicate (n = 3), and the results are expressed by mean ± SD. Also, the results are presented in terms of the volume of water retained in the PVC tube (assuming a water density of 1.00 g cm^{-3}).

2.6 Determination of the electrical conductivity of distilled and leached water

The determination of the electrical conductivity was performed at the end of the analysis (148th day), using a portable Knup conductivity meter with an accuracy of approximately 2.0%. The water leached from the PVC tubes was transferred into a 50 mL beaker for the conductivity measure.

2.7 Statistical analyses

The obtained data were submitted to statistical analysis using one-way Analysis of Variance (ANOVA) and Tukey's test. The analyses were performed in the software Minitab® 19, working with a significance level of 95%.

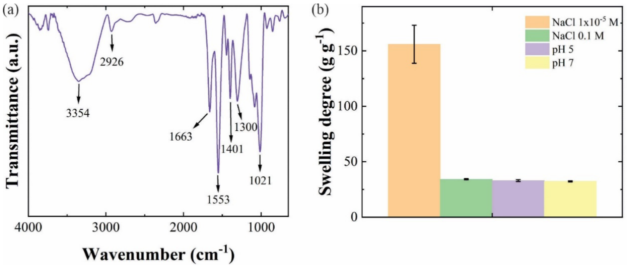
3 Results and Discussion

3.1 Characterization of the starch-based hydrogel

The ATR-FTIR spectra of HG (Figure 2(a)) presented the characteristic bands expected in a starch-based sample such as the broad band centered at 3354 cm^{-1}, attributed to the stretching of hydroxyl (-OH) groups (Peets *et al.*, 2019). However, this band also reflects the stretching of amine (-NH_2) groups grafted onto starch by a chemical modification reaction. The bands at 1663 cm^{-1} and 1401 cm^{-1} also confirm the presence of amide groups in the structure of the matrix. They are attributed to the stretching of amide carbonyl groups (-$CONH_2$) (Hamou; Djadoun, 2011; Meaurio; Cesteros; Katime, 1997) and C-N bonds (Peets *et al.*, 2019), respectively.

The polymer matrix of HG also had carboxylate (-COO^-) groups grafted onto its structure. The band at 1553 cm^{-1} matches the stretching of these groups (Peets *et al.*, 2019). The other bands observed in the spectra (2926 and 1300 cm^{-1}) describe the stretching and bending vibration of -CH bonds, respectively. The stretching of the several types of C=O bonds in the matrix justifies the band at 1021 cm^{-1} (Kizil; Irudayaraj; Seetharaman, 2002).

Figure 2 - (a) ATR- FTIR spectra of the dry starch-g-poly (2-propenamide-co-2-propenoic acid) potassium salt hydrogel and its (b) swelling degree under different pH and ionic strengths



Source: research data.

Given the ionic nature of the hydrogel matrix, parameters like pH and ionic strength might affect the swelling capacity. It was evaluated the swelling of the samples under two pH values (pH 5 and pH 7; to simulate soil conditions), and two ionic strengths (using 1x10^{-5} mol L^{-1} and 0.1 mol L^{-1} NaCl solutions). The results from Figure 2(b) evidence the similarity in swelling when the sample is exposed to pH 5 and 7. This lack of difference might be the result of the proximity between both pH values. It is also important to consider that the pK_a of carboxylic acids ranges at around 4.8 (Bruice, 2017). Above this pH, the groups are deprotonated and below pH 4.8, they are protonated. Therefore, it is also possible that the carboxylate groups were still in the negatively charged form in both pH. This result suggests that the HG would display a very similar performance within the pH range between pH 5 and pH 7.

Very different results were observed when the concentration of ions dissolved in the medium increased from $1x10^{-5}$ mol L^{-1} to 0.1 mol L^{-1}. These ions form ion-dipole interaction with the charged groups from the matrix and ultimately stabilize them. By doing so, the matrix experiences weaker repulsive forces between adjacent charged groups and inevitably swells less water. At the lowest ionic strength evaluated in this work ($1x10^{-5}$ mol L^{-1}), the swelling degree reached 155.9 ± 17.1 g of water per gram of HG. When the ionic strength increased to 0.1 mol L^{-1}, the swelling degree decreased to 34.2 ± 0.2 g g^{-1}.

The swelling degree at the ionic strength of 0.1 mol L^{-1} was very similar to the ones observed for the samples assessed at different pH values. It happens because the pH was assessed using PBS, which also is rich in dissolved ions. The obtained swelling results suggest that this matrix would be able to retain large amounts of water if exposed to nutrient-poor soils, but its water-retaining capacity would drastically decrease when exposed to nutrient-rich soil.

The ionic strength-responsiveness of this starch-g-poly(2-propenamide-co-2-propenoic acid) potassium salt hydrogel represents a significant drawback because, as a water-retaining system for agricultural purposes, it would be exposed to soils containing ionic species like magnesium (Mg^{2+}), calcium (Ca^{2+}), iron (Fe^{3+}), aluminum (Al^{3+}), chloride (Cl^-), carbonates (CO_3^{2-}), and nitrates (NO_3^-) (Kazanskii; Dubrovskii, 1992), for example. Hence, its effectiveness would potentially be conditioned to the concentration of ions in the soil.

3.2 Characterization of the clay and sandy soils

The clay and sandy soils were first characterized regarding their physical-chemical parameters. Table 1 presents the obtained results on the first day (for the control groups). As will be discussed in the following section, the sandy soil displayed a more appealing water-retaining capacity compared to the clay soils and was, therefore, chosen for further analysis. Table 1 also presents the results of the sandy soil containing dry and swollen HG after 148 days.

Table 1 - Physical and chemical analysis of clay and sandy soils with dry and swollen HG, before and after 148 days

Physical and Chemical Analysis	Day 0		Day 148		
	Control		Dry HG		Swollen HG
	Clay soil	Sandy soil	Clay soil	Sandy soil	Sandy soil
Clay (%)	66.55	13.35	–	–	–
Silt (%)	20.75	1.50	–	–	–
Sand (%)	12.7	85.15	–	–	–
pH-$CaCl_2$ (mol dm^{-3})	4.50	6.08	4.67	6.16	5.66
PO_4^{3-} (mg dm^{-3})	4.60	5.90	0.80	16.40	29.10
K^+ (mol dm^{-3})	0.10	0.15	0.31	0.33	0.46
Al^{3+} (mol dm^{-3})	0.30	1.50	0.00	0.00	0.00
Ca^{2+} (mol dm^{-3})	1.75	2.13	1.00	1.00	1.50
Mg^{2+} (mol dm^{-3})	1.00	1.25	0.50	0.25	0.50
I.E.C.*	7.81	5.04	6.48	3.33	4.08

*I.E.C. stands for ion exchange capacity.

Source: research data.

As expected, sandy soil has a high sand percentage, while clay soil has a high clay percentage. Regarding the chemical analysis, the sandy soil had the highest ionic character, since it contains the highest amounts of ions (PO_4^{3-}, K^+, Al^{3+}, Ca^{2+}, and Mg^{2+}). Despite the higher ionic content, clay soil still presented a higher ion exchange capacity.

The HG matrix would probably degrade, and it would inevitably lead to the leaching of groups from the matrix into the soil. The results from Table 1 confirm this hypothesis for sandy soils. The sandy soil containing the dry HG samples presented higher pH, PO_4^{3-}, and K^+ content. On the other hand, the Al^{3+}, Ca^{2+}, and Mg^{2+} content decreased after 148 days. As an anionic matrix, HG could interact with positively charged ions. Since the afore mentioned ions had more than one electron missing in their orbitals, they could also form more than one physical (coordination) bond with the matrix. By doing so, the K^+ ions from the matrix would be replaced by the bi or trivalent ions. Since the K^+ ions were no longer needed to stabilize the negatively charged groups in the matrix, they leached onto the soil. The Al^{3+}, Ca^{2+}, and Mg^{2+} content also decreased for the clay soil, confirming that the HG exchanged its K^+ ions. Distilled water (conductivity of 80 µS cm^{-1}) was added into tubes containing sandy soil without any HG addition and containing HG (added in the dry and swollen state). Table 2 portrays the results of nutrient leaching.

Table 2 - Electrical conductivity of the water leached from the tubes* containing sandy soil without (control group) and with HG, added in the dry and swollen state

Tube (with mixed hydrogel)	Conductivity (µS cm^{-1})
Distilled water	80
Control sandy soil	1221
Sandy soil + dry HG	558
Sandy soil + swollen HG	520

*The conductivity of the distilled water added to the tubes was not subtracted from the values presented above.

Source: research data.

Table 2 shows that the distilled water conductivity increased 15 times after leaching from the sandy soil without HG (control group). This result shows that the leaching process contributes to the removal of ionic nutrients from the soil. However, in the presence of HG, the soils tend to lose fewer nutrients (~56% considering the average between 558 and 520 μS cm^{-1}). This result is particularly appealing for agriculture since it suggests that the HG would not only retain water, but nutrients as well. This result is in agreement with the literature. For example, a study carried out by Navroski *et al.* (2015) indicated that the dosage of 4.5 g L^{-1} of hydrogel contributed to increasing the amount of macro and micronutrients in plant tissues of *Eucalyptus dunnii* seedlings (Navroski *et al.*, 2015). The nutrient retention by the hydrogel reached 22, 2.8, and 10 g kg^{-1} of N, P, and K, respectively. In another study, conducted by Fagundes *et al*. (2015), the incorporation of 2 g L^{-1} of hydrogel into the substrate reduced nutrient losses by leaching, helping the growth of passion fruit seedlings.

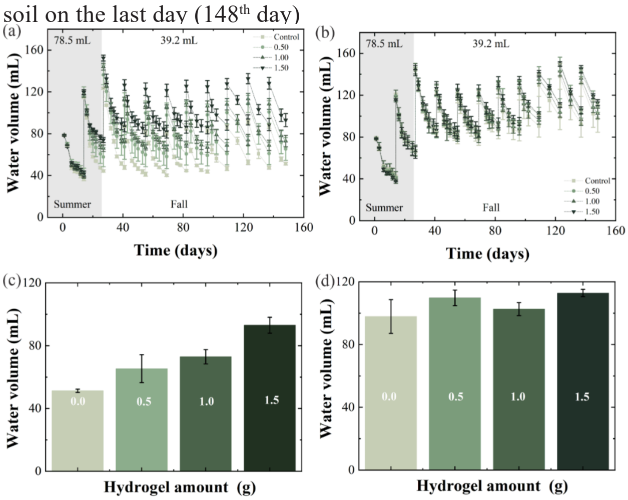
Another interesting aspect observed in Table 2 is that, although the swollen HG applied mixed in the soil did not show a positive result in water retention (as will be discussed in the following section), it was still able to retain ionic species in practically the same amount as the dry HG mixed with the soil. It reinforces the hypothesis of the formation of strong physical interactions between the matrix and the polyvalent cations.

3.3 Water-retaining capacity of the HG applied in different conditions

Each type of soil has its unique characteristics. On the one hand clay soils are known for their rich nutrient content, moderate pH, and good water-retaining capacity (Letey, 1958), sandy soils, on the other hand, are poor in nutrients and lose water more easily (Huang; Hartemink, 2020)these soils are increasingly used to provide food, feed, fiber, energy, and other services to our society. In this paper, we summarize some recent studies on sandy soils and review the main soil and environmental issues related to the understanding, use, and management. We classify the soil issues into three categories: 1. Figure 3 presents the results of the dry HG in retaining water in the afore mentioned soils, which comprised the end of the summer (27 days) and fall (121 days). The peaks represent water additions to the PVC tubes (a total of eleven additions), and the exponential decay represents water lost by the soil throughout the 15 days in-between water additions.

The results indicate that the sandy soil lost water from one addition to another (Figure 3(a)) even during summer. However, the samples containing HG lost less water than the control. This soil also portrayed a more homogeneous behavior in the first six water additions carried out during fall. Nevertheless, the water retained by the soil slowly increased during the last two water additions performed in this season. Considering that (a) the HG has ionic groups in its structure, (b) it is formed by a biodegradable polymer, (c) it was exposed to natural conditions (presence of bacteria, soil compression, temperature changes, etc.), and (d) the HG structure might break if prolongedly exposed to aqueous environments. One could assume the sandy soil absorbed some of the charged groups leached from the HG during the time experiments, which corroborates the results from section 3.2. It probably changed the ion exchange capacity of the sandy soil and contributed to the retention of water molecules.

Figure 3 - Water variation volume as a function of time for (a) sandy soil, and (b) clay soil containing different amounts of HG (0.0, 0.50, 1.00, and 1.50 g; added while dry) mixed in the soil, and the amount of water retained by (c) sandy soil and (d) clay soil on the last day (148th day)



Source: research data.

From (Figure 3(b)), in the water additions performed during summer, the HG was not at all efficient in retaining water in clay soil, losing even more water than the control (clay soil without any added hydrogel). The ionic strength-responsiveness (Figure 2(b)) presented by this hydrogel might justify this behaviour. As mentioned before, clay soils are rich in nutrients, which are mostly formed by salts, and have a high water-retaining capacity. The HG would not be efficient in moisture contents close to field capacity because the soil itself would be highly hydrated. However, as the soil loses moisture and its inherent water retention forces decrease, the HG should effectively contribute to higher water retention. It happened during fall when the volume of water added to the tubes changed from 78.5 to 39.2 mL.

The HG became slightly more efficient in retaining water in the clay soil after the sixth water addition during fall. In this case, the lower moisture content of the soil plus the lower ionic strength probably favoured the swelling of the matrix, which agrees with the results discussed in Sections 3.1 and 3.2.

Despite increasing water retention in clay soils, the HG was not as effective as it could have been. Besides the effects of the moisture content and ionic strength, the pressure from the soil might have also compromised water retention. As the matrix swells water, its chains expand. If they cannot expand, they will probably not swell as much water as they could.

It is also possible that the late positive effect of the HG in the clay soil was the result of chemical changes in the matrix. This work used a matrix with ionic groups in its structure, as discussed in Section 3.1. Hence, it is possible that the acidic pH of the soil (pH = 4.50; Table 1) led to a partial neutralization of the negatively charged groups. It would inevitably decrease the ionic strength responsiveness presented by the matrix and could probably increase its swelling capacity in high ionic strength mediums (like clay soil). However, even though the increase in potassium content in the clay soil supports the hypothesis of chemical changes to the matrix (Table 1), it is impossible to quantify the extent of this change, especially because the overall ionic content of the soil decreased throughout the experiments. Hence, it is not possible to affirm which possibility contributed more to the behaviour observed in Figure 3(b).

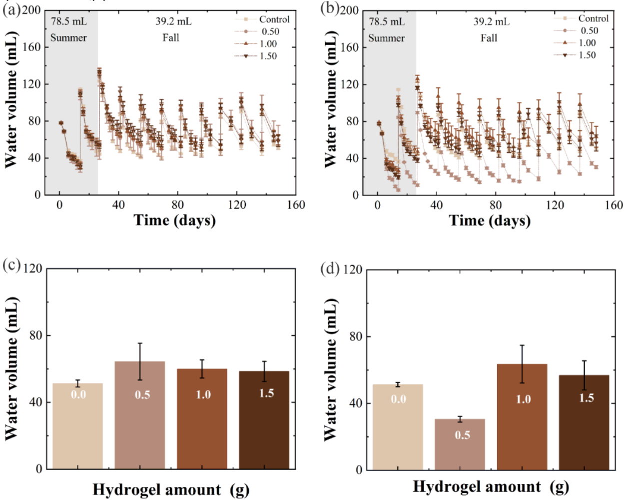
Comparing the results for the different soils evaluated in this work, the dry HG was not immediately effective in clay soil. On the other hand, in sandy soil, it started retaining water even since the first days (Figure 3(a) and (b)). Intriguingly, in terms of water-retaining capacity, the matrices retained more water in clay soil (Figure 3(d)) than in sandy soil (Figure 3(c)). The air permeability of each soil might justify this behaviour. Sandy soil has higher air permeability than clay soil. As a consequence, the soil loses more water regardless of whether it has hydrogel or not (Letey, 1958).

Regarding the effect of the amount of HG added to the soil, Figures 3(a) and (c) suggest almost a linear tendency in water retaining capacity in sandy soils by increasing the amount of the hydrogel from 0.00 g to 1.50 g. The same cannot be said about clay soils (Figure 3(b) and (d)). While the effect of the amount of HG was clearly seen in the sandy soil after 20 days, for clay soil, it only started to appear after 100 days and was still not statistically different at 95% significance. It suggests that increasing the amount of HG in clay soil might be neither efficient nor cost-effective. It would not represent an issue for sandy soil, as confirmed by the statistical comparisons.

Similar results were found in the literature. It was found an increase in water availability as a function of the increasing hydrogel doses, especially for sandy soil. Additionally, the hydrogel behaviour was studied in three different doses in sandy soil, observed that the treatment with the highest dose (40 g per pot) reported the highest values of water retention in the soil (Idrobo *et al.,* 2010).

Figure 4 portrays the results of the application of the HG in the sandwiched form, which is, a layer of hydrogel between two layers of soil (Figure 1(c)). The samples containing initially dry HG (Figure 4(a)) presented a similar behaviour to the ones displayed in Figure 3. The results started indicating higher water-retention by the samples (compared to the control group) only after 20 days. Three factors might justify this behaviour. First, the air permeability in sandy soils is higher than in clay soils. It increases the loss of moisture content. One also has to consider that (2) the HG matrix is highly hydrophilic and (3) the swelling of outer HG portions is faster than inner portions (Ganji; Vasheghani-Farahani; Vasheghani-Farahani, 2010). Therefore, it is possible that, during summer, the amount of water added to the tubes was not enough to ensure the reaching of the swelling equilibrium. In this case, the water retained by the HG would be more prone to be lost due to the higher air permeability. As the water started being retained in the inner portions of the gel, its loss became more complicated (because it depended on the combination of chain relaxation and diffusion processes) (Ganji; Vasheghani-Farahani; Vasheghani-Farahani, 2010) and a slower process. It would consequently improve the efficiency of the HG as a water retaining system.

Figure 4 - Water variation volume as a function of time in sandy soils containing different sandwiched amounts of HG (0.0, 0.50, 1.00, and 1.50 g) administrated in (a) dry state, and (b) swollen; and the amount of water retained by the sandy soil with sandwiched (c) dry and (d) swollen HG on the last day (148th day)



Source: research data.

The water-retaining results during fall corroborate the hypotheses presented in the paragraph above. As new water additions were done, less water was lost by the matrixes. However, the tubes containing 1.5 g of HG were expected to retain more water than the ones containing fewer amounts. The amount of water retained on the last experiment day was very similar in all of the samples (Figure 4(c)). They were even statistically equal to the control group. It suggests that adding the hydrogel in a dry state and sandwiched between layers of soil would neither be efficient nor effective. Table 3, analyse the water retention on the 148th day of the experiment for the sandwiched HG added to the sandy soil in the dry and swollen form.

Table 3 - Water retention on the 148th day of the experiment for the sandwiched HG added to the sandy soil in the dry and swollen form*

Amount of HG (g)	Dry HG	Swollen HG
0.00	51.30 ± 1.30^{aA}	51.30 ± 1.30^{abA}
0.50	64.39 ± 11.01^{aA}	30.55 ± 1.69^{bA}
1.00	59.96 ± 5.42^{aA}	64.86 ± 13.34^{aA}
1.50	58.55 ± 6.01^{aA}	56.80 ± 8.72^{aA}

*(mean ± SD)^{aA} that does not share the same letter are statistically different at 95% of significance. Lower case letters refer to the comparison between different amounts of hydrogen under the same condition (same type of soil) while upper case letters refer to the comparison of the same amount of hydrogen under different conditions (sandy or clay soil).

Source: research data.

A very different behaviour was achieved when the HG added between two layers of soil was already swollen (Figure 4(b)). Even though the matrices were not exposed to an aqueous environment for a time long enough to reach the swelling equilibrium before being placed in the tubes containing sandy soil, they probably retained more water in inner portions than they could have retained during the first water additions (if they had been placed in the tubes in the dry state). Ironically, during the first 15 days (interval between the first and second water addition), all tubes containing HG lost even more water than the control group. After the second water addition, only the tube containing 0.50 g of HG lost more water than the control, and this behaviour was consistent throughout the entire experiment.

The higher air permeability in sandy soils might, one more time, explain the observed behaviour. However, it is important to acknowledge that the tubes containing the swollen HG had more water to lose than the control. Considering the principle of osmosis, the hydrogels (medium more concentrated, in this case) might have released higher amounts of water into the soil (medium less concentrated, in this case). Since sandy soil is not efficient in retaining water, the water released from the HG was inevitably lost by evaporation.

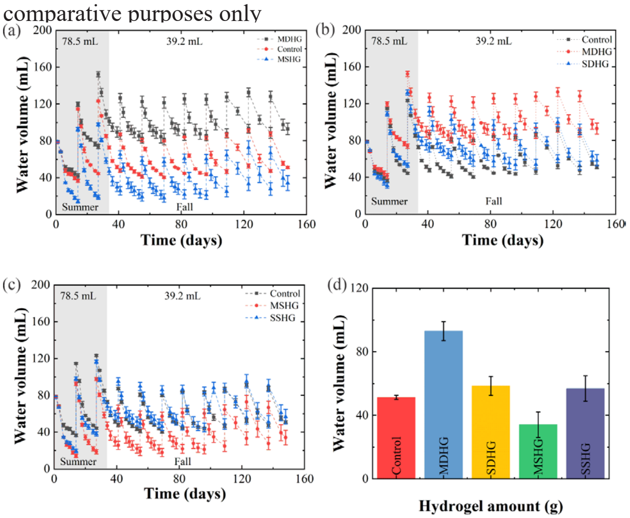
A smaller amount of water was lost with 1.00 and 1.50 g of HG compared to the control. The formation of a thicker hydrogel layer might have aided water retention. In this case, the physical interactions formed between adjacent HG particles may have created what would resemble a new hydrogel matrix (physically combined), formed by inner and outer portions. Hence, the thicker the layer, the harder would be to lose water retained in inner portions. Although the results confirm this hypothesis (Figure 4(d)), statistical analysis confirms that the water-retaining capacity of the tubes containing 1.00 and 1.50 g was statistically equal to the water-retaining capacity of the control group

Figure 5(a) compares the water-retaining behaviour of the HG, mixed with the sandy soil, administrated in dry (MDHG) and swollen (MSHG) states. The results evidence the better performance of the dry HG mixed in the soil. This condition led to the best results among all the experimental conditions, retaining ≈ 93 mL of water on the 148th day of the experiment, Figure 5(d).

Comparing the mixed dry HG (MDHG) and sandwiched dry HG (SDHG) (Figure 5(b)), MDHG displayed a better performance. As the amount of HG increased, the retention efficiency also increased in the MDHG samples, which retained 58% more water than the SDHG samples, and 83% more than the control group. The best performance might be the result of (1) the leaching of ionic groups from the mixed HG followed by the absorption of these groups by the soil, and (2) a potentially higher swelling behaviour in MDHG. However, it is also possible that (3) the mixed HG had more space to expand as it swelled water, allowing the HG pieces to reach their full swelling capacity.

The HG administrated in swollen form (mixed swollen HG (MSHG) and sandwiched swollen HG (SSHG); Figure 5(c)) had an inferior performance compared to the HGs administrated in a dry state.

Figure 5 - The general comparison regarding the water variation volume (mL) as a function of time for sandy soil with HG (1.50 g) administrated as (a) mixed dry HG (MDHG) and swollen HG (MSHG), (b) mixed dry HG (MDHG) and sandwiched dry HG (SDHG), and (c) mixed swollen HG (MSHG) and sandwiched swollen HG (SSHG) throughout 148 days; (d) and the amount of water retained by the sandy soil (containing 1.5 g applied in different conditions) on the last day of the experiment. The control group consisted of sandy soil without HG. The data for the control, MDHG, SDHG, and SSHG were repeated here for comparative purposes only



Source: research data.

Despite the different water-retaining efficiencies, which can be clearly observed in Figure 5(d), the statistical results confirm that MDHG retained the highest amount of water among all samples, and it was statistically different from all of them at 95% significance. The MSHG condition led to the worst results among all (even worse than the control group), and it was also statistically different them the other samples at 95% of significance. Even though the conditions SDHG and SSHG retained more water than the control group, they were still statistically equal at 95%.

The results presented in this work indicate that HG would be effective if mixed with sandy soils in a dry state. The results also indicate that, in this condition (MDHG), higher amounts of HG would be beneficial for water-retaining purposes. For the other conditions, no significant gain was observed by increasing the amount of hydrogel.

In a recent paper, it was observed productivity increases (up to 15%) in tomato crops by adding 35 kg per hectare of the same hydrogel evaluated in the present work (Jeevan *et al.*, 2023). The authors also reported a more efficient use of nutrients (nitrogen, phosphorous, and potassium) in irrigated soils containing the hydrogel (Kathi *et al.,* 2021)water scarcity and nutrient availability are major constraints for food production. Excess fertilization to make up for the limited nutrient availability in dry soils leads to nitrogen runoff and groundwater contamination. Reducing nitrogen leaching into surface water while providing adequate nutrition remains a major challenge. Superabsorbent polymers (SAPs.

4 Conclusion

By the ionic-strength responsiveness that this particular matrix would is more effective as a water-retaining system in soils with low nutrient content. Also, the matrices displayed very similar swelling capacities at pH 5 and 7, suggesting that they would be equally effective in retaining water under common pH conditions of soils. Dry HG mixed in the soil retains more water in clay soil than in sandy soil. However, the HG would still be a more efficient water-retaining system in sandy soil than in clay soil, especially because sandy soils lose water more easily than clay soil. Also, sandy soil displays an amount-dependent water-retaining efficiency, which is not observed for clay soil. Therefore, further experiments were performed only for sandy soil. The water-retaining capacity considerably decreased when the hydrogels were mixed in the soil in a swollen state or sandwiched in both (dry and swollen) states.

Despite the different effectiveness, soil characterization analyses indicated that the hydrogels exchanged ions with the soil. The potassium content increased in all cases while the amount of Al^{3+}, Ca^{2+}, and Mg^{2+} decreased. Hence, HG would be effective as a water-retaining matrix and would still potentially be a nutrient-retentor as well. However, further studies about the nutrient-retaining capacity of HG are still prospects of this work.

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