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CARLA DANIELLE VASCONCELOS DO NASCIMENTO

HYDROGELS FOR APPLICATION IN SOILS UNDER ABIOTIC STRESSES OF DRYLANDS

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2020

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Thesis presented to the Graduate Program in Soil Science of the Federal University of Ceará, as a partial requirement to obtain Doctor's degree in Soil Science. Area of concentration: Management and conservation of soil and water.

Advisor: Professor Mirian Cristina Gomes Costa.

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To the Supreme Creator of the universe. To my parents Augusto and Zenilda. To my brother Ícaro and my husband Alan.

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ABSTRACT

The use of superabsorbent hydrogels for application in soils has been studied once they can retain water to improve soil water availability for plant growth. However, the loss of water absorption/retention capacity of hydrogels raises doubts about their long-term efficacy, since there are evidences that abiotic factors affect their efficiency, degradation, and residual levels of acrylamide. Three laboratory studies were carried out to evaluate hydrogels under temperature and salinity stresses. In the first study, the effects of salinity on hydrogel efficiency and potential degradation were evaluated through an experiment in split plot design with four evaluation times (30, 60, 90 and 120 days), five salinity levels (0.003, 0.5; 1.5; 3.0 and 6.0 dS m^{-1}), and four repetitions. The swelling, composition, and residual acrylamide concentration of a commercial hydrogel were evaluated. In the second study, the effect of temperatures on the physical attributes of soil amended with commercial hydrogel was evaluated through an experiment in split plot scheme with four temperatures (30; 45; 65 and 105 °C), four exposure times (40, 70, 100, and 130 days), and four repetitions. Moisture at field capacity and permanent wilting point, available water, soil density and porosity were evaluated. The third study was a factorial experimental design in a (3x4x2) scheme. The treatments were three hydrogels (A, B, and C), four temperatures (20, 30, 40, and 65 °C), and two salinities (0.003 and 3.0 dS m^{-1}) with four replications. The swelling degree and the residual acrylamide concentration of the hydrogels were measured. Data were analyzed with univariate (for all studies) and multivariate statistics (for the third study). The first study revealed that there is a reduction in the hydrogel capacity for water absorption over time and with increasing salinity levels. Despite abiotic factors compromising water absorption by the hydrogel, in the second study beneficial effects on soil water storage capacity (up to three times increase), density (reduction of up to 15%), and porosity (up to 15% increase) were observed. Temperature tolerance of the hydrogels evaluated in the third study should be improved so they can be used in regions with high temperatures and salinity levels. Residual acrylamide levels of hydrogels decreased up to 95% over 30 days and are safe for application to soils. In general, anionic superabsorbent co-polymers have the potential to contribute to soil management under abiotic stresses typical of drylands.

Keywords: Superabsorbent polymers. Water management. Hydrogel in agriculture. Hydrogel for reforestation.

RESUMO

O uso de hidrogéis superabsorventes para aplicação em solos tem sido estudado uma vez que podem reter água, melhorando sua disponibilidade no solo para o crescimento das plantas. No entanto, a perda da capacidade de absorção/retenção de água dos hidrogéis levanta dúvidas sobre sua eficácia a longo prazo, uma vez que há evidências que fatores abióticos afetam sua eficiência, degradação e níveis residuais de acrilamida. Três estudos de laboratório foram realizados para avaliar hidrogéis sob estresse térmico e salino. No primeiro estudo, os efeitos da salinidade na eficiência e degradação do hidrogel foram avaliados através de um experimento em parcelas subdivididas, com quatro tempos de avaliação (30, 60, 90 e 120 dias), cinco níveis de salinidade (0,003, 0,5; 1,5; 3,0 e 6,0 dS m^{-1}) e quatro repetições. O intumescimento, a composição e a acrilamida residual de um hidrogel comercial foram avaliados. No segundo estudo, o efeito das temperaturas nos atributos físicos do solo adicionado de hidrogel foi avaliado através de um experimento em parcelas subdivididas com quatro temperaturas (30; 45; 65 e 105 °C), quatro tempos de exposição (40, 70, 100 e 130 dias) e quatro repetições. Foram avaliadas a umidade na capacidade de campo e ponto de murcha permanente, água disponível, densidade e porosidade do solo. O terceiro estudo apresentou esquema (3x4x2) fatorial. Os tratamentos foram três hidrogéis (A, B e C), quatro temperaturas (20, 30, 40 e 65 °C) e duas salinidades (0,003 e 3,0 dS m^{-1}) com quatro repetições. O grau de intumescimento e a acrilamida residual dos hidrogéis foram medidos. Os dados foram analisados com estatística univariada (para todos os estudos) e multivariada (para o terceiro estudo). O primeiro estudo indicou que há redução na capacidade de absorção de água do hidrogel com o aumento do tempo e salinidade. Apesar dos fatores abióticos comprometerem a absorção de água pelo hidrogel, no segundo estudo foram observados efeitos benéficos na capacidade de armazenamento de água no solo (aumento de até três vezes), densidade (redução de até 15%) e porosidade (aumento de até 15%). A tolerância à temperatura dos hidrogéis avaliados no terceiro estudo deve ser aprimorada para que possam ser utilizados em regiões com altas temperaturas e níveis de salinidade. Os níveis residuais de acrilamida dos hidrogéis diminuíram até 95% em 30 dias, sendo seguros para aplicação em solos. Em geral, copolímeros aniônicos superabsorventes têm o potencial de contribuir no manejo do solo sob estresses abióticos típicos de regiões secas.

Palavras-chave: Polímeros superabsorventes. Manejo da água. Hidrogel na agricultura. Hidrogel para reflorestamento.

CONTENTS

1 INTRODUCTION

Drylands play an important role in global ecosystems, housing more than two billion people. The climate in these regions is characterized by seasonal rains, recurrent drought years, and a high rate of evapotranspiration. Soils in these areas are often characterized as poorly weathered and shallow resulting in a low water storage capacity and high vulnerability to erosion. High temperatures and salinity are also aspects observed in drylands.

Semi-arid regions fall under the classification of Drylands. Agriculture in these regions has been suffering from water scarcity and decreased crop yields, being the forest sector also affected by water limitations. To feed a growing global population and increase water use efficiency, it is essential to carefully use natural resources, including the soil, in these regions. Global expansions of Drylands will increase the population affected by water scarcity and land degradation. This has led to a growing interest in the development of practical and accessible solutions.

Considering the severe water limitation in arid and semi-arid regions for irrigation, the use of soil conditioners is an alternative that can improve water availability for plant establishment and survival. Between these conditioners are the hydrogels that started to be studied since they allow to minimize the problems associated with water scarcity. However, there are doubts about their long-term effectiveness because there is evidence that their efficiency and degradation are affected by high temperatures, excess of salts in the medium in which they are used (abiotic factors typical of semiarid regions), and time since application.

Previous studies have indicate that increased temperature compromises the functionality of agricultural hydrogels since the absorption/retention of water is reduced with temperature rises. The valence of charges and the concentration of salts in the swelling solution of the hydrogels reduce water absorption, as electrical conductivity of the solution increases. In addition, the degradation of hydrogels can be accelerated by the high concentration of salts in the irrigation water. Further, the efficiency of hydrogels has been reported to decrease a few months after application.

Thus, there is a need to study existing and develop new hydrogels, which are more tolerant of adverse abiotic factors that occur in arid and semi-arid regions. Also, the level of acrylamide monomer (C_3H_5NO), remaining in the synthesis process, is an important issue due to its toxicity. Anionic PAM is most commonly used as a soil conditioner because it has low mobility and is associated with residual acrylamide monomer levels of <0.05%.

Given the need for knowledge on the use of hydrogels for the development of crops of interest and for revegetation of degraded areas in edaphoclimatic conditions of arid and semi-arid regions, the following hypotheses were raised: i) despite the interaction between salinity and time affecting the efficiency and degradation of commercial hydrogels, reducing their long-term durability, it is possible to obtain benefits from their use in dry regions; ii) even in the face of thermal stress and prolonged exposure times, commercial hydrogel provide beneficial effects on water storage capacity, soil density, and porosity; iii) given the interaction between salinity and temperature, and the characteristics of a hydrogel that provides improvements in the soils of dry regions can be identified; iv) the intrinsically low residual acrylamide content of hydrogels does not increase under the abiotic stresses of high temperatures and/or salinity and therefore does not represent an environmental risk.

The general objective of the study was to evaluate the efficiency, potential degradation, and residual acrylamide concentration of superabsorbent polymers (hydrogels) using abiotic factors (temperature and salinity), with the aim to promote their use as conditioners for agriculture and for revegetation of arid and semi-arid regions.

2 LITERATURE REVIEW

2.1 Land degradation in Drylands

In the global context, agriculture is predominantly dependent on rainfall. Uncertainties in the frequency and pattern of rainfall in arid and semi-arid areas result in crop losses every year. However, to feed a global population in constant growth, it is necessary to use the lands of these regions, in addition to using natural resources judiciously (THOMBARE *et al*., 2018).

Drylands, which include arid and semi-arid ecosystems, cover 41% of the earth's surface, play an important role in the global ecosystem, and are home to more than two billion people (HOOVER *et al*., 2020). The semi-arid regions are those in which the addition of water by precipitation is less than losses due to evaporation and plant transpiration. These regions comprise 1/3 of the planet's continental land mass, are home to 1.0 billion people, and are responsible for 22% of food production (SANTOS *et al*., 2016). Water scarcity, high intensity and low-frequency precipitation characterize semi-arid regions (SANTOS *et al*., 2016). High temperatures, poorly weathered soils, and small biomass production are also associated with these regions (ARAÚJO FILHO, 2013).

To characterize the semi-arid areas, the Aridity Index (AI) was defined, which is the ratio between precipitation and evapotranspiration. Semi-arid regions are associated with an AI value ranging from 0.20 to 0.50 and arid regions an value ranging 0.05 to 0.20 (MELO FILHO; SOUZA, 2009). Severe water scarcity is becoming common in many arid and semi-arid regions of the world (MOHAMMADINEZHAD; AHMADVAND, 2020), with water management being one of the biggest challenges for these regions (ABOBATTA, 2018).

Global Drylands have expanded over the past sixty years and will continue to expand into the 21st century. At the end of this century, the dry areas of the world are projected to be 10% higher than in 1961-1990 climatology. The greatest predicted expansion of semiarid regions will occur in the northern Mediterranean, southern Africa, and North and South America. Global expansions of arid lands will increase the population affected by water scarcity and land degradation (FENG; FU, 2013).

Soils in arid and semi-arid regions are being rapidly degraded (PROSDOCIMI *et al*., 2016). Natural factors that cause degradation problems are based mainly on climate, hydrology, topography, geology, and vegetation. On the other hand, anthropic factors are related, for example, to land use (IBAÑEZ *et al*., 2014; MUNOZ-ROJAS *et al*., 2015). Additionally, in arid and semi-arid regions there is a greater potential for salinization due to high evaporation, low precipitation, and soil characteristics (such as its mineralogy) (ACOSTA *et al*., 2011).

The Brazilian semiarid region is one of the largest and most populous in the world. More than eighteen million people live in this region, with eight million in rural areas (FILHO; SOUZA, 2009). The Brazilian semi-arid region comprises an area of approximately 970,000 km^2 (LAPOLA *et al*., 2014), and it is estimated that only 54% of the native vegetation known as "Caatinga" is preserved (ALTHOFF *et al*., 2018; LAPOLA *et al*., 2014).

The soils in the Brazilian semiarid region are poorly developed, mineral-rich, stony, and shallow. This compromises water infiltration and reduces water retention capacity, the latter being an important limiting factor for plant production in that region. Soil classes of LUVISSOLOS, PLANOSSOLOS, and NEOSSOLOS predominate in this region of Brazil (OLIVEIRA *et al*., 2009).

The removal of the Caatinga, combined with long periods of drought and the characteristics of the soils favours accentuated degradation of the soils, leaving them uncovered and exposed for a longer time to the action of climatic agents. This reduces their productive potential causing often irreversible damage to the environment (TREVISAN *et al*., 2002).

Semiarid soils are undergoing an intense process of desertification, as in conventional agriculture, there is a replacement of natural vegetation by crops and/or pasture without the adoption of conservationist practices, which is exemplified by the use of fire in the preparation of agricultural areas. Conventional agricultural systems in the Brazilian semiarid region are associated with reduced soil organic carbon stocks (MEDEIROS *et al*., 2020). The reduction in organic matter content is a problem associated with soil degradation, with a negative effect mainly on availability of nutrients, the stability of aggregates, and microbial activity (BAYER; MIELNICZUK, 1999). Deforestation and irrigated crops are leading to soil salinization, further increasing the evaporation of the water contained in them and accelerating the desertification process (GARDA, 1996).

The combination of anthropic pressure and aridity led to the extreme degradation of large expanses of Caatinga in the Brazilian semi-arid region, giving rise to so-called ‘desertification hotspots’. Thus, means of preserving biodiversity and developing strategies to recover these areas are urgent (SILVA *et al*., 2014). Additionally, soil degradation implies a reduction or loss of its productive potential. Consequently, it is necessary to find alternatives to maintain/improve agricultural production. The use of soil conditioners, as hydrogels, that can favor the revegetation of degraded areas as well as agricultural production in semi-arid regions is a strategy to be studied aiming at the functioning of ecosystems and agro-ecosystems.

2.2 Importance of soil cover for the rehabilitation of degraded soils

Regardless of the purpose of an environmental rehabilitation program, the actions presuppose the use of soil protection measures, among which is the formation and maintenance of soil cover (LONGO; RIBEIRO; MELO, 2010). Soil cover is considered the most important factor controlling the movement of runoff the soil surface. Vegetation reduces runoff velocity, strengthens and maintains soil structure and soil retention by plant roots (ARAÚJO FILHO, 2013).

The lack of soil cover contributes to the increase of the erodibility and soil density, being preponderant for the beginning of the runoff (ARTEMI CERDÀ; MORERA; BODÍ, 2009). Changes in soil cover, such as transition from forest to non-forest systems, results in increased soil loss due to higher rates of runoff and erosion (RICHEY *et al*., 2002). The lack of soil cover resulting from the low biomass production of agricultural crops also favors soil degradation.

Revegetation and generation of high biomass added into the soil as crop residues are considered an effective tool for improving soil quality and for rehabilitating degraded environments (WANG *et al*., 2012). Furthermore, revegetation is an effective method to control desertification, especially in arid and semi-arid regions, as an example from China, where revegetation has been consistently implemented since the 1950s (CHEN *et al*., 2017).

2.3 Abiotic factors affecting soil cover in arid and semi-arid regions

2.3.1 Soil temperature

Temperature is a factor that plays an important role in soil chemical, hydrological and biological processes (BHATTI *et al*., 2000). It influences the decomposition of organic matter, availability of nutrients, soil thermal dynamics (YI *et al*., 2009), seedling emergence and mortality (TER HEERDT *et al*., 2017), plant growth (WANG; SHAO; LIU, 2013), respiration of soil organisms, nitrification and denitrification - which also influences CO_2 and N_2O emissions (LUO *et al*., 2012). Soil temperature also has an influence on the physical properties of water (movement and availability) and soil air (GASPARIM *et al*., 2005). Soil temperature is a dynamic property since it changes with climatic variability and other processes (AWE; REICHERT; WENDROTH, 2015).

In general, the greatest changes in soil temperature occur after the removal of vegetation which increases solar radiation incidence on the soil surface and decreases plant transpiration and interception of water by the canopy (SCHARENBROCH; BOCKHEIM, 2007).

Vegetation removal is common in semi-arid regions, where extractive agricultural systems and overgrazing for livestock are observed (ARAÚJO FILHO, 2013). Agriculture is developed at the expense of indiscriminate deforestation, burning, and inadequate fallow periods. There is also intense extraction of firewood and wood, contributing to the reduction of vegetation in the Caatinga (ARAÚJO FILHO, 2013). The removal of the Caatinga, combined with long periods of drought, causes marked degradation, leaving the soil exposed for long periods to the actions of water, temperature and wind (SOUTO *et al.*, 2005).

The Brazilian semi-arid region has high air temperature, with an annual average of around 26.0 to 27.5 °C. At the soil surface, in the driest months, the temperature reaches 60 ºC (CORREIA *et al.*, 2012). In the semi-arid region of Brazil, a temperature value for a degraded soil of 30.8 °C at a depth of 10 cm has been recorded (SOUTO *et al.*, 2005).

The maximum soil temperature in an agroforestry system in the Brazilian semi-arid region on which *Gliricidia sepium* was intercropped with *Zea mays* L. was 30 °C in the middle of drought season. Outside the area of *Gliricidia sepium* influence the maximum soil temperature was 41 °C (MARIN *et al.*, 2006a), showing the effects of soil cover in reducing soil temperature.

In the semiarid region of China, at soil depths of 5 and 25 cm, temperature values of around 25 ºC were observed (WU *et al.*, 2017; XIAO *et al.*, 2016). In the semi-arid region of Chile, at a depth of 0-10 cm, values of 35.3 °C were found in summer and 38.4 °C in spring (REYES *et al.*, 2016).

2.3.2 Soil and water salinity

Salinity is one of the main abiotic stresses that limit plant development and crop productivity worldwide (PIÑERO *et al.*, 2016). In arid and semi-arid regions the excess of salts in the soil limits agricultural production (ANDRÉO-SOUZA *et al.*, 2010). Soil salinization is the main environmental problem in arid and semi-arid regions and seriously restricts regional ecological security and sustainable agricultural development (YANG *et al.*, 2020).

Consequently, soil salinity represents a threat to food security and environmental conservation (SINGH; PANDA, 2012).

Salinity negatively affects plant growth and crop yields. In arid and semi-arid non-agricultural areas, it affects urban structures due to the reduction of groundwater quality, leading to soil erosion and land degradation (ABUELGASIM; AMMAD, 2019).

Soils affected by salts are an important category of degraded soils because they occupy a large global extent and due to the serious effects they have on agricultural productivity (WICKE *et al*., 2013). Saline soils occupy more than 7% of the planet's terrestrial surface and play an important role in the landscape of the arid and semi-arid regions of the world (SETIA *et al*., 2011).

This is because arid and semi-arid regions have greater potential for salinization due to high evaporation, low precipitation, and inherent soil characteristics such as its mineralogy (ACOSTA *et al*., 2011). Poor internal drainage common in soils in these areas, together with excessive evaporation, promotes the accumulation of soluble salts and an increase in exchangeable sodium on the surface and/or sub-surface of the soils (BARROS *et al*., 2004).

High concentrations of salts in the soil restrict plant growth due to an inhibition of metabolic processes, increased osmotic potential, decreased hydraulic conductivity and nutrient imbalances, resulting in low plant yields (SALL *et al*., 2015). High soil salinity can also lead to flocculation or dispersion of particles of organic material, which influences the solubility of soil organic matter and the mineralization of carbon (C), nitrogen (N), sulfur (S) and phosphorus (P) (LU *et al*., 2015; WONG *et al*., 2010).

Sodicity alters physical properties of the soil, causing a decline in soil structure at a sub-aggregate scale due to increased expansion and dispersion of clays. This leads to an increase in rainfall induced structural crusts and increased crust cohesion on drying, with a concomitant decline in soil permeability, infiltration, and hydraulic conductivity (WONG *et al*., 2010).

In addition to soil salinity problems, arid and semi-arid regions have salinity problems associated with irrigation water. Water of suitable quality for irrigation is a limited resource in these regions (SINGH; PANDA, 2012), with water stress being one of the main limiting factors that affects crop growth and productivity (NIRMALA; GUVVALI, 2019). In the Northeast of Brazil, the water used for irrigation, in most cases, have salt concentration in the range of 1 to 30 mmolc L^{-1}, corresponding to an electrical conductivity (EC) ranging from 0.1 to 3.0 dS m^{-1} (GHEYI; QUEIROZ; MEDEIROS, 1997).

In many cases, this saline water is the only source of water for irrigation both for agriculture and for revegetation programs in semi-arid Brazil. The classification of water according to the risk of salinity was established according to the University of California Committee of Consultants (UCCC) with the following limits: low (Class 1: <0.75 dS/m), medium (Class 2: 0.75 - 1.5 dS m^{-1}), high (Class 3: 1.5 - 3.0 dS m^{-1}) and very high (Class 4:> 3.0 dS m^{-1}) (FRENKEL, 1984). According to the FAO classification, the level of restrictions for the use of irrigation water is: None (<0.7 dS m^{-1}), slight to moderate (0.7 - 3.0 dS m^{-1}) and severe restriction (> 3.0 dS m^{-1}) (AYERS; WESTCOT, 1985).

To overcome the difficulties brought about by abiotic factors for agriculture and revegetation of degraded areas in semi-arid Brazil, it is necessary to search for alternatives such as the use of soil conditioners.

2.4 Superabsorbent polymers or hydrogels as soil conditioners

The soil conditioners known as superabsorbent polymers or ‘hydrogels’ - an employed generic term in many areas, including agriculture (FERREIRA *et al*., 2014) - absorb many times their weight in water, and have been successfully used in dry areas to improve the capacity of the soil to absorb and retain water (ZAIN *et al*., 2018).

Hydrogels are among the most widely used synthetic soil conditioners in agriculture, horticulture, and the forestry sector (PARADELO; BASANTA; BARRAL, 2019). In agriculture they can be used to preserve water in the soil and to release nutrients; however, the main characteristic of hydrogels is their ability to absorb and retain large amounts of water (GUILHERME *et al*., 2015). Due to their high-water absorption capacity, superabsorbent hydrogels are being extensively studied as soil conditioners to increase water use efficiency in agriculture (CHEN *et al*., 2017; COELLO *et al*., 2018; PARADELO; BASANTA; BARRAL, 2019; SONG *et al*., 2020; THOMBARE *et al*., 2018; VASCONCELOS *et al*., 2020; YANG *et al*., 2018; ZAIN *et al*., 2018).

Hydrogels are cross-linked hydrophilic polymers that have a high water-holding capacity. They are considered superabsorbent when their retention capacity is >100 times their original mass (ESSAWY *et al*., 2016). Hydrophilic polymers can absorb and conserve large amounts of water, even under a hostile external environment, such as heat or pressure, compared to other traditional absorbents (WANG *et al*., 2019). The fact that hydrophilic polymers swell, absorbing large volumes of water or aqueous solutions, has led to many practical applications of these materials (such as in horticulture), particularly in arid regions, to improve soil water retention and water supply to plants (ANDRY *et al.*, 2009).

The term "polyacrylamide" is loosely used to describe any acrylamide polymer present as one of the monomers. More strictly, its nomenclature according to IUPAC (International Union of Pure and Applied Chemistry) is poly (prop-2-enamide), which defines it as a water-soluble polymer formed by the polymerization of acrylamide monomers (XIONG *et al.*, 2018). Polyacrylamide (PAM) with only acrylamide monomers is non-ionic; other monomers such as acrylate can be copolymerized in various percentages to form anionic PAM (XIONG *et al.*, 2018). Currently, most agricultural hydrogels on the market are manufactured from acrylate and polyacrylamide monomers or polymers (SONG *et al.*, 2020).

The ability of hydrogels to absorb water depends on the hydrophilic functional groups linked to the polymer backbone, while their resistance to dissolution is linked to the cross-links between the chains of the polymeric network (ZAIN *et al.*, 2018). The retention and release of water by the polymeric material applied to the soil is a function of soil texture, granulometry, and hydrogel type. As for the type of hydrogel, the water retention capacity is directly related to the elasticity of the polymeric network, the presence of hydrophilic functional groups in the polymeric chain, such as -OH, -COOH, $-CONH_2$, $-SO_3H$, the degree of crosslinking and the porosity level of the material (DORKOOSH *et al.*, 2000).

Concerning the application of hydrogel as soil conditioners results have already been reported regarding the following aspects: erosion control, control of nutrient loss, stabilization of steep slopes (CHEN *et al.*, 2017), in the structural stability of soils (BUCHMANN; BENTZ; SCHAUMANN, 2015), in mitigating post-fire erosion (INBAR *et al.*, 2015), in soil biochemical properties (EL-SAIED *et al.*, 2016), in-plant morphophysiological indicators and soil physical-hydric attributes (GALEŞ *et al.*, 2016). In order for hydrogels to be considered as an alternative to favor plant development in dry regions they must contribute to a significant improvement in soil physical-hydric attributes.

2.4.1 Hydrogel effects on soil physical-hydric parameters

Hydrogels have been used to improve the physical properties of soils, increasing soil water storage capacity and the efficiency in water use by plants (HOU *et al.*, 2018; THOMBARE *et al.*, 2018). When superabsorbent polymers are applied, evaporation and water infiltration on the soil surface can be reduced (THOMBARE *et al.*, 2018). These polymers are effective in increasing water holding capacity, decreasing the percolation depth, reducing evaporation losses in sandy soils (EL SHAFEI *et al*., 1992) and improving the water supply to cultivated plants (ANDRY *et al*., 2009)

Hydrogels applied to the soil can improve water supply to the plants by increasing soil capacity to store water (WOLTER *et al*., 2002). A three-fold increase in water availability to the plants was verified by adding 0.2 % w w^{-1} of hydrogel to a sandy soil (VARENNES *et al*., 1997). At least 95% of the water retained in the polymers, in potential matrices greater than -1500 kPa, were available to plants in a study where a PAM hydrogel was added to sandy substrates (FONTENO; BILDERBACK, 1993).

The soil available water content increased 2.2 and 3.2 times in loamy and sandy soil, respectively, with the application of 8 g of hydrogel per kg of soil. The hydrogel dose of 2 g kg^{-1} increased the soil moisture by 40% in a loam-clay-sandy soil, compared to the treatment without hydrogel, and also increased the total plant water availability by 125% (ABEDI KOUPAI; SOHRAB; SWARBRICK, 2008). There was more water available lasting longer for *Agrostis stolonifera* species grown in soil treated with a PAM polymer as a hydrogel, which reduced the irrigation frequency (AGABA *et al*., 2011).

Hydrogel addition increased the easily available soil water; however, for sandy soil, the water availability increase last longer (about 22 days, which corresponds to the irrigation interval of most crops) than in loam-clay soil on which critical water content was reached more quickly (4 -7 days). These findings suggest that hydrogels have greater potential application in sandy soils (NARJARY *et al*., 2012).

The water retention capacity of superabsorbent PAM polymers subjected to an extreme water deficit was less than in the absence of deficit. This suggests that the water retention capacity of hydrogels is related to initial soil moisture and that when soil moisture is below a critical limit, the water retention capacity of the hydrogel is greatly reduced (BAI *et al*., 2010).

In addition to water retention, hydrogels can improve other soil attributes, such as bulk density and porosity. The hydrogel increases soil porosity, improving oxygenation to plant roots (ULLAH *et al*., 2015). Amounts of potassium polyacrylate hydrogel applied to the soil increased porosity and decreased soil density (HOU *et al*., 2018). The changes in soil porosity and density were attributed to the fact that the hydrogel tested favored the formation of macropores in the soil, helping in the water infiltration process (HOU *et al*., 2018). The application of two superabsorbent hydrogels to the soil improved water retention and significantly promoted potato growth and productivity (HOU *et al*., 2018).

With the incorporation of a PAM hydrogel “Aquastock” (with a bulk density of 0.85 g/cm^{-3}, it has 10% N and 19% C) to a depth of 20 cm, it was verified that the bulk density decreased from 1420 kg m^{-3} to 1150 kg m^{-3} in the sand, and from 1200 kg m^{-3} to 920 kg m^{-3} in the clay soil evaluated. Total porosity and water availability increased, while soil permeability decreased, especially in the sandy soil (BAASIRI *et al.*, 1986).

Although multiple studies demonstrate beneficial effects of hydrogels on soil physical-hydric parameters, there are external factors that can compromise the efficiency of the hydrogels and promote their degradation.

2.4.2 Effects of salinity and temperature on efficiency and degradation of PAM hydrogel in the soil

The presence of salts in the swelling solution interferes with the hydrogels' ability to retain water. Thus, when an irrigation water source contains high levels of dissolved salts, or when effluents are used for irrigation or when there are salts applied through fertilizers, hydrogels significantly lose their water holding capacity (WANG; GREGG, 1990).

Water absorption efficiency of hydrophilic polymers is reduced by increases of water electrical conductivity (ANDRY *et al.*, 2009). Subtle increases in water-soluble wetting salts reduce the absorption capacity of PAM-based polymers (COELHO *et al.*, 2008). A high-water absorption capacity by the hydrogel was found in deionized water; however, upon saturation in saline solutions containing monovalent cations (NaCl and KCl,), the hydrogel showed a reduction in water absorption capacity of approximately 80%. (VARENNES *et al.*, 1997).

Salinity impairs water absorption since hydrophilic groups of PAM hydrogels bind to salts, blocking water ingress (XIONG *et al.*, 2018). Salts also suppress the electrostatic interactions between the hydrogel and water molecules (XIONG *et al.*, 2018; ZHAO *et al.*, 2019). Thus, the efficiency of PAM hydrogels is affected by salinity of both soil and irrigation water, a common condition in arid and semi-arid regions.

The reduction in swelling of hydrogels in saline conditions is attributed to a “charge-screening effect” of additional cations, causing non-perfect anionic electrostatic repulsion (KWON; BAE; SUNG WAN KIM, 1991; MIRDARIKVANDE *et al.*, 2014; SADEGHI; GHASEMI; YARAHMADI, 2011). This term refers to the protection of carboxylate anions by additional cations, which prevents effective anion-anion repulsion. Therefore, the decrease in osmotic pressure results in a decrease in the concentration of mobile ions between the hydrogel and the aqueous phases, decreasing the water absorption by the PAM hydrogels.

The characteristics of the external solution, such as the charge valency of the ions present and their concentration (e.g. Na^+, Mg^{2+}), influence the expansion of hydrogels (RAJU; RAJU; MOHAN, 2003). In the case of saline solutions with multivalent cations, ionic crosslinking on the surface of the polymer particles decreases the swelling capacity (FLORY, 1953; HEIDARI *et al*., 2018; MIRDARIKVANDE *et al*., 2014). The decrease in swelling depends on the type and concentration of salts present in the solution (HEIDARI *et al*., 2018; MIRDARIKVANDE *et al*., 2014).

Divalent elements, such as Ca^{2+} and Mg^{2+}, can decrease the swelling of hydrogels. This is due to their ability to bind ions with the carboxamide or carboxylate groups of hydrogels forming inter and intramolecular complexes (SADEGHI; GHASEMI; YARAHMADI, 2011). Monovalent cations, such as Na^+, can shield the carboxylate anions of the hydrogel polymeric structure, contributing to reducing the three-dimensional structure due to the lower repulsion between the fixed charges of the hydrogel polymeric network, leading to a decrease in the osmotic pressure difference between the hydrogel framework and the external solution. This in consequence leads to a decrease in water retention capacity (MAGALHÃES *et al*., 2013; SADEGHI; GHASEMI; YARAHMADI, 2011).

For greater absorption of saline solution by hydrogels, it is recommended to introduce hydrophilic groups that are more prone to ionization, such as sulfonic and phosphate groups in which the degree of association with mobile ions present in saline solution would be lower than that observed in the carboxylic acid group (ZAIN *et al*., 2018).

The efficiency of PAM hydrogel (at a rate 1 g per l and 0.75 m deep) has been reported to be decreasing over time, with a marked reduction in water retention capacity 18 months after polymer application to the soil (HOLLIMAN *et al*., 2005). However, significant reduction of water retention of a PAM hydrogel (0.3-0.6% w/w) capacity was observed after 5 months in a substrate with *Salvia officinalis* (SAVI *et al*., 2014). Additionally, hydrogels can be degraded in the soil. Some authors claim that degradation of PAM hydrogels occurs slowly in the soil as a result of chemical, photochemical and mechanical processes and due to the large size of the molecule that is broken into progressively smaller units over time by abiotic processes (ENTRY; SOJKA; HICKS, 2008).

Considering the characteristics of arid and semi-arid regions, it is also necessary to understand how high temperatures affect the hydrogel applied to the soil. Studies indicate that the increase in temperature compromises the functionality of agricultural hydrogels, highlighting a reduction of up to 60% of the water retention capacity in the soil that received hydrogel at temperatures up to 35 °C (ANDRY *et al*., 2009). The absorption of water by a hydrogel from poly(aspartic acid) decreased with increasing temperature from 30 to 60 °C (ZHAO *et al*., 2005).

Hydrogels can absorb and lose water in a reversible way, being related to intrinsic factors of the external environment, such as temperature, which in turn can contribute to the collapse or phase change (AHMED, 2015). At a critical temperature, the elasticity of the polymeric network is reduced to zero and the gel becomes infinitely compressible (MOLLOY; SMITH; COWLING, 2000). At a constant temperature of 37 °C, it has been reported that a PAM hydrogel can change its physical properties (SMITH; PRUES; OEHME, 1996a).

In arid and semi-arid regions of the world, soil temperature values can range from 25 to 60 °C (CORREIA *et al*., 2012; GAO *et al*., 2007; REYES *et al*., 2016; WU *et al*., 2017; XIAO *et al*., 2016). Inappropriate management practices (eg deforestation) are commonly adopted in semi-arid regions, leaving the soil exposed to the effects of temperature, as solar radiation starts to directly affect the soil (SOUTO *et al*., 2005; SCHARENBROCH, BOCHEIM, 2007). Thus, it is important to know to what extent the temperature negatively affects the functionality of hydrogels for agricultural use.

2.4.3 Acrylamide from hydrogels

Hydrogels synthesized from acrylamide have greater potential for water use due to their high-water absorption capacity. However, potential environmental pollution must be considered, because, in the last decades, acrylamide has gained an important place, especially in food science and technology, as well as in environmental science, due to its carcinogenic effect on human health (TEPE; ÇEBI, 2017; XIONG *et al*., 2018).

Although polyacrylamide is considered a non-toxic and inert substance, its monomeric form, acrylamide, has been studied because of its neurotoxic, genotoxic and carcinogenic impacts on human health (XIONG *et al*., 2018). Acrylamide-based hydrogels may contain residual acrylamide monomer as a result of incomplete polymerization (XIONG *et al*., 2018). The content of acrylamide monomer in commercial hydrogels has been an important issue, particularly for applications in which human contact is involved (CAULFIELD *et al*., 2003). The useful life of PAM hydrogels and the potential for degradation and release of toxic by-products remain, in part, unknown (HOLLIMAN *et al*., 2005).

Acrylamide ($CH_2 = CH - CONH_2$), also known as 2-propenamide, is a solid monomer, which has a white color with crystalline and odorless characteristics. Its chemical structure has a polar group and a vinyl function, which allows the polymerization of acrylamide (MATOSO *et al.*, 2019). Anionic PAM is most commonly used as a soil conditioner because it has low mobility and is associated with residual acrylamide monomer levels of <0.05% (XIONG *et al.*, 2018). Typically, acrylamide monomer levels in agricultural polymers are around 200-500 mg kg^{-1} (0.02-0.05 %) based on dry weight (CASTLE, 1993).

The World Health Organization (WHO) has set the concentration of acrylamide in drinking water at 0.5 µg L^{-1}. The European Union (EU) has established a minimum quality requirement of 0.1 µg L^{-1} in water for human consumption (MARIN *et al.*, 2006b). The maximum levels of residual acrylamide found in water are 5 to 480 times lower than those found in frequently consumed foods (TEPE; ÇEBI, 2017). The acrylamide monomer can be adsorbed through dermal exposure and inhalation and is lethal (LD50) at 150-200 mg kg^{-1} of body weight (MATOSO *et al.*, 2019).

As acrylamide does not bind to the soil, it is highly soluble and mobile in water, and moves quickly with infiltration, causing an even greater risk of contamination of the surface or groundwater (TEPE; ÇEBI, 2017). On the other hand, acrylamide is susceptible to biodegradation in soil and surface water, which reduces the risk of accumulation in the environment (NEELY; BRANSON; BLAU, 1974; TEPE; ÇEBI, 2017). Acrylamide is biodegraded in days (LANDE; BOSCH; HOWARD, 1979), is rapidly decomposed into propionamide and propanoic acid. Propanoic acid is a fatty acid metabolized by plants, while propionamide is degraded to CO_2, NH_4^+, and H_2O (HOLLIMAN *et al.*, 2005).

Some authors claim that PAM is stable at room temperature, stable under fluorescent lights, and does not release detectable acrylamide in an aqueous solution at 95 °C (CAULFIELD *et al.*, 2003). Under artificial environmental conditions, it was found that PAM did not degrade to acrylamide, but residual acrylamide degraded to ammonium and these ammonium concentrations increased as residual acrylamide levels decreased (SMITH; PRUES; OEHME, 1996b). Based on the chemical structure of acrylamide, ammonium is a possible product of the acrylamide degradation process and may contribute to plant development, as ammonium is one of the ways in which plants absorb N which is an essential element of their development (MOREAU *et al.*, 2019; SMITH; PRUES; OEHME, 1996b).

The release of acrylamide into the soil solution from hydrogel applications is a concern for its environmental contamination. There is currently, a paucity of information on the degradation of residual acrylamide under semi-arid conditions.

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3 DURABILITY INDICATIVES OF HYDROGEL FOR AGRICULTURAL AND FORESTRY USE IN SALINE CONDITIONS

ABSTRACT

Hydrogels are hydrophilic polymers that absorb >100 times their mass of water, presenting the potential enhancing water use efficiency for agricultural and forestry use, especially in semi-arid regions. High durability is an informed feature in commercial products, but little is known about how time and salinity affect hydrogel efficacy. In this laboratory study, the hypothesis tested was that the interaction between time and salinity reduces water absorption potential of a commercial hydrogel, promoting chemical degradation and residual acrylamide monomer. The experimental design was completely randomized split plot with four replications. The treatments were four time periods (30, 60, 90 and 120 days) and five levels of salinity (distilled water = 0.003, 0.5; 1.5; 3.0 and 6.0 dS m^{-1}). Swelling, hydrogel composition, and residual acrylamide monomer concentration were evaluated. The hydrogel showed less swelling (8.1 g g^{-1}) in a saline solution of 4.20 dS m^{-1} after 120 days. The C/N ratio of the polymer increased up to 47% in the EC 4.4 dS m^{-1} at 120 days and there was a shift in the wavelength of the methylene, amide and acrylate bands. Residual acrylamide monomer was up to 0.5 mg g^{-1} only in the hydrogel before the experiment; however, the values were within the acceptable range. After 120 days up to 85% of the residual acrylamide monomer was degraded. For the hydrogel evaluated in this study, under laboratory conditions and without mixing with soil, there is an interaction between time and salinity, reducing water absorption and promoting the chemical degradation of the polymer and the residual acrylamide monomer. This suggest that under semi-arid conditions hydrogel durability may be impaired for forestry and permanent crops applications.

Keywords: Soil conditioner. Acrylamide and potassium acrylate copolymer. Irrigation water salinity.

1 INTRODUCTION

Semi-arid regions comprise 1/3 of the planet's continental masses, are home to a billion people and are responsible for 22% of food production (ARAÚJO FILHO, 2013). Research the facilitates agricultural and forestry production in semiarid regions are important since dry areas of the world have expanded in recent years and will continue to expand (FENG; FU, 2013).

In addition to the water deficit, salinity in the soil solution and irrigation water limits plant development in semiarid regions (PIÑERO *et al.,* 2016). Dry regions are susceptible to salinization due to high evaporation, low precipitation and inherent soil characteristics (ACOSTA *et al*., 2011). The water used for irrigation becomes more concentrated in salts because in the dry season there is a reduction in the volume of water in reservoirs. In the Brazilian semiarid region, the waters used for irrigation is saline with an electrical conductivity (EC) of 0.1 to 3.0 dS m^{-1} (GHEYI; QUEIROZ; MEDEIROS, 1997). According to the FAO classification, the level of restrictions for the use of irrigation water is: None (<0.7 dS m^{-1}), slight to moderate (0.7 - 3.0 dS m^{-1}) and severe restriction (> 3.0 dS m^{-1}) (AYERS; WESTCOT, 1985).

As agriculture and forestry are affected by water deficit and salinity, it is necessary to develop solutions for the sustainable management of water resources in semiarid regions. Among the alternatives for supplying water to plants are hydrogels, which are materials that often absorb >100x their weight in water and have been used in dry regions to improve soil water storage and the efficiency of water use by plants (HOU *et al*., 2018; THOMBARE *et al*., 2018; ZAIN *et al*., 2018).

Questions about the viability of using hydrogels in an agricultural and forestry context have arisen from studies that have shown reduced water retention capacity at 150 and 540 days after application of the hydrogel to the soil (HOLLIMAN *et al*., 2005; SAVI *et al*., 2014) and reduction in water absorption efficiency with increased EC of the wetting solution (ANDRY *et al.*, 2009). Although there is a study indicating that hydrogels can absorb and conserve large amounts of water (> up to 1000 w w^{-1}), even in adverse external environments (WANG *et al*., 2019), it is common in commercial products to find high durability listed as a key performance indicator of the hydrogel for agricultural and forestry use. These aspects indicate the need to better understand the functioning of hydrogels over time and in saline conditions.

The absorption of water by hydrogels depends on the hydrophilic functional groups linked to the polymeric backbone while its resistance to dissolution is associated with the crosslinks between the chains of the polymeric network (ZAIN *et al.*, 2018). Salinity impairs water absorption, as hydrophilic groups of hydrogels bind to salts, blocking water from entering; also, salts suppress electrostatic interactions between the polymer and water molecules (XIONG *et al.*, 2018; ZHAO *et al.*, 2019). The reduction in swelling of hydrogels in saline conditions is attributed to a "charge screening effect" of additional cations, causing non-perfect anionic electrostatic repulsion (KWON; BAE; SUNG WAN KIM, 1991; MIRDARIKVANDE *et al.*, 2014; SADEGHI; GHASEMI; YARAHMADI, 2011).

Most agricultural hydrogels on the market consist of monomers or polymers of acrylic acid and polyacrylamide (SONG *et al.*, 2020) that are non-toxic. However, hydrogels also contain residual acrylamide monomer as a result of the synthesis process (XIONG *et al.*, 2018) and there is concern that this will be released into the environment by applying the product to the soil. The release of acrylamide monomer in the environment is undesirable due to its toxic effects (XIONG *et al.*, 2018).

Based on the above, the hypothesis was tested that there is an interaction between time and salinity reducing the water absorption potential of a commercial hydrogel, promoting its chemical degradation as well as the degradation of residual acrylamide. The objective of the study was to evaluate water absorption efficiency, residual acrylamide monomer concentration and the degradation of the commercial hydrogel in response to time and salinity, to obtain information to recommend its application to the soil of semiarid regions.

2 MATERIAL AND METHODS

2.1 Characterization of the hydrogel

Hydrogel characterization was performed at the Polymer Laboratory of the Department of Organic and Inorganic Chemistry at the Federal University of Ceará (Fortaleza, CE, Brazil). The hydrogel used was a commercial product (Forth Gel®), characterized on the manufacturer's label as a copolymer of acrylamide and potassium acrylate. To refine the characterization of the product, the following analyses were performed: elementary, X-ray fluorescence spectrometry (FRX), particle size and residual acrylamide monomer concentration of the hydrogel before exposure to experimental salinity and time treatments.

Elementary analysis of carbon (C), hydrogen (H) and nitrogen (N) was performed using a Carlo Erba EA 1108 microanalyzer; with the C/N ratio was obtained by the ratio between C and N; the elemental composition of the acrylate was determined by X-ray fluorescence spectrometry (FRX) using X-ray fluorescence spectrometer, model ZSXMini II (Rigaku); the particle size fraction was determined using 24 mesh (0.710 mm), 35 mesh (0.425 mm) and 48 mesh (0.300 mm) sieves and residual acrylamide monomer was determined by high-performance liquid chromatography (HPLC) in a chromatograph model LC-20AD from Shimadzu, coupled to the diode array detector model SPD-M20A, at a wavelength of 197 nm.

Infrared spectroscopy (FTIR) absorption spectroscopy and X-ray diffraction were also performed for the characterization of the polymer. Infrared absorption spectroscopy (FTIR) was performed on equipment FT IR-8500 (Shimadzu), operating in the 400-4000 cm^{-1} range; X-ray diffraction was performed using an XPert Pro MPD diffractometer (Panalytical), with Cu-Kα radiation, varying 2θ from 5 to 70º.

The swelling of the commercial hydrogel in distilled water and saline solutions was characterized. To obtain the saline solution, sodium chloride (NaCl), calcium chloride ($CaCl_2.2H_2O$) and magnesium chloride ($MgCl_2.6H_2O$) solutions were dissolved in the ratio of 7:2:1, assuming the existing relationship between the electrical conductivity of irrigation water (ECw) and its concentration [Cs ($mmol_c$ L^{-1}) = EC x 10]; where: Cs = concentration of salts; EC = pre-established electrical conductivity (RHOADES *et al.*, 1989).

To determine the swelling kinetics, 30 mg of the polymer was weighed in a 30 mL filter crucible (porosity Nº0) previously moistened. This set was then completely submerged in the liquid medium (distilled or saline water). The set (crucible+gel) was removed at intervals of time (2, 4, 6, 8, 10, 12, 15, 30, 45, 60, 90, 120, 180, 240 minutes), the outer wall of the crucible was dried and weight was measured. The procedure was performed in triplicate. The hydrogel in granular form was screened to obtain a particle size between 24 and 35 mesh that was used in this swelling study. To calculate the swelling, formula 1 was used:

$$S = \frac{Wt - W0}{W0} \qquad (1)$$

Where: W0 represents the mass (g) of the hydrogel dried at 65 °C and Wt is the mass (g) of the hydrogel expanded at time t.

Thus, the hydrogel swelling curve in distilled water (0.003 dS/m) and saline solutions with electrical conductivities of 0.5, 1.5, 3.0 and 6.0 dS m^{-1} were obtained. Some characteristics of the gel (W_{eq}, $t_{eq,}$ and Wt = 6 min) were obtained through the swelling curves (RAY; OKAMOTO, 2003).

2.2 Experiment to assess the effects of time and salinity levels in the hydrogel

The experiment was installed on 10/04/2017 and conducted for 120 days at the Soil Management Laboratory of the Department of Soil Science at the Federal University of Ceará (Fortaleza, CE, Brazil).

The experimental design was completely randomized split plot in time with four repetitions (4x5) x 4, totalling 80 experimental units. Four hydration time periods were evaluated (30, 60, 90 and 120 days) with five levels of salinity of the hydration solution (distilled water = 0.003, 0.5; 1.5; 3.0 and 6.0 dS m^{-1}). The electrical conductivity values of the solutions were equivalent to 5, 15, 30, 60 $mmol_c$ L^{-1}, corresponding, respectively, to the risks of low salinity (Class 1: <0.75 dS m^{-1}), medium (Class 2: 0,75 – 1.5 dS m^{-1}), high (Class 3: 1.5 – 3.0 dS m^{-1}) and very high (Class 4: > 3.0 dS m^{-1}) (FRENKEL, 1984).

Each experimental unit consisted of a PVC column (10 x 20 cm), opened at the surface and closed at the base by a perforated PVC cap (for drainage). Each experimental unit was filled with 3g of hydrogel (Figure 3a). To install the experiment, the gels were initially dried at 65 °C. After reaching constant mass, they were hydrated with the solution for each treatment.

Figure 3 – Experimental unit (a); experimental units in the oven (b); overview of experimental units distributed on a bench (c).

Source: elaborated by the author.

For swelling inside the PVC cylinders, the dry hydrogel was inserted, and the swelling solution was inserted in the lid so that the swelling would occur by capillarity. When all hydrogels showed equilibrium in their swelling (~30 minutes), the units were weighed to calculate the initial swelling.

The hydrogel samples were submitted to the treatments (distilled water and with increasing levels of salinity), applying each solution corresponding to the treatments in individual reservoirs on which the PVC columns were placed, to keep the hydrogel in permanent contact with the solution. The cylinders were randomly placed on a bench and the solution was replaced daily (Figure 3b). At the end of each hydration period the respective columns were weighed to calculate the final swelling and then the samples were dried (65°C) to a constant mass (Figure 3c).

2.2.1 Response variables

At the end of the hydration periods tested, the experimental units were suspended until drainage ceased and subjected to the process used to determine the degree of final swelling, according to formula 1. With the dry hydrogel, the levels of C, H, and N in samples submitted to treatments, using Carlo ERBA EA 1108 microanalyst, as performed in the hydrogel characterization.

After the respective hydration period, the concentration of residual acrylamide monomer of the hydrogel was determined. For this, the dry hydrogel was submerged in deionized water for 4 h. This time of immersion of the hydrogel in deionized water was necessary to achieve equilibrium in the medium and provide the displacement of all residual monomer to the immersion water, following Bezerra (2015).

The immersion water was analyzed to determine the presence of residual acrylamide monomer by the technique of high-performance liquid chromatography (HPLC) in a chromatograph model LC-20AD from Shimadzu, coupled to the diode array detector model SPD-M20A, at a wavelength of 197 nm. The acrylamide monomer was quantified from the area of its respective chromatographic peak, with elution time of 2.2 min, using a calibration curve obtained by diluting a 10-ppm solution of acrylamide monomers in deionized water. The results were expressed in mg of monomer/g of hydrogel (BEZERRA, 2015).

Also, the degradation of residual acrylamide monomers in the gel immersion water was quantified. With the results about the initial (new gel) and final (at the end of the experiment) contents of residual acrylamide monomers, the degradation of residual acrylamide (mg g^{-1}) was calculated using the formula 2:

$$\text{Initial acrylamide (mg g}^{-1}\text{) - final acrylamide (mg g}^{-1}\text{)} \qquad (2)$$

X-ray diffraction analysis was performed as reported for the hydrogel characterization. To obtain the diffractogram of the hydrogels after the experiment, contrasting treatments were selected to facilitate the understanding of the results: shorter time (30 days) and longer evaluation time (120 days); distilled water and 3 dS m^{-1} saline solution.

2.2.2 Statistical analysis

The homogeneity of variance and the normality of the residues were tested before conducting the analysis of variance (Two-way-ANOVA) with level of significance $p < 0.01$ (99%). When the interaction between factors and/or each isolated factor was significant, linear regressions were performed. All statistical analyzes were performed using SAS 9.3 (“SAS 9.3 Software”, 2011).

3 RESULTS AND DISCUSSION

3.1 Characterization of the hydrogel

The hydrogel used in the study showed 39.7% C; 6.7% H; 15.0% N; C/N ratio of 2.65 (Table 1). In the elementary chemical composition of the acrylate present in the hydrogel, the presence of a greater amount (99.2%) of potassium (K) and the occurrence of 0.8% of sulfur (S) was found (Table 1). The high amount of K confirms that the acrylate used in the synthesis of the hydrogel evaluated was K and, therefore, confirms that the material is a copolymer of acrylamide and K-acrylate.

Table 1 – Elementary analysis of carbon (% C), hydrogen (% H), nitrogen (% N), carbon/nitrogen ratio (C/N) of the hydrogel; elementary chemical composition of the acrylate (%) with potassium (K) and sulfur (S) contents, granulometric distribution and residual acrylamide of the commercial hydrogel before applying the treatments (new gel).

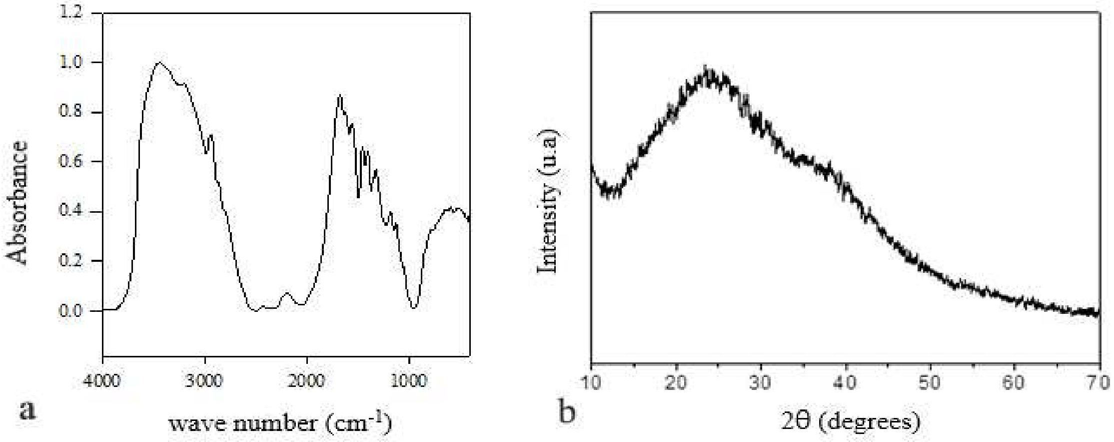
---- Elementary analysis (%)----				Acrylate elementary composition (%)	
C	H	N	C/N	K	S
39.7	6.70	15.0	2.65	99.2	0.8
Particle size fraction (%)				Residual acrylamide	
<24 mesh	24-35 mesh	35-48 mesh	>48 mesh	(mg g^{-1})	
12	37	15	36	0.50	

Source: elaborated by the author.

In the granulometric fraction, greater amounts of hydrogel (37 and 36%) were observed in the fractions of 24-35 mesh and the >48 mesh, respectively (Table 1). The residual acrylamide monomer content (0.5 mg g^{-1}) corresponds to 500 mg kg^{-1} and is within the manufacturing limits reported in the literature for agricultural PAMs (200-500 mg kg^{-1}) and within the manufacturing level considered as low (<0.05%) (CASTLE, 1993; XIONG *et al.*, 2018).

The bands of the spectrum (Figure 1a) show the formation of a copolymer due to the appearance of the band in 1682 cm^{-1}, referring to the C=O stretch of amide (amide band I), coming from acrylamide, and in the band in 1560 cm^{-1}, referring to the asymmetric stretching of the carboxylate ion (COO^-) from the acrylate (MAGALHÃES *et al.*, 2012). The hydrogel X-ray diffractogram (Figure 1b) shows an absence of crystallinity, indicating that it is an amorphous material.

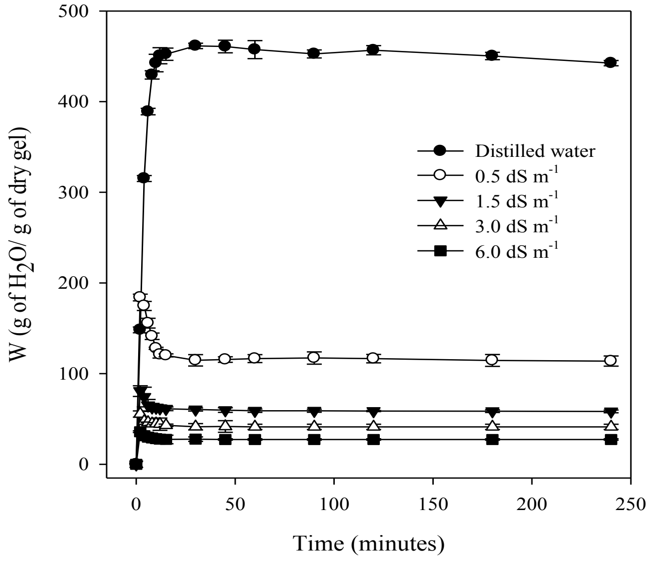
Figure 1 – Infrared spectrum (a) and diffractogram (b) of the commercial acrylamide and acrylate hydrogel studied.



Source: elaborated by the author.

Graph 1 shows the curve obtained from the swelling of the commercial hydrogel Forth Gel®. The swelling curve of the hydrogel in distilled water indicates a rapid initial absorption followed by an equilibrium level (W_{eq}).

Graph 1 – Hydrogel swelling curve in distilled water and solutions of sodium chloride (NaCl), calcium chloride ($CaCl_2.2H_2O$) and magnesium chloride ($MgCl_2.6H_2O$) dissolved in a 7:2:1 ratio at electrical conductivity of 0.5, 1.5 3.0 and 6.0 dS/m (d) at 25 °C.



Source: elaborated by the author.

Swelling is an important parameter in the characterization of crosslinked hydrogels (KIPCAK *et al.*, 2014). The degree of maximum swelling is defined as the ratio of the mass of the swelled hydrogel, in equilibrium, and the mass of the dry hydrogel. The profiles of the swelling curves for the hydrogel in saline solutions differ significantly from the profile in distilled water. These show a rapid mass gain in the first minutes followed by deceleration until equilibrium (W_{eq}) is achieved (Graph 1). The 0.5 dS m^{-1} saline solution is associated with a 75% reduction in at 240 minutes as compared with the hydrogel hydrated with distilled water (Graph 1). For the hydration solutions of 1.5, 3.0 and 6.0 dS m^{-1} the reduction in swelling of the hydrogel is 87, 91 and 94%, respectively as compared with the distilled water control.

When swollen, the polymeric nets of hydrogels are more elastic. The osmotic force that assists in carrying the solution into the polymeric network is counterbalanced by a retractive elastic force (FLORY; REHNER, 1943). Thus, when the osmotic and elastic forces are equal, the hydrogel will have reached the state of swelling equilibrium, obtaining the maximum water absorption value (W_{eq}) at a certain time (t_{eq}). The hydrogel obtained, in distilled water, W_{eq} = 462 ± 3.0g of water/g of the hydrogel, Wt (6 min) = 389 ± 3.5 and reached equilibrium with t_{eq} = 30 min (Table 2).

Table 2 – Swelling kinetics in distilled water and 0.5, 1.5, 3.0 and 6.0 dS/m hydration solutions of the hydrogel of potassium acrylate-co-acrylamide.

Forth Gel®	W_{eq} (g of water/g of gel)	t_{eq} (min)	$W_{t = 6\ min}$
Distilled water	462 ± 3.0	30	389 ± 3.5
0.5 dS/m	184 ± 3.6	25	156 ± 5.4
1.5 dS/m	81 ± 5.9	25	65 ± 6.5
3.0 dS/m	56 ± 3.4	25	46 ± 0.4
6.0 dS/m	36 ± 1.0	25	30 ± 1.1

Attributes of swelling kinetics (W_{eq} - swelling in equilibrium, t_{eq} - equilibrium time and $W_{t = 6\ min}$ - swelling in time = 6 minutes). Source: elaborated by the author.

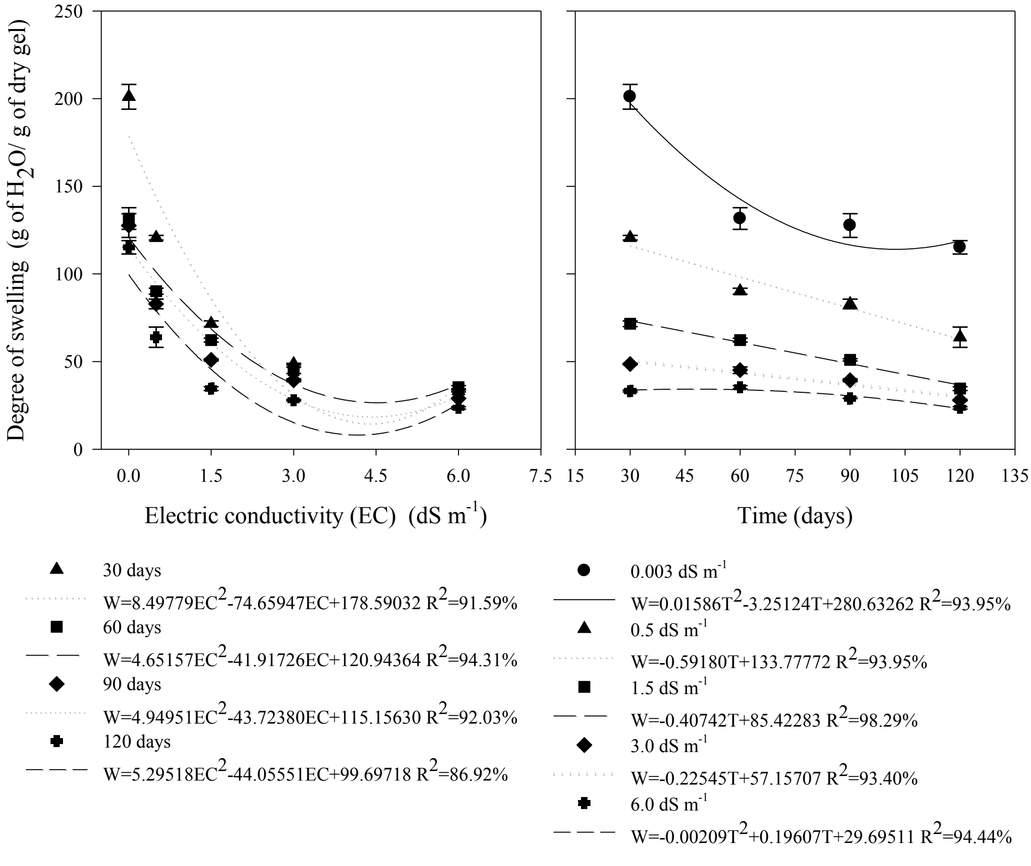
The hydrogel can be considered superabsorbent, as it absorbed more than 300 times its dry mass in water (THOMBARE *et al.*, 2018). In the presence of saline solutions, W_{eq} gradually decreased. For solutions of 0.5, 1.5, 3.0 and 6.0 dS m^{-1} the W_{eq} was 184 ± 3.6, 81 ± 5.9, 56 ± 3.4, and 36 ± 1.0 g of water/g of hydrogel, respectively. For all saline solutions, the hydrogel had an equilibrium time of 25 minutes (Table 2).

3.2 Experiment to assess the effects of time and salinity levels on the hydrogel

By the F test of the analysis of variance (Table 1 - ANNEX A), the interaction between the factors (salinity*time) was significant, proceeding the study split from one factor into the other for the variables: final swelling (W_{final}), residual acrylamide monomer concentration, acrylamide degradation, and C/N, as discussed below.

The Forth Gel® hydrogel studied exhibited different water absorption capacities, depending on salinity and time (Graph 2a and b).

Graph 2 – Swelling degree (g H_2O/g dry gel) of hydrogel of potassium acrylate-co-acrylamide as a function of salinity levels (0.003, 0.5, 1.5, 3.0 and 6.0 dS m^{-1} = 0.03, 5, 15, 30 and 60 mmol/L) of hydration solution (a) and time (30, 60, 90 and 120 days) (b).



Source: elaborated by the author.

At 30 days, the smallest swelling statistically significant was 14.61 g g^{-1} in EC 4.40 dS m^{-1} (Graph 2a). At 60, 90 and 120 days the smallest swellings (26.5, 18.6 and 8.1 g g^{-1}, respectively) occurred in ECs 4.5, 4.42 and 4.16 dS m^{-1}, respectively, 4.20 dS m^{-1} is therefore considered to be a critical value of EC to the reduction in the swelling of the commercial hydrogel, since in all the evaluation times the reduction of the swelling was accentuated already in this conductivity. The swelling of hydrogels that have ionic functional groups depends on the concentration and valence of ions in the swelling solution (GŁOWIŃSKA; TROCHIMCZUK; JAKUBIAK-MARCINKOWSKA, 2019).

The reduction in swelling is attributed to a "charge screening effect" of the additional cations in the solution, causing non-perfect anionic electrostatic repulsion (KWON; BAE; SUNG WAN KIM, 1991; MIRDARIKVANDE *et al*., 2014; SADEGHI; GHASEMI; YARAHMADI, 2011). This term refers to the protection of carboxylate anions by additional cations, which prevents an effective anion-anion repulsion. Therefore, the reduction of osmotic pressure results in a decrease in the concentration of mobile ions between the hydrogel and the aqueous phases, decreasing the water absorption by the hydrogel. Also, in the case of saline solutions with multivalent cations, such as the one used in the present study, ionic cross-linking on the surface of the polymeric network causes a decrease in the swelling capacity (FLORY, 1953; HEIDARI *et al*., 2018; MIRDARIKVANDE *et al*., 2014).

The decrease in swelling depends on the type and concentration of salts present in the solution (HEIDARI *et al*., 2018; MIRDARIKVANDE *et al*., 2014). Divalent elements, such as those found in the saline solution of the present study (Ca^{2+} and Mg^{2+}), can decrease the swelling of hydrogels. This is due to the binding of ions with the carboxamide or carboxylate groups of hydrogel and the formation of inter and intramolecular complexes (SADEGHI; GHASEMI; YARAHMADI, 2011).

Monovalent cations, such as Na^{+}, can shield the carboxylate anions of the polymeric structure, contributing to compact the three-dimensional structure due to the lower repulsion between fixed network charges, leading to a decrease in the osmotic pressure difference between the polymeric network and the external solution and, consequently, a decrease in the water holding capacity (MAGALHÃES *et al*., 2013; SADEGHI; GHASEMI; YARAHMADI, 2011).

The improvement in the absorption of saline solutions is a critical point in the development of hydrogels (LIM *et al*., 2001). For greater absorption of saline solutions by hydrogels, it is recommended to introduce hydrophilic groups (into the polymeric network) that are more prone to ionization, such as sulfonic and phosphate groups, in which the degree of association with mobile ions present in the saline solution would be lower than that observed in the carboxylic acid group (ZAIN *et al*., 2018).

In distilled water (EC 0.003 dS/m) there was a minimum point in the swelling of the hydrogel (114.01 g g^{-1}) at 102 days (Graph 2b). For ECs 0.5, 1.5 and 3.0 dS m^{-1}, decreasing functions were observed, so that for each elapsed day there was a reduction in the swelling of the hydrogel of 0.60, 0.40 and 0.22 g g^{-1}, respectively. For the 6.0 dS m^{-1} hydration solution, the swelling of the hydrogel was markedly reduced, with the maximum value (34.25 g g^{-1}) being reached at 47 days.

The observed reduction in swelling indicates that the hydrogel does not remain with the same functionality over time, even in distilled water. This is not favorable for agricultural or forestry use, and there is a need to improve the hydrogel so that its effects (Water absorption potential) are durable. Other studies have also shown a reduction in hydrogel functionality over time. The absorption of water by the hydrogel has been reported to decrease over time, showing a marked decrease 540 days after application to the soil (HOLLIMAN *et al.*, 2005). A significant loss of hydrogel water retention capacity was observed after 150 days in a substrate with *Salvia officinalis* (SAVI *et al.*, 2014).

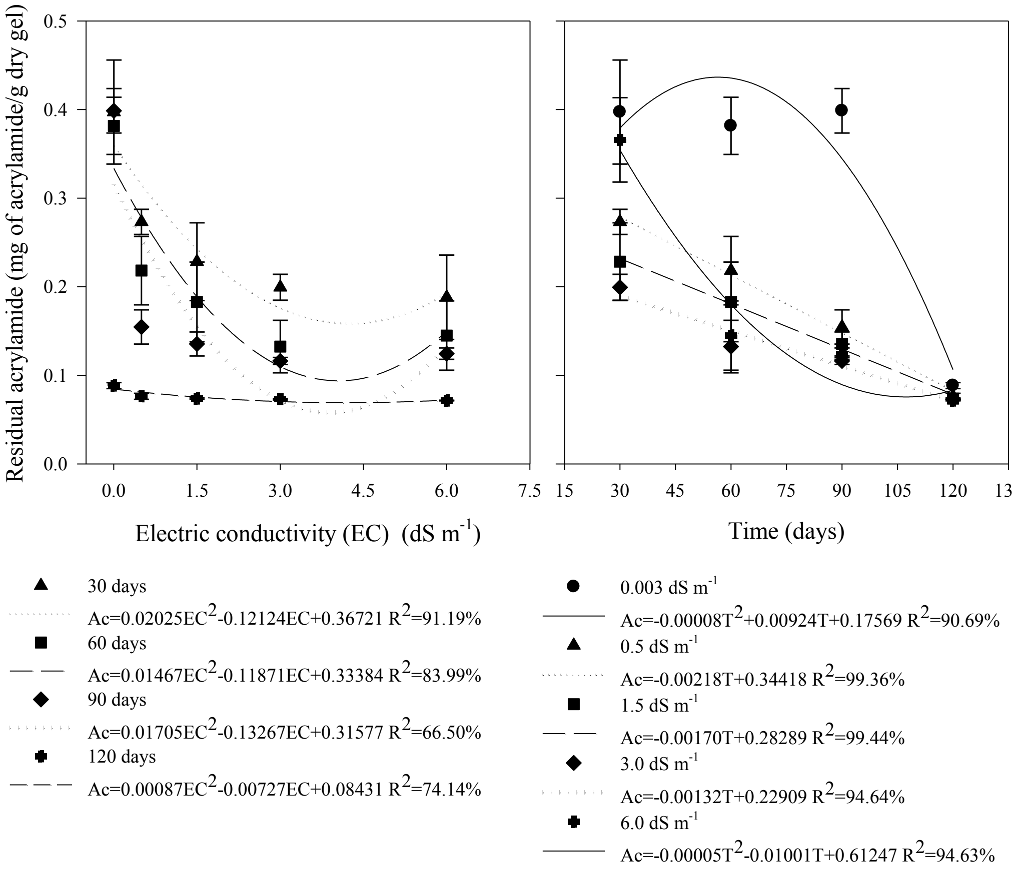
Concerning residual acrylamide, at 30 days the EC 3.0 dS m^{-1} provided a minimum value (0.19 mg g^{-1}) (Graph 3a). At 60, 90 and 120 days, ECs 4.05, 3.9 and 4.2 dS m^{-1} provided minimum values of 0.09, 0.06 and 0.07 mg g^{-1} of residual acrylamide monomer (RA_m), respectively. In distilled water, the maximum residual acrylamide monomer concentration (0.44 mg g^{-1}) is estimated to occurred at 56 days (Graph 3b), which is the highest value observed between treatments. This maximum level of residual acrylamide monomer (0.44 mg g^{-1}) corresponds to 440 mg kg^{-1} and is within the manufacturing limits reported in the literature for agricultural PAMs (200-500 mg kg^{-1}) and within the manufacturing level considered low (<0.05%) (CASTLE, 1993; XIONG *et al.*, 2018). These low levels found are due to the efforts of the industry that have been encouraged to change methods to reduce levels of residual acrylamide monomer in PAMs (SATHESH PRABU; THATHEYUS, 2007).

In ECs 0.5, 1.5 and 3 dS m^{-1} decreasing functions were found, with a reduction in RA_m concentrations of 0.00218, 0.0017 and 0.00132 mg g^{-1} per day, respectively (Graph 3b). For the maximum EC (6 dS m^{-1}), a minimum value (0.11 mg g^{-1}) of residual acrylamide was observed at 100 days (Graph 3b).

The hydrogel investigated has acceptable initial levels of potentially toxic RA_m. It is also considered to be stable as there was no increase in acrylamide concentrations resulting from possible depolymerization of acrylamide in the hydrogel polymeric chain (HOLLIMAN *et al.*, 2005; XIONG *et al.*, 2018). This corroborates a study which showed that the addition of 1% (w w^{-1}) of PAM soil conditioner in tomato and wheat plantations did not pollute the soil with acrylamide monomers resulting from depolymerization (KUSNIN; SYED; AHMAD, 2015).

Residual acrylamide was analyzed in corn, potatoes, sugar beet and beans produced following PAM application to the soil. The tested cultures showed <10 ppb of acrylamide, concluding that, over time, acrylamide is reduced in plant tissue (BOLOGNA; ANDRAWES; BARVENIK, 1999).

Graph 3 – Final residual acrylamide (mg acrylamide/g dry gel) of a hydrogel of potassium acrylate-co-acrylamide as a function of salinity levels (0.003, 0.5, 1.5, 3.0 and 6.0 dS m^{-1}) of hydration solution (a) and time (30, 60, 90 and120 days) (b).



Source: elaborated by the author.

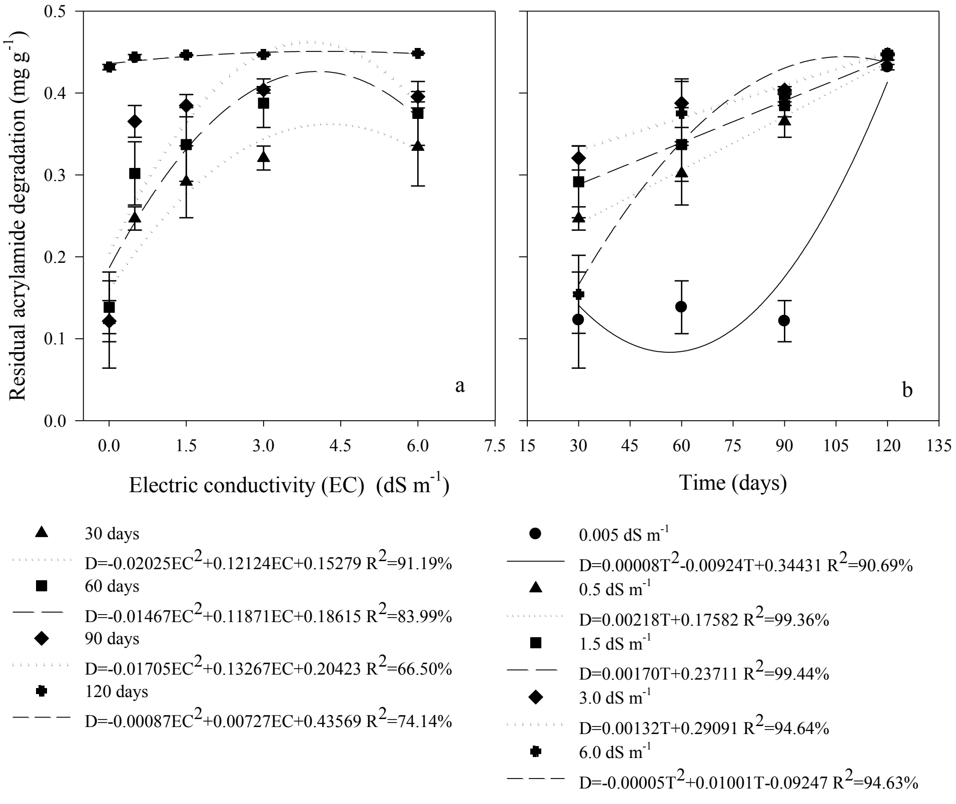
Although acrylamide levels are within the tolerable limit, it is suggested that the post-synthesis polymer washing process should be improved, since some of the monomer values found were located at the upper limit (Initial pre-testing hydrogel RA_m concentration of 0.5 mg g^{-1} - Table 1) and close to the upper limit (hydrogel in distilled water at 56 days; 0.44 mg g^{-1} - graph 3b). This improvement in washing after hydrogel synthesis would further reduce RA_m levels and increase safety when applying the hydrogel to the soil (BEZERRA, 2015).

Monomeric acrylamide contains an unsaturated vinyl group that is vulnerable to various chemical reactions (MATOSO *et al.*, 2019) facilitating its degradation. The acrylamide monomer is decomposed into propionamide and propanoic acid. Propanoic acid is a fatty acid metabolized by plants, while propionamide is degraded to CO_2, NH_4^+, and H_2O (HOLLIMAN *et al.*, 2005).

In the current study, at 30 days the greatest degradation of 0.33 mg g^{-1} was observed at an EC of 3.0 dS m^{-1}. At 60 days the maximum degradation was 0.40 mg g^{-1} in EC 4.0 dS m^{-1}. At 90 and 120 days, the degradation was similar (0.43 and 0.42 mg g^{-1}) and maximum in ECs 3.0 and 4.2 dS m^{-1}, respectively (Graph 4a). Between the ECs of 3.0 to 4.2 dS m^{-1}, the maximum degradation of RA_m occurred for the longest evaluation times (90 and 120 days).

Under simulated environmental conditions, it was found that PAM hydrogel did not degrade to acrylamide, but RA_m did degrade to NH_4^+ and NH_4^+ concentrations increased as the levels of RA_m decreased (SMITH; PRUES; OEHME, 1997). According to the polymer characterization analysis (Table 1), NH_4^+ is a measurable product of RA_m degradation and can contribute to the development of plants, since NH_4^+ is one form of how plants absorb N, which is essential for plant metabolism (MOREAU *et al.*, 2019; SMITH; PRUES; OEHME, 1996a). The accumulation of N in forest seedlings increased over time and with the increase of Forth Gel® doses in a substrate (ALBUQUERQUE, 2019), proving the use of N from the hydrogel by the plants.

Graphic 4 – Residual acrylamide degradation (mg acrylamide/g dry gel) of a hydrogel of potassium acrylate-co-acrylamide as a function of salinity levels (0.003, 0.5, 1.5, 3.0 and 6.0 dS m^{-1}) of hydration solution (a) and as a function of time (30, 60, 90 e 120 days) (b).



Source: elaborated by the author.

In distilled water, less degradation of RA_m (0.08 mg g^{-1}) was observed at 56 days (Graph 4b). For ECs 0.5, 1.5 and 3.0 dS m^{-1}, RA_m degradation was observed in increasing functions, so that daily degradation of 0.0022, 0.0017 and 0.0013 mg g^{-1}, respectively, occurs. For the EC 6 dS m^{-1} treatment, a maximum point of RA_m degradation of 0.41 mg g^{-1} was observed at 100 days (Graph 4b). These results show that RA_m is degraded rapidly, especially at low concentrations. However, higher concentrations of acrylamide require more time to degrade, remaining stable for more than 60 days in tap water (BROWN *et al.*, 1980).

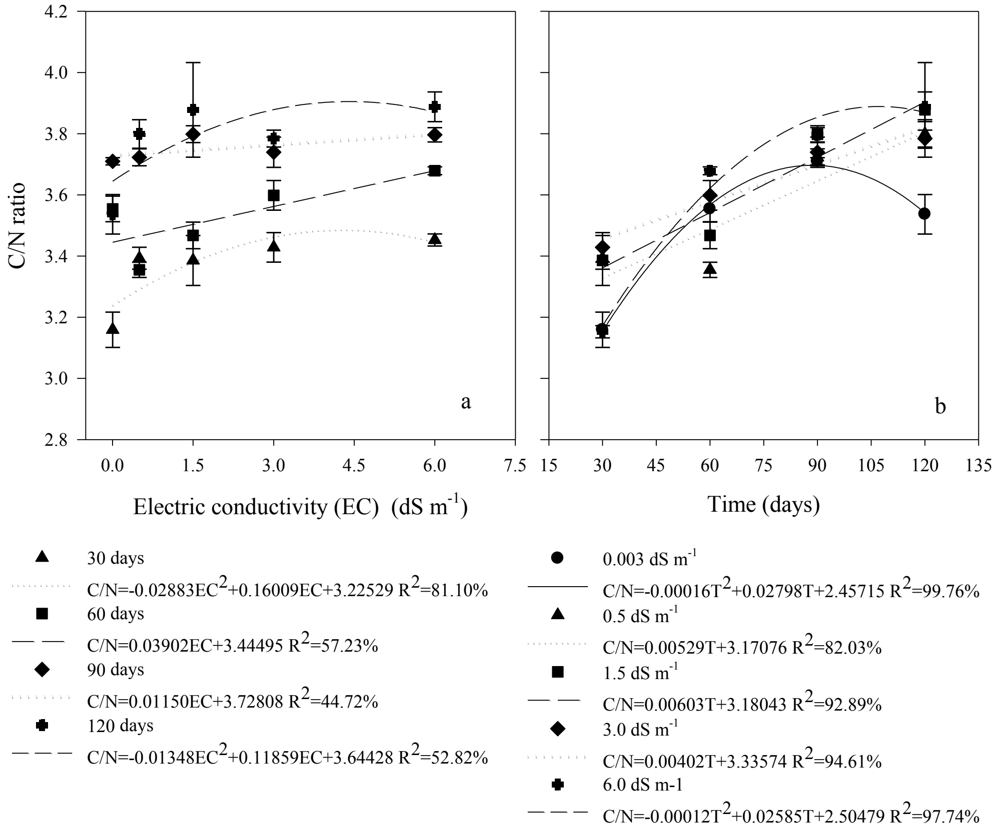
The degradation of RA_m, at all salinity levels, is greater with the increase in the evaluation time (Graph 4b), confirming that acrylamide is degraded in days (LANDE; BOSCH; HOWARD, 1979) and is susceptible to biodegradation in soil and surface water, which reduces the risk of accumulation in the environment (NEELY; BRANSON; BLAU, 1974; TEPE; ÇEBI, 2017).

At 30 days, the C/N was estimated to be maximum (3.45) at an EC of 2.80 dS m^{-1} (Figure 5a). At 60 and 90 days, increasing functions were observed, with daily increments in the C/N of 0.039 and 0.012, respectively. At 120 days, the maximum C/N (3.90) was observed for an estimated EC of 4.40 dS m^{-1}. In distilled water, maximum C/N (3.68) was observed at an estimated 87 days (Graph 5b). For ECs 0.5, 1.5 and 3.0 dS m^{-1}, increasing functions were found, with daily increments in the C/N of 0.005, 0.006 and 0.004, respectively. For the EC 6.0 dS m^{-1} hydration solution, the maximum C/N value (3.9) occurred at an estimated 108 days.

The C/N ratio of the hydrogel evaluated increased with time and salinity levels in relation to the C/N of the hydrogel pre-testing (2.60 - Table 1), being close to 4.0 (Graph 5a and b). With the increase in C/N in relation to the hydrogel pre-testing, the degradation and the greater release of N from the polymer chain is confirmed in contrast to C. The increase in the C/N ratio of the hydrogel about the hydrogel pre-testing is attributed to hydrolysis, as well as the possible microbial growth inside the hydrogel, since the average microbial C:N is about 7:1 (HOLLIMAN *et al.*, 2005).

While monomeric acrylamide contains an unsaturated vinyl group that is vulnerable to a wide range of chemical reactions (MATOSO *et al.*, 2019), once polymerized, the double bond disappears leaving only the amide group exposed and susceptible to typical amide reactions (for example, hydrolysis or Hoffman's rearrangement) (HOLLIMAN *et al.*, 2005). The results of this study indicate the hydrolysis of the amide groups of the hydrogel tested increased the C/N ratio above that of the re-testing level. The results of increasing the C/N for the samples for 120 days suggest that hydrolysis is an important degradation pathway.

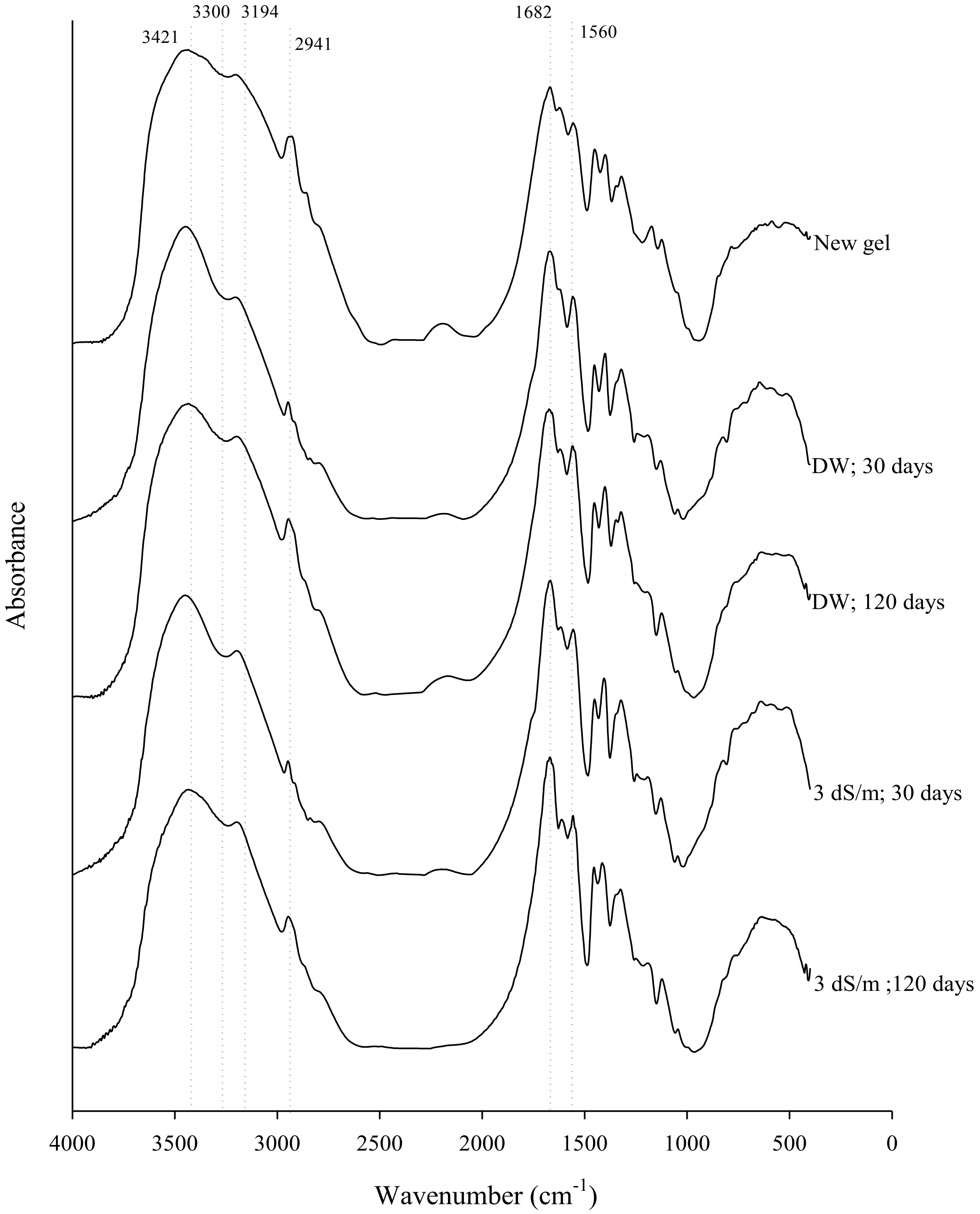
Graph 5 – C/N ratio of commercial hydrogel of a hydrogel of potassium acrylate-co-acrylamide as a function of salinity levels (0.003, 0.5, 1.5, 3.0 and 6.0 dS m^{-1}) of hydration solution (a) and as a function of time (30, 60, 90 and 120 days) (b).



Source: elaborated by the author.

The spectra of the acrylamide and potassium acrylate copolymer before the experiment (Graph 1a), in distilled water and time = 30 days, distilled water and time = 120 days, 3dS m^{-1} saline solution and time = 30 days, 3 dS m^{-1} saline solution and time = 120 days are shown in Graph 6.

Graph 6 – Fourier-transform infrared spectroscopy (FTIR) spectra of Forth Gel®.



New gel: hydrogel before the experiment; DW; 30 days: hydrogel in distilled water at 30 days; DW; 120 days: hydrogel in distilled water at 120 days; 3dS m^{-1}; 30 days: hydrogel in 3 dS m^{-1} solution at 30 days; 3dS m^{-1}; 120 days: hydrogel in a 3 dS m^{-1} solution at 120 days. Source: elaborated by the author.

Table 3 lists the assignments of the main bands highlighted in Graph 6.

Table 3 – Attribution of main bands in FTIR (Fourier-transform infrared spectroscopy) spectra of Forth Gel®

Forth gel®	Assignment
3421	ν_{as} NH_2 of acrylamide unit
3300	υ OH of adsorbed water
3194	ν_S NH_2 of acrylamide unit
2941, 2860	nCH and nCH_2
1682	n C=O of acrylamide
1560	COO^- of acrylate

Source: Magalhães *et al.* (2012).

The bands at 3421 cm^{-1} (ν_{as} NH_2), 3194 cm^{-1} (ν_S NH_2) and 1682 cm^{-1} (n C = O) are characteristic of acrylamide. The band at 1560 cm^{-1} occurs due to the asymmetric stretching of the carboxylate group from the acrylate (MAGALHÃES *et al.*, 2012). The presence of adsorbed water can be seen by the band at 3300 cm^{-1} in all spectra and the displacement in the band 2941 cm^{-1} indicates a change in methylene - main chain of Forth Gel® (polymeric backbone).

In the peaks referring to acrylamide (3401, 3194, 1687 cm^{-1}), little change was observed, with a more noticeable change being observed in 1682 cm^{-1}, with an increase in the more pronounced peak in the spectrum of the swollen hydrogel in EC 3 dS m^{-1} at 120 days, in the band referring to the amide I of the acrylamide (stretch C=O of amide).

In all the curves shown in Graph 6, it is observed that, after contact with distilled water or saline solution over time, there was a change in the chemical structure of the hydrogel, in different proportions, since there was a shift in the wavelength of the bands of the methylene, amides, and acrylate. In this case, it is possible to observe that the level of salinity and/or time period are altering the chemical structure of the hydrogel, indicating its degradation. These results confirm that the degradation of the hydrogel evaluated can be accelerated in the presence of solutions containing Ca, Mg salts and by the concentration of salts contained in the soils (FREITAS *et al.*, 2019) and over time (HOLLIMAN *et al.*, 2005). This degradation occurs without any release of RA_m but represents limitations to the hydrogel's functionality in the long term.

4 CONCLUSIONS

It is accepted the hypothesis that there is an interaction between time and salinity levels, reducing the water absorption potential of the commercial hydrogel tested, favoring its chemical degradation as well as the degradation of the RA_m. This implies a reduction in the durability of the hydrogel.

There is a reduction in the absorption capacity with an increase in the time of use in all salinity levels demonstrating that the hydrogel loses absorption capacity. This may be an obstacle for agricultural and forestry use if high water absorption is required for periods >120 days. Therefore, there is a need for further studies to evaluate the durability of the hydrogel when applied to the soil in forest and agricultural contexts. Future research should be based on improving the characteristics of hydrogels and their functionality over long periods and in adverse conditions (such as salinity) in irrigation water and soil.

It is recommended to use the Forth Gel® in the lowest salinity levels (~ 0.003 dS m^{-1}) of the irrigation water possible to obtain swelling >150 g g^{-1} since small additions of salts (0.003–0.5 dS m^{-1}) reduce water holding capacity drastically (~40%). However, it should be noted that even in distilled water, changes in water absorption occur over time (reduction of ~43% of the swelling when compare 30 with 120 days); water with salinity levels provide changes in the swelling, reducing this drastically but the levels of acrylamide monomer are lower under these conditions.

The studied hydrogel does not present any problems regarding RA_m levels since both the initial and the final concentrations were within acceptable levels and there was no formation of the monomer in the salinity range of the immersion solutions (water, saline solution) and in the studied times. Up to 85% of the residual monomer was degraded within 120 days. Although the RA_m levels found are not considered high, it is recommended to improve the post-synthesis polymer washing process, which would further reduce the levels and increase environmental safety and handling with its use.

The level of salinity and/or time changes the chemical structure of the hydrogel, indicating a degradation process which has the potential to compromise its durability.

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4 TIME OF EXPOSURE TO TEMPERATURES AS A LIMITATION ON AGRICULTURAL USE OF HYDROGELS

ABSTRACT

Due to their water retention capacity, hydrogels are considered promising to improve plant available water in the soil in semi-arid environments; however, little is known about how temperature affects the functionality of hydrogels. In this study, the effect of temperature on physical attributes of soil amended with hydrogel was evaluated. A laboratory experiment was installed in a scheme (4x4) x 4 - four temperatures (30; 45; 65 and 105 °C), four exposure times (40, 70, 100, and 130 days) with four repetitions. Soil moisture at field capacity (θ_{FC}) and permanent wilting point (θ_{WP}), plant available water (AW), bulk density, and soil porosity were evaluated. The data were submitted to analysis of variance. The hydrogel increased the θ_{FC} of the soil, from 0.140 to 0.178 and 0.179 m^3 m^{-3} at 40 and 70 days, respectively, up to a soil temperature of 69°C. At 40 days, a minimum θ_{WP} (0.05 m^3 m^{-3}) was observed at 92 °C. Field capacity increased, while the θ_{WP} decreased, providing improved soil water storage. AW was higher in soil with hydrogel even at temperatures above 60°C. In all treatments evaluated, the soil bulk density and porosity were improved in comparison to the un-amended control. This constitutes an advantage in the use of the hydrogel as a soil conditioner. Even with the interaction of abiotic factors acting on the hydrogel, there are beneficial effects on the water storage capacity, soil bulk density, and soil porosity.

Keywords: Hydrogel. Superabsorbent copolymer. Physical soil properties. Water storage.

1 INTRODUCTION

Drylands, which include arid and semiarid ecosystems, cover 41% of the earth's surface, play an important role in the global ecosystem, and are home to more than two billion people (HOOVER *et al*., 2020). Arid and semiarid environments are peculiar in terms of landforms, soil, fauna, flora, and water balance. Water scarcity and high-intensity, low-frequency rainfall are characteristic of these regions (SANTOS *et al*., 2016).

The global expansion of arid lands will increase the population affected by water scarcity and land degradation (FENG; FU, 2013). To feed an increasing global population, it is necessary to take advantage of drylands and use their natural resources sustainably (THOMBARE *et al*., 2018). Severe water scarcity is becoming common in many arid and semiarid regions of the world (MOHAMMADINEZHAD; AHMADVAND, 2020), with water management being one of the biggest challenges for these regions (ABOBATTA, 2018).

Among the alternatives for supplying water to plants in arid and semiarid regions, soil conditioners stand out, which helps to overcome adverse conditions, favoring plant development. Hydrogels proved to increase water use efficiency where irrigation water is limited (BAKASS; MOKHLISSE; LALLEMANT, 2002), and have been used in dry regions to increase the soil's capacity to absorb and retain water (ZAIN *et al*., 2018) and improve crop growth (YANG *et al*., 2018). Positive effects of hydrogels have also been related to increased soil porosity, providing better oxygenation to plant roots (ULLAH *et al*., 2015) and reduced soil bulk density (HOU *et al*., 2018).

Considering the characteristics of arid and semiarid regions, it is necessary to understand how high temperatures affect the hydrogel applied to the soil. Studies have indicated that increasing temperature compromises the functionality of agricultural hydrogels, highlighting a reduction of up to 60% of the water retention capacity in soil amended with hydrogel at temperatures up to 35 °C (ANDRY *et al*., 2009). The absorption of water by a hydrophilic polymer decreased with increasing temperature from 30 to 60 °C (ZHAO *et al*., 2005).

Hydrogels can absorb and lose water in a reversible way, being related to intrinsic factors of the external environment, such as temperature, which in turn can contribute to the collapse or phase change (AHMED, 2015). At a critical temperature, the elasticity of the hydrogel reaches zero and the hydrogel becomes infinitely compressible (MOLLOY; SMITH; COWLING, 2000). At a constant temperature of 37 °C, it has been reported that the hydrogel can change its physical properties (SMITH; PRUES; OEHME, 1996a).

In arid and semiarid regions of the world, soil temperature values ranging from 25 to 60 ºC have been recorded (CORREIA *et al*., 2012; GAO *et al*., 2007; REYES *et al*., 2016; WU *et al*., 2017; XIAO *et al*., 2016). Inappropriate management practices (e.g. deforestation) are commonly adopted in semiarid regions, leaving the soil exposed to the effects of temperature, as solar radiation starts to directly affect the soil (SCHARENBROCH; BOCKHEIM, 2007; SOUTO *et al*., 2005). Thus, it is important to know the extent to which temperature negatively affects the functionality of hydrogels for agricultural use.

Thus, the hypothesis was tested that even in the face of thermal stress and exposure time, a commercial hydrogel provides beneficial effects by improving the water storage capacity, soil bulk density, and soil porosity. The objective of the study was to evaluate physical attributes of soil that received hydrogel through times of exposure to temperatures that are indicative of arid and semiarid regions, to obtain information for the use of hydrogels as a strategy for improving water availability in adverse conditions.

2 MATERIAL AND METHODS

2.1 Experimental site and soil used

The study was carried out from January to June 2018 through an experiment installed and conducted at the Soil Physics laboratory of the Federal University of Ceará, located at the Campus do Pici (Fortaleza, CE, Brazil). The soil used in the experiment was a Leptsol with a sandy loam texture, collected at the Vale do Curu Experimental Farm (Pentecoste, CE). The surface layer of 0-0.2 m of soil was collected with visible signs of degradation (absence of vegetation, erosion processes, signs of fire use, and compaction). The collected samples were air-dried, ground, to pass a < 2 mm sieve and homogenised prior to physical and chemical characterization (Table 1).

Table 1 – Physical and chemical attributes of the 0-0.2m litter of the Leptsol used in the study, from Pentecoste-CE.

Physical attributes	**Depth (0-0.2m)**	**Chemical attributes**	**Depth (0-0.2 m)**
Sand (g kg^{-1})	736	pH water 1:2,5	6.82
Silt (g kg^{-1})	225	Ca^{2+} (cmol$_c$ kg^{-1})	7.0
Clay (g kg^{-1})	39	Mg^{2+}(cmol$_c$ kg^{-1})	1.90
Disp. clay (g kg^{-1})^1	25	K^+(cmol$_c$ kg^{-1})	0.56
DF (%)^2	37	Na^+(cmol$_c$ kg^{-1})	0.08
Silt/clay	5.8	S (cmol$_c$ kg^{-1})^9	9.54
Texture	Sandy loam	Al^{3+} (cmol$_c$ kg^{-1})	0.10
Ds (g cm^{-3})^3	1.49	H^+ (cmol$_c$ kg^{-1})	2.20
P (%)^4	44.0	CEC (cmol$_c$ kg^{-1})^{10}	11.8
θ_{sat} (m^3 m^{-3})^5	0.44	C org (g kg^{-1})^{11}	13.0
θ_{fc} (m^3 m^{-3})^6	0.14	V (%)^{12}	80.6
θ_{wp} (m^3 m^{-3})^7	0.10	m (%)^{13}	1.08
AW (m^3 m^{-3})^8	0.04	PST (%)^{14}	0.68

^{1}dispersed clay in water; ^{2}degree of flocculation;^{3}soil density; ^{4}total porosity; ^{5}saturation humidity; ^{6}soil moisture at the field capacity; ^{7}soil moisture at the point of permanent wilt; ^{8}available water; ^{9}sum of bases; ^{10}cation exchange capacity; ^{11}organic carbon; ^{12}base saturation; ^{13}aluminium saturation; ^{14}percentage of sodium saturation.
Source: elaborated by the author.

In the granulometric analysis, the clay was quantified by the pipette method, sand by wet sieving, and silt by the difference between the initial mass of the sample and the masses of clay and sand (GEE; BAUDER, 1986). The soil bulk density was determined by the beaker method (ALMEIDA *et al.*, 2017) and the particle density according to Blake and Hartge (1986). Soil porosity was obtained when the density of the soil and particles was known, according to formula 1:

$$\alpha = \left(1 - \frac{\rho_s}{\rho_p}\right), \tag{1}$$

Where: α - porosity (m^3 m^{-3}), ρ_p and ρ_s - particle and soil densities (kg m^{-3}), respectively.

For chemical characterization of the soil, the following analyzes were performed: pH, which was measured in H_2O (1: 2.5) by potentiometry; potential acidity (H + Al), which was extracted with calcium acetate buffered at pH 7.0 and determined by titration; Ca^{2+} and Mg^{2+}, which were extracted with 1M KCl solution and determined by atomic absorption spectrometry; exchangeable aluminum (Al^{3+}), was extracted with 1M KCl solution and determined by titration. Phosphorus (P), sodium (Na^+) and potassium (K^+) were extracted with Mehlich 1 solution, with P determined by colorimetry and K^+ and Na^+ by flame photometry (TEIXEIRA *et al.*, 2017).

Total organic carbon (TOC) was determined by wet oxidation (YEOMANS; BREMNER, 1988). The cation exchange capacity (CEC), the sum of bases (SB), base saturation (V%), aluminium saturation (m%), and sodium saturation percentage (PST) were calculated following Teixeira *et al.* (2017).

2.2 Characterization of the hydrogel

The hydrogel used was a commercial product (Forth Gel®), characterized on the manufacturer's label as a copolymer of acrylamide and potassium acrylate. To refine the characterization of the product, elemental analysis, X-ray fluorescence spectrometry (FRX), particle size, and residual acrylamide of the gel was carried out before exposure to temperature and time (Table 2).

Elementary analysis of carbon (C), hydrogen (H) and nitrogen (N) was performed using a Carlo Erba EA 1108 microanalyzer; the C/N ratio was obtained by the ratio between C and N; the elemental composition of the acrylate was determined by X-ray fluorescence spectrometry (FRX) using X-ray fluorescence spectrometer, model ZSXMini II (Rigaku); the particle size fraction was determined using 24 mesh (0.710 mm), 35 mesh (0.425 mm) and 48 mesh (0.300 mm) sieves and residual acrylamide were determined by high-performance liquid chromatography (HPLC) in a chromatograph model LC-20AD from Shimadzu, coupled to the diode array detector model SPD-M20A, at a wavelength of 197 nm.

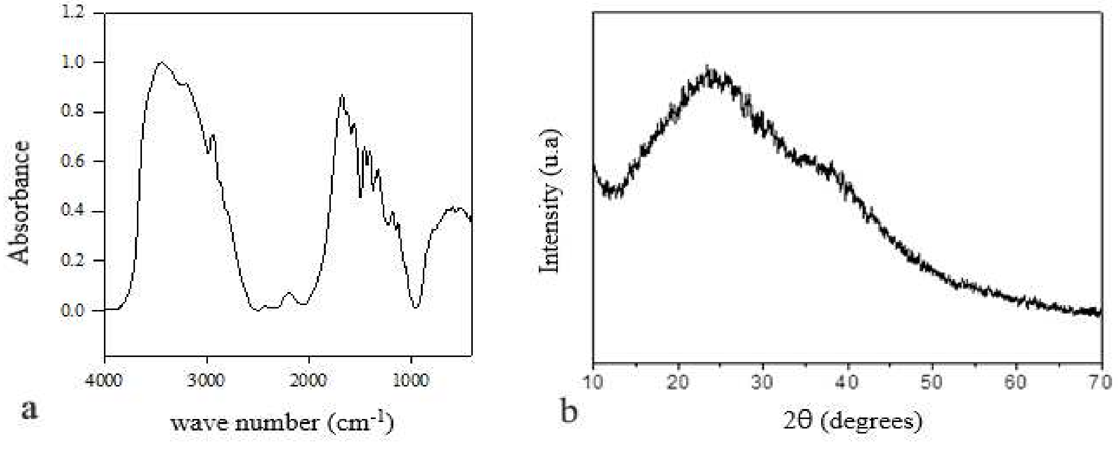
Table 2 – Elementary analysis of carbon (%C), hydrogen (%H), nitrogen (% N), carbon/nitrogen ratio (C/N) of the hydrogel; elementary chemical composition of the acrylate (%) with potassium (K) and sulfur (S) contents, granulometric distribution and RA_m of the commercial hydrogel before applying the treatments (new gel).

---- Elementary analysis (%)----				Acrylate Elementary composition (%)	
C	H	N	C/N	K	S
39.7	6.70	15.0	2.65	99.2	0.8
Particle size fraction (%)				Residual acrylamide (mg g^{-1})	
<24 mesh	24-35 mesh	35-48 mesh	<48 mesh		
12	37	15	36	0.50	

Source: elaborated by the author.

Infrared spectroscopy (FTIR) and X-ray diffraction were also performed for the characterization of the hydrogel. Infrared absorption spectroscopy (FTIR) was performed on FT equipment IR-8500 (Shimadzu), operating in the 400-4000 cm^{-1} range; X-ray diffraction was performed using an XPert Pro MPD diffractometer (Panalytical), with Cu-Kα radiation, varying 2θ from 5 to 70° (Figure 1).

Figure 1 – Infrared spectrum (a) and diffractogram (b) of the commercial acrylamide and acrylate hydrogel studied.



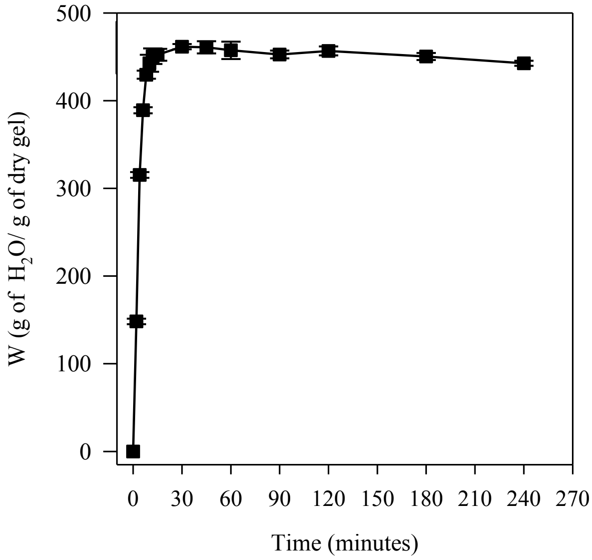
Source: elaborated by the author.

To determine the swelling curve, 30 mg of the hydrogel were weighed in a 30 mL filter crucible (N° 0 porosity) previously moistened. This set was completely submerged in the liquid medium (distilled water). The set (crucible + gel) was removed at intervals of time (2, 4, 6, 8, 10, 12, 15, 30, 45, 60, 90, 120, 180, 240 minutes), the outer wall of the crucible was the dry and heavy system. The procedure was performed in triplicate. The hydrogel was screened to obtain the particle size between 24 and 35 mesh that was used in this swelling study. To calculate the swelling, formula 2 was used:

$$S = \frac{Wt - W0}{W0} \quad (2)$$

W0 represents the mass (g) of the hydrogel dried at 65 °C and Wt is the mass (g) of the hydrogel expanded at time t. This resulted in the hydrogel swelling curve in distilled water (0.003 dS m^{-1}) (Graph 1).

Graph 1 – Hydrogel swelling curve in distilled water.



Source: elaborated by the author.

2.3 Experimental design and treatments

The experimental design was entirely randomized, in split plot system (4 x 4) x 4, with two factors (temperature and time), each with 4 levels. The dose of hydrogel used was 0.1% (w w^{-1}), determined experimentally so that there is no visible structural alteration in the soil confined to a 100 cm^3 cylinder after wetting and drying in an oven.

The treatments were as follows: I) temperatures (T1 = 30 °C; T2 = 45°C; T3 = 65 °C and T4 = 105 °C); II) evaluation times (40, 70, 100 and 120 days). The treatments were evaluated with four replications, totalling 64 experimental units. Each experimental unit consisted of a stainless-steel cylinder with dimensions of 5 x 5 cm (100 cm^3) filled with homogenized soil with hydrogel at a dose of 0.1% w w^{-1}, sealed with tissue at the bottom.

2.4 Experiment installation, conduction, and evaluations

The sealed stainless-steel cylinders of known mass (experimental units) were placed in plastic trays. Each experimental unit was filled with soil homogenized with the dry hydrogel and, later, they were moistened by capillarity. Each sample consisting of a stainless-steel cylinder filled with soil + hydrogel was saturated for 24 hours and, after saturation, showed an initial density of 1.15 g cm^{-3}.

Subsequently, the samples were placed in an oven and subjected to treatments with temperatures (T1= 30 °C; T2= 45 °C; T3= 65 °C and T4= 105 °C). At the end of each evaluation period (40, 70, 100, and 120 days), the samples were analyzed for soil moisture at field capacity (θ_{FC}) and permanent wilting point (θ_{WP}), plant available water (AW), bulk density and porosity.

The field capacity (θ_{FC}) was determined in deformed samples, after equilibrium at a tension of 10 kPa, using the gravimetric method in a Haines funnel. Soil moisture at permanent wilting point (θ_{WP}) was determined in deformed samples, using a gravimetric method in a Richards extractor after equilibrium at a tension of 1500 kPa (KLUTE, 1986). Plant available water (AW) was calculated as the difference between θ_{WP} and θ_{WP}.

The samples were taken to an oven at 105 ºC until constant mass was attained. Soil density was determined using formula 3:

$$\mathrm{Ds} = \frac{\mathrm{Ms}}{\mathrm{Vs}} \qquad (3)$$

Ds (g cm^{-3}) = Density of the soil; Ms (g)= Mass of dry soil; Vs (cm^{-3}) = Total soil volume.

Soil porosity was obtained with soil and particle density, according to formula 1.

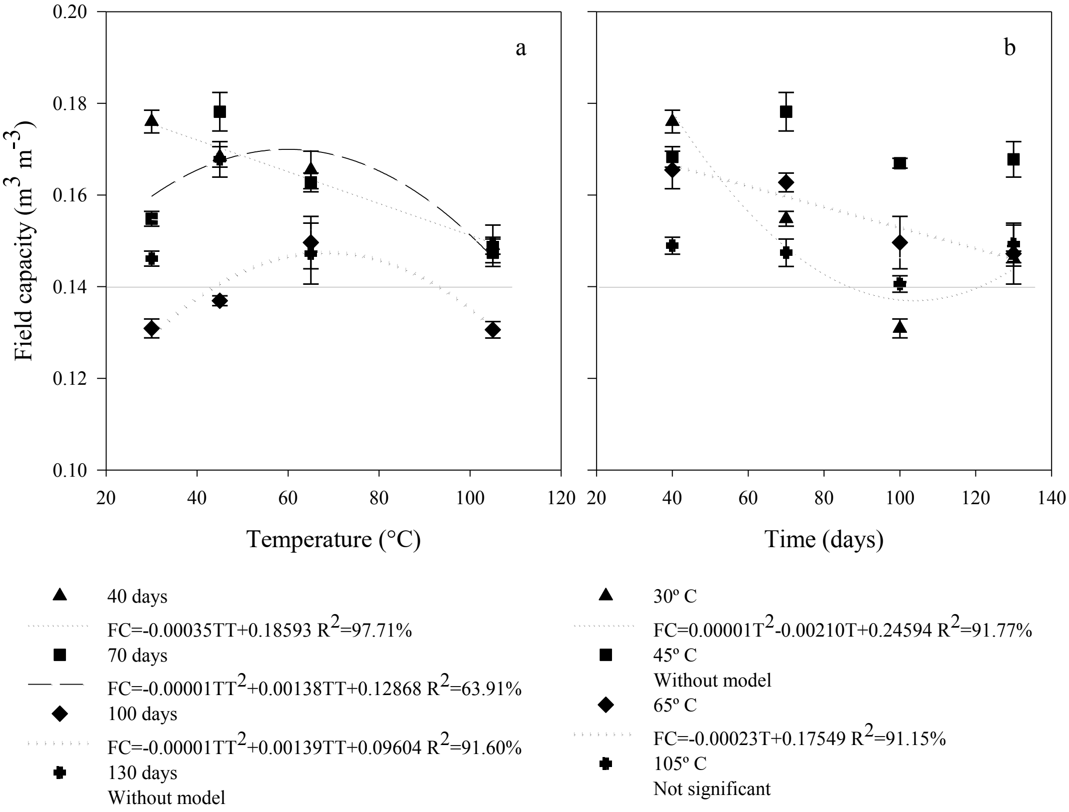
The homogeneity of variance and the normality of the residuals were tested before conducting the analysis of variance (Two-way factorial ANOVA), with level of significance of 99% ($p < 0.01$). When the interaction between factors and/or each isolated factor was significant, linear regressions were performed. All statistical analyzes were performed using SAS 9.3 (“SAS 9.3 Software”, 2011).

3 RESULTS AND DISCUSSION

With the F test of analysis of variance (ANOVA), a significant interaction was found for all sources of variation: Field capacity, wilting point, available water, bulk density, and porosity (Table 2 - ANNEX A). With that, the factors were unfolded where the models were adjusted.

At 40 days, the relationship between θ_{FC} and temperature is represented by a decreasing linear function (Graph 2a), so that there is a decrease in θ_{FC} of 0.0004 $m^3\ m^{-3}$ for each 1 °C increase in temperature (Graph 2a). For 70 and 100 days, the model to which the experimental data fitted was quadratic; at 70 days a maximum point was found for θ_{FC}, 0.170 $m^3\ m^{-3}$, at 69 °C. At 100 days the maximum value of θ_{FC} was 0.147 $m^3\ m^{-3}$ (Graph 2a) and at 130 days there was no adjustable mathematical model to the equation.

Graphic 2 – Field capacity ($m^3\ m^{-3}$) of a 0-0.2m layer of the Leptsol plus 0.1% ($w\ w^{-1}$) of the hydrogel as a function of air temperatures (30, 45, 65 and 105 °C) (a) and time of exposure to temperature (40, 70, 100 and 130 days) (b). The continuous gray line indicates the field capacity of the soil without hydrogel.



Source: elaborated by the author.

The addition of the hydrogel increased the value of θ_{FC} of the soil (0.140 m^3 m^{-3}) by up to 28%, especially at 40 and 70 days at temperatures of up to 69 °C, reaching maximum values of 0.178 and 0.179 m^3 m^{-3}. This confirms that the hydrogel improves water storage in the soil (MANDAL *et al.*, 2015). However, there is a decline in θ_{FC} with a rise in temperature >69 °C.

The increase in the θ_{FC} of the soil caused by the addition of the hydrogel did not affect the free porosity of water (or aeration), which was around 30% in the condition of maximum θ_{FC}. It is recognised that there is a restriction in the development of plants when the volume of pores with air in the soil is < 0.1 cm^3 of air per cm^3 of soil, that is, porosity free of water less than 10% (GRABLE; SIEMER, 1968).

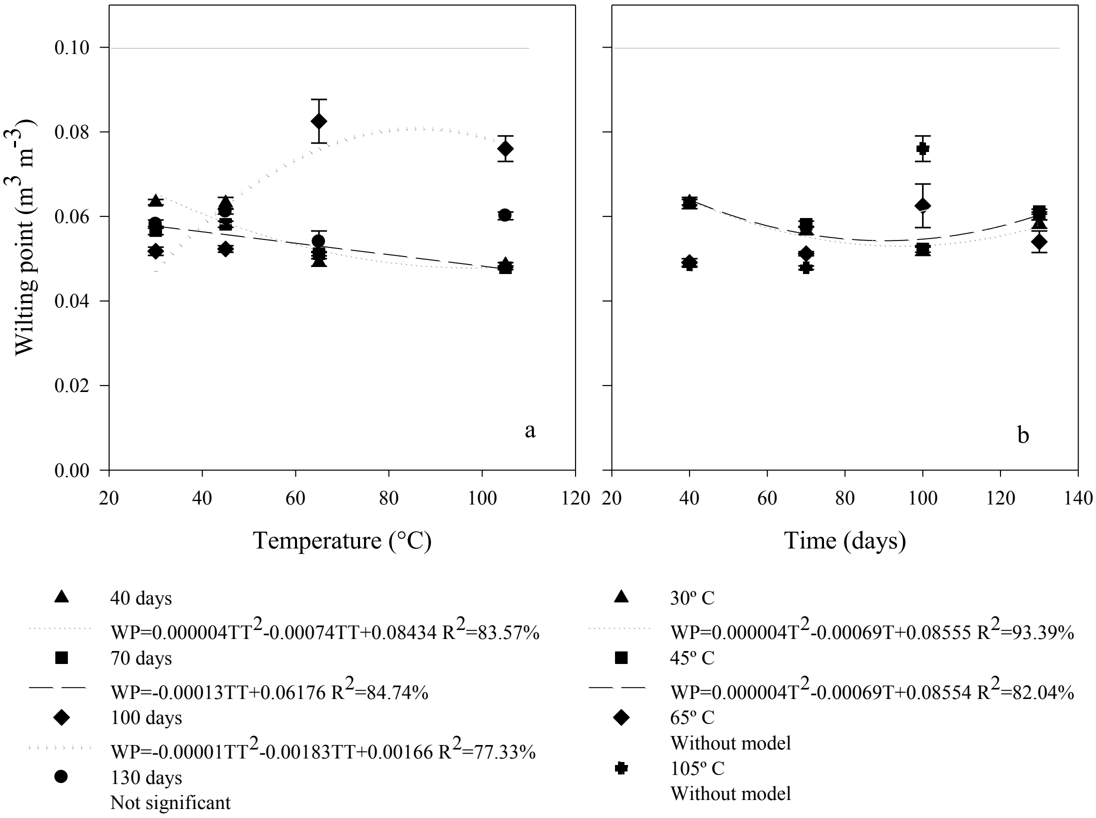
The water retention efficiency of hydrophilic hydrogel applied to a sandy soil decreased by up to 60% when the temperature increased from 15 to 35 °C (ANDRY *et al.*, 2009). In the present study, higher tolerance of the hydrogel to temperatures was observed, with a reduction of up to 15% in water retention in θ_{FC} (in 10 kPa) with temperature increases from 30 to 105 °C. Minimal effects of temperature up to 40 °C have already been reported in hydrophilic agricultural hydrogels immersed in saline solutions (MOLLOY; SMITH; COWLING, 2000).

The term “polymeric network” refers to cross-linking, which has the function of preventing the dissolution of hydrophilic polymeric chains from the hydrogel to the aqueous phase (HENNINK; NOSTRUM, 2012) being N, N′-methylene- (bis) -acrylamide (BAA) the water-soluble cross-linking agent most used in the production of superabsorbent hydrogels (WU *et al.*, 2001). The water retention capacity is related to the degree of crosslinking of the hydrogel (DORKOOSH *et al.*, 2000) providing a different three-dimensional expansion and porous structure (AHMED, 2015).

At 30 °C, there was a minimum value of θ_{FC} (0.140 m^3 m^{-3}) at 105 days (Graph 2b). At 65 °C, a decreasing function is observed, with daily reductions of 0.0002 m^3 m^{-3} in θ_{FC}. At 45 °C, there was no adjustment model to the equation and at 105 °C, there was no statistical differentiation between the treatments (Graph 2b). Another study shows a significant loss of water retention capacity in a hydrogel substrate after 150 days (SAVI *et al.*, 2014). In the present study, there was a loss of water-holding capacity in the soil with hydrogel after about 100 days.

Just as there was a change in the water retention efficiency at 100 days (greater reduction of θ_{FC} - Graph 2a), at 100 days a change in retention efficiency at 1500 kPa was also observed (maximum point θ_{WP} (0.08 m^3 m^{-3} - Graph 3a)) - at 91 °C. This reduction in θ_{FC} and increase in θ_{WP} implies a reduction in the water available to plants. This θ_{WP} value is close to the soil condition without adding the hydrogel (0.10 m³ m⁻³ - Table 1), indicating a change in the hydrogel's retention capacity with the combination of higher values of the temperature x time.

Graphic 3 – Permanent wilting point ($m^3\ m^{-3}$) of a 0-0.2m layer of the Leptsol plus 0.1% ($w\ w^{-1}$) of the hydrogel as a function of air temperatures (30, 45, 65 and 105 °C) (a) and times of exposure to temperatures (40, 70, 100 and 130 days) (b). Continuous gray line indicates the permanent wilting point of the soil without hydrogel



Source: elaborated by the author.

At 40 days, the lowest θ_{WP} (0.05 m³ m⁻³) was observed at 92 °C (Graph 3a). This combination of time and temperature favored an increase in the range of water available to plants. At 70 days, the response was obtained in the form of a decreasing function, with a reduction of 0.0001 m³ m⁻³ in θ_{WP} per °C increased. At 130 days there was no statistical significance. At 30 and 45 °C, points of minimum θ_{WP} (0.06 m³ m⁻³) were observed at 86 days. For 65 and 105 °C, there was no adjustable model to the equation (Graph 3b).

When the samples were subjected to 1500 kPa, even under different conditions of temperature and exposure times, 82-90% of the water absorbed by the soil + hydrogel mixture was released, indicating that a large part of the water is not strongly retained, which would make it unavailable to plants. The effect of adding a polyacrylamide (PAM) hydrogel to sandy substrates was evaluated in another study in which the authors found that at least 95% of the water retained in the hydrogel, at stresses below 1500 kPa, were available to plants (FONTENO; BILDERBACK, 1993).

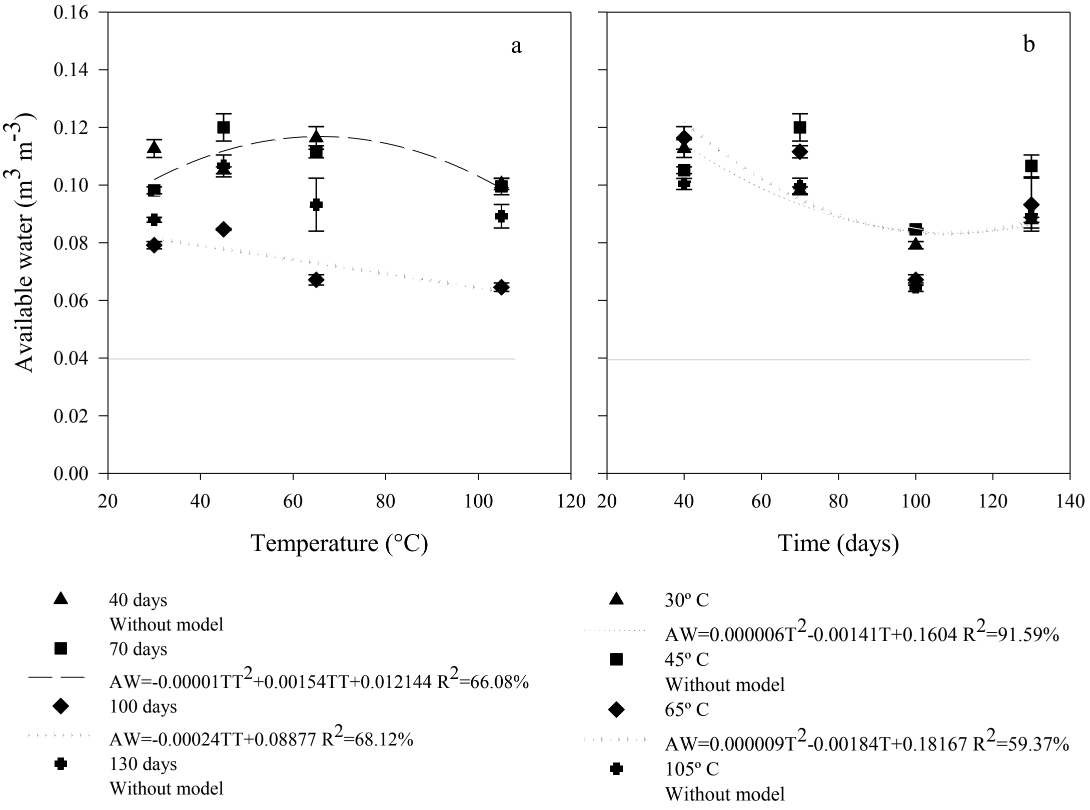
It is interesting to note that the time taken for soil samples amended with the hydrogel to reach equilibrium at the tension of 1500 kPa was longer than the unamended control. An increase in the number of days to reach θ_{WP} has been previously reported in cultivation systems amended with hydrogels (ABEDI KOUPAI; SOHRAB; SWARBRICK, 2008). The WP of sand without added hydrogel was achieved between 2 and 3 days, compared to 6-7 days for sand treated with hydrogel (amount of 1 g kg^{-1}) and 9-10 days for sand treated with hydrogel in the amount of 2 g kg^{-1} (ABEDI KOUPAI; SOHRAB; SWARBRICK, 2008; BAASIRI *et al.*, 1986).

Considering the range of temperatures and time periods evaluated, the addition of hydrogel to the soil causes the θ_{WP} to shift below that of the soil without hydrogel (Figure 3). This effect, associated with the increase in soil moisture at θ_{FC} (Figure 2) is an advantage, as it offers more AW to plants.

Hydrogels, when applied to the soil, can improve the water supply to plants due to the increase in the soil's capacity to store water (WOLTER *et al.*, 2002). In this study, at 70 days, the maximum AW value (Graph 4a) was 0.11 m^3 m^{-3} at 77 °C (higher than that observed for the unamended soil (0.04 m^3 m^{-3} - Table 1). The AW to plants (between 10 and 100 kPa) for all soil types without hydrogel was lower compared to samples with hydrogel (NARJARY *et al.*, 2012). Water retention in the soil, between 10 and 1500 kPa (range corresponding to AW for plants), increased with levels of polymers composed of sodium acrylate incorporated (VARENNES *et al.*, 1997).

In the current study, an increase of up to 3 times in AW was verified after addition of 0.1% w w^{-1} of the commercial hydrogel to the sandy-loam soil evaluated, similar to that found by Varennes *et al.* (1997) by adding 0.2% (w w^{-1}) of hydrogel to a sandy soil. The AW content increased 2.2 and 3.2 times in a loamy and sandy soil, respectively, with the application of 8 g of hydrogel per kg of soil (ABEDI KOUPAI; SOHRAB; SWARBRICK, 2008). A hydrogel dose of 2 g kg^{-1} increased the humidity by 40% in a loam-clay-sandy soil, compared to an unamended treatment, and also increased the AW by 125% (ABEDI KOUPAI; SOHRAB; SWARBRICK, 2008).

Graphic 4 – Available water ($m^3\ m^{-3}$) of a 0-0.2m layer of the Leptsol plus 0.1% (w w^{-1}) of the hydrogel as a function of air temperatures (30, 45, 65 and 105 °C) (a) and times of exposure to temperatures (40, 70, 100 and 130 days) (b). The continuous gray line indicates the water available from the soil without hydrogel.



Source: elaborated by the author.

At 100 days, a decreasing function was observed in the AW, with a reduction of 0.0002 $m^3\ m^{-3}$ per 1 °C increment (Graph 4a). At 40 and 130 days and 45 °C and 105 °C there was no adjustment model; at 30 °C and 65 °C, points with minimum values of available water (0.08 $m^3\ m^{-3}$) were observed at 117 and 102 days, respectively (Graph 4b). Even under increasing conditions of temperature and time, the soil with hydrogel showed greater AW for longer. A study with the application of acrylamide polymer in the soil in which the species *Agrostis stolonifera* was cultivated, there was a higher AW value for a longer time, reducing the frequency of irrigation (AGABA *et al.*, 2011). The application of hydrogels can result in a significant reduction in the frequency of irrigation required, especially for sandy soils, being an important issue in arid and semi-arid regions of the world to improve water management in these soils (KOUPAI; ESLAMIAN; KAZEMI, 2008).

The AW was higher than that initially observed in the unamended soil even at temperatures above 60 °C, and a gradual release of part of the AW could be expected with changes in the soil temperature. The increase in AW in response to the hydrogel is explained by the addition of hydrophilic functional groups to the soil. Therefore, the greater capacity of the soil to retain water with hydrogel was attributed to its chemical structure containing the hydrophilic functional group's acrylamide and potassium acrylate, capable of producing more hydrogen bridges with water (ABEDI KOUPAI; SOHRAB; SWARBRICK, 2008; MARANDI; REZA, 2008).

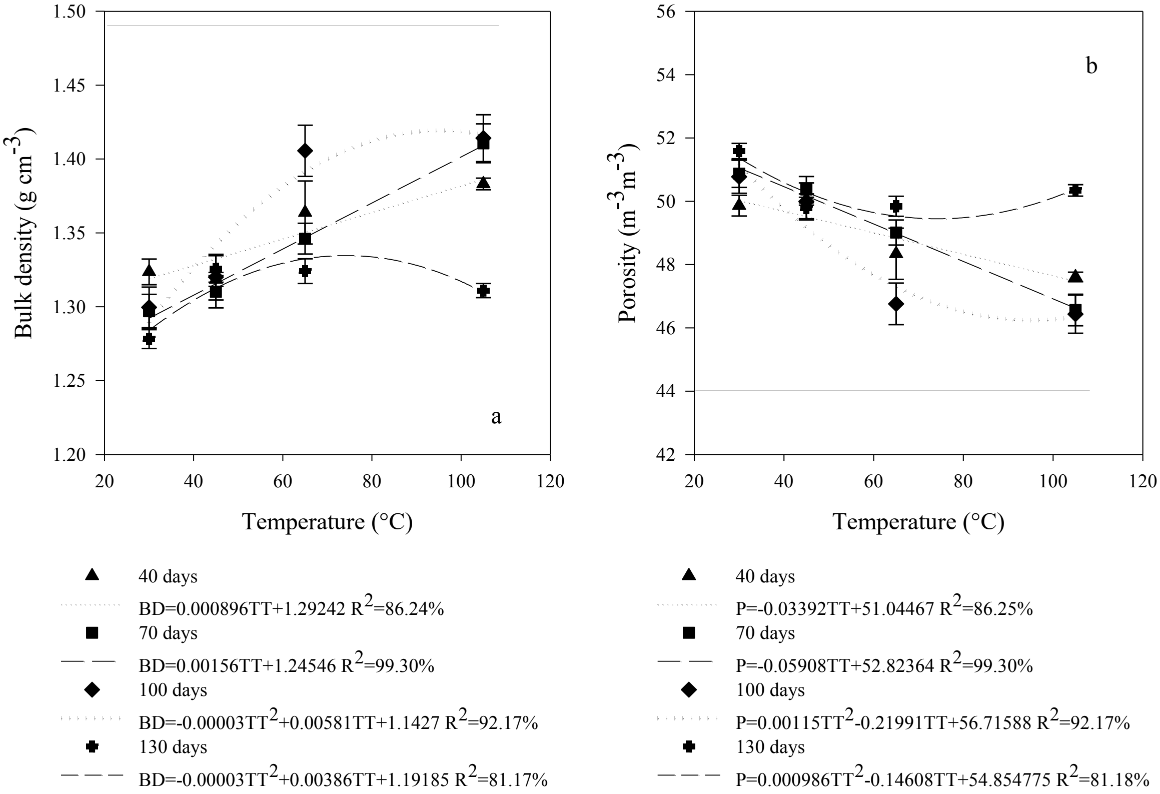
Considering an area of 1 ha and a homogeneous soil layer of 0.2 m, the water storage in the soil without hydrogel is 80 m^3 ha^{-1}. In the condition of maximum water storage with the incorporated hydrogel, the soil water storage was 220 m^3 ha^{-1}, representing an increase of 140 m^3 ha^{-1}. These results show that the tested hydrogel has a good potential to contribute to water management in soils in arid and semi-arid regions and are a strategy for increasing water use efficiency and plant production in drylands.

Concerning bulk density, at 40- and 70-days increasing equations were found, with increments of 0.0009 and 0.0016 g cm^{-3} in density, respectively, by a unitary increase in temperature (°C). For 100 and 130 days, points of maximum soil density (1.42 and 1.32 g cm^{-3}) were observed at 97 and 64 °C, respectively (Graph 5a).

With the addition of the studied hydrogel, the density of the soil increased significantly by 12% (considering conditions of maximum time and temperature). However, even in these conditions, the density was lower than the unamended soil (1.49 g cm^{-3} - Table 1). The density of the soil was reduced at all temperatures studied (Graph 5a). The soil density decreases with the application of superabsorbent hydrogel (BAASIRI *et al.*, 1986; BAI *et al.*, 2010; HOU *et al.*, 2018) because the product favors the formation of macropores in the soil (HOU *et al.*, 2018).

There was an increase in density with the increase in temperature, indicating that temperatures change the efficiency of the hydrogel in improving the physical properties of the soil. Hydrogels can absorb and lose water in a reversible way, being related to intrinsic factors of the external environment, such as temperature, which in turn can contribute to the collapse or phase change (AHMED, 2015). With the collapse of the hydrogel, there is a rearrangement of particles or aggregates, so that spaces previously occupied by hydrated hydrogel suffer volume reduction and, therefore, the density of the soil is increased. At a critical temperature, the elasticity reaches zero and the hydrogel becomes infinitely compressible (MOLLOY; SMITH; COWLING, 2000). At a constant temperature of 37 °C, it has been reported that a PAM hydrogel can change its physical properties, becoming softened when wet and brittle when dry (SMITH; PRUES; OEHME, 1996a).

Graphic 5 – Density (g cm^{-3}) (a) and soil porosity (%) (b) of a 0-0.2m layer of the Leptsol plus 0.1% (w w^{-1}) of the hydrogel as a function of air temperatures (30, 45, 65 and 105 °C). The continuous gray line indicates the bulk density and porosity from the soil without hydrogel.



Source: elaborated by the author.

Regarding soil porosity, at 40 and 70 days, decreasing functions in the equations were observed, so that for each 1 °C increase in temperature, a decrease in porosity of 0.0339 and 0.0591 m^3 m^{-3} occurs, respectively (Graph 5b). For 100 and 130 days, there are minimum values of soil porosity (46 and 49%) at temperatures of 96 and 74 °C, respectively. In the studied conditions of temperatures and time period, the porosity of the soil increased as compared with the unamended soil (PT = 44% - Table 1).

In the semi-arid region of China, it was observed that the density of the soil decreased with the addition of a potassium polyacrylate hydrogel, improving the total porosity of the soil (HOU *et al.*, 2018). This improvement, as already discussed, was attributed to the fact that the product favors the formation of macropores in the soil (HOU *et al.*, 2018). The wetting and drying cycles promote loosening of the soil structure and increased aeration because during the expansion of the hydrogel there is a detachment of the soil mass and an increase in its total porosity (PALUSZEK, 2011). Due to the considerable reduction in the volume of the hydrogel as the water is released to the plant, the hydrogel allows the appearance of free pore volume, providing more space for the infiltration of air and water, movement of gases and root growth (MILANI *et al*., 2017).

The soil porosity decreased with increasing temperature, with a decrease of up to 10% when the temperature is raised from 30 to 105 °C. For all temperatures studied, in the 40-day time period, greater soil porosity was found, a condition in which less time for the hydrogel application has elapsed and the polymer still has its functionality little changed by the gradual degradation provided by the action of time. There is evidence that the degradation of PAM hydrogels occurs as a result of chemical, photochemical and mechanical processes and due to the large size of the molecule, and that abiotic processes break the molecule into progressively smaller units over time (ENTRY; SOJKA; HICKS, 2008).

In all the evaluated treatments, the density and porosity of the soil were improved in comparison to unamended soil (Graph 5), which constitutes an advantage in the use of the hydrogel as a soil conditioner. Despite the negative effects of abiotic factors on the efficiency of the hydrogel, the results confirm that the presence of the hydrogel reduces the density and increases the porosity of the soil even under these conditions, which causes better oxygenation to the roots of the plants (ULLAH *et al*., 2015).

After adding hydrogel to the soil, even under thermal stress, total porosity and θ_{FC} increased, while the permanent wilting point decreased, providing improvement in soil water storage. In another study carried out in a semi-arid region, it was found that the application of hydrogel improves soil properties, increases soil water retention capacity, irrigation efficiency, crop growth, and productivity (DAR *et al*., 2017). The hydrogel was used to increase the water reservoir close to the plant's root system, where it increased the θ_{FC} of different soils and increased the AW to the plants and the period of their availability (MONTESANO *et al*., 2015).

4 CONCLUSIONS

The hypothesis is confirmed that even with the interaction of abiotic factors, the hydrogel provides beneficial effects at all temperatures and exposure times evaluated, improving the water storage capacity, density, and porosity of the soil. Thus, the tested hydrogel has good potential to contribute to water management in soils in arid and semi-arid regions.

The addition of the hydrogel increased the value of θ_{FC} of the soil (0.140 $m^3 m^{-3}$) by up to 28%, especially at 40 and 70 days at temperatures of up to 69 °C. However, the increase in the θ_{FC} of the soil caused by the addition of the hydrogel did not affect the free porosity of water (or aeration), which was around 30% in the condition of maximum θ_{FC}. Was observed a reduction of up to 15% in water retention in θ_{FC} (10 kPa) with temperature increases from 30 to 105 °C.

When the soil + hydrogel were subjected to 1500 kPa, even under different conditions of temperature and exposure times, 82-90% of the water absorbed by the soil + hydrogel mixture was released, indicating that a large part of the water is not strongly retained, which would make it unavailable to plants. Considering the range of temperatures and time periods evaluated, the addition of hydrogel to the soil causes the θ_{WP} to shift below that of the soil without hydrogel. This effect, associated with the increase in soil moisture at θ_{FC} is an advantage, as it offers more AW to plants.

In the current study, an increase of up to 3 times in AW was verified after addition of 0.1% w w^{-1} of the commercial hydrogel to the sandy-loam soil evaluated. Considering a condition of maximum water storage with the incorporated hydrogel, the soil water storage had an increase of 140 $m^3 ha^{-1}$. These results show that the tested hydrogel has a good potential to contribute to water management in soils in arid and semi-arid regions and are a strategy for increasing water use efficiency and plant production in drylands.

Temperatures in arid and semi-arid environments and time lead to a progressive loss of hydrogel effectiveness. Thus, there is a potential benefit for crops with a short growth cycle. Future research should be based on improving the characteristics of hydrogels and their effects over long periods and in adverse conditions typical of arid and semiarid environments.

The density and porosity of the soil were improved in comparison to unamended soil , which constitutes an advantage in the use of the hydrogel as a soil conditioner. Despite the negative effects of abiotic factors on the efficiency of the hydrogel, the results confirm that the presence of the hydrogel reduces the density and increases the porosity of the soil even under these conditions, which causes better oxygenation to the roots of the plants.

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5 POTENTIAL OF SUPERABSORBENT HYDROGELS TO BE USED IN AGRICULTURE UNDER ABIOTIC STRESSES

ABSTRACT

Hydrogels are a promising management option to increase the efficiency of water use in agriculture in arid and semi-arid regions. However, abiotic factors may affect hydrogel efficacy. This study evaluated the effect of abiotic stress on the swelling and rate of residual acrylamide degradation in hydrogels The response of three hydrogels to the abiotic stresses of temperature and salinity were quantified. The experimental design was completely randomized in a 3x4x2 scheme with four replications. The treatments were three hydrogels (A, B and C), four temperatures (20, 30, 40 and 65 °C) and two salinities (0.003 and 3.0 dS/m). At the end of 30 days, the swelling degree and the residual acrylamide concentration of the hydrogels were measured. Data were analyzed with univariate and multivariate statistics. The swelling order of hydrogels under low salinity was A>C>B; at high salinity was B>A>C. All hydrogels presented significant swelling reduction at high salinity, with swelling reductions in A and C of 97% and 85%, respectively, while B presented a swelling reduction of 37% at 20 °C and greater than 89% at higher temperatures. Hydrogel B achieved good swelling under saline conditions, but only at 20 °C. Thus, the temperature tolerance of this hydrogel should be improved so it can be used to improve water use efficiency in regions with high temperatures and salinity levels. Residual acrylamide levels of hydrogels decreased by 95% over 30 days, to levels well below the maximum permissible levels for agricultural use.

Keywords: Super absorbent hydrogels. Polyacrylamide. Water use efficiency.

1 INTRODUCTION

Semi-arid and arid areas comprise 41% of the global land area and provide food to more than 38% of the global population (REYNOLDS *et al*., 2007). Careful management of soil and water resources in these regions is essential in order to feed growing populations (THOMBARE *et al*., 2018).

Arid and semi-arid regions around the world regularly face increasing problems of water scarcity for domestic, industrial and agricultural use. Rainfed agriculture is the predominant cropping system in these areas, but aridity and climate uncertainty are the main challenges facing farmers (AMMAR *et al*., 2016). Water scarcity has compromised agricultural productivity in many developing countries, leading to a growing interest in developing practical and affordable solutions (ZAIN *et al*., 2018). Due to their high-water absorption capacity, superabsorbent hydrogels are being extensively studied as soil conditioners to increase water use efficiency in agriculture (CHEN *et al*., 2017; COELLO *et al*., 2018; PARADELO; BASANTA; BARRAL, 2019; THOMBARE *et al*., 2018; YANG *et al*., 2018; ZAIN *et al*., 2018).

Hydrogels are crosslinked hydrophilic polymers that can absorb large amounts (>100x their mass) of water (GUILHERME *et al*., 2015).The characteristics of the external solution, such as charge valency and mineral salts concentration (e.g. Na^+, Mg^{2+}), influence the expansion of hydrogels (RAJU; RAJU; MOHAN, 2003). Water absorption efficiency of hydrogels decreases with increasing solution electrical conductivity (ANDRY *et al*., 2009). Salinity impairs water absorption because hydrophilic groups of hydrogels bind to salts, blocking water ingress. Salts also suppress the electrostatic interactions between the hydrogel and water molecules (XIONG *et al*., 2018; ZHAO *et al*., 2019).

Andry *et al*., (2009) also observed that hydrophilic polymers can exhibit thermal sensitivity. When hydrogels are applied to the soil, increasing temperature increases the adsorption of anionic hydrogels to clays due to the reduction of hydrogen bonds between the polymer and water molecules which increases polymer penetration in the internal clay structure (XIONG *et al*., 2018). Thus, the efficiency of hydrogels is affected by the salinity of the soil and/or irrigation water applied as well as temperature. Both these abiotic stresses characterise arid and semiarid regions.

Anionic polyacrylamide (PAM) is the most commonly used hydrogel as a soil conditioner and, although it is an inert polymer, may contain residual acrylamide monomer (RA_m) as a result of incomplete polymerization (XIONG *et al*., 2018). Acrylamide has been studied for agricultural use because of its potential toxic effects (HOLLIMAN *et al*., 2005). Residual acrylamide concentrations in commercial PAM products are typically <500 mg/kg as regulated by the Food and Drug Administration (FDA), the U.S. Environmental Protection Agency (EPA), and the National Resources Conservation Services (NRCS) (XIONG *et al*., 2018).

Residual acrylamide although soluble and mobile in the soil is susceptible to biodegradation in soil and surface waters, which significantly reduces the risks of accumulation in the environment (NEELY; BRANSON; BLAU, 1974; TEPE; ÇEBI, 2017). Residual acrylamide associated with PAMs is subject to rapid biological degradation in soils with a half-life of 18-45 hrs (BARVENIK, 1994).

In arid and semiarid regions superabsorbent hydrogels are increasingly seen as a viable option to significantly increase water retention in soils and increase plant available water. However, as salinity and high temperatures compromise water absorption by hydrogels, it is necessary to develop polymers tolerant of these conditions. Further, there is a paucity of data on the effect of salinity and temperatures commonly associated with arid and semiarid regions on the efficacy of superabsorbent polymers.

The objective of this study was to evaluate the water absorption potential and RA_m degradation rate of three hydrogels subjected to thermal and saline stress. The hypotheses tested were: i) anionic hydrogels can contribute to water absorption efficiency under abiotic conditions of arid and semiarid regions; ii) despite the adverse effects of temperature and salinity on the efficiency of hydrogels, a polymer that provides improvements in the soil of arid and semi-arid regions can be identified; iii) the rate of RA_m degradation is influenced by the abiotic stresses of high temperatures and/or salinity and RA_m levels do not pose an environmental risk.

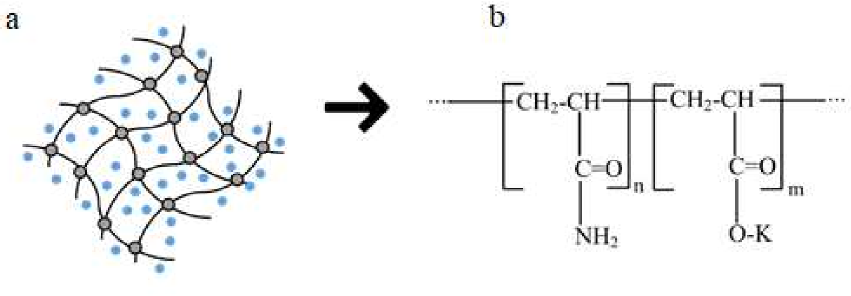
2 MATERIAL AND METHODS

This laboratory experiment was conducted at Cranfield University (UK). The experimental design was completely randomized in a 3x4x2 scheme in which the treatment factors were: hydrogel type (A, B and C), air temperature (20, 30, 40 and 65 °C) and salinity level of hydration solution (low - deionized water with electrical conductivity (EC) = 0.003 dS/m, and high - saline solution with EC = 3.0 dS/m). The treatments were replicated in quadruplicate, totalling 96 experimental units. Each experimental unit consisted of a PVC pipe (0.06m internal diameter x 0.1m long) filled with 2.0g of de-hydrated hydrogel to which the respective hydration solution was applied.

To determine the amount of hydration solution to be applied, swelling tests were performed using deionized and saline water, to achieve maximum swelling and all swelling solution not absorbed by the hydrogel was drained (~ 2 hours). Subsequently, the following volumes were used: hydrogel A - 600 ml of deionized water and 300 ml of saline solution; hydrogel B - 400 ml of deionized water and 400 ml of saline solution; hydrogel C 600 ml of deionized water and 300 ml of saline solution.

The three hydrogels tested were cross-linked acrylamide and potassium acrylate copolymers (Figure 1).

Figure 1. a. Representation of copolymer swollen in water. The lattice represents the cross-linking and the grey circles the hydrogel cross-linking points. The blue circles represent the water molecules inside the hydrogel. b. Structural representation of acrylamide and potassium acrylate copolymer. c. description of the polymers used in this study.



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Gel	Polymer characteristics	Crosslinking	Counterion	Residual acrylamide (mg/g)
A	acrylamide/acrylic acid	Yes	Potassium	0.189
B	acrylamide/acrylic acid	Yes	Potassium	0.272
C	acrylamide/acrylic acid	Yes	Potassium	0.095

Source: elaborated by the author.

All the hydrogels contain initial residual acrylamide levels well below the allowable values (<500 mg/kg) set by the Food and Drug Administration (FDA), the U.S. Environmental Protection Agency (EPA), and the U.S. National Resources Conservation Services (NRCS) (XIONG *et al.*, 2018).

The treatment for high salinity was established based on the classification of saline waters, in which Class 3 presents an EC in the range of 1.5 to 3.0 dS/m (FRENKEL, 1984). In the Northeast of Brazil, the waters used for irrigation have, in most cases, a salt concentration ranging from 1 to 30 mmol_c/L, corresponding to an EC ranging from 0.1 to 3.0 dS/m (GHEYI; QUEIROZ; MEDEIROS, 1997).

The high salinity hydration solution was prepared with sodium chloride (NaCl), calcium chloride ($CaCl_2.2H_2O$) and magnesium chloride ($MgCl_2.6H_2O$) dissolved in a 7:2:1 ratio, assuming the ratio between the EC of the irrigation water (ECW) and its concentration [CS (mmolc/L) = EC x 10], as proposed by (RHOADES *et al.*, 1989); where: Cs = salt concentration; EC = pre-established electrical conductivity.

In semi-arid regions of China, soil temperature values of about 25 °C were recorded between 5 and 25 cm depth (WU *et al.*, 2017; XIAO *et al.*, 2016); 38.4 °C in summer (REYES *et al.*, 2016) and 41 °C in agroforestry systems in Brazilian semiarid regions (MARIN *et al.*, 2006a), reaching up to 60 °C (CORREIA *et al.*, 2012). The minimum treatment temperature of 20 °C was established as a laboratory control in order to be able to critically evaluate hydrogel performance at higher temperatures. The treatments with temperatures of 30, 40 and 65 °C were obtained by placing the experimental units in Weiss Technik growth chambers. After 30 days of exposure to the temperature treatments, the samples were weighed and oven-dried at 65 °C until a constant mass was attained. Then, the experimental units were re-hydrated with the respective hydration solutions.

The final swelling of the hydrogels (g/g) was calculated as follows:

$$S=\frac{Wt-W0}{W0} \qquad (2)$$

W0 represents the mass (g) of the hydrogel dried at 65 °C and Wt is the mass (g) of hydrogel swollen in the time t.

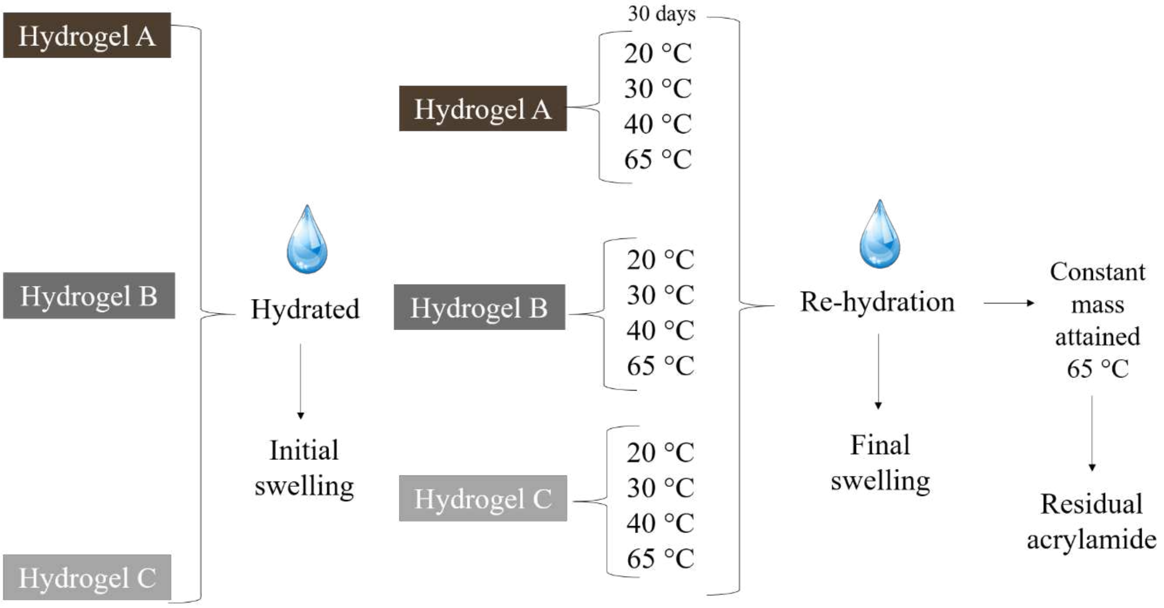
The dimensionless swelling factor of the hydrogels was obtained by the following calculation:

$$\alpha = \frac{W(\text{Salt})}{W(\text{Water})} \qquad (3)$$

which is defined as the ratio between the absorption capacity of saline solution and the absorption in a salt-free solution.

A summary of the experimental methodology is presented in Figure 2.

Figure 2. Schematic summary of the experimental method showing: swelling sequence, temperatures applied, drying protocol, rehydration and residual acrylamide analysis.



Source: elaborated by the author.

Residual acrylamide was determined by submerging 100 mg of the dry hydrogels (at the end of the experiment) in deionized water for 4 hours. The resulting immersion solution was filtered using a 0.22 μm pore 13 mm diameter cellulose ester GS membrane (Millipore) and injected into a high-performance liquid chromatography (HPLC) system. A Shimadzu model LC-20AD chromatograph coupled to a SPD-M20A diode array detector at a wavelength of 197 nm was used. For separation of the acrylamide monomer, a 250 mm long 4.6 mm internal diameter Kinetex 5u C18 100 A column was used in a CTO-20A model thermostated oven. The elution solvent (mobile phase) was 25:75 acetonitrile solution and ultrapure water, with a flow rate of 1.25 mL/min and elution time of 5 minutes. The volume used for sample injection was 50 μL.

The RA_m was quantified from the area of its respective chromatographic peak, with an elution time of 2.2 min, using a calibration curve obtained by diluting 10 ppm solution of the RA_m in deionized water. Monomer contents were expressed in mg/g (BEZERRA, 2015).

The % RA_m, which corresponds to % that remained in the hydrogels immersion solution after the 30 day treatment period, was calculated as follows:

$$\% \text{ residual acrylamide} = \left(\frac{\text{final residual acrylamide}}{\text{initial residual acrylamide}}\right) . 100 \qquad (4)$$

In addition, to access RA_m degradation the following calculation was adopted:

$$\text{residual acrylamide degradation } (\%) = \left(\frac{\text{Initial residual acrylamide-final residual acrylamide}}{\text{Initial residual acrylamide}}\right) .100 \qquad (5)$$

Experiment treatments consist of all combinations of three main factors: hydrogel acrylamide and potassium acrylate polymers (hydrogels A, B, C), four air temperatures (20, 30, 40, 65 °C) and two ECs of the swelling solution (0.003 and 3 dS/m). The homogeneity of variance and residual normality of each variable were tested for each parameter before conducting the Two-way analysis of variance (ANOVA). Data were transformed using Box-Cox techniques (BOX; COX, 1964), outliers were removed when appropriate before submitting data for ANOVA. When the interaction between factors and/or each isolated factor was significant, the means were compared by the Duncan test ($\alpha = 0.05$) ("SAS 9.3 Software", 2011). The performance of the hydrogels under the experimental temperatures and EC of the swelling solution was evaluated using the final swelling, final RA_m, residual acrylamide degradation and dimensionless swelling factor.

3 RESULTS AND DISCUSSION

The three hydrogels studied are considered superabsorbent since they absorbed > 100 times their dry mass of water (THOMBARE *et al.*, 2018). However, there are records in the literature of hydrogels that absorb more than 1000 times their dry mass in water (GUILHERME *et al.*, 2015).

In the absence of salts, at a temperature of 20°C, the degree of swelling was in the order hydrogel A> C> B, whereas in the presence of salts, at 20 °C, the order was hydrogel B> A> C (Table 2).

Table 2 – Comparison test of means for final swelling degree (g/g) of three acrylamide and potassium acrylate copolymer hydrogels at four temperatures and two levels of electrical conductivity of the hydration solution.

Treatment			**Mean ± SE**	**Duncan Grouping**
Hydrogel	°C	dS(m)	(g/g)	
A	30	0.003	431±12.1	a
A	20	0.003	366±5.68	b
C	40	0.003	324 ±6.53	bc
C	20	0.003	313±2.60	cd
C	30	0.003	286±2.11	cde
C	65	0.003	284±2.83	cde
A	40	0.003	273±6.42	de
A	65	0.003	262±5.83	e
B	30	0.003	212±3.37	f
B	20	0.003	209±5.63	f
B	40	0.003	195±4.86	f
B	65	0.003	192±1.41	f
B	20	3	134±1.85	g
A	20	3	62.0±0.42	h
C	20	3	40.8±0.67	i
C	40	3	31.8±1.54	j
C	65	3	29.9±0.16	j
C	65	3	24.8±0.46	k
B	65	3	23.2±0.61	k
B	40	3	21.2±0.63	k
C	30	3	21.0±1.58	k
B	30	3	16.6±0.31	l
A	40	3	16.2±0.34	l
A	30	3	13.3±0.32	m

Means with the same letter are not significantly different ($p<0.05$) by Duncan test
Variable with transformation $x^{0.1}$; SE -standard error.
Source: elaborated by the author.

The initial swelling order hydrogel A>C> B in the absence of salts could be explained by the degree of crosslinking of the studied hydrogels which are assigned as: low for

A and C and high for B. The degree of crosslinking is an important factor controlling the swelling of hydrogels, determining the mechanical strength, swelling ratio and other properties of PAM hydrogels, so that even small changes in crosslinking alter swelling characteristics (THOMBARE *et al.*, 2018).

More crosslinked hydrogels show greater rigidity in the polymeric mesh (Hydrogel B), which causes less swelling (MOLLOY; SMITH; COWLING, 2000). This is because as the crosslinking rate increases, the number of crosslinks per unit volume increases, thus causing a decrease in the free space available between crosslinks to accommodate water molecules (BAJPAI; SINGH, 2006).

The swelling degree of the three hydrogels decreased upon exposure to the high salinity hydration solution (EC = 3 dS/m) (Tables 2 and 3). Maximum swelling (431 g water/g hydrogel) was observed for hydrogel A at 30 °C exposed to low salinity deionized water. The second-largest swelling (366 g/g) was also observed for hydrogel A in deionized water but at a temperature of 20 °C (Table 2). However, when hydrogel A, at 30 °C, was subjected to the saline solution, it presented the lowest swelling value (13.3 g/g), representing a 97% reduction in swelling in response to salinity (Tables 2 and 3).

Table 3 – Comparison test of means for final swelling (g/g) ± standard error of three copolymeric acrylamide and potassium acrylate hydrogels submitted to four temperatures and two levels of electrical conductivity (dS/m) of the hydration solution.

	Deionized water	Saline solution	Deionized water	Saline solution
Hydrogel	20°C		30°C	
A	366±5.68a	61.9±0.42b	431±12.13a	13.3±0.32b
B	209±5.63a	134±1.85b	212±3.37a	16.6±0.31b
C	313±2.60a	40.8±0.67b	286±2.11a	21.2±0.63b
Hydrogel	40°C		65°C	
A	273±6.42a	13.3±0.32b	262±5.83a	24.8±0.46b
B	195±4.86a	16.6±0.31b	192±1.41a	23.2±0.61b
C	323±6.53a	21.2±0.63b	284±2.83a	29.9±0.16b

Values followed by the same lower case letters in the lines that compare the same hydrogel at the same temperature between deionized water and saline are not significantly different (p <0.05) by Duncan test.
Source: elaborated by the author.

In the saline hydration solution the swelling of the three studied hydrogels was significantly reduced (Tables 2 and 3), confirming water absorption efficiency of hydrophilic hydrogels decreases with increasing salts and EC of the hydration solution (ANDRY *et al.*, 2009). The reduction in swelling under saline conditions is attributed to a "charge-screening effect" of additional cations, causing non-perfect anionic electrostatic repulsion (KWON; BAE; SUNG WAN KIM, 1991; MIRDARIKVANDE *et al.*, 2014; SADEGHI; GHASEMI;

YARAHMADI, 2011). Therefore, decreasing osmotic pressure results in decreased concentration of mobile ions between the hydrogel and aqueous phases resulting in a decrease in water molecule absorption by the PAM co-polymers. Also, in the case of multivalent cation saline solutions such as that used in the present study, ionic crosslinking of PAM co-polymer particles causes a decrease in swelling capacity (FLORY, 1953; HEIDARI *et al.*, 2018; MIRDARIKVANDE *et al.*, 2014).

Decreased swelling depends on the type and concentration of salts present in the solution (HEIDARI *et al.*, 2018; MIRDARIKVANDE *et al.*, 2014). Divalent elements, such as those found in the saline hydration solution of the present study (Ca^{2+} and Mg^{2+}), may decrease the swelling of hydrogels. This is due to the ability of ions to bind with the carboxamide or carboxylate groups of the PAM co-polymers and form inter and intramolecular complexes (SADEGHI; GHASEMI; YARAHMADI, 2011).

Monovalent cations, such as Na^{+}, can shield the carboxylate anions of the hydrogel polymeric network contributing to a compact three-dimensional structure due to the lower repulsion between the fixed polymeric network charges. This leads to a decrease in the osmotic pressure difference between the hydrogel framework and the external solution and, consequently, a decrease in water retention capacity (MAGALHÃES et al., 2013; SADEGHI; GHASEMI; YARAHMADI, 2011).

For the temperatures evaluated, in deionized water hydrogel B presented significantly lower swelling values (212-192 g/g) as compared with hydrogel C (323-284 g/g) and hydrogel A (431-262 g/g), without any significant differences associated with temperature changes (Table 2), indicating that hydrogel B in salt-free water maintains its water absorption potential in the temperature range of 20 °C to 65 °C. When exposed to salinity, hydrogel B showed greater swelling at 20 °C (134 g/g), presenting only a 37% reduction in response to salinity (Tables 2 and 3), which represents a significantly improved tolerance to salinity for hydrogel B at 20 °C as compared with the other hydrogels tested (Table 2). However, hydrogel B showed a marked reduction in swelling (from 89 to 92%) with increasing temperature (Table 2). Hydrogel C obtained maximum swelling (324 g/g) at 40 °C in deionized water, but this swelling dropped by 90% in the saline hydration solution, for the same temperature (Table 2).

The interaction between salinity and high temperatures influenced swelling, resulting in the swelling characteristics of hydrogel B at temperatures >30 °C being statistically comparable to C and A (Table 2).

The reduction in swelling with salinity demonstrates that the tested hydrogels exhibit aspects of physical crosslinking, such as that characterized by electrostatic bonds or hydrogen bonds between polymer chains (FAJARDO *et al.*, 2013; GUILHERME *et al.*, 2015). Physical crosslinking is reversible and the PAM co-polymer matrix can be destroyed under adverse conditions such salinity, reducing the hydrogel's water absorption capacity (GUILHERME *et al.*, 2015; ZHANG; CHEN; WANG, 2006).

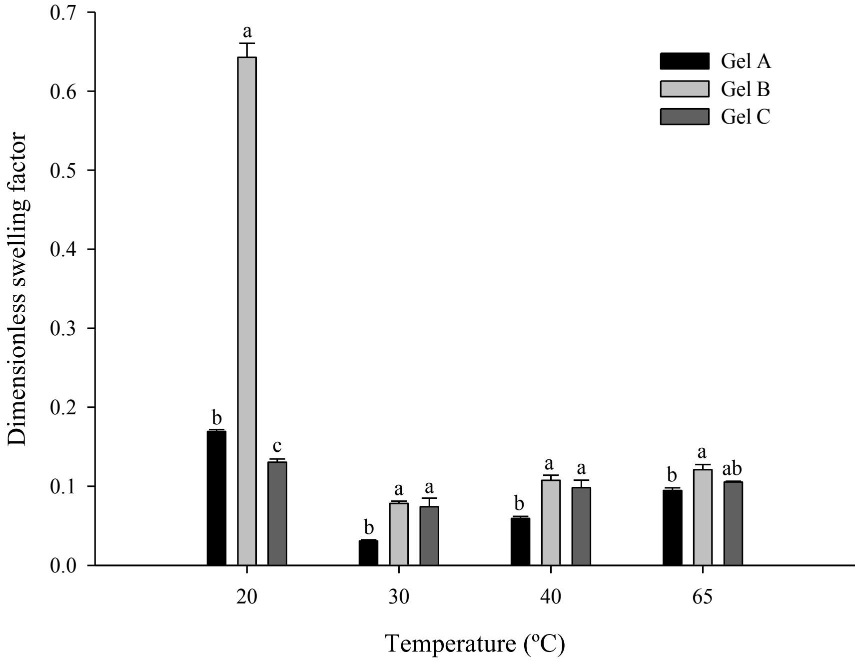
The higher swelling of hydrogel A at 20 and 30°C suggests this temperature range is ideal for obtaining the maximum swelling efficiency of this polymer (Table 2) which is attributed, based on the results, to low crosslinking and higher anionicity. However, in the saline solution hydrogel A showed the lowest swelling efficiency. This may be due to salts causing a reversal of crosslinking, leading to the loss of mechanical strength that is required for hydrogels to expand and retain water (THOMBARE *et al.*, 2018). Hydrogel A, despite having a good degree of swelling (>100x dry mass) in deionized water, is not recommended for regions with soil/water salinity problems.

Increasing the number of ionic groups in hydrogels is known to increase their swelling capacities. This is mainly due to the simultaneous increase of the number of counterions inside the hydrogel, which produces an additional osmotic pressure that causes swelling (FLORY, 1953). Hydrogel A was characterized by low crosslinking and high anionicity; hydrogel B exhibited a higher degree of crosslinking than A and C and lower anionicity; hydrogel C presented a lower degree of crosslinking and higher anionicity (less than hydrogel A). Regarding crosslinking, the sequence is: B> C~A; the sequence for anionicity is: A> C> B.

The swelling factor was significantly higher (0.644) for hydrogel B at 20 °C as compared with < 0.2 for hydrogels A and C (Figure 3). From 30 °C onwards, the swelling factor of hydrogel B was also reduced to < 0.2, becoming not significantly different for hydrogel C but significantly higher than that found for hydrogel A (Figure 3).

This factor is defined as the ratio of hydrogel water absorption capacity in saline to salt-free water and can be a measure of the absorption sensitivity of a hydrogel upon changes in salinity. The higher the swelling factor (ranging from 0-1) the lower the sensitivity of the hydrogel to salinity (MOHAN; MURTHY; RAJU, 2005; OMIDIAN *et al.*, 1999).

Figure 3 – Dimensionless swelling factor (α) the three copolymeric acrylamide and potassium acrylate hydrogels tested as a function of temperature. Lowercase letters compare averages within the same temperature. Error bars represent the standard error of the mean.



Source: elaborated by the author.

Since contrasting salinities (deionized water and 3 dS/m saline solution) were used, an experiment was carried out with the three gels, a fixed temperature of 20 °C over an increased range of salinity (0.003, 0.5, 1.5, 3.0 and 6.0 dS/m) in order to verify whether hydrogel B maintains the greatest swelling factor. The results can be verified in annex B, and confirmed the significantly greater swelling performance of hydrogel B as compared with A and C in hydration solutions with EC of 0.5 to 6.0 dS/m, at a temperature of 20 °C. In contrast, the absorption of deionized water from hydrogel B is significantly lower as compared to hydrogels A and C which are associated with less crosslinking. However, hydrogel B exhibits high potential for application in regions with problems related to salinity in irrigation water, as it maintains a certain capacity swelling under saline conditions.

The crosslinking of hydrogel B was less impaired by the presence of salts than hydrogels A and C. The swelling of hydrogels with a high degree of crosslinking is less sensitive to salinity change, since crosslinking itself prevents polymeric network expansion, just as salinity does (MOHAN; MURTHY; RAJU, 2005; OMIDIAN *et al.*, 1999). Hydrogel B presented lower sensitivity to the saline hydration solution, which is advantageous for regions with soil/water affected by salts. However, for wider applicability, there is a need to increase this tolerance to salinity also at higher temperatures typical of soil temperatures in arid and semi-arid regions.

For greater absorption of saline hydration solution by hydrogels, it is recommended to introduce hydrophilic groups that are more prone to ionization, such as sulfonic and phosphate groups in which the degree of association with mobile ions present in saline solution would be lower than that observed in the carboxylic acid group (ZAIN *et al.*, 2018).

Across all hydrogels, temperatures and EC of hydration solution, at the end of the 30 days, RA_m levels ranged from 0.013 to 0.113 mg/g (Table 4).

Table 4 – Comparison test of means for final RA_m (mg/g) of three acrylamide and potassium acrylate copolymer hydrogels at four temperatures and two levels of electrical conductivity of the swelling solution.

Treatment			**Mean ± SE**	**Duncan Grouping**
Gel	°C	dS/m	(mg/g)	
B	20	3	0.113±0.001	a
A	40	0.003	0.111±0.001	a
C	20	3	0.097±0.002	ab
A	20	0.003	0.082±0.001	abc
A	30	0.003	0.076±0.001	abcd
C	40	3	0.068±0.001	abcde
C	20	0.003	0.046±0.001	abcde
C	30	0.003	0.046±0.006	abcde
A	20	3	0.043±0.002	abcde
A	40	3	0.038±0.003	cdef
C	40	0.003	0.034±0.002	cdef
A	65	0.003	0.032±0.002	cdef
C	30	3	0.029±0.001	def
B	65	3	0.028±0.003	ef
B	40	3	0.027±0.001	fg
C	65	3	0.027±0.004	fgh
B	30	3	0.019±0.003	fgh
A	30	3	0.019±0.002	fghi
C	65	0.003	0.019±0.001	fghi
B	65	0.003	0.017±0.001	fghi
A	65	3	0.017±0.003	hij
B	20	0.003	0.016±0.005	ij
B	30	0.003	0.013±0.001	j
B	40	0.003	0.013±0.009	j

Means followed by the same letter are not significantly different ($p<0.05$) by Duncan test.
Variable with transformation $x^{0.1}$; SE -standard error.
Source: elaborated by the author.

The highest final RA_m contents (0.113 and 0.111 mg/g) were found, respectively, for hydrogel B at 20 °C under saline conditions and for hydrogel A at 40 °C in deionized water

(Table 4). However, this is still a significant reduction in concentration as compared with the initial RA$_m$ content for these hydrogels. The lowest RA$_m$ content (0.013 mg/g) was observed for hydrogel B at temperatures of 30 and 40 °C in deionized water (Table 4), significantly lower that hydrogel C which was associated with a significantly lower initial RA$_m$ content as compared with hydrogels A and B (Table 1). Hydrogel B was associated with a significantly higher initial RA$_m$ content (0.272 mg/g) (Table 1) and greater RA$_m$ degradation (0.256 mg/g) in deionized water as compared with hydrogels A and C and significantly lower RA$_m$ degradation (0.159 mg/g) under saline conditions (Table 5).

Table 5 – Comparison test of means (n=4) for residual acrylamide (RA$_m$) degradation (mg/g) ± standard error of three acrylamide and potassium acrylate copolymer hydrogels at four temperatures and two levels of electrical conductivity of the swelling solution.

	Deionized water	Saline solution	Deionized water	Saline solution
Gel	20°C		30°C	
A	0.107±0.019a	0.146±0.003a	0.113±0.002b	0.170±0.004a
B	0.256±0.029a	0.159±0.002b	0.259±0.001a	0.253±0.006a
C	0.049±0.002a	0.002±0.004a	0.049±0.001a	0.066±0.002a
Gel	40°C		65°C	
A	0.078±0.001a	0.151±0.005a	0.157±0.004b	0.172±0.005a
B	0.259±0.017a	0.245±0.001a	0.255±0.002a	0.244±0.005a
C	0.061±0.003a	0.027±0.003b	0.076±0.002a	0.071±0.009a

Values followed by the same lower case letters in the lines that compare the same hydrogel at the same temperature between deionized water and saline are not significantly different ($p < 0.05$) by Duncan test.
Source: elaborated by the author.

Initial levels of the RA$_m$ in the hydrogels tested were, respectively: A = 0.189, B = 0.272 and C = 0.095 mg/g (Table 1). These values correspond to 189, 272 and 95 mg/kg, which are well below the permissible levels (100-500 mg/kg) stipulated by the U.S. Food and Drug Administration (FDA), Environmental Protection Agency (EPA), and the National Resources Conservation Services (NRCS). For the hydrogels tested the RA$_m$ contents were within the range considered low (<0.05%) (XIONG *et al*., 2018).

The RA$_m$ in hydrogel A was degraded in greater quantities at 65 °C, with 83% degradation within 30 days. For hydrogel B the greatest degradation of RA$_m$ occurred at 30 and 45 °C, with 95% degradation over the 30 days. For hydrogel C the greatest degradation was at 65 °C, with 80% of RA$_m$ degraded within 30 days. These results suggest that higher temperatures promote a higher RA$_m$ degradation rate. Under simulated environmental conditions, it was found that polyacrylamide did not degrade to acrylamide, but RAm degraded to ammonium (NH_4^+) and that ammonium concentrations increased as RA$_m$ levels decreased (SMITH; PRUES; OEHME, 1996b). Based on the chemical structure of RA$_m$, ammonium is a possible product of the RA_m degradation process and may contribute to plant development, as ammonium is one of the ways in which plants absorb N which is an essential element of their development (MOREAU *et al*., 2019; SMITH; PRUES; OEHME, 1996b).

Principal component analysis (PCA) results indicate that the best behaviour of the hydrogels was composed of PC1 and PC2 (Table 6).

Table 6. Matrix of superabsorbent hydrogel variable scores in the two selected main components (PC1 and PC2).

Variables	PCA 1	PCA2
Final swelling	0.42	-0.58
Swelling reduction	-0.50	0.50
Final RA_m concentration	0.52	0.48
% RA_m degradation	0.55	0.43
Eigenvalues	1.95	1.54
Variances (%)	48.86	38.39
Accumulated variances (%)	48.86	87.25

Source: elaborated by the author.

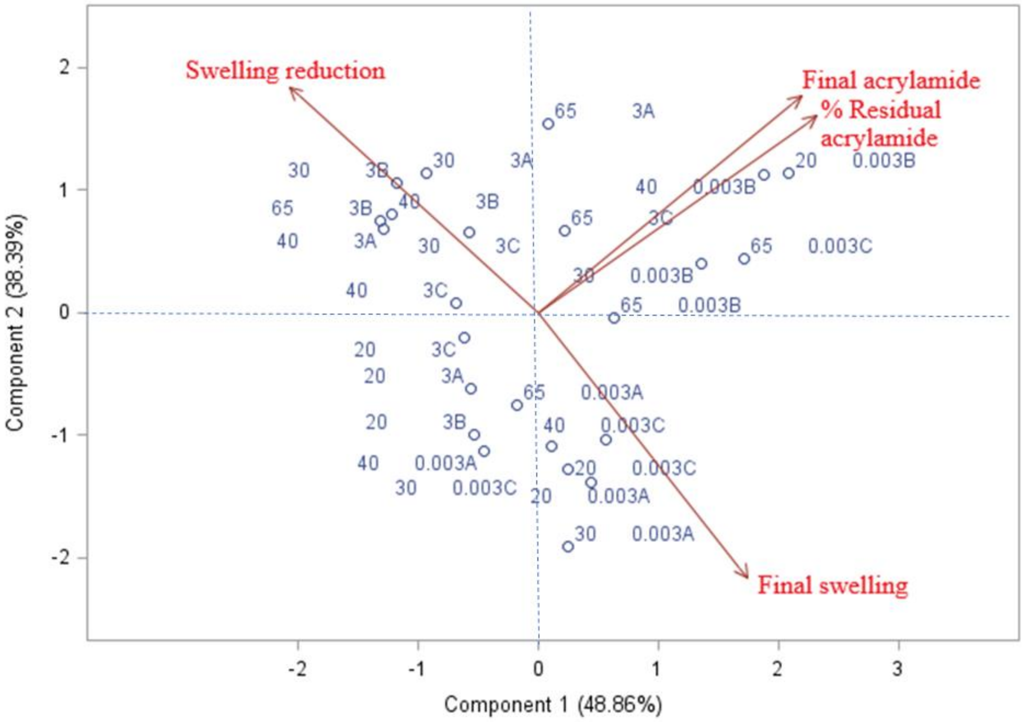
The variables with the highest discriminatory power in CP1 were % RA_m degradation (0.55) and final RA_m concentration (0.52). The values of final RA_m concentration, % RA_m degradation and final swelling were inverse to the reduction in swelling. The variables with the highest discriminatory power in CP2 were final swelling (-0.58) and reduction in swelling (0.50), which were also inversely associated. Thus, these variables highlighted in the main components CP1 and CP2 are considered important for the selection of hydrogels for use under conditions of high temperature and salinity indicative of semi-arid and arid regions.

The two components determined by the PCA explain 87.3% of the total variance of the original variables. The highest score values indicate those that are the most expressive variables in each component. The first component explains 48.9% of the variability of the variables and is associated with the variables indicating the RA_m contents (% RA_m degradation and final RA_m concentration). The CP2 explains 38.4% of the total variance of the matrix of standardized variables and is associated with the variables indicating the swelling of the hydrogels (final swelling and reduction in swelling).

In the Biplot plot of PCA data were separated into different quadrants (Figure 4). Deionized water is represented by (DW) and saline water by (SW). In the 1st quadrant, statistically comparable and with higher final final RA_m concentration and a higher (% RA_m degradation the treatments were: 20 DW-B (20°C, DW, hydrogel B), 30 DW-B (30°C, DW, hydrogel B), 40 DW-B (40°C, DW, hydrogel B), 65 DW-C (65°C, DW, hydrogel C), 65 SW-A (65°C, SW, hydrogel A) 65 SW-C (65°C, SW, hydrogel C) (Figure 4).

The variables final RA_m concentration and % RA_m degradation are strongly and positively related and were located in the 1st quadrant (Figure 4). The variables final swelling (4th quadrant) and reduction of swelling (2nd quadrant) are inversely related (Figure 4 and Table 6). For maximum swelling and for smaller swelling reductions over time, hydrogels in the 4th quadrant: A and C at temperatures of 20 to 40 °C in a low salinity solution are recommended (Figure 4).

Figure 4. PCA biplot graph with two main components.



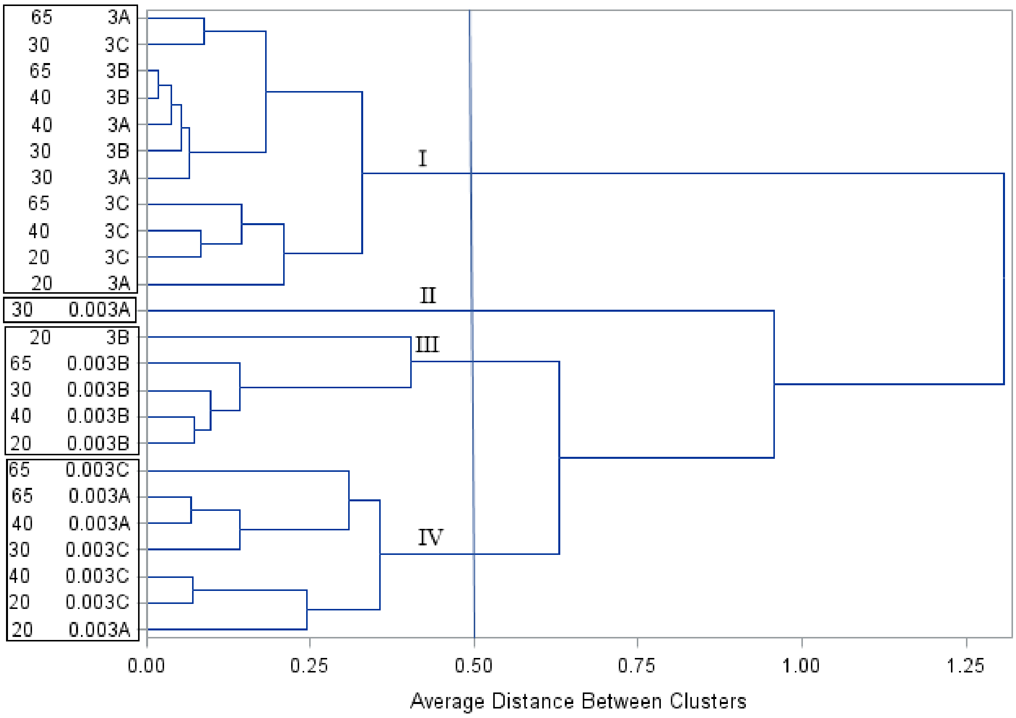
Source: elaborated by the author.

Steeper reductions in swelling and low final swelling were observed for treatments in the 2nd quadrant: 30 SW-A (30°C, SW, hydrogel A), 30 SW-B (30°C, SW, hydrogel B), 40 SW-A (40°C, SW, hydrogel A), 30 SW-C (30°C, SW, hydrogel C), 40 SW-B (40°C, SW, hydrogel B), 40 SW-C (40°C, SW, hydrogel C), 65 SW-B (65°C, SW, hydrogel B).

The treatments in the 3rd quadrant were characterized by having low levels of final RA_m concentration and % RA_m degradation. The treatments grouped in the 3rd quadrant were: 20 SW-A (20°C, SW, hydrogel A), 20 SW-B (20°C, SW, hydrogel B), 20 SW-C (20°C, SW, hydrogel C), 40 DW-A (40°C, DW, hydrogel A) and 65 DW-A (65°C, DW, hydrogel A). Treatments with high final swelling rates and low swelling reduction rates were in the 4th quadrant: 40 DW-C (40°C, DW, hydrogel C), 30 DW-A (30°C, DW, hydrogel A), 20 DW-A (20°C, DW, hydrogel A), 20 DW-C (20°C, DW, hydrogel C).

In the dendrogram (Figure 5) four clusters were formed, obeying the Euclidean distance cut-off point (0.5). In group I, hydrogels subjected to saline stress at different temperatures were identified, but hydrogel B at 20°C subjected to saline stress appeared in group III which, together with groups II and IV, concentrated the treatments subjected to deionized water.

Figure 5. Dendrogram showing the main subdivisions.



Source: elaborated by the author.

The dendrogram (Figure 5) shows that in group I the hydrogels exposed to high salinity were identified. In group II, hydrogel A was identified alone at 30 °C in deionized water. In group III, hydrogel B treatments in deionized water were identified, together with hydrogel B in saline solution at 20 °C. In group IV, hydrogels A and C were identified in deionized water. The formation of the groups in the dendrogram was primarily due to the response of the hydrogels to the salinity of the hydration solution. Emphasis is given to hydrogel B exposed to the high salinity hydration solution (3 dS/m) and at a temperature of 20 °C that was in the same group as swollen hydrogel B in deionized water, thus having a salinity response behaviour similar to that in deionized water at 20 °C, which is advantageous because of the lower sensitivity of this hydrogel to salinity at this temperature.

CONCLUSIONS

Anionic superabsorbent PAM co-polymers ‘hydrogels’ have the potential to contribute to soil management under abiotic conditions indicative of arid and semiarid regions.

The absorption of deionized water from hydrogel B is lower as compared to hydrogels that exhibit less crosslinking (A and C), but its use is a good strategy for regions with problems related to salinity in irrigation water, as it maintains a certain capacity swelling in saline conditions. However, hydrogel B achieved good swelling performance under saline conditions only at 20 °C. Thus, the temperature tolerance of hydrogel B should be improved so that it can be used in regions with high temperatures and salinity levels of soil and/or water.

With regards the RA_m concentration, all of the hydrogels tested can be recommended for use in agriculture as both initial and final RA_m contents were well below permissible levels and there was no release of RA_m across the temperature range (20 to 65 °C) and swelling solution salinities tested. Further, 80 to 95% of the RA_m was degraded within 30 days indicating negligible environmental persistence.

6 FINAL CONSIDERATIONS

Regarding Forth Gel®, it is recommended their use in the lowest salinity levels (~ 0.003 dS m^{-1}) of the irrigation water possible to obtain swelling >150 g g^{-1} since small additions of salts (0.003–0.5 dS m^{-1}) reduce water holding capacity drastically (~40%). However, it should be noted that even in distilled water, changes in water absorption occur over time (reduction of ~43% of the swelling when compare 30 with 120 days); water with salinity levels provide changes in the swelling, reducing this drastically but the levels of acrylamide monomer are lower under these conditions.

Forth Gel® does not present any problems regarding RA_m levels since both the initial and the final concentrations were within acceptable levels (<0.5 mg g^{-1}) and there was no formation of the monomer in the salinity range of the immersion solutions (water, saline solution) and in the studied times. Up to 85% of the residual monomer was degraded within 120 days.

After adding Forth Gel® to the soil, even under thermal stress, total porosity and θ_{FC} increased, while the permanent wilting point decreased, providing improvement in soil water storage. Temperatures in arid and semi-arid environments and time lead to a progressive loss of hydrogel effectiveness. Thus, there is a potential benefit for crops with a short growth cycle. Future research should be based on improving the characteristics of hydrogels and their effects over long periods and in adverse conditions typical of arid and semiarid environments.

Regarding the hydrogels A, B and C, the absorption of deionized water from hydrogel B is lower as compared to hydrogels A and C, but its use is a good strategy for regions with problems related to salinity in irrigation water, as it maintains a certain capacity swelling in saline conditions. However, hydrogel B achieved good swelling performance under saline conditions only at 20 °C. Thus, the temperature tolerance of hydrogel B should be improved so that it can be used in regions with high temperatures and salinity levels of soil and/or water.

With regards the RA_m concentration, all of the hydrogels (A, B and C) tested can be recommended for use in agriculture as both initial and final RA_m contents were well below permissible levels and there was no release of RA_m across the temperature range (20 to 65 °C) and swelling solution salinities tested.

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ANNEX A - ANOVA SUMMARY

Table 1. Summary of Analysis of Variance (ANOVA) for final swelling (W_{final}), residual acrylamide, acrylamide degradation and C/N.

SV	$W_{(final)}$	Residual acrylamide	Acrylamide degradation	C/N
Salinity	1437,715**	27,874**	27,874**	7,004**
Time	131,437**	47,81**	47,81**	77,786**
Salinity*time	18,689**	4,342**	4,342**	4,209**
CV 1 (%)	6,78	28,64	16,74	2,67
CV 2 (%)	9,55	30,11	17,6	3,13

Source: elaborated by the author.

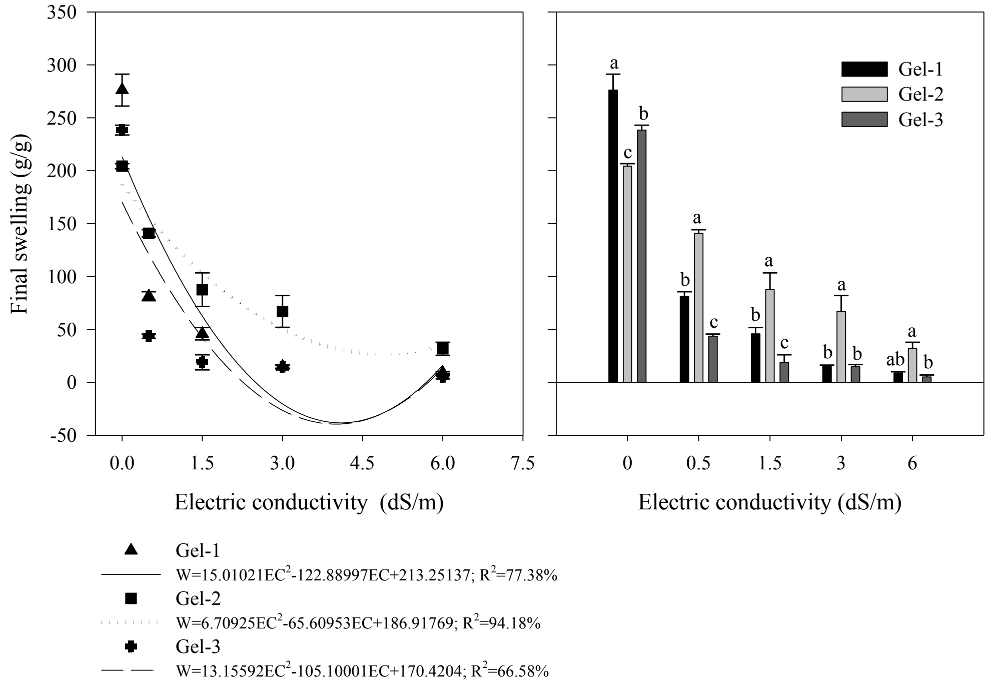
Table 2. Summary of Analysis of Variance (ANOVA) for field capacity, wilting point, available water, bulk density and porosity

SV	Field capacity	Wilting point	Available water	Bulk density	Porosity
Temperature	12.652**	1.063^{ns}	15.133**	25.734**	25.737**
Time	47.494**	30.759**	86.022**	15.029**	15.029**
Temperature *Time	8.970**	33.097**	4.301**	5.664**	5.664**
CV 1 (%)	5.00	4.88	6.96	2.17	2.23
CV 2 (%)	4.18	6.47	7.25	1.64	1.69

Source: elaborated by the author.

ANNEX B – FINAL SWELLING AND DIMENSIONLESS SWELLING FACTOR

Graph 1 – Final swelling (g H_2O/g dry gel) of three hydrogels of potassium acrylate-co-acrylamide as a function of salinity levels (0.003, 0.5, 1.5, 3.0 and 6.0 dS/m = 0.03, 5, 15, 30 and 60 mmol/L) of swelling water.



Graph 2 – Dimensionless swelling factor of three hydrogels tested as a function of electric conductivity (EC) (dS/m).