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# Controlled-Release Fertilizer Based on Chitosan Hydrogel: Phosphorus Release Kinetics

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## *Abstract*

This paper describes the phosphorus release behavior of controlled-release fertilizer (CRF) hydrogels, which were prepared from polyvinyl alcohol (PVA), chitosan (CS) and the blend of these two polymers, using glutaraldehyde as a crosslinker. The mechanisms of phosphorus release from the CRF hydrogels were investigated using the Korsmeyer-Peppas model. It was found that, both in deionized water and in soil, the values of $n$ for all the CRF hydrogels are smaller than 0.5, indicating that the releases of nutrients from CRF hydrogels are a quasi-Fickian diffusion mechanism. Swelling ratio and water retention in soil of CRF hydrogels were investigated. The PVA hydrogel showed the highest value of equilibrium water absorbency and water retention among all the synthesized hydrogels. This is due to PVA is more hydrophilic than CS. The chemical structure, therefore, was important factors that affected the swelling ratio of the hydrogels which is directly related to the release rate of phosphorus from the CRF hydrogels.

*Keywords*: Controlled release, Hydrogel, Diffusion, Chitosan, Polyvinyl alcohol.

## 1. Introduction

In agriculture, loss of nutrient elements is one of large problems. It causes the insufficient of plant nutrients, increases process cost and pollutes the environment. Controlled release is a method used to solve this problem. With the use of controlled-released systems, nutrients are released at a slower rate throughout the season, plants are able to take up most of the nutrients without waste by leaching [1-2]. Polymer hydrogels can be defined as three-dimensional polymeric networks that can retain a significant amount of water within their structures, and swell without dissolving in water [3]. Polymer hydrogels have been used for agricultural as controlled release fertilizer [4]. In the recent years, research on slow and controlled-release fertilizer has been mainly focused on regulating nutrients-release rate and on coating slow and controlled release fertilizers.

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Han et al. have recently developed a new slow controlled-release fertilizer by coating the fertilizers with starch/polyvinyl alcohol (PVA) [5]. Liang et al. developed a controlled-release fertilizer from poly (acrylic acid-co-acrylamide)/kaolin composite [2]. In this study, the controlled release fertilizer (CRF) hydrogels were prepared from chitosan, polyvinyl alcohol and polyvinyl alcohol/-chitosan, using glutaldehyde 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 [6]. In addition, the phosphorus release mechanism of each CRF hydrogel was investigated.

## 2. Materials and Methods

The CRF hydrogels were prepared by mixing 10%w/v PVA solution with 1%w/v chitosan solution in 2%w/v acetic acid. The mixture was stirred constantly until homogeneous and the appropriate amount of fertilizer solution and the crosslinking agent were added into the mixture under constant stirring. After homogeneous mixing, the gel was formed within 30 minutes. The CRF hydrogel product was dried at 40 $^{o}$C in a vacuum oven overnight. The amount of PVA, CS, glutaraldehyde, fertilizer solution and crosslink solution used for preparing the CRF hydro-gels, are shown in Table 1.

**Table 1.** Formulation of CRF hydrogels.

| CRF hydrogels | CS solution (mL) | PVA solution (mL) | Fertilizer solution [(a)] (mL) | 1.25% (w/v) of GA (mL) | Crosslink solution [(b)] (mL) |
|---|---|---|---|---|---|
| PVA | - | 10.00 | 2.50 | - | 5.71 |
| PVA1/CS2 | 7.50 | 2.50 | 2.50 | 0.06 | 1.43 |
| PVA1/CS1 | 5.00 | 5.00 | 2.50 | 0.04 | 2.86 |
| PVA2/CS1 | 2.50 | 7.50 | 2.50 | 0.02 | 4.28 |
| CS | 10.00 | - | 2.50 | 0.08 | - |

[(a)] 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.

[(b)]Crosslinking solution was prepared by mixing 50% methanol, 10% acetic acid, 1.25% glutaraldehyde and 10% sulfuric acid together, making up a 3:2:1:1 weight ratio solution.

Swelling ratio of the CRF hydrogels was studied using the equation [7]

$$\%SR = \frac{W_s - W_d}{W_d} \times 100 \qquad (1)$$

where $W_s$ and $W_d$ referred to the weight of swollen and dry CRF hydrogels, respectively. To study water retention of soil containing the CRF hydrogels, a dry sample of CRF hydrogel was buried in dry soil, which was placed in a cup (A). The other of dry soil without CRF hydrogel was placed in an identical cup (B), 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 and were weighed every day ($W_t$) over a period of 30 days. Water retention (%$WR$) of soil was then calculated by the equation [7]

$$\%WR = \frac{W_t - W}{W_o - W} \times 100 \qquad (2)$$

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 pipette into a 25.00 mL volumetric flask, then, 5.00 mL of molybdovanadate reagent was added. Deionized water was also added to make a 25.00 mL solution. After 30 minutes, at the room temperature. The absorbance of the sample solution was measured at a wavelength of 420 nm by UV spectrophotometer. The amount of phosphorrus in the sample solution was calculated using the calibration curve. [6].

In this present study, the mechanism of phosphorus release from the CRF hydrogels was investigated using a semi-empirical model, known as the power law or the Korsmeyer-Peppas model [8-9]

$$\frac{M_t}{M_\infty} = kt^n \qquad (3)$$

where $M_t$ and $M_\infty$ represent the amount of nutrient released at a time t and at equilibrium, respectively, k is the constant characteristic of fertilizer-polymer system, and n is the diffusion exponent characteristic of the release mechanism. For quasi-Fickian diffusion the value of n < 0.5, Fickian diffusion n = 0.5, non-Fickain or anomalus transport n = 0.5-1.0 and Case II transport n = 1.0. Initial diffusion coefficient (D) can be calculated from the following equation [9]

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi l^2}\right)^{0.5} \qquad (4)$$

where $l$ is the thickness of the hydrogel sample.

## 3. Results and Discussion

Figure 1 represents water retention beha-vior of the soil containing CRF hydrogels. Each data point represented in the figure is the average value of three measure-ments with standard deviation of 4%. It was found that, the water retention of soil reduces with time. However, all the CRF hydrogels increased the water retention of soil. The soil without the CRF hydrogels had remained water around 2% on the 20$^{th}$ day, while the soil containing PVA-, PVA2/CS1-, PVA1/ CS1-, PVA1/CS2- and CS-hydrogels had remained water around 20, 16, 15, 10 and 9%, respectively. On the 30$^{th}$ day, the water retention of soil containing PVA-, PVA2 /CS1-, PVA1 /CS1-, PVA1/CS2- and CS-hydrogels were 20, 15, 14, 9 and 8%, respectively. While the soil without the CRF hydrogels had already given off most of the water. In addition, the PVA/CS ratio of CRF hydrogels affected the water retention. That is the water retention of the soil increased with increasing PVA content.

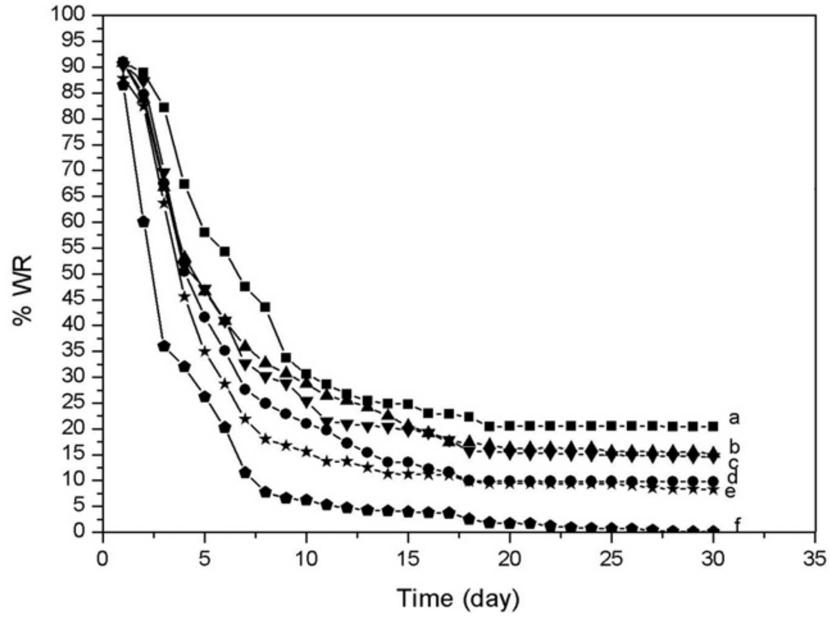


**Figure 1.** Water retention of soil containing (a) PVA-, (b) PVA2/CS1-, (c) PVA1/CS1-, (d) PVA1/CS2-, (e) CS-hydrogels and (f) without hydrogel.

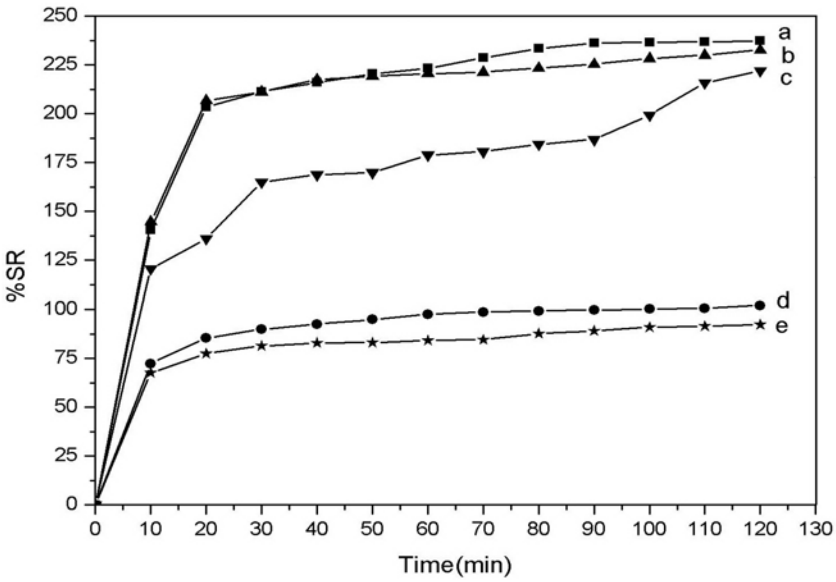


**Figure 2.** Swelling ratio of (a) PVA-, (b) PVA2/CS1-, (c) PVA1/CS1-, (d) PVA1/CS2- and (e) CS-hydrogels.

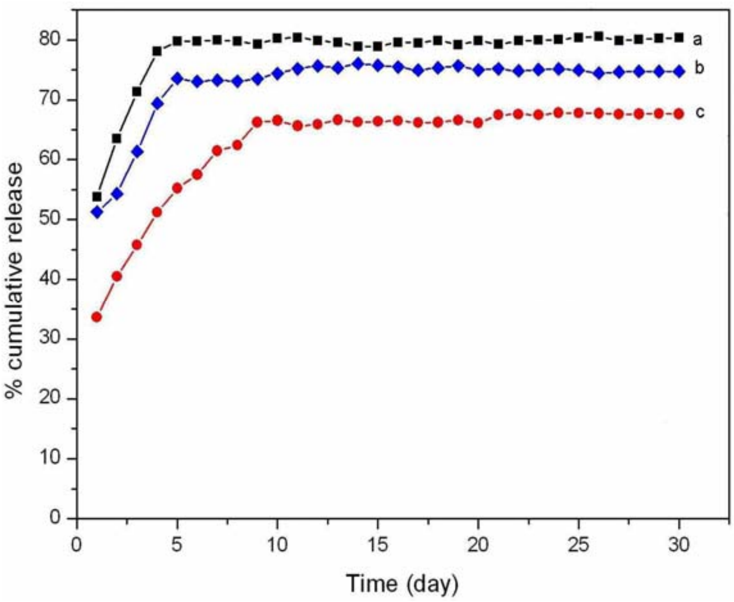


**Figure 3.** Release behaviors of phosphorus in water of (a) PVA-, (b) PVA1/CS1- and (c) CS-hydrogels.

The water absorbency of CRF hydrogels, in form of the swelling ratio, is shown in Figure 2. Each data point represented in the figure is the average value of three measurements with standard deviation of 3%. The equilibrium swelling ratio of PVA-, PVA2/CS1-, PVA1/CS1-, PVA1/CS2- and CS-hydrogels are 237, 232, 222, 102 and 92%, 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, the higher water absorbency is [10].

The phosphorus release behaviors of the CRF hydrogels in the deionized water at the room temperature are shown in Figure 3. All the CRF hydrogels exhibited initial burst release. PVA-, PVA1/CS1- and CS-hydrogels showed percent cumulative release of phosphorus, at day 30th, of 80, 75 and 67 %, respectively. The PVA hydrogels is appeared to show the highest release amount of phosphorus, both initial and at equilibrium, due to its high hydrophilicity. Phosphorus (in form of diammonium phosphate) in the CRF hydrogels released after the hydrogels absorbed water, leading hydrolysis process taking place [2]. Therefore, phosphorus diffused out the of the CRF hydrogels more easily at high swelling ratio than the lower one.

Figure 4 shows the percent phosphorus cumulative release in soil of CRF hydrogels. It was found that on the 30th day, the percent cumulative release of phosphorus of PVA-, PVA1/CS1- and CS-hydrogels were 16, 24 and 31%, respectively. In contrast with phosphorus release behavior in water, the CS hydrogel exhibited the highest the percent cumulative release. This is because chitosan is an excellent biodegradable material and is easily degraded by microorganisms and ions existing in soil [11-12]. Therefore, the existing of many kinds of ions and microorganisms in soil solution, possibly increases the degradation rate of the CRF hydrogels [13].

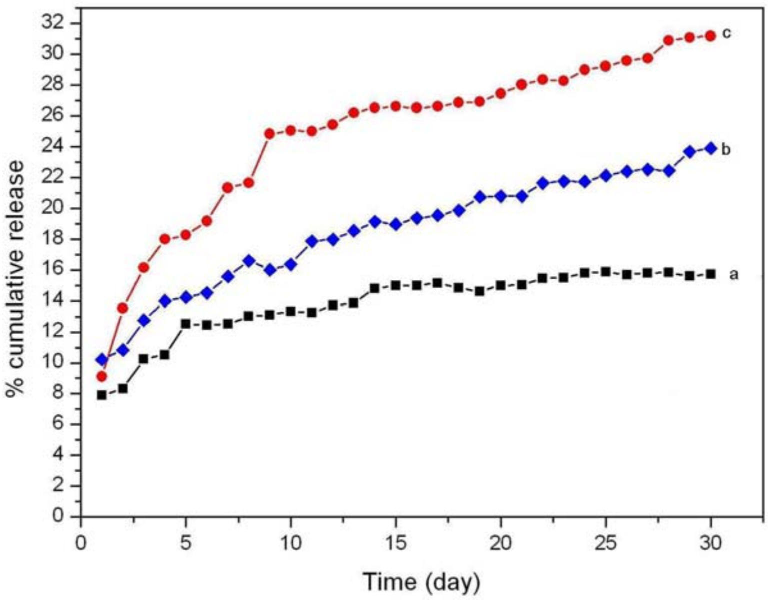


**Figure 4.** Release behaviors of phosphorus in soil of (a) PVA- (b) PVA1/CS1- and (c) CS-hydrogels in soil.

These contribute to such high percent cumulative release of phosphorus from the CS hydrogel.

In the present study the release patterns of phosphorus in soil and in deionized water have been studied. In order to investigate the release mechanism, the data were fitted to Eq. (3), the Korsmeyer-Peppas exponential equation. The release exponent, *n*, correlation coefficient, $R^2$ and release factor, *k* of each CRF hydrogel were obtained by plotting of log ($M_t / M_\infty$) versus log time. To further calculate the initial diffusion coefficient (*D*), Eq. (4) has been employed. Results of diffusion exponent, release factor and initial diffusion coefficient for the selected swell-lable CRF hydrogels are listed in Table 2. It was found that the PVA-, PVA1/CS1- and CS-hydrogels have *n* values, in soil, of 0.24, 0.21 and 0.41, respectively. The values of *n* for all the CRF hydrogels are smaller than 0.5, indicating that the releases of phosphorus from the CRF hydrogels are a quasi-Fickian diffusion mechanism. In addition, in deionized water all the CRF hydrogels also show *n* values that is smaller than 0.5, which also corresponds to quasi-Fickian diffusion mechanism. This mechanism indicates that phosphorus diffuses partially through a swollen matrix and water filled pores in the CRF hydrogels [14].

**Table 2.** Released exponent (*n*), correlation coefficient ($R^2$), release factor (*k*) and diffusion coefficient (*D*) of phosphorous release in deionized water and in soil for the swellable CRF hydrogels.

| CRF hydrogels | Release exponent, *n* | Correlation coefficient, $R^2$ | Release factor, *k* | Diffusion coefficient, *D* ($cm^2/s$) |
|---|---|---|---|---|
| In soil | | | | |
| PVA | 0.24 | 0.99 | 0.5901 | $1.48 \times 10^{-8}$ |
| PVA1/CS1 | 0.21 | 0.98 | 0.6240 | $7.35 \times 10^{-9}$ |
| CS | 0.41 | 0.98 | 0.3867 | $1.25 \times 10^{-9}$ |
| In deionized water | | | | |
| PVA | 0.26 | 0.99 | 0.6733 | $3.01 \times 10^{-8}$ |
| PVA1/CS1 | 0.22 | 0.96 | 0.6875 | $1.47 \times 10^{-8}$ |
| CS | 0.31 | 0.99 | 0.6016 | $1.67 \times 10^{-9}$ |

## 4. Conclusions

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 some remained 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 structure. 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. The release of nutrients from all the CRF hydrogels, both in deionized water and in soil, are a quasi-Fickian diffusion mechanism, in which nutrients diffuse partially through a swollen matrix and water filled pores in the CRF hydrogels. The initial diffusion coefficient (*D*) of nutrients, both in soil and in deionized water, related to PVA content of the CRF hydrogels. The higher the PVA content, the higher swelling ratio and the more the initial diffusion coefficient is.

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