

Process Optimization for the Production of Potassium-Carrageenan Nanofertilizer by Ionic Crosslinking

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Abstract. The effects of nutrient loading, mixing temperature, time and type of drying method (freeze and oven drying) on the total K content of the potassium-carrageenan fertilizer formulated through ionic crosslinking was evaluated. Direct effect on the total K was observed at varying nutrient loading at nutrient-to-carrier mass ratios 1:2 and 2:1 with no significant effect at varying mixing conditions and drying. Instead, variations are observed on the qualitative properties of potassium-carrageenan such as viscosity due to the thermoreversible properties of kappa-carrageenan. A linear model based on the significant factor was generated to predict the potassium content at the range of nutrient ratio adjusted to 1:2 to 1.5:1 to obtain a center ratio 1:1, with a maximum predicted value of 26.64% w/w. Potassium and carrageenan crosslinking yield an organized helix structure based on SEM micrograph with crystalline structure. Freeze dried fertilizers yield smaller particle sizes about 300nm due to its easily size reducible physical appearance than in oven-drying where film like particles are observed. Further, a decrease in absorbance is observed at increased potassium concentration. Evaluation of release pattern using buffer system shows slower release of nutrient using carrageenan carrier compared to conventional fertilizer at pH sensitive environment.

1 Introduction

Environmental pollution and low crop productivity brought about by inefficient conventional fertilizer use can be minimized through encapsulating the essential nutrient in carriers which promotes slow and controlled release based on environmental triggers. This can be obtained through the incorporation of nanotechnology in line with sustainable agriculture through the production of nanofertilizers.

In the Philippines, the most commonly used fertilizer is nitrogen-based, representing 50% of the total fertilizer production [1]. This limited the supplied nutrients to plants only using nitrogen-containing fertilizers, thereby limiting the other essential macronutrients such as potassium. Excessive use of this type of fertilizer has caused negative significant impacts in the environment such as degradation of soil fertility and algal bloom. With this, there has been an imbalanced nutrient intake for plants because of loss and minimal or often incomplete input of essential nutrients.

Incorporating nanotechnology in agriculture is an innovation to address this concern. Nanofertilizers containing the major nutrients or macronutrients essential for plant growth (Nitrogen, Phosphorus, Potassium) are encapsulated in nanoparticles to minimize surface run-off and leaching of nutrient contents, thus maximizing absorption. It promotes controlled release using fertilizer carriers at targeted delivery, diminishing nutrient losses [2]. Few of the

carriers used for encapsulation includes chitosan and carrageenan. Carrageenan is a polysaccharide extracted from red seaweeds of class Rhodophyceae such as *Eucheuma Spinosum* and *Cottonii* which are most commonly distributed in Philippine waters. These carriers are charged polysaccharides interacting with ionic NPK [3].

One of the major essential nutrients which highly affect plant development is potassium which is involved in improving product quality and resistance of plant against drought and diseases. Out of the total potassium fertilizer input, only 30%-50% are absorbed by plants and the remaining portion are lost to the environment [4]. This nutrient can be encapsulated using different nanocarriers such as carrageenan to improve plant nutrient intake, maximize resource costs and minimize nutrient loss.

Hence, this study aims to produce potassium nanofertilizer using kappa-carrageenan which is a potassium-sensitive polymer as carrier through ionic crosslinking and to evaluate its nutrient release pattern and compare it with the conventional potassium fertilizer as indication of its potential for nanofertilizer applications.

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2 Material and Methods

2.1 Materials and Reagents

Commercial refined food-grade kappa-carrageenan obtained from Ricogel Hydrocolloids Inc., Metro Manila, Philippines was used for the nanocarrier preparation. For the nutrient source, fertilizer grade muriate of potash (0-0-60) was obtained from Amigo Planters, Metro Manila.

2.2 Nanocarrier Preparation

The carrier solution of 10mg/mL concentration was produced by dissolving 0.5g of the powdered kappa-carrageenan in 50 mL distilled water and heated at 60°C for 30 minutes to facilitate dissolution. The carrageenan aggregates were further sonicated for 60 minutes at 37 kHz, 550 W to depolymerize the aggregated polymeric chains, forming the nanoparticles.

2.3 Nutrient Preparation

Different amounts of potash were prepared and weighed using analytical balance at high and low ratio of potassium-to-carrageenan ratio with a constant carrier mass. The mass of muriate of potash for high and low ratio are 1.5058 g and 0.5019 g corresponding to 1.5:1 (w/w) and 1:2 (w/w) potassium-to-carrier ratio, respectively, which were determined using stoichiometric analysis.

The weighed muriate of potash were dissolved in 50mL distilled water and sonicated for 30 minutes.

2.4 Ionic Cross-linking of Potassium-Carrageenan Fertilizer

For the ionic crosslinking, carrier and nutrient solutions were mixed using the experimental set-up shown in Figure 1.

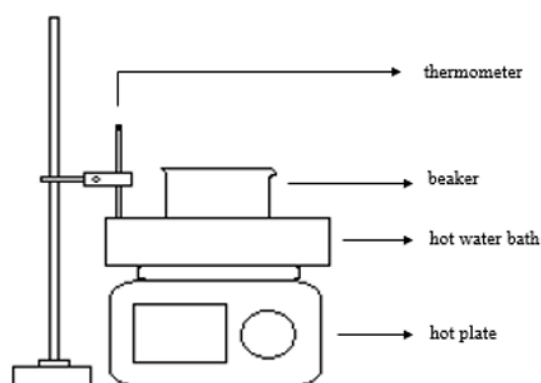


Fig 1. Experimental set-up for ionic cross-linking.

The nutrient and polymer solutions were mixed at 1:1 volume ratio, forming a 100mL potassium-carrageenan mixture. Nanoparticle formation occurs spontaneously through gradual addition of nutrient to the carrier solution at varying mixing time of range 30-60 minutes and temperature range from 40-70°C. Water bath was used to maintain the temperature at the specified condition using a hot plate and thermometer. The gel suspension obtained were sonicated at 37 kHz, 550 W for 60 minutes, cooled for equilibration at room temperature and filtered for gel recovery. The obtained nanosuspension were dried using freeze drying at 100 mTorr-300 mTorr and oven drying at 70°C, respectively to complete dryness.

The parametric experimental matrix was designed using three-factor two-level (2^3) full factorial design and the generated model was optimized using Response Surface Methodology to maximize the Total Potassium content of the synthesized fertilizer. The experimental data were analyzed by determining the potassium content of fertilizers produced at different conditions and evaluated using statistical analysis at $\alpha=0.05$ using Design Expert version 11.0.0.

The response was obtained using a calibrated Sherwood Model 410 Flame Photometer to determine the amount of potassium in the sample. Prior to photometric analysis, the sample undergone sample treatment through dry ashing to remove the residual organic compounds in the nanofertilizer. Using standard solutions, a calibration curve was obtained to relate the flame photometric reading versus the total potassium content.

2.5 Release Pattern Evaluation using Buffer

The release pattern of the potassium-carrageenan fertilizer formulated at optimum conditions was evaluated using Britton Robinson buffer solution which is composed of equal amounts of 0.04M Boric acid, 0.04M phosphoric acid and 0.04M acetic acid. A mass of 0.08 g formulated fertilizer was weighed and applied in 1L buffer system. The set-up was allowed to stand for 2 days and 5-ml samples were collected at time 0, 2, 4, 12, 24 and 48 hours and stored in vials for potassium content analysis via flame photometry. The same procedure was performed for the blank buffer solution and buffer loaded with 0.1 g muriate of potash for comparison.

The potassium content for the three different solutions at each collection interval were tabulated and compared for the purpose of comparing the fertilizers' capacity to release nutrients at minimized loss with respect to time. Consequently, the theoretical potassium content of the fertilizer inputted was calculated to determine the maximum amount of nutrient that can be released, and this was compared to the final potassium content determined at $t=48$ hours to compare the encapsulation efficiency of the carrier.

3 Results and Discussion

3.1 Effects of Process Conditions on Total Potassium Content

Statistical analysis using ANOVA ($\alpha = 0.05$) revealed that only the nutrient-to-carrier ratio significantly affects the total potassium content of the synthesized nanofertilizer. Variation in mixing temperature and time has no significant effect on the nutrient content due to the spontaneous gel formation upon addition of muriate of potash, which contains about 49.81%w/w theoretical Total Potassium content. This is because the crosslinking of potassium to the anionic blocks of the carrier occurred spontaneously upon gradual addition of nutrient, as shown by the instantaneous gel formation as indication of the abrupt binding of potassium ion to kappa-carrageenan's OSO_3^- group. At high temperature, decreased viscosity of the gel suspension was observed due to the conformational transformation of aggregated double helices into coils. However, the cooling of the suspension at room temperature before drying facilitated equilibration where the coils transition back to double helix aggregates. This is due to the thermoreversible characteristics of kappa-carrageenan where there is a reversible transition of aggregated double helices into coils and vice versa at changing temperature. At high temperatures, *gel melting* is favored where the aggregated helices regain its coil conformation [5] and reverts back to double helix aggregates segmented by crosslinkers (e.g., potassium) during cooling [6]. During cooling phase, the potassium ions present in the suspension crosslinks altogether with the sulphate groups of kappa-carrageenan, hereby neglecting the initial effect of mixing condition variations.

At increased nutrient loading, increased viscosity of the gel suspension was observed due to the increased binding of potassium to the negatively charged sulfate groups of kappa-carrageenan. However, the gel properties were not further evaluated since the gel recovered where dried. The amount of nutrient loading has shown direct positive effect on the total potassium content encapsulated due to abundance of potassium source. At increased nutrient loading, high amount of potassium is available for crosslinking and vice versa, hence an increase in the final potassium content.

Further, the type of drying method was determined to have no significant effect on the total potassium content of the potassium-carrageenan nanofertilizer analyzed statistically at $\alpha=0.05$ with a p-value of 0.1213. Hence, oven drying was employed for the proceeding of experimentation due to its cost and energy efficiency. The model generated was optimized via one-factor optimization to maximize the total potassium content of the nanofertilizer. and it was experimentally verified that increased nutrient loading yields higher Total Potassium (%w/w) content at a constant carrier concentration because of the increased direct attachment of K^+ ions to the OSO_3^- ends of the polymer via cross linking, with a

maximum Total potassium content of 30%w/w, approximately six to seven percent of which is inherent to the kappa-carrageenan. Maximum response was obtained at 1.5:1 nutrient-carrier mass ratio at 40°C and 30 minutes mixing.

3.2 Characterization of Potassium-Carrageenan Nanofertilizer

The SEM images for both drying methods of the synthesized fertilizer as observed in Figure 3 show crystalline structures formed during cross-linking due to formation and organization of helices aggregate.

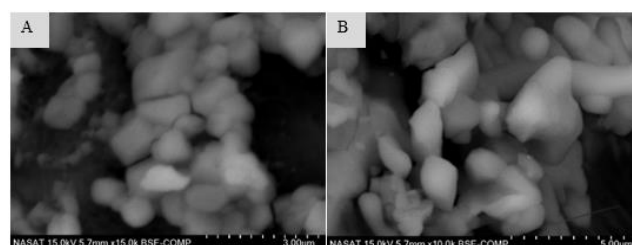


Fig 3. Scanning electron micrograph (SEM) of oven dried (A) and freeze dried (B) potassium-carrageenan fertilizer synthesized at optimum conditions.

Formation of these crystalline structures indicates the cross-linking of kappa carrageenan with potassium ions during gelation. This is more evident in the oven dried samples. The image obtained from the freeze-dried samples shows aggregation of the particles, hence the crystalline structures are less evident.

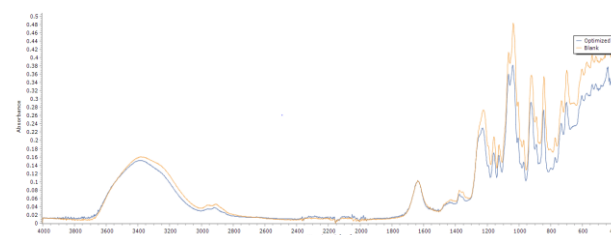


Fig 4. Comparison of FTIR spectra of kappa-carrageenan with and without nutrient loading.

As shown in Figure 4 by comparing the FTIR spectrum of the potassium-carrageenan fertilizer versus the raw carrageenan, the same bands or wavenumber for both was observed. However, variation in absorbance occurred from the deviation on the infrared light absorbance where it is observed to decrease upon loading of nutrient, represented by the blue spectrum. This is explained by Beer's law where concentration has direct effect on the absorbance. At high nutrient loading, the concentration of potassium in the sample is high which directly links with the sulphate groups of kappa-carrageenan, hence lesser sulphate molecules are available to absorb the light emitted, thus a decrease in absorbance.

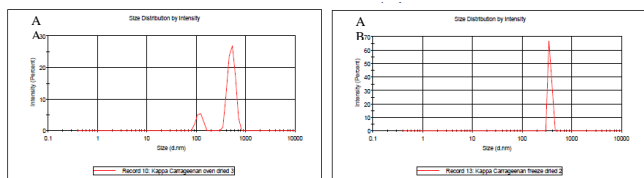


Fig 5. Size distribution intensity graph of oven dried (A) and freeze-dried (B) potassium carrageenan nanofertilizer.

Using Dynamic Light Scattering, the particle size of the formulated nanofertilizer obtained from both drying methods were compared and analyzed as shown in Figure 5. The oven-dried sample was polydisperse and exhibits aggregation as observed by the extended decay of curves and multiple peaks, with the highest observed at 516.5nm and the remaining at 116nm. Meanwhile, a smaller particle size of 360nm was observed for the freeze-dried samples because of its porous appearance, making it easier to size reduce unlike in oven-drying where film-like particles were observed. Due to the thermo-reversible property of kappa-carrageenan, the fertilizer exhibited swelling behavior upon prolonged contact with water, which was used as dispersant, resulting to high particle size. For nanoparticles derived from polymers, higher particle sizes are generally observed since it exists as a colloidal system, with an upper limit of 1000nm [7]. Based on this criterion, the synthesized potassium-carrageenan fertilizer is considered a nanofertilizer.

3.3 Nutrient Release Characteristics of the Potassium-Carrageenan Fertilizer using Britton Robinson Buffer

The 2-day release pattern of potassium-carrageenan fertilizer was analyzed and compared with raw fertilizer grade muriate of potash. The obtained data for the overall sampling for $t=0$ to $t=48$ hours for all samples were summarized as shown in Figure 6.

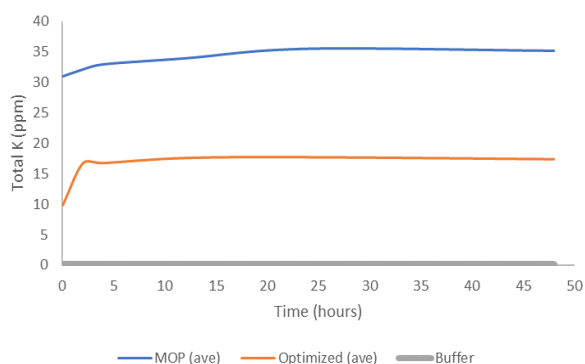


Fig 6. Graph of cumulative average Total Potassium content (ppm) released at $t=0$ to $t=48$ hours.

At time 0, an average initial reading of 31 ppm and 9.8 ppm potassium were analyzed using flame photometry for the muriate of potash (MOP) and potassium-carrageenan fertilizer, respectively. Since the

environment is acidic with pH 5.5, decrease in association of the cross-linked polymer was favored due to competing electrostatic interactions. At an increased time, an increase in the potassium content was observed specifically at the interval of 0 to 4 hours. This can be attributed to the potassium in the synthesized fertilizer that is not linked and may only be adhered on the carrageenan surface. The obtained data were compared to the theoretical maximum potassium content that can be potentially released by the muriate of potash and potassium-carrageenan fertilizers. After $t=48$, nutrient release tended to level off at 17.40 ppm which represents 74.07% of the total potassium that can be potentially released. Meanwhile, nutrient release for the muriate of potash reached 35.21 ppm at $t=48$, presenting 99.40% of the total potassium available in the fertilizer.

Table 1. Comparison of average Total Potassium released at $t=48$ vs maximum Total Potassium capacity.

Sample	Total K at $t=48$ hours (ppm)	Theoretical Total K_{max} (ppm)
Muriate of Potash	35.21	35.42
Potassium-Carrageenan	17.40	23.49
Britton-Robinson	0	0

After 48 hours, the muriate of potash almost reached the maximum Total Potassium it is available to be released from the fertilizer. Meanwhile, the potassium-carrageenan fertilizer would still be capable to release more potassium even after 48 hours based on the significant gap of maximum and at $t=48$ Total Potassium values determined as shown in Table 1. Relative to the release pattern of the conventional fertilizer, smaller amounts of potassium are released from the potassium-carrageenan fertilizer at cumulative time, indicating that there is a strong affinity between the carrier and the potassium nutrient.

4 Conclusion

Environmental pollution Potassium fertilizer was synthesized using food grade kappa-carrageenan as carrier and fertilizer grade muriate of potash through ionic crosslinking which involves linking of the K^+ ion with carrageenan's SO_3^- group to form gel. The effect of mixing time and temperature was determined to be insignificant on the Total Potassium content, instead the stated parameters were observed to affect only the qualitative properties of the fertilizer such as viscosity. Moreover, increased Total Potassium content was observed at increased potassium-to-carrageenan ratio which was analyzed using flame photometry. Different drying methods were also employed namely oven drying and freeze drying which was observed to have no significant effect on the potassium content. After determining the significant factors, a model representing the response was generated using one factor optimization with two center points. Numerical optimization was done to maximize the total potassium content of the

formulated fertilizer and the optimum condition was experimentally verified. Optimum conditions were obtained at high level nutrient loading (1.5058 g) and low-level mixing temperature (40°C) and time (30 min) for economic advantages, with an optimum Total Potassium content of 29.37% (w/w). It was validated that the generated model is adequate and can be used to predict the potassium content. Further, the aggregation of double helices during crosslinking yield crystalline microstructures. The potassium-carrageenan nanofertilizer have lower absorbance compared to the raw kappa-carrageenan (which initially contains few amounts of potassium), hereby hindering vibrations of available functional groups due to increased binding. Comparing both drying methods used, freeze-dried fertilizer yields smaller particles than oven-dried samples.

Relative to the conventional muriate of potash, a slower accumulated release of potassium was observed for the synthesized potassium-carrageenan fertilizer. Because of the wide availability of carrageenan and its properties, it is considered a good carrier for delivery systems especially with potassium because of its effective cross-linking compatibility.

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