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POTENTIAL OF SUPERABSORBENT HYDROGELS TO IMPROVE AGRICULTURE UNDER ABIOTIC STRESSES

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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. The effect of abiotic stress on the swelling and residual acrylamide in hydrogels was evaluated. 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}). 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 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, being safe for agricultural applications.

Keywords: Anionic co-polymers; soil science; soil conservation; water use efficiency.

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1 Introduction

Semiarid 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 natural resources in these regions is essential in order to feed growing populations (Thombare et al., 2018).

Arid and semi-arid regions around the world face increasing problems of water scarcity for both domestic and agricultural water 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 et al., 2019; Thombare et al., 2018; Yang et al., 2018; Zain et al., 2018).

Hydrogels are crosslinked hydrophilic polymers that can absorb large amounts 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 superabsorbent polymers (Raju et al., 2003). Water absorption efficiency of hydrophilic polymers 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 among the polymer 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 polymers to clays due to the reduction of hydrogen bonds among the polymer and water molecules which increases polymer penetration in the internal clay structure (Xiong et al., 2018). Thus, the efficiency of superabsorbent polymers 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 as a result of incomplete polymerization (Xiong et al., 2018). 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 et al., 1974; Tepe and 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).

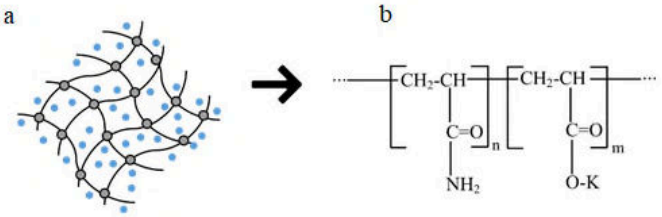
In arid and semiarid regions superabsorbent hydrogels are increasingly seen as a viable option to significantly increase water retention in soils and increase plant available water. However, as salinity and high temperatures compromise water absorption by hydrogels, it is necessary to develop polymers 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 superabsorbent polymers.

The objective of this study was to evaluate the water absorption potential and residual acrylamide degradation rate of three superabsorbent polymers subjected to thermal and saline stress. The hypotheses tested were: i) anionic superabsorbent polymers 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 superabsorbent polymers, a polymer that provides improvements in the soil of arid and semi-arid regions can be indicated; iii) the rate of residual acrylamide degradation is influenced by the abiotic stresses of high temperatures and/or salinity and does 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 factorial 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 swelling water (low - deionized water with electrical conductivity (EC) = 0.003 dS m^{-1}, and high - saline solution with EC = 3.0 dS m^{-1}). 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 water/experimental saline solution was applied.

The three hydrogels evaluated were commercial products characterised as anionic cross-linked acrylamide and potassium acrylate copolymers (Figure 1). As shown in Figure 1, these exhibited differences in their swelling rates in water and saline solution, swelling factor and level of residual acrylamide.



c

Gel	Copolymer characteristics	Counterion	Swelling degree (water) (g g^{-1})	Swelling degree (saline solution) (g g^{-1})	Swelling factor (20 °C)	Residual acrylamide (mg g^{-1})
A	AA	potassium	365	62	0.18	0.189
B	AA	potassium	208	134	0.64	0.272
C	AA	potassium	313	40	0.10	0.095

AA- acrylamide/acrylic acid.

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 hydrogels used in this study.

All the hydrogels contain initial residual acrylamide levels well below the allowable values (<500 mg kg^{-1}) set by the U.S. FDA, EPA, and NRCS (Xiong et al., 2018).

Since soil temperature varies linearly with air temperature (Sharma et al., 2010), in this study increasing air temperature was adopted to simulate soil temperatures that are observed in arid and semi-arid regions. The minimum treatment temperature of 20 °C was established as a laboratory control to critically evaluate hydrogel performance at the higher temperatures tested. The treatments temperatures of 30, 40 and 65 °C were obtained by placing the experimental units in Weiss Technik growth chambers for 30 days. The hydrogel temperatures would have equilibrated with the growth room temperatures after 24h. Using the growth chambers to regulate temperature also ensured that temperature within the experimental units was uniform. This allowed differences in the response of the hydrogels to be observed.

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^{-1} (Frenkel, 1984). The high salinity 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 among the EC of the irrigation water (EC) and its concentration [CS ($mmol_c$ L^{-1}) = EC x 10], as proposed by (Rhoades et al., 1989); where: Cs = salt concentration; EC = pre-established electrical conductivity.

To determine the amount of water/saline solution to be applied, tests were performed using deionized and saline solution to achieve maximum swelling and all water/saline solution not absorbed by the hydrogels was drained (~ 2 hours). The amounts of water and saline solution applied in the

experiment were, respectively, 600 and 300 ml for hydrogel A, 400 and 400 ml for hydrogel B, and 600 and 300 ml for hydrogel C.
The PVC columns containing the hydrogels received the amount of water/saline solution for the initial swelling and were exposed to the temperature treatments for 30 days. Subsequently, the material was re-hydrated with the same amount of water/saline solution initially used, with drainage of excess (~ 2 hours). Then, samples were weighed and oven-dried at 65 °C until a constant mass was attained. The value of the mass of the PVC column + hydrogel was subtracted from the value of the total mass (PVC column + re-hydrated hydrogel) to obtain the mass of the swollen hydrogels (W). The oven-dried hydrogels were then removed from the columns and weighed, thus obtaining the dry mass (W0). With the wet and dry mass values of the samples, the final swelling of the hydrogels was calculated as follows:

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

S represents the final swelling of the hydrogels (g g^{-1}), W0 represents the mass (g) of the hydrogel dried at 65 °C, and W is the mass (g) of hydrogel swollen.

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

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

which is defined as the ratio among the absorption capacity of water in each saline solution and the absorption in a salt-free solution. A summary of the experimental methodology is presented in Figure 2.

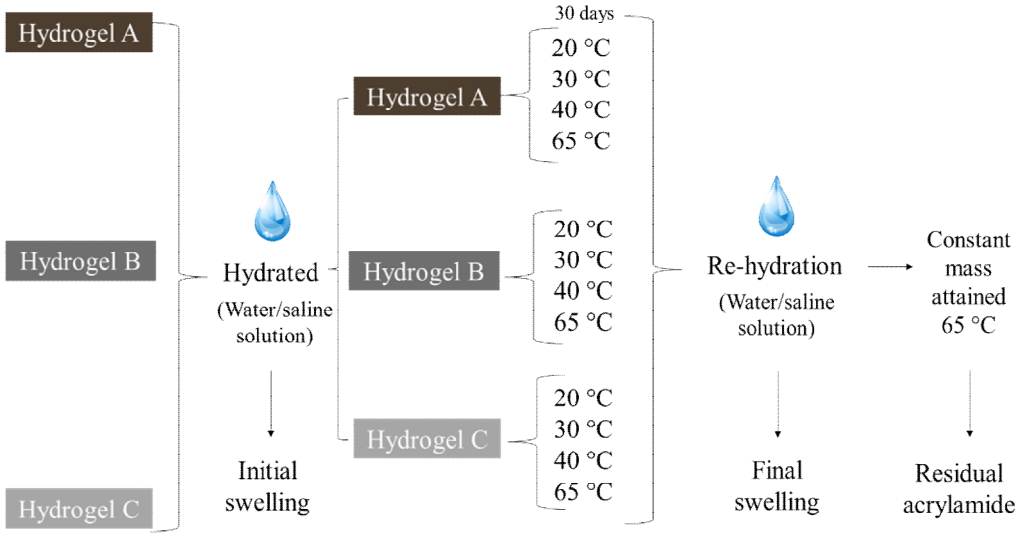


Figure 2. Schematic summary of the experimental method showing: swelling sequence, temperatures applied, drying protocol, rehydration and residual acrylamide analysis.

Residual acrylamide was determined by submerging 100 mg of the oven-dried 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 residual acrylamide monomer 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 residual acrylamide monomers in deionized water. Monomer contents were expressed in mg g^{-1} (Bezerra, 2015).
To access residual acrylamide degradation the following calculation adopted:

$$\text{residual acrylamide degradation } (\%) = \left(\frac{\text{Initial residual acrylamide-final residual acrylamide}}{\text{Initial residual acrylamide}}\right).100 \quad (4)$$

Experiment treatments consist of all combinations of three main factors: hydrogel type (A, B, C), four air temperatures (20, 30, 40, 65 °C) and two ECs of the swelling solution (0.003 and 3 dS m^{-1}). The homogeneity of variance and residual normality of each variable were tested for each parameter before conducting the Two-way analysis of variance (ANOVA). For the variables level of final swelling and final residual acrylamide, the transformation $x^{0.1}$ was used to solve problems of lack of normality in the residues, homogeneity of variance of treatments and outliers. Therefore, Box-Cox optimal power procedure via SAS was used (Box and Cox, 1964), before submitting data for ANOVA. When the interaction among factors and/or each isolated factor was significant, the means were compared by the Duncan test ($\alpha = 0.05$) ("SAS 9.3 free Software," 2011). The performance of the hydrogels under the experimental temperatures and EC of the swelling solution was evaluated using the final swelling, final residual acrylamide, residual acrylamide degradation and dimensionless swelling factor.
In the multivariate analysis, the following data were considered: degree of final swelling, swelling reduction, final residual acrylamide and % residual acrylamide degradation. Cluster analysis was carried out to verify similarities among treatments using the method of the average link among groups or UPGMA (Unweighted Pair Group Method with Arithmetic Mean) and Euclidean distance, with the elaboration of a dendrogram with emphasis on the treatment groups; and the analysis of the main components, including the Biplot chart ("SAS 9.3 free Software," 2011).

3 Results

In the absence of salts, the degree of swelling was in the order hydrogel A> C> B, whereas in the presence of salts, at a temperature of 20 °C, the order was hydrogel B> A> C (Figure 3).
The swelling degree of the three hydrogels decreased upon exposure to the high salinity solution (EC = 3 dS m^{-1}). Maximum swelling (431 g of water/g of hydrogel) was observed for hydrogel A at 30 °C exposed to low salinity deionized water. The second-largest swelling (366 g g^{-1}) was also observed for hydrogel A in deionized water but at a temperature of 20 °C. However, when hydrogel A, at 30 °C, was subjected to the saline solution, it presented the lowest swelling value (13.3 g g^{-1}), representing a 97% reduction in swelling in response to salinity (Figure 3).

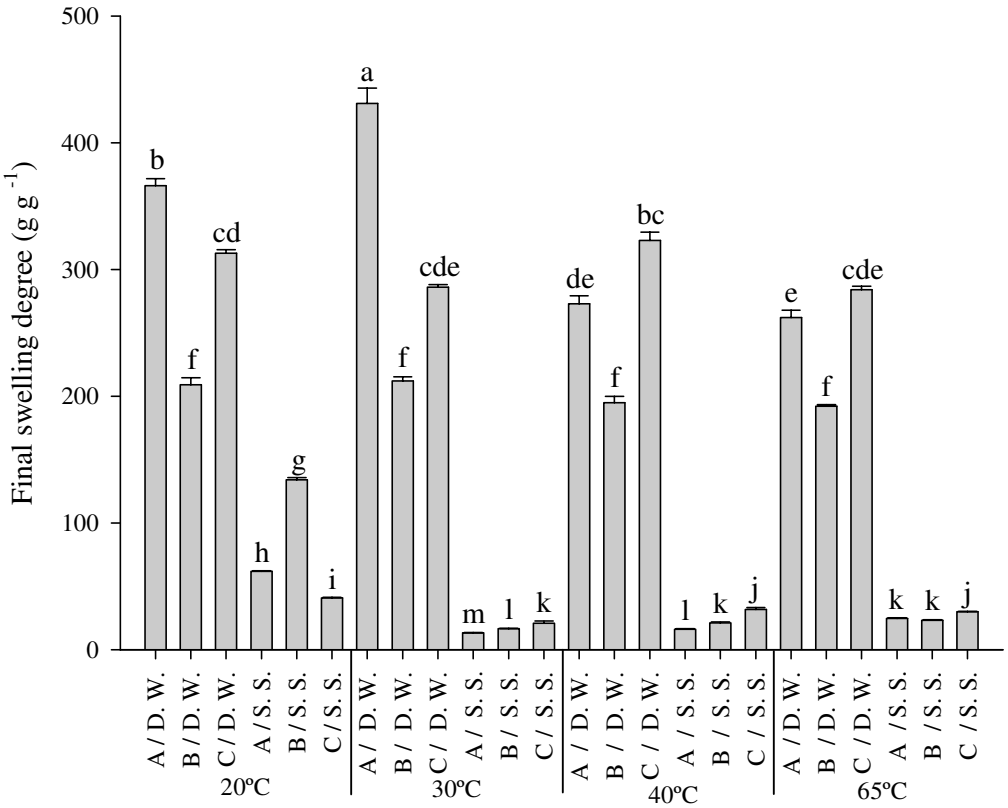


Figure 3. Comparison test of means for final swelling degree (g g^{-1}) of three acrylamide and potassium acrylate copolymer hydrogels at four temperatures and two levels of electrical conductivity of the swelling solution.

Means with the same letter are not significantly different (α = 0.05) by Duncan test

Variable with transformation $x^{0.1}$; SE -standard error.

DW: deionized water; SS: saline solution.

In deionized water hydrogel B presented significantly lower swelling values (212-192 g g^{-1}) as compared with hydrogel C (323-284 g g^{-1}) and hydrogel A (431-262 g g^{-1}), without any significant differences associated with temperature changes (Figure 3), 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^{-1}), presenting only a 37% reduction in response to salinity (Figure 3), which represents a significantly improved tolerance to salinity of hydrogel B at 20 °C. However, hydrogel B showed a marked reduction in swelling (from 89 to 92%) with increasing temperature (Figure 3).

Hydrogel C obtained maximum swelling (324 g g^{-1}) at 40 °C in deionized water, but this swelling dropped by 90% in the saline solution, for the same temperature (Figure 3).

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 4). From 30 °C onwards, the swelling factor of hydrogel B was also reduced to < 0.2, becoming not significantly different for hydrogel C and significantly higher than that found for hydrogel A (Figure 4).

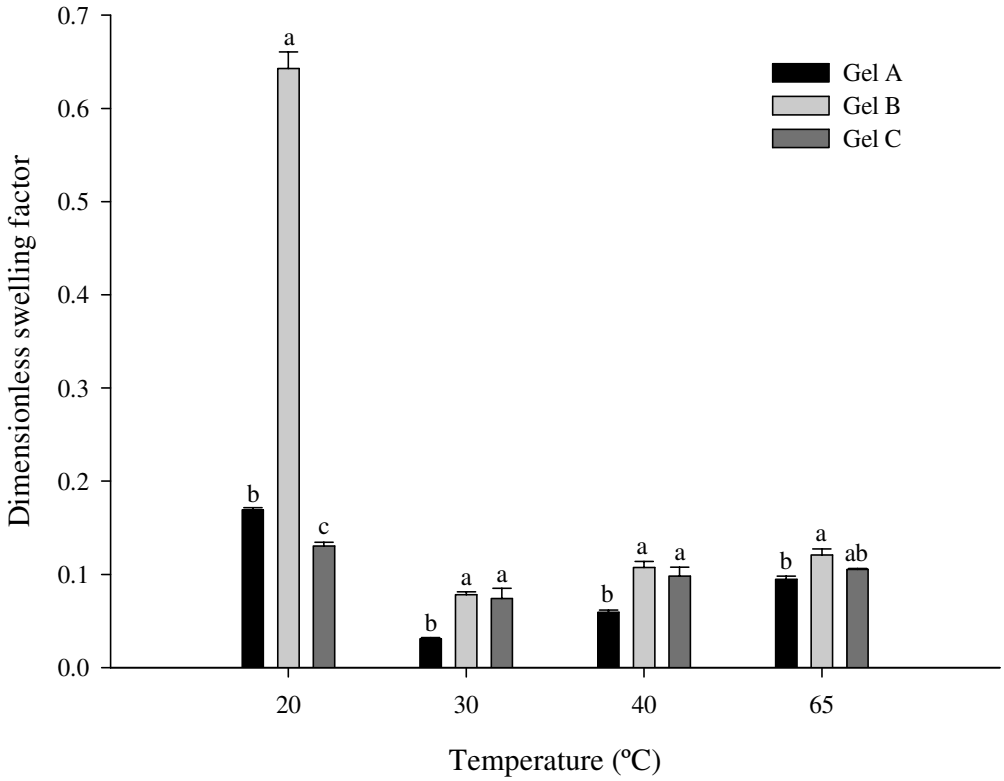


Figure 4. Dimensionless swelling factor (α) of three hydrogels tested as a function of temperature. Lowercase letters compare averages within the same temperature (α = 0.05). Error bars represent the standard error of the mean.

Across all hydrogels, temperatures and EC of swelling solution, at the end of the 30 days, residual acrylamide levels ranged from 0.013 to <0.11 mg g^{-1} (Figure 5). The highest final residual acrylamide contents (0.11 mg g^{-1}) were found, respectively, for hydrogel B at 20 °C under saline conditions and for hydrogel A at 40 °C in deionized water, but this is still a significant reduction in concentration as compared with the initial residual acrylamide content (Figure 1c). The lowest residual acrylamide content (0.013 mg g^{-1}) was observed for hydrogel B at temperatures of 30 and 40 °C in deionized water, significantly lower that hydrogel C which was associated with a significantly lower initial residual acrylamide content as compared with hydrogels A and B.

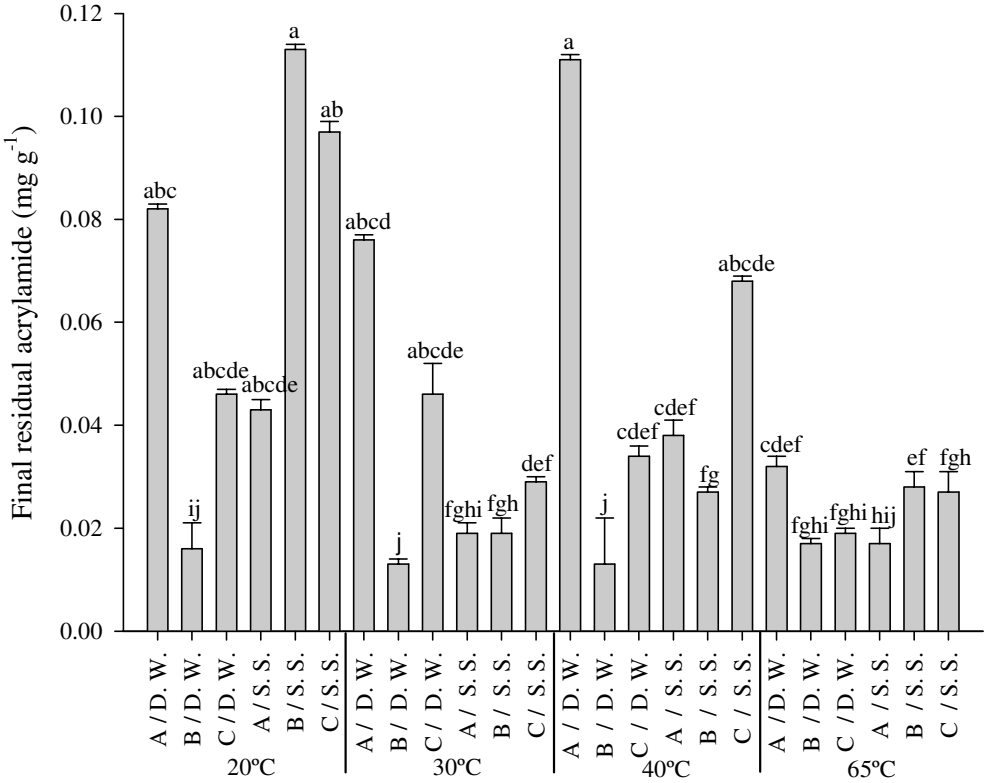


Figure 5. Comparison test of means for final residual acrylamide (mg g^{-1}) of three acrylamide and potassium acrylate copolymer hydrogels at four temperatures and two levels of electrical conductivity of the swelling solution.

Means followed by the same letter are not significantly different (α = 0.05) by Duncan test.
Variable with transformation $x^{0.1}$; SE -standard error.
DW: deionized water; SS: saline solution.

In general, there was a high rate of degradation of residual acrylamide from hydrogels in the period of 30 days, with values of 30% (hydrogel C at 65 °C in deionized water) to 95% (hydrogel B at 20 °C in saline solution) (Figure 6). It was observed that the highest degradation rates of acrylamide are associated with hydrogels swollen in saline solution.

Hydrogel B was associated with a significantly higher initial residual acrylamide content (0.272 mg g^{-1}) (Figure 1) but had greater residual acrylamide degradation in saline solution as compared with hydrogels A and C.

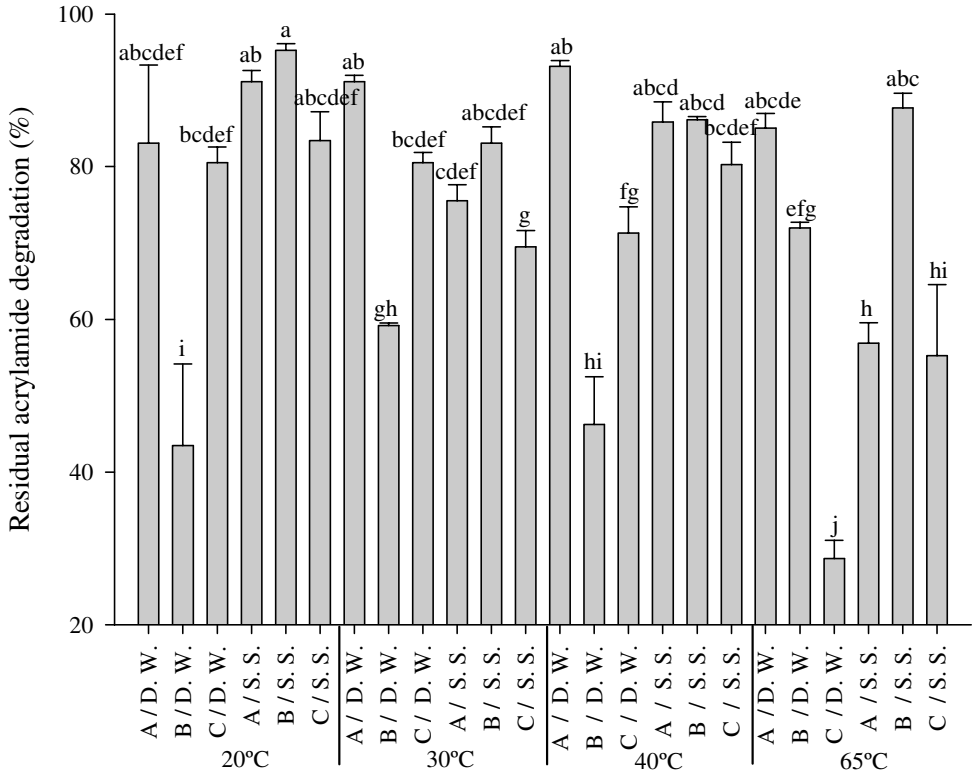


Figure 6. Comparison test of means for residual acrylamide degradation (%) of three acrylamide and potassium acrylate copolymer hydrogels at four temperatures and two levels of electrical conductivity of the swelling solution.

Means followed by the same letter are not significantly different (α = 0.05) by Duncan test.

SE -standard error; DW: deionized water; SS: saline solution.

The principal component analysis (PCA) results indicate that the best behaviour of the hydrogels was composed of PC1 and PC2 (Table 1).

Table 1. Matrix of superabsorbent hydrogels 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 acrylamide	0.52	0.48
% residual acrylamide degradation	0.55	0.43
Eigenvalues	1.95	1.54
Variances (%)	48.86	38.39
Accumulated variances (%)	48.86	87.25

In the Biplot of PCA data were separated into different quadrants (Figure 7). For deionized water was used (DW) and saline water (SW). In the 1st quadrant, statistically comparable and with higher final residual acrylamide content and a higher percentage of residual acrylamide 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).

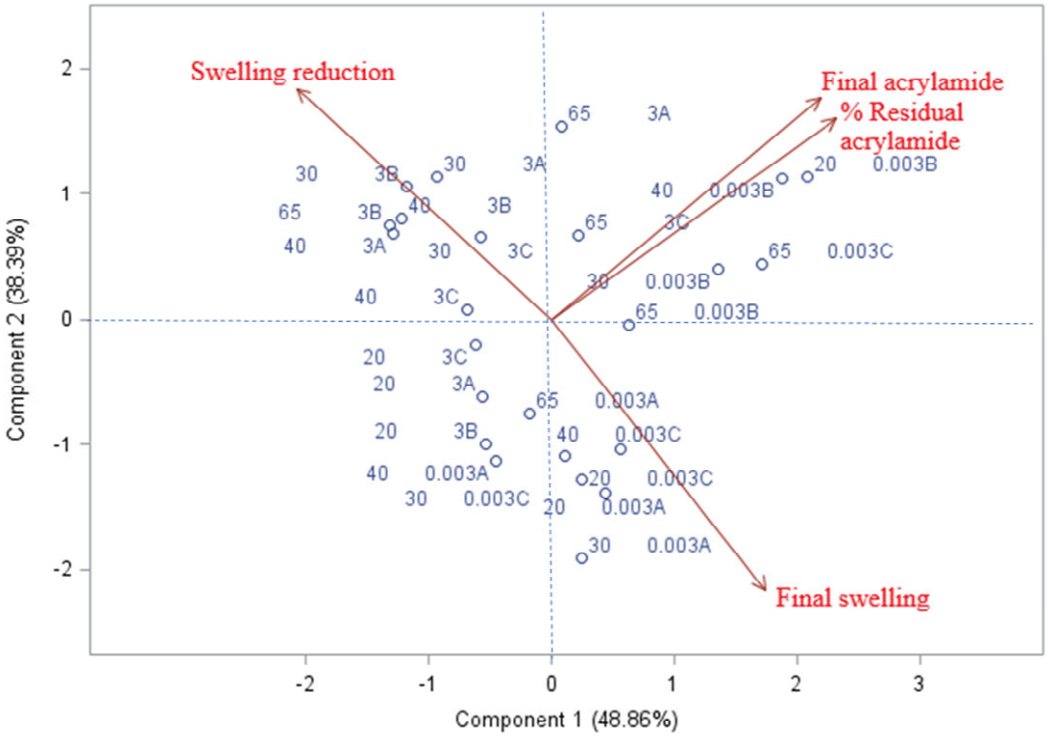


Figure 7. PCA biplot graph with two main components.

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 residual acrylamide and % residual acrylamide. 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 8) 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.

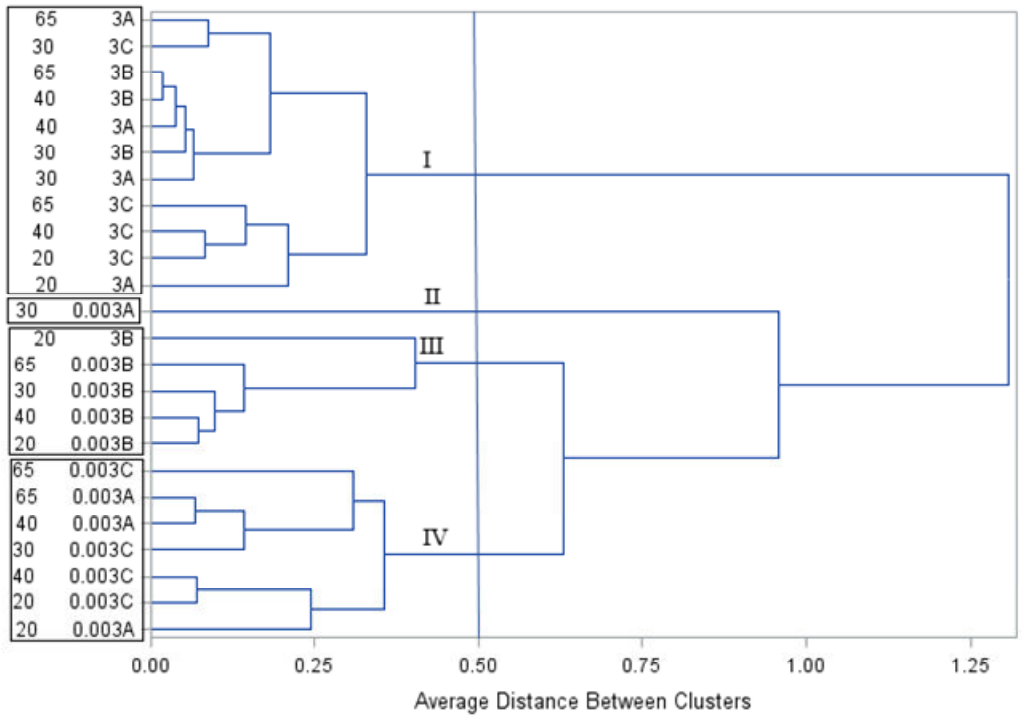


Figure 8. Dendrogram showing the main subdivisions. Each treatment is represented by temperature (20, 30, 40 or 65 °C), level of salinity (0.003 or 3 dS m^{-1}) and hydrogel type (A, B or C) respectively.

4 Discussion

The three hydrogels studied are considered superabsorbent since they absorbed > 100 times their dry mass of water (Zhao et al., 2019). However, there are records in the literature of polymers that absorb more than 1000 times their dry mass in water (Guilherme et al., 2015).

The initial swelling order hydrogel A>C> B in the absence of salts could be explained by the degree of cross-linking 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 small changes in crosslinking alter swelling characteristics (Thombare et al., 2018).

More crosslinked polymers show greater rigidity in the polymeric mesh (Hydrogel B), which causes less swelling (Molloy et al., 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 among crosslinks to accommodate water molecules (Bajpai and Singh, 2006).

In the saline solution the swelling of the three studied hydrogels was significantly reduced (Figure 3), confirming water absorption efficiency of hydrophilic polymers decreases with increasing salts and EC of the 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 et al., 1991; Mirdarikvande et al., 2014; Sadeghi et al., 2011). Therefore, decreasing osmotic pressure results in decreased concentration of mobile ions among 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 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 et al., 2011). Monovalent cations, such as Na^{+}, can shield the carboxylate anions of the polymeric structure, contributing to a compact three-dimensional

structure due to the lower repulsion among the fixed network charges. This leads to a decrease in the osmotic pressure difference among the hydrogel framework and the external solution and, consequently, a decrease in water retention capacity (Magalhães et al., 2013; Sadeghi et al., 2011). 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 (Figure 3) 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 retain water (Thombare et al., 2018). Hydrogel A, despite having a good degree of swelling in deionized water, is not recommended for regions with soil/water salinity problems.

Hydrogel B exhibited higher swelling under saline conditions when compared to hydrogels A and C (Figure 3). However, this greater swelling in saline conditions occurred only at 20 °C. The interaction among 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 (Figure 3).

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 gel, which produces an additional osmotic pressure that causes swelling of the hydrogel (Flory, 1953). Hydrogel A was characterized by low crosslinking and high anionicity; hydrogel B had a high degree of crosslinking than A and C and low anionicity; hydrogel C presented a low degree of crosslinking and high anionicity (less than gel A). Regarding crosslinking, the sequence is: B> C~A; the sequence for anionicity is: A> C> B.

The dimensionless swelling factor (α) confirmed the improved performance of hydrogel B under saline conditions at 20 °C as compared with the other hydrogels tested, with a value of 0.644 (Figure 4). 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 et al., 2005; Omidian et al., 1999).

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 network expansion, just as salinity does (Mohan et al., 2005; Omidian et al., 1999). Hydrogel B presented lower sensitivity to the saline solution, being an advantage 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 arid and semi-arid regions.

Although this study evaluated hydrogels without mixing with soil, the results strongly suggest that hydrogel B has potential to be used as a soil conditioner under high salinity conditions. It is recommended therefore that further studies should be undertaken mixing hydrogel B with saline soil in plant growth trials to validate the results of this study.

The absorption of deionized water from hydrogel B is lower compared to hydrogels that have 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 the capacity swelling in saline conditions.

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).

Initial levels of the residual acrylamide in the hydrogels tested were, respectively: A = 0.189, B = 0.272 and C = 0.095 mg g^{-1} (Figure 1). These values correspond to 189, 272 and 95 mg kg^{-1}, which is well below the permissible levels (100-500 mg kg^{-1}) 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 residual acrylamide contents were within the range considered low (<0.05%) (Xiong et al., 2018).

In general, the higher degradation rates of residual acrylamide are associated with hydrogels in saline solution (Figure 6). These results suggest that higher salinities promote a higher residual acrylamide

degradation rate. Under artificial environmental conditions, it was found that polyacrylamide did not degrade to acrylamide, but residual acrylamide degraded to ammonium and these ammonium concentrations increased as residual acrylamide levels decreased (Smith et al., 1996). Based on the chemical structure of acrylamide, ammonium is a possible product of the degradation process and may contribute to plant development, as ammonium is one of the ways in which plants absorb nitrogen which is an essential element of their development (Moreau et al., 2019; Smith et al., 1996).
In the multivariate analysis of the data from the present study (Table 2), the variables with the highest discriminatory power in PC1 were % residual acrylamide (0.55) and final residual acrylamide (0.52). The values of final residual acrylamide, % residual acrylamide and final swelling were inverse to the reduction in swelling. The variables with the highest discriminatory power in PC2 were final swelling (-0.58) and reduction in swelling (0.50), which were also inversely associated. Thus, these variables highlighted in the main components PC1 and PC2 are considered important for the selection of hydrogels for use under conditions of high temperature and salinity levels.
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 acrylamide contents (% residual acrylamide and final residual acrylamide content). The PC2 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).
The variables final residual acrylamide content and % residual acrylamide are strongly and positively related and were located in the 1st quadrant (Figure 7). The variables final swelling (4th quadrant) and reduction of swelling (2nd quadrant) are inversely related. 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.
The dendrogram (Figure 8) 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 swelling solution. Emphasis is given to hydrogel B exposed to the high salinity solution (3 dS m^{-1}) and at a temperature of 20 °C that was in the same group of 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.

5 Conclusion

Anionic superabsorbent PAM co-polymers ‘hydrogels’ have the potential to contribute to water use efficiency under abiotic conditions indicative of arid and semiarid regions.
The absorption of deionized water from hydrogel B is lower 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 the capacity swelling in saline conditions. However, hydrogel B achieved good swelling performance under saline conditions 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. It is recommended therefore that further studies should be undertaken mixing hydrogel B with saline soil in plant growth trials to validate the results of this study.
With regarding the residual acrylamide contents, all of the hydrogels tested can be recommended for use in agriculture as both initial and final residual acrylamide contents were well below permissible levels and there was no release of acrylamide monomer across the temperature range (20 to 65 °C) and swelling solution salinities tested. Further, up to 95% of the residual acrylamide was degraded within 30 days indicating negligible environmental persistence.

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Potential of superabsorbent hydrogels to improve agriculture under abiotic stresses

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