Eggshell As An Alternative Source Of Calcium For Nitrate Fertilizer Bead Gel

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The chicken eggshell was applied as an alternative calcium source to produce calcium nitrate fertilizer. 12 g of eggshell waste was used as raw material for extraction into liquid calcium nitrate by a 100 mL of 10%(v/v) nitric acid solution. The liquid calcium nitrate fertilizer was encapsulated through the wet-extrusion process, in which calcium ions from liquid calcium nitrate as crosslinking agents and sodium alginate as an absorbent polymer. 73.57% of nitrate was absorbed by the droplet of 2%(w/v) sodium alginate, forming sphericallike gel structures. The optimal hardening time for bead gel formation was 120 min. The average size of wet bead gels was 4.29 ± 0.34 mm. The bead gels were oven-dried at 45°C for 1 hour to maintain their shapes. Among other controlled release agents, pectin showed the slowest nitrate release from fertilizer bead gel. The chemical nature of bead gels characterized by FTIR indicated that nitrate was absorbed by alginate polymer incorporated with pectin, binding with the Ca^{2+} ions.

Keywords: bead gel, calcium nitrate, control release agent, eggshell, encapsulation, fertilizer

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1. Introduction

Eggshells are an agricultural solid waste generated several tons per day from food processing plants, restaurants, and households and cumulated on-site without pre-treatment [1, 2]. The high production of eggs relates to the enormous generation of eggshell waste, which is typically discarded and disposed of in various landfills [3]. The Food and Agriculture Organization (FAO) reported that 6.4 million tons of eggshell waste are sent to landfills [4], with a high management cost [1]. To reduce the amount and prevent environmental problems, eggshell wastes should be recycled, reused, and transformed into valuable products [5]. Eggshell consists of 94% calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate, and 4% organic substances in its composition [6, 7]. Therefore, it is economical to transform the eggshell waste to create new value from these waste materials.

In the literature reviews, eggshell waste can be used for many applications as a valuable product, such as a biodiesel catalyst, a low-cost adsorbent for the removal of ionic pollutants, a possible bone substitute, fertilizer, and calcium supplements in nutrition for plants, animals, and humans [1] due to its rich source of mineral salts, mainly calcium carbonate [6–8]. In addition, as a fertilizer, eggshell has a large amount of calcium which increases the pH value and enriches the calcium content of the soil. This enrichment benefits tomato and berry plants suffering from blossom-end rot disease [9].

It is generally known that nitrogen is an essential mineral nutrient for plant growth. Most non-legume cropping systems need more nitrogen inputs from the soil in different growth stages. Nitrogen availability to crops is a significant limiting factor in the productivity of crops [10]. Therefore, nitrogen is the scarce primary nutrient for crop production. To enhance agricultural production, nitrogen fertilizers have increased over the last fifty years [11].

However, nitrogen fertilizers contain a large amount of ammonium and amine nitrogen, making the soil acidified. Therefore, ammonium-based fertilizer is suitable for irrigation areas with high pH, and ammonium nitrogen and sulfur accelerate the soil acidification process, becoming a neutralizing effect [12]. Calcium nitrate fertilizer contains nitrogen and calcium, two essential nutritional elements for the plants' needs. Calcium, together with nitrate, does not cause the formation of remaining in the roots of plants because nitrate-nitrogen elevates the absorption of soluble calcium by the plant roots, supporting the supply of calcium to the plant [13].

However, the intensive use of fertilizer nitrogen can cause the deterioration of the soil because conventional fertilizers are highly soluble and immediately lost through leaching and runoff [11]. The encapsulation has been used to control the release of agrochemicals to enhance the efficiency of nutrient use, improve stability, and reduce environmental impact [14]. Agrochemical substances are coated with polymers to allow slow release. Water will diffuse through the coating and slowly dissolve the fertilizer materials inside. The dissolved fertilizer slowly diffuses back out of the coating [15]. It has been reported that the duration and timing of the release depend on the coating properties. The controlled release can decrease the potential for leaching, runoff, and volatilization. In addition, encapsulation can protect agrochemicals from water and microorganism degradation and reduce phytotoxicity [16].

Alginate is a polysaccharide extracted from brown seaweeds. In acidic environments, alginate carboxyl groups protonate, limiting drug release. In addition, alginate can crosslink with Ca^{2+} ions through ionotropic gelation [17]. Furthermore, calcium can be extracted from eggshells and shells. Therefore, the use of alginate for encapsulation can provide several advantages, such as ease of preparation, biocompatibility, biodegradability, and nontoxicity, making alginate one of the biopolymers with biomedical and other applicability [18–20].

In agriculture, alginate gels have served as excellent matrices for the slow release of agrochemicals due to their biodegradability and easy incorporation of agrochemicals using an aqueous system at ambient temperatures [21]. For example, carboxymethyl cellulose and sodium alginate hydrogel beads were prepared by Ca^{2+} ions crosslinking followed by gamma irradiation, which can be used for the controlled release of ammonium nitrate used as an agrochemical [22]. Joshi et al. [23] synthesized sodium alginate-based hydrogel microbeads using calcium chloride as the crosslinking agent in the wet-extrusion process to encapsulate fertilizers and pesticides. Encapsulation helps slow the release of inorganic fertilizers (KNO_3 and K_2HPO_4) into the environment and protects the biopesticide *Bacillus thuringiensis* from harsh environments. These encapsulation materials are organic and completely biodegradable. In addition, urea, a nitrogen-source fertilizer, was entrapped within chitosan-alginate and gelatin-alginate beads. It found that chitosan-alginate beads possessed better urea entrapping efficiency than gelatin-alginate beads, while gelatin-alginate beads showed slower fertilizer release than those of the chitosan-alginate beads. These biodegradable polymer-based urea fertilizers can help reduce soil pollution by acting as efficient soil conditioners, allowing for the slow and steady release of urea into the soil [20].

The objective in this study was to encapsulate nitrate fertilizer within biopolymeric beads of sodium alginate crosslinked with divalent calcium ions derived from the eggshell using the wet extrusion technique. Cellulose, guar gum, and pectin were examined in order to facilitate the controlled release of nitrate. Chicken eggshell waste was used as a calcium source for calcium nitrate fertilizer. The extrusion technique was used for preparing calcium nitrate fertilizer beads with sodium alginate combined with the controlled-release agents cellulose, guar gum, and pectin. The loading capacity and the encapsulation efficiency of nitrate, the morphology, swelling, and potential of the controlled release of nitrate from beads as encapsulated fertilizer were investigated.

2. Materials and methods

2.1. Preparation of chicken eggshell powder

Chicken eggshell waste was collected from a canteen of King Mongkut's University of Technology North Bangkok. First, the membrane of eggshell waste was removed, then eggshell waste was washed and desiccated at room temperature. After that, the dried eggshell was crushed into small particles and oven-dried at 105°C for 24h (Fig. 1a). Finally, the dried crushed eggshell was pulverized by a miller into powder (Fig. 1b) and then sieved using mesh sizes of 35.

2.2. Extraction of liquid calcium nitrate

The ratio of an eggshell powder to 10% (w/v) HNO_3 solution used for extraction was 6, 8, 10, 12, 14, 16, 18, and 20%(w/v). The eggshell powder was gradually added to the HNO_3 solution and continuously mixed. After that, liquid calcium nitrate was analyzed for the solubility of eggshell powder. The undissolved eggshell powder in the solution was filtered through filter paper, oven-dried at 105°C for 24 h, and weighed. The pH value of liquid calcium nitrate was also measured. The optimum amount for extracting liquid calcium nitrate from eggshell waste with a 10% nitric acid solution was chosen for the further preparation of calcium nitrate beads.

2.3. Preparation of calcium nitrate beads

A 2%(w/v) sodium alginate solution was prepared by adding 2 g of sodium alginate (Sigma-Aldrich, USA) dissolved in 100 mL of distilled water. After that, 50 mL of 2%(w/v) sodium alginate was loaded into a plastic syringe and then added dropwise into 100 mL of 12% (w/v) liquid calcium nitrate solution under 100 rpm to form spherical-like beads. To analyze the loading capacity (LC) and the encapsulation efficiency (EE), the $Ca\,(NO_3)_2$ residual amount in an aqueous solution was determined after withdrawing the $Ca\,(NO_3)_2$-alginate bead at 30, 60, 90, 120, and 150 minutes.

2.4. Hydration of calcium nitrate bead

All $Ca(NO_3)_2$-alginate beads prepared in section 2.3 with an optimum hardening time were weighed and oven-dried at 45°C for 1 and 2 h to remove humidity from the bead. After drying, the dried beads were weighed and measured.

2.5. Preparation of beads load with the controlled-release agent

Cellulose, pectin, and guar gum were used as the controlled-release agent. A- 0.2% of each controlled-release agent was added to a 2% sodium alginate solution before the dropwise step, which used a similar protocol to section 2.3. After a hardening time of 120 min, the beads were harvested from the solution and absorbed with paper. The beads were counted, weighed, and measured to determine bead size distribution by vernier caliper (HI-TECH, Germany). In capacity (LC-%) and encapsulation efficiency (EE-%) of nitrate, which was calculated using Eqs. (1) and (2), respectively, according to Sun et al. [24].

$$LC = \left[\frac{\text{amount of encapsulated NO3}}{\text{total bead weight}}\right] \times 100\% \quad (1)$$

$$EC = \left[\frac{\text{initial amount of NO3-residaul amont of NO3 in soslution}}{\text{initial amount of NO3}}\right] \times 100\% \quad (2)$$

2.6. Fourier transform infrared (FTIR) spectroscopy

The surface chemical functional groups were analyzed using Fourier transform infrared spectroscopy (FTIR) (PerkinElmer Spectrum UATR Two, USA), and the FTIR spectra were scanned with the range of $4000 - 400\ \text{cm}^{-1}$ at a resolution of $4\ \text{cm}^{-1}$.

2.7. Release experiment of nitrate from beads

All $Ca\,(NO_3)_2$-alginate beads (control bead, NA), $Ca\,(NO_3)_2$-alginate-cellulose beads (NAC), $Ca\,(NO_3)_2$-alginate-pectin beads (NAP), and $Ca\,(NO_3)_2$-alginate-guar gum beads (NAG) were immersed in 200 mL of distilled (DI) water under 100 rpm at room temperature for 2hrs. After that, 2 mL of the solution, in which nitrate was released from each bead type, was taken and measured by the chromotropic acid method (HI93766-50 reagent kit, Hanna Instruments, USA) and calculated with Eq. (3) according to Nornberg et al. [25]. Each experiment was done in duplicate.

$$\text{NO3 released} = \left[\frac{\text{amount of NO3 in solution}}{\text{amount of NO3 encapsulated}}\right] \times 100\% \quad (3)$$

2.8. Swelling and shrinking of calcium nitrate beads

All bead gel types were soaked in 200 mL of distilled water under 100 rpm at room temperature. Twenty swollen and shrunk bead gels for each bead type were taken from day 7 and 30 to measure the size by vernier caliper (HI-TECH, Germany). After each time interval, the swelling and shrinking rates were calculated in Eq. (4) [25] and Eq. (5), respectively.

$$\text{Swelling }(\%) = \left[\left(\frac{\text{swollen weight of beads}}{\text{dryweight of beads}}\right) - 1\right] \times 100\% \quad (4)$$

$$Shrinking(\%) = \left[\left(\frac{\text{shrunk weight of beads}}{\text{dry weight of beads}}\right) - 1\right] \times 100\% \quad (5)$$


(a) (b)

Fig. 1. (a) Crushed dried chicken eggshell and (b) dried chicken eggshell powder

3. Result discussions

3.1. Effect of amount of eggshell powder on calcium nitrate extraction

The amount of eggshell powder varied from 6% up to 20%(w/v) in 10%(w/v)HNO_3 solution. It was found that an amount of eggshell powder of 6%, 8%, 10%, and 12%(w/v) had high solubility in the 10%(w/v)HNO_3 solution (Fig. 2).

When the amount of eggshell was increased from 6% up to 8%, 10%, and 12%(w/v) in HNO_3 solution, the solubility was slowly decreased from 98.54% to 98.25 , to 97.75 , and 96.82%, respectively. However, when the amount of eggshell was increased from 12% to 14%, a drop in solubility was observed from 96.82% to 83.56%. Solubility was continuously decreased with an increase of eggshell powder from 14% to 16%, to 18% and 20% (w/v) counted to 73.36%, 64.58%, and 59.29%, respectively. Therefore, 12%(w/v) of eggshell was an optimum amount for extracting liquid calcium nitrate fertilizer.

The pH value from the extraction of eggshell powder at 6% to 12%(w/v) in 10%(w/v) HNO_3 solution ranges from 0.25 to 0.84 , which leads to high solubility, as shown in Fig. 2. The increase in eggshells increased the pH value because eggshells consist of 94% calcium carbonate, which can raise the pH by consuming hydrogen ions to form bicarbonate ions [26]. When the amount of eggshell was increased from 12% to 14%, to 16%, to 18%, and 20%, the pH value increased to 4.34, 4.44, 4.82, and 5.18 , respectively, resulting in a decrease in the solubility.

3.2. Effect of hardening time and hydration on the formation of calcium nitrate beads

Usually, the forming of alginate beads was prepared from sodium alginate ionically crosslinked by divalent calcium ions $\left(Ca^{2+}\right)$ [25]. The carboxyl groups in the alginate

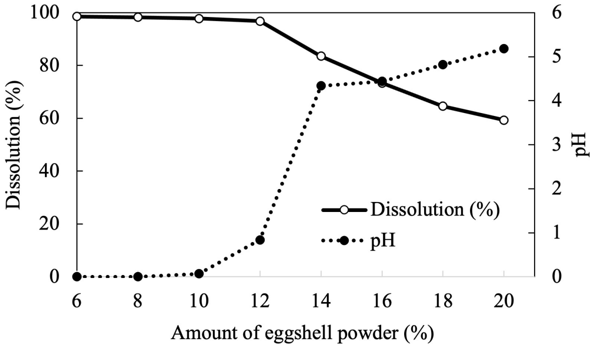
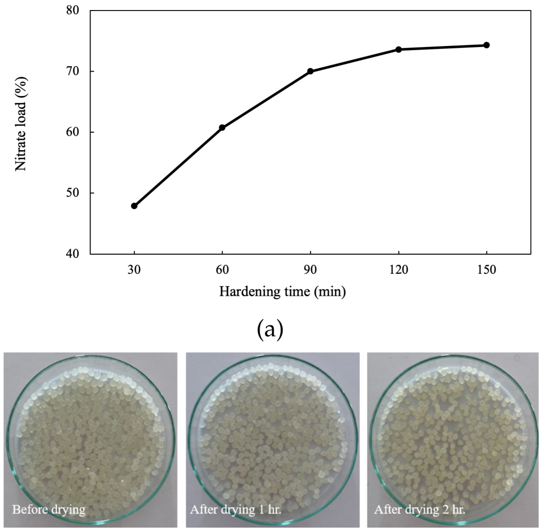


Fig. 2. The amount of eggshell powder dissolved with 12% nitric acid on the extraction of calcium nitrate and pH value

polymer will bind with the Ca^{2+} ions during immersion [23]. However, liquid calcium nitrate produced from the eggshell powder also contained calcium in this study. Therefore, alginate beads were formed without adding $CaCl_2$ as the crosslinking agent. To investigate the optimum time for bead forming, the amount of nitrate absorbed into the bead was analyzed by measuring the residual nitrate in liquid calcium nitrate.

When the time of bead forming in liquid calcium nitrate was increased from 30 min to 60 , to 90 , to 120 , and 150 min, the absorption capacity of alginate beads from 47.86% was also increased to 60.72%, to 70.00%, to 73.57%, and 74.29%, respectively. Therefore, the time required for bead forming in liquid calcium nitrate was 120 min, which was the optimal time to produce nitrate bead gel (Fig. 3a). The spherical with a smooth surface and comparable size of all encapsulated beads were found (Fig. 3b).

After oven-dried at 45°C, it was found that one h of drying was sufficient for the stability of the beads (Table 1). The weight of the beads was reduced by 18.67%, and the



(b)

Fig. 3. (a) The absorption capacity of alginate beads against time and (b) the morphology of alginate bead after hydration.

Table 1. Shape and weight of bead after oven drying for hydration test

The oven dries at 45°C	Weight (g)	Size (mm)
Before oven dries	14.817	4.00 ± 0.00
Drying for 1 h	12.050	3.70 ± 0.30
Drying for 2 h	9.072	3.27 ± 0.30

bead's surface was dry. The shape of the beads was round. When the drying time was increased to 2 h, the weight of the beads was reduced by 38.77%, and the bead's surface was wrinkled. The size of the dried bead was decreased and related to the drying time. The bead size incubated for 1 and 2 h was reduced by 7.5 and 18.25%, respectively (Fig. 3b).

3.3. Morphology of calcium nitrate bead incorporated with the controlled-release agents

Carboxyl groups in alginate polymers can bind with Ca^{2+} ions after immersion in an aqueous solution of Ca^{2+} ions. Then, alginate chains rapidly crosslink via stacking of G-blocks to form an egg-box structure into a spherical shape because the G-block of alginate has a high affinity for divalent ions [23]. However, it has been reported that alginate alone does not have sufficient mechanical properties.

Therefore, alginate should be combined with other polyelectronegative polymers such as cellulose [25], guar gum [27], and pectin [28, 29] to form bridges with other chains and become hydrogel networks. Alginate and other polyelectronegative polymers interact via intermolecular hydrogen bonds [30, 31]. The molecule of guar gum [32] and cellulose [25] also contains a hydroxyl groups. Therefore, an interaction between the alginate/cellulose and alginate/guar gum will occur by hydrogen bonding activity.

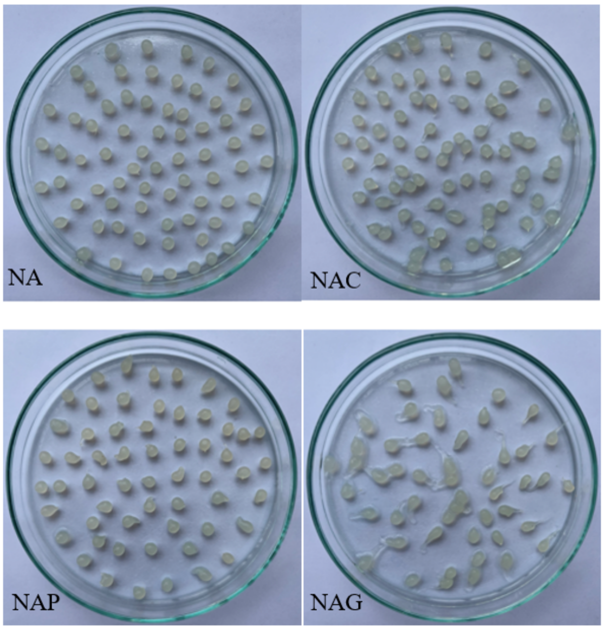


Fig. 4. Bead shape encapsulated with the controlled-release agents

The addition of the controlled-release agents affected on the bead yield and the bead shape. That is, the beads containing cellulose (NAC), bead containing pectin (NAP), and beads containing guar gum (NAG) yielded 637.5, 647.5, and 565 bead/g, respectively, compared with alginate (NA) beads, which yielded 670 bead/g. The shape and size of beads are known to be linked to their mechanical and chemical stability. Fig. 4 shows a bead shape encapsulated with the controlled-release agent compared with an alginate bead. It was found that the type of controlled-release agent added with sodium alginate to form a bead affected the shape of the bead. The aspherical shape was observed from the NAC beads, relatively the same as an NA bead.

Therefore, beads with well-defined sizes and shapes lead to the development of highly reproducible reactions or controlled release rates [33]. A less rounded shape was detected in some NAP beads due to an increase in the viscosity of the solution. In addition, a round shape with a tail was observed from the NAG bead. The non-spherical shape of the beads has been reported to decrease gel bead strength compared to spherical beads. In addition, breakage and cracking were observed on the tear-shaped beads and non-spherical beads, leading to the release of the encapsulant [33].

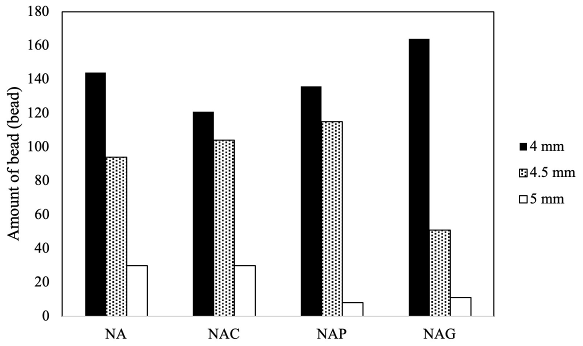


Fig. 5. Size distribution of each bead type

Calcium nitrate bead encapsulated by alginate, cellulose-alginate, pectin-alginate, and guar gum-alginate is divided into three sizes: 4, 4.5, and 5.0 mm (Fig. 5). It can be seen that the size of 4 mm was counted as the highest proportion, followed by 4.5 and 5.0 mm for all bead types. The size 4.0, 4.5, and 5.0 mm of NA, NAC and NAP beads counted 47.45 − 53.73%, 35.07 − 44.40%, and 3.09 − 11.79%, respectively. However, the size of 4.0 mm of the NAG bead counted 72.57%, followed by 22.57% of 4.5 mm, and 4.87% of 5.0 mm.

3.4. Potential of the controlled-release agent to encapsulate and control the release of nitrate

For the loading capacity of nitrate, the NA bead provided the highest loading capacity, followed by the NAG, NAC, and NAP beads, respectively. The same as the results of loading capacity, the highest encapsulation efficiency was detected from the NA bead, followed by the NAG, NAC, and NAP beads, respectively. It revealed that the controlled-release agent did not assist the bead in absorbing more nitrate compared to alginate (Table 2). For the release experiment, adding the controlled-release agent could control and prolong nitrate release from the bead. As a result, the NAP bead could control nitrate release longer than the NAC, NAG, and NA beads, respectively.

Guar gum [32] and cellulose [25] interact with alginate by hydrogen bonding, whereas pectin interacts with Ca^{2+} like alginate. Both pectin and alginate are natural ionic polysaccharides that form crosslinked hydrogels with the addition of Ca^{2+}. Then, the Ca^{2+} ions interact with guluronic acid and galacturonic acid in alginate and pectin, respectively [34]. Therefore, pectin can create an egg-box structure in the presence of Ca^{2+} ions as well as alginate [28].

In terms of NAP beads, an increase in Ca^{2+} concentration can generate a dense and elastic gel network, resulting in an improvement in gel viscosity and elasticity. That is, gel strength will increase with an increase in Ca^{2+} concentration [35]. In the previous studies, the concentration of CaCl$_2$ solution used as a crosslinking agent ranged from 0.1% to 5%(w/v) [23, 25, 28, 29, 36], whereas in this study, calcium nitrate solution was used as a crosslinking agent because calcium was extracted from eggshells with nitric acid. Therefore, the Ca^{2+} ion is sufficient for a crosslink of alginate and pectin to form a dense and elastic gel.

3.5. Effect of controlled-release agent on swelling and shrinking of beads

It was found that the NA and NAC beads showed an enlarged swelling of 3.73% and 5.63%, respectively, after soaking in DI water for 7 days, while the NAP and NAG beads were shrunk by 2.96 and 4.38%, respectively. When all encapsulated beads were soaked for 30 days, the size of all encapsulated bead types decreased. The smallest size was observed from the NAG bead, which decreased by 25%, followed by the NAC, NAP, and NA beads reduced by 16.25, 13.60, and 8.81%, respectively.

Fig. 6 shows the IR peaks of calcium nitrate fertilizer beads prepared with sodium alginate and sodium alginate combined with pectin. The FTIR spectra of liquid calcium nitrate presented distinct peaks at 3,351, 1,653, and 1,315 cm^{-1}, indicating the stretching of O − H, N − O (symmetric), and N − O (asymmetric) bonds, respectively. The spectra of sodium alginate showed peaks around 1,598, 1,403, and 1,026 cm^{-1}, indicating the stretching of COO(asymmetric), COO^{-}(symmetric), and C − O − C bonds, respectively [37]. The spectra of sodium alginate are similar to those of Agulhon et al. [17], which showed distinct peaks at 1,593.9 and 1,406.4 cm^{-1} because of asymmetric and symmetric stretching vibrations of carboxyl anions [38]. When liquid calcium nitrate is encapsulated with sodium alginate, Ca^{2+} ions will replace Na^{+}ions in the uronic acid of sodium alginate [39].

The spectrum of the NA beads presented all characteristic peaks of calcium nitrate and sodium alginate with some discrepancies. That is, the peaks associated with the O − H stretching $(3,340\ \mathrm{cm}^{-1})$, COO^{-}asymmetric stretching $(1,606\ \mathrm{cm}^{-1})$, COO^{-}symmetric stretching $(1,408\ \mathrm{cm}^{-1})$, N-O symmetric stretching $(1,340\ \mathrm{cm}^{-1})$, and C − O − C stretching $(1,030\ \mathrm{cm}^{-1})$ [37, 40], indicating the successful crosslinking of the alginate- Ca^{2+} network and the encapsulation of nitrate within this network. In the pectin spectra, the broad peak at 1,726, 1,014, and 839 cm^{-1} corresponds to the C = O stretching [37], C − O − C stretching [37], and = C − H stretching, respectively. When liquid calcium nitrate was encapsulated with sodium alginate and pectin, all peaks of the NAP bead showed slight dis-

Table 2. Loading capacity, encapsulation efficiency, and the release of nitrate from each encapsulated bead type and swelling and shrinking of bead gels

Bead sample type	LC (%)	EE (%)	Release (%)	Bead size (mm)		
				Initial	7 days	30 days
NA bead gel	19.87	70.84	44.71	4.03 ± 0.11	4.18 ± 0.24	3.67 ± 0.34
NAC bead gel	16.65	61.67	35.12	4.00 ± 0.00	4.23 ± 0.26	3.35 ± 0.24
NAP bead gel	14.66	55.01	28.80	4.23 ± 0.26	4.10 ± 0.21	3.65 ± 0.33
NAG bead	18.45	63.34	31.58	4.00 ± 0.00	3.83 ± 0.29	3.00 ± 0.23

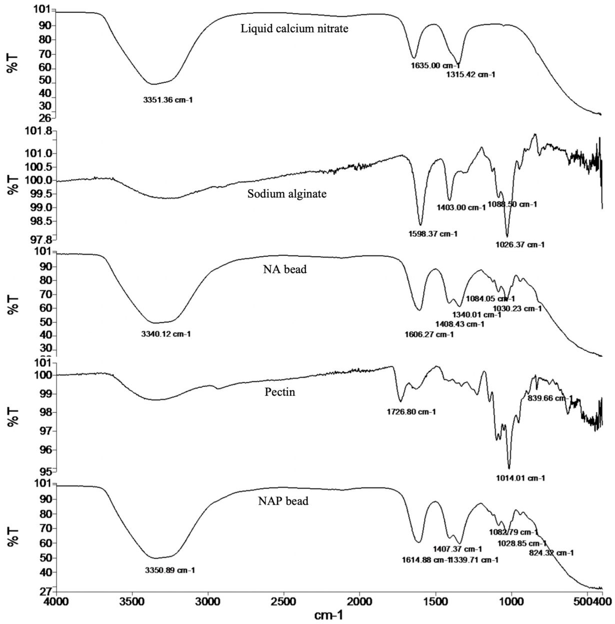


Fig. 6. FTIR spectra of liquid calcium nitrate, sodium alginate, pectin, NA bead, and NAP bead

crepancies, with the new peak at 824 cm^{-1} associated with the $= \mathrm{C} - \mathrm{H}$ stretching emerging as compared to the NA spectrum. This confirmed that pectin could interact with the alginate- Ca^{2+} network.

4. Conclusions

12%(w/v) of eggshell was an optimum amount for extracting liquid calcium nitrate fertilizer by 10%(v/v) nitric acid. The nitrate fertilizer beads were prepared via crosslinking alginate chains by Ca^{2+} ions from liquid calcium nitrate. The optimal time required for bead forming by 2%(w/v) sodium alginate in liquid calcium nitrate was 120 min. An oven-dried $\mathrm{Ca}\left(\mathrm{NO}_3\right)_2$ beads at 45°C for 1 hour is sufficient to maintain their shape. The controlled-release agent could control and prolong nitrate release from the beads, but it did not assist the bead in absorbing more nitrate. The release experiments revealed that the presence of 0.2%(w/v) pectin in the beads could slow the release of nitrate the longest among other controlled-release agents. However, the shape of calcium nitrate fertilizer bead gels with pectin should be optimized for further development.

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