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Synthesis, Characterization, and Controlled Release Property Evaluation of Carboxymethyl Cellulose/Alginate (CMC/Alg) Encapsulated NPK Fertilizers

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This work described the successful preparation of encapsulated nitrogen-phosphorus-potassium (NPK) fertilizers with the use of carboxymethyl cellulose/alginate (CMC/Alg) blend employing citric acid (CA) as the crosslinking agent. The study involved the preparation, characterization, release studies, and efficacy evaluation of the said fertilizer system. Fourier transform infrared (FTIR) and fluorescence spectroscopic methods, scanning electron microscopy (SEM), particle size analysis, and zeta potential measurements showed the successful formation of spherical particles with varying sizes (ranging from 733–1200 nm) *via* crosslinking. Release profiles of the CMC/Alg NPK conformed to the standards of controlled-release fertilizer with a maximum release rate of 50% for CMC/Alg NPK in 30 d. Investigation of the release mechanism using the Korsmeyer-Peppas mathematical model showed that the release of nutrients is governed by both coating material relaxation and diffusion processes. Controlled release behavior was demonstrated as confirmed in the efficacy evaluation of the prepared fertilizer in a 2-mo pot experiment using mung bean.

Keywords: controlled release, crosslinking, encapsulation, NPK fertilizers

INTRODUCTION

One efficient strategy of slowly releasing nutrients for sustained feeding of plants is through encapsulated fertilizer. Aside from being more efficient in terms of nutrient management, the encapsulation of chemical inputs like fertilizers is more environment-friendly as opposed to soluble fertilizers since nutrients are more efficiently absorbed by the plant when released slowly. This also avoids being washed away or leached through the soil where the possibility of fertilizers entering the groundwater is high. Studies on fertilizer leaching indicate about 40–70% of nitrogen, 80–90% of phosphorus, and 50–70% of potassium of the applied fertilizers can be lost to the environment (Saigusa *et al.* 2001). Controlled release fertilizer using a biodegradable polymer is one viable option for an efficient nutrient management strategy. It can release the nutrient contents gradually while also minimize environmental pollution that came with the leaching of fertilizers and other chemical inputs. Polymers, especially in the form of hydrogels, are widely used for the controlled release of agrochemicals and nutrients in agricultural and horticultural applications (Rafaat *et al.* 2012) while acting as compost after their degradation (Campos *et al.* 2014).

CMC is one of the most common derivatives of cellulose. It is the product of carboxymethylation using monochloroacetic acid *via* base-induced mechanism (Heinze and Koschella 2005). Unlike cellulose, CMC is soluble in aqueous media (Kim *et al.* 2012) to some extent because of the attached ionic carboxylate (Riyajan and Nuim 2013), thus making it easier to handle. Alginate, on the other hand, is also a good material for controlled

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*Corresponding Author: david.penaloza.jr@dlsu.edu.ph release applications. Because it is very soluble in aqueous media, alginate is less stable in holding nutrients. The instability, however, can be addressed by crosslinking – as such strategy forms a three-dimensional network that adds up to its structural stability (Chen *et al.* 2013). Recent studies showed that alginate, cellulose, and its derivatives can be crosslinked to form a more stable network (Anirudhan *et al.* 2015; Mesias *et al*. 2019; Agu *et al.* 2019). Considering the carboxylate groups of alginate and hydroxyl groups of cellulose and its derivatives, CA is an excellent candidate for a crosslinking agent to chemically connect cellulose and alginate (Demitri *et al.* 2008; Mesias *et al.* 2019). Here, we describe the successful preparation of encapsulated NPK fertilizers with the use of crosslinked CMC/Alg NPK. The study involved the preparation, characterization, release studies, and efficacy evaluation of the said fertilizer.

MATERIALS AND METHODS

Materials

CMC (low molecular weight) and alginate (low molecular weight) were obtained as sodium salts analytical grade reagent. In addition, glacial acetic acid (AR Labscan), CA monohydrate (AR Himedia), potassium dihydrogen phosphate (AR Himedia), calcium chloride dehydrate (AR Himedia), ammonium chloride (AR Himedia), pH buffers (AR Labscan), and sodium 8-anilino-1-naphthalenesulfonate (ANS; AR Fluka) were used as received.

Preparation of CMC/Alg Encapsulated NPK Fertilizer

The 3.0 % (wt/vol) dispersions of sodium alginate and CMC were prepared by dispersing appropriate amounts of each polymer in deionized water with continuous stirring up to 2 h. This was followed by the addition of NPK fertilizers in the form of NH_4Cl and KH_2PO_4 to the alginate dispersion which was stirred at 1000 rpm for 30 min. After this, the CMC dispersion with an appropriate amount of CA crosslinker was added to the alginate dispersion and was continuously stirred for 30 min at the same temperature. The NPK loaded polymer blends were then removed and were placed in a syringe. This was then followed by its addition to 20 mL of 2% (wt/vol) calcium chloride solution in a dropwise manner while stirring at 1000 rpm and heating at 80 °C. The polymer ratios were varied as 1:2, 1:1, and 2:1 at a constant amount of CA crosslinker of 5% (wt/wt polymer), and the amount of crosslinker was varied as 5% and 10% (wt/wt polymer) at constant polymer volume ratio (1:1). They were prepared as described and each product was subjected to encapsulation efficiency, particle size analysis, and zeta potential measurements.

Encapsulation Efficiency of the Encapsulated CMC/Alg NPK Fertilizer

The polymer dispersion was centrifuged at 10,000 rpm for 15 min then the residue was washed and filtered. The supernatant liquid was collected and added to the filtrate then diluted with deionized water and was subjected to the chemical determination of NPK in terms of parts per million (ppm). The excess or uncoated mass of each element was calculated using the total volume of liquid and concentration from NPK analysis. After this, the mass was subtracted to the total mass of NPK to obtain the mass encapsulated. The encapsulation efficiency is calculated as:

$$\begin{matrix}\mathit{Encapsulation}\\ \mathit{efficiency}\end{matrix} = \frac{\mathit{Mass\ encapsulated\ (g)}}{\mathit{Total\ mass\ (g)}} \text{ x } 100\%$$

Characterization Methodologies Employed

The particle size distribution and zeta potential of each formulation were determined by Malvern ZetaSizer Nano ZS. FTIR spectra were obtained on a Nicolet 6700 FTIR spectrophotometer, after which all samples from different stages of each reaction were dried at 40 °C for 12 h. The reaction was monitored as follows: the first portion was obtained from the alginate-NPK mixture, next was when chitosan was added, and the last one was after the CA crosslinking at the end of the preparation process. The encapsulation of substance onto the matrix was investigated by Spectrum ASCII fluorescence spectrometer using ANS dye as a fluorophore; 50 mL of 5% (wt/vol) dye was prepared and divided into three 15-mL portions. The samples tested were dispersions in water containing 1) ANS dye only, 2) polymer blend without the crosslinker, and 3) polymer blend with the crosslinker, respectively. They were stirred for 1 h at 700 ppm prior to fluorescence spectroscopic measurements. The morphology of CMC/Alg NPK with the highest encapsulation efficiency was checked by SEM.

Controlled Release Studies of the Encapsulated CMC/Alg NPK Fertilizer under Different pH Conditions

Three buffer solutions were used in the release study at various pH 5.0, 7.0, and 8.5. Exactly 1.0 g CMC/Alg NPK with the highest encapsulation efficiency was weighed and analyzed to determine the total content of NPK. While the same mass of polymer-coated fertilizer was placed in each 100-mL buffer, dispersed, and kept at room temperature. The NPK released was examined for 5, 10, 15, 20, and 30 d by getting 5-mL portions of the buffer from each container, after which it was diluted to 50 mL with deionized water prior to NPK chemical analysis. Lastly, the % release was plotted against the time variable for each nutrient at a given pH and the release kinetics of CMC/Alg NPK fertilizers was investigated using the Korsmeyer-Peppas equation.

Fertilizer Efficacy Evaluation of the Encapsulated CMC/Alg NPK Fertilizer

This involved three setups: A – untreated; B – with uncoated NPK; C – with CMC/Alg NPK. Each setup was prepared in triplicates; approximately 700 g of loam soil was placed on each pot. Thereafter, an amount of soil on each pot was subjected to soil analysis of total NPK to ensure that they have comparable nutrient content. The mung bean seeds were placed in water overnight to swell, then five seeds were placed in each pot. After 2 d of sprouting, respective treatments were added. Finally, all pots were placed under direct sunlight and observed for growth. Plant height, leaf height, leaf width, and the number of leaves were all obtained weekly. All of these growth parameters were obtained weekly up to 8 wk and the fruiting time was also noted for each setup.

RESULTS AND DISCUSSION

In general, NPK dissolution is necessary in order for the particle distribution to occur resulting in a better encapsulation upon crosslinking (Ma *et al.* 2013). Alginate dispersion was chosen as the fertilizer core because of its resistance to dissolution at slightly acidic pH; hence, good quality of controlled delivery in acidic soils occurs. However, a modification was done because the presence of more water would reduce the encapsulation due to the NPK solubility in aqueous solution as some of them will escape the polymer crosslinking process (Ren *et al.*. 2016). The heating process is needed for the CA crosslinking mechanism to occur (Demitri *et al.* 2008). CA has been widely used to crosslink the hydroxyl group of various polymers in making films, so there is a possibility of compromising the encapsulation process in terms of the shape of the particles (Reddy and Yang 2010). In light of this, multivalent ions must be employed to ensure bead formation (Kim *et al.* 2012); hence, calcium chloride was chosen as it tends to react to carboxylate of CMC and alginate adapting an eggshell model (Olukman 2012), resulting to encapsulation. Continuous stirring was done under heating for the CA crosslinking as well as to increase the gelling while preventing particle growth.

Encapsulation Efficiency of the Encapsulated CMC/Alg NPK Fertilizer

The encapsulation efficiency of various CMC/Alg formulations obtained from varying the composition of polymers (CMC/Alg) and the amount of CA crosslinker are presented in Figure 1. It is clearly seen that an increase in CA contributed to the encapsulation efficiency of CMC/Alg. This is because crosslinking introduces a three-dimensional network structure (Chen *et al.* 2013) that entraps the substance to the polymer matrix (Shi *et al.* 2008; Mesias *et al.* 2019). Furthermore, when the amount of crosslinker is fixed among treatments while varying CMC/Alg ratios, the encapsulation efficiency is also affected. In Figure 1, variations of 1:2 and 2:1 CMC/Alg ratios have a smaller efficiency compared to that of 1:1. This is due to the imbalance of interaction caused by the dominance of one component over the other, resulting in less organized network (Riyajan and Nuim 2013).

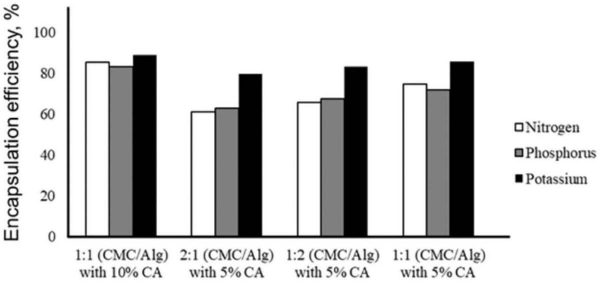

Figure 1. Encapsulation efficiency (%) of various CMC/Alg/CA/NPK formulations.

Particle Size Analysis of the Encapsulated CMC/Alg NPK Fertilizer

It is shown in Figure 2 that various particle sizes (with average values from 733–1200 nm) can be made by varying the CMC/Alg weight ratios as well as the concentration of the added CA crosslinker. At constant crosslinker concentration, the imbalance of interaction given by 1:2 CMC/Alg and 2:1 CMC/Alg formulation – resulting in average sizes of 797 nm and 733 nm, respectively – reduced the mutual interaction. A balanced interaction between two negatively charged polymers, as

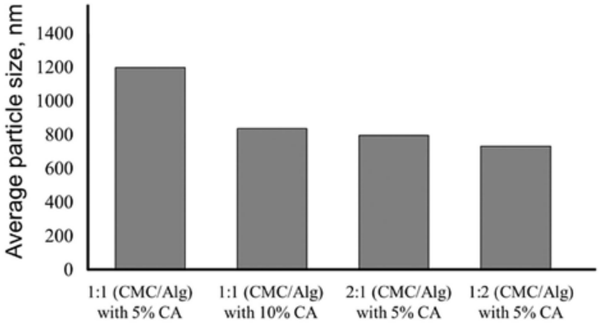

Figure 2. Average particle size (nm) of various CMC/Alg/CA/NPK formulations.

had been observed in 1:1 CMC/Alg, resulted in a larger average particle size (1200 nm) due to repulsive forces (Kim *et al.* 2012). In all these treatments, 5% (wt/wt) CA as the crosslinker was added. With regards to the concentration of the crosslinker, 10%(wt/wt) CA added to 1:1 CMC/Alg resulted in smaller particles (838 nm average size).

Zeta Potential Measurements of the Encapsulated CMC/Alg NPK Fertilizer

By observation, as in the case of CMC/Alg, the particles settled after about 3 d. All values – disregarding the negative sign for the charge of the crosslinked particles – were small, suggesting low stability. Low zeta values suggest that particles will settle eventually.

The reason for low zeta potential values is the dominance of van der Waals interaction over electrostatic repulsion (Zhang *et al.* 2011). In reference to the preparation method, the concentration of the polymers was 3% (wt/vol). Hence, the higher amounts of the polymer will introduce more van der Waals interaction overcoming the effect of electrostatic repulsion since more particles are forming and the distance between them reduces. It can be observed from Figure 3 that the magnitude of zeta potential reduces as the amount of crosslinker is increased from 5% to 10% of 1:1 CMC/Alg formulations. That is accounted for the formation of an organized network upon crosslinking (Maitra and Shukla 2014) and this promotes more van der Waals interaction over electrostatic repulsion (Zhang *et al*. 2011), hence leading to the aggregation of particles. Low zeta potential values of CMC/Alg (1:2) with 5% CA is attributed to the excess alginate polymers in which the charge is being neutralized by Ca^{+2} (Kim *et al.* 2012). Since alginate is more capable of bonding with Ca^{+2} than CMC (Olukman 2012), the zeta potential of 2:1 CMC/Alg formulation remains higher than 1:2 CMC/Alg. In general, the sign of zeta potential dictates the dominant ionic charge in the surface and negative values obtained in this study are reasonable since both CMC and alginate are negatively charged in its sodium salt form (Kumar *et al.* 2015).

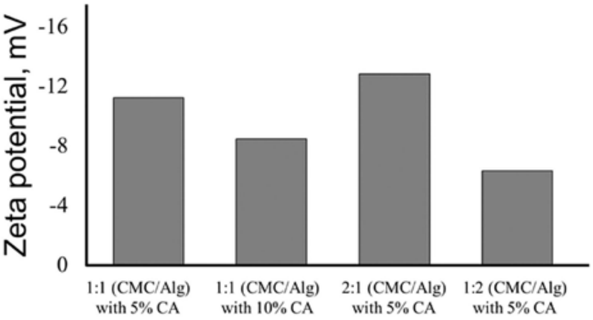

Figure 3. Zeta potential (mV) of various CMC/Alg/CA/NPK formulations.

FTIR Spectroscopy to Follow the Crosslinking Process of the Encapsulated CMC/Alg NPK Fertilizer

To monitor the progress of the CMC/Alg reaction, the micro-scale setup was performed to ensure that sufficient CA is present for IR spectra evaluation. Figure 4 shows the changes in the IR profile as the reaction of CMC/Alg proceeds to completion from Stage 1 to Stage 3.

The first portion (Stage 1) was obtained from a mixture containing NPK and alginate. Next was when CMC was added (Stage 2). The last one was after the CA was added as the crosslinking agent at the end of the preparation process (Stage 3). As the reaction stage proceeded from Stage 1 to Stage 2, the peak at 1086 cm^{-1} was maintained. However, its intensity decreases as the CA crosslinking occurred. Here, the hydroxyl groups reacted to form esters (Demitri *et al.* 2008). However, the broad peak from 3800 to 2500 cm^{-1} had continued to change when CMC was added and further shifted upon crosslinking. These confirmed the crosslinking of the CMC and Alg. This was further supported by the intensity reduction at 1430 cm^{-1} and the shifting of carboxylate stretch due to its interaction with calcium ions and the carboxylate ions of alginate and CMC (Kim *et al.* 2012). Lastly, the appearance of the peak at 1740 cm^{-1} in Stage 3 indicated an ester formation between CA and CMC/Alg (Reddy and Yang 2010).

Fluorescence Spectroscopy to Evaluate Encapsulation Efficiency of the CMC/Alg Materials

The experiment was done using ANS dye as a fluorescing agent. This dye is slightly soluble in pure water and provides a stronger fluorescence emission in a hydrophobic environment compared to that of hydrophilic one (Penaloza *et al*. 2013), which means that an encapsulation process using CMC/Alg can be confirmed if the emission intensity maximizes as the process proceeds to completion. In Figure 5, the ANS dye had the lowest emission intensity followed by CMC/Alg without the CA crosslinker whose intensity was just slightly higher. This indicated that the dye molecules were not yet restricted to the hydrophobic part of the polymer. However, after the crosslinking process, there was an abrupt increase in the emission intensity. What this means is the ANS molecules were within the hydrophobic domain (Penaloza *et al.* 2013) and, therefore, restricted in the CMC/Alg (Mesias *et al.* 2019). Hence, the concept of encapsulation was confirmed.

SEM of the Encapsulated CMC/Alg NPK Fertilizer

The SEM image of CMC/Alg (1:1) with 10% CA at different magnifications is shown in Figure 6. Most of the particles are spherical and their sizes complemented what we have reported in the particle size analysis.

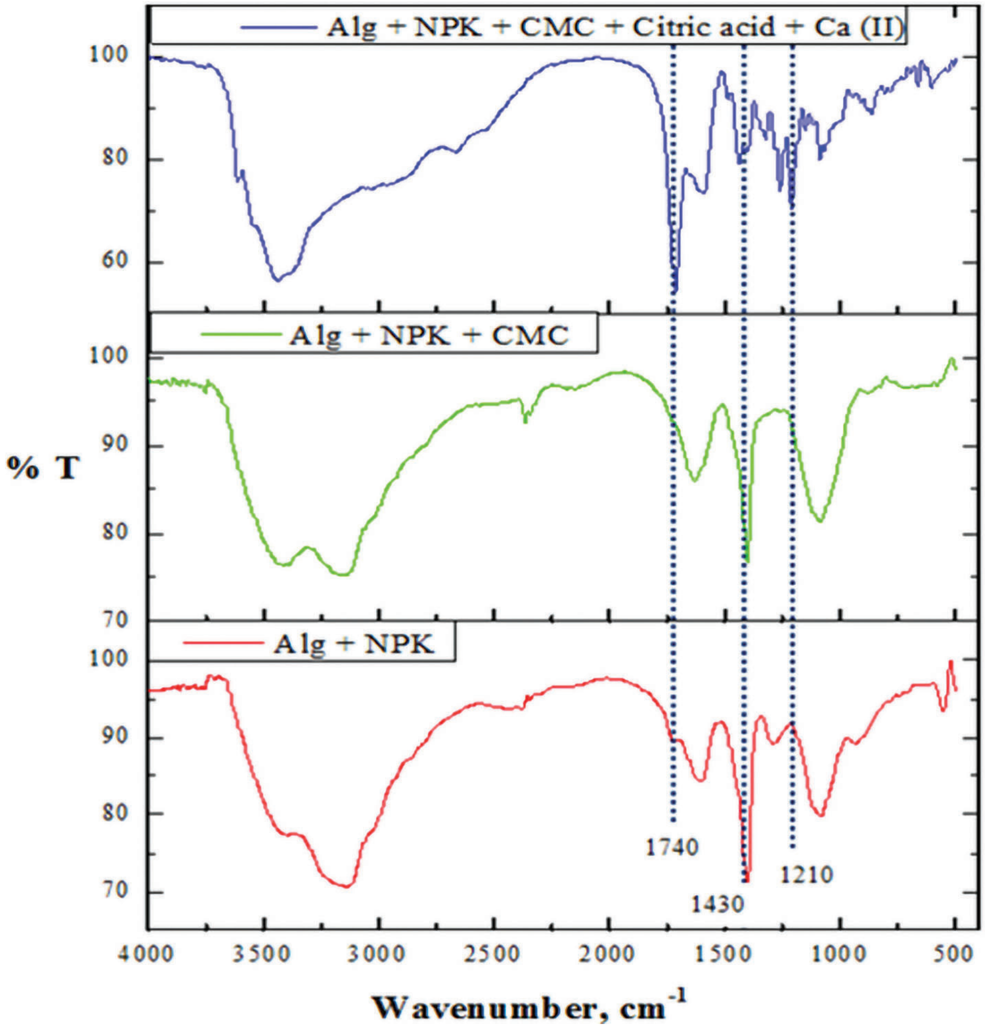

Figure 4. IR spectra for each of the reaction stages presented as follows: (A) NPK fertilizer in alginate dispersion, here labeled as Alg + NPK; (B) CMC added to alginate and NPK, here labeled as Alg + NPK + CMC; (C) CA-crosslinked CMC/Alg NPK, here labeled as Alg + NPK + CMC + CA + Ca(II).

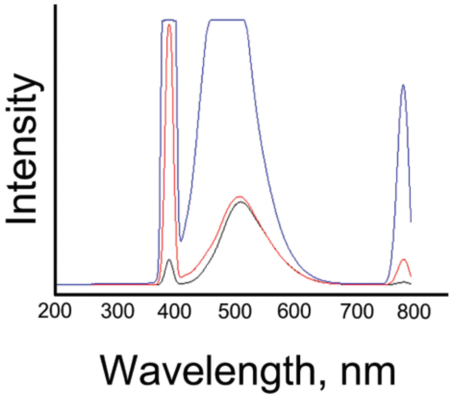

Figure 5. A fluorescent dye (ANS) is used as a model active to be encapsulated. The fluorescence measurement of the ANS dye in water (in black); water containing CMC/Alg (before crosslinking) (in red); and water containing chitosan/alginate and CA (after crosslinking) (in blue).

The formation of spheres itself is a good indication of encapsulation. It has a similarity with the SEM micrograph of a related study by Riyajan and Nuim (2013). It can also be noticed upon further magnification that the surface of the particles was rough and appeared to be porous. This can be due to void structures upon the interaction of CMC-alginate, as described by Kim *et al*. (2012).

Release Studies of the Encapsulated CMC/Alg Fertilizer under Various pH Conditions

The release profiles of CMC/Alg (1:1) with 10% wt/wt CA at various pH levels are shown in Figure 7.

The CMC/Alg NPK exhibits controlled release behavior. It can be seen by curve inspection that the release rate increases with pH. This demonstrates the solubility of polymer components at slightly basic conditions (Kim *et al.* 2012) and it also demonstrates the resistance alginate

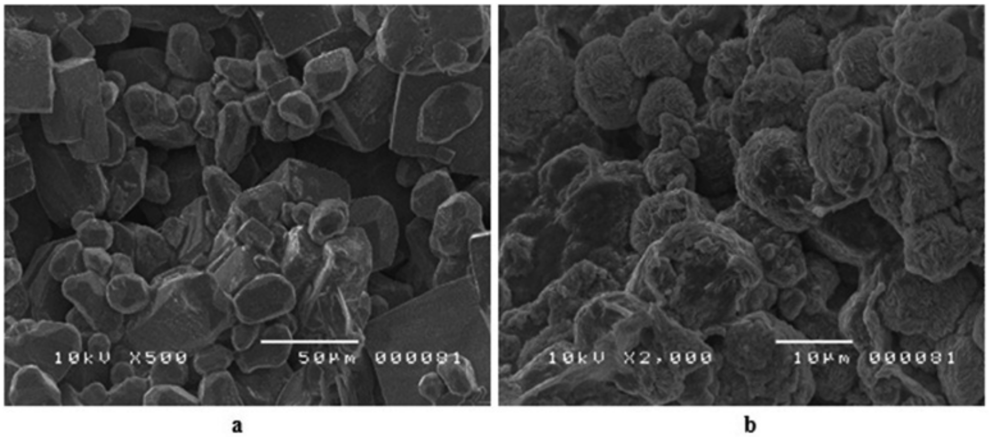

Figure 6. SEM image of the crosslinked polymer (CMC/Alg reacted with CA) containing NPK fertilizer at 500x magnification (a) and 2000x (b).

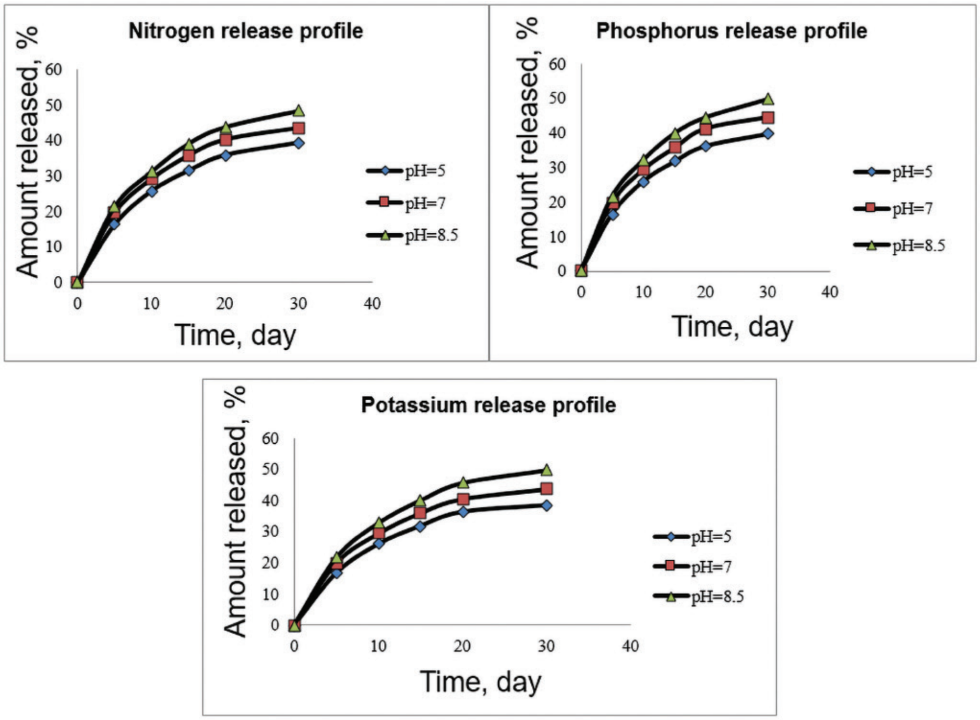

Figure 7. Release profiles of CMC/Alg (1:1) NPK with 10% (w/w) CA at pH 5 (diamond plots), 7 (square plots), and 8.5 (triangle plots).

at slightly acidic medium. Alginate is compensated by CMC by reducing its solubility at neutral to slightly basic pH (Kim *et al*. 2012). It is also revealed that for neutral and slightly basic conditions, about 50 % of NPK were released for the span of 30 d, and this complies with the standard of less than 70% for 28 d (Liu *et al.* 2014).

The release profiles for each nutrient at various pH were fitted into the Korsmeyer-Peppas model. Upon linearization of the said model, an equation of the line is generated for each variable in which y is log release, x is log time, the y-intercept is log release rate constant, and the slope is the release exponent (n), which defines the release mechanism (Anal *et al*. 2010). Based on Figure 8, all nutrients and pH levels had slope ranging from 0.43–0.85, which is an indication of both diffusion-controlled and matrix-based release behaviors (Li *et al.* 2008). Also, the values of the y-intercepts increase with pH. This supports the observation that the % release was highest at basic conditions because of the solubility of the matrix.

Fertilizer Efficacy Evaluation of the Encapsulated CMC/Alg NPK Fertilizer

In the first few weeks, plants in all treatments registered continued growth with their growth parameters (plant height, leaf length, leaf width, and the number of leaves) seemed identical. However, in the later weeks, the setup containing the encapsulated NPK fertilizer was growing faster. Based on Figure 9, CMC/Alg NPK fertilizer treatment had significantly higher values in all parameters measured after 8 wk. This could be attributed to its

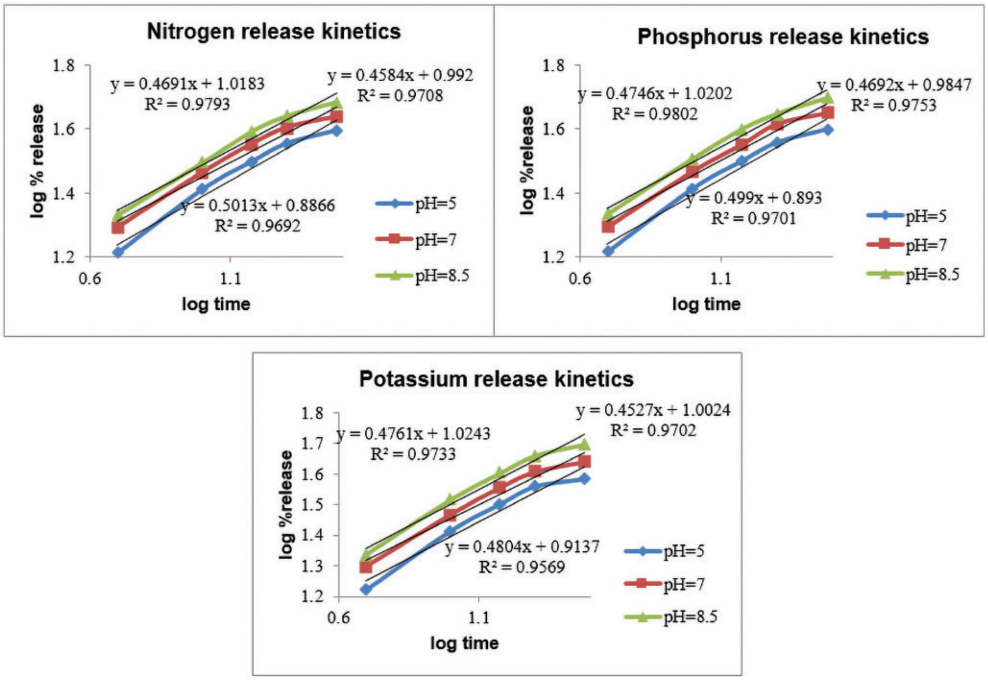

Figure 8. Release kinetics of CMC/Alg (1:1) NPK with 10% (w/w) CA at pH 5 (diamond plots), 7 (square plots), and 8.5 (triangle plots).

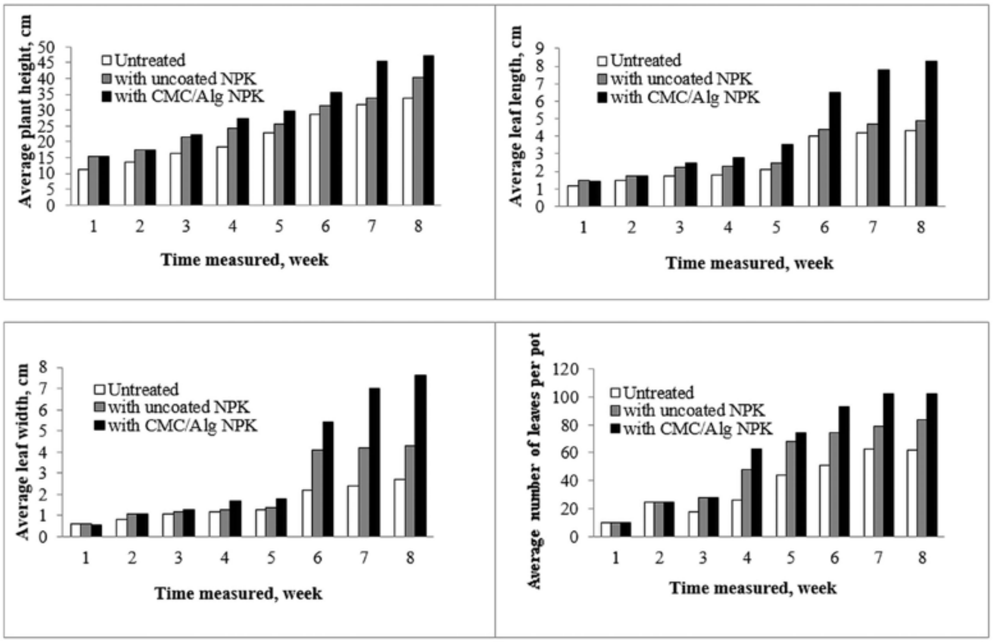

Figure 9. Growth parameters in terms of plant height, leaf length, and leaf width of mung bean studied for 8 wk in various setups: untreated (gray); with uncoated NPK fertilizer (white); and with CMC/Alg coated NPK fertilizer (black).

encapsulating capability exhibiting a slower release of NPK nutrients (Corradini *et al.* 2010). Hence, controlled release property was observed.

CONCLUSION

The encapsulated NPK fertilizers in the form of CMC/Alg using CA as the crosslinking agent was successfully prepared as a polymer dispersion. Particle size analysis revealed various sizes as a result of varying CMC/Alg ratios and the amount of crosslinking agent. Zeta potential measurements confirm that crosslinking of the CMC/Alg results in stable dispersion. The highest encapsulation efficiency, which ranges from 86–91%, was observed in the 1:1 CMC/Alg ratio with 10% CA (per weight polymer) formulation. SEM images reveal spherical particles for the crosslinked CMC/Alg. FTIR spectroscopic measurements confirmed the successful crosslinking of CMC/Alg using CA as the crosslinker. Moreover, fluorescence spectroscopic experiments carried out confirmed that encapsulation was successfully established for CMC/Alg matrix. The encapsulated NPK fertilizer demonstrated controlled release behavior at various pH levels and is established to follow the Korsmeyer-Peppas profile, meaning the release behavior is both governed by polymer relaxation and diffusion. Lastly, these dispersions showed a good controlled release performance in the conducted pot experiments, establishing its great potential to encapsulate chemical inputs like fertilizers.

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