

DURABILITY INDICATORS OF A HYDROGEL FOR AGRICULTURAL AND FORESTRY USE UNDER SALINE CONDITIONS

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Abstract

This research tested the hypothesis that the interaction between time and salinity reduces the water absorption potential of a hydrogel – Poly (Acrylamide-*co*-Potassium Acrylate) and influence the degradation of residual acrylamide monomer. The experimental design was completely randomized split-plot with four replications. The treatments were time periods (30, 60, 90 and 120 days) and levels of salinity of the hydrating solution (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 lowest water absorption potential (8.1 g g⁻¹) in a saline solution of 4.20 dS m⁻¹ after 120 days. The C/N ratio of the hydrogel increased by up to 47% in a hydrating solution with an EC of 4.4 dS m⁻¹ at 120 days. Additionally, there was an observed shift in the wavelength of methylene, amide, and acrylate bands, that indicates degradation. Residual acrylamide monomer concentration was < 0.5 mg g⁻¹ (safe for agricultural use). After 120 days up to 85% of the residual acrylamide monomer was degraded. About the water absorption potential, the results suggest that under semi-arid conditions hydrogel durability for forestry and crops applications may be impaired by the salinity of the hydrating solution.

Keywords: Soil conditioner. Poly (Acrylamide-*co*-Potassium Acrylate). 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 that facilitates agricultural and forestry production in semi-arid regions is critical in since these regions have expanded in recent years and will continue to expand (Feng and Fu, 2013). 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 and Ammad, 2019).

In addition to the water deficit, salinity in the soil solution and irrigation water limits plant development in semi-arid 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. Salt presence induces higher ion concentration in the soil relative to that in the roots, disabling water uptake, and resulting a reduction in root system volume and under extreme cases, cessation of vegetative growth. The leaf area gradually decreases, followed by defoliation (Ljubojević et al., 2017).

In the Brazilian semi-arid region, the waters used for irrigation are typically saline with an electrical conductivity (EC) of 0.1 to 3.0 dS m⁻¹ (Gheyi et al., 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 and Westcot, 1985). Consequently, irrigation water quality in semi-arid regions of Brazil poses a major challenge to sustainable crop and agroforestry production systems.

Salinity is also of great importance in urban landscaping, as an increase in the green urban areas combined with scarcity in freshwater scarcity mandates wastewater reuse for irrigation. Application of hydrogels is one of the easiest and cheapest measures for water preservation and reduction of salt-induced stress (Ljubojević et al., 2017). As agriculture, forestry and urban greenery are affected by water deficit and salinity, it is necessary to develop solutions for the sustainable management of water resources in semi-arid regions.

Hydrogels are a viable option to improve plant available water. Hydrogels 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, forestry and urban 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). Wang et al., (2019) demonstrated that hydrogels can absorb and conserve large amounts of water ($> \text{up to } 1000 \text{ w w}^{-1}$), even in adverse external environments. As a consequence, it is common in commercial products to find high durability listed as a key performance indicator of the hydrogel for agricultural and forestry use. However, there remains a need to better understand the durability and performance of hydrogels over time and under 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 crosslinking 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. In addition, 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 et al., 1991; Mirdarikhvande et al., 2014; Sadeghi et al., 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 when hydrogels are applied to the soil. The release of acrylamide monomer in the environment is undesirable due to its toxic effects (Xiong et al., 2018).

This research tested the hypothesis that the interaction between time and salinity reduce the water absorption potential of a hydrogel – Poly (Acrylamide-*co*-Potassium Acrylate), and influence the degradation of residual acrylamide. The objective of the study was to evaluate water absorption efficiency, residual acrylamide monomer concentration and the degradation of a commercially available hydrogel in response to time and salinity to inform decisions regarding hydrogel application to the soil in semi-arid 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 characterized on the manufacturer's label as a copolymer of acrylamide and potassium acrylate – Poly (Acrylamide-*co*-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 obtained by the ratio between C and N. The elemental composition of the acrylate was determined by X-ray fluorescence spectrometry (FRX) using an X-ray fluorescence spectrometer, model ZSXMini II (Rigaku). Particle size fraction was determined using 24 mesh (0.710 mm), 35 mesh (0.425 mm) and 48 mesh (0.300 mm) sieves.

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

The swelling of the commercial hydrogel in distilled water and saline solutions was characterized. To obtain the saline solution, sodium chloride (NaCl), calcium chloride (CaCl₂.2H₂O) and magnesium chloride (MgCl₂.6H₂O) solutions were dissolved in the ratio of 7:2:1, assuming the existing relationship between the electrical conductivity of irrigation water (EC_w) 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 N°0) previously moistened. This set was then completely submerged in the hydration solution (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:

$$S = \frac{W_t - W_0}{W_0}, \quad (1)$$

Where: W_0 represents the mass (g) of the hydrogel dried at 65 °C and W_t is the mass (g) of the hydrogel expanded at time t .

Thus, the hydrogel swelling curve in distilled water (0.003 dS m⁻¹) and saline hydration solutions with EC's of 0.5, 1.5, 3.0 and 6.0 dS m⁻¹ were obtained. Some characteristics of the gel (W_{eq} - swelling in equilibrium, t_{eq} - equilibrium time and $W_t = 6$ min - swelling in time = 6 minutes) were obtained through the swelling curves (Ray and 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 EC values of the solutions were equivalent to 5, 15, 30, 60 mmol_e 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. Prior to installing the experiment, the gels were initially dried at 65 °C. After reaching constant mass, they were hydrated with the solution appropriate for each treatment.

For swelling inside the PVC cylinders, the dry hydrogel was inserted, and the swelling solution applied 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. 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.

2.2.1 Response variables

At the end of the hydration periods tested, the experimental units were suspended until drainage ceased and degree of final swelling calculated, according to formula 1. Samples of the dry hydrogel, were determined for levels of C, H, and N using Carlo ERBA EA 1108 microanalyst, as performed in the initial hydrogel characterization.

After the respective hydration period, the concentration of residual acrylamide monomer of the hydrogel was also 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 concentration of residual acrylamide monomer by high-performance liquid chromatography (HPLC) in a chromatograph model LC-20AD from Shimadzu, coupled to a diode array detector model SPD-M20A, at a wavelength of 197 nm. The residual acrylamide monomer (RA_m) 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 $mg\ g^{-1}$ of hydrogel (Nascimento et al., 2021). To access residual acrylamide degradation the following calculation adopted:

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

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 residuals 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 free Software,” 2011).

3 Results

3.1 Characterization of the hydrogel

The hydrogel used in the study contained 39.7%, 6.7% and 15.0% C, H, and N and had a C/N ratio of 2.65 (Table 1). The elementary chemical composition of the acrylate present in the hydrogel (Table 1), was 99.2% potassium (K) and 0.8% of sulfur (S).

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 monomer of the commercial hydrogel before applying the treatments (Gel pre-testing).

---- 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 monomer	
<24 mesh	24-35 mesh	35-48 mesh	>48 mesh	(mg g ⁻¹)	
12	37	15	36	0.50	

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. The level of residual acrylamide concentrations in the commercial hydrogel is with the regulatory limit established by Food and Drug Administration (FDA), the U.S. Environmental Protection Agency (EPA), and the National Resources Conservation Services (NRCS) (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 and in the band in 1560 cm⁻¹. The hydrogel X-ray diffractogram (Figure 1b) shows an absence of crystallinity.

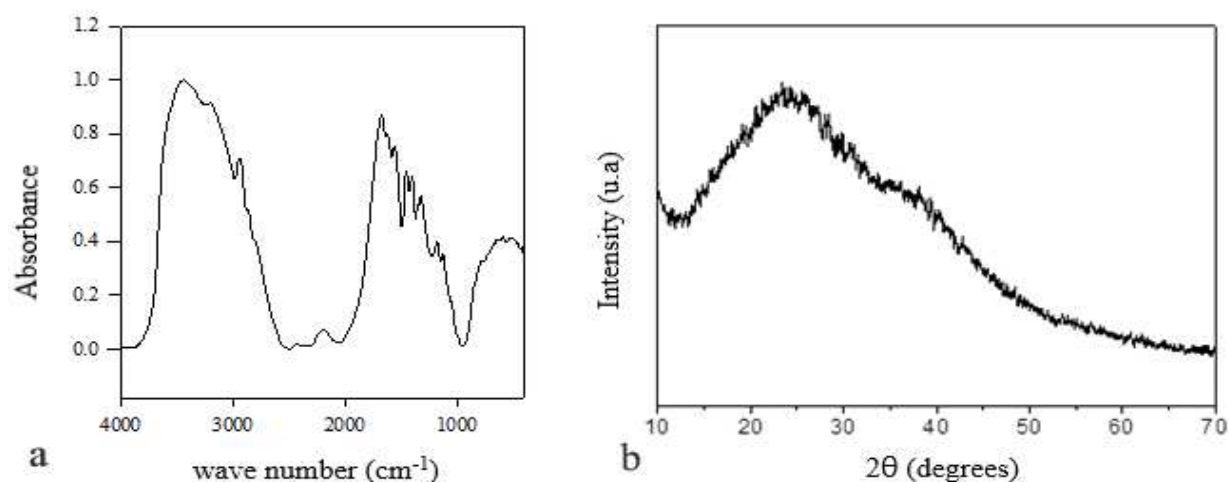


Figure 1. Infrared spectrum (a) and diffractogram (b) of the commercial Acrylamide-*co*-Potassium Acrylate hydrogel studied.

Figure 2 shows the curve obtained from the swelling of the commercial hydrogel – Poly (Acrylamide-*co*-Potassium Acrylate). The 0.5 dS m^{-1} saline solution is associated with a 75% reduction in swelling at 240 minutes as compared with the hydrogel hydrated with distilled water (Figure 2). 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.

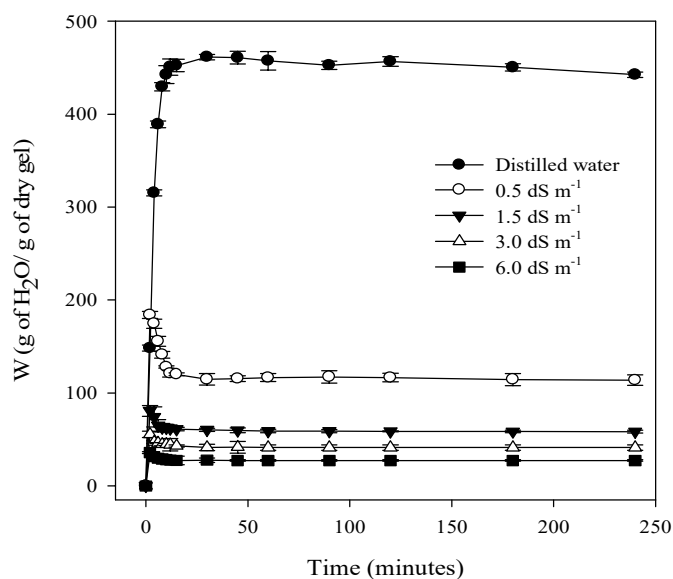


Figure 2. Hydrogel swelling curve in distilled water and solutions of sodium chloride (NaCl), calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) dissolved in a 7:2:1 ratio at EC's of 0.5, 1.5 3.0 and 6.0 dS m^{-1} (d) at 25 °C.

The hydrogel obtained, in distilled water, $W_{\text{eq}} = 462 \pm 3.0$ g of water g^{-1} of the hydrogel, W_t (6 min) = 389 ± 3.5 and reached equilibrium with $t_{\text{eq}} = 30$ min (Table 2).

Table 2. Swelling kinetics in distilled water and 0.5, 1.5, 3.0 and 6.0 dS m^{-1} hydration solutions of the commercial hydrogel – Poly (Acrylamide-*co*-Potassium Acrylate).

Poly (Acrylamide- <i>co</i> -Potassium Acrylate)	W_{eq} (g of water/g of gel)	t_{eq} (min)	$W_{t=6 \text{ min}}$
Distilled water	462 ± 3.0	30	389 ± 3.5
0.5 dS m^{-1}	184 ± 3.6	25	156 ± 5.4
1.5 dS m^{-1}	81 ± 5.9	25	65 ± 6.5
3.0 dS m^{-1}	56 ± 3.4	25	46 ± 0.4
6.0 dS m^{-1}	36 ± 1.0	25	30 ± 1.1

Attributes of swelling kinetics (W_{eq} - swelling in equilibrium, t_{eq} - equilibrium time and $W_{t=6 \text{ min}}$ - swelling in time = 6 minutes).

In the presence of saline solutions, W_{eq} gradually decreased. For saline hydration 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 hydration 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

The interaction between the factors (salinity*time) was significant for the variables: final swelling (W_{final}), residual acrylamide monomer concentration, acrylamide degradation, and C/N.

The hydrogel studied exhibited significantly different water absorption capacities, depending on salinity of the hydration solution and duration of exposure (Figure 3a and b). At 30 days, the lowest swelling was 14.61 g g^{-1} at an EC of 4.40 dS m^{-1} (Figure 3a). At 60, 90 and 120 days the lowest swellings were 26.5, 18.6 and 8.1 g g^{-1} , respectively which occurred in ECs of 4.5, 4.42 and 4.16 dS m^{-1} , respectively.

An EC of 4.20 dS m⁻¹ is therefore considered to be a critical value for reduction in the swelling potential of the commercial hydrogel, since in all the evaluation times the reduction in swelling was accentuated at this conductivity.

In distilled water (EC 0.003 dS m⁻¹) there was a minimum point in the swelling of the hydrogel (114.01 g g⁻¹) at 102 days (Figure 3b). 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 a maximum value 34.25 g g⁻¹ being reached at 47 days.

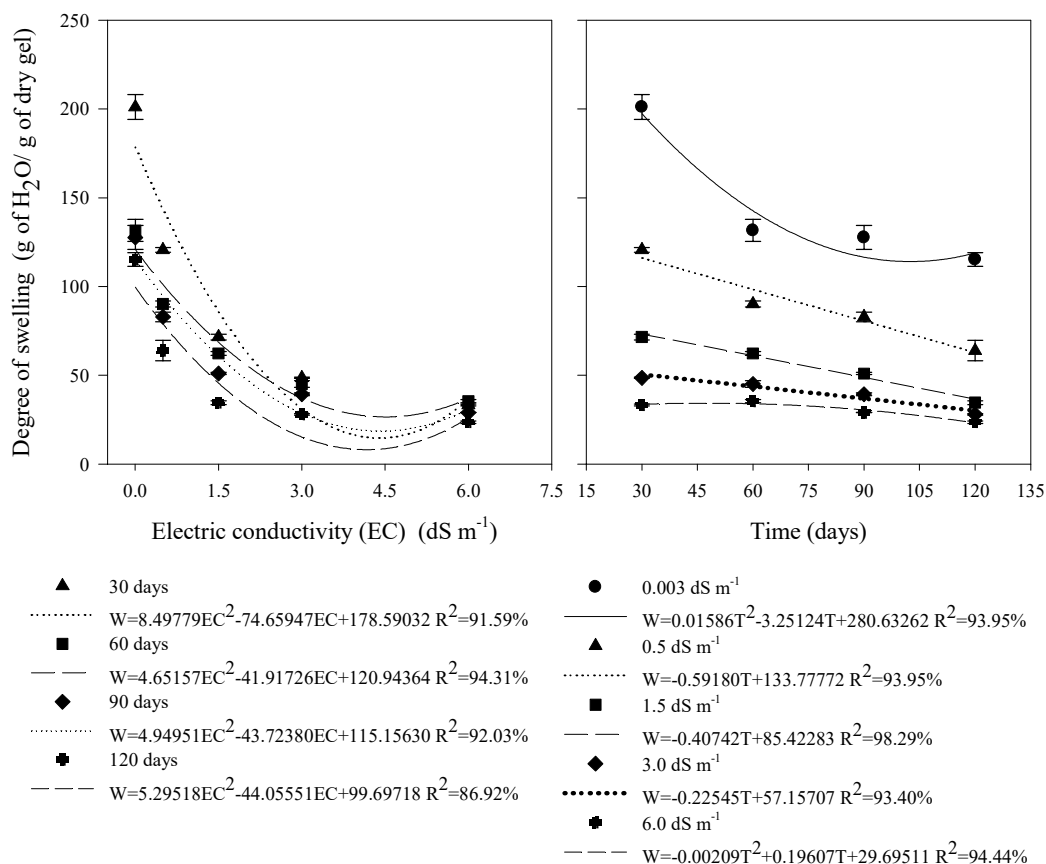


Figure 3. Swelling degree (g H₂O g dry gel⁻¹) of hydrogel Poly (Acrylamide-co-Potassium Acrylate) as a function of salinity (0.003, 0.5, 1.5, 3.0 and 6.0 dS m⁻¹ = 0.03, 5, 15, 30 and 60 mmol/L) of the hydration solution (a) and exposure time (30, 60, 90 and 120 days) (b).

With regards the residual acrylamide monomer, at 30 days the EC 3.0 dS m⁻¹ provided a minimum value of 0.19 mg g⁻¹ (Figure 4a). 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 of 0.44 mg g^{-1} is estimated to occurred at 56 days (Figure 4), which is the highest value observed across all treatments.

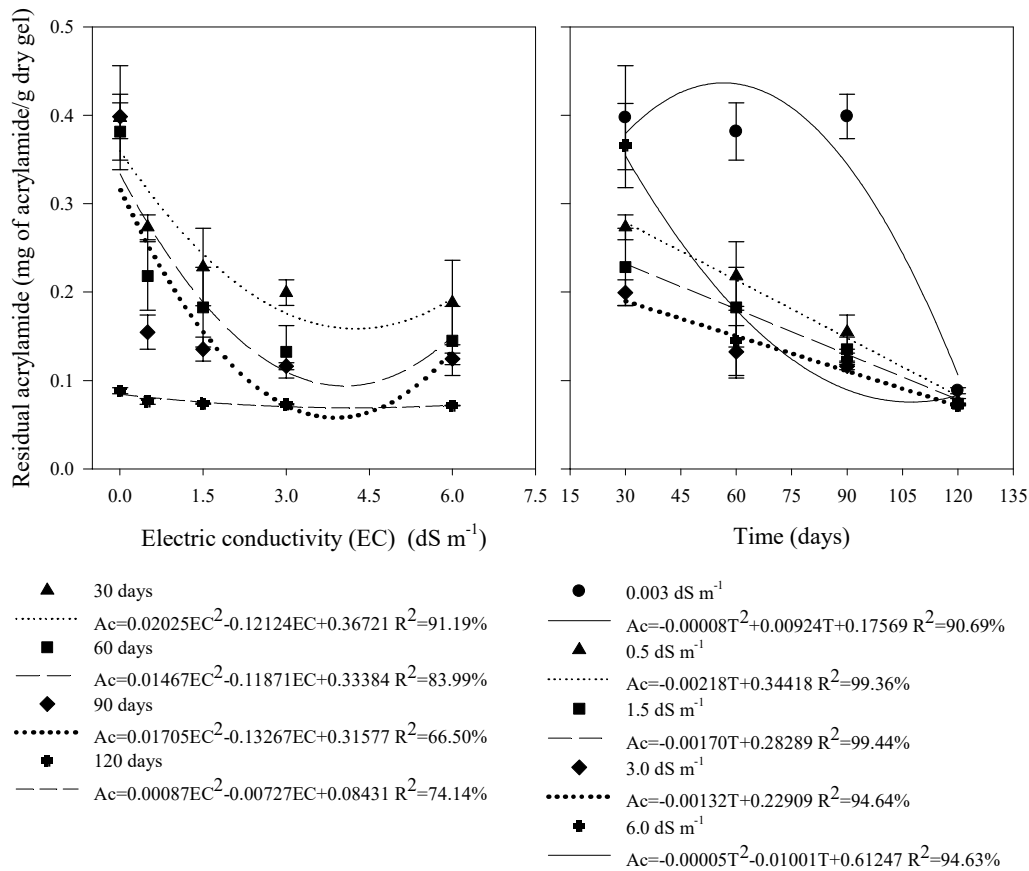


Figure 4. Final residual acrylamide monomer (mg RA_m/g dry gel) of a hydrogel of Poly (Acrylamide-*co*-Potassium Acrylate) as a function of salinity (0.003, 0.5, 1.5, 3.0 and 6.0 dS m⁻¹) of hydration solution (a) and exposure time (30, 60, 90 and 120 days) (b).

For the saline hydration solutions with 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 (Figure 4). For the highest EC (6 dS m⁻¹), a minimum value (0.11 mg g⁻¹) of residual acrylamide monomer was observed at 100 days (Figure 4).

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} at an 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 of 3.0 and 4.2 dS m⁻¹,

respectively (Figure 5). Between the ECs of 3.0 to 4.2 dS m⁻¹, the maximum degradation of RA_m occurred at the longest evaluation times (90 and 120 days).

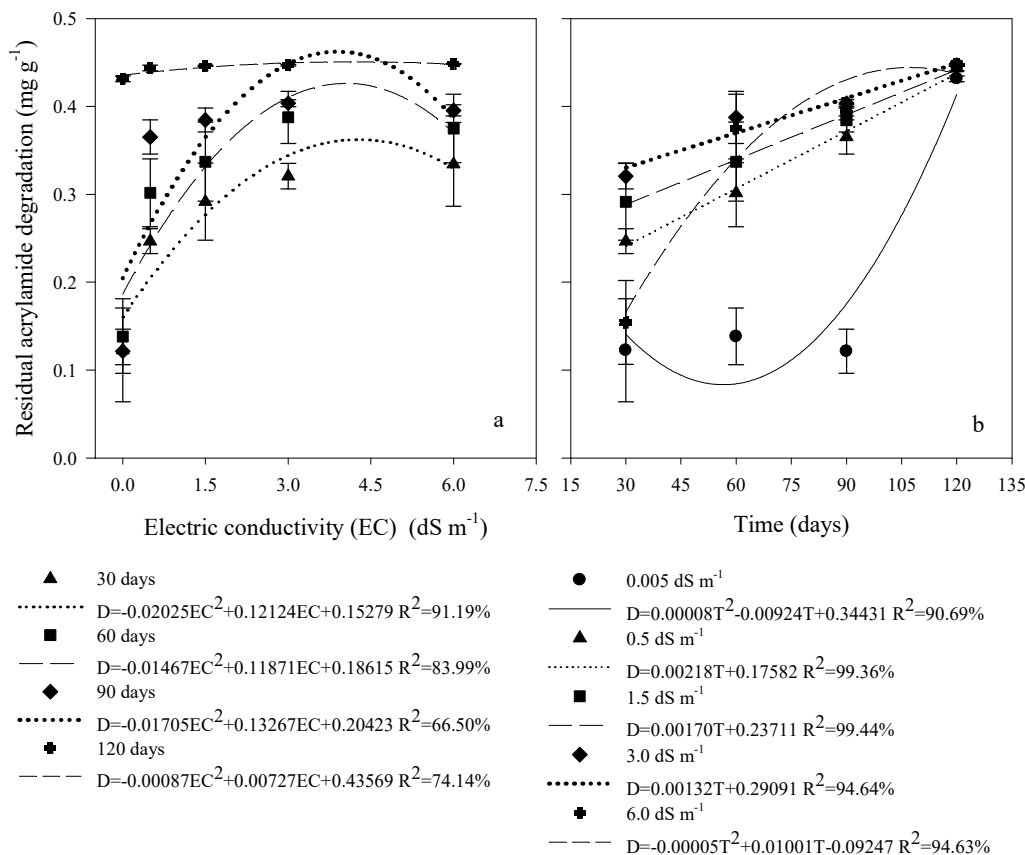


Figure 5. Residual acrylamide degradation monomer (mg RA_m/g dry gel) of a hydrogel of Poly (Acrylamide-co-Potassium Acrylate) as a function of salinity (0.003, 0.5, 1.5, 3.0 and 6.0 dS m⁻¹) of the hydration solution (a) and exposure time (30, 60, 90 e 120 days) (b).

In distilled water, the least degradation of RA_m (0.08 mg g⁻¹) was observed at 56 days (Figure 5). For ECs 0.5, 1.5 and 3.0 dS m⁻¹, RA_m degradation was observed in increasing functions, with daily degradation values of 0.0022, 0.0017 and 0.0013 mg g⁻¹, respectively. For the EC 6 dS m⁻¹ treatment, a maximum value of RA_m degradation of 0.41 mg g⁻¹ was observed at 100 days (Figure 5).

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, a maximum C/N (3.68) was observed at an estimated 87 days (Figure 6b). For

hydration solutions with ECs of 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 (Figure 6a and b).

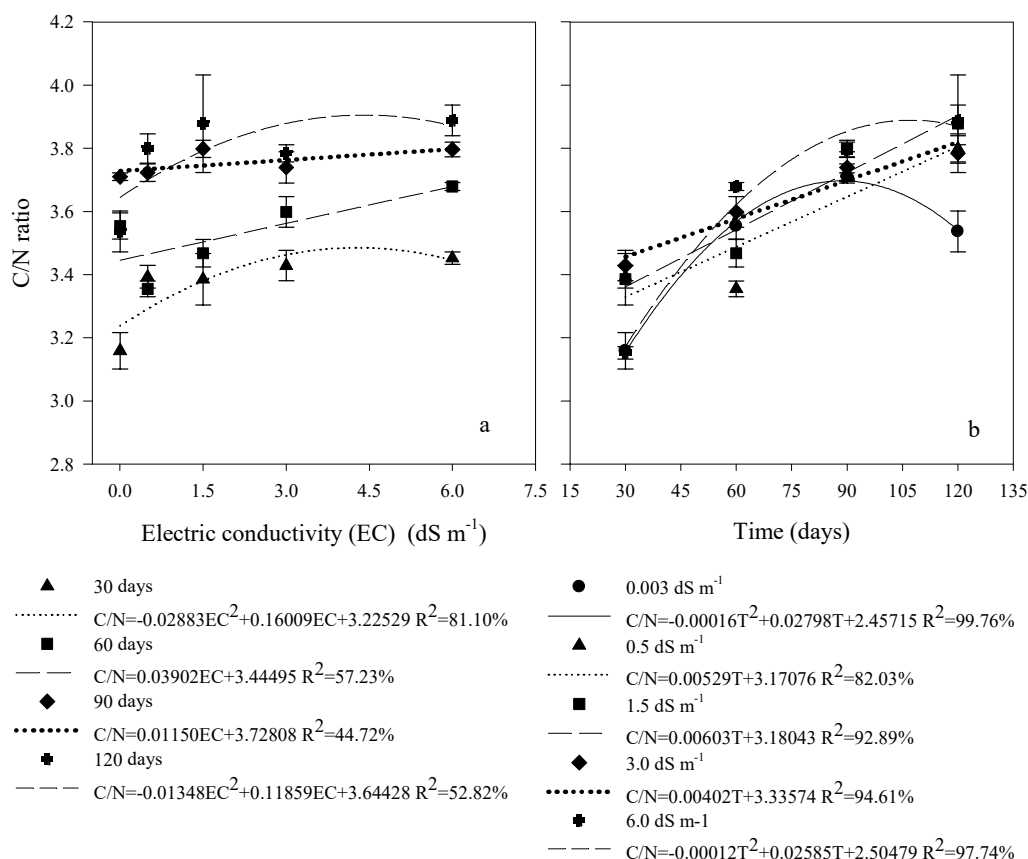


Figure 6. C/N ratio of the commercial hydrogel of a hydrogel of of Poly (Acrylamide-*co*-Potassium Acrylate) as a function of salinity level (0.003, 0.5, 1.5, 3.0 and 6.0 dS m⁻¹) of hydration solution (a) and exposure time (30, 60, 90 and 120 days) (b).

The spectra of the acrylamide and potassium acrylate copolymer pre-testing , in distilled water and exposure 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 Figure 7.

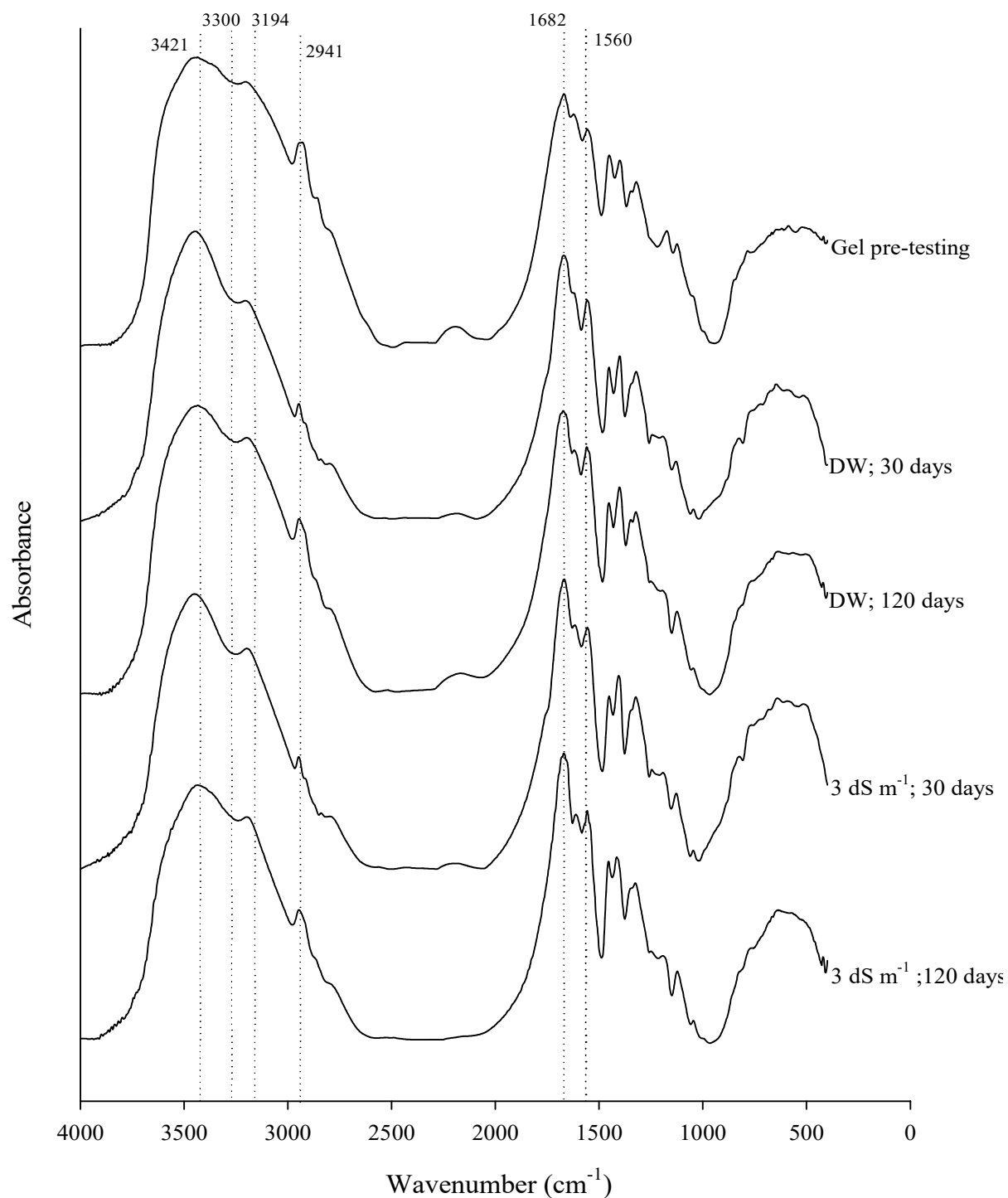


Figure 7. Fourier-transform infrared spectroscopy (FTIR) spectra of the hydrogel – Poly (Acrylamide-*co*-Potassium Acrylate).

Gel pre-testing: Commercial 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.

Table 3 lists the assignments of the main bands highlighted in Figure 7.

Table 3. Attribution of main bands in FTIR (Fourier-transform infrared spectroscopy) spectra of the hydrogel – Poly (Acrylamide-*co*-Potassium Acrylate).

Poly (Acrylamide- <i>co</i> -Potassium Acrylate)	Assignment
3421	ν_{as} NH ₂ of acrylamide unit
3300	ν 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).

4 Discussion

4.1 Characterization of the commercial hydrogel

In the elementary chemical composition of the acrylate present in the hydrogel, the presence of a greater amount (99.2%) of K and the occurrence of 0.8% of 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.

The residual acrylamide monomer content (0.5 mg g⁻¹ Table 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.

The swelling curve of the hydrogel in distilled water (Figure 2) indicates a rapid initial absorption followed by equilibrium (W_{eq}). 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 W_{eq} and the mass of the dry hydrogel. The profiles of the swelling curves for the hydrogel in saline hydration solutions differ significantly from the profile in distilled water. These show a rapid mass gain in the first minutes followed by deceleration until W_{eq} is achieved (Figure 2).

When swollen, the polymeric nets of hydrogels are more elastic. The osmotic force that assists in carrying the hydration solution into the polymeric network is counterbalanced by a retractive elastic force (Flory and Rehner, 1943). Thus, when the osmotic and elastic forces are equal, the hydrogel will have reached W_{eq} at a certain time (t_{eq}). The commercial hydrogel evaluated in this study can be considered a superabsorbent, as it absorbed more than 300 times its dry mass in water (Thombare et al., 2018).

4.2 Experiment to assess the effects of time and hydration solution salinity levels on the hydrogel

The reduction in swelling (Figure 3a) is attributed to a “charge screening effect” of the additional cations in the hydration solution, causing non-perfect anionic electrostatic repulsion (Kwon et al., 1991; Mirdarikhvande et al., 2014; Sadeghi et al., 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 hydration 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; Mirdarikhvande et al., 2014).

The decrease in swelling depends on the type and concentration of salts present in the solution (Heidari et al., 2018; Mirdarikhvande et al., 2014). Divalent elements, such as those found in the saline hydration solutions used in 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 the hydrogel and the formation of inter and intramolecular complexes (Sadeghi et al., 2011). Monovalent cations, such as Na^+ , can shield the carboxylate anions of the polymeric structure, contributing to compact three-dimensional structures due to the lower repulsion between fixed network charges. This leads 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 et al., 2011).

The observed reduction in swelling (Figure 3b) indicates that the hydrogel does not retain the same functionality over time, even in distilled water. This is not favorable for agricultural, forestry and

urban use, and there is a need to improve the hydrogel so that its water absorption potential is durable. Other studies have also shown a reduction in hydrogel functionality over time. The absorption of water by hydrogels 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).

Salinity is one of the main abiotic stresses that limit plant development and crop productivity worldwide (Piñero et al., 2016). Despite the reduction in swelling with an increase in the salinity of the hydration solution, the high water retention obtained by the hydrogel can favor plant growth. Previous studies have indicated that hydrogel amendment can result in better plant establishment and growth through improvements in nutrient availability and moisture retention, which is highly relevant in the context of prevailing global climate change (Ljubojević et al., 2017).

The maximum level of residual acrylamide monomer (0.44 mg g^{-1} Figure 4a) corresponds to 440 mg kg^{-1} and is within the manufacturing limits reported in the literature for agricultural PAMs ($200\text{--}500 \text{ mg kg}^{-1}$) 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 RA_m in PAMs (Sathesh Prabu and Thatheyus, 2007).

The hydrogel investigated in this study has acceptable initial levels of potentially toxic RA_m . It is also considered to be stable as there was no increase in RA_m 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 $1\% (\text{w w}^{-1})$ of PAM soil conditioner in tomato and wheat plantations did not pollute the soil with acrylamide monomers resulting from depolymerization (Kusnin et al., 2015).

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 RA_m value was 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} – Figure 4). 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).

Under simulated environmental conditions, it was found that PAM hydrogel did not degrade to acrylamide, but RA_m did degrade to NH_4^+ with, NH_4^+ concentrations increasing as the level of RA_m decreased (Smith et al., 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 a form of N absorbed by plants and is essential for plant metabolism (Moreau et al., 2019; Smith et al., 1996).

The results of this study (Figure 5) show that RA_m is degraded rapidly. The degradation of RA_m , at all salinity levels increases with evaluation time confirming that acrylamide is degraded in days (Lande et al., 1979). Up to 95% of the RA_m was degraded within 30 days in hydrogels Poly (Acrylamide-co-Potassium Acrylate) under temperatures and salinity, indicating negligible environmental persistence (Nascimento et al., 2021). Also, RA_m is susceptible to biodegradation in soil and surface water, which reduces the risk of accumulation in the environment (Neely et al., 1974; Tepe and Çebi, 2017).

Under simulated environmental conditions, it was found that polyacrylamide did not degrade to acrylamide, but RA_m degraded to ammonium (NH_4^+) and that ammonium concentrations increased as RA_m levels decreased (Smith et al., 1996). 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 et al., 1996).

With the increase in C/N as compared to the hydrogel pre-testing (Figure 6), the degradation of RA_m and the 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 pre-testing level. The results of increasing the C/N for the samples for 120 days suggest that hydrolysis is an important degradation pathway.

The bands at 3421 cm^{-1} ($\nu_{\text{as}}\text{ NH}_2$), 3194 cm^{-1} ($\nu_{\text{s}}\text{ NH}_2$) and 1682 cm^{-1} ($\text{n C}=\text{O}$) 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. The displacement in the band 2941 cm^{-1} indicates a change in methylene which is main chain of the hydrogel (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 $\text{C}=\text{O}$ of amide).

In all the curves shown in Figure 7, it was observed that, after contact with distilled water or saline hydration 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 of the hydration solution and/or time are altering the chemical structure of the hydrogel, indicating its degradation. These results confirm that the degradation of the hydrogel evaluated in this study can be accelerated in the presence of hydration solutions containing Ca, Mg salts and therefore potentially by salts contained in 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 durability in the long term.

5 Conclusions

It is accepted the hypothesis that there is an interaction between time and salinity levels, reducing the water absorption potential of the 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 water absorption capacity over time across all salinity levels of the hydrating solution demonstrating that the hydrogel loses water absorption capacity. This may be an obstacle for agricultural, forestry and urban 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, agricultural and urban 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 hydrogel – Poly (Acrylamide-*co*-Potassium Acrylate) in the lowest salinity levels ($\sim 0.003 \text{ dS m}^{-1}$) of irrigation water possible to obtain swelling $>150 \text{ g g}^{-1}$ since small additions of salts in solution ($0.003\text{--}0.5 \text{ dS m}^{-1}$) reduce water holding capacity drastically ($\sim 40\%$).

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 RA_m in the salinity range of the hydration solutions (water, saline solution) over the studied times. Up to 85% of the RA_m was degraded within 120 days. Although the RA_m levels found are not considered high, it is recommended that the post-synthesis polymer washing process be improve, to further reduce RA_m levels and increase environmental safety.

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Durability indicatives of hydrogel for agricultural and forestry use in saline conditions

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