Malaysian Journal of Chemistry, 2023, Vol. 25(5), 36-45
(Special Issue: *4th International Symposium on Multidisciplinary Science 2022*)

Evaluation of Gellan Gum-glufosinate Ammonium Beads and its Release Study Performance

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The aim of this study is to prepare hydrogel beads that contain the herbicide of glufosinate ammonium (GA). Gellan gum (GG) is used as a host material, due to its interesting properties which are biodegradable and biocompatible. Hydrogel having the hydrophilic structure of which renders them capable of holding large amounts of water in their three-dimensional networks. GA is a type of contact herbicide that is used to control weeds and unwanted plants in agriculture industry. GA acts as a guest species to be incorporated into host, GG to produce controlled release formulation of herbicide. GG beads were prepared by ionotropic gelation using calcium chloride solution as a crosslinker. In the preparation of GG hydrogel beads loaded with GA, different concentrations of GA which are 0.4 M, 0.8 M, 1.2 M and 1.6 M were prepared. From the results obtained, FTIR spectrum showed the combination of both functional groups from the host and guest species even when different concentrations of GA were used. Elemental analysis of CHNS showed that the GG loaded with GA have an increase in the carbon, hydrogen, nitrogen and sulfur contents which is due to the successful incorporation of various concentrations of GA into the GG. From the TGA-DTG thermogram, thermal stability showed that the weight loss was influenced by the concentrations of the incorporated GA. The release profile of the GA from the gellan gum beads showed the release of GA completed on the sixth day.

Keywords: Gellan gum; glufosinate ammonium; hydrogel; beads; herbicide

Received: September 2022; Accepted: May 2023

GA or generally known as glufosinate is a widely used chemical as herbicide. It exists in white to light yellow crystalline powder, slightly pungent odor, non-corrosive and stable with exposure to light [1]. It is used to control a wide range of weeds after the crop emerges or for total vegetation control on land not used for cultivation. Plants absorb this substance primarily through their leaves and stem. As a contact herbicide, GA is effective only when it comes into contact with the plant. Therefore, this allows it to control weeds without affecting the roots or soils which is vital especially in erosion-prone areas such as slopes. Besides weeds, this herbicide also can be used to destroy other unwanted vegetation such as grasses and woody plants [2]. GA is a phosphorus containing amino acid that inhibits the activity of an enzyme, glutamine synthetase, which is necessary for the production of the amino acid glutamine and for ammonia detoxification [3]. The application of GA leads to reduced glutamine and increased ammonia levels in the plant's tissue. This causes photosynthesis to stop and the plant dies within a few days. GA has become one of the key herbicides in global agriculture. Farmers often use this herbicide because it ensures a high degree of crop safety as it only affects the parts of plant where it is applied and it offers a unique, simple and effective weed control in a variety of crops [4].

However, this herbicide carries unacceptable risks to human, especially to the environment and to agricultural biodiversity because during the crop spraying, it is unacceptably have high effect even when protective clothing is worn. GA **(**Figure 1) cause toxic effects to humans as large quantities of this formulation can lead to death in humans [5]. The widespread use of GA herbicides could have a number of impacts on the arable environment. It can inhibit some beneficial bacteria or fungi and may increase the susceptibility of some crop plants to disease. Over long period of continuous use, weeds may become tolerant to GA and this can cause the increase in the application of other agrochemicals including fertilizers, insecticides,

†Paper presented at the 4th International Symposium on Multidisciplinary Science 2022 (SMS 2022)

fungicides, and herbicides [6]. One way to overcome this problem is by using control release technology at which the glufosinate will be incorporated in to a chosen host, in this case, by using GG in a form of hydrogel.

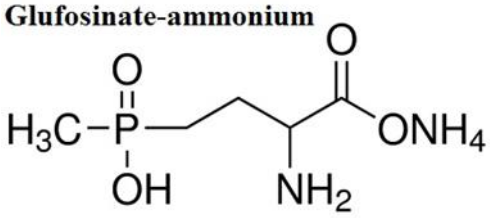

Figure 1. Chemical structure of GA

A hydrogel is a macromolecular polymer gel that was constructed by a network of crosslinked polymer chains [7]. Hydrogels are synthesized from hydrophilic monomers together with a functional crosslinker to promote network formation where in this study, calcium chloride solution is used as a medium of crosslinker to form the GG beads. A net-like structure with void imperfections has enabled the hydrogels to absorb large amount of water via hydrogen bonding. As a result, hydrogels have good elastic mechanical properties and firm as it resemble the self-healing structure. Self-healing is the spontaneous formation of new bonds when old bonds are broken within a material. As mentioned above, hydrogels as three-dimensional crosslinked hydrophilic polymer networks are capable of swelling or de-swelling reversibly in water and retaining large volume of liquid in swollen state [8].

A variety of renewable biopolymers such as GG is receiving greater attention than synthetic petrochemicals-based polymers due to the environmental concerns. In general, GG is a water-soluble anionic polysaccharide produced by the bacterium Sphingo-monas elodea [9]. The use of GG as a natural hydrogel application to form gellan beads in the presence of calcium ions make the beads nontoxic when taken orally and since the dried GG beads have the property of reswelling, they can act as controlled release system. The hydrogels have the response that can be controlled when it swells or expand due to the conditions changes from the environment [10]. Therefore, from the recent studies, hydrogels were found in formulating controlled and mucoadhesive drug delivery system because of their hydrophilic and three-dimensional network structure helps to encapsulate and regulate the release of the drug. The applications of gellan gum have been used in a variety of fields such as a tablet binder, a gelling agent, and as a controlled released polymer in a pharmaceutical industry [11]. Besides, gellan gum is used in food industry to make jelly, as a food additive, stabilizer, and emulsifier [12]. In textile industry, gellan gum give excellent film forming and thickening properties when used for textile sizing, finishing and printing [13]. It reduces dusting while sizing and gives better efficiency in production. In cosmetic industry, gellan gum is used as a protective colloid in skin care products, creams and lotions [14].

In this study, gellan gum is used as the host for the controlled released system containing the herbicide of GA. GG is biodegradable and biocompatible which makes it suitable to be used in agriculture purposes. The influence of various concentrations of GA used to be incorporated into the GG beads were studied. The obtained beads were then analyzed and characterized by using different analytical techniques. The release profile of gellan gum hydrogels containing GA were studied using the Ultraviolet-Visible Spectroscopy and real sample analysis. It is expected that by encapsulating this herbicide into the host of GG and functioning as controlled release system, it will partly contribute to the safe and economical of herbicide application. The targeted plant will be protected, high yield of crop could be obtained and the chemicals pollution to the environment would be minimized.

EXPERIMENTAL

Chemicals and Materials

Gellan gum (Gelzan™ CM), glycerin (99.5%), CH_3COOH (99.9%) and sodium acetate, $C_2H_3NaO_2$ (99.0%) were purchased from Sigma Aldrich, United State. Glufosinate ammonium powder was kindly provided by Dr Norhayu Asib from Faculty of Agriculture, UPM. All chemicals and reagents were used directly without further purification.

Preparation of GG-GA Beads

The beads were prepared according to the ionotropic gelation technique. Gellan solution was prepared by dissolving 1 g of GG powder in 100 ml of distilled water under constant magnetic stirring of 500 rpm at temperature 70 °C. Then, 4 ml of glycerin was added to this solution that acts as a plasticizer. After the GG solution was completely dissolved, 0.4 of GA solution was dropped slowly into the homogeneous gellan gum solution. After that, the mixture was stirred for 1 hour to ensure that the solution is fully homogeneous by using hot plate stirred. To prepare the GG-GA beads, different concentrations of GA (0.4 M, 0.8 M, 1.2 M and 1.6 M) were prepared by dissolving specific masses of GA in distilled water at room temperature. The formulation is shown in Table 1. To improve the physical crosslink to form the hydrogel beads, the solution that was prepared before was added drop wise by using a micropipette into calcium chloride solution under gentle stirring and curing time 5 min to provide sufficient mechanical strength. The beads were separated by filtration, washed with distilled water and dried in oven at 37 °C for 12 hours. GG-GA beads were stored in desiccators at room temperature for further characterization. The steps above were then repeated with different concentrations of GA which were 0.8 M, 1.2 M and 1.6 M respectively.

Table 1. Amount of weight and volume in each of the GG-GA beads.

Sample	Weight of GG (g)	Vol. of Glycerol (mL)	Weight of GA (%)
GG	1	4	0
GG-GA0.4	1	4	0.4
GG-GA0.8	1	4	0.8
GG-GA1.2	1	4	1.2
GG-GA1.6	1	4	1.6

Characterization

The prepared GG-GA beads were then analyzed and characterized by using different analytical techniques to study the interactions of the GG hydrogel with GA. The techniques involved in this study were Fourier transform infrared spectroscopy (FTIR), Carbon, hydrogen, nitrogen and sulphur analyzer (CHNS), thermogravimetric and differential thermogravimetric analysis (TGA-DTG) and ultraviolet-visible spectroscopy (UV-Vis).

FTIR is the most common equipment use to characterize sample as it can determine the functional group of the sample tested. In this study, it was used to detect the presence of the functional group of both GG beads with GA and neat gellan gum beads. All samples were tested using Perkin Elmer model 1725X in the wave number range from 4000 to 400 cm^{-1}.

The CHNS analysis was carried out to determine the mass fractions or the amount of carbon(C), hydrogen (H), nitrogen (N), and sulphur (S) in the samples by using CE440 Elemental Analyzer - CHNS instrument. The beads obtained were finely dried, weighed and mixed in a tin capsule that contains an oxidizer which is vanadium pentoxide, V_2O_5. Then, it was combusted in a reactor at high temperature of 1000 °C. The weight percentage can be obtained from the products produced from the combustion process. The data of the combustion analysis of gellan gum and GG-GA beads with different concentrations of GA were recorded.

TGA-DTG is use to determine the compositions and to investigate the thermal behaviour of the samples by measuring the amount and rate of changes in the weight of a material as a function of temperature or time under controlled heating atmosphere. The change of mass of the sample was analyzed by using Perkin-Elmer THA 700 thermal analyzer. The thermal analysis of the samples was conducted in the range of 35 °C to 1000 °C with a constant heating rate of 10 °C/min under nitrogen atmosphere.

In-vitro release study was carried out by using UV-Vis Spectrophotometer Perkin Elmer UV-Vis LAMBDA 20. Firstly, buffer solution was prepared at pH 6 by dissolving 41.83 g of sodium acetate in 300 ml of distilled water. The solution was stirred until it was fully dissolved. Then, 1.0 M of acetic acid was added drop wise until the solution reached pH 6. After that, distilled water was added to the solution until it reached approximately 500 ml while maintaining the pH. 10 g of 1.6 GG-GA were added to this solution. For every 5 minutes interval, 3 ml of this buffer solution was taken by using a syringe. This reaction was continued for one week. This buffer solution was then used for further analysis by using UV-vis. The controlled release study of GG-GA beads at concentration of 1.6 for one week was transferred in the cuvette. The absorbance peak was then observed and recorded at wavelength of 292.4 nm.

Real Sample Analysis

Crabgrass weeds were planted and grown in polybags with open sunlight condition. The plant was watered every day. GG-GA1.6 beads were scattered in the polybag. The reaction of the crabgrass weeds to the beads were observed and analysed.

RESULTS AND DISCUSSION

FTIR Analysis

Infrared spectroscopy was used to determine and identify the functional groups present in the hydrogel beads. The vital usefulness of infrared spectroscopy arises because different chemical structures or molecules produce different spectral fingerprints. In this study, the present of herbicide GA in the gellan gum beads were evaluated to confirm the GA binding into the gellan gum beads. Figure 2 displays the spectra obtained for the GA, GG, and GG-GA beads at different concentrations of GA and the details is presented in Table 2. Based on Figure 2, the spectrum of GA shows the existence of the hydroxyl group (O-H) stretching vibration at the absorption bands in the range of 3000 – 3055 cm^{-1}. The absorption bands at 2968.45 cm^{-1} shows the C-H stretching. The absorption range at peak 1340–1420 cm^{-1} indicates the present of CH_2 symmetrical bending and overlapping of CH_2 and O-H in plane bending. Besides, there is the existence of a broad weak absorption band at 2827.64 cm^{-1} that corresponds to the hydroxyl stretch of carboxylic acid group. The peak located in the range of 1550–1640 cm^{-1} is showing the N-H bending vibration in amide structure. The presence of functional group carbonyl (C-O) appears at 1722.43 cm^{-1}. The

presence of absorption peak at 1465.90 cm^{-1} shows the CH_2 bending vibrations. Most importantly is the presence of (P=O) stretching at absorption band of 1280 – 1300 cm^{-1} showing the active ingredient in GA which is phosphinothricin (PPT) that caused the plant to die by inhibiting the action of enzyme glutamine synthetase [15].

In the spectrum of GG beads, at 3302.13 cm^{-1}, there is the presence of strong broad peak that correspond to the stretching frequency of hydroxyl group, -OH that are presence in alcohols and carboxylic acids. For GG beads containing GA, it was shown to have almost similar wavenumber which is in the range of 3292–3304 cm^{-1}. The peaks of O-H group for GG and GG-GA beads have the same intensity from the Figure 2. At wavenumber 2937.59 cm^{-1}, C-H bending group has shown the absorption while in the GG-GA, the absorption can also be seen in the range of 2937-2943 cm^{-1}. The absorption band at 2885.51 cm^{-1} was attributed to the carboxyl, COOH group that can also be seen in the range of 2885-2887 cm^{-1} in GG-GA. Moreover, due to the presence of glycosidic link in the GG beads, there is a weak absorption peak at 1616.35 cm^{-1} that is correspond to the C=O stretching. For the gellan gum beads loaded with GA, there is the shifting of the carbonyl, C-O stretching at 1633.71 cm^{-1}. From the absorption band in the spectrum of GG, C=O shift can be seen at 1413.82 cm^{-1} that is due to the carboxylate functional group. At different concentrations of GA for GG-GA beads, shifting of C=O appeared in the range of 1411–1413 cm^{-1}. The strong and sharp peak of the carbonyl group is because of the large dipole of the bond. The presence of narrow and sharp peak at 1033.85 cm^{-1} shows the functional group from C-O stretching vibration that was presence in alcohol and carboxylic acid. The same goes to the spectrum for GG-GA beads where the C-O stretching can be seen in the range of 1031-1033 cm^{-1}. To prove the existence of GA in the GG beads at different concentrations, there is the presence of (P=O) stretching at 1296.16 cm^{-1}. However, the narrow peak located in the range of 1595-1639 cm^{-1} that was correspond to the N-H bending in amide group of GA has a weak absorption intensity due to the hindrance from the presence of water in GG-GA beads. The significance ability of hydrogel in this study is to absorb water that arises from the hydrophilic functional group that was presented by carboxyl and hydroxyl group [7].

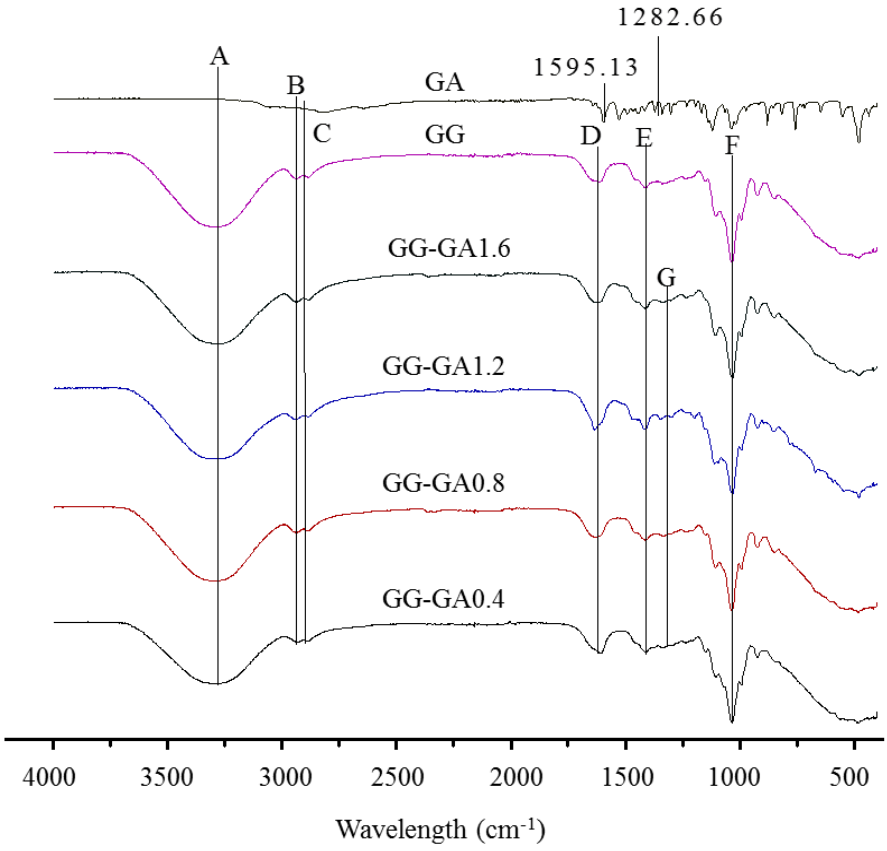

Figure 2. FTIR spectra of GA, GG, GG-GA beads at different concentrations of GA.

Table 2. FTIR details of GG and GG-GA beads at different concentrations of GA.

Type of vibrations	Sample				
	GG	GG-GA0.4	GG-GA0.8	GG-GA1.2	GG-GA1.6
(A) Hydroxyl, O-H stretch	3302.13	3304.06	3294.42	3292.49	3304.06
(B) Alkane, C-H	2937.59	2937.59	2939.52	2943.37	2939.52
(C) Carboxyl, COOH	2885.51	2887.44	2887.44	2887.44	2885.51
(D) Carbonyl, C=O stretch	1616.35	1608.63	1637.56	1633.71	1627.92
(E) C=O shift	1413.82	1411.89	1413.82	1411.89	1413.82
(F) C-O stretch	1033.85	1033.85	1033.85	1031.92	1031.92
(G) Phosphoric acid, P=O	-	1296.16	1296.16	1296.16	1296.16
Amide, N-H bending	-	1595-1639	1595-1639	1595-1639	1595-1639

CHNS Elemental Analysis

A CHNS analyzer is a scientific instrument use to determine the contents of carbon, hydrogen, nitrogen and sulphur in the GG powder, GA powder, GG beads and GG-GA beads. Table 3 present the data obtained for this analysis. Based on Table 3, the contents of carbon, hydrogen, nitrogen and sulfur in gellan gum powder were 35.57%, 5.465%, 0.0821% and 1.492% respectively. In GA powder, the presence of C, H and N were observed to be 29.84%, 7.146% and 13.69% respectively. There was 0% content of sulfur in GA showed that there is no sulfur content in GA. Besides, the C and H content of the GG beads were 30.01% and 7.072% which shows the increase in amount due to the presence of polysaccharides in gellan gum beads. The content of hydrogen was found to be high due to the hydroxyl group, O-H in the hydrogel structure. Nitrogen content is smaller because of the process of fermentation and hindrance from the water molecule. Moreover, there is an increase in the percentage content of carbon, hydrogen, nitrogen and sulfur of the GG beads loaded with GA compared to the GG beads without GA. This can be well explained to show the successful incorporation of the active ingredient of GA into the gellan gum beads [16]. Carbon content is observed to increase with further increase of GA content. The percentage content of nitrogen also increases starting from 0.656% for GG-GA0.4 to 5.107% for GG-GA1.6 beads. This is due to the presence of nitrogen in GA and as the concentration of GA increases, the percentage content of nitrogen also increases. In other words, higher concentration of GA will result in the higher amount of elements in the compound [17]. The beads that were picked at random to be sent for analysis might influence the results of the contained elements because the weight of the chosen beads might differ for all the beads that were prepared.

Table 3. The percentage contents of C, H, N and S in GG powder, GA powder, GG beads and GG-GA beads at various concentrations of GA.

Sample	**Carbon (%)**	**Hydrogen (%)**	**Nitrogen (%)**	**Sulfur (%)**
GG	35.57	5.465	0.082	1.492
GA	29.84	7.146	13.69	0
GG beads	30.01	7.072	0.134	1.027
GG-GA0.4	30.44	7.367	0.656	1.094
GG-GA0.8	30.26	7.354	2.015	1.085
GG-GA1.2	30.67	7.541	1.989	1.162
GG-GA1.6	32.18	7.603	4.107	1.168

Thermogravimetric Analysis

Thermogravimetric analysis is a method of thermal analysis in which changes in physical and chemical properties of materials such as changes in weight loss are measured as a function of increasing temperature. GG and GG-GA beads were heated from 45 °C to 600 °C. The thermograms are shown in Figure 3 and the details of thermal analysis of GG and GG-GA beads are summarized in Table 4. Figure 3a shows that GG beads experiences three stages of weight loss while GG-GA beads (Figure 3b to Figure 3e) experiences a two stages of weight loss from the thermogram. The first weight loss was observed at ~100 °C that is due to the loss of residual water or moisture from the samples and can be well explain by the loss of weight in terms of the loss of plasticizers, small molecular weight and volatile liquid components in the samples [18]. The thermogram shows that GG beads undergoes the first thermal decomposition at 46.07 °C–169.15 °C with a total percentage of 9.29% mass loss. The second stage starts at 171.40 °C–382.29 °C with a total percentage of 54.181% that correspond to the decomposition stage of the hydrogel beads. The third stage shows about 27.32% weight loss at 383.04 °C-543.8 °C that can be well explained by the removal of the loosely held interlayer between the molecules in the hydrogel.

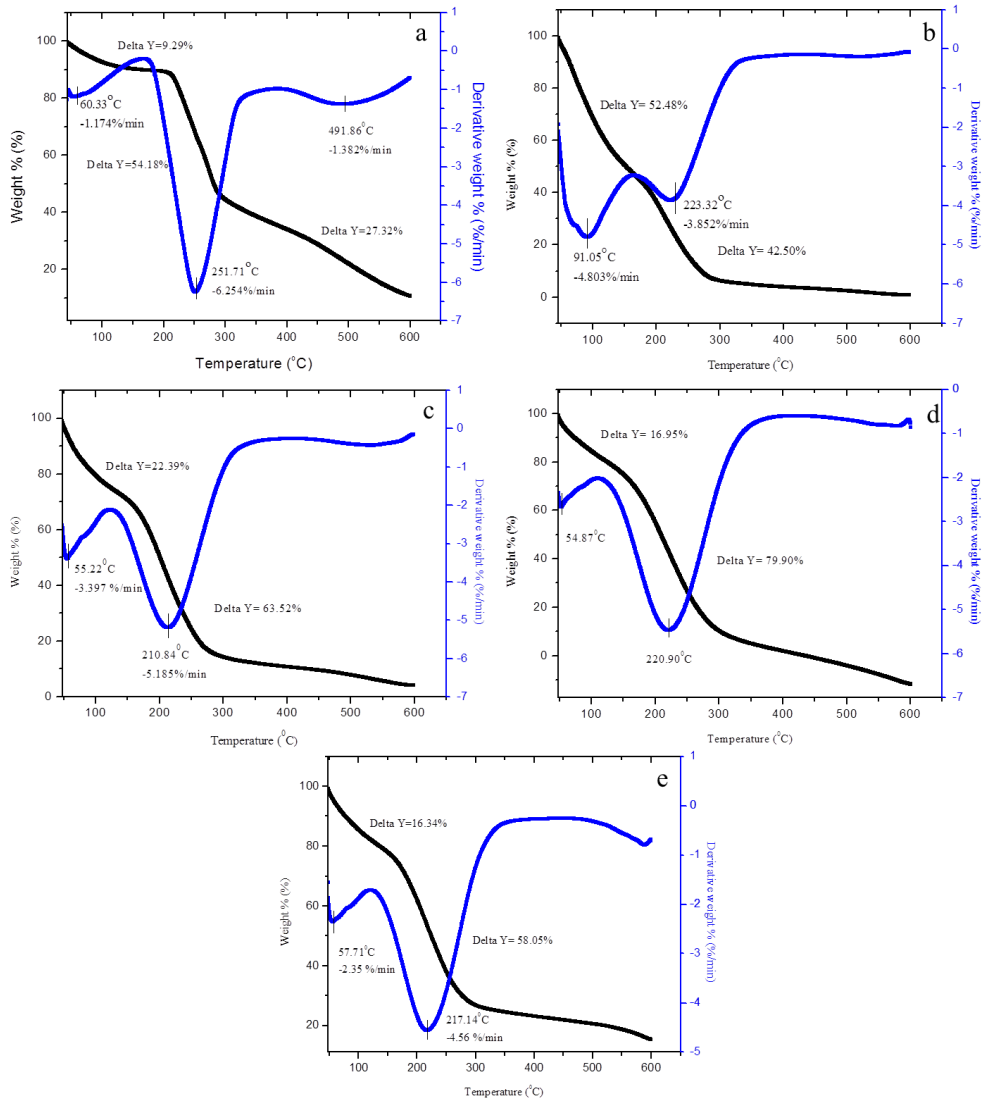

Figure 3. TGA-DTG thermograms of (a) GG beads, (b) GG-GA0.4, (c) GG-GA0.8, (d) GG-GA1.2 and (e) GG-GA1.6.

Table 4. Thermal decomposition data of GG-B and GG-GA beads.

Sample	Stage number	Temperature (°C) from TGA	Temperature (°C) from DTG	Mass loss (%)
GG	1	46.07– 169.15	60.33	9.29
	2	171.40– 382.29	251.71	54.18
	3	383.04-543.8	491.86	27.32
GG-GA0.4	1	45.69 – 165.93	91.05	52.48
	2	167.03 – 396.03	223.32	42.50
GG-GA0.8	1	49.19 – 124.26	55.22	22.40
	2	125.91 – 383.44	210.84	63.52
GG-GA1.2	1	48.48 – 112.32	54.87	16.95
	2	113.96 – 393.79	220.90	79.90
GG-GA1.6	1	50.04 – 124.55	57.71	16.34
	2	125.10 – 386.97	217.14	58.05

TGA graph of GG-GA beads reveals the initial loss of mass of 52.48% (GG-GA0.4), 22.40% (GG-GA0.8), 16.95% (GG-GA1.2) and 16.34% (GG-GA1.6). The introduction of GA to GG brought the impact towards the thermal behaviour of the hydrogels. This shows that when concentration of GA increases, the initial loss of mass decreases that indicate the interaction between the GA molecule and gellan gum. The second stage then showed a loss of mass at about 42.50% (GG-GA0.4), 63.52% (GG-GA0.8), 79.90% (GG-GA1.2) and 58.05% (GG-GA1.6) are observed and associated with the sample degradation and loss of polymer chains in the samples [19]. These show the successful incorporation of GA onto the polymer chains.

The DTG curve provides information about the temperature range in which the sample degrades or lost in derivative weight percentage. The point at which the peak starts showing the degradation temperature of the component while the point where the peak ends indicate the temperature at which the component is lost. The lowest point in the peaks represents the highest mass loss rate with respect to temperature. The presents of the unique peaks of these degradations were observed from the lowest point in the peaks at 251.71°C (GG), 223.32 °C (GG-GA0.4), 210.84 °C (GG-GA0.8), 220.90 °C (GG-GA1.2) and 217.14 °C (GG-GA1.6). From the TGA curve, it was clearly seen that the hydrogel beads with the highest concentration of GA decomposed at the lowest temperature compared to the hydrogel beads with the lowest GA concentration content. Higher concentration of GA limits the absorption of moisture into the GG beads. Therefore, GG-GA1.6 beads will degrade slowly due to the formation of the rigid structure. Based on their DTG curve as well, the lowest point in the peak of GG beads with the highest concentration of GA was lower than that of the lowest content of GA. This means that the thermal stability of the gellan gum beads containing GA decreases when concentration of the GA increases [20]. Moreover, GG is observed to have the highest degradation temperature than GG-GA beads.

UV-vis and Real Sample Analysis

Release study of the GG-GA1.6 was conducted in the buffer solution at pH of 6 which is resembled to the condition of soil over 6 days at room temperature to study the controlled release of GA from the GG beads. Hydrogels are hydrophilic polymer network that can absorb large amount of water that led to the increase in volume [21]. During the immersion, the beads were in contact with the buffer solution. The samples of buffer solution containing beads that release GA were taken every minute and were evaluated by using UV-Vis spectroscopy. This was done to obtain the absorbance for each sample over time. The data was then used to calculate the percentage release of GA over time. Figure 4 shows the release profile of GG-GA1.6 and it showed a rapid release on the first day of experiment. But at around 420 minutes at the first day, a much slower release was observed. Then, on the 2nd day of experiment, at 1980 minutes, a slightly increase in percentage release was observed from 65% to 71% at 2100 minutes. After that, the release of GA showed much slower than on the first day until it reached 7260 minutes on the 6th day.

The amount of accumulated release for GG-GA1.6 and the time taken to achieve equilibrium release was observed to be 90% at 7260 minutes on the 6th day of experiment. From the observation, it was clearly shown that the contents in the polymer network of hydrogel can diffuse out into the immersed buffer solution and same goes with the solution that able to enter the hydrogel beads that causes the hydrogel to swell until it reached the equilibrium state. This is due

to the cross-linking of hydrogel which the content of hydrogel will increase as the cross-link increases. The cross-link formation is a network in which the solvent enters and did not dissolve but it tends to swell that causes the increase in the total volume of the network [22]. High concentration of GA had made the structure of the hydrogel beads become more rigid because the binding of GA compound to the host, gellan gum hydrogel have completely covered the surface of the guest species [23].

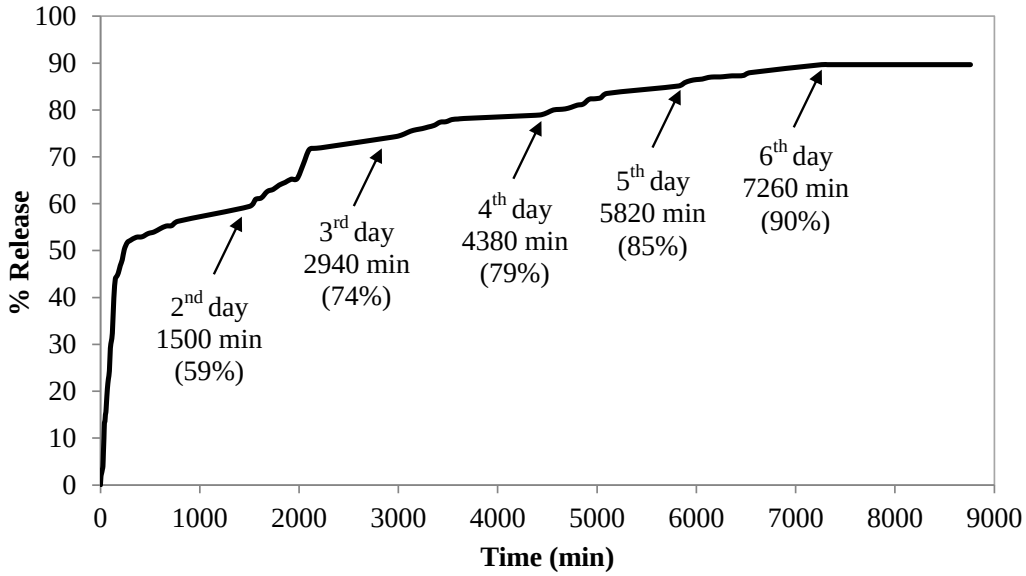

Figure 4. The release profile of GG-GA1.6 beads for 6 days.

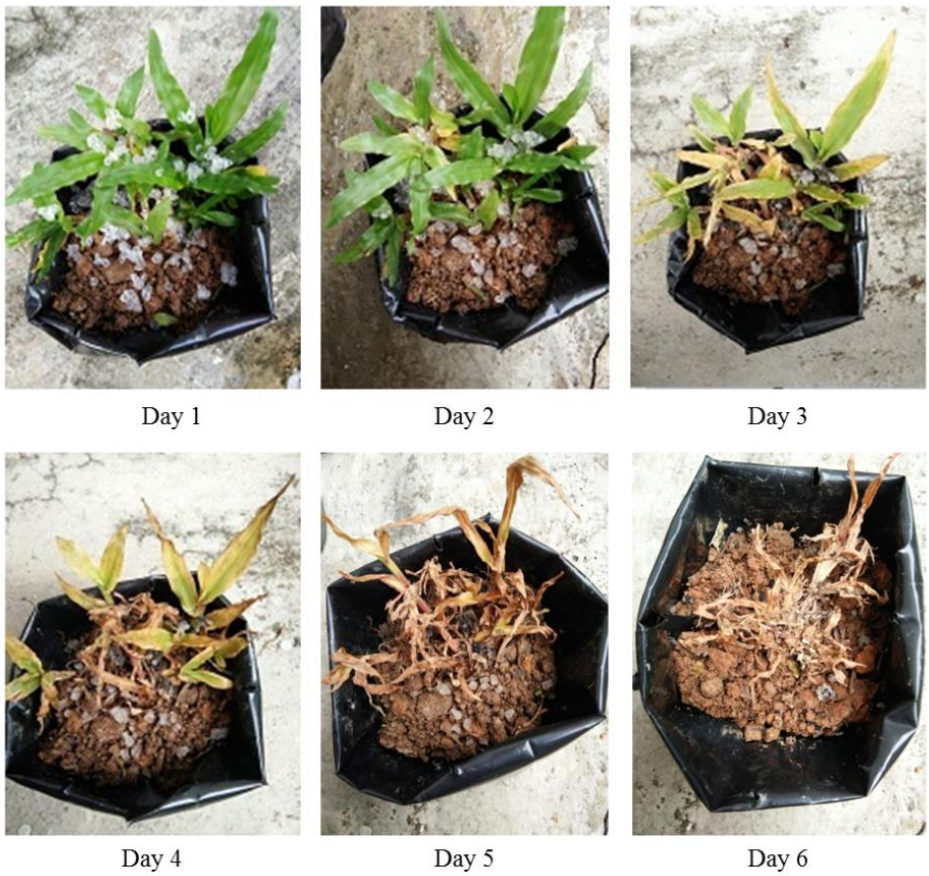

Figure 5. The weeds (crabgrass) died completely on the 6th day after being in contact with GG-GA1.6 bead.

Figure 5 shows the weeds died on the 6th day after being in contact with the GG beads with 1.6 M concentration of GA. This study shows the equivalent response to the release study experiment that the amount of accumulated release for GG-GA1.6 beads to achieve equilibrium release was observed to be on the 6th day of experiment. The porosity in the GG beads had make it for fast release of incorporated GA for controlled release of herbicides GA into the weeds [24].

CONCLUSION

In this study, the GG beads and the GG-GA beads with different concentrations of GA have been successfully prepared and characterized using FTIR, CHNS, TGA-DTG and UV-Vis spectroscopy. Different concentrations of GA in the range of 0.4 M to 1.6 M were managed to be incorporated into the GG beads by using ionotropic gelation method. This study was able to observe the controlled release process for agricultural purposes where herbicide GA was used as a guest species to be incorporated into the host of GG beads. FTIR analysis had confirmed from the GA powder, GG and GG-GA that the GA with various concentrations was successfully bind into the GG beads. This is caused by the presence of both functional group of GA and GG in the gellan gum beads that contain different concentrations of GA. The CHNS analyzer had determine the percentage of elements in the hydrogel beads that shows an increase in the percentage contents of carbon, hydrogen, nitrogen and sulfur. When the concentration of GA increases, the percentage of elements presence in the hydrogel beads also increases. The presence of nitrogen in GA had caused the increase in the percentage content of nitrogen in higher concentration of GG-GA beads. Therefore, these observations can confirm the successful incorporation of GA into the GG beads. Conclusively, the GG-GG beads show a potential to be applied with the control release technology for the agricultural application.

ACKNOWLEDGEMENTS

The author thanks Universiti Putra Malaysia for the financial support through the GP-IPS 9456600 grant.

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