Modeling of Swelling and pH-Dependent Nutrient Release Kinetics of HPC/CMC/Alginate Hydrogel Blends for Agricultural Applications

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Abstract. The swelling and nutrient release behaviors of a novel hydrogel blend of hydroxypropyl cellulose (HPC), carboxymethyl cellulose (CMC), and sodium alginate (NaAlg) was investigated to determine its applicability as an agricultural soil conditioner. Hydrogel swelling and nutrient release data were obtained over time at varying temperatures and pH conditions. The experimental data were fit into the power law, Tsai and Strieder, and Johansson's models to determine the kinetic parameters for the swelling behavior and nutrient release. Under the experimental swelling conditions, the maximum and minimum swelling capacities of the hydrogel blend were 322.9245% and 228.0483%, respectively. The data fit to the power law suggested that a pseudo Fickian behavior describes the diffusion mechanism. The data fit to the Tsai and Strieder and Johansson's models provided the experimental values for the α and temperature correlation as 3.69×10^{-5} and 0.0278, respectively, which implies that the diffusion behavior within the hydrogel does not vary significantly within the temperature range. Lastly, the inconsistency observed in the nutrient release behaviors at varying pH suggested that additional trials may be required in order to establish a clearer relation between pH and nutrient release behavior.

Index Terms: Hydrogels, modeling, swelling, nutrient release

I. INTRODUCTION

Hydrogels are polymeric materials which are gaining interest in the field of agriculture due to their superabsorbent properties demonstrated by their high-water holding capacity and soil moisture retention, as well as controlled solute release properties [1]. Hydrogels present commercially are made of acrylate materials which are non-renewable and could also pose toxicity to the environment. Therefore, a hydrogel made from renewable and safe materials is desired.

Renewable materials that could be used for hydrogel synthesis are cellulose derivatives such as sodium carboxymethyl cellulose (NaCMC) and hydroxypropyl cellulose (HPC). NaCMC is a smart cellulose derivative as it is sensitive to pH and ionic strength changes [2]. NaAlg is the gel forming component in controlled proportion of cations [3]. HPC is the temperature responsive material which also creates a network based on the hydrophilicity and hydrophobicity balance [4]. The use of temperature and pH-responsive materials as components in hydrogels give the hydrogels even more flexibility in terms of applications. It is also important especially in studying behaviors or mechanisms in fluctuating environmental conditions since these are known to show active responses to small environmental changes by exhibiting reversible changes in their structure, physiological or chemical properties [5].

A hydrogel was synthesized from these cellulose derivatives and sodium alginate (NaAlg), with aluminum sulfate ($Al_2(SO_4)_3$) used as the crosslinking agent [6]. The optimum blend of the hydrogel was obtained based on the properties of swelling capacity and nutrient loading capacity. It was found to decrease fertilizer runoff by 28% and increase field capacity to 55%. It can also accommodate 1585% moisture and 8.39% fertilizer on a dry basis.

Hydrogel performance is affected by factors such as varying temperatures and pH [7]. Since the agricultural environment is exposed to varying temperatures and pH, hydrogels used for agricultural purposes may act differently when exposed to these varying parameters. The previously developed hydrogel from an optimal blend of NaCMC, NaAlg, and HPC is a good alternative to current hydrogels in the market due to its renewability. No known studies yet have been done on testing this hydrogel blend's performance in varying temperature and pH conditions.

The main objective of this research is to evaluate the applicability of the NaCMC/NaAlg/HPC hydrogel in agricultural applications. Specifically, the research aims to observe the behavior of the hydrogel by gathering swelling and solute release data in varying temperature and pH, and fit them into existing models, and to determine the model parameters from the fitted data.

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The research will not delve into the effects of different blending techniques in the synthesis of hydrogels. The different internal structure of each batch of hydrogel will also not be accounted in the calculations for the parameters of the models. Additionally, the swelling and nutrient release parameters of the hydrogel will only be tested in laboratory scale experiments. Furthermore, the research will be utilizing values for pH, temperature, and fertilizer composition parameters based on local experience and most common recurrence.

II. MATERIALS AND METHODS

2.1 Materials and Equipment

The preparation of the hydrogel involved the following materials: sodium carboxymethyl cellulose (NaCMC), hydroxypropyl cellulose (HPC), and sodium alginate (NaAlg) for the polymer solution, and calcium chloride ($CaCl_2$) for the physical crosslinker solution. NaAlg, HPC, and $CaCl_2$ were already available in the laboratory, while NaCMC was procured from Kemrad Incorporated.

For the nutrient release studies, a 30-10-10 NPK fertilizer was procured from a local hardware. Phosphate buffer of pH 7 and 1.0 M HCl were also used to prepare the different buffer solutions needed for the experiment. The equipment used in the experiment were analytical balance, hot plate, pH meters, thermocouple and conductivity meter.

2.2 Hydrogel Synthesis

A ratio of NaCMC, NaAlg, and HPC was dissolved to form a 3 wt% polymer solution. At ambient temperature, the polymer was continuously stirred with the use of a magnetic stirrer. Once the solution became homogeneous, it was covered and left to settle overnight to remove any air bubbles. Simultaneously, the crosslinking solution was made. Five (5) wt% $CaCl_2$ was dissolved in distilled water and stirred vigorously until all $CaCl_2$ was dissolved.

Once the bubbles of the polymer solution had settled, 20 mL of the solution was measured and then poured into a dry petri dish. The petri dish was tilted several times to allow the solution to cover the whole surface area, afterwards the crosslinking solution was poured on top of the polymer solution. Making sure that the crosslinking solution covered the top layer of the polymer solution, the sample was left to physically crosslink for an hour. Excess solution from crosslinking was then washed off and the formed hydrogel was left to air dry for 30 minutes.

2.3 Swelling Studies for Hydrogels

Air-dried hydrogels were weighed using an analytical balance to determine their initial weight before swelling, afterwards, the hydrogels were immersed in a water bath. The samples were kept at room temperature. At certain time intervals, the hydrogels were removed from the water bath and weighed using an analytical balance. The swelling capacity of the sample was then calculated using (1), where W_s is the final weight of the swollen hydrogel and W_i the initial weight of the air-dried hydrogel.

$$\text{swelling capacity} = \frac{W_s - W_i}{W_i} \times 100\% \tag{1}$$

2.4 Nutrient Release Studies

For the nutrient release kinetic studies, the hydrogels submerged in fertilizer solution were air-dried for an hour. Afterwards, the thickness and diameter of the hydrogels were measured using a Vernier caliper.

In determining the rate of the nutrient release of the hydrogel, a 200-mL water bath was prepared. The water bath was heated to the desired temperature of the system using a hot plate. The temperature was varied from 25°C to 50°C and was monitored using a thermocouple. Once the desired temperature of the water bath has been reached, the loaded hydrogel was then submerged inside the water bath and the conductivity of the solution was monitored over time using a conductivity meter.

2.5 Data Fitting

The data gathered from observing the conductivity of the solution over time from the nutrient release studies were used to plot the fractional release of the hydrogel at different temperatures. The data were then fitted into the truncated 2-D model that describes the relationship of the rate of fractional release and the solute diffusion in a gel (D_g) of the hydrogel as shown in (2).

$$\frac{M_t}{M_\infty} = 4\left(\frac{D_g t}{\pi a^2}\right)^{\frac{1}{2}} - \pi\left(\frac{D_g t}{\pi a^2}\right) - \frac{\pi}{3}\left(\frac{D_g t}{\pi a^2}\right)^{\frac{3}{2}} + 4\left(\frac{D_g t}{\pi l^2}\right)^{\frac{1}{2}} - \frac{2a}{l}\left[8\left(\frac{D_g t}{\pi a^2}\right) - 2\pi\left(\frac{D_g t}{\pi a^2}\right)^{\frac{3}{2}} - \frac{2\pi}{3}\left(\frac{D_g t}{\pi a^2}\right)^2\right] \tag{2}$$

Before determining the parameters of the diffusion models, the diffusion coefficient of the solute in liquid at infinite dilution (D_0) was first determined using the Stokes-Einstein model as described in (3), where k_B is the Boltzmann constant, T is temperature, and η is the viscosity of water at T, and r_s is the hydrodynamic radius of the solute.

$$D_0 = \frac{k_B T}{6\pi\eta r_s} \tag{3}$$

Finally, the diffusion models used to determine the parameters of diffusion of the hydrogels were the obstruction model developed by Johansson, et al. (1991), and Tsai and Strieder (1985) shown in (4) and (5), respectively.

$$\frac{D_g}{D_0} = \exp\left(-0.84\alpha^{1.09}\right) \tag{4}$$

$$\frac{D_g}{D_0} = \left(1 + \frac{2}{3}\alpha\right)^{-1} \tag{5}$$

III. RESULTS AND DISCUSSION

3.1. Characteristics of Hydrogel Swelling

The swelling capacities of the hydrogel samples synthesized using $CaCl_2$ were calculated and summarized as shown in Table 1. On average, the swelling capacity of the novel hydrogels is 264.4051%. In contrast to the 1585% swelling capacity achieved by the novel hydrogels synthesized previously [6], the hydrogels synthesized achieved only up to 16.6817% of this value. The difference between the swelling capacity of the hydrogels can be attributed to difference in geometry as well as the use $CaCl_2$ as a crosslinker.

Table 1. Initial weight, final weight, and swelling capacity of hydrogels

Trial	Initial Weight (W_i)	Final Weight	Swelling Capacity
1	0.2813	0.9228	228.0483%
2	0.2927	1.2379	322.9245%
3	0.2533	0.8669	242.2424%
Mean			264.4051% ± 0.5117%

The samples used in the three trials were shaped into thin disks, as opposed to the spherical hydrogels in the previous study. The geometry of the hydrogel can affect its swelling capacity [8]. The internal stress fields of the center as well as the top and bottom of a hydrogel in thin disk are different. The edge of the hydrogels achieve equilibrium faster than the center [8], which may explain why the hydrogels in thin disks had lower swelling capacity compared to the spherical hydrogels.

The lower swelling capacity can also be attributed to the difference in complexation of NaAlg with various cations. It can be noted that NaAlg forms stronger crosslinked hydrogels with $CaCl_2$ compared to $Al_2(SO_4)_3$ [9]. Similarly, in another study, the amount of time the polymer solution was left to crosslink also affected the water uptake or the hydrogel's swelling capacity [10]. Both novel hydrogels synthesized previously and hydrogels synthesized for this experiment were left for 30 minutes in a crosslinking solution. However, hydrogels that use $CaCl_2$ would have a higher swelling capacity if allowed to crosslink at lesser time intervals as it would prevent the tight structure from forming inside the hydrogel [10].

It can also be observed that the final weight of the hydrogels after 150 hours is not the maximum swelling capacity of the hydrogels. As shown in Fig. 1, the hydrogels reached their maximum weight after 70 hours of swelling.

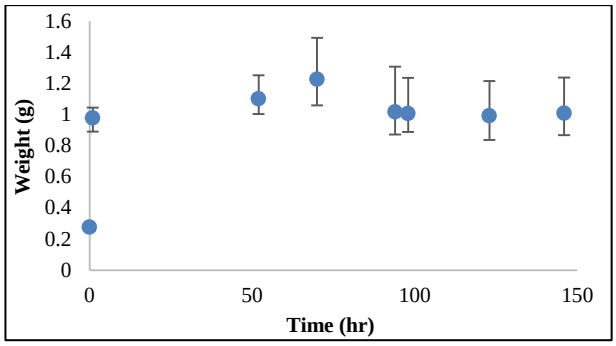

Figure 1. Weight vs. time of hydrogel samples

Swelling can be described as a continuous process wherein hydrogels transition from glassy to partially rubbery state, and can be described depending on the solvent diffusion rate (Rdiff) and polymer chain relaxation rate (Rrelax) [11]. According to the same study, slab samples often follow Case I wherein the diffusion asymptotically approaches a fixed equilibrium. However, when diffusion is more rapid than the relaxation of the polymer (Case II), the mass uptake is directly proportional to time. A third case called anomalous transport can also be observed when the diffusion and relaxation rates are comparable.

In determining the type of mechanism that the swelling of hydrogel followed, the power law was utilized [12]. The values for the diffusion constant (n) are summarized in Table 2. The vast difference in values of the diffusion constant between each trial can be traced back to the effect of the hydrogel's geometry in its swelling capacity and its polymer network. When the hydrogels were air-dried before swelling, some of the hydrogels failed to maintain their thin disk shape. Due to the loss of moisture content, some of the hydrogels curled up and their geometries were distorted.

Another important aspect to consider with the swelling of the hydrogel is that the Fickian model is used to describe the small volume difference experienced by the hydrogel at shorter amount of time. In a similar swelling study, the weight of the hydrogel was monitored over an hour with 10 minutes interval instead of across the week [13].

Table 2. Initial weight, final weight, and swelling capacity of hydrogels

Trial	Diffusion Constant (n)	ln k	Type of Transport
1	-0.0199	0.1466	Less Fickian
2	0.0605	-0.2114	Less Fickian
3	0.0028	3.6376	Less Fickian

3.2. Effect of Temperature on Nutrient Release Kinetics

The low correlation of D_g against temperature, as shown in Fig. 2, implies that it has no direct relation with temperature. This observation may further be verified if a

clearer trend could be seen with more data points, e.g., at smaller temperature intervals.

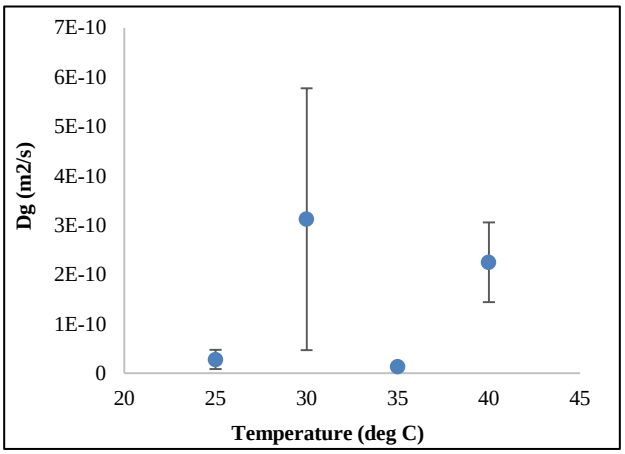

Figure 2. Calculated D_g at varying temperatures D_0 (m^2/s)

The value of r_s for the fertilizer at 25°C was calculated from the average ionic D_0 values of the constituent ions of a model 30-30-30 NPK fertilizer [14]. The density and viscosity of water at the temperature range was calculated using guidelines provided by IAPWS 2008 [15]. These values, together with r_s, were used in extrapolating the values of D_0. By fixing these values, alpha (α) against temperature was calculated for Tsai and Johansson's models. It was found that for both models, α had extremely low correlation with temperature. Since α is correlated to the radius of the fibers and the solute, this could imply that changing the temperatures in this range may not have a significant effect on the diffusion behavior of hydrogels.

Table 3. Calculated α for Tsai and Johansson models

Temperature (°C)	Tsai and Strieder model	Johansson model
25	15.7319	2.9063
30	251.5008	6.1047
35	8.3369	2.2389
40	95.0151	4.9574

The greatest spread in the data is found in the samples recorded at 30°C and 40°C, with 40°C spread about four times more than that at 25°C. The runs performed at 35°C generated D_g values with the least spread in the data. The spread of the data can be attributed to several factors, such as the instability of heating, and the crumpled geometry of the hydrogel.

Distorted geometry may introduce an additional factor. The crumpling of the hydrogel due to drying causes deviations from the model being flat, circular disks. These variations are minimized by making sure that the hydrogels are dried at similar times, and that multiple trials are done to average out the values.

3.3. Effect of pH on Nutrient Release Kinetics

pH is classified as a chemical stimulus which can cause changes on the polymer chains of a hydrogel that leads to changes in its swelling and nutrient release [16]. The effect of pH on the nutrient release of hydrogels is also dependent on other factors such as size, shape, crosslinking density, and ionic groups present. Fig. 3 shows the effect of pH on the nutrient release of the post-loaded hydrogels. Among the three pH conditions, the two trials under pH 6.00 behaved more similarly with each other as they had a linear increase at first and continued to plateau over time. On the other hand, the behavior of the other two trials under pH 5.00 and pH 4.00 were vastly different from each other. This problem can be attributed to: (i) lack of further experimental data, and (ii) the nature of natural hydrogels.

The erratic behavior can be explained through understanding the nature of the hydrogel. The hydrogel is classified as a polysaccharide-based natural hydrogel. Natural hydrogels are ideal for agricultural applications due to their biocompatibility and biodegradability; however, they have a high batch-to-batch variation and lower mechanical properties [17]. These properties of natural hydrogels make them harder to control experimentally and to produce reproducible data.

On the other hand, this problem with natural hydrogels can be offset with the presence of alginate. The anionic nature of alginate allows it to control nutrient release at different pH [16]. At lower pH values like 1.2, the acidic groups in the blends would remain unionized, which slows down the nutrient release. Meanwhile at pH 7.4, the acidic pendant groups are ionized and cause the blend to swell extensively.

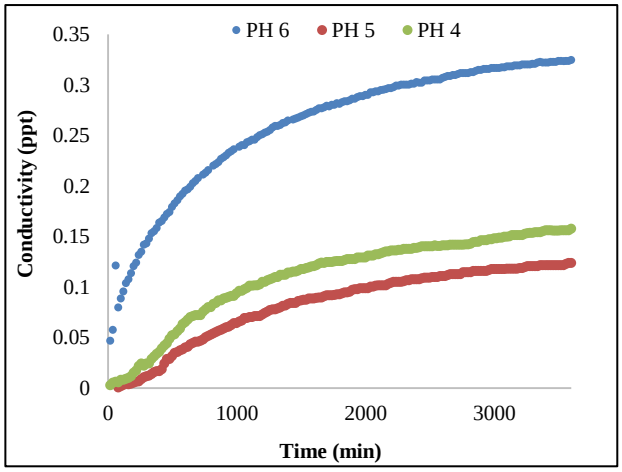

Figure 3. Effect of pH on nutrient release

IV. CONCLUSION

Due to the innate properties of natural hydrogels to have low mechanical properties and high batch to batch variations, the characteristics of the swelling rate of the hydrogel were vastly different from one sample to another with the highest swelling capacity recorded as 322.9245% and the lowest being 228.0483%. Moreover, in determining the transport mechanism exhibited by the

hydrogel, all samples used in the experiment did not follow Fickian diffusion.

On investigating the effect of temperature on the nutrient release of the hydrogel, data fitted to Tsai and Strieder, and Johansson's models resulted to low correlation values for alpha and temperature at 0.0000369 and 0.0278, respectively. This implies that temperature may not have a significant effect on the diffusion behavior of the hydrogel. On the study of varying pH, inconsistent nutrient release behaviors of the hydrogel were observed for pH 4 and 5 trials while a linear increase eventually leading to a plateau behavior was observed for pH 6 trials. However, due to the limited number of experimental trials and data, an overall conclusion on the effect of pH on nutrient release cannot be derived.

Natural hydrogels have a high batch to batch variation; therefore, it is recommended to investigate different swelling methods such as the tea bag swelling method to explore the effect of the hydrogel variation in the results of the swelling analysis. Additionally, researchers may also explore how the characterization of each hydrogel changes overtime using different imaging studies such as FTIR and SEM. Future research may also explore other novel combinations of hydrogel and determine their behavior against pH and temperature in terms of solute release behavior and swelling.

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