pH-Sensitive Crosslinked Guar Gum-Based Superabsorbent Hydrogels: Swelling Response in Simulated Environments and Water Retention Behavior in Plant Growth Media

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ABSTRACT: Crosslinked guar gum-*g*-polyacrylate (cl-GG-*g*-PA) superabsorbent hydrogels were prepared to explore their potential as soil conditioners and carriers. The hydrogels were prepared by *in situ* grafting polymerization and crosslinking of acrylamide onto a natural GG followed by hydrolysis. Microwave-initiated synthesis under the chosen experimental conditions did not exhibit any significant improvement over the conventional technique. The optimization studies of various synthesis parameters, namely, monomer concentration, crosslinker concentration, initiator concentration, quantity of water per unit reaction mass, particle size of backbone, and concentration of alkali were performed. The hydrogels were characterized by wide-angle X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy, and solid-state ^{13}C-NMR spectroscopy. Swelling behavior of a candidate hydrogel [GG-superabsorbent polymer (SAP)] in response to external stimuli, namely, salt solutions, fertilizer solutions, temperature, and pH, was studied. The GG-SAP exhibited significant swelling in various environments. The effect of GG-SAP on water absorption and the retention characteristics of sandy loam soil and soil-less medium were also studied as a function of temperature and moisture tensions. The addition of GG-SAP significantly improved the moisture characteristics of plant growth media (both soil and soil-less), showing that it has tremendous potential for diverse applications in moisture stress agriculture. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41060.

INTRODUCTION

In view of the fast depletion of groundwater reserves, uncertainty of rains in arid and semiarid regions of the world, coupled with the growing food demands of the burgeoning human population, efficient use of water available for crops has become highly relevant. In the recent years, the use of superabsorbent polymers (SAPs) has been viewed as an innovative tool to improve water use efficiency in agricultural operations. Since the report of the first SAP by the US Department of Agriculture,[1] the research on developing better products for use in agriculture continues worldwide. Polymeric soil conditioners have been known since 1950s.[2–5] In addition, purely synthetic as well as semisynthetic hydrogels have been used for the removal of heavy metals from water as well as controlled release

agro-input devices in agriculture.[6] However, the effects of hydrogel technology in agriculture are inconclusive because contradictory effects on physical properties of growing media have been reported.[6–18] The use on large scale remains limited primarily because of high cost and rate of application and their inability to perform under harsh agro-climatic conditions.[9,19] A SAP of semisynthetic origin "Pusa gel" has already been developed and commercialized from our laboratory.[20] Its potential as a water-retentive aid in agriculture is well established. Most of the soil conditioners reported so far, although possess impressive fluid absorption characteristics, a candidate SAP for use under alkaline soil conditions is still elusive. The SAP studied in this work was developed to explore its potential as an alternative with superior characteristics.

This article was published online on 17 June 2014. An error was subsequently identified. This notice is included in the online and print versions to indicate that both have been corrected 03 July 2014.

Biopolymeric superabsorbent hydrogels have been receiving great attention because of the enhanced properties over purely synthetic hydrogels.[19–23] Guar gum (GG), a nonionic galactomannan polysaccharide seed gum derived from *Cymaposis tetragonolobus*, is one such biopolymer of interest in SAP chemistry that has been exploited in various areas, for example, thickening agent, ion exchange, suspending agent, and controlled release devices for biomedical applications.[24] It has also been used in discrete studies to develop SAPs and SAP composites with pH-sensitive characteristics.[25–27] In agriculture, a balance of water/nutrient retention-release characteristics favorable to plant and ability to perform under extremes of environmental conditions such as temperature, pH, salinity in soil, and so forth is an area of interest. In the current study, crosslinked GG-*graft*-polyacrylate (GG-*g*-PA) hydrogels have been synthesized by free radical solution polymerization, and the effect of various synthesis parameters on their water absorbency (WAC) has been reported and supported by structural characterization. In the second part of this study, an exhaustive evaluation of their performance as a function of external stimuli, namely, temperature, pH, salts, and fertilizers, as well as water absorption, retention, and release characteristics in sandy loam, soil, and soil-less media has been presented.

EXPERIMENTAL

Materials

Commercial GG, acrylamide, *N,N*-methylenebisacrylamide crosslinker, and a persulfate initiator were purchased locally from Thomas Baker, Mumbai, India, and used as such without further purification.

Preparation of Guar Gum-g-Polyacrylate Hydrogels

The process of synthesis of biopolymeric superabsorbent materials for agricultural applications has been standardized previously in our laboratory, and the same was used here with minor modifications.[23] Briefly, SAPs were prepared by *in situ* grafting polymerization and crosslinking of acrylamide on the GG backbone in the presence of crosslinker using persulfate initiator. The details of the various reaction factors and their levels are given in Table I. To optimize the concentration of various synthesis parameters, a sequential completely randomized design was adopted. A typical procedure used was as follows: to an aqueous solution containing different weight ratios of monomer, crosslinker, and GG, different amounts of initiator were added under ambient conditions (under air) at 50°C. The feed mixture was kept as undisturbed for 8 h. The gel mass was treated with different molar ratios of alkali for 8 h under ambient conditions, washed with distilled water, and either air dried or with the help of methanol. The dehydrated sample was vacuum dried till constant weight. The dried product was milled and screened through 100–120 mesh-size screen. Fourier transform infrared (FTIR) spectra of native GG and an optimized GG-SAP were recorded in KBr discs on a Bruker FTIR spectrophotometer under dry air at room temperature. Solid-state ^{13}C-NMR spectra of optimized GG-SAP were recorded on a Bruker DSX 300 spectroscopy operating at 7.04 T with carbon frequency at 75.47 MHz. Crosslinker and monomer were characterized by liquid-state ^{13}C-NMR using Bruker Avance 400 instrument. Wide-angle X-ray diffraction

(XRD) measurements were performed using a Philips PW1710 diffractometer control equipped with Philips PW1728 X-ray generator. The scanning range was 3°–20° 2θ, with a scanning rate of 1.2° 2θ/min. Scanning electron microscopy (SEM) images were obtained with a Zeiss EVO series SEM (EVO 50) with a resolution of 2.0 nm at 30 kV.

Water Absorbency Measurements

Each sample weighing 0.1 g (particle size 100–240 mesh size) was immersed in the excess of distilled water (pH 7.0, EC 0.001 mhos/cm) in triplicate and kept at two temperatures, 25 and 50°C, until equilibrium was attained. Free water was filtered through a nylon sieve (200 mesh size), gel allowed to drain on sieve for 10 min, and finally weighed. The WAC (Q_{H_2O}) was calculated using the following equation:

$$Q_{H_2O} \ (g/g) = (w_2 - w_1)/w_1,$$

where w_1 is the weight of xerogel (dry absorbent) and w_2 is the weight of swollen gel. Q_{H_2O} was calculated as grams of water per gram of dry sample. The GG-SAP exhibiting maximum absorption in distilled water was further evaluated in different salt solutions.

Grafting Efficiency

The grafting efficiency (G_e) used to characterize the nature of the copolymer was calculated using the following equation:

$$G_e = (W_g - W_o)/W_m,$$

where W_g, W_o, and W_m are the weights of grafted copolymer, GG, and monomer, respectively.

Salt Solution Absorbency Measurements

Vacuum-dried GG-SAP exhibiting maximum Q_{H_2O} in distilled water was milled to achieve particle size in the range of 100–240 mesh size. Aqueous solutions of different strengths (5, 10, 15, and 20 mM) of four salts, ammonium sulfate, ammonium nitrate, potassium nitrate, and sodium chloride, and one fertilizer, urea, were prepared and used. The dried and milled sample (0.1 g) was immersed in salt solution of a particular strength at 50°C. The swollen gel was weighed after 24 h, and Q_{H_2O} was calculated using the same equation as above. Another similar experiment was repeated in tap water (pH 7.7, EC 2.04 mhos/cm), hard water, and aqueous solutions of pH 4, 7, and 9. Hard waters of three different strengths were prepared in the laboratory according to CIPAC standard method and labeled as hard water A (hardness 20 ppm, pH 5–6, and Ca : Mg ratio 50 : 50), hard water B (hardness 20 ppm, pH 8–9, and Ca : Mg ratio 80 : 20), and hard water C (hardness 500 ppm, pH 7–8, and Ca : Mg ratio 80 : 20).

Water Absorption and Retention Measurement in Soil and Soil-Less Media

Sandy loam soil [pH 7.8 measured at 1 : 1.25 soil to water ratio; organic carbon (OC) content: 0.51% for natural soil (determined by the Walkley and Black method)[28]; soil mechanical fractions: sand 78%, silt 10%, and clay 12.4%, using the Bouycos hygrometer method[29]; cation exchange capacity 11.2 cmol/kg by the normal ammonium acetate[28] (pH 7.0) method] and

Table I. Various Constituents Used in the Preparation of GG-SAP

Monomer concentration[a] (wt %/feed)	Crosslinker concentration[b] (wt %/feed)	Initiator concentration[c] (wt %/feed)	Water volume[d] (mL/g feed)	Molar ratio of NaOH to monomer[e]	Particle size[f]
2.5	0.05	0.03	2.84	0.5	25–100
3.75	0.1	0.06	5.68	1.0	100–240
5	0.5	0.3	8.52	1.5	>240
7.5	1.0	0.6	11.36	2.0	
10	5.0	3.0	14.2	2.5	
15	10.0	4.5	16.5	3.0	
		5.0			
		5.5			

[a] Synthesis parameters: crosslinker (wt %): 0.5, and initiator (wt %): 3.0; $V_{H_2O} = 11.36$ mL/g feed.
[b] Synthesis parameters: monomer (wt %): 3.75, and initiator (wt %): 3.0; $V_{H_2O} = 11.36$ mL/g feed.
[c] Synthesis parameters: monomer (wt %): 3.75, and crosslinker (wt %): 1.0; $V_{H_2O} = 11.36$ mL/g feed.
[d] Synthesis parameters: monomer (wt %): 3.75, crosslinker (wt %): 1.0, and initiator (wt %): 3.0.
[e] Synthesis parameters: monomer (wt %): 3.75, crosslinker (wt %): 1.0, and initiator (wt %): 3.0; $V_{H_2O} = 11.36$ mL/g feed.
[f] Synthesis parameters: monomer (wt %): 3.75, crosslinker (wt %): 1.0, and initiator (wt %): 3.0; $V_{H_2O} = 11.36$ mL/g feed.

soil-less media (a sterilized mixture of coco peat, vermiculite, and perlite in the ratio 3: 1: 1 on volume basis) were collected from institute farm and protected cultivation nursery, respectively. Air-dried soil sample was passed through the 2-mm sieve and mixed with GG-SAP at the rate of 0.5% and 0.75% each. Soil-less medium was dried till constant weight was attained and used as such. For WAC measurement, desired amounts of amended soil (50 g) or soil-less medium (20 g) were taken separately in preweighed plastic cups having perforated bases fitted with filter papers. Subsequently, each cup was immersed overnight in water to saturate. Water held by the sample was determined gravimetrically. Water holding capacity (WHC) of soil and soil-less medium was calculated by the following equation:

$$\text{WHC } (\%) = M - m/m \times 100,$$

where M denotes the weight of wet sample (g) and m denotes the weight of oven-dried sample (g).

Water retention study was done using pressure plate apparatus at different tensions (2.3, 2.8, 3.0, 3.7, 4.0, and 4.2 pF). Ceramic plates were kept overnight in water for saturation. Amended soil and soil-less media were filled in rubber rings arranged on bar plates and allowed to saturate overnight. The saturated samples along with ceramic plates were placed in pressure chamber pertaining to different tensions. Pressure was applied and maintained till water stopped flowing out of the chamber. Dehydrated moist and final samples were transferred to moisture boxes immediately and weighed. The moist samples were dried in a hot air oven at 105°C for 24 h, air cooled, and reweighed. The amount of water held at particular pressure was calculated using the following equation:

$$\text{WC } (\% \text{ w/w}) = [(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}] \times 100,$$

where WC is the percent water content of soil or soil-less media on weight basis, W_{wet} is the mass of wet soil or soil-less media

at a particular tension, and W_{dry} is the weight of oven-dried soil or soil-less medium.

Statistical Analysis

The experiments on the effect of various parameters on WAC values were conducted using factorial completely randomized design. To identify the best treatment combinations, the data were analyzed by one-way classified analysis using PROC GLM procedure of SAS package (SAS Institute, Cary, NC).

RESULTS AND DISCUSSION

The grafting efficiency of the hydrogel with optimized swelling behavior was as follows: grafting efficiency $(G_e) = 0.98$. The details of grafting efficiency of other constituents are given in Table III.

Synthesis Technique Selection: Comparison of Microwave- and Thermally Initiated Polymerization

It is clear from Table II that under the chosen experimental conditions, microwave-assisted synthesis resulted in hydrogel with inferior swelling ratios when compared with the conventional technique. This observation is in contrast to the one reported by Sen et al.[30] When compared with the conventional technique, the microwave-assisted synthesis exhibited continuous increase in swelling ratio of generated hydrogels. Sen et al. reported a threshold monomer content of ∼ 15 wt %, which is the highest monomer content in the current work. The inferior swelling ratios of microwave-irradiated hydrogels relative to the corresponding thermally initiated ones can be explained in terms of instantaneous formation of highly compact hydrogels in the former technique, which in turn is possible due to extremely fast generation of free radicals when compared with thermally initiated polymerization. Another factor favoring this behavior could be further lowering of energy of activation for the grafting reaction by taking preheated water (40°C), thus enabling GG chains to expand and participate in the reaction effectively.

Table II. Swelling Response of GG-SAP Prepared by Conventional and Microwave Techniques

Monomer (wt %)	Q_{H_2O} (g/g)	
	Conventional[a]	Microwave[b]
2.5	154.9	26
3.75	492.3	48
5.0	464.2	95
7.5	423.4	106.7
10	394.3	125.6
15	354.4	189.6

[a] Synthesis parameters: crosslinker (wt %): 0.5, and initiator (wt %): 3.0; V_{H_2O} = 11.36 mL/g feed.
[b] Synthesis parameters: crosslinker (wt %): 0.5, and initiator (wt %): 3.0; V_{H_2O} = 11.36 mL/g feed.

Characterization of Superabsorbent Hydrogels

FTIR Analysis. The FTIR spectra of native GG, crosslinked PA hydrogel, and crosslinked GG-g-PA hydrogel are shown in Figure 1. The absorption bands of GG at 1661 cm^{-1} assigned to H—OH bending and at 1439 cm^{-1} assigned to C—OH bending vibration almost disappeared in FTIR of the hydrogel (Figure 1), where new bands at 1654 cm^{-1} (C=O stretching of COO$^-$ groups), 1570 cm^{-1} (asymmetric stretching of COO$^-$), and 1411 cm^{-1} (symmetric stretching of COO$^-$) appeared. Bands of GG at 1020 cm^{-1} (C—O stretching), 1082 cm^{-1} (C—OH stretching), and 1158 cm^{-1} (C—O—C stretching), although are visible in the spectrum of hydrogel, the intensity is weaker. Shift of $\approx$ 30 cm^{-1} toward longer wavelength in the O—H stretching band in hydrogel can be attributed to intermolecular/intramolecular H-bonding. The absence of all the characteristic peaks of CONH$_2$ group of acrylamide [3361 cm^{-1} (v_aNH$_2$), 3198 cm^{-1} (v_sNH$_2$), 1670 cm^{-1} (vC=O), 1429 cm^{-1} (vC—N), 1352 cm^{-1}
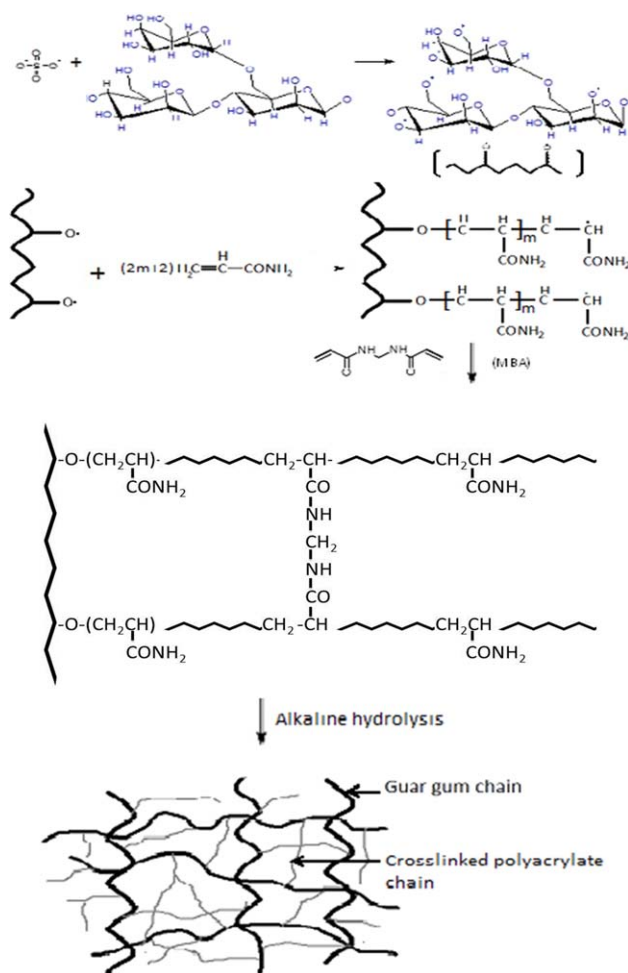

Figure 2. Diagrammatic representation of formation of a typical crosslinked guar gum-g-polyacrylate hydrogel. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
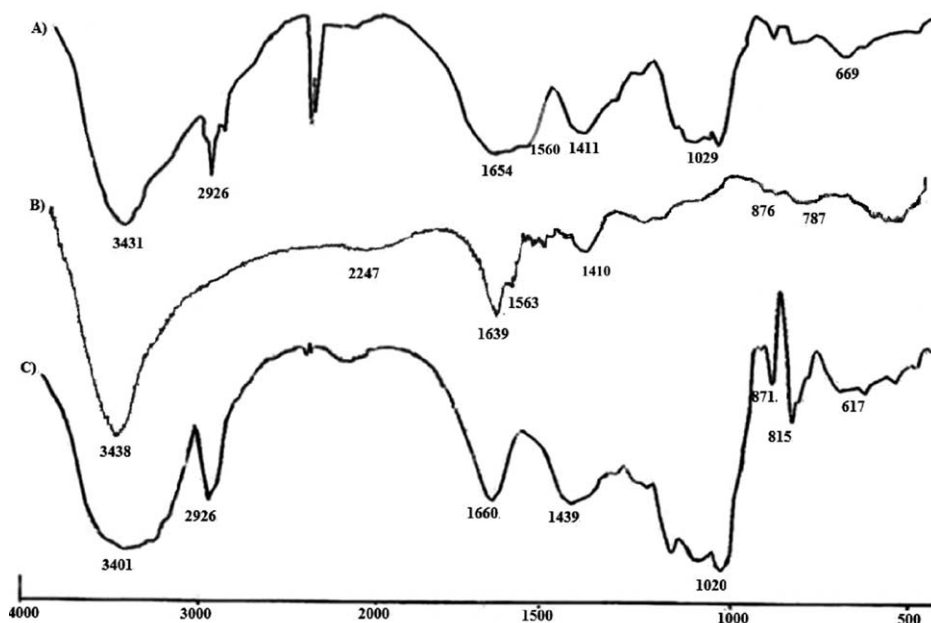

Figure 1. FTIR spectra of GG-SAP (A), polyacrylate hydrogel (B), and guar gum (C).
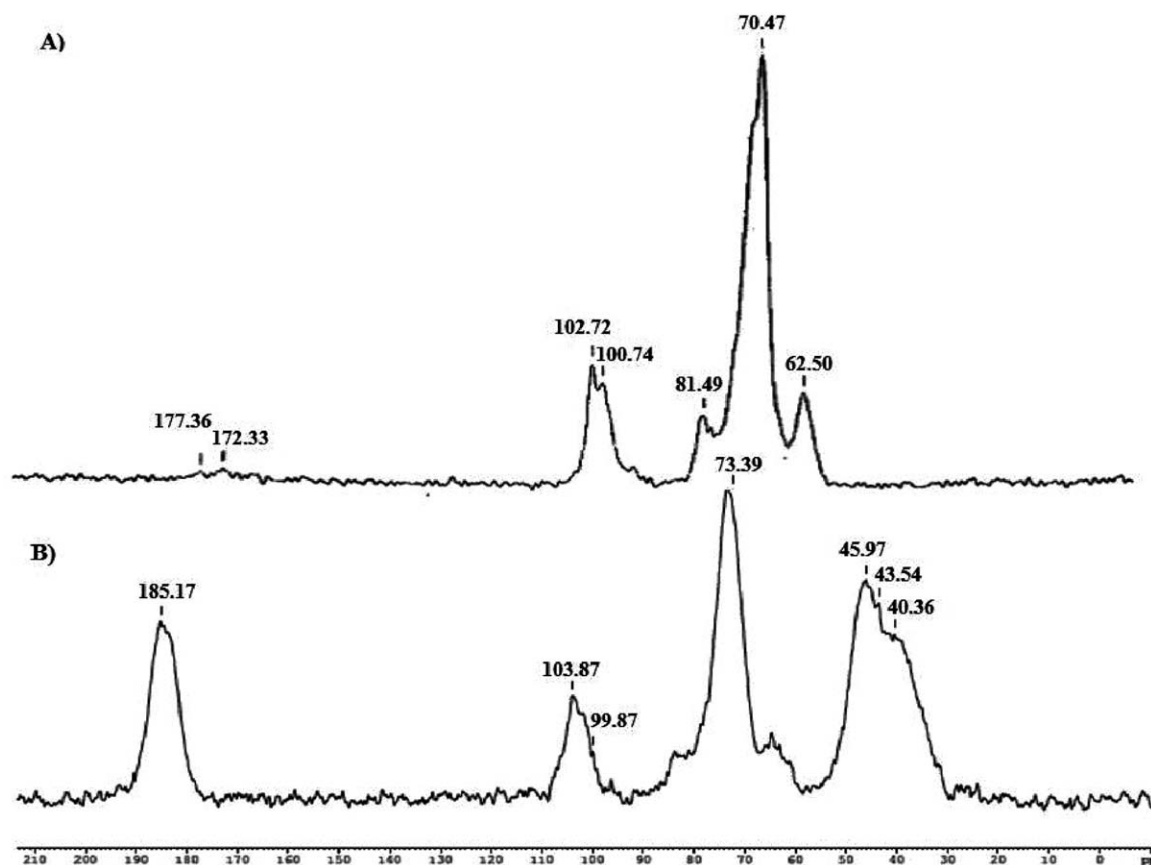
Figure 3. ^{13}C-NMR spectra of guar gum (A) and GG-SAP (B) (solid-state ^{13}C).

($ NH_2$), 1280 cm^{-1} ($\gamma$ NH$_2$), and 961 cm^{-1} (ω NH$_2$)] and the appearance of the characteristic peaks of COOH and COO$^-$ group as described above confirm successful conversion of amide into COO$^-$ moiety. A tentative scheme of the formation of developed SAPs is depicted in Figure 2.

Solid-State ^{13}C-NMR Analysis. Figure 3 depicts ^{13}C-NMR spectrum of an optimized crosslinked GG-g-PA hydrogel. NMR peaks in the spectrum were compared with the peaks of native GG.[31] A signal at 185.7 ppm can be ascribed to the COO$^-$ group of Cs in the grafted PA network. This peak is not visible in the spectrum of GG. Assignments characteristic of the GG are clearly visible in the spectrum of the hydrogel and are as follows[32]: 108.8 ppm (C-1 of galactose and mannose units), 99.88 ppm (C$_1$ of β-D-mannose-reducing chain end), 73.39 ppm (C$_2$– C$_5$ of galactose and mannose), and 64 ppm broad peak (C$_6$ of galactose and mannose units). Additional peaks at 40.30–45.97 ppm can be assigned to various Cs (CH$_2$—CH$_2$—) of the polacrylate network grafted onto the GG. The absence of peaks in this region in the backbone's spectrum confirms *in situ* grafting and crosslinking.

Morphological SEM. Figure 4 compares the surface morphology of crosslinked GG-g-PA hydrogel (GG-SAP) *vis-à-vis* native GG examined under scanning microscope to investigate the effect of grafting and crosslinking on the surface morphology of the backbone polymer. SEM photograph of GG displays dense

and smooth surface of the backbone. As is evident from Figure 4, grafting and crosslinking of PA chains onto the backbone resulted in homogeneous but fractured topography.[33]

Another noteworthy feature in the SEM micrographs is uniform porous appearance on the surface of the hydrogel. In most of the previous work performed on GG-g-PA hydrogels, nonporous, uniform morphology has been reported, which is caused by the incorporation of clay minerals.[24] In contrast to this, hydrogel prepared in the current study exhibit ragged and porous topography. This observation highlights the impact of the reaction conditions and drying techniques used in the preparation of hydrogels. Porous morphology of hydrogels in our work can be attributed to the solvent-assisted drying technique. This fact has also been confirmed in our previous studies.[23]

XRD Analysis. X-ray diffraction patterns of native GG and GG-SAP are presented in Figure 5. The XRD peaks of both the materials confirm their amorphous character. A very low degree of crystallinity in GG is indicated by its characteristic diffraction band ($2\theta = 20°$). XRD of GG-SAP also showed major diffraction band at the same position ($2\theta = 20°$), indicating that grafting and crosslinking of PA chains onto the GG backbone did not influence the crystallinity of the latter. However, as is evident from Figure 4, an additional peak ($2\theta = 9°$) appears in the XRD of GG-SAP, which can be ascribed to the lateral bilayering of the PA chains.
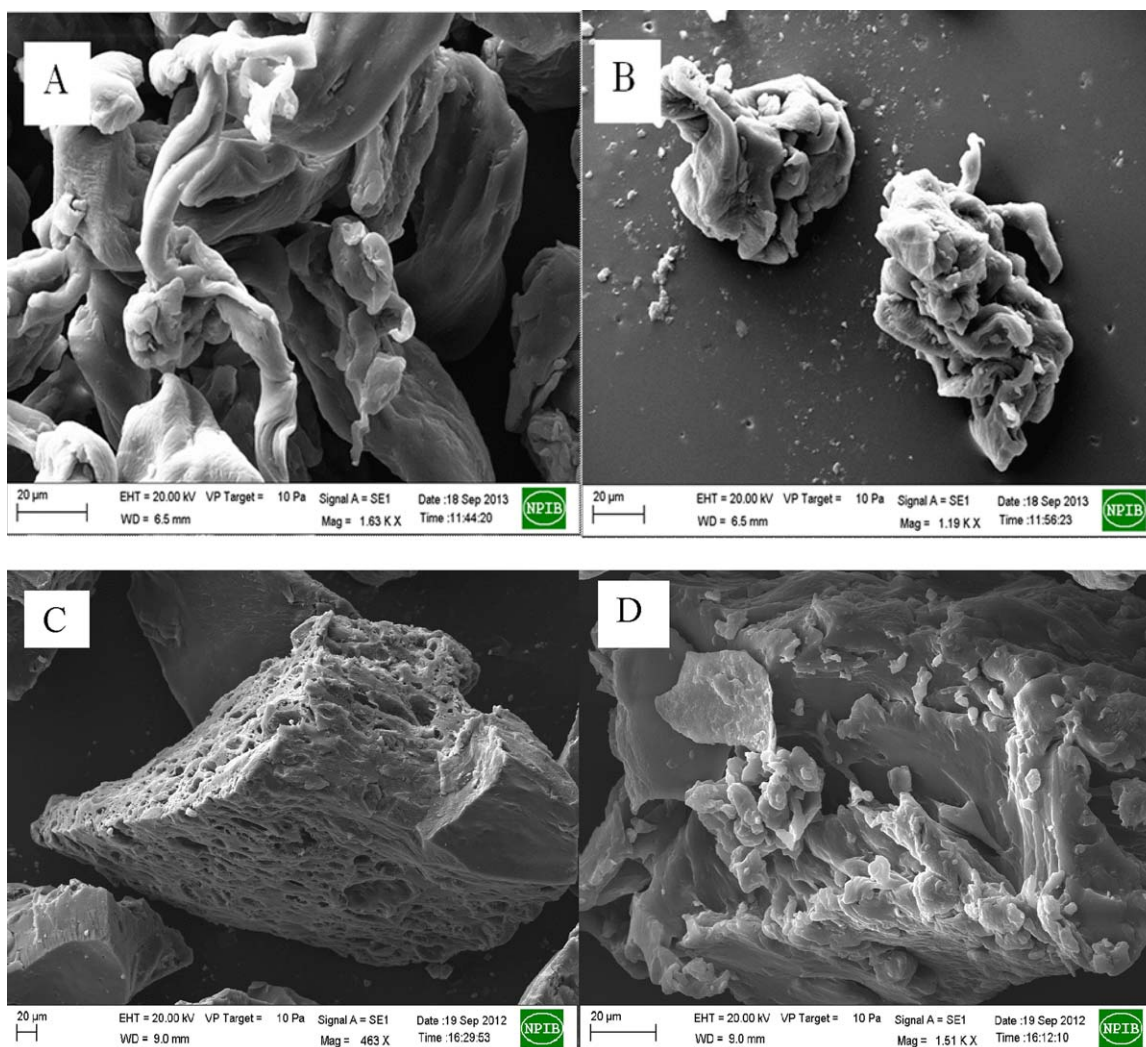
Figure 4. SEM images of guar gum (A and B) and GG-SAP (C and D). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of Monomer Content on Water Absorbency

The effect of different monomer to backbone ratios recorded on WAC of prepared hydrogels is shown in Table III. It can be seen that initially the equilibrium WAC increased with the increase in monomer content up to monomer backbone ratio of 3.75 : 1. Further increase up to the investigated ratio of 15:1, the Q_{H_2O} exhibited consistent fall. Initial increase in the amount of acrylamide leads to an increase in the fraction of PA chains, containing sufficient number of polar —COO$^-$ groups. The electrostatic repulsion up to this point seems to favor the water absorption characteristics of the polymer. The decrease of Q_{H_2O} beyond weight ratio 3.75 : 1 can be attributed to the increase in homopolymer content, resulting in the increase in soluble fraction at fixed crosslinker and initiator amount in the feed.[23,25] In a related work on GG-g-PA hydrogels, similar trend was reported, although the maximum equilibrium WAC was achieved at much higher monomer content in the feed.[24] The variations can be ascribed to the difference in reaction process conditions reported earlier and in the current study.

Effect of Crosslinker and Initiator Concentration on Water Absorbency

The effect of crosslinker content on WAC behavior of prepared hydrogels is shown in Table III. It is clear from Table III that at a fixed monomer and initiator concentration, the swelling ratio exhibited significant increase with crosslinker concentration increase in the range 1.0 wt %, beyond which it significantly decreased with the increase in crosslinker concentration. The initial increase may be understood in terms of decrease in homopolymer and soluble fractions in the feed due to expansion in crosslinked network. The decrease in water uptake above 1.0 wt % can be easily explained in terms of Flory's theory, according to which a high concentration will induce extensive crosslink points, resulting in the increase of crosslinking density.[34] As a result, the network relaxation and the voids for holding water decrease, leading to a decrease in water absorption. Under experimental conditions chosen in the current study, concentration of the crosslinker should be higher than 0.03 wt %, otherwise gel setting cannot be achieved. This can
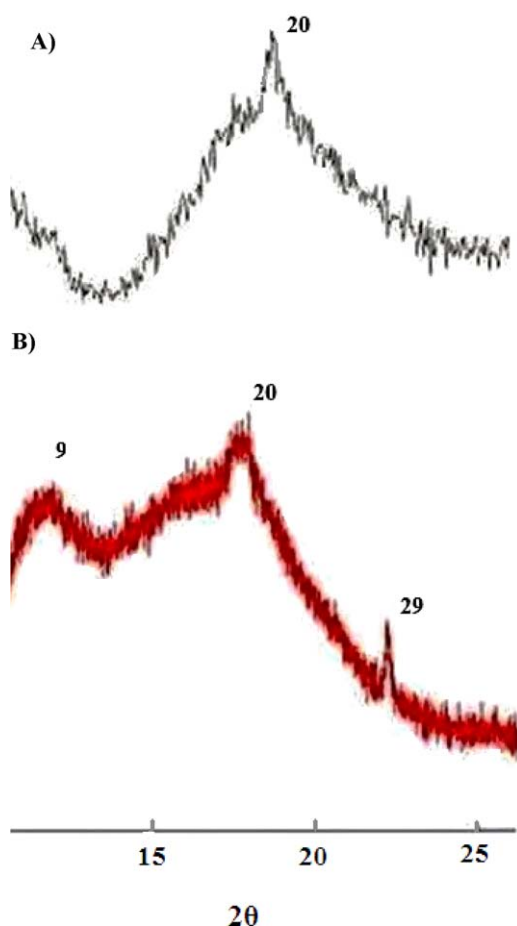
Figure 5. X-ray diffractogram of guar gum (A) and GG-SAP (B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

be understood in terms of the insufficient number of crosslinker molecules need to graft and create stable polymer network. GG and PA although are hydrophilic in nature, lack of proper crosslinking leads to sol–gel states in water, and Q_{H_2O} cannot be measured.

The amount of initiator, as can be seen from Table III, plays a significant role in the graft polymerization reaction. It is evident that under constant reaction conditions used in the current work, the WAC reaches maxima at 3.0 wt % initiator concentration. Furthermore, at lower and higher concentrations, the inferior selling is exhibited. An initial increase up to 3.0 wt % can be easily understood in terms of the increase in the active sites in the feed leading to enhanced grafting efficiency and network structure favoring higher water uptake. The decreasing swelling behavior beyond 3.0 wt % can be explained as follows. The increase in initiator concentration beyond an optimum value, which is a function of the process conditions and reaction parameters and the nature of the reactants and the backbone, leads to an increase in the reaction velocity leading to bimolecular collisions favoring chain-terminating step of the reaction. Consequently, the rate of graft polymerization and the generation of polymer network onto the backbone decreases, whereas the homopolymer content in the feed increases.[33] The degradation of backbone polymer due to higher free radical content also serves as another key factor to this effect.

Effect of Volume of Water in the Feed on Water Absorbency

The variation of Q_{H_2O} with the quantity of water in the feed mixture, expressed as milliliter per gram of reaction mass, is shown in Table IV. It is evident that the increase in quantity of water from 2.8 to 11 g/mL of feed mass showed consistent increase in the Q_{H_2O} values of hydrogels. An optimum network formation requires effective collisions between various reaction moieties, for

Table III. Effect of Monomer to Backbone Ratio, Crosslinker, and Initiator Concentration on the Water Absorption and Grafting of GG-SAP

Monomer concentration[a] (wt %)	Q_{H_2O} (g/g)	G_e	Crosslinker concentration[b] (wt %)	Q_{H_2O} (g/g)	G_e	Initiator[c] (wt %)	Q_{H_2O} (g/g)	G_e
2.5	154.9[f]	0.68	0.05	48.2[f]	0.32	0.03	47.8[g]	0.60
3.75	492.3[a]	0.93	0.1	192.8[e]	0.53	0.06	182.4[f]	0.68
5	464.2[b]	0.98	0.5	490.5[b]	0.56	0.3	320.3[e]	0.80
7.5	423.4[c]	0.80	1.0	513.1[a]	0.57	0.6	354.6[d]	0.85
10	394.3[d]	0.85	5.0	449.2[c]	0.60	3.0	507.8[a]	0.98
15	354.4[e]	0.87	10.0	350.8[d]	0.61	4.5	482.4[b]	0.87
						5.0	421.9[c]	0.80
						5.5	404.2[d]	0.78
LSD at 5%	6.96			10.07			7.07	
CV	1.0064			1.6259			1.2710	
F value	2990.48			3351.77			5504.92	

G_e, grafting efficiency (g/g). Means within a column followed by different letters are significantly different at 5% level of significance and those followed by the same letter are not significantly different at 5% level of significance.
[a] Synthesis parameters: crosslinker (wt %): 0.5, and initiator (wt %): 3.0; $V_{H_2O} = 11.36$ mL/g feed.
[b] Synthesis parameters: monomer (wt %): 3.75, and initiator (wt %): 3.0; $V_{H_2O} = 11.36$ mL/g feed.
[c] Synthesis parameters monomer (wt %): 3.75, and crosslinker (wt %): 1.0; $V_{H_2O} = 11.36$ mL/g feed.

Table IV. Effect of Water Volume, Molar Ratio of Alkali to Monomer, and Particle Size of Backbone on Water Absorbency of Optimized GG-SAP

Water volume[a] (mL/g)	Q_{H_2O} (g/g)	Molar ratio of NaOH to monomer[b]	Q_{H_2O} (g/g)	Particle size[c]	Q_{H_2O} (g/g)
2.84	88.2[f]	0.5	178.3[f]	25-100	484.4[c]
5.68	195.1[e]	1.0	354.9[e]	100-240	603.2[a]
8.52	351.7[c]	1.5	426.9[d]	>240	516.9[b]
11.36	517.1[a]	2.0	518.4[a]		
14.2	434.2[b]	2.5	498.3[b]		
16.5	288.4[d]	3.0	467.2[c]		
LSD at 5%	7.39		6.91		17.18
CV	1.2376		0.9431		1.4173
F value	5943.34		3889.66		196.61

Means within a column followed by different letters are significantly different at 5% level of significance and those followed by the same letter are not significantly different at 5% level of significance.
[a] Synthesis parameters: monomer (wt %): 3.75, crosslinker (wt %): 1.0, and initiator (wt %): 3.0.
[b] Synthesis parameters: monomer (wt %): 3.75, crosslinker (wt %): 1.0, and initiator (wt %): 3.0; V_{H_2O} = 11.36 mL/g feed.
[c] Synthesis parameters: monomer (wt %): 3.75, crosslinker (wt %): 1.0, and initiator (wt %): 3.0; V_{H_2O} = 11.36 mL/g feed.

which water plays a significant role as reaction medium. At volume less than 11 mL/g, low Q_{H_2O} values are due to tightly crosslinked hydrogel network formation. The increase of V_{H_2O} beyond 11 mL/g leads to an increase in the soluble fraction due to dilution of crosslinker, thus leading to poor network formation. This fact is reflected in the decrease in WAC on the increase of V_{H_2O} from 11 to 16.5 mL/g under our experimental conditions. These findings have also been described in our previous study.[23]

Effect of Molar Ratio of Alkali to Monomer on Water Absorbency

According to Flory's network theory, the fixed charges on the polymer network contribute significantly to the swelling of superabsorbent. The effect is exerted by these charges through electrostatic repulsion and osmotic potential difference between the network and surrounding solution. Therefore, the type and amount of hydrophilic groups are important in determining fluid absorption properties of hydrogels. The effect of molar ratio of alkali to acrylamide on equilibrium WAC of GG-SAP in distilled water is shown in Table IV; the Q_{H_2O} increases with the increase in molar ratio from 0.5 to 2.0 under experimental conditions of the current study. Further increase led to a fall in the Q_{H_2O}. On saponification of polyacrylamide by NaOH, the ionic hydrophilic moieties in polymer structure increase that cause increase in osmotic potential difference, and the electrostatic repulsion causes disentanglement of polymer chains resulting in expansion of the network. Concentrations of NaOH higher than 2.0 molar ratio, however, led to the generation of low-swelling superabsorbent. The swelling loss at higher concentration can be related to build up of residual cations content in the hydrogel matrix after the completion of hydrolysis reaction. These excess cations shield the carboxylate anions and eliminate the main anion–anion electrostatic repulsive forces. Consequently, the less expanded network of hydrogel absorbs less water, manifesting in low WAC values. This phenomenon is often referred to as charge screening effect.[33] Alkaline degradation of the backbone polymer could also be another reason for the observed behavior.

Table V. Effect of Temperature, Water Quality, and pH on Swelling of GG-SAP

Temperature (°C)	Q_{H_2O} (g/g)	Water quality	Q_{H_2O} (g/g)	pH	Q_{H_2O} (g/g)
10	490.7[e]	Deionized water	675.8[a]	4.0	466.8[c]
25	519.2[d]	Distilled water	611.9[b]	7.0	669.2[b]
35	542.4[c]	Tap water	452.2[c]	9.0	744.3[a]
45	593.8[b]	Hard water A	361.0[d]		
50	621.1[a]	Hard water B	250.3[e]		
		Hard water C	215.6[f]		
LSD at 5%	3.39		6.54		5.82
CV	0.3205		0.8407		0.4102
F value	4915.60		8211.97		9349.45

Means within a column followed by different letters are significantly different at 5% level of significance and those followed by the same letter are not significantly different at 5% level of significance.

Effect of Particle Size of Backbone Polymer on the Water Absorbency

As seen in Table IV, a decrease in the particle size of GG used in hydrogel preparation up to 100–240 mesh led to an increase in the swelling ratio under experimental temperature (50°C). Finer particles of size >240 mesh size led to the formation of hydrogels with reduced Q_{H_2O}. GG is well known to generate highly viscous solutions even at low concentrations.[35] Finer particle-sized GG resulted in instantaneous and highly viscous solution development. The increase in viscosity leads to a decrease in the grafting polymerization by limiting the mobility of the reactants and the macroradicals.[36] This resulted in the formation of sticky material with poor network stability. This was further substantiated by the visible material loss through the nylon bag at the time of swelling measurements.

Effect of Temperature and pH on Swelling

In our previous studies and other studies, the equilibrium swelling of hydrogels in water was found to be dependent on the temperature.[23,37] As is clear from Table V, the Q_{H_2O} increases significantly with an increase in the temperature from 10 to 55°C. The temperature in the range of 25–50°C is of particular interest to assess the suitability of hydrogels in agriculture.

As in seen in Table V, Q_{H_2O} of anionic GG-SAP exhibited significant response as a function of pH of swelling medium. GG-g-PA hydrogels contain hydrophilic —COOH and —COO⁻ groups, which ionize further at pH 9.0 and exert electrostatic repulsion leading to expansion of polymer network and hence the increase in Q_{H_2O}. Similar finding has been described by Kiatkamjornwong and Phuncharcon.[38] Comparatively, lower WAC at pH 4.0 can be attributed to nonionization of —CONH₂ groups and —COOH groups. Our laboratory has developed a cellulosic superabsorbent, P-gel,[20] which has been established as water-retentive aid in agriculture. However, its use in problem soils (acidic and alkaline) is restricted due to its low Q_{H_2O} values in acidic and alkaline pH environment. Superior swelling characteristics of GG-SAP at pH 4–9 and more particularly 9
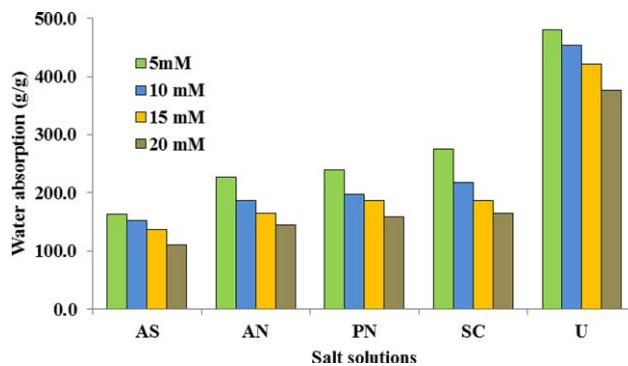
Figure 7. Effect of salt/fertilizer type and their strength on water absorbency. AS, ammonium sulfate; AN, ammonium nitrate; PN, potassium nitrate; SC, sodium chloride; U, urea. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

point toward a potential soil conditioner for the acidic and alkaline soils.

Effect of Quality of Water on Absorbency

Water quality plays an important role in determining the performance of superabsorbents in agriculture under most practical use conditions; hard water is available for agricultural use. The effect of water quality on the swelling ratio of GG-SAP is shown in Table V. When compared with maximum Q_{H_2O} values of the product obtained in distilled and deionized water, the swelling in tap water (EC = 2.04 mhos/cm, pH = 7.7) and hard water of different simulated ionic strengths decreased, but not drastically in comparison with our earlier reports on swelling behaviors of P-gel and biopolymeric superabsorbent nanocomposite.[23] The decrease of WAC with the increase in its ionic strength of hard water may be explained in terms of screening of —COO⁻ anions by the cations present in water. Similar observation has been described by Pourjavadi et al.[39]

Effect of Time Period on Water Absorbency

As can be seen from Figure 6, water absorption rates of the optimized GG-SAP were measured at 25 and 50°C. The results shown in Figure 5 indicate that the GG-SAP attains equilibrium WAC in 14 h at 50°C, whereas at 25°C, the same is attained in 18 h. Swelling of SAP involves large segmental motion that further results in increased expansion of macromolecular chains.[40]

Buchanan et al.[41] suggested that swelling rate of hydrogel is a function of chemical structure, surface area, particle size, and density of the polymer. Initially, low swelling rates at both the temperatures may be explained in terms of slow diffusion and restricted capillarity in the initial polymer network. The absorbency rates of biopolymeric hydrogels can be significantly improved by the addition of hydrophilic clays and through the generation of porosity.[42]

Effect of Salt Type and Strength on Water Absorbency

Evaluation of the swelling behavior of GG-SAP in salt solutions, particularly those applied as fertilizers and present in saline soil, is very important in view of their agricultural and horticultural applications. Figure 7 depicts the comparative swelling response of the optimized GG-SAP in solutions of varying strengths of
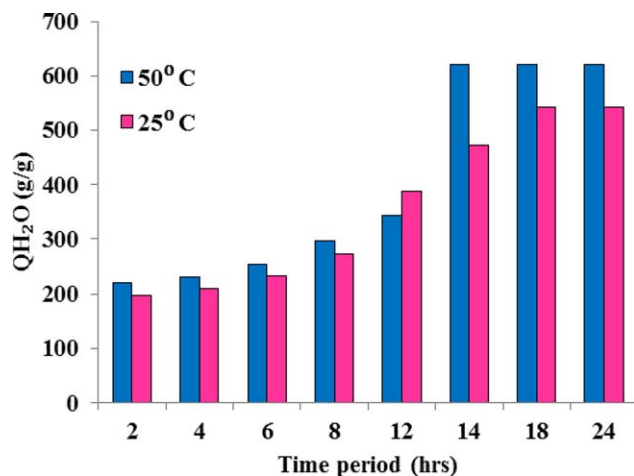
Figure 6. Swelling of GG-SAP as a function of time period at 25 and 50°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VI. Water Absorbency Behaviors of GG-SAP in Soil and Soil-Less Medium at 25 and 50°C

Hydrogel content (wt %)	Soil		Soil-less medium	
	25°C	50°C	25°C	50°C
0.0	42[j]	41.5[j]	283.3[e]	284.6[c]
0.5	94.9[i]	112.7[h]	402.3[d]	428.1[c]
0.75	145.4[g]	186.7[f]	454.9[b]	476.1[a]
LSD at 5%	6.39			
CV	1.4922			
F value	5884.59			

Means within a column followed by different letters are significantly different at 5% level of significance and those followed by the same letter are not significantly different at 5% level of significance.

$(NH_4)_2SO_4$, NH_4NO_3, KNO_3, NaCl, and urea. In all the salt solutions, absorption was less compared with that in distilled water. The hydrogel exhibited minimum reduction in Q_{H_2O} in urea solutions at all test concentrations. This observation is of interest because for most of the crops in agriculture, urea comprises an important agro-input. In general, decrease in Q_{H_2O} with increase in concentration of salt solutions may be understood in terms of reduction in osmotic pressure difference between gel matrix and external salt solution.
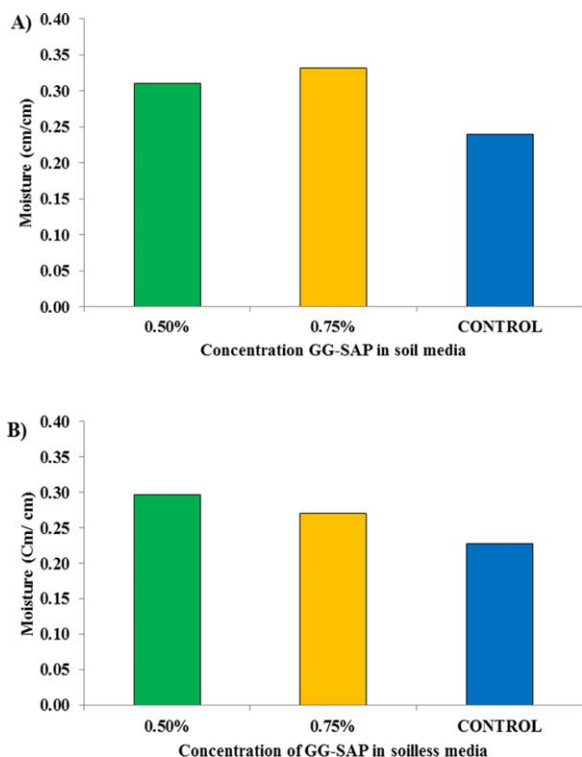
Effect of Hydrogel Addition on Water Absorption and Retention Capacity of Plant Growth Media (Sandy Loam Soil and Soil-Less Medium)

Water absorption capacity of the test sandy loam soil and soil-less medium significant increased with the addition of GG-SAP hydrogel. As is clear from the Table VI, at both the experimental temperatures (25 and 45°C), the hydrogel-amended soil and soil-less medium absorbed more water than respective controls. Amendment with hydrogel at 0.75% exhibited significantly higher WAC than at 0.5% in both the plant growth media. In case of soil, the amended samples at 50°C exhibited higher WAC than at 25°C at both 0.5% and 0.75% amendment levels. Similar pattern, although less pronounced, was exhibited by the amended soil-less medium. GG-SAP exhibits an increase in Q_{H_2O} with the increase in temperature due to expansion of the polymer network as described earlier, and the same behavior is also manifested in the amended media. Similar observation was described in our earlier reports on biopolymeric hydrogels.[20]

The use of the developed superabsorbent material (GG-SAP) for agricultural and horticultural applications was evaluated in terms of its effect on the moisture characteristics of the plant growth media under different matric tensions. When compared with the control, the WHC of the hydrogel (GG-SAP) amended soil at both rates 0.5% and 0.75% remained higher at field capacity and also at all matric tension, respectively, although the difference between 0.5% and 0.75% amended soils became narrower at matric tensions above 2.53 pF. Similar behavior was observed for the soil-less medium. The hydrogel (GG-SAP)-
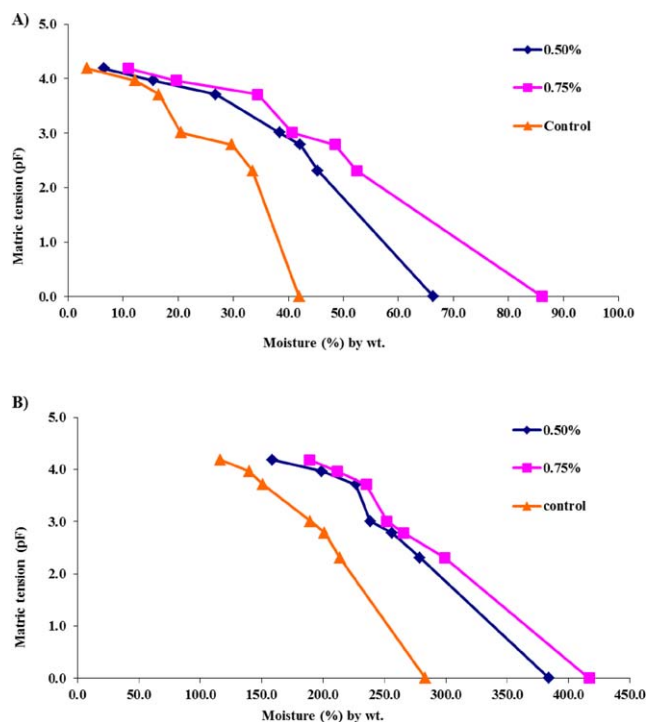

Figure 8. Effect of gel addition on available water from soil (A) and soil-less (B) media. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9. Moisture retention characteristics of soil (A) and soil-less (B) media with unamended and gel amended condition under different matric tensions (pF). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
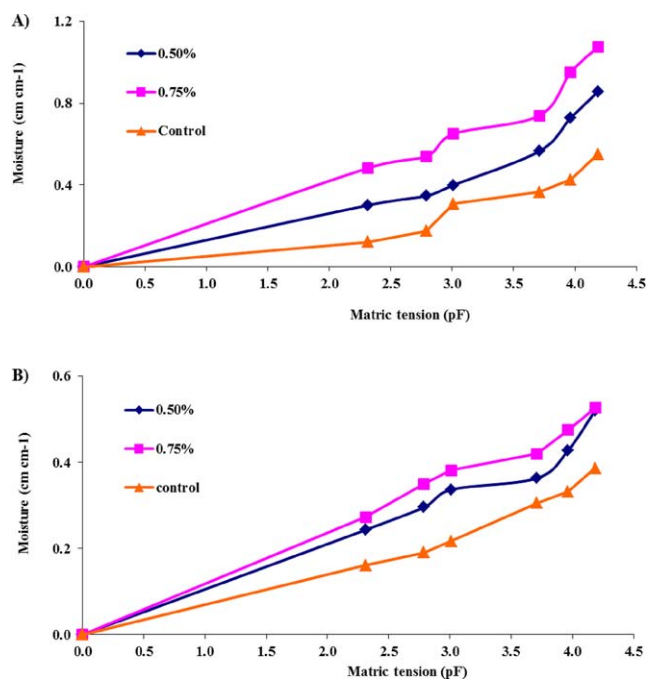
Figure 10. Moisture release curves of soil (A) and soil-less (B) media with unamended and gel amended condition under different matric tensions (pF). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

amended soil-less medium at 0.5% and 0.75% showed higher WHC values (65.2% and 85.29% respectively) when compared with the control. Irrespective of the type of absorbent material, the percent moisture absorbed by free SAP is more relative to when it is present in a plant growth medium. This is because in such situations, the gel particles are surrounded by the soil or media particles, which subject it to confirming pressure and limit the degree of swelling.[43]

Water harvested by the hydrogel should be readily available to plant, thus avoiding water stress and enable its survival.[44] Thus, it is expressed in terms of the available water capacity (AWC) or readily available water (RAW; Figure 8) that refers to the difference between field capacity and soil moisture at a threshold value of matric tension that is calculated using the following expression[45]:

$$\text{Available water capacity } (\text{AWC}) = (\text{FC} - \text{PWP}) \times \rho/100,$$

where FC is field capacity, PWP is permanent wilting point, and ρ is bulk density of media used.

The addition of GG-SAP to soil and soil-less medium increased the water availability to plant when compared with the respective control. In case of soil-less medium, the values of RAW at both amendment levels, whereas in case of soil amended at 0.75%, were able to make more water available. As is clear from Figure 9, when compared with the control, WHC of soil and soil-less medium amended with the GG-SAP remained higher with the increase in matric tension. At field capacity, in both soil and soil-less media, hydrogel addition led to higher percent retention when compared with the unamended controls.

Moisture release curves [Figure 10(A,B)], expressed as moisture cm/cm of the hydrogel-amended soil and soil-less media, show that when compared with the individual controls, the gel-amended soil and soil-less media exhibited significantly higher release of moisture. The moisture release was calculated as follows[46]:

$$(M_p - M_0) \times \rho/100,$$

where M_p is the moisture held at particular pressure, M_o is the moisture held at zero pressure, and ρ is the bulk density of soil or soil-less medium. At 4.2 pF (corresponding to permanent wilting point), hydrogel-amended soil released (21–37%) more water than control. Similar behavior was observed in case of soil-less medium. Relative moisture release was higher in soil-less medium when compared with the soil at both amendment levels. This can be attributed to the loose texture of the soil-less medium.

CONCLUSIONS

The probability of scale up of a laboratory process depends on its simplicity and ease of handling. Emphasis in our laboratory has always been to develop agricultural and ecofriendly and economic soil conditioners as water-retentive aids in agriculture. The hydrogels developed in this study has exhibited all the characteristics that qualify it as a potential candidate for agricultural use. When compared with earlier soil conditioners developed by us, GG-SAP possesses additional advantage and merits in terms of superior WAC behavior under acidic and alkaline conditions, in the presence of salts and fertilizers, and the moisture retention and release characteristics imparted to the plant growth media. GG, being a biopolymer with hydrophilic biocompatible characteristics, the hydrogels based on it will be exploited as potential bioformulations. The study showed that the backbone monomer ratio, crosslinker concentration, and quantity of water per unit reaction mass were critical parameters in determining the swelling properties. Structural characterization confirmed the successful formation of the hydrogels based on GG.

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