Alginate-chitosan hydrogel as controlled release of NPK macronutrient

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Abstract. Alginate-chitosan hydrogel as controlled release of Nitrogen, Phosphorus, and Potassium (NPK) macronutrient has been studied. Variations of alginate and chitosan mass, N; P and K concentration, pH solution, swelling ratio and mass ratio of alginate and chitosan were optimized. Hydrogel was prepared by mixing alginate, chitosan and CaCl₂ as a cross linker in the water media. Hydrogel product was characterized by Fourier Transform Infrared (FTIR). N; P; and K release were measured by UV-Vis spectrophotomer and Atomic Absorption Spectrophotometer (AAS). The result showed that addition of chitosan in the hydrogel caused a decrease of swelling ratio hydrogel and a decrease of N; P and K release. The release of N; P and K was affected by N; P and K concentration and pH solution. The higher N; P and K concentrations and lower pH solution caused an increase of release rate of N; P and K. The mechanism of N; P and K release from the alginate-chitosan hydrogel followed the Korsmeyer-Peppas model. The ratio of alginate and chitosan in the hydrogel also affected to the the release rate of N; P and K.

1. Introduction

Plants are basically composed of 14 essential macronutrients as nitrogen, phosphorus, and potassium[6]. Generally, plants are capable to adapt at low pH in uptaking NH₄⁺ and at high pH solution in uptaking NO₃⁻. Inorganic phosphorus as nutrient for plant in soil is found in the form of H₂PO₄⁻, HPO₄²⁻ and potassium cation⁵. Nutrients were taken by plants through step by step absorption. In this case, the utilisation of conventional fertilizers may not effective as the rest nutrients which are not absorbed may loose due to leaching, run-off, gaseous emission, and fixation by soil and the following effects, soil degradation, reducing the quality of water and environmental degradation may occur⁵. Therefore, the use of nutrient-control release may help to solve the problems. The control release makes nutrients are slowly released to the media following by nutrients absorption by plants without any waste due to leaching⁵. Here, a media that is to keep and to release nutrient in nutrient uptaking of plants is needed. In this study, bio-copolymer of alginate is studied as the media that acts for nutrient control release. Alginate is a polysaccharide consisting of 1-4 linked α-D-mannuronat and β-L-guluronat where in the presence of divalent cations will form a crosslinked cation-alginate gel and form

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distinctive eggbox structure\cite{13,10}. The nutrition leaching during preparation of hydrogel can be solved by synthesizing bi-polymeric alginate beads with other natural polysaccharides\cite{9}. Due to owing negative-charge surface, alginate can interact with chitosan which has positive charge to form polyelectrolyte complex\cite{11}. Here, the aim of the study is to form hydrogel from alginate and chitosan with the presence of CaCl$_2$ crosslinker as controlled release of nutrient.

2. Experimental

2.1. Materials

The material used in the study are Na-Alginate, Chitosan, Calcium Chloride (CaCl$_2$), Ammonium nitrate (NH$_4$NO$_3$), Diammonium Hydrogen Phosphate (NH$_4$H$_2$PO$_4$), Potassium Nitrate (KNO$_3$) from Merck (all are analytical grade). Ammonium molibdat ((NH$_4$)$_6$Mo$_7$O$_{24}$H$_2$O), ethanol 96%, ammonium vanadate (NH$_4$VO$_3$), Nitric Acid (HNO$_3$), Hydrochloric Acid (HCl), para dimetilamo benzaldehyde (p-DAB) were purchased from Mallinckrodt.

2.2. Instrumental

Fourier Transform Infrared/FTIR (Shimadzu FT-IR-821 PC) was used to characterize the hydrogel product. Spectroscopy UV-Visible (Thermo Scientific Evolution 201), and Atomic Absorption Spectroscopy/AAS (Parkin Elmer 3110) was used to measure the release performance.

2.3. Preparation of alginate-chitosan hydrogel

The fertilizer solution was prepared by dissolving ammonium nitrate, diammonium phosphate, and potassium nitrate in 100 mL deionized water\cite{10}. The alginate-chitosan hydrogel was prepared by dissolving alginate 2% (b/v) and chitosan into fertilizer solution with mass ratio of alginate: chitosan (10:0); (8:2); (7:3); (6:4). Acetic acid (2%) was added into solution under constant stirring. The mixture was injected into syringe and then dropped into CaCl$_2$ 0.5 M solution to form viscous gel. Gel formed was rinsed with distilled water and dried in the room temperature.

2.4. Swelling ratio of alginate-chitosan hydrogel

Alginate-chitosan hydrogel was weighed firstly in the dry form. The hydrogel was then immersed into deionization water and various pH solution for 100 minutes before filtration and weighing. The swelling ratio of hydrogel was calculated using equation:

\[ \text{SR} = \frac{W_x - W_d}{W_d} \times 100\% \]  

(1)

Where $W_x$ referred to weigh of swollen hydrogel and $W_d$ is dried hydrogel.

2.5. Optimisation of N; P and K release in various condition

The hydrogels made with various mass ratio and various N; P; K concentration were immersed into 20 mL deionized water. The solution (3 mL) was sampled and measured for N; P; and K concentration every 24h until for 12 days. The mother solutions were added with 3 mL deionized water after each measurement done. The content of N; P; and K was determined with UV-Vis Spectrophotometer and AAS. N; P; and K content was also determined at pH 3; 5; and 6.8.

2.6. Modelling and release kinetics

The release mechanism of N; P; and K was investigated using a semi-empirical model, known as Korsmeyer-Peppas which correlates nutrient release from polymer as following equation:

\[ \frac{M_t}{M_\infty} = k t^n \]  

(2)
Where $M_t$ and $M_\infty$ represent the amount of released nutrient at a time $t$ and equilibrium condition, $k$ is constant characteristic of fertilizer-polymer system, and $n$ is the diffusion exponent characteristic of the release mechanism (Quasi-Fickian diffusion $n = 0.5$; non-Fickian or anomalous transport $n = 0.5 – 1.0$ and Case II transport $n = 1.0$)

3. Results and Discussion

3.1. Characterization of alginate-chitosan hydrogel by FTIR

The IR spectra of alginate (figure 1) showed a peak at 3448 cm$^{-1}$ indicated -OH group from carboxyl and peaks at 1620 and 1420 cm$^{-1}$ showed asymmetric and symmetric vibration of -COOH groups and strong peak at 1126 cm$^{-1}$ indicated the presence of C-O vibration from carboxylic acid. Chitosan was identified with N-H peak at 1651 cm$^{-1}$ and at 3448 cm$^{-1}$ (overlapping of O-H and NH$_2$ vibration), at 1080 cm$^{-1}$ (C-N stretching vibration) and at 1309 – 1419 cm$^{-1}$ (deformation from C-OH vibration). The complex formation of alginate-chitosan as polyelectrolyte was indicated by the decrease of absorption intensity at 3425 cm$^{-1}$ (-OH and NH$_2$ vibration). It was caused by protonation of -COOH group into COO$^-$ and NH$_2$ into NH$_3^+$ which affects to ionic interaction between the carbonyl group of alginate and the amino group of chitosan. The peak shift at 1651 cm$^{-1}$ to 1635 cm$^{-1}$ and 1420 cm$^{-1}$ to 1381 cm$^{-1}$ indicated that complexation between alginate and chitosan occurred.

![FTIR Spectra of (a) chitosan, (b) alginate, (c) alginate-chitosan](image)

**Figure 1.** FTIR Spectra of (a) chitosan, (b) alginate, (c) alginate-chitosan

3.2 Swelling ratios of alginate-chitosan hydrogel

The swelling ratio of alginate-chitosan hydrogel in deionized water is shown in figure 2. The swelling ratio of hydrogel decreased with the increase of chitosan in the hydrogel. This decrease of swelling ratio is well known, due to hydrophobic of chitosan more than alginate. The lowest swelling ratio was achieved in the alginate-chitosan hydrogel with 8:2 mass ratio. Here, the large number of alginate with negative groups that were bonded by cross linker caused the increase of hydrogel stability in deionized water.
The swelling ratio of alginate-chitosan hydrogel with 8:2 mass ratio in various pH solutions is shown in figure 3. From the figure, it was concluded that the swelling ratio decreased with the increase of pH solutions. It was because of unreacted NH$_2$ group that was protonated to NH$_3^+$ in acidic solution and leaded to dissociation of the hydrogen bonding of the amino groups$^{[9]}$. As consequence, the entrance of solvent into hydrogel and the release of nitrogen, phosphorus and potassium was higher. The increase of pH solution caused weakness of the protonation of unreacted NH$_2$ group which also caused lower swelling ratios of hydrogel.

3.3 Optimisation of N; P and K release in various condition.

The N; P; and K release from the hydrogel in the media of deionized water at variations of alginate-chitosan mass ratios are shown in figure 4. From the data, the release of N; P; and K decreased with the increase of chitosan content in hydrogel. The alginate-chitosan hydrogel at 8:2 mass ratio showed the lowest release of N; P; and K. The release of N; P; and K out of hydrogel occured after absorption of water by hydrogel and then N; P; and K was released by diffusion out of hydrogel. The diffusion of N; P; K is more easily at higher swelling ratio than lower swelling ratio. On the other hand, the hydrogel with the higher chitosan content caused the increase of ionic interaction between amine groups of chitosan and carboxylic groups of alginate and decrease of interaction between alginate and Ca$^{2+}$.$^{[12]}$ This phenomenon contributed to the decrease of hydrogel swelling.
Figure 4. The release of (a) N; (b) P; and (c) K with the variations of alginate-chitosan mass ratios

The release of N; P; and K with the variations of N; P; and K concentration are shown in figure 5. It was shown that the released amount of N; P; and K was increased with higher content of N; P; and K concentration in hydrogel.
Figure 5. The release of (a) N; (b) P; and (c) K with the variations of N; P; and K concentrations in the hydrogel

The release of N; P; and K macronutrient at the variation of pH is shown in figure 6. It was showed that the release of N; P; and K at lower pH was higher than at higher pH. It was due to the unreacted NH₂ group was protonated in acidic solution, that also caused polymer chains exert repulsive forces and dissociation of secondary interaction. As consequence, the hydrogel could absorb more water and increase the swelling ratio of hydrogel.

Figure 6. The release of (a) N; (b) P; and (c) K with pH solution variation
The release mechanism of N; P; and K macronutrient that was investigated using semi empirical equation known as Korsmeyer-Peppas was correlated with the release exponent, $n$, correlation coefficient ($R^2$) and release factor ($k$) of each hydrogel. The values were obtained by potting $\ln (M_t/M_{\infty})$ vs $\ln t$. The values of $n$ for released of N; P; and K with mass variation are listed in table 1 and table 2.

| Nutrient | Alginate: chitosan | Corelation coefficient | Korsmeyer-Peppas |
|----------|------------------|-----------------------|------------------|
|          |                  | $R^2$ | $n$ | $k$ (mg/day) |
| N        | 10:0             | 0.99 | 0.50 | 0.25 |
|          | 8:2              | 0.85 | 0.78 | 0.10 |
|          | 7:3              | 0.94 | 0.78 | 0.13 |
|          | 6:4              | 0.95 | 0.77 | 0.17 |
| P        | 10:0             | 0.97 | 0.50 | 0.25 |
|          | 8:2              | 0.98 | 0.44 | 0.11 |
|          | 7:3              | 0.98 | 0.54 | 0.19 |
|          | 6:4              | 0.97 | 0.50 | 0.18 |
| K        | 10:0             | 0.99 | 0.50 | 0.25 |
|          | 8:2              | 0.93 | 0.51 | 0.17 |
|          | 7:3              | 0.96 | 0.51 | 0.22 |
|          | 6:4              | 0.95 | 0.50 | 0.21 |

| Nutrient | Concentration | Corelation coefficient | Korsmeyer-Peppas |
|----------|---------------|-----------------------|------------------|
|          |               | $R^2$ | $n$ | $k$ (mg/hari) |
| N        | A             | 0.82 | 0.85 | 0.11 |
|          | B             | 0.97 | 0.82 | 0.13 |
|          | C             | 0.98 | 0.74 | 0.14 |
| P        | A             | 0.99 | 0.50 | 0.035 |
|          | B             | 0.97 | 0.58 | 0.098 |
|          | C             | 0.95 | 0.42 | 0.13 |
| K        | A             | 0.99 | 0.30 | 0.11 |
|          | B             | 0.99 | 0.36 | 0.19 |
|          | C             | 0.98 | 0.37 | 0.30 |

The mechanism release of nitrogen, phosphorus, and potassium showed that $n$ value was 0.5 – 1.0, indicated that the release of N; P; and K was a Non-Fickian diffusion. This mechanism indicated that N; P; and K was diffused by controlled swelling and controlled diffusion. The different $n$ value was seen in the phosphorus release at 8:2 mass variation. It was affected by the different chemical structure of the hydrogel. The $n$ value for the release of nitrogen and phosphorus by variation of concentration of N; P; and K was 0.5 -1.0 indicated that the release of nitrogen and phosphorus was Non-Fickian diffusion. $n$ value for potassium release was smaller than 0.5, indicated that the release of N; P; and K
from hydrogel was a quasi Fickian. This mechanism indicated that N; P; and K diffused partially through swollen hydrogels and water filled pores of the hydrogel.

4. Conclusion
The alginate-chitosan hydrogel as control release of N; P and K showed as good media for nutrient release. The swelling ratio of hydrogel decreased by the content increase of chitosan in the hydrogel. The release of N; P; and K decreased with the content increase of chitosan. The increase of N; P; K concentration in the hydrogel affected the release increase of N; P; and K. The lower pH solution affected to the higher swelling ratio of hydrogel and therefore, the release of N; P; and K also increased. From the mechanism study, it was found that the mass variation generally exhibited the small value of release exponent that is only 0.5-1.0, indicated a non-Fickian diffusion mechanism. N; P; and K concentration was following Quasi-Fickian and Non-Fickian diffusion. Release of N; P and K could be controlled by ratio of the alginate-chitosan content in the hydrogel.

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