

Study of different methods to induce crosslinking of polyacrylamide for agriculture process

Mohamed Ahmed Elhady^{1*}, Hussien Elnahas¹, Gamal Meligi², Ahmed Ammar³

¹Department of Polymers, Industrial Irradiation Division, National Centre for Radiation Research and Technology (NCRRT), Atomic Energy Authority, Nasr City, Cairo 11371, Egypt

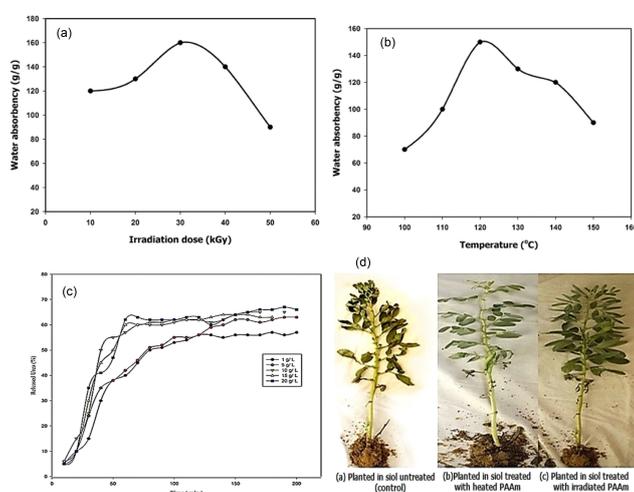
²Department of Chemistry, Faculty of Science, Ain Shams University, Abbassia, Cairo 11566, Egypt

³Environmental Department, Egyptian Airports Company, Cairo, Egypt

HIGHLIGHTS

- Preparation of superabsorbent polyacrylamide (PAAm) hydrogels radiation or thermal.
- Application of PAAm hydrogels in farming of sandy soil.
- The PAAm hydrogel samples were loaded with urea and their release behavior was examined in water.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study describes two different methods for the preparation of superabsorbent polyacrylamide (PAAm) hydrogels for application in farming of sandy soil. The two methods were employed to induce the crosslinking of the polymer matrix. In the first method a PAAm paste was exposed to gamma rays, while in the second method the polymer was thermally treated in the solid phase. Crosslinked PAAm hydrogel samples prepared by both methods were characterized by gel content, water absorbance, Fourier transform infrared (FTIR) spectroscopy, X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The parameters affecting the gel content, including the irradiation dose and temperature, were investigated. The obtained results suggested that the gel content of the PAAm hydrogel crosslinked by radiation and thermal treatments increases as the irradiation dose and temperature increased. Furthermore, the results indicated that the water absorbance reaches the maximum values at an irradiation dose of 30 kGy and a temperature of 120 °C. SEM showed that the synthesized hydrogels have a porous morphology. The PAAm hydrogel samples were loaded with urea and their release behavior was examined in water. Finally, the effect of hydrogels on the growth of beans (*Vicia faba L.*) was studied. The radiation crosslinked samples displayed better stability during the farming period and enhanced plant growth in comparison with the samples crosslinked by thermal treatment.

* Corresponding author: Tel.: +201016415657 ; Fax: +20222876031 ; E-mail address: mohamedelhady2000@yahoo.com

1. Introduction

Recently, water resources have decreased and water saving has become an important issue. Thus, soil management techniques, which reduce evaporation, and efficient irrigation programming, through the monitoring of soil water content, could be adopted in water scarcity scenarios [1,2]. On the other hand, superabsorbent polymers are three-dimensional crosslinked polymeric structures that are capable of absorbing large quantities of water without disintegrating [3-5]. Hydrogel is a kind of hydrophilic polymer with three dimensionally crosslinked structures.

The use of hydrogels for agricultural applications has shown encouraging results, as they have been observed to help reduce irrigation water consumption, lower the death rate of plants, improve fertilizer retention in the soil, and increase plant growth rate [6]. Hydrogels are now recognized as a well-established class of polymers with widespread applications in agriculture, medicine, the food industry and environmental sciences because they can retain significant fractions of water within their structure but do not dissolve into the soil [7-9]. These structures are capable of absorbing and holding a large amount of water, and the preserved water is difficult to removed even under high pressure. Hydrogel could also improve the amount of fertilizer retained in soil [10-12].

PAAm is a polymer that is formed from units of acrylamide, a known neurotoxin. PAAm is used in wide range in various applications such as foods, hygienics, cosmetics, and agriculture. Because PAAm is chemically inert and stable over various conditions, PAAm has been employed, whether clinically or under development, to serve as a useful matrix for several types of extracorporeal toxin removal [13,14].

The crosslink property has been used to improve the insolubility, mechanical strength, stiffness, and rigidity of polymer microbeads with potential applications in solid-phase synthesis, solid-phase extraction, and biomedical fields. A crosslink polymer is an important engineering material due to its excellent stability, which is more than the same polymer without crosslinking [15-17]. Crosslinking modification, including chemical crosslinking and thermal crosslinking, is a promising method to improve and enhance the thermal and chemical stabilities of polymeric membrane. The thermal rearrangement and crosslinking occur in the chain segments of polymer to form a stable three-dimensional

network structure during thermal crosslinking [18].

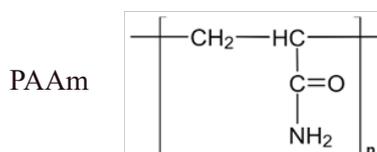
Fertilizers and water are important factors that limit the production of agriculture, so it is very important to improve the utilization of water resources and fertilizer nutrients. Nitrogen, the most widely applied plant nutrient, has commonly been considered to be the one limiting yield. However, the degree of utilization of nitrogen fertilizers is in the range of 30–50% [19-22]. Among the nitrogen fertilizers, the most widely used is urea because of its high nitrogen content (46%) and comparatively low cost of production.

The purpose of this work is to induce crosslinked PAAm hydrogels by thermal treatment and ionizing irradiation without using chemical crosslinkers. The two methods were selected to produce a PAAm hydrogel with controllable gelation for use on the practical scale, and then to study their impact on the gel content, water absorbance, and finally to make a comparison between them and radiation effect on PAAm. The parameters affecting the hydrogel swelling properties, including irradiation doses and temperature degree, were studied. The results refer to the ability of these hydrogels to enhance sandy soil water retention as well as aid in bean emergence and performance.

2. Experimental

2.1. Materials

PAAm with an average M.W. App. of 5,000,000–6,000,000 was obtained from Merck, Germany. Urea was purchased from El-Nasr Co. from Chemical Industries, Egypt and used without further purification.



2.2. Preparation of hydrogels

2.2.1. Preparation of PAAm hydrogel by gamma irradiation

To prepare PAAm hydrogel by gamma irradiation, about 50g PAAm was wet with 10g water and continuous mechanically stirred to convert the conete to paste. The paste PAAm was exposed to a gamma irradiation dose

ranging from 10-50 kGy at a dose rate of 1.08 kGy/h. The extracted hydrogels were dried in an oven at 45°C for three days. The dried hydrogels were boiled in hot water to determine the gel content. It is noteworthy to mention that the source of gamma irradiation was generated from a cobalt-60 gamma cell facility at the Atomic Energy Authority of Egypt.

2.2.2. Preparation of PAAm hydrogel by thermal treatment

To prepare PAAm hydrogels, 50g of PAAm were heated in an oven at temperatures of 100, 120, 130 and 150 °C for 20 min, then were boiled in hot water to determine the gel content.

2.3. Water absorbency measurement

The dry sample was weighed and immersed in water for 24 h to reach absorption equilibrium. The fully swollen hydrogel was separated from the unabsorbed water through a 65-mesh (100 μm) sieve until water ceased to drop. Then, the hydrogel was weighed. Relative water absorbency was calculated by the Eq. (1).

$$\text{Water Absorbency (g/g)} = \frac{\text{Mass of swollen hydrogel} - \text{Mass of dry sample}}{\text{Mass of dry sample}} \quad (1)$$

2.4. Gel Content

To extract the insoluble parts of the hydrogels (i.e., the gelled part), the prepared hydrogels were soaked in water for 24 h at 60 °C. Then, they were taken out and washed with hot water to remove the soluble part, dried, and weighed. The gel percentage in the hydrogel was determined from the Eq. (2).

$$\text{Gel Content (\%)} = \frac{W_e}{W_d} \times 100 \quad (2)$$

where, W_e and W_d represent the weights of the dry hydrogel after and before extraction, respectively.

2.5. Loading and release of urea

Urea loading was carried out by immersing pre-weighed dry PAAm hydrogels into different concentrations of urea solution for 24 h. Thereafter, the

swollen gels were dried at room temperature for 3 days. The loading percentage was calculated by the Eq. (3).

$$\text{Loading (\%)} = \frac{W_1 - W_0}{W_0} \times 100 \quad (3)$$

where, W_0 and W_1 are the weights of unloaded and loaded dry hydrogels, respectively.

The released amounts of urea from PAAm hydrogel matrices were measured by soaking the dried loaded hydrogel samples in a vessel containing 100 ml deionized water at room temperature. At various times, aliquots of 3 ml were drawn from the medium to detect the quantity of urea released, which was determined by an ultraviolet spectrophotometer (adouble-beam UV visible Sp200, Pye-Unicam, England at 217 nm) and placed again into the same vessel to keep the volume constant [23].

2.6. Fourier transform infrared spectroscopy (ATR-FTIR)

This study used an attenuated total reflectance-Fourier transform infrared ATR-FTIR spectroscopy Vertex 70 FTIR spectrometer equipped with a HYPERION™ series microscope, Bruker Optik GmbH, Ettlingen, Germany, over the 4000-500 cm⁻¹ range, at a resolution of 4 cm⁻¹. Software OPUS 6.0 (Bruker) was used for data processing, which was a baseline corrected by the rubber band method with CO₂ bands excluded.

2.7. X-Ray diffraction (XRD)

X-ray diffraction (XRD) patterns were recorded using a Shimadzu diffractometer XRD-6000, at an operating voltage of 40 kV and an electric current of 30 mA. The pattern was recorded at a scanning rate of 4°/min and angular range of 10~100° 2θ.

2.8. Scanning electron microscope (SEM)

The fraction surface of polymeric films was studied by scanning electron microscope (SEM), JEOL, JSM-5400 at a voltage of 30 kV. The fraction surface was pre-coated with a thin gold layer to reduce charging in the SEM.

3. Results and Discussion

3.1. Water absorbency studies

Fig. 1 shows the effect of irradiation dose on water

absorbency of PAAm hydrogel. The results indicated that the hydrogel swelling enhanced as the irradiation dose increased up to 30 kGy, then decreases until it reaches almost the same value of absorbency at 50 kGy. At low irradiation doses (below 30 kGy) the reduction in water absorbance may be due to the possible degradation in crosslinking density. This trend copes up with the outcome results of gel content. Further, at high doses (above 30 kGy), the PAAm formed a high percentage of crosslinking which could lead to the forming of narrow pores in the hydrogels causing not enough space for water molecules to enter the polymer networks, resulting in a lower water absorbency. Therefore, there is an ultimate crosslink content to maximal water absorbency [24-26].

The impact of temperature on water absorbency is shown in Fig. 2. The results indicate that the water absorbance increases as the temperature increases until it reaches a maximum value at 120 °C. This temperature represents the highest value of water absorbency of hydrogel. During the thermal treatment the PAAm sample might be linked to a loss of the NH_2 groups which then evolve into a form of ammonia gas during the heating process, this might be responsible for the more porous structure of the hydrogel. This explanation agrees with the work of Kabiri *et al.* [27-29]. The porosity favours a better water diffusion through the hydrogel network. Above 120 °C, the water absorbency slightly decreased due to burning the sample and degradation of the cells.

3.2. Gel Content study

Gel content indicates the degree of crosslinking formed in the hydrogel. A high degree of crosslinking

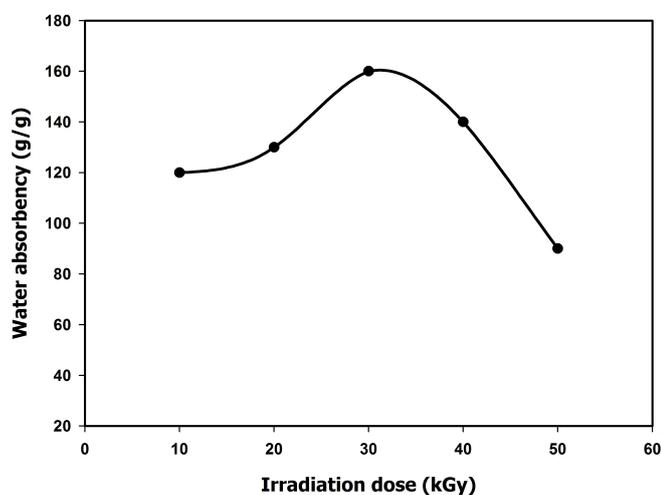


Fig. 1. Effect of irradiation dose on water absorbency of PAAm hydrogel.

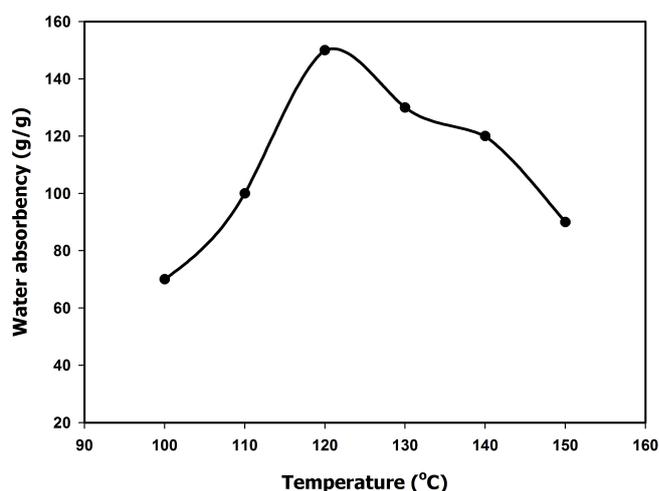


Fig. 2. Effect of temperature on water absorbency of PAAm hydrogel.

will make the structure become rigid and reduces the ability of the hydrogel to absorb water [24].

Fig. 3 illustrates the relationship between the gel content and the irradiation dose. The gel content (%) rises as the irradiation dose increases until reaching a maximum stable level (98.5%) at 30 kGy. No significant change of gel content (%) was observed above 30 kGy. Similar results completely agree with those reported in the literature [14]. This trend occurred due to the presence of liquid radiolysis, which enhances the mobility and elasticity of the rigid PAAm chains.

As a consequence, molecular movement takes place, allowing macroradicals to recombine and to enhance intermolecular and intermolecular recombination reactions. Furthermore, the presence of water radiolysis creates the macroradicals by abstracting H from the polymer chains. Thus, the crosslinking process of PAAm occurs faster and easier in the presence of water.

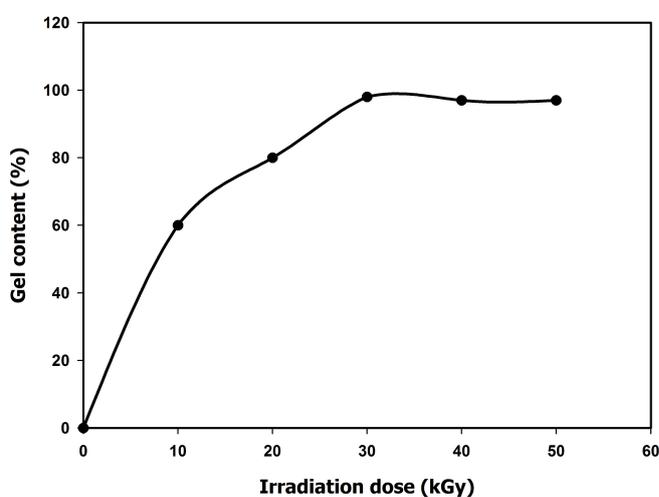


Fig. 3. Effect of the irradiation dose on the gel content of irradiated PAAm hydrogel.

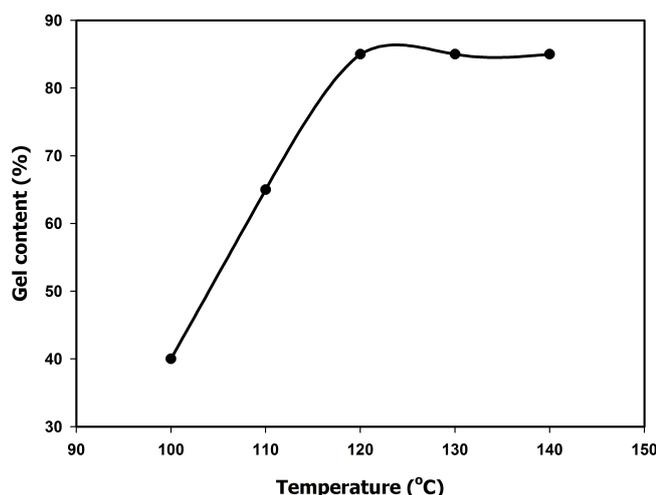


Fig. 4. Effect of temperature on the gel content of heated PAAm hydrogel.

Therefore, the presence of water is necessary to form easy homogenous hydrogel [14].

Fig. 4 shows the relationship between the PAAm gel content and the temperature. The gel content (%) increases with as the temperature increases until it reaches the maximum stable level (87.5 %) at 120°C. Then no more gel content was formed by increasing the temperature. It is confirmed that the crosslinking density reached a maximum by increasing the temperature and no more crosslinking density occurred above 120°C. The gel content test confirmed that 98.5% of crosslinking was recorded through the irradiation process; however, 87.5% was recorded for the temperature process as seen in Figures 3 and 4. Therefore, the gel content of hydrogel induced by gamma irradiation is higher than that prepared by the thermal process.

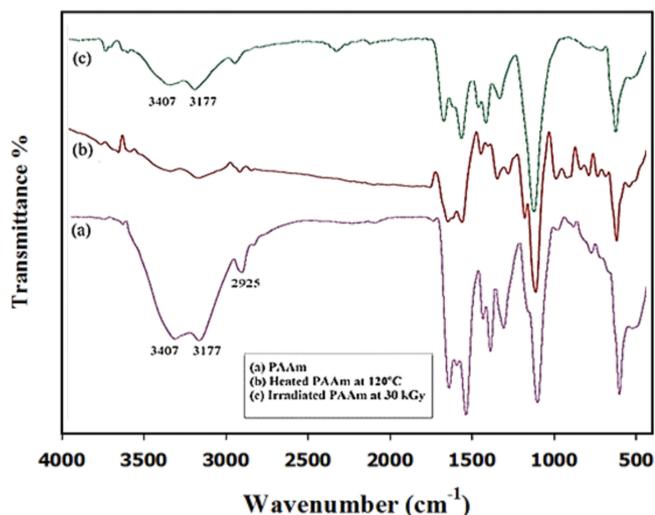
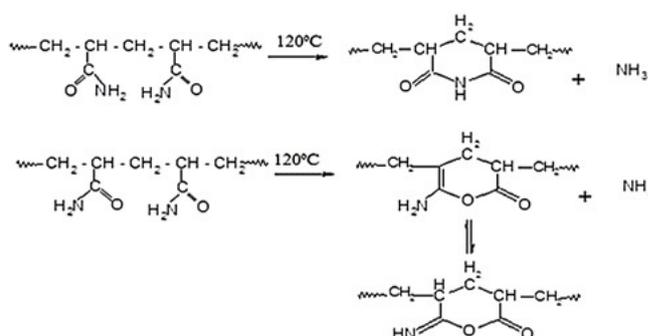


Fig. 5. FTIR spectra for (a) PAAm, (b) crosslinked PAAm by heating (at 120 °C), and (c) crosslinked PAAm by gamma irradiation (at 30 kGy).

3.3. FT-IR spectra analysis

FT-IR spectra for PAAm (a) and crosslinked PAAm by heating (b) or by gamma irradiation (c) are presented in Fig. 5. The FT-IR spectrum of PAAm shows the bands characteristics located at 3407, 3177 cm^{-1} are ascribed to the NH_2 (two beak) as shown in Fig. 5 (a) and (c), while in Fig. 5 (b) the band NH_2 disappeared. This is due to the release of ammonia as a gas when heating PAAm, which is known as the thermal degradation behavior of PAAm. As the temperature further increases, decomposition of the polymers begin [30]. From the suggested Scheme 1, it is clear that the thermal process causes the deammonation and dehydration of PAAm.



Scheme 1. The suggested reaction mechanisms in the thermal decomposition of PAAm.

3.4. X-ray diffraction analysis

Fig. 6 presents X-ray diffraction patterns for both PAAm and treated PAAm hydrogel (irradiated at 30 kGy or heated at 120 °C). It was observed that the peak intensities of PAAm hydrogel either prepared by gamma irradiation or thermal are a little broad. This is due to the crosslinking density of hydrogel and disruption of the original ordered structure [31].

3.5. Morphological properties

Fig.7 shows the photomicrographs of scan electronic microscopy (SEM) of PAAm (Fig. 7(a)) and PAAm hydrogels by irradiation (Fig. 7(b)) or by thermal (Fig.7(c)). As can be seen, pore sizes of the crosslinking hydrogel of PAAm is clearly observed, and both images of SEM are approximately similar compared to PAAm. The cavities between the network of the crosslinked PAAm appear to absorb the water, but there are no cavities in the PAAm. Finally, porous hydrogels are characterized by relatively rapid

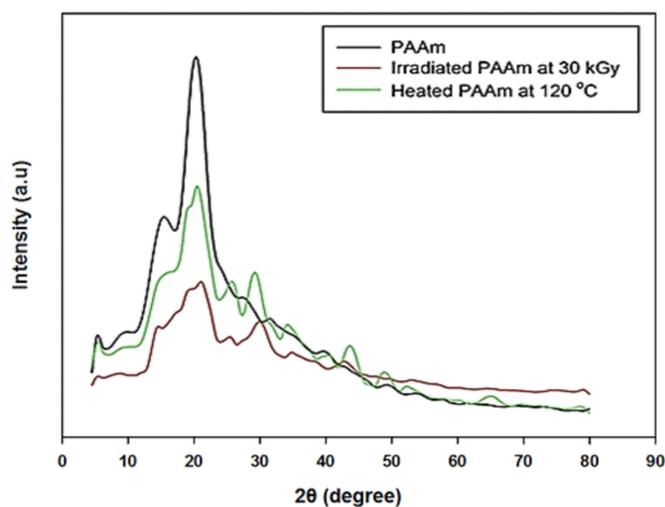


Fig. 6. XRD patterns of PAAm, heated PAAm at 120 °C, and irradiated PAAm at 30 kGy.

swelling kinetics with hydrogel samples reaching their equilibrium swelling in several minutes to a few hours because of their large pores and open structure [32].

3.6. Effect of bulk density on swelling particle and porosity of hydrogel

The bulk density of the hydrogel of PAAm is investigated in this section. In Fig. 8, the thermal method was used as a blowing agent to obtain the light bulk density of hydrogel, where at 120°C for 20 min was enough for 0.4 g/cm³ with an obvious pore structure. Heating PAAm in an oven at 120°C for 20 min led to changes in the crosslinking of PAAm to become in a popcorn shape as shown in Fig. 9. The result indicated that bulk density increased as the water absorbance increased due to the longitudinal formation of the porous structures resulting from the gas evolving effect, gas rising from the bottom to the top of the composite surface resulted in a porous hydrogel with oriented pore

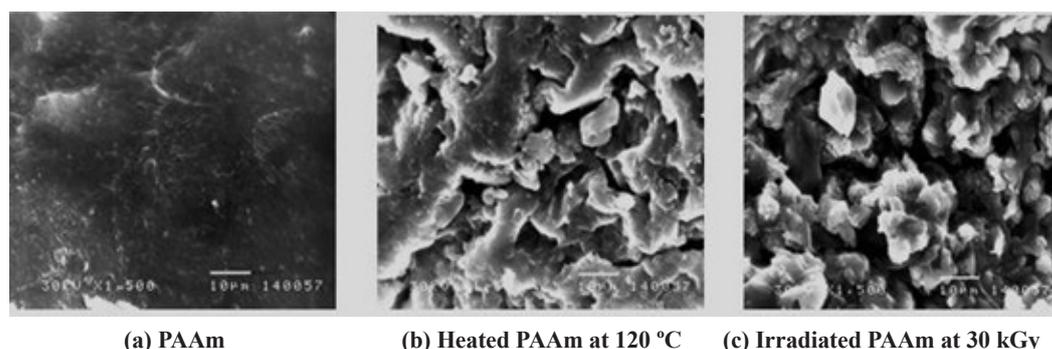
structures and fast swelling properties. The swelling of porous hydrogel in the aqueous solution is due to the absorption of water by capillary pressure through interconnected pores (i.e., open channels).

3.7. Urea loading and release behaviour

Different factors, such as soaking time, hydrogel size and active material concentration, could affect the loading of hydrogels within active matrices. The effect of urea concentration on hydrogel loading is shown in Fig. 10. Different urea concentrations had a lower impact on water absorbency but a greater effect on urea loading percentage. The different urea concentrations in the aqueous solution hardly changed the water absorbency of PAAm hydrogel. It can be seen that the loading percentage was increased by increasing the urea concentration of the loading solution. These results may be due to the increase of urea diffusion inside the hydrogel matrix. The dependence of urea loading percentage on urea concentration may be due to the fact that urea is a neutral molecule that does not affect the electrostatic repulsion force of the carboxylate groups on the hydrogel chains.

The addition of urea in water would not change the hydrogel-solvent interaction. Therefore, aqueous solutions of urea with different concentrations scarcely change the swelling process of PAAm hydrogel.

It is well known that most fertilizers are water-soluble and prone to evaporate at room temperature. Due to surface runoff, leaching, and vaporization the utilization efficiency or plant uptake of urea is generally low and most of the urea escapes into the environment, resulting not only in huge economic and resource losses but also in very serious environmental problems [33,34].



(a) PAAm

(b) Heated PAAm at 120 °C

(c) Irradiated PAAm at 30 kGy

Fig. 7. SEM of (a) PAAm, (b) PAAm hydrogel by heating at 120 °C, and (c) PAAm hydrogel by irradiation at 30 kGy.

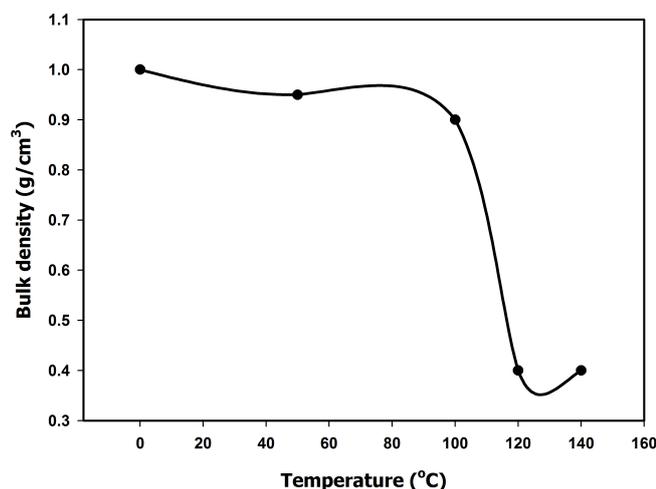


Fig. 8. Effect of temperature on bulk density of PAAm hydrogel.

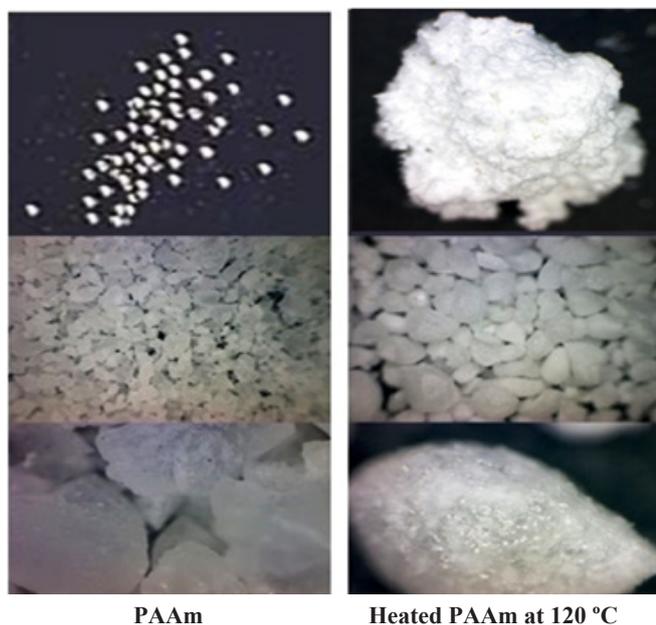


Fig. 9. Optical images of PAAm and heated PAAm at 120 °C.

3.8. Release of urea from loaded PAAm in water

The release behaviour based on the glassy-rubbery transition of the hydrogel occurs as a result of water penetration into the hydrogel matrix. Thus, it is important to study its release behaviour in PAAm. The release of the loaded hydrogel is closely related to its water sorption as it has been already established that a highly swollen hydrogel should release a greater amount of solute entrapped within the gel [35]. The release profiles of urea from the loaded PAAm hydrogel with different urea loading percentages in water at 25°C (swollen in aqueous urea solutions with different concentrations) are depicted in Fig. 11. The release profile indicates

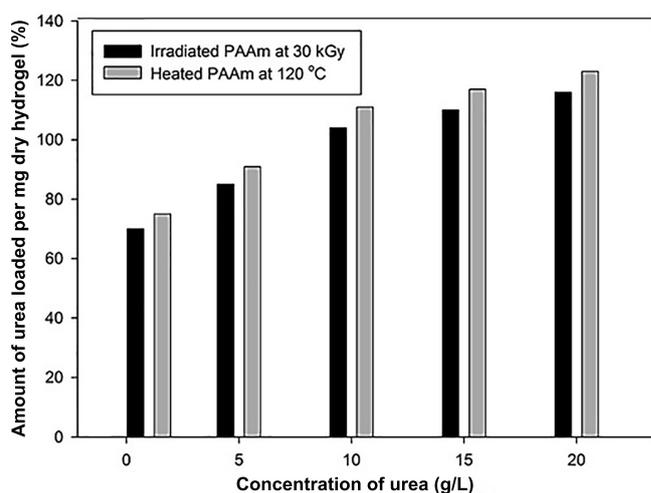


Fig.10. Effect of urea solution concentration on the loading (%) of PAAm hydrogel by heating at 120°C and PAAm hydrogel by irradiation at 30 kGy.

that the amount of the released urea increased as the loading percentage of the hydrogel increased. This is due to the fact that the larger the initial load, the faster the movement is of the solvent when penetrating the surface of the loaded hydrogel [32,36].

The period of high speed release lasted for 60 min, after this process the samples that were swollen in the 1 and 5 g/L aqueous urea solutions attained 75% of the whole release, while the rest achieved 85% to 95%. The release of urea is closely related to the swelling characteristic of the PAAm hydrogel. Firstly, the PAAm hydrogel is highly water absorbent and the polymer network extends immediately. Then, the urea molecules rapidly release from it. When PAAm swell to a certain degree, the extension of the polymer network is restricted, resulting in a slowing of the release of urea molecules. Furthermore, as can be deduced from Fig. 10, the higher the urea loading percentage was the faster the release of urea molecules appeared to be. This may be due to the fact that the high load of urea accelerates the absorption of water in the loaded samples, which facilitates the relaxation of macromolecular chains [37]. Therefore, swelling in aqueous urea solutions with different concentrations is an effective way to regulate the load and release of urea from the hydrogel composite.

3.9. Application of hydrogel in agriculture field

Polymer hydrogels are a commonly available product to ensure adequate hydration as they have the ability to absorb large quantities of water. Among these hydrogels

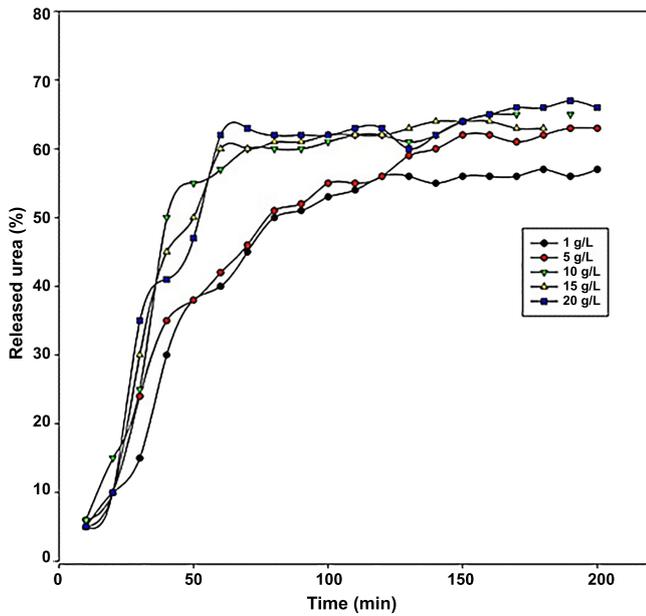


Fig.11. The release profile of urea loaded PAAm hydrogel with different urea loading percentages.

PAAm is one of the most popular, having also been used to reduce water runoff and increase infiltration rates in agriculture field [38,39] in addition to increasing water holding capacity for horticultural and agricultural applications [40-42].

3.10. Effect of the prepared hydrogels on the time to wilting for plant

The shelf-life (time to wilting) of bean plants grown in sandy soil treated with PAAm hydrogel (irradiated PAAm and heated PAAm) was investigated and is shown in Fig. 12 and Table 1. It is observed that the time to wilting of bean plants planted in the presence of

hydrogels is longer than that for the control and follows the order: irradiated PAAm>heated PAAm>control. The addition of the hydrogel in the soil led to a significant raise in the wilting time of the bean (*Vicia faba L.*) plants.

Fig. 12 shows three sets of pots (a, b and c). It was observed that the water retention of sandy soil without hydrogel (control) is lower than that of the sandy soil containing absorbent hydrogel. The presence of hydrogel improved the water retention of the sandy soil. The water retention time of sandy soil containing 2% irradiated PAAm/Soil weight (b) is more than 2% of the heated PAAm/Soil weight (c). Therefore, in sample (a) the growth of the bean plant was poor while in sample (b and c) the growth was high. Hence, the prepared hydrogels are more beneficial for areas in which seeds are not grown in soils due to a deficiency of water.

4. Conclusions

In this study, a complete system of producing water absorbent hydrogels from different methods to induce crosslinking of PAAm is suggested. The first method is a radiation process and the second method is using the effect of temperature to induce crosslinking of PAAm for possible applications in the agricultural field of sandy soil was studied. The water retained by hydrogels can be used by the plants and this addition enhanced plant growth and improved water use efficiency. The preperde hydrogels were charaterzied by diffrenet techniques such as FT-IR, XRD and SEM. In addition to this, the decrease in bulk density of the hydrogel prepared using the thermal process achieved an excellent improvement in water absorbency by reducing the



Fig. 12. Time to wilting of Bean (*Vicia faba L.*) plant planted in (a) soil untreated (control), (b) treated with heated PAAm, and (c) treated with irradiated PAAm.

Table 1. Time to wilting of plant planted in sandy soil treated with different types of PAAm hydrogel.

Hydrogel types	Hydrogel amount (g/m ²)	Time to wilting (h)
Control (a)	0	204
Heated PAAm (b)	10	336
Irradiated PAAm (c)	10	384

time and increasing the rate of absorbency. Hydrogel absorption of the urea (as fertilizer) was also studied and its retention was also found to have the ability to absorb and retain a high concentration of urea (20 g/L). From the obtained results it was suggested that PAAm super absorbent hydrogels may be used as potential eco-friendly water saving materials for agriculture applications in sandy soil as a soil conditioner in view of increasing their water-holding capacity and/or nutrient retention. The water retention of the soil was enhanced by using PAAm hydrogel. The use of the prepared hydrogels for the growth of bean seeds was also investigated. Our results showed that the thermal treatment method is preferable to the radiation method, as the thermal process is a quicker, easier and cheaper process.

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