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Studies on guar gum and cellulose acetate superabsorbent hydrogel beads with high water retention properties for rejuvenation of dryland wettability

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The guar gum-polyethylene glycol (GG-PEG) and cellulose acetate-polyethylene glycol (CA-PEG) hydrogel beads have been synthesized using crosslinking agent polyethylene glycol with drop cast method. The newly fabricated beads have been characterized by FTIR, FESEM, TGA and swelling studies. Water retention, water holding, and soil porosity tests have been conducted on both hydrogel beads. The results showed that the swelling ratios for GG-PEG and CA-PEG were 350 g/g and 250 g/g, respectively. At high pressures, GG-PEG retained 20% more water than untreated soil, whereas CA-PEG retained 17.5%. The soil's water-holding capacity improved to 16.05% when treated with GG-PEG, compared to 9.69% with CA-PEG. The porosity of soil increased to 69.45% in the case of GG-PEG hydrogel beads and 65.17% in the case of CA-PEG when compared to untreated soil. The biodegradable studies of the hydrogel beads showed that GG-PEG was more susceptible to degradability since it was a natural polymer. As a result, GG-PEG is more efficient than CA-PEG, and this study demonstrates how natural polymers may be employed as superabsorbents to improve soil qualities by serving as conditioners.

Keywords: Cellulose acetate, Guar gum, Hydrogel beads, Superabsorbent, Water retention

Introduction

Agriculture is mostly dependent on rainfall across the world. Every year, crop losses are caused by uncertainties in the frequency and distribution of rainfall in dry areas. Water scarcity and soil desertification are two of the most serious anthropogenic concerns in around one-third of the world's regions[1]. Various strategies are being used to improve agricultural water usage efficiency. Hydrogel materials, particularly superabsorbent hydrogels, are being extensively researched for water retention and soil conditioning in agriculture due to their large water-absorbing and slow-releasing capacity[2]. Superabsorbents are hydrophilic polymers that are crosslinked and therefore they absorb and store water as much as hundred times of their weight. The absorbed water is rarely retrieved, even under moderate pressure. This property had been utilized extensively in horticulture and agriculture[3]. Soil conditioners which can retain water are as important as that of humus which helps in the growth of plants by providing sufficient nutrition. Such soil conditioners could be used along with the humus which helps during a drought condition. The addition of superabsorbents benefits the soil, otherwise could not be provided by the humus alone justifying their role as soil conditioners[4]. Due to the appealing qualities, including biodegradability, nontoxicity, and renewable capacity, cellulose has been the subject of intensive research over the past few decades[5]. It is possible that the biological degradation and biological compatibility of the hydrogels made from cellulose would be advantageous for bioengineering processes and agricultural uses[6]. In the field of agriculture, synthetic polymers are widely used. But the disadvantage is, they are non-biodegradable and the products obtained after their degradation are hazardous in nature[7]. Hence, natural polymers are the better substitutes in the field of agriculture[8]. Starch-based hydrogels being soil conditioners are used to increase the soil health which enhances plant development. Different natural polymers crosslinked with aluminium sulphate were examined for their water retention capacity. Results from the literature revealed that the water retention capacities for cassava starch, maize starch, potato starch, and yam starch were 66%, 56%, 73% and 65%, respectively[9].

Cellulose acetate, which is derived from a natural polymer, cellulose, could be called as a semi-synthetic polymer has several applications such as the manufacture of photographic films, adhesives and also in the separation process such as filtration and reverse osmosis[10–15]. So, in the present study, cellulose acetate has been crosslinked with polyethylene glycol to form a hydrogel in the form of beads.

Alternatively, non-toxic guar gum hydrogel beads could be used. Guar gum (GG) is obtained from the beans of the *"Cyanaposis tetragonolobus"* family of guar plants which belong to Leguminosae. It is a naturally occurring nonionic polymer with (1-4) linkages of β-D-mannopyranosyl units connected to (1-6) linkages of α-D-galactopyranosyl units appearing as side branches. It has a wide application in industries pertaining to textile, paper, pharmaceutical, food and cosmetics[16]. It is biodegradable, and has controlled release properties unfortunately susceptible to microbial breakdown in the environment. There are several modified products based on guar gum that have been used for different applications, especially in the medical field. But still, there is a huge scope for the products synthesized from guar gum to use in the field of agriculture which has a limited literature[17]. It was reported that an efficient guar gum crosslinked with ethylene glycol di methacrylic acid was used in agricultural applications with water retention capacity of 51.6%[18]. By considering this aspect, a novel superabsorbent hydrogel beads were synthesized to use as superabsorbent in agricultural field.

The intention of synthesizing hydrogels in the form of beads is due to the advantages of microbeads over a mere hydrogel. These beads of diameter less than 10 µm were spherical with increased porosity, expanded polymer chains, increased surface area with increased access to internal sorption sites. Hence, these hydrogel beads are gaining more importance in the field of food industry, pharmaceuticals and agricultural sectors. Moreover, the hydrogel beads could be introduced to the soil around the plants or saplings easily. The polyethylene glycol (PEG) was chosen as a crosslinker due to its high hydrophilic features and enhanced membrane performances such as porosity and swelling properties[19].

Hence, the work presented here is about the synthesis and characterization of hydrogel beads with some of the important agricultural applications such as water holding capacity, water retention, soil density and porosity. The agricultural applications and the efficiency for both guar gum-polyethylene glycol (GG-PEG) and cellulose acetate-polyethylene glycol (CA-PEG) hydrogel beads were determined and compared.

Experimental Section

Materials

Cellulose acetate which was used as a raw material for the preparation of hydrogel beads was purchased from Molychem, Mumbai, India. Guar gum, Acrylamide (AAM), Acrylic acid (AA) and PEG-400 required for the experiment were procured from Loba Chemie Lab, Reagents and Fine chemicals Mumbai, India. Dimethylformamide (DMF) was obtained from Spectrochem Pvt. Ltd., Mumbai, India. Ammonium persulphate (APS) was purchased from Himedia Mumbai, India.

Synthesis of guar gum and cellulose acetate based hydrogel beads

The guar gum (GG) and cellulose acetate (CA) hydrogel beads were synthesized by dropping method. In the synthesis of both the beads, ammonium persulphate (APS) was used as the initiator and polyethylene glycol (PEG) was added as crosslinker.

The GG was dissolved in water by stirring followed by the addition of APS which was added to initiate the reaction. The reaction mixture was irradiated with microwave for 2 min at a power of 60W. The reaction mixture was added with acrylic acid and acrylamide for the co-polymerization reaction followed by the addition of a crosslinker. The GG-PEG hydrogel beads were synthesized by drop-cast method with acetone as the coagulating agent. In the case of CA-based hydrogel beads, the CA was dissolved in DMF followed by the addition of APS and kept for stirring until all the raw materials dissolves. The reaction mixture was irradiated to microwave for 1 min at a power of 50W. The reaction mixture was kept for stirring upon the addition of the crosslinker and the CA-PEG hydrogel beads were synthesized using the dropping method with water as the coagulating agent. After both the hydrogel beads were synthesized, they were dried and stored for further use.

Swelling studies of the hydrogel beads

Studies in aqueous medium

The hydrogel beads prepared were subjected to swelling studies under the influence of distilled water (DW) and compared for the maximum swelling ability of the hydrogel beads. Both GG-PEG and CA-

PEG hydrogel beads were immersed in two separate beakers containing DW (100 mL each). The swelling rate was calculated at different time intervals. The hydrogel was removed at different time intervals and the weight of the swollen hydrogel was measured to check the maximum swelling rate. The swelling ratio of both the hydrogel beads was calculated and compared using Eq. (1),

$$Swelling\ rate = (M_2 - M_1)/M_1 \quad \ldots (1)$$

where, M_2 is the mass of the swollen hydrogel beads and M_1 is the mass of the dry hydrogel beads

Studies at different pH conditions

To examine the maximal swelling ability at various time intervals, the GG-PEG and CA-PEG hydrogel beads were exposed to various pH solutions. Standard buffer solutions of pH 4, 7 and 9 were initially prepared by dissolving the required buffer capsule in 100 mL distilled water. Different acidic pH solutions were adjusted using 0.1 M HCl solution and basic pH solutions were adjusted using 0.1 M NaOH solution. A similar procedure as that conducted for DW was done for different pH solutions at room temperature. The rate of swelling was determined using Eq. (1). The swelling rate was compared for both GG-PEG and CA-PEG hydrogel beads.

Instrumental details

The GG-PEG and CA-PEG hydrogel beads were subjected to FTIR analysis at a frequency of 400-4000 cm^{-1} which confirmed the structure of the samples (Shimadzu IR Prestige 21 (Japan) FTIR spectrometer). The surface morphological studies were analyzed using FESEM by gold sputtering the beads for 15 min. The micrograms obtained were recorded at a magnification of 100 -10000 at an accelerating voltage of 5 kV (Carl Zeiss Microscopy Ltd). The modification caused by the thermal behaviour was analyzed using a thermogravimetric analyzer (Model; SDTQ600, TA Instruments, UK) at a temperature range of 25–700 °C for all the samples. The samples were injected into a nitrogen atmosphere at a gas flow rate of 100 mL min^{-1} and a heating rate was 10 °C min^{-1}.

Applications of GG-PEG and CA-PEG in agriculture

The effects of synthetic hydrogels on certain physical features of soil, such as maximum water holding capacity, particle density, porosity, bulk density and water retention capacity were examined to assess their suitability for use in agriculture as soil modifiers. The soil used for the analysis was a garden laterite soil located in Kumpala area of Mangalore district, Karnataka, India.

Soil density and soil porosity

In order to determine the density of the soil, it was dried at 100 °C and filtered using a 3 mm sieve to get soil particles of uniform size. Bulk density and particle density were calculated using a pycnometer[20].

For the determination of bulk density, the hydrogel beads (both GG-PEG and CA-PEG) were mixed along with the soil at different amounts like 0.1, 0.2, 0.3, 0.4 and 0.5 g and the soil without hydrogel was taken as control. All these samples were taken in 6 different pycnometers. The initial weight of the pycnometer was noted and taken as W_p. The mass of pycnometer and soil with hydrogel was considered as $W_p + W_s$. All the samples were added with water slowly so that the soil and the hydrogel absorb water to its maximum. The weight was again noted. From the values obtained, the bulk density and particle density were determined for both GG-PEG and CA-PEG hydrogel beads. As the bulk density and particle density was determined, the soil porosity was determined by the equation,

$$Porosity = \left[1 - \frac{(Bulk\ density)}{(Particle\ density)}\right] \times 100 \quad \ldots (2)$$

Water holding capacity

The air-dried soil was filtered through a 3 mm sieve and was treated with 0.1,0.2,0.3,0.4 and 0.5 g of hydrogel beads (both GG-PEG and CA-PEG), whereas the untreated soil was kept as control. To estimate the maximum water-holding capacity of the soil, a measured quantity of soil was taken in a glass crucible and at the inner side of the crucible, a filter paper was placed at the bottom. The soil was allowed to absorb the water to the point of saturation in a water tub with all six samples inside. The crucible was taken out after 8 h, and extra gravitational water was removed. Each crucible's weight was recorded. The weight of the wet filter paper and empty crucible were subtracted to get the net quantity of water absorbed by the soil. The experimental setup for water holding capacity is shown in Fig. 1.

Water retention of soil

The water retention analysis was done using the standard method “EN ISO 11274:2019” for which the apparatus is shown in Fig. 2. The water retention capacity was determined by applying suction using a pressure difference in the rubber tube. The burette was filled with water. The funnel was placed with

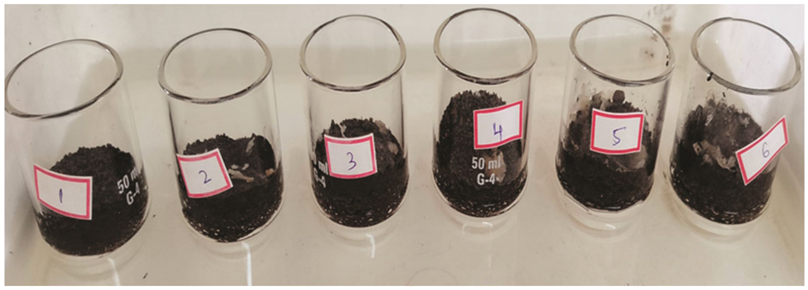


Fig. 1 — Set-up for determining water holding capacity

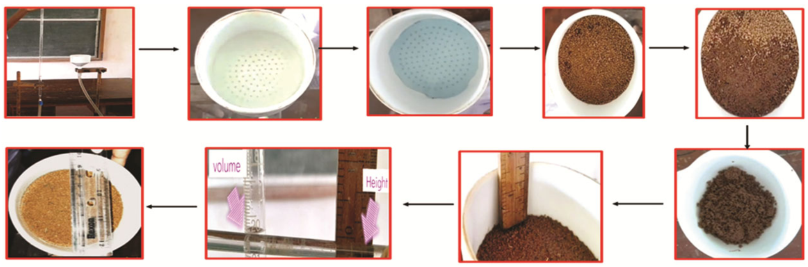


Fig. 2 — Apparatus for the water retention of soil

filter paper followed by a membrane filter. It was filled with 50 g of dry soil. This was considered as control. The thickness of the soil layer was maintained to be 1 to 2 cm. The burette was slowly raised so that water present in the funnel was wetted. The process was continued until the soil was saturated with water. The procedure was repeated for 0.1, 0.2, 0.3, 0.4 and 0.5 g of GG-PEG and CA-PEG hydrogel beads. The water retention level was calculated.

Biodegradation studies

The biodegradation studies of both the hydrogels were studied by soil burial methodology[21–23]. A measured quantity of GG-PEG and CA-PEG hydrogels were buried inside the soil and the moisture content of the soil was maintained at 1/3rd of its water retention capacity throughout the analysis. The hydrogel samples were removed from the soil at a particular interval of time, washed and dried followed by weighing. The degradation percentage was calculated using the Eq. (3),

$$\%\ of\ Hydrogel\ remaining = \frac{Weight\ of\ hydrogel\ after\ degradation}{Initial\ weight\ of\ the\ hydrogel} \times 100 \quad \dots (3)$$

Results and Discussion

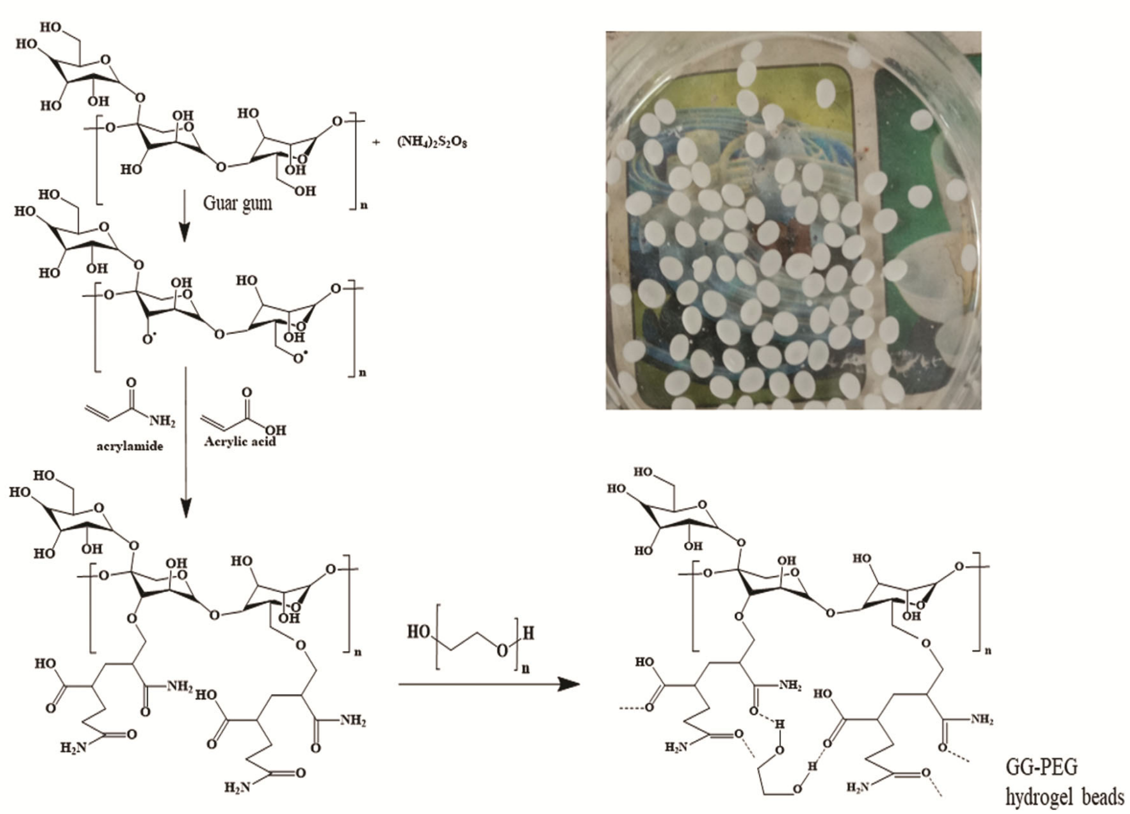
Mechanism for the formation of GG-PEG and CA-PEG beads

Guar gum was dissolved in water with ammonium persulfate (APS) acting as the initiator and PEG as the crosslinker to synthesize the guar gum hydrogel beads. Free radicals were formed from the initiator, APS, which helped the GG macroradicals to develop. On the GG radical sites, AA and AAM radicals add up to give acid-amide pendant groups, which upon interaction with PEG, resulted in a porous network developed through H-bonding between the highly polar -CONH$_2$ and -COOH groups. The hydrogel beads were produced by coagulating with acetone using the dropping method by introducing the solution through the syringe.

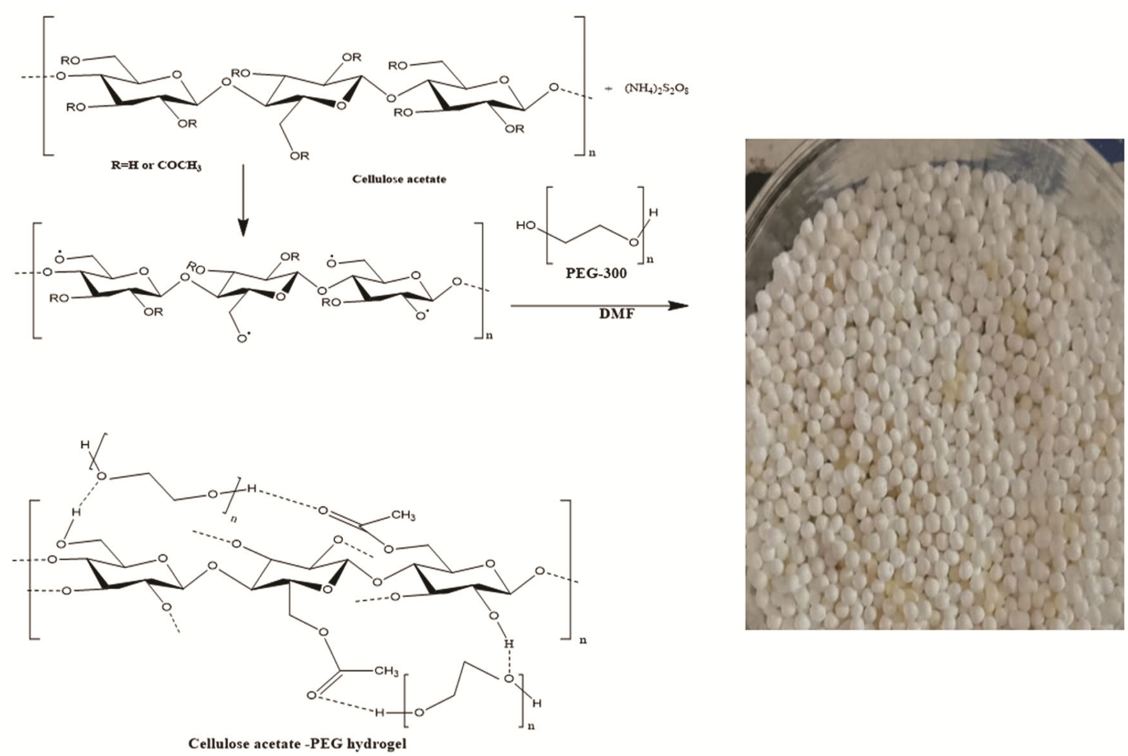
The CA-PEG hydrogel beads were synthesized by the dissolution of CA with APS as the initiator and the crosslinker PEG. The initiator free radicals helped in the development of CA macroradicals. In the case of CA, the pendant acetate groups present, help in forming a network of hydrogel by crosslinking with PEG through H-bonding. The use of AA and AAM was avoided because of the presence of a pendant acetate group which helps in networking. The hydrogel hence formed was introduced into a syringe to form hydrogel beads in water which acts as a coagulating agent. In both cases, by regulating the rate of addition, uniform-sized beads were obtained. The plausible mechanism for the formation of the hydrogel beads of GG-PEG and CA-PEG are illustrated in Scheme 1 and 2.

FTIR analysis

In order to confirm the structural integrity of GG, GG-PEG, CA and CA-PEG, FTIR spectra were recorded. Fig. 3 displays the FTIR spectra of GG,



Scheme 1 — Mechanism of formation of Guar gum-PEG hydrogel beads (GG-PEG) and synthesized hydrogel beads



Scheme 2 — Mechanism of formation of cellulose acetate-PEG hydrogel beads (CA-PEG) and synthesized hydrogel beads

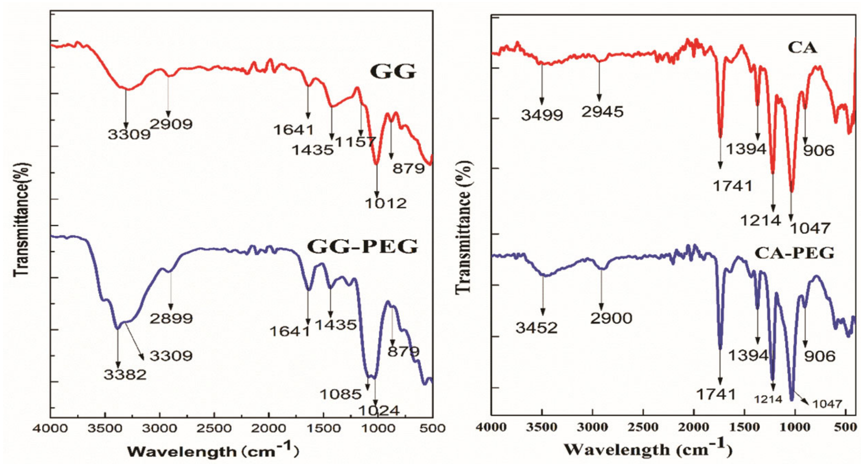


Fig. 3 — FTIR spectra of (a) GG, GG-PEG and (b) CA, CA-PEG hydrogel beads

GG-PEG, CA, and CA-PEG. The FTIR spectrum of GG showed an absorption band at 3309 cm^{-1} due to -OH stretching, 2909 cm^{-1} due to C-H stretching vibrations[24]. The crosslinked GG-PEG hydrogel beads showed a sharp band at 3382 cm^{-1} which corresponded to -OH stretching vibrations of polyethylene glycol and indicated the crosslinking of GG into the polymer matrix. The crosslinking can also be concluded by the shift in the broad band to a sharp band from 3309 cm^{-1} to 3382 cm^{-1}. The addition of AA and AAM to GG backbone was confirmed by the appearance of other absorption bands at 2899 cm^{-1} and 1024 cm^{-1} corresponding to N-H stretching and C-H stretching vibrations. It is noteworthy that in the GG-PEG hydrogel beads, in addition to 3309 cm^{-1} of GG an additional sharp band at 3382 cm^{-1} indicated that the -OH of PEG has been crosslinked to GG.

The absorption bands at 906, 1047, 1214, 1394, 1741, and 2939 cm^{-1} that were found in the spectra of CA and CA-PEG hydrogel beads were associated to the stretching vibrations of C-O, C-OH, C-O-C, $-CH_2$ and C-H, respectively. The FTIR spectrum of CA showed an absorption band at 2945 cm^{-1} due to C-H stretching of the methyl group which was shifted to 2900 cm^{-1} in the spectrum of CA-PEG. The absorption band at 3499 cm^{-1} in CA was due to -OH group, whereas in the case of CA-PEG the absorption band was further widened due to intermolecular hydrogen bonding with -OH group and showed a band at 3452 cm^{-1}, which indicated the involvement of -OH in the hydrogen bonding[25].

Scanning electron microscopy

Fig. 4 displays the FESEM images of GG and GG-PEG as well as CA and CA-PEG under a scanning electron microscope. The surface of cellulose acetate looks rough, complex, continuous, irregular and heterogeneous. The cellulose-based hydrogel beads have uniform polyethylene glycol dispersion throughout the system and a smooth surface.

Under a scanning electron microscope, the surface of guar gum seems to be non-porous and dense. With the addition of crosslinker into the matrix, the surface of the GG-PEG hydrogel beads exhibited a smooth appearance indicating hydrogel formation.

The reaction of acrylic acid and acrylamide with macroradicals causes functional pendant groups of amide and carboxylic molecules. So, PEG not only intercalates with OH groups present in polymer backbone, but also forms hydrogen bond with highly polar carboxylic and amide groups. This results in larger networking resulting in increased porosity in hydrogel matrix of the beads. The voids hence generated can hold higher amount of water and making it a superabsorbent material, where as in the case of CA-PEG only, the extent of networking decreased due to the lack of large polar pendant groups. However, acetate groups do participate in hydrogen bonding with polyethylene glycol and this makes the system compact. But, when the two beads were compared the porous nature is largely seen in GG-PEG than that of CA-PEG and hence this results in the higher swelling ability of GG-PEG hydrogel beads.

Thermogravimetric analysis

It is believed that a cross-linking in polymeric network results in greater thermal stability than its source material. Therefore, comparative thermal investigations were carried out to verify cross-linking in the synthesized hydrogel.

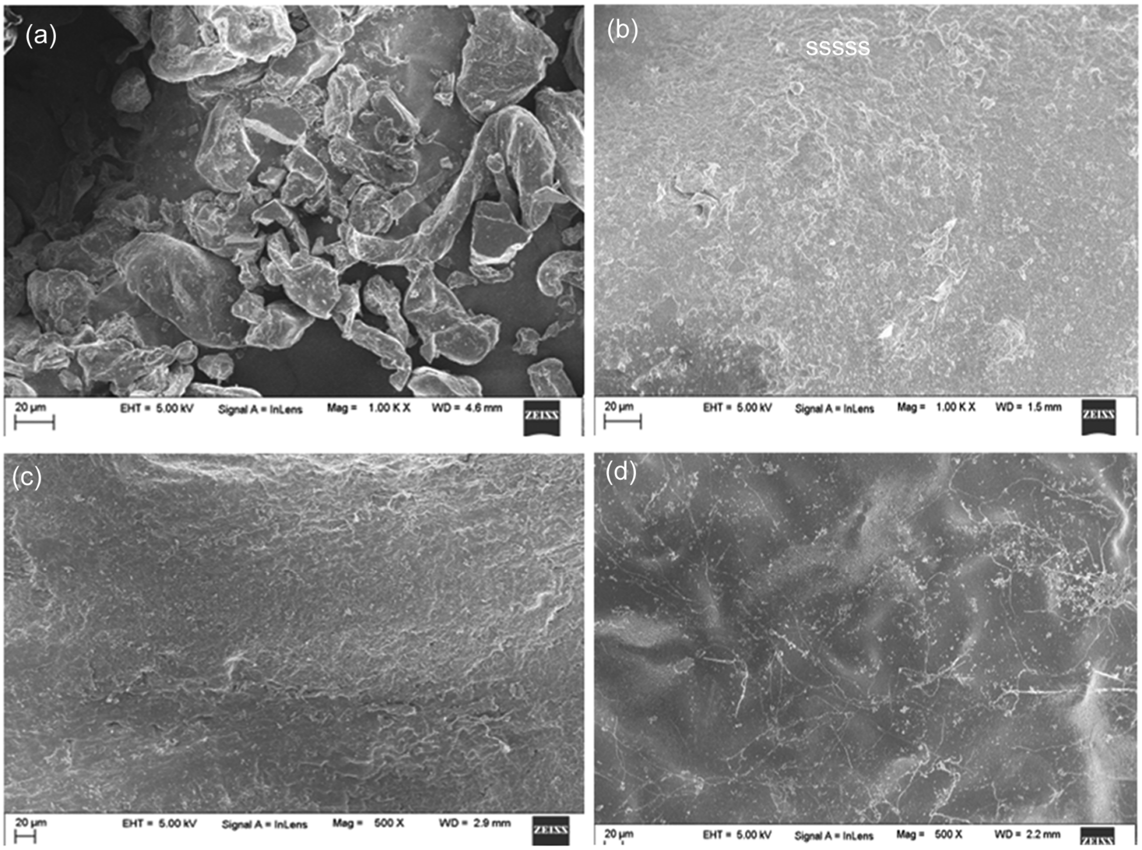


Fig. 4 — FESEM images showing the morphology of (a) guar gum, (b) GG-PEG hydrogel beads (c) cellulose acetate, (d) CA-PEG hydrogel beads

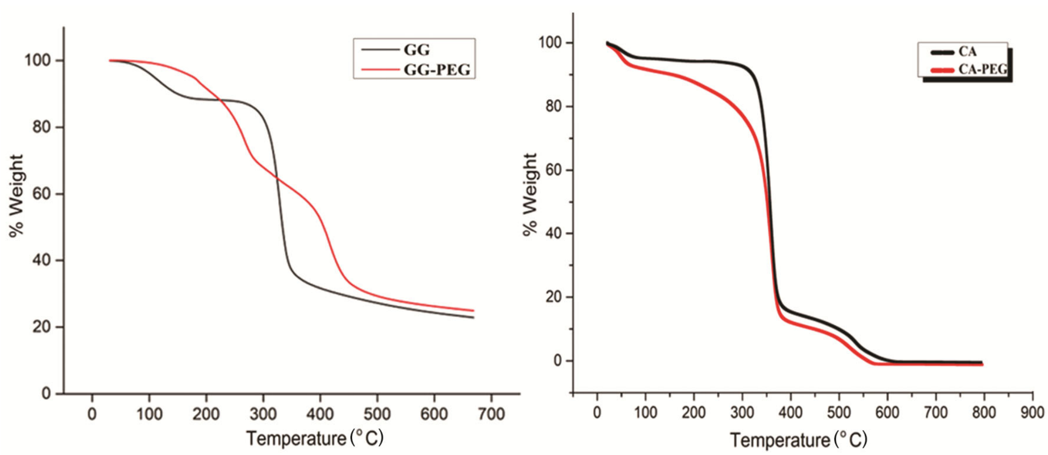


Fig. 5 — Thermograms of GG, GG-PEG, CA and CA-PEG hydrogel beads

In Fig. 5, the thermograms of GG, GG-PEG, CA and CA-PEG are displayed. In the case of GG, three different zones of weight reduction were observed. The initial stage of weight loss of 9.76% was observed at 30-275 °C and it was due to the loss of moisture present in the guar gum.[18] The second stage of weight loss (51.45%) at 275-350 °C which indicated the decomposition of the hydrogel groups as water molecules present in the guar gum, wherein a major weight loss is observed[26]. The third stage was the complete combustion of the polymer at 350 -650 °C with 25% weight loss[27].

However, in the case of GG-PEG hydrogel beads, the weight loss was observed in four stages. The initial stage of weight loss of 28.17% was observed at 30-300 ℃ and it was due to the loss of moisture adsorbed and absorbed. The second stage of weight loss (17.83%) was at 300-410 ℃ which indicated the decomposition of the polymer. The third stage indicated the breakdown of crosslinking bonds between the hydroxyl groups present in the polymer backbone at a temperature of 410-490 ℃ with a weight loss of 22.17%. The GGB had a mass percentage of around 45% when heated to 400 ℃ while the GG had a mass percentage of 30% at the same temperature. The fourth stage indicated the complete combustion of the product at 490-700 ℃ at about 9% weight loss.

The sample investigations of CA and CA-PEG revealed three stages of deterioration at various temperatures which led to proportionate weight loss. The first stage of weight loss for CA happened between 25 and 275 ℃ as a result of the loss of H_2O molecules from the sample. The disintegration of the polysaccharide backbone led to the second stage, which took place between 275 to 400 ℃[28]. The third and last degradation lasted from 400 ℃ to 650 ℃. The material lost all of its properties at 650 ℃ converting into ash. This study showed the change in the crystalline state of CA to amorphous state of CA-PEG which complemented FESEM results.

Swelling studies

Studies in aqueous medium

The swelling studies for GG-PEG and CA-PEG hydrogel beads were investigated in aqueous medium and it was found that the maximum swelling took place at 80 min after which the weight of the swollen hydrogel was constant for GG-PEG hydrogel beads and 480 min for CA-PEG hydrogel beads. The swelling ratio of GG-PEG was found to be 350 g/g and that of CA-PEG was 250 g/g. So, the swelling ability of GG-PEG hydrogels showed superior results than that of CA-PEG hydrogel beads. The porosity of the GG-PEG beads might have influenced quick and higher absorption of water. This was due to the larger networking caused by the additions of AA and AAM. The results are shown in Fig 6.

Under different conditions of pH

The swelling studies for different pH solutions were carried out for both GG-PEG hydrogel beads and CA-PEG hydrogel beads. In the case of GG-PEG hydrogel beads, initially, the swelling ratio slowly increased from pH 2 to 9.2. Under acidic environment, swelling was minimum because of the inefficient protonation in the cross-linked polymer units. On the other hand, at higher pH the hydrogel matrix converted into anionic form at carboxylic acid pendent groups. This caused the increase in the electrostatic repulsion brought by the anionic nature of carboxylate ions increasing the volume of the voids in the hydrogel[16]. This influenced easy entry of solution through hydrogen bonding which in turn resulted in the increased swelling at pH 9.2 and the swelling ratio was found to be 1400 g/g.

But, in the case of CA-PEG hydrogel beads, the maximum swelling ratio was found at pH 7 with a swelling ratio of 250 g/g. The swelling ratio increased gradually from pH 1.3 to 7.0 and then at pH 7, the swelling ratio was found to be highest. As the pH turned alkaline, the swelling ratio again decreased due

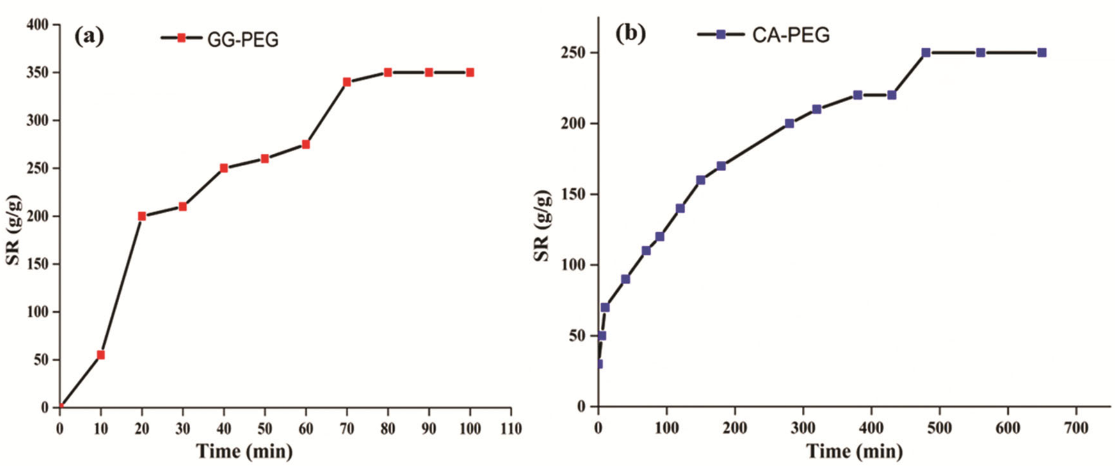


Fig. 6 — Swelling studies of (a) GG-PEG and (b) CA-PEG

to the fact that the crosslinker, PEG changes into a supra-polyelectrolyte in the anionic form from a neutral polymer. The hydrogen bonding between the acetate group and PEG disrupted at alkaline pH. Even at pH 7 (DW) the GG-PEG hydrogel beads were more efficient than CA-PEG hydrogel beads. The results are shown in Fig. 7.

Applications of GG-PEG and CA-PEG in agriculture

Analysis of water holding capacity

It was concluded from the experiment that, the water-holding capacity of the soil increased by the treatment of hydrogel beads. The water-holding capacity of soil treated with GG-PEG and CA-PEG hydrogel beads are shown in Table 1. The soil treated with 0.1,0.2,0.3,0.4 and 0.5 g GG-PEG hydrogel beads showed an increase of 4.61, 5.68, 6.84, 11.65 and 16.05%, respectively, to that of control.

Similarly, in the case of the soil treated with 0.1,0.2,0.3,0.4 and 0.5 g of CA-PEG hydrogel beads showed an increase of 4.48,5.38,5.57,7.37 and 9.69%, respectively, than that of control. The results are shown in Fig. 8. Hence it can be concluded that GG-PEG hydrogel beads were more effective in holding maximum water capacity than the CA-PEG hydrogel beads. However, both beads have shown efficiency towards water holding capacity.

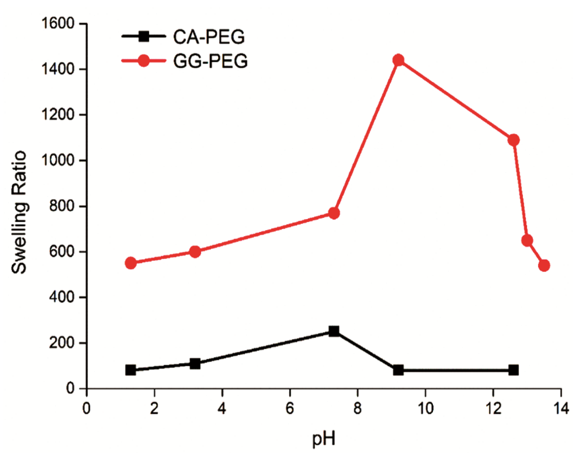


Fig. 7 — Swelling ratio at different pH conditions

Soil density and porosity determination

The porosity of the soil was determined by calculating the bulk and the particle density of soil with different concentrations of the hydrogel. The particle density of the soil was found to be 2.36 g/cm^3. From the obtained value of particle density, the bulk density and the porosity of the soil were calculated and tabulated in Table 2. Fig. 9 shows the change in bulk density and soil porosity for control soil and soil treated with hydrogels.

Table 1 — Water holding capacity of soil treated with GG-PEG and CA-PEG hydrogel beads

	Water holding capacity (%)	
Hydrogel beads (g)	GG-PEG	CA-PEG
Control	72.95	72.95
0.1	77.56	77.43
0.2	78.63	78.33
0.3	79.79	78.52
0.4	84.59	80.32
0.5	89.00	82.61

Table 2 — Density and porosity of soil treated with GG-PEG and CA-PEG hydrogel beads

	Bulk density(g/cm^3)		Soil porosity (%)	
Hydrogel beads (g)	GG-PEG	CA-PEG	GG-PEG	CA-PEG
Control	1.042	1.042	55.85	55.85
0.1	0.987	0.962	59.24	58.18
0.2	0.930	0.934	61.45	60.43
0.3	0.862	0.890	63.48	62.29
0.4	0.769	0.834	67.42	64.67
0.5	0.721	0.822	69.45	65.17

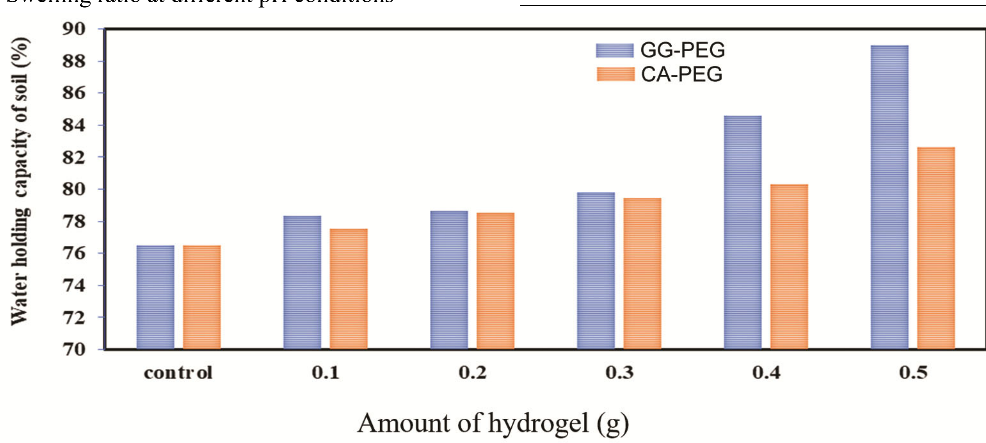


Fig. 8 — Analysis of water holding capacity of hydrogel beads

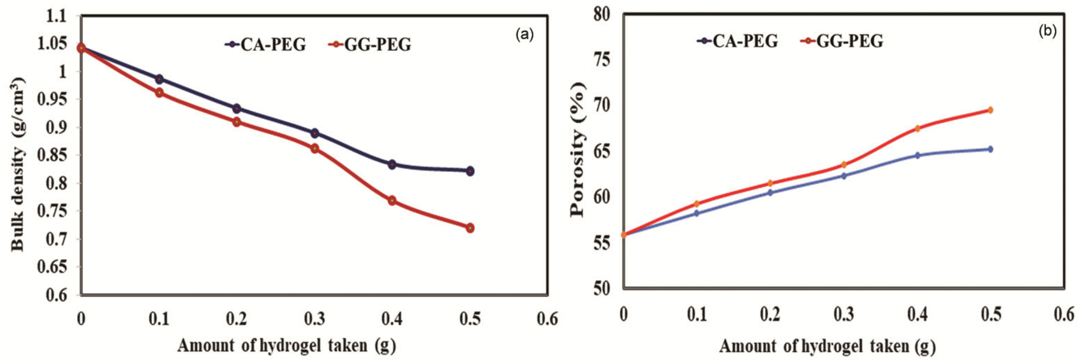


Fig. 9 — Analysis of soil density and porosity using hydrogel beads

The soil treated with 0.1, 0.2, 0.3, 0.4, and 0.5g of GG-PEG hydrogel beads decreased in bulk density by 5.5, 11.2, 17.3, 27.3, and 32%, respectively, compared to the control. A decrease in density enhanced the soil's porosity. The porosity percentage of the soil before treatment with hydrogel beads was 55.85%, but with 0.1, 0.2, 0.3, 0.4, and 0.5 g, it was 59.24, 61.45, 63.48, 67.42, and 69.45%.

Similar results were seen when CA-PEG hydrogel beads were applied to the soil. The soil treated with 0.1, 0.2, 0.3, 0.4, and 0.5 g of hydrogel beads had a porosity of 58.18, 60.43, 62.29, 64.67, and 65.17%, and a decrease in bulk density of 8.0, 10.8, 15.2, 20.8, and 22.0%, respectively, compared to the control. The moisture loss of hydrogel particles causes voids in the soil that aid in the soil's increased porosity.

Hence, it could be concluded that GG-PEG was more porous than that of CA-PEG in increasing the porosity of the soil to promote better plant growth by retaining the water content. However, both beads have shown efficiency towards porosity.

Determination of water retention capacity

A very essential factor determining the amount of water available to plants is how much water is retained under varying soil matric potentials. This is crucial under the situations of stress and drought and a little increase in the soil's ability to retain water under pressure could benefit the health of the crop and increase the probability that it could withstand a severe condition of drought. The use of GG-PEG and CA-PEG hydrogel beads had improved the water retention ability of the soil and the graph is plotted for both the hydrogel beads shown in Fig. 10 and compared.

When GG-PEG hydrogel beads were introduced, the untreated soil (control) had a 60% capacity to retain water, but as the hydrogel concentration increased the percentage of water retention increased. Water retention capacity for 0.1,0.2,0.3,0.4 and 0.5 g was 72, 74, 76, 78 and 80% respectively. When the pressure was raised, the soil's ability to retain water followed a similar pattern, although at a lower rate than soil that wasn't under pressure. This difference decreased and control soil could maintain 19.0% moisture in comparison to 19.5% for 0.1% hydrogel, 20.0% for 0.2% hydrogel, 20.5% for 0.3% hydrogel, 21.0% for 0.4% hydrogel and 21.5% for 0.5% hydrogel at a pressure of 10 bar.

In the case of CA-PEG hydrogel beads, the water retention capacity was 64, 66, 68, 70 and 74% respectively. When the pressure was raised, the difference decreased and control soil could maintain 15.0% moisture in comparison to 15.5% for 0.1% hydrogel, 16.0% for 0.2% hydrogel, 16.5% for 0.3% hydrogel, 17.0% for 0.4% hydrogel and 17.5% for 0.5% hydrogel at a pressure of 10 bar.

But, when the two hydrogel beads were compared the results showed that the GG-PEG hydrogel beads were more efficient than the CA-PEG hydrogel beads in retaining the water from the soil. However, both beads have shown efficiency towards water retention capacity.

Biodegradation studies

Most polymeric hydrogels with superabsorbent properties cannot be widely used in agriculture due to their low soil degradability and accumulation which results in the pollution of soil and environment[30]. In the present work, GG-PEG and CA-PEG hydrogel beads were synthesised by crosslinking synthetic monomer along with natural polymers and a semi-synthetic polymer in order to increase its biodegradability. Fig. 11 shows the biodegradation studies of both

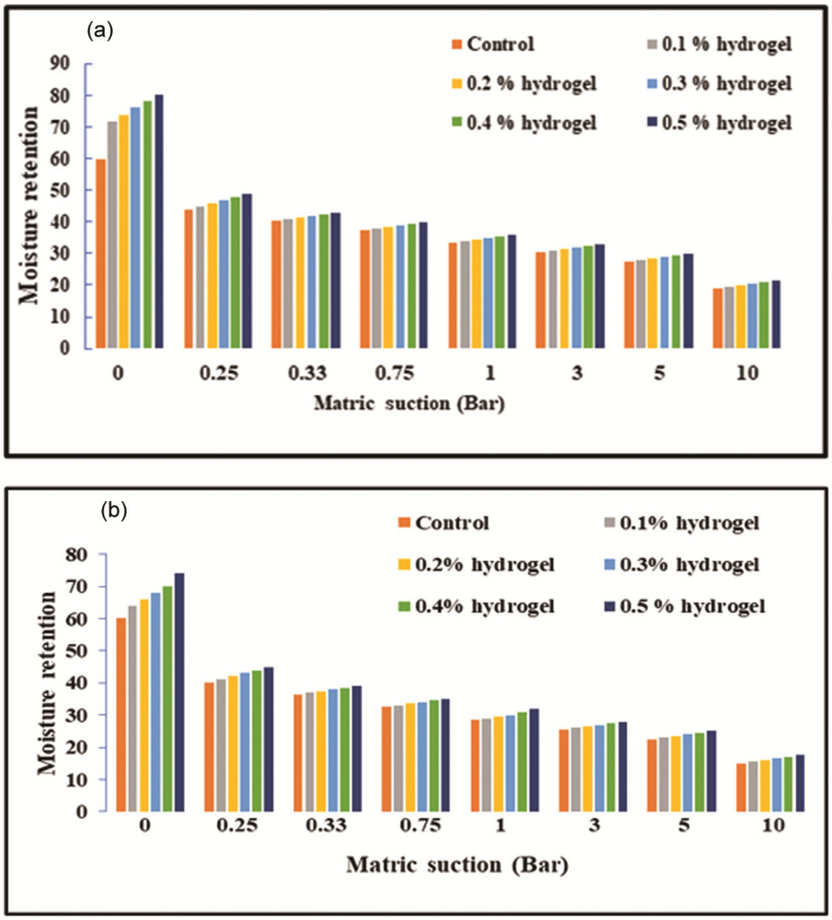


Fig. 10 — Water retention capacity (a) GG-PEG and (b) CA-PEG hydrogel beads

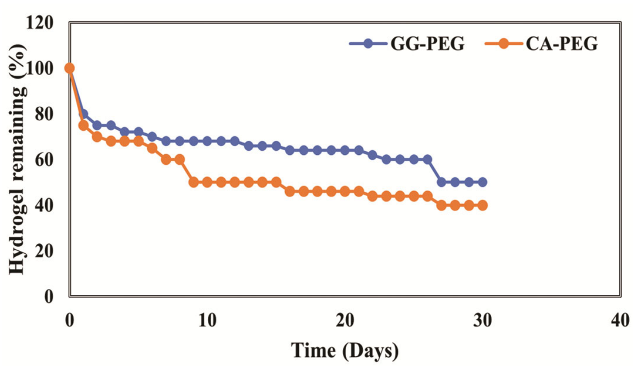


Fig. 11 — Biodegradation studies of GG-PEG and CA-PEG

GG-PEG and CA-PEG hydrogel beads. The degradation studies showed that the hydrogels were degraded due to the microorganisms present in the soil which resulted in the decrease of weight in the hydrogel. In some of the phases, the degradation was constant due to the water present in the hydrogel could hinder the growth of microorganisms resulting to form anaerobic environment[21].

Table 3 — Comparison of water retention capacity of the GG-PEG and CA-PEG hydrogel beads with other hydrogels

Hydrogel	Water retention (%)	References
GG-AA-EGDMA hydrogel	51.6	18
Cassava starch-Aluminum sulphate hydrogel	66	9
Corn starch-aluminum sulphate hydrogel	56	9
Potato starch-aluminum sulphate hydrogel	73	9
Yam starch-aluminum sulphate hydrogel	65	9
GG-PEG hydrogel	80.0	Present work
CA-PEG hydrogel	74.0	Present work

Table 3 shows the water retention capacity for different hydrogels and it was found that GG-PEG and CA-PEG (present work) were more efficient than other hydrogels.

Conclusion

In this article, the use of GG-PEG and CA-PEG hydrogel beads in agricultural applications were studied. The newly synthesized hydrogel beads were characterized to understand the structural modifications. The GG-PEG and CA-PEG hydrogel beads upon addition to the soil (100 g) improved the absorption of moisture as well as the capacity to retain the moisture content at a low dosage of the hydrogel beads (0.1-0.5 g). The water holding capacity of GG-PEG was 6.36% compared to CA-PEG whose retention capacity was 2.5%. The introduction of hydrogel beads to the soil improved its porosity with GG-PEG showing 4.28% greater than that of CA-PEG. The biodegradable studies of the beads showed that both GG-PEG and CA-PEG hydrogel beads were biodegradable but, almost stable during the study period of 30 days. By considering the agricultural applications, it could be concluded that the hydrogel beads of natural and semi-synthetic polymers are an excellent superabsorbent that would hold water, retain water and increase the porous nature of the soil. In this study, GG-PEG hydrogel beads emerged with better characteristics than those of CA-PEG hydrogel beads.

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References

1 Owesis T & Hachum A, Water harvesting and supplemental irrigation for improved water-use efficiency in dry areas, *Agric Water Manage*, 80 (2006) 57.

2 Xie L, Liu M, Ni B, Zhang X & Wang Y, Slow-release nitrogen and boron fertilizer from a functional superabsorbent formulation based on wheat straw and attapulgite, *Chem Eng J*, 167 (2011) 342.

3 Wu L & Liu M, Preparation and properties of chitosan-coated NPK compound fertilizer with controlled-release and water-retention, *Carbohydr Polym*, 72 (2008) 240.

4 Huttermann A, Orikiriza L J B & Hillary A, Application of superabsorbent polymers for improving the ecological chemistry of degraded or polluted lands, *Clean*, 37 (2009) 517.

5 Bello K, Sarojini B K, Narayana B, Rao A & Byrappa K, A study on adsorption behavior of newly synthesized banana pseudo-stem derived superabsorbent hydrogels for cationic and anionic dye removal from effluents, *Carbohydr Polym*, 181 (2018) 605.

6 Wang J, Zhou X & Xiao H, Structure and properties of cellulose/poly(N-isopropylacrylamide) hydrogels prepared by SIPN strategy, *Carbohydr Polym*, 94 (2013) 749.

7 Barth H G & Smith D A, High-performance size-exclusion chromatography of guar gum, *J Chromatogr A*, 206 (1981) 410.

8 Thombare N, Jha U, Mishra S & Siddiqui M Z, Guar gum as a promising starting material for diverse applications: A review, *Int J Biol Macromol*, 88 (2016) 361.

9 Nnadi F & Brave C, Environmentally friendly superabsorbent polymers for water conservation in agricultural lands, *J Soil Sci Environ Manage*, 2 (2015) 206.

10 Schulten H R, The three-dimensional structure of humic substances and soil organic matter studied by computational analytical chemistry, *Fresenius J Anal Chem*, 351 (1995) 62.

11 Kanmoni V G G, Daniel S & Raj G, Photocatalytic degradation of chlorpyrifos in aqueous suspensions using nanocrystals of ZnO and TiO_2, *React Kinet Mech Catal*, 106 (2012) 325.

12 Ma G, Zhang J, Chen L, Liu T, Yu L, Liu X & Lu C, Amino-functionalized ordered mesoporous silica SBA-15, a rapid and efficient adsorbent for the adsorption of (-)-epigallocatechin gallate from green tea extract, *RSC Adv*, 40 (2014) 41341.

13 Senna A M, Novack K M & Botaro V R, Synthesis and characterization of hydrogels from cellulose acetate by esterification crosslinking with EDTA dianhydride, *Carbohydr Polym*, 114 (2014) 260.

14 Dantas P A & Botaro V R, Synthesis and characterization of a new cellulose acetate-propionate gel: Crosslinking density determination, *Open J Polym Chem*, 2 (2012) 144.

15 Tsioptsias C, Sakellariou K G, Tsivintzelis I, Papadopoulou L & Panayiotou C, Preparation and characterization of cellulose acetate-Fe_2O_3 composite nanofibrous materials, *Carbohydr Polym*, 81 (2010) 925.

16 Wang W & Wang A, Preparation, swelling and water-retention properties of crosslinked superabsorbent hydrogels based on guar gum, *Adv Mater Res*, 96 (2010) 177.

17 Vijayendran B R & Bone T, Absolute molecular weight and molecular weight distribution of guar by size exclusion chromatography and low-angle laser light scattering, *Carbohydr Polym*, 4 (1984) 299.

18 Thombare N, Mishra S, Siddiqui M Z, Jha U, Singh D & Mahajan G R, Design and development of guar gum-based novel, superabsorbent and moisture retaining hydrogels for agricultural applications, *Carbohydr Polym*, 185 (2018) 169.

19 Lee S, Tong X & Yang F, Effects of the poly (ethylene glycol) hydrogel crosslinking mechanism on protein release, *Biomater Sci*, 4 (2016) 405.

20 Blake G R & Hartge K H, Methods of soil analysis, *Am Soc Agron Soil Sci Soc*, 101 (1986) 363.

21 Ni B, Liu M, Lu S, Xie L & Wang Y, Multifunctional slow-release organic-inorganic compound fertilizer, *J Agric Food Chem*, 58 (2010) 12373.

22 Ni B, Liu M & Lu S, Multifunctional slow-release urea fertilizer from ethylcellulose and superabsorbent coated formulations, *Chem Eng J*, 155 (2009) 892.

23 Sharma K, Kaith B S, Kumar V, Kalia S, Kumar V & Swart H C, Synthesis and biodegradation studies of gamma irradiated electrically conductive hydrogels, *Polym Degrad Stab*, 107 (2014) 166.

24 Prasad S S, Rao K M, Reddy P R S, Reddy N S, Rao K S V K & Subha M C S, Synthesis and characterisation of guar gum-g-poly (Acrylamidoglycolic

acid) by Redox initiator, *Indian J Adv Chem Sci*, 1 (2012) 28.

25 Fei B, Chen C, Wu H, Peng S, Wang X & Dong L, Quantitative FTIR study of PHBV/bisphenol a blends, *Eur Polym J*, 39 (2003) 1939.

26 Soppirnath K S & Aminabhavi T M, Water transport and drug release study from cross-linked polyacrylamide grafted guar gum hydrogel microspheres for the controlled release application, *Eur J Pharm Biopharm*, 53 (2002) 87

27 Thombare N, Jha U, Mishra S & Siddiqui M Z, Borax cross-linked guar gum hydrogels as potential adsorbents for water purification, *Carbohydr Polym*, 168 (2017) 274.

28 Zhou W, Yuan S, Chen Y & Bao L, Morphology and hydrogen-bond restricted crystallization of poly (butylene succinate)/cellulose diacetate blends, *J Appl Polym Sci*, 124 (2012) 3124.

29 Stahl J D, Cameron M D, Haselbach J & Aust S D, Biodegradation of superabsorbent polymers in soil, *Environ Sci Pollut Res*, 7 (2000) 83.