



Up-Scalable Synthesis of High Porous Superabsorbent Polymer via Alkaline Hydrolysis of Acrylamide using Microwave Irradiation: Application in Agriculture

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Abstract

We present a new one-pot industrial organic synthesis method of poly(acrylate-co-acrylamide) superabsorbent polymer via partial alkaline hydrolysis of acrylamide using microwave irradiation. The method allows the hydrolysis, polymerization and gelation to take place in one pot during a very short reaction time (120 s), and with no need to operate under inert atmosphere. The gel is compact and has a water absorbency of 1031 g/g. The degree of hydrolysis of the gel is determined by a back titration method. FTIR spectroscopy is used to confirm the hydrolysis and the formation of sodium acrylate. Scanning electron microscopy (SEM) reveals that the synthesized hydrogel has a high porous structure. The influence of the environmental parameters on water absorbency such as the pH and the ionic strength is also investigated. The product is tested for agricultural application as a soil moisture retention agent using onion as example. An enhancement in the growth of onion plant is proved in comparison to the growth of the onion without the superabsorbent polymer. Due to the simplicity of the preparation process associated with the high absorbency of the gel, the process can be scaled up for industrial applications.

1. Introduction

The increased need of arid and semi-arid regions for more arable land for agriculture has intensified the research for novel soil conditioner materials with new synthesis methods and low cost. In this respect, superabsorbent polymers (SAPs) are promising candidates to be used as soil conditioners and the development of new synthesis methods of SAPs is still challenging.

SAPs as three-dimensional cross-linked polymeric structures are capable of absorbing large quantities of water without disintegrating [1-3]. They are widely used in various applications such as hygienic, foods, cosmetics, and agriculture [4,5]. Therefore the synthesis and the investigation of new SAPs with high absorbency, better mechanical strength and fast initial absorption rate, have been the goal of several research groups in the past decades [6,7]. Acrylic-based SAPs have been widely studied because of their good swelling behaviors and chemical stability [8].

On the other hand, using microwave irradiation in organic synthesis has received increasing interest due to the specificity of microwave heating in terms of reactivity associated with control of very fast heating rate [9-11]. Microwave energy can be directly and uniformly absorbed throughout the entire volume of the reactive medium, causing it to heat up evenly and rapidly [12]. The microwave irradiation has been successfully used in the graft polymerization of chitosan with polyacrylic acid [13], the cellulose-g- polyacrylamide [14] and bentonite-g- poly(sodium acrylate-co-acrylamide) [15,16].

The preparation of poly(sodium acrylate-co-acrylamide) with conventional heating methods is very common. It can be prepared from its comonomers [17], or via alkaline hydrolysis of polyacrylonitrile, polyacrylamide or poly (acrylamide-co-acrylonitrile) [18-21].

To the best of our knowledge, the synthesis of poly(sodium acrylate-co-acrylamide) starting from acrylamide only and performing the hydrolysis, polymerization and crosslinking in one step have not investigated before.

In this paper, we aim to synthesize a high absorbency gel of poly(sodium acrylate-co-acrylamide) in one reaction pot starting from the acrylamide monomer under partial alkaline hydrolysis and using microwave irradiation. Owing to the simplicity of the proposed process, in comparison with the well known industrial method for synthesis of superabsorbent polymers, suggests the potentiality of mass production of the new absorbent copolymer on the industrial scale [22-24].

2. Material and Methods

2.1. Materials

Acrylamide (AM) for synthesis (Merck) was used as purchased. Potassium peroxydisulfate $K_2S_2O_8$ (KPS) GR for analysis as an initiator and N,N-methylene bisacrylamide (MBA) for electrophoresis as a crosslinker were also obtained from Merck. Sodium hydroxide NaOH microgranular pure (POCH) was used as a hydrolysis agent. Solvents: methanol and ethanol (GR for analysis) were obtained from Merck. Saline sodium chloride (NaCl) (Merck), calcium chloride ($CaCl_2$) (Panreac) and aluminum chloride ($AlCl_3$) (Merck) were prepared with distilled water.

2.2 Instrumental Analysis

The IR spectra in the 400-4000 cm^{-1} range were recorded at room temperature on the infrared spectrophotometer (Bruker, Vector 22) with a resolution at 2 cm^{-1} and 6 scans. For recording IR spectra, powders were mixed with Potassium bromide (KBr), as KBr disk, in the ratio 1:250 by weight to ensure uniform dispersion in the KBr pellet. The mixed powders were then pressed in a cylindrical die to obtain clean discs of approximately 1 mm thickness.

Morphology of the dried gels was studied by scanning electron microscope (Vega Tescan SEM). Dried superabsorbent powder was coated with a thin layer of graphite and imaged in a SEM instrument.

Water absorbency of the gel is measured by the free swelling method and is calculated in grams of water per one gram of the dried product [22,25]. Thus, an accurately weighed quantity of the polymer under investigation (0.1 g) is immersed in 500mL of distilled water at room temperature for at least 3 hours. Then the swollen sample is filtered through weighed 100-mesh (150 μm) sieve until water ceased to drop. The weight of the gel containing absorbed water is measured after draining for 1 hour, and the water absorbency is calculated according to the following equation:

$$Q = (m_2 - m_1) / m_1$$

Where, m_1 and m_2 are the masses (g) of dry and swollen samples, respectively. All results related to water absorbency are repeated three times.

2.3. Copolymer preparation from acrylamide in alkaline medium:

In this section, we aim to prepare poly(sodium acrylate-co-acrylamide), starting from acrylamide in an alkaline medium. To this end, sodium hydroxide 0.04 mol are added to a solution of acrylamide (0.169 mol in ca. 24mL of distilled water) under vigorous stirring. Then, 0.08g of KPS, as an initiator, (in ca. 7 mL of distilled water) and 0.08g of MBA, as a crosslinker, (in ca. 5 mL of distilled water) are added to the above solution. The total mass of the reactive mixture is brought to 100g by adding distilled water. The mixture is stirred for 15 min at 750rpm. Then, it is treated in a microwave oven at the power of 950W. The gelation point is reached after 120s and an odor of ammoniac has accompanied the gel formation. The product (as an elastic gel) is cut to small pieces. Then it is washed several times with methanol to dissolve non reacting reagents, and last washed by ethanol, and dried for several hours at 60°C until it becomes solid and brittle. At this point the solid is ground and dried in the oven at 60°C for 24 hours. Fig. 1 illustrates a proposed mechanism of the reaction.

2.4. Determination of the degree of hydrolysis

The hydrolysis degree of the synthesized SAP is determined by acid-base titration of carboxylate groups produced by alkaline hydrolysis of acrylamide, after adding a saturated solution of NaCl to a precisely pre-weighed mass of the copolymer [26].

Hydrochloric acid (0.1M) solution is dripped over the sample solution until the pH is reached 3. This solution is then back titrated with aqueous solution of sodium hydroxide (0.1M) until the pH was raised to 7. The number of equivalents of sodium hydroxide consumed is equal to the number of acrylate content in the SAP [23]. The result shows that percentage of acrylate groups is 18.83% for the synthesized SAP.

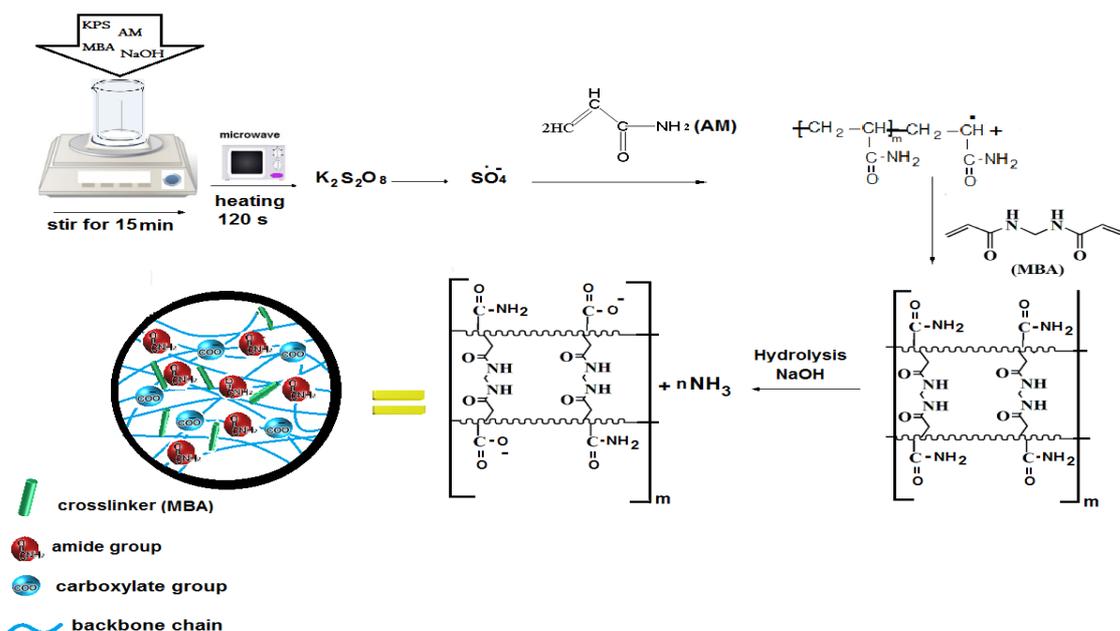


Fig. 1 : Proposed scheme of mechanism of preparation of superabsorbent polymer by hydrolysis of acrylamide.

2.5. Determination of the gel content

In order to measure the gel content, accurately weighed dried samples of SAPs are dispersed in distilled water to swell completely. Then the swollen SAPs are filtered and washed with distilled water frequently. The samples are dewatered in excess ethanol for 48 h, and dried at 50°C for 12 h until the SAPs have a constant weight. The gel content is defined as the following equation:

$$\text{Gel}(\%) = \frac{W_d}{W_i} \times 100$$

Where W_d is the weight of dried SAP after extraction and W_i is the initial weight of the SAP.

2.6. Agricultural Application

The synthesized SAP is used as a soil moisture retention agent for growing onions (taken as a field trial). Two sets of onion cultivation, with and without SAP, are performed in an area of 2 m² for each.

1.5 g of dried SAP is swelled using tap water and distributed evenly around the onion roots in set 1. The cultivation lasts 5 months during the period from January until May. Then, the onions are collected from each set. Statistical study of the data is performed using the statistical software spss 17.

3. Results and discussion

In the abovementioned synthesis, each of the polymerization, the alkaline hydrolysis of amide groups and the cross-linking will take place in one stage and during a very short period of time not exceeding 120 s (prototype reactor). Since the reaction time is very short, there's no need to operate under inert atmosphere. In this process, we obtain a superabsorbent polymer with high absorbency and high porosity without using any foaming aid. The simplicity of the synthesis procedure associated with high gel content (about 90.6%) suggests the suitability of the procedure to be scaled up to the industrial level. The use of this SAP as a soil conditioner is also investigated. The hydrogel can be a promising substitute of polyacrylamide or partially neutralized polyacrylate SAPs, traditionally used in agricultural applications. Acrylamide repeating units contribute in enhancing the mechanical strength of the resultant gel, while the acrylate repeating units endow better swelling capacity to the hydrogel. The optimization of reaction parameters, i.e. the concentration of acrylamide, NaOH and MBA has been performed in order to get the hydrogel with maximum absorbency and good mechanical strength.

The parameters, which are chosen to be optimized, are the concentrations of monomer, NaOH and MBA. The optimized value of each one is determined by performing experiments in which the values of the parameter of interest are changing, while maintaining the values of other parameters fixed. For each experiment, the value of water absorbency is measured and mechanical strength and compactness of the gel are examined. Then, the optimized value of the parameter corresponds to the gel with the highest water absorbency and good mechanical strength.

3.1. Influence of monomer concentration on water absorbency

Table 1 depicts water absorbencies of different samples of SAPs prepared as mentioned in section 2.3. with different concentrations of acrylamide and MBA 1%w/w_{monomer} and KPS 0.08g and without NaOH.

Table 1 Water absorbencies of different samples of SAPs prepared with different concentration of acrylamide

Exp. n°	number of moles of AM (mol)	Water absorbency (g/g)	Gel consistency
1	0.084	-	no-gel
2	0.169	37	compact
3	0.25	21	compact
4	0.34	18	compact
5	0.42	19	compact

It is obvious from Table 1 that the increase in AM concentration leads to a decrease in water absorbency. In fact, the increase in AM concentration leads to a rapprochement between the polymeric chains and creates accordingly electrostatic cross-linked polymer chains by hydrogen bonds, and eventually it decreases water absorbency [27].

3.2. Influence of hydrolysis degree on water absorbency

Table 2 depicts water absorbencies of different samples of SAPs prepared as mentioned in section 2.3 with different hydrolysis degrees and with AM 0.169 mol, MBA 0.08 g and KPS 0.08g.

Table 2 : Water absorbencies of different samples of SAPs prepared with different hydrolysis degrees

Exp. n°	number of moles of NaOH (mol)	Water absorbency (g/g)	Gel consistency
1	0	37	compact
2	0.02	706	compact
3	0.03	728	compact
4	0.04	1031	compact
5	0.05	1134	compact
6	0.06	1162	loose
7	0.08	-	no-gel

From Table 2, we can conclude that the alkaline hydrolysis plays a positive role in increasing water absorbency of the gel, by rendering it more hydrophilic and by increasing the inter-chains repulsion due to the electrostatic repulsion of acrylate groups. But increasing NaOH above a certain threshold affects the gel consistency, as the secondary amide group of the crosslinker may undergo alkaline hydrolysis.

In the course of the hydrolysis, the formation of ammonia gas is the driving force that displaces the equilibrium of the alkaline hydrolysis of acrylamide towards the formation of acrylates, and it favors the hydrolysis of the primary amide groups of the acrylamide in comparison to the hydrolysis of secondary amide groups of the crosslinker MBA, Fig. 2.

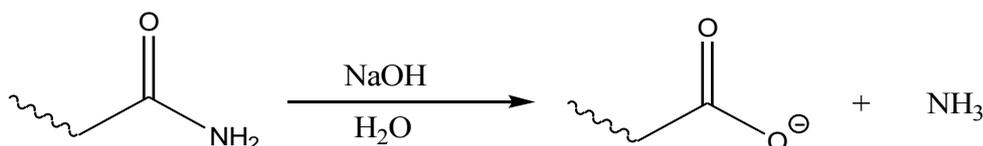


Fig. 2 : Alkaline hydrolysis of acrylamide and the formation of ammonia gas as the driving force for the displacement of the equilibrium.

There are two important factors contributing to the increase in water absorbency

a) The first one is the arrangement of the co-monomers along the polymeric network. In fact, during the hydrolysis of acrylamide, the formation of carboxylate groups occurs randomly along the polymeric chains. So, it's expected to be statistical. The electrostatic repulsion of the polymeric chains is more efficient in the case of a statistical copolymer and this provides better swelling properties.

b) The second factor might be linked to the formation of NH_3 gas during the alkaline hydrolysis and might be responsible of more porous structure of the gel [28]. In fact, during the reaction in the microwave oven, the reaction mixture becomes jelly or pasty, which prevents the removal of the evolved NH_3 and water vapors from the pasty medium. Eventually, the removed vapors create porosity in the gel. The porosity favors better water diffusion through the hydrogel network.

We have to notice that water absorbencies of the copolymers from hydrolysis of acrylamide prepared by microwave heating are higher than the water absorbency of the same copolymer when prepared by conventional heating methods [18]. This also may be linked to the specificity of microwave heating that induces shorter gelation time (not exceeding 120 s) and more progeny bubbles trapped in the viscous reaction mixture, and results in products with higher porosity [28].

3.3. Influence of MBA concentration on water absorbency

Table 3 presents water absorbencies of different samples of SAPs prepared with different amounts of MBA and with AM 0.169 mol, NaOH 0.04 mol and KPS 0.08g.

Table 3 : Water absorbencies of different samples of SAPs prepared with different amount of MBA

Exp. N ^o	MBA (g)	Water absorbency (g/g)	Gel consistency
1	0.04	-	no-gel
2	0.06	1128	compact
3	0.08	1031	compact
4	0.12	551	compact

It is obvious from Table 3 that the increase in MBA concentration leads to a decrease in water absorbency. The cross-linking agent MBA has a very large effect on both the network structure and the water absorbency. In order to form a network structure, some MBA is needed. More MBA will produce too many cross-linked points, which affects negatively the water absorbency of the samples.

According to boldfaced results of Tables 1, 2 and 3, one can deduce that the prepared SAP in section 2.3 is the optimized one. Therefore, the reported previous measurements in 3.1, 3.2 and 3.3 sections are promising.

3.4. FTIR spectra:

Fig. 3 shows the FTIR spectrum of polyacrylamide gel synthesized without alkaline hydrolysis (A), and the spectrum of the synthesized SAP prepared from the alkaline hydrolysis of the acrylamide (B).

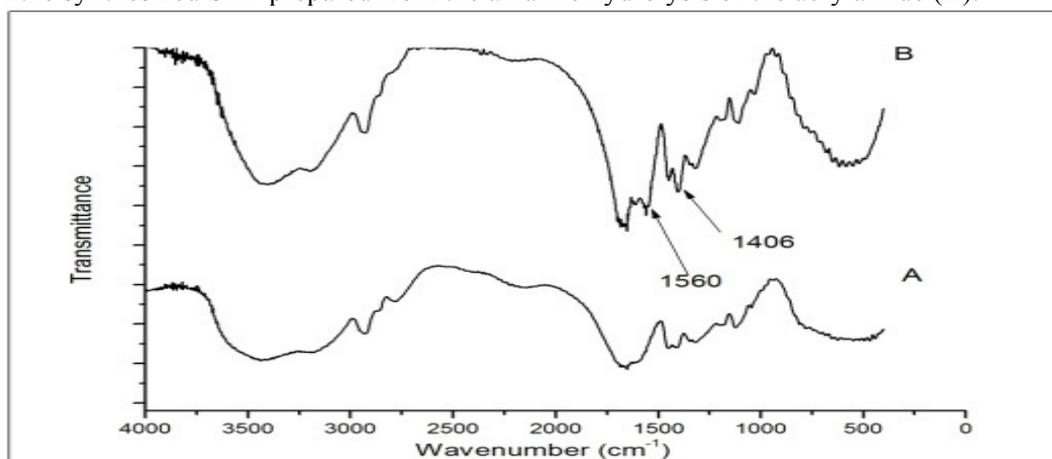


Fig. 3 : FTIR spectra of (A) polyacrylamide gel without alkaline hydrolysis and (B) poly (acrylamide–co-sodium acrylate) hydrogel prepared from alkaline hydrolysis of acrylamide (hydrolysis degree 18.83%).

Both spectra in Fig. 3 exhibit the characteristic absorption bands at 1654 cm^{-1} and 3450 cm^{-1} , corresponding to the C=O stretching vibration of the amide groups and amide N-H stretching respectively. By comparing the two spectra, it can be seen clearly the appearance, in spectrum (B), of additional two peaks characteristics of the carboxylate ion due to the partials alkaline hydrolysis of the amide groups. The first peak at about 1406 cm^{-1} corresponds to the symmetric stretching mode of the carboxylate ion. While, the second peak at 1560 cm^{-1} corresponds to the asymmetric stretching mode of this ion.

3.5. Scanning Electron Microscopy:

One of the most important properties that must be considered when studying hydrogels is its microstructure morphology. Fig. 4 shows the scanning electron microscope micrographs of the synthesized SAP with the hydrolysis degree 18.83%.

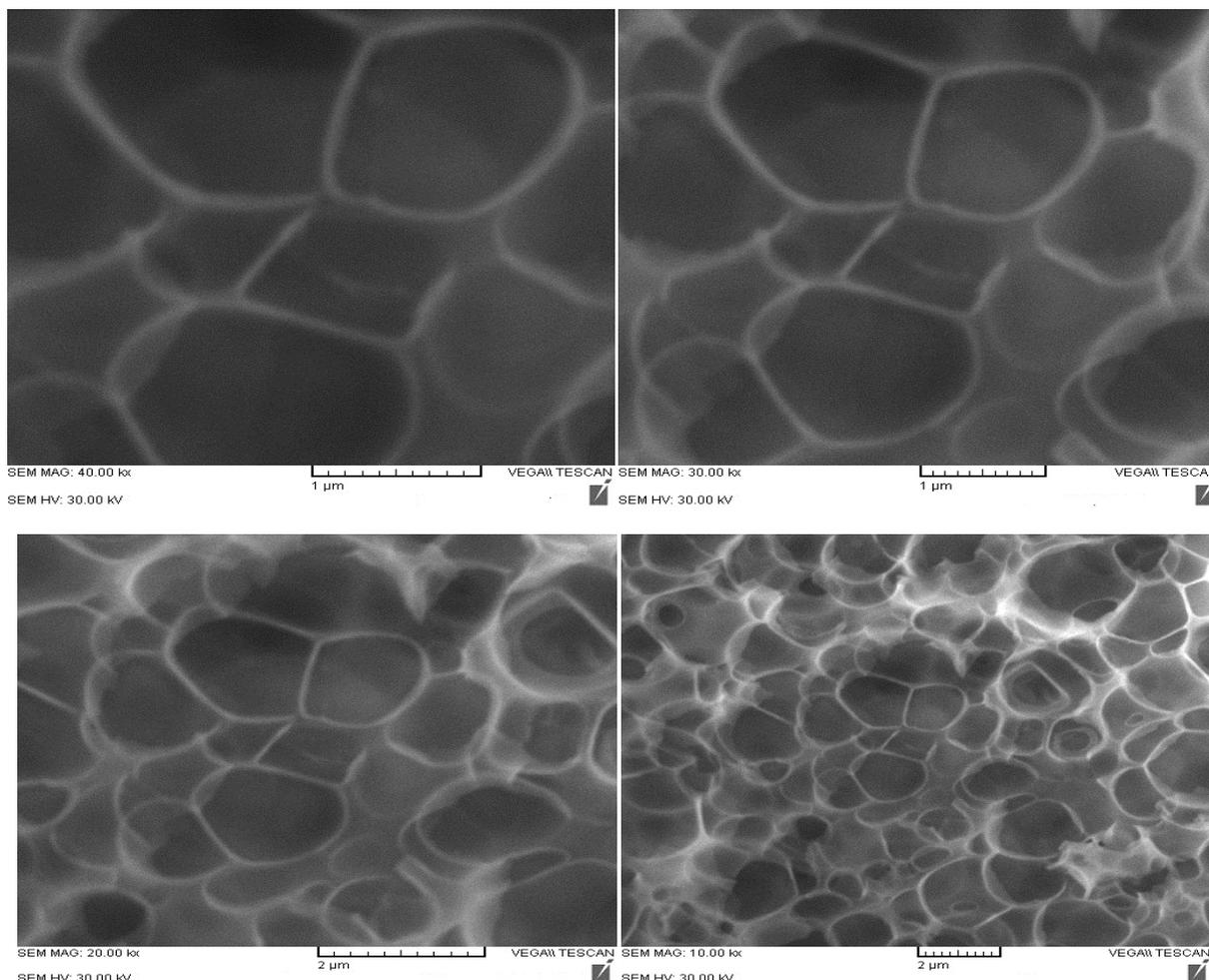


Fig. 4: SEM micrographs of the dried poly (acrylamide–co-sodium acrylate) gel prepared from the alkaline hydrolysis of acrylamide (hydrolysis degree 18.83%) with different magnification scales.

The micrographs of Fig. 4 verify that the synthesized polymer has a porous structure, with the effective pore sizes in the 1-2 µm range. So this copolymer is classified as a macroporous hydrogel [29,30]. It is supposed that these pores are regions of water permeation and interaction sites between external stimuli and the hydrophilic groups of the gel. These pores were simply produced from NH_3 gas formation and water evaporation during hydrogel synthesis.

3.6. Effect of the environmental parameters on water absorbency

3.6.1. Effects of salt solution on water absorbency:

The synthesized SAP with the hydrolysis degree 18.83% was tested for the effect of water salinity on its swelling capacity. Different concentration of NaCl , CaCl_2 , AlCl_3 solutions were prepared in order to study the effect of ion charge and ion concentration on water absorption, Fig. 5.

Fig. 5 shows that water absorption decreases with increasing the ionic strength of the saline solution as cited in Flory equation [31,32]. The ionic strength of the solution depends on both the concentration and the charge of each individual ion. In fact the presence of ions in the solution decreases the osmotic pressure difference, the driving force for swelling, between the gel and the solution. In addition, multivalent cations (Ca^{2+} and Al^{3+}) can neutralize several charges inside the gel by complex formation with carboxamide or carboxylate groups, leading to increased ionic crosslinking degree and consequently loss of swelling.

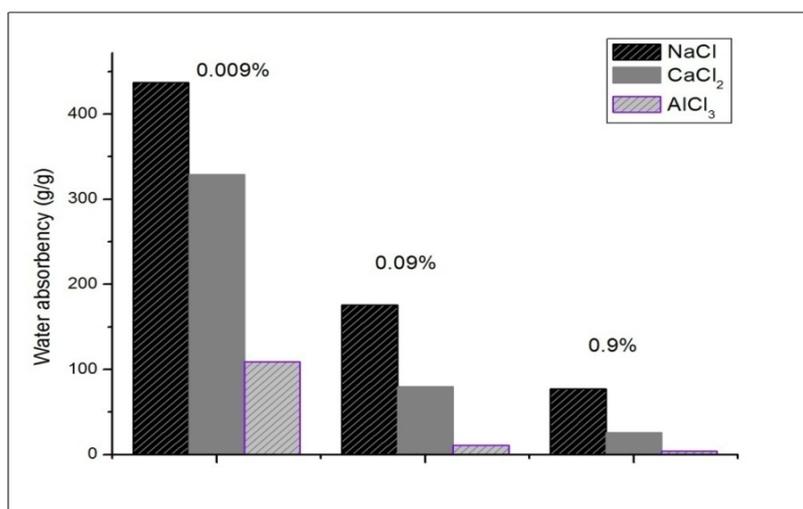


Fig. 5 : Effect of salt solution on water absorbency of the synthesized SAP with the hydrolysis degree 18.83%.

3.6.2. Effects of the environmental pH on water absorbency:

The swelling behavior of the synthesized SAP with the hydrolysis degree 18.83% was studied at various pH values between 2.0 and 12.0, at room temperature, Fig. 6. To clearly observe the net effect of pH, buffer solutions containing lots of ionic species, were not used as swelling media, as the swelling is strongly decreased by ionic strength. Therefore, a stock of concentrated solution HCl and NaOH were diluted with distilled water to reach the desired acidic or basic pH.

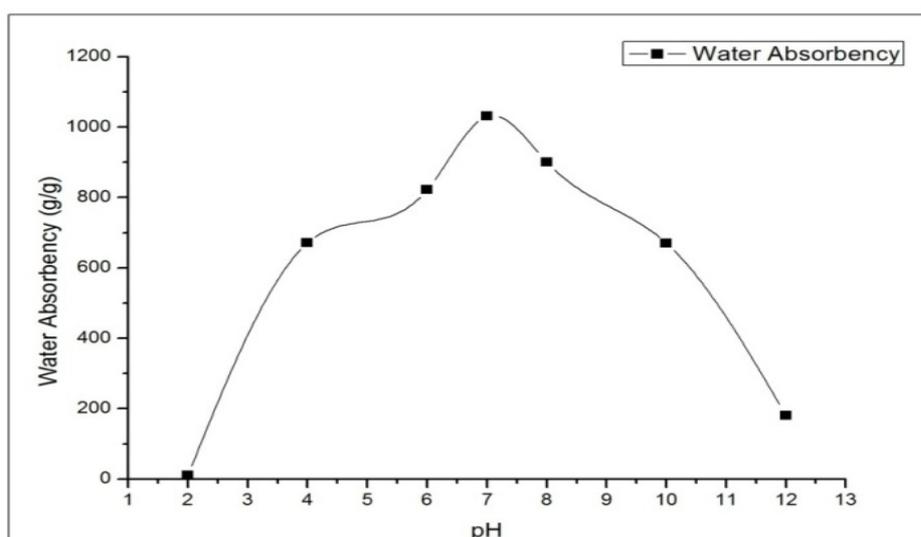


Fig. 6 : Effect of environmental pH on water absorbency of the synthesized SAP with the hydrolysis degree 18.83%.

Studies have indicated that water absorption of hydrogels are sensitive to environmental pH [33]. Fig. 6 shows that at low pH, the swelling capacity decreases as the sodium carboxylate groups on the polymer network are protonated. The polymer shrinks and becomes hydrophobic. This in turn decreases the degree of ionization and hence decreases the swelling ratio. At high pH, the swelling capacity also decreases by “charge screening effect” of excess Na⁺ in the swelling media, which shields the carboxylate anions and prevents effective anion-anion repulsion [33]. In the interval pH=4 to pH=8, some of carboxylic acid groups are ionized and the electrostatic repulsion between COO⁻ groups causes an enhancement of the water absorbency.

3.7. Agricultural Application

Tables 4 and 5 show the results of statistical analysis performed on the studied samples of onions grown in the presence of SAP and in its absence, respectively.

Table 4: Statistical analysis of onions crops grown in the presence of SAP.

	Weight of plant(g)	Length of leaves(cm)	Number of roots	Length of roots (cm)	Diameter of roots (mm)	Number of leaves
Mean	102.96	49.71	55.25	23.73	1.12	9.00
Minimum	78.68	38.60	42	17.50	0.83	7
Maximum	160.20	64.80	73	38.70	1.28	12
Range	81.52	26.20	31	21.20	0.45	5
Std. Error-Mean	7.48	1.93	2.88	1.63	0.042	0.41
Std. Deviation	25.92	6.68	9.97	5.64	0.14	1.41
Variance	671.84	44.66	99.48	31.78	0.02	2.00
Skewness	1.55	0.74	0.46	1.77	-1.04	0.93
Kurtosis	1.50	1.63	-1.07	4.37	0.17	0.62

Table 5: Statistical analysis of onions crops grown in the absence of SAP

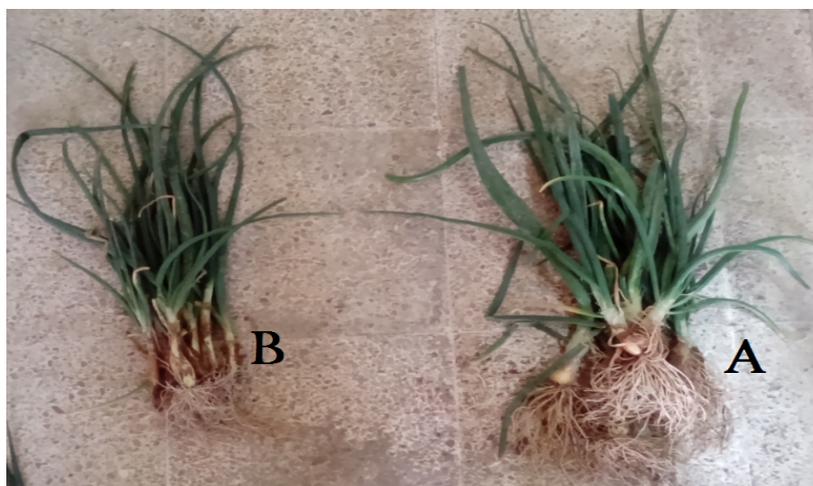
	Weight of plant(g)	Length of leaves(cm)	Number of roots	Length of roots (cm)	Diameter of roots (mm)	Number of leaves
Mean	43.65	37.56	36.42	18.37	0.66	6.50
Minimum	16.75	25.20	28	10.10	0.53	4
Maximum	65.50	53.60	51	26.20	0.83	8
Range	48.75	28.40	23	16.10	0.30	4
Std. Error-Mean	4.79	2.44	2.01	1.34	0.029	0.40
Std. Deviation	16.58740	8.43677	6.973	4.62549	0.09931	1.382
Variance	275.14	71.18	48.63	21.40	0.010	1.91
Skewness	-0.39	0.45	0.66	-0.01	0.38	-0.37
Kurtosis	-1.27	-0.44	0.005	-0.33	-0.73	-1.02

It can be clearly noticed that adding SAP to the soil has a beneficial effect on the plant growth. The weight of the plant is increased of about 135%. The lengths, number and diameters of roots, and the length and number of leaves are also enhanced, Table 6.

Table 6: Summary of the results of the agricultural application.

Weight of plant	Increase in the plant weight of about 135%
Length of leaves	Increase in the length of leaves of about 32.4%
Number of roots	Increase in the number of roots of about 51.7%
Length of roots	Increase in the length of roots of about 29.1%
Diameter of roots	Increase in the diameter of roots of about 69.2%
Number of leaves	Increase in the number of leaves of about 38.4%

Fig. 7 shows the difference between two onion samples cultivated (a) with SAP added to the soil and (b) without SAP.

**Fig. 7 :** Onion samples planted (A) with adding SAP to the soil and (B) without adding SAP.

Conclusion

Poly(sodium acrylate-co-acrylamide) has been synthesized by a simple and fast method using a domestic microwave oven by partially hydrolyzed acrylamide. This method enables to get high water absorbency. The enhancement of the absorbency is linked to the statistical nature of the copolymer and the high porosity of the copolymer due to gassing of ammonia. The relatively higher value of water absorbency of the copolymer compared to the absorbency of similar copolymers prepared via classical heating is related to the very short gelation time induced by microwave heating that leads up to more progeny bubbles trapped in the viscous reaction mixture, and results in products with higher porosity. SEM micrographs demonstrate the macroporous nature of the gel. Owing to the good results of the synthesis process (high gel content 90.6%) and its simplicity at the laboratory scale, it can be up scalable for industrial production. The current SAP is evaluated as a soil moisture retention agent using onion plant as an example, and it exhibits very satisfactory results.

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