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SYNTHESIS OF CHITOSAN BASED POLYVINYLALCOHOL HYDROGEL FOR LOADING WITH CONTROLLED-RELEASED FERTILIZER

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Abstract

The use of controlled-released fertilizer hydrogel has become a new trend to save fertilizer consumption, and to reduce environmental pollution and safety application in agriculture. In agriculture, loss of nutrient elements is one of the large problems. So controlled-release is a method used to slove this problem. This paper describes the phosphorus release behavior of controlled-released fertilizer (CRF) hydrogels. The CRF hydrogel was prepared by mixing chitosan solution, polyvinyl alcohol hydrogel and fertilizer solution. The swelling ratio, water retention and fertilizer release behavior of prepared CRF hydrogel in water and soil were investigated. Therefore, the chemical nature was important that affected the degree of swelling of the hydrogel. Cultivation of chilli and maize seed tested using the various amount of prepared CRF hydrogel samples. The investigation of agronomical characters of the generation seeds were described.

Keywords: controlled-release fertilizer, hydrogel, chitosan, polyvinyl alcohol

Introduction

Nowadays, fertilizer specially NPK is the vital material for the grough of crops and plays an important role in food security. These NPK fertilizers are added into soil to save the necessary nutrients for plant growth. However, various environmental and economic drawbacks associated with the use of conventional fertilizers have become a focus of worldwide concern. The main problem facing the agrochemical industry is the huge loss of fertilizers added to the soil. One method for overcoming these shortcomings involves the use of slow-release fertilizers, which has demonstrated many advantages over the conventional types, such as decreasing fertilizer loss rate, supplying nutrient sustainably, lowering application frequency, and minimizing potential negative effects associated with over dosage (Diwani *et al.*, 2013).

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The growth of plants and its quality are mainly a function of the fertilizer quantity and water used. Depending on application methods and soil condition, some amount of the nutrients from the conventional fertilizers cannot be absorbed by plants and is lost to the environment. This phenomenon not only causes large economic and resource losses, but also causes serious environmental pollution (Salmiaton and Firoozeh, 2015).

Controlled release is a method that release or deliver a compound in a response of time. This method firstly practiced in medical field to optimize the dosage, to minimize the cost and toxic effect, and to increase the drugs overall efficiency. In agriculture field, this method is used to make a controlled release fertilizer. The advantages in this method are (1) to minimize the effect of excess fertilizer, (2) to decrease the operational cost, (3) to release the fertilizer directly to the root of the plants, (4) to decrease the fertilizer loss, and (5) to reduce water and soil pollution (Han *et al.,* 2008).

Chitosan, the second great amount of natural polysaccharide on earth crust, as a compound of chitin deacetylation is a biodegradable and non-toxic material for environment. Chitosan is widely used to produce controlled release materials in various fields, particularly in controlled-released fertilizer (CRF) manufacturing. Chitosan can be successfully processed by a variety of chemical reactions owing to its. Few works have applied chitosan particles in the agricultural field such as incorporation of NPK fertilizer into the chitosan nanoparticles to make fertilizer consumption more efficient. Furthermore, chitosan coated NPK compound fertilizers have demonstrated controlled release properties (Roshanravan *et al.*, 2015).

In this study, the controlled- released fertilizer (CRF) hydrogels were prepared from chitosan, polyvinyl alcohol and polyvinyl alcohol - chitosan, using glutaraldehyde as a crosslinker. Water absorbency, water retention and phosphorus release behavior of such the CRF hydrogels in water and in soil were investigated. The water and soil samples were analyzed for total amount of phosphorus by UV-visible spectrophotometry. In addition, the phosphorus release mechanism of each CRF hydrogel was investigated.

The objective of this research was to obtain materials possessing controlled release properties. This was done by covering granules of mineral fertilizer with a layer of chitosan as an example of biodegradable, natural polymer.

Materials and Methods

Materials

Commercial chitosan sample from shrimp shell was purchased from Asian Technology Groups Co., Ltd., Local Industry, Yangon, Myanmar. Polyvinyl alcohol (Molecular weight 20, 000, degree of hydrolysis 98%) was purchased from the British Drug House (BDH) Chemical Ltd, England. All other chemicals used were of analytical reagent grade. In all investigations, the recommended standard methods and techniques involving both conventional and modern methods were provided.

Preparation of Controlled-Release Fertilizer (CRF) Hydrogel Film

Chitosan solution 1% w/v was prepared by dissolving 1 g of CS in 100 mL of 1% v/v acetic acid to get a clear solution. Clear solution of PVA 20 % w/v in water was put in an autoclave for 20 min at 121 ºC and 0.1 MPa. The fertilizer solution was prepared by dissolving 2.0010 g of ammonium nitrate, 3.3015 g of diammonium phosphate and 2.5275 g of potassium nitrate to make 100 mL aqueous solution. Crosslinking solution was prepared by mixing 50 % methanol, 10 % acetic acid, 1.25 % glutaraldehyde and 10 % sulphuric acid together, making up a 3:2:1:1 weight ratio solution.

The prepared CS solution , PVA solution, glutaraldehyde, fertilizer solution and crosslink solution were mixed with appropriate proportions under constant stirring to obtain a series of CRF hydrogel films. After homogeneous mixing, the gel was formed within 30 min. The CRF hydrogel solutions were kept for sufficient time to remove any bubble formation and were dried on melamine plates at 40 °C in vacuum for overnight.

Determination of Degree of Swelling

The prepared CRF hydrogel film (1×1 cm^2) were dipped in 25 mL of water at room temperature. The swelling time was kept as various time intervals. The films were removed from water, blotted gently with tissue paper and weighed. Based on these values, swelling (%) were determined. Each experiment was replicated for three times. The degree of swelling was calculated by the following equation and the results are shown in Table 1 and

Figure 1. DS (%) = $\frac{W_s - W_d}{W_d} \times 100\%$, where W_s and W_d referred to the weight of swollen and dry CRF hydrogels, respectively.

Determination of Water Retention of Soil

A dry sample of CRF hydrogel was buried in dry soil, which was placed in a cup (A). The other dry soil without CRF hydrogel was placed in an identical cup (B) and then each cup was weighed (W). After that, deionized water was added into both cups and reweighed (W_o). The cups were kept under identical conditions at room temperature (Figure 1) and were weighed every day (W_t) over a period of 30 days. Water retention (% WR) of soil was then calculated by the following equation (Cheng and Sun, 2005).

$$WR\ (\%) = \frac{W_t - W}{W_o - W} \times 100\%$$

Figure 1: Experiment for determination of water retention of soil

Determination of Phosphorus Release Behaviors

The release behaviors of phosphorus from the CRF hydrogels, both in deionized water and in soil, were investigated by UV-visible spectrophotometry. A 5.00 mL fertilizer sample solution was pipetted into a 25.00 mL volumetric flask, and then 5.00 mL of molybdovanadate reagent was added. Deionized water was also added to make a 25.00 mL solution. After 30 min, at the room temperature the absorbance of the sample solution was measured at a wavelength of 420 nm by UV spectrophotometer. The amount of phosphorus in the sample solution was calculated using the calibration curve (AOAC,1990).

Cultivation of Chilli and Maize Plants

Cultivation of Chilli and Maize seed samples were conducted in plots of beside fields Chemistry Department, University of Yangon. Five experimental plots (1.5' x 2') were prepared for sowing in 10^{th} November 2016. After 14 days, the germination of plant started. Plant height, number of branches per plant and number of pod per branches were measure and counted in the investigation of agronomical characterization of chilli and maize plant. The selected plant was taken to record height, number of branches and number pod in all investigation.

Results and Discussion

Aspect of Degree of Swelling of CRF Hydrogel Films

The degree of swelling of a series of CRF hydrogel, in form of the water absorbency, films are shown in Table 1 and Figure 2 as a function of immersion time .

As seen in figure the highest degree of swelling of CS-PVA(1:4), CS-PVA(2:3), CS-PVA(3:2) and CS-PVA(4:1) are 877.97, 812.91, 728.64 and 674.23 % respectively. The water absorbency of the hydrogels increases with increasing PVA content. Hydrophilic groups are responsible for such results. This is because PVA is more hydrophilic than CS. Thus, the higher PVA content within the CRF hydrogels caused the higher water absorbency.

It can be seen that all the CRF hydrogels reached maximum amount of swelling in 90 min with in 5 h. The swelling ratio of CS-PVA(1:4) system was found to be higher than other systems.

Table 1: Degree of Swelling of CRF Hydrogels

Time (min)	Degree of Swelling (%) of CRF Hydrogels			
	CS-PVA (1:4)	CS-PVA (2:3)	CS-PVA (3:2)	CS-PVA (4:1)
30	251.47	234.12	197.45	176.29
60	763.80	720.65	630.98	569.29
90	877.97	812.91	728.64	674.23
120	847.94	803.45	709.91	654.47
150	730.75	727.12	692.11	562.19
180	726.43	727.01	672.12	539.98
210	687.11	675.44	614.54	400.19
240	689.25	687.76	524.20	386.13
270	630.32	543.13	510.22	378.98
300	539.99	537.23	493.12	298.87

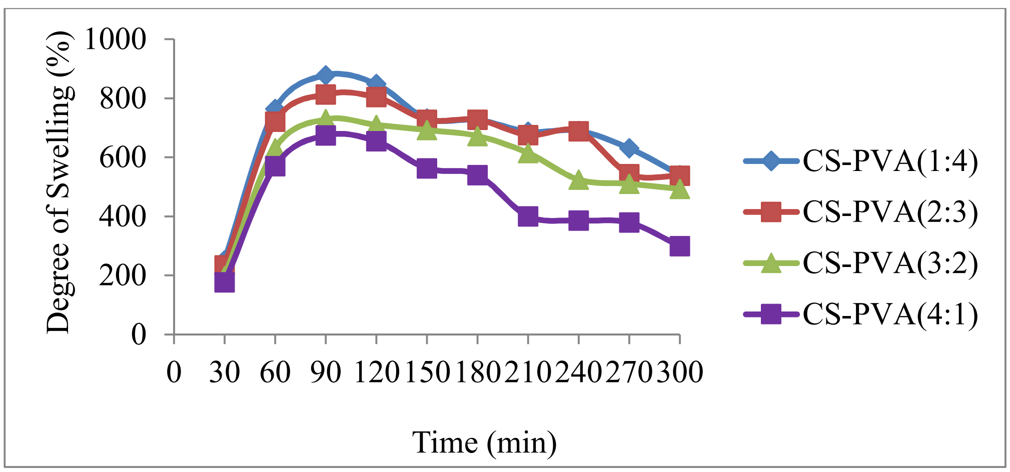

Figure 2: Degree of swelling of CRF hydrogels consisting of different ratios pH1

Aspect of Water Retention Behavior of CRF Hydrogel Films

Table 2 and Figure 3 represent water retention behavior of the soil containing CRF hydrogels. The CS-PVA ratios (1:4, 2:3, 3:2, 4:1) were investigated for water retention of the soil. Table 2 and Figure 2 show that on the 14 days, the soil containing CS-PVA(1:4), CS-PVA (2:3), CS-PVA (3:2) and CS-PVA (4:1) hydrogels have remained water around 15, 12, 10 and 3 % respectively. Therefore the CS-PVA(1:4) ratio of CRF hydrogels affected the highest water retention and CS-PVA(4:1) ratio of CRF hydrogel affected the lowest water retention. That is the water retention of the soil increased with increasing PVA content.

Table 2: Water Retention of Soil Containing CRF Hydrogel Films

Time (Day)	Samples			
	CS-PVA (1:4)	CS-PVA (2:3)	CS-PVA (3:2)	CS-PVA (4:1)
1	89	87	78	68
2	77	74	73	66
3	72	68	61	57
4	60	59	55	52
5	58	52	47	42
6	40	34	31	28
7	36	31	29	23
8	34	27	25	21
9	31	25	23	17
10	29	21	19	16
11	26	17	14	11
12	22	15	13	9
13	19	14	11	5
14	15	12	10	3

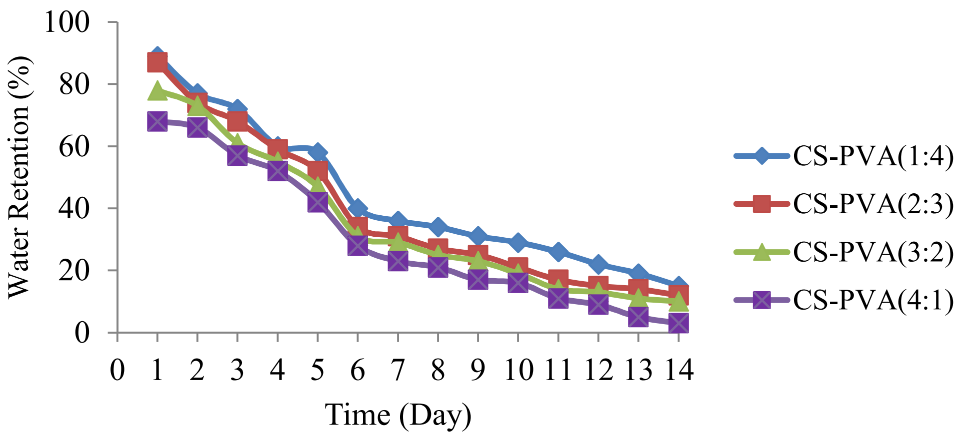

Figure 3: Water retention of soil containing CRF hydrogel films

The Behavior of of CRF Hydrogel Films for Release Phosphorus

The release behaviors of phosphorus of the CRF hydrogels in deionized water at room temperature are shown in Table 3 and Figure 4. It was found that all the CRF hydrogels exhibited initial increased release. The percent cumulative release of phosphorus CS-PVA(1:4), CS-PVA (2:3), CS-PVA (3:2) and CS-PVA (4:1) hydrogels showed of 76, 69, 67 and 63 %, on14th day, respectively. The PVA hydrogels both initial and at equilibrium appeared to show the highest release amount of phosphorus due to its high hydrophilicity. Phosphorus (in the form of diammonium phosphate) in the CRF hydrogels released after the hydrogels absorbed water, leading hydrolysis process taking place.

Table 4 and Figure 5 show the percent phosphorus cumulative release in soil of CRF hydrogels. It was found that the percent cumulative release of phosphorus of CS-PVA(1:4), CS-PVA (2:3), CS-PVA (3:2) and CS-PVA (4:1) hydrogels were 20, 20.8, 22.7 and 25.7 % on the 14th day, respectively. In contrast with phosphorus release behavior in water, the CS-PVA(1:4) hydrogel exhibited the highest percent cumulative release. This is because chitosan is an excellent biodegradable material and is easily degraded by microorganisms and ions existing in soil . Therefore, the existing of different kinds of ions and microorganisms in soil solution, probably increases the degradation rate of the CRF hydrogels.

Table 3: Release Behavior of Phosphorus of CRF Hydrogel Films in Water

Time (Day)	Phosphorus release (%)			
	CS-PVA (1:4)	CS-PVA (2:3)	CS-PVA (3:2)	CS-PVA (4:1)
1	24	21	21	20
2	32	27	26	24
3	34	31	31	26
4	41	39	35	32
5	52	50	47	44
6	62	57	54	51
7	68	63	61	53
8	72	65	64	60
9	75	68	64	61
10	77	72	65	64
11	83	73	71	69
12	81	71	70	69
13	79	69	70	65
14	76	69	67	63

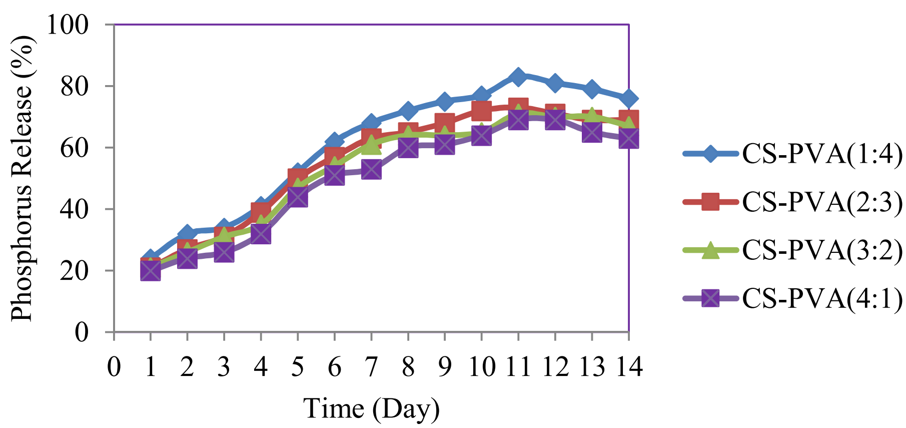

Figure 4: Release behavior of phosphorus of CRF hydrogel films in water

Table 4: Release Behavior of Phosphorus of CRF Hydrogel Films in Soil

Time (Day)	Phosphorus release (%)			
	CS-PVA (1:4)	CS-PVA (2:3)	CS-PVA (3:2)	CS-PVA (4:1)
1	6.0	7.2	7.4	8.5
2	6.5	7.8	8.1	9.4
3	7.2	8.1	8.6	9.7
4	9.5	9.7	10.5	10.6
5	10.2	11.0	11.9	12.6
6	12.4	12.9	13.2	14.2
7	12.9	13.6	14.5	15.3
8	14.0	14.8	15.7	16.7
9	14.9	15.3	16.5	17.2
10	16	16.4	16.9	18.9
11	16.9	16.7	17.3	19.8
12	17.4	17.9	18.4	20.1
13	18.5	19.2	19.9	22.3
14	20.0	20.8	22.7	25.7

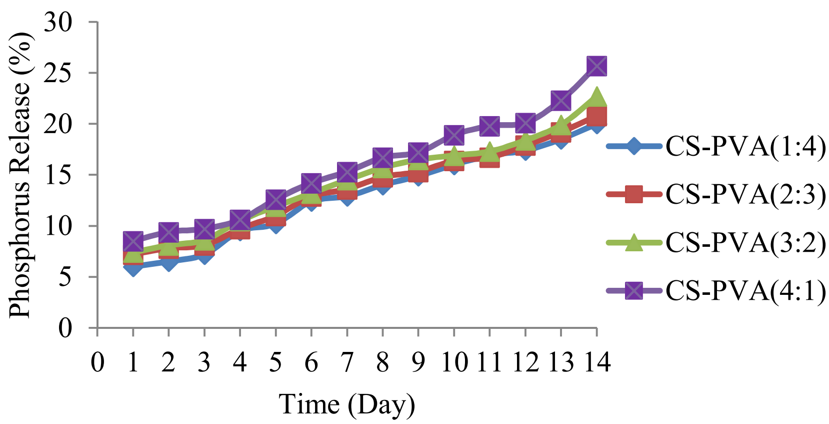

Figure 5: Release behavior of phosphorus of CRF hydrogel films in soil

Application

The growth of plants Chilli using CRF hydrogel were recorded by photos in Figure 6. As seen in Table 5, in all cultivation of the agronomical characteristics of chilli plant, CRF hydrogel showed longer plant height, increasing number of branches and pads when compared with control. According to the data, CS-PVA (3:2) and CS-PVA (4;1)are the more effective than the other hydrogel films. So all CRF hydrogels films have the greater cumulative effect than the control. The growth of plant Maize using CS-PVA (3:2) CRF hydrogel were further investigated by photos in Figure 7. As seen in Figure 7, CS-PVA (3:2) CRF hydrogel showed longer plant height. It can be concluded that all CRF hydrogel films have the greater cumulative effect and these by reducing the environmental pollution.

Control CS-PVA (1:4) CS-PVA (2:3) CS-PVA (3:2) CS-PVA (4:1)

(A) Growing chilli after 1 months

Control CS-PVA (1:4) CS-PVA (2:3) CS-PVA (3:2) CS-PVA (4:1)

(B) Growing chilli after 1.5 months

Control CS-PVA (1:4) CS-PVA (2:3) CS-PVA (3:2) CS-PVA (4:1)

(C) Growing chilli after 2 months

Figure 6: Growing plants of Chilli (A) after 1 month (B) after1.5 months (C) after 2

Table 5: Agronomical Characteristic of Chilli Plant

Sample	**Plant height (cm)**			**Number of branches per plant**			**Number of pad per branch**		
	Month			**Month**			**Month**		
	1	1.5	2	1	1.5	2	1	1.5	2
control	15.74	19.30	20.32	3	3	3	2	3	4
CS:PVA(1:4)	29.97	33.52	35.81	4	4	4	4	6	7
CS:PVA(2:3)	30.73	34.54	36.83	4	4	4	6	8	11
CS:PVA(3:2)	33.27	34.79	37.08	4	6	6	6	8	13
CS:PVA(4:1)	33.27	35.05	37.59	4	6	6	7	8	13

CS-PVA (2:3)

(A) Growing maize after after 20 days , (15.24 cm) height

CS-PVA (2:3)

(B) Growing maize after 1.5 months , (91.44 cm) height

CS-PVA (2:3)

(C) Growing maize after 2 months, 152.4 cm and above height

Figure 7: Growing plant (A) Maize after 1 month (B) Maize after1.5 months (C)Maize after 2 months

Conclusion

All the synthesized CRF hydrogels exhibited high swelling ratio. With increasing PVA content within the CRF hydrogels, the water absorbency of the hydrogels increases. The soil containing the CRF hydrogels had retained some water, while the soil without CRF hydrogels had already given off most of the water. The amount of the remained water depends on the PVA content in the CRF hydrogel. In deionized water, the release behavior of phosphorus related to PVA content of the CRF hydrogels. The higher the PVA content, the higher the swelling ratio and the more the release amount is. CS hydrogel exhibited the highest the percent cumulative release of phosphorus in soil among the CRF prepared hydrogels. Various agronomical characteristics so measured revealed that CRF hydrogel showed significant changes in terms of retaining water and release of phosphorus when compared with control. So all CRF hydrogels films have the greater cumulative effect than the control. It can be recommended that the synthesis of chitosan based polyvinyl alcohol CRF hydrogel film and its application become a new trend to save fertilizer consumption and to reduce environmental pollution from agriculture.

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