Synthesis of Superabsorbent from Wheat Straw Cellulose and Its Application on Eggplant

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Abstract

Despite the many transformations taking place in Myanmar, its agricultural sector is lagging. Increasement in agricultural productivity is urgently needed. In this research, superabsorbent was prepared by graft copolymerization with acrylamide (AM) and wheat straw cellulose using N,N-methylene-bis-acrylamide (NNMBA) as a cross-linker, potassium persulphate (KPS) as initiator and bentonites as inorganic compound. Wheat straw cellulose was prepared by soda process. The various cellulose to acrylamide ratioswas applied for graft copolymerization at 65°C. The morphologies and structure of the wheat straw cellulose and superabsorbent were characterized by Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and X-rays diffraction (XRD) method. The effect of cellulose and acrylamide ratio on grafting efficiency and swelling degree and effect of superabsorbent on plant growth parameters were studied. Eggplant (*Solanummelongena*) was used as cultivar for superabsorbent application. The results indicated that the sample with superabsorbent synthesized by cellulose to AM ratio (1:3), 0.5 wt % KPS and 0.1 wt % NNMBA produced a high yield.

Keywords:Superabsorbent, Cellulose, Eggplant, Growth parameters.

Introduction

Superabsorbent is a new class of polymeric material with strong hydrophilic groups and can absorb 100- 1000 times water of its own weight, [6]. Owing to its super strong water absorption ability, it has been extensively used in agriculture and forestry construction, medical and public health and daily life supplies. [14]. When superabsorbent polymers (SAPs) are incorporated with soil, it is resumed that they retain large quantities of water and nutrients. These stores water and nutrients release as required by the plants. Thus, plant growth could be improved with limited water supply [13].

Myanmar is an agricultural country and wheat production by year is 1000 metric tons. Wheat straw (WS) is an abundant, renewable and inexpensive whose main components are cellulose, hemicellulose and lignin [10]. So it was selected as raw material for cellulose production.Wheat straw consisted of natural cellulose (32.1 %), hemicellulose (29.2 %), lignin (16.4 %) and other components 22.3 %. It is one of the best-known fiber crops [8]. Cellulose is natural polymer that has biodegradable, biocompatible and non-toxic properties. Cellulose is possible to develop as superabsorbent polymer through grafting modification to the main backbone of cellulose [7].

Superabsorbent polymers (SAPs) are hydrophilic and three dimensional networks that exhibit the ability to highly swell in water and retain significant amount of water within the structure [7]. SAPs are widely used in many applications including

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hygienic products, agriculture, waste water treatment and heavy metal removal [10]. Furthermore, SAPs may be an excellent soil conditioner, it will affect the physical, chemical and biological properties of the soil as well as on plant growth parameters [8].

In this study, wheat straw cellulose was used as skeletal material and acrylamide monomer was expected to graft on the structural bodies to crosslink into superabsorbent polymer. The grafting of acrylamide onto wheat straw cellulose was performed by free radical polymerization method. The effect of acrylamide monomer concentration on superabsorbent characterization such as grafting efficiency, swelling property in urea and water was attempted to reveal. The present study focused to evaluate the effects of SAPs on growth of eggplant.The aim of this research is to produce superabsorbent from wheat straw forplant growth promoter in agricultural application and to increase the crop yield by using superabsorbent.

Materials and Methods

In this research, wheat straw was collected from Chae-Yar-Taw village, Myinmu Township, Sagaing Region, Myanmar. Wheat straw was used as a raw material. Sodium hydroxide (NaOH) was used to extract cellulose from wheat straw. Acrylamide (AM) monomer as grafting agent, potassium hydroxide (KOH), hydrogen peroxide (H_2O_2) as an impurity removal of wheat straw cellulose, potassium persulphate as initiator, N, N-methylene-bis-acrylamide as cross-linker, bentonite as inorganic compound, sodium hypochlorite, acetic acid and ethanol were used[5].

Preparation of Cellulose from Wheat Straw

The wheat straw (WS) was washed by distilled water and sun dried. The dried straw was cut into small pieces and grinded with a grinder. The wheat straw powder was sieved by using 40 mesh size sieves. Cellulose was prepared by soda process[1,11].

Superabsorbent Synthesis

Cellulose was mixed with distilled water and stirred at 350 rpm at room temperature for about 1 hour. Then acrylamide monomer was added into the mixture and stirred at 65°C for 1 hour to get homogeneous mixture. The resulting solution was refluxed in water bath at 65°C for 30 min. The resulting solution was transferred into the beaker containing certain amounts of NNMBA, KPS and bentonite which was kept stirring with magnetic stirrer at 65°C until pasty product was obtained and then the product was cut into small pieces. Then the samples were dewatered with ethanol and dried at 65°C to constant weight. Experiments were carried out with a variation on cellulose, acrylamide, potassium persulphate and N, N-methylene-bis-acrylamide [7].

Scanning Electron Microscope (SEM) Analysis of Cellulose and Superabsorbent

Scanning electron microscopy was used to study the morphological structures of cellulose and grafted copolymer by detecting the presence of connected microporosity. Original wheat straw cellulose and grafted copolymers were qualitatively analysed by SEM method.

Determination of Grafting Efficiency

The grafting efficiency is the ratio the mass grafted of monomer on cellulose with the initial monomers. The grafting efficiency was determined by using the following equation 1 [2].

$$\text{Grafting Efficiency} = \frac{W_h - W_S}{W_m} \times 100\ \% \qquad (1)$$

where, W_h is the weight of the cellulose-acrylamide graft copolymer, W_s is the weight of cellulose and W_m is the weight of the acrylamide monomer.

Determination of Swelling Degree

The Japanese Industrial Standard K 8150 method has been used to measure the swelling. For determination of swelling degree, superabsorbent was immersed in deionized water for 48 hours at room temperature occasionally stirring. After swelling, the swollen superabsorbent was filtered and the swelling degree was calculated as shown in equation 2 [2].

$$\text{Swelling Degree} = \frac{\text{Wss} - \text{Wd}}{\text{Wd}} \times 100\% \qquad (2)$$

where, W_{ss} is the weight of superabsorbent in swollen state and W_d is the weight of dry superabsorbent.

FT IR Analysis

The Fourier Transform Infrared (FT IR) Spectroscopy was used to identify the functional group of the active compounds based on the peak value in the region of infrared radiation. The FT IR spectra of the original wheat straw cellulose and grafted cellulose-acrylamide copolymer were recorded by FT IR spectrophotometer (Perkin Elmer, UK, L1600400) in the wave number range 400-4000 cm^{-1}.

Crystallization Analyzed by XRD

The crystallization of wheat straw cellulose and superabsorbent were examined by XRD measurement performed on a multiplex 2 kW (Rigaku, Japan) using Cu/K-alpha (λ = 1.54056 Å) at 40 kV and 50 mA.

Scherrer equation was used for calculating crystallite size in plane.

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (3)$$

where λ is wavelength of X-ray tube λ = 1.54056 Å, β is the pure integral of width of the reflection at half maximum height (FWHM, full width at half maximum) of 012 peak at 2θ about 22° and 0.89 is the Scherrer constant.

$$\%Cr = \frac{\text{Icrystallinity} - \text{Inoncrystallinity}}{\text{Icrystallinity}} \times 100 \qquad (4)$$

Where $I_{crystallinity}$ is the intensity at maximum of crystalline peak ($22^{\circ}<2\theta<23^{\circ}$) and $I_{noncrystallinity}$is the intensity at minimum ($16^{\circ}<2\theta<17^{\circ}$).

Water Retention Test for Superabsorbent Copolymer

The usedsoil was firstly dried in oven for two days at 60 ºC to remove moisture from soil. The superabsorbent was mixed in container with 300 g of soil. The mixture was irrigated with 200 ml of water, and the container was weighed at different set intervals. This measurement was carried out at room temperature. The weight loss of the mixtures against time was calculated at every interval time and so water retention capacity of superabsorbent was obtained. Controlled experiment without superabsorbent was also performed as reference. Water retention (WR) percentage of soil treated with superabsorbent was determined as the following equation 3 [4].

$$WR\,(\%) = \frac{M_1 - M_2}{M_2} \times 100\% \quad \text{———} \quad (5)$$

Where, M_1 is the weight of wet soil at certain interval time and M_2 is the weight of oven dry soil.

Application of Superabsorbent on Eggplant

The pot test of eggplants was carried out at Lun – Taung village, Madayar Township, Mandalay Region, Myanmar, during August to December, 2019.

Sowing the seeds

Eggplant seeds were sowed into the prepared ground and watering daily until seeding.

Preparing soil media

The soil samples were collected from near the Lun – Taung village. The soil was thoroughly mixed with natural fertilizer and cow dung. Each pot was supplied with 1.5 kg prepared soil. Sixteen pot soil media were prepared.

Method and Experimental Design

One month after sowing, one seedling was transplanted in each pot. Superabsorbent polymer (SAP) 5g per 1.5 kg of growth soil media was added to fifteen plant samples. The same watering intervals three days a time were applied in this experiment as shown in table.

Table 1. Types of plant sample treated superabsorbent polymers (SAPs).

Types of sample	Cellulose : AM	Apply SAP (g)	Types of sample	Cellulose : AM	Apply SAP (g)	Type of sample	Cellulose : AM	Apply SAP (g)
B_1	1:2	5	B_6	1:3	5	B_{11}	1:4	5
B_2	1:2	5	B_7	1:3	5	B_{12}	1:4	5
B3	1:2	5	B_8	1:3	5	B_{13}	1:4	5
B_4	1:2	5	B_9	1:3	5	B_4	1:4	5
B_5	1:2	5	B_{10}	1:3	5	B_{15}	1:4	5
						B_{16} control	-	-

The transplanting plants were watered daily for seven days until plants were well established. After seven days, some soils at the bottom of the plants were removed to add SAPs. After that 5g of SAPs were soaked in water for six hours and then filtered the swelling SAPs and added into the bottom of the plants. During the period of flowering and fruiting fermented cattle manure solution were mixed with water and used twice over the given period. Intercultural operations like weeding and pest control of the experiment were carried out when necessary. Every three weeks, equal volume of foliar fertilizer was applied to each plant.

Fig-1. Seedling process

Fig-2. Transplanting the plants

Results and Discussion

Yield of Wheat straw cellulose

Wheat straw cellulose was prepared by soda process using 4% NaOH. The yield of wheat straw cellulose was found to be 58.3%.

Effect of Cellulose to Acrylamide Ratio on Grafting Efficiency and Swelling Degree

Grafting efficiency and swelling degree of superabsorbent with bentonite in urea and water were investigated. The results are shown in Table 2.

Table 2.Effect of Cellulose to Acrylamide Ratio on Grafting Efficiency and Swelling Degree(with bentonite) 0.5 wt % KPS, 0.1 wt % NNMBA

No.	Cellulose : AM	Grafting Efficiency (%)	Swelling Degree (%)	
			Urea	Water
1	1 : 1	78	305.72	254.54
2	1 : 2	80	700.18	450.31
3	1 : 3	81	1600	1050
4	1 : 4	99	1317.64	950

According to the results, grafting efficiency and swelling degree increased with increasing monomer ratio (cellulose to AM ratio 1 : 1 - 1 : 3). At cellulose : AM (1 : 4), it was found that swelling degree decreased. This result could be explained in term of cross-linked density. The increased monomer concentration made more cross-linked density. Higher in cross-linked density reduced the free volume available for swelling by increasing the tightness of the network structure[2]. For agriculture application, swelling property of the superabsorbent network is more important than other factors. The results of swelling capacity showed that superabsorbent of wheat straw cellulose with bentonite had the highest swelling capacity in urea and water. The maximum swelling capacity of wheat straw cellulose superabsorbent in urea and water were 1600 % and 1050 % at cellulose to AM ratio (1 : 3), 0.5 wt % KPS and 0.1 wt % NNMBA.

Characterization of Cellulose and Grafted Copolymer using FT IR Spectroscopy

In Fig. 3, the absorption at 3332.39 cm^{-1} is assigned to the stretching of OH groups which was diminished after graft copolymerization. It can be explained that the partial hydrogen bond of cellulose is destroyed enhancing the new formation of cross-links with acrylamide monomer. The changed spectra can be seen with the peaks at 3833.3 cm^{-1}, 3191.04cm^{-1} in Fig. 4, Those two bands indicate the unsymmetric and symmetric stretching of NH_2 group, which are characteristics of the – $CONH_2$ group present in the acrylamide monomer [9].

The absorption band at 1650.94 cm^{-1} in Fig. 4 is assigned to the stretching of the C = O which indicated the presence of i amide in the grafted copolymer. This absorption band is not observed in cellulose. These changes provide strong evidence of the grafting of acrylamide onto cellulose. The peak at 1023.45 cm^{-1} in Fig. 3 indicates the C – O – C stretching of cellulose. The band observed in at 1416.13 cm^{-1} (Fig. 4) is assigned the stretching CN of grafted copolymer [9].

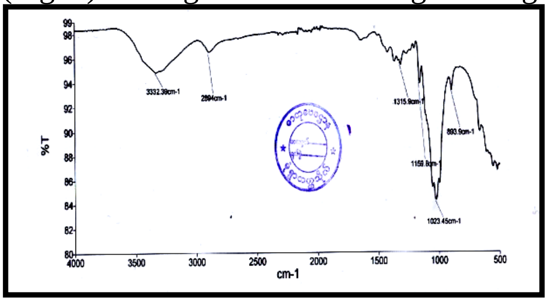


Fig. 3. FT IR Spectrum of Wheat Straw Cellulose

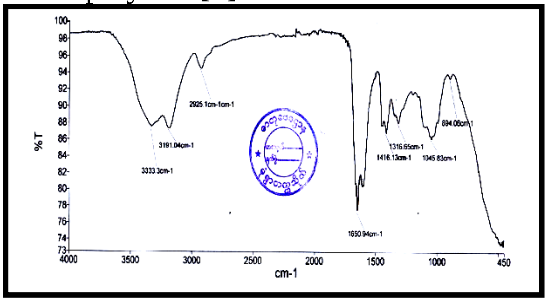


Fig. 4. FT IR Spectrum of Grafted Copolymer

Morphologies of the Superabsorbent

SEM image of WS cellulose and dried superabsorbent nanocomposite are depicted in Fig. 5. It can be observed that WS cellulose displays a fibrous morphology. However, superabsorbent nanocomposite presents an undulant and coarse surface with many microporous holes which can facilitate the permeation of water into polymer network. This indicates that WS superabsorbent nanocomposite has good water absorption[10].

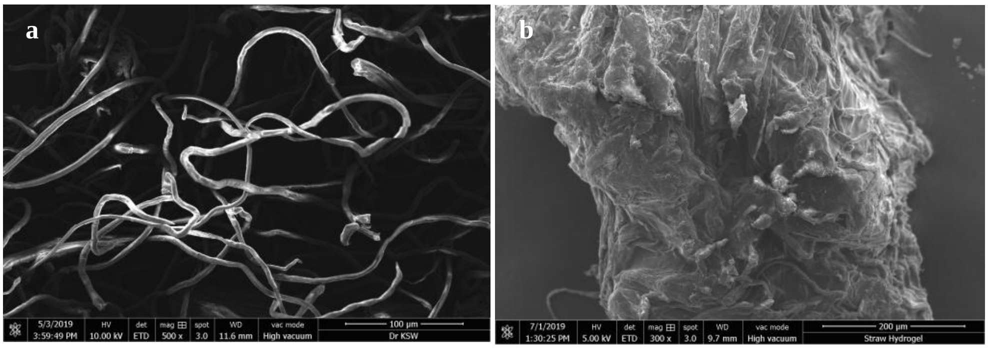
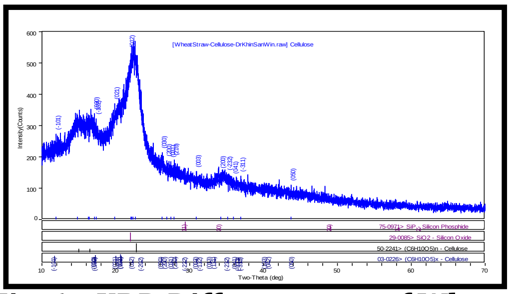


Fig. 5. SEM Image of (a) Wheat Straw Cellulose and (b) Superabsorbent Copolymer

XRD Analysis of the Superabsorbent

XRD patterns of wheat straw cellulose and WS superabsorbent nanocomposite are shown in Fig. 6 and 7. In Fig. 6, it can be seen the diffraction pattern of wheat straw cellulose with sharp peak at 22.33° as intensity of crystalline.The peak at 17.12 ° called intensity of amorphous. The percent crystallinity of cellulose is 32.2% means cellulose is semi- crystalline. The size of cellulose calculated by Scherrer's law was 9.2 nm, which indicates nanocrystal size. Fig. 7 shows that the diffraction pattern of superabsorbent nanocomposite indicates the amorphous structure due to appearance of diffused maximum [4]. The amorphous structure of the superabsorbent nanocomposite will increase the swelling capacity due to its irregular composition, so the solution would be easy to get in and bind with the superabsorbent [5].



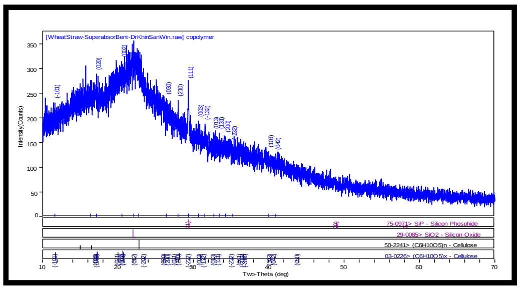


Fig. 6. XRD Diffractogram of Wheat Straw **Fig. 7. XRD Diffractogram of Superabsorbent**

Water Retention in Soil

The addition of micro-porous superabsorbent in soils can markedly increase water holding abilities by absorbing and retaining large amount of water which indirectly increase the nutrient availability in plant roots. Water retention test in soils with and without the addition of superabsorbent was carried out under room temperature and results are shown in Figure (8).

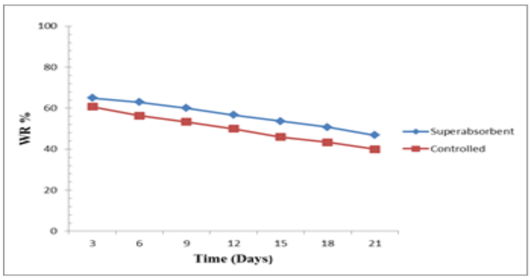


Fig. 8 Water Retention Testin Soil

According to the results, water retention in soil decreased as the time was prolonged and soil containing superabsorbent possessed higher water retention over controlled one. This result indicates that superabsorbent can enhance the water retention capacity in soil**.**

Effect of superabsorbent polymer (SAP) on Eggplant Growth and Yield

In this study, plant growth and yield of eggplant were investigated to know the effect of SAP on plant. The effect of three types of SAPs on the plant height and fruit yield was shown in Table 3. It was found that the plant height of SAP applied samples was higher than control one. Among them, the eggplant height using SAP -2 type, B_7 was the highest, These results indicate that application of SAPs had tremendous effect on growth of eggplant. Figure (9) shows eggplant (a) before (b) after adding SAPs and (c) fruiting stage.

Fig (9) Eggplant (a) before (b) after adding SAPs and (c) fruiting stage

Eggplant was grown with SAP in the soil on (6.9.2019). After about two month flowering process of eggplant started. In addition, the eggplant fruits began to produce in the plant after about two and half month. According to results, it was found that SAP-2 applied sample(B_6 to B_{10}) had earlier flowery and the harvesting period. Results revealed that total fruit weight of SAPs applied plant was higher than control one. It was observed that SAP-2 applied sample(B_6 to B_{10}) had higher fruit yield than other samples. The best producing weight was obtained from plant grownin soil with SAP-2 synthesized by cellulose : AM (1:3), 0.5 wt % KPS and 0.1wt% NNMBA.

Table (3) Effect of SAPs on Eggplant Growth and Yield

Type of Sample	Type of SAP	Plant Height (cm)			Total Fruit Weight/ plant (g)
		After one month	After two month	After three month	
B_1	SAP-1	12.5	29.5	99	936.27
B_2	SAP-1	13	29.5	97	898.10
B_3	SAP-1	12.5	43.5	100	918.10
B_4	SAP-1	10.5	40	92	1000.96
B_5	SAP-1	14	29.5	94	946.92
B_6	SAP-2	14	43	100	1218.30
B_7	SAP-2	16	45	110	1356.80
B_8	SAP-2	14.5	32	92	1110.00
B_9	SAP-2	14.5	34	92	1096.09
B_{10}	SAP-2	14	46	102	1011.96
B_{11}	SAP-3	13.5	29.5	89	990.61
B_{12}	SAP-3	13	33	89	899.21
B_{13}	SAP-3	14	30	91	903.90
B_{14}	SAP-3	10.5	40	98	896.52
B_{15}	SAP-3	10.5	29.5	94	906.21
B_{16}		10	39	88	650.06

Conclusion

A novel superabsorbent, wheat straw cellulose graft copolymer was synthesized via graft copolymerization reaction of wheat straw cellulose and acrylamide using NNMBA as cross-linker and KPS as an initiator. Base on the present study, it can be concluded that superabsorbent polymer (SAP) has progressive impact on eggplant in terms of plant height and total fruit weight. According to the result of eggplant, it showed different responses to SAP synthesized by different cellulose to acrylamide ratio. From this study, it was found that the highest fruit weight (1356.80 g) was recorded in eggplant with application of SAP synthesized by cellulose: acrylamide 1:3, 0.5 wt % KPS and 0.1 wt% NNMBA. In contrast, the lowest yield (650.06 g) was recorded in control plant. Therefore it can be said that application of SAP can improve total fruit weight of eggplant nearly twice than control. The superabsorbent polymer found applicable in agriculture, especially in drought prone areas or water stress condition where the availability of water is less.

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