

RELEASE BEHAVIOUR STUDY ON CONTROLLED-RELEASE PHOSPHOROUS FERTILIZER ENCAPSULATED BY STARCH- ALGINATE SUPERABSORBENT COMPOSITE

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Abstract

Controlled-release fertilizer is used as a promising green technology in preventing excessive application and leaching into undesired places. A hydrogel is a polymer matrix that is able to hold water and release its active ingredient at a controlled pace. This work presents the release behaviour study on the starch-alginate encapsulation of diammonium hydrogen phosphate (phosphorous) fertilizer using calcium chloride as an effective crosslinking agent. The FTIR peaks showed the successful interaction between O-H stretching bonds in starch with COO⁻ in alginate. Furthermore, the peak at 3430cm⁻¹ verified that crosslinking action was successfully employed. At the same time, the phosphate group was successfully retained in its own form. The amount of phosphorous released into distilled water was measured using HPLC with a mobile phase of water to methanol ratio of 80:20 v/v% under the wavelength of 240nm for phosphate compound detection. The swelling and dissolution study of hydrogel was carried out using the weighing technique. Microscopy images at magnification of 40X verified that calcium chloride was able to improve the surface morphology of the hydrogel. TGA results of the controlled-release fertilizer showed that hydrogel with high CaCl₂ content have low thermal stability. The variation of calcium chloride content showed a more stable trend in release rate, swelling and dissolution in comparison to the variation of starch and alginate. Formulation S13 showed optimum results whereby it released 7wt% phosphorous into distilled water after 30 days with 40% swelling and 80% dissolution. Therefore, it was concluded that the main effect is CaCl₂ and sample S13 (12 wt% St, 1 wt% Alg, 3.5M CaCl₂) produces the best controlled-release fertilizer.

Keywords: Controlled-release, Hydrogel, Phosphorous, Starch-Alginate, Swelling.

1. Introduction

In the agricultural industry, phosphorous is important for the production of nucleotides in plants [1]. One of the main challenges is the loss of nutrient elements resulting in the inefficiency of plant nutrients uptake due to excessive application. Subsequently, phosphorous based fertilizers is the primary cause of excessive algae growth in lakes and rivers which can negatively impact the environment [1]. The formulation of controlled release fertilizers (CRF) has been vastly used to resolve this challenge whereby nutrients are released at a controlled pace through a polymer matrix for maximum utilization by plants [2-4]. A polymer hydrogel is a three-dimensional polymeric network having large water retention property that is able to swell without dissolving in water [1]. Thus, the right formulation will produce a CRF out of the polymer matrix. Therefore, the material of the controlled-release formulation is the key in solving this challenge.

Controlled release formulation has been investigated over the past 50 years to determine the compatibility of various encapsulation materials for fertilizers. There are three broad categories for these formulations which are organic, inorganic and superabsorbent material [5]. More recently, the use of superabsorbent composite is found to be favourable due to its low cost and biodegradability, hence this is the main research area for this study. Previous test by other researchers show that a conventional fertilizer without controlled-release formulation gave a full release after two days; whereas wheat other superabsorbent material such as straw as was found demonstrating a full release after five days [6, 7]. However, a more promising controlled release results were reported by various researchers on using sodium alginate (Na-Alg), montmorillonite (MMT), and starch-matrix composite material on coated pesticide, where the complete release of the active ingredient were lasted up to 60 days and beyond [8, 9]. With these results, superabsorbent materials gained high attention in the controlled-release formulation especially starch due to its excellent water retention properties.

However, starch based formulation has a high potential to burst due to high water absorbency. Therefore, researchers are trying to improve the polymer matrix of controlled release fertilizer through addition of another material. A. Roy et al. continued this work by adding alginate to starch using calcium chloride (CaCl_2) as the cross-linking agent [10]. The combination has reduced the release rate of pesticide by 30%. A similar trend was shown by B. Singh et al. whereby the release rate is further reduced by 35% [11, 12]. This justifies that these superabsorbent composites have the potential to reduce the release rate of encapsulated ingredient. Na-alg is a type of copolymer known to be able to hold the matrix together due to its good gelation property [12]. Furthermore, the molecular structure and porosity of the polymer is enhanced by CaCl_2 as a crosslinking agent [12, 13].

There are several ways to synthesize controlled release fertilizer such as the coating, extrusion and encapsulation method. It is more economical to use the encapsulation method whereby the active ingredient is loaded into the superabsorbent material to form hydrogel beads [12]. Due to the research findings which demonstrated the good properties of starch, sodium alginate and calcium chloride, it is worth the investigation. The application of these superabsorbent materials was only tested on several active ingredients such as urea, pesticide and fungicide. However, there is currently no research on the application of these materials for phosphorous fertilizer.

Nevertheless, the objective of this project is to study the effect of each material variation on phosphorous release rate for a total of 13 formulations. The project scope includes the release behaviour study which covers the mechanism of swelling, dissolution as well as the diffusion of phosphorous into distilled water. Physical characterization was also carried out to justify the release behaviour of each formulation.

2. Methodology

2.1. Material

Analytical grade of Sodium Alginate C.P., Calcium Chloride anhydrous granular C.P. and Di-Ammonium Hydrogen Phosphate A.R. were obtained from R&M Chemical, UK; whereas food grade cassava starch, brand Kapal ABC, manufactured in Thailand, was purchased off the shelf from grocery shop in Malaysia.

2.2. Synthesis of starch-alginate hydrogel beads

The synthesis method followed the methodology suggested by Singh et al. [12]. Total of 13 formulations divided into three categories: variation of St, Na-Alg and CaCl₂ as shown in Table 1. St and Na-Alg at various amounts (as per Table 1) were mixed in 100 ml distilled water together with phosphorous at 5 w/v%. The solution was mixed using a magnetic hot plate stirrer (Thermo Scientific MSH-300, Malaysia) at 40°C, 600RPM for 30 minutes until the solution reaches its homogeneity. CaCl₂ solution was prepared by dissolving CaCl₂ into 100ml of water. The starch-alginate-phosphorous solution was dripped into the CaCl₂ solution using a 1.2mm diameter syringe. The formed hydrogel beads were then rinsed with distilled water, filtered through a 200-mesh stainless steel sphere-shaped net. Excess water was removed by tapping the beads with tissue paper. The beads were dried at a temperature of 80°C for 24 hours using natural convection oven (Mettler Universal Oven UN55). The dried samples were cooled and stored in bottles sealed with parafilm for further analysis.

Table 1. Controlled-release formulations.

Material Variation	Sample	Cassava Starch (w/v) %	Sodium Alginate (w/v) %	Calcium Chloride (M)
Starch	S1	3	1	1.5
	S2	6	1	1.5
	S3	9	1	1.5
	S4	12	1	1.5
	S5	15	1	1.5
Sodium Alginate	S6	12	0.5	1.5
	S7	12	1.5	1.5
	S8	12	2	1.5
	S9	12	2.5	1.5
Calcium Chloride	S10	12	1	2.0
	S11	12	1	2.5
	S12	12	1	3.0
	S13	12	1	3.5

2.3. Fourier transform infrared (FTIR)

Fourier Transform Infrared Spectrometer (FTIR Spectrum 100, Perkin Elmer) was used to identify the functional groups of materials used in sample synthesis. Attenuated Total Reflectance (ATR) sampling method was employed with a total of 16 scans under the operating range of 4000 - 650 cm^{-1} .

2.4. Thermogravimetric analyzer (TGA)

Thermogravimetric Analyzer (TGA 8000, Perkin Elmer) was carried out over a temperature range of 30 - 700°C with a constant heating rate of 20°C/min under nitrogen atmosphere to determine the thermal degradation of the beads.

2.5. Digital microscope

The surface morphology was visually analysed using a digital microscope (M10DB-MP, Motic) under a magnification of 40X.

2.6. High performance liquid chromatography (HPLC)

The amount of phosphate released into distilled water was determined through the calibration curve of known concentration of pure phosphate. This was carried out using High Performance Liquid Chromatography (1220 Infinity LC, Agilent Technologies Co.). The mobile phase was prepared at methanol to water ratio of 20:80 v/v. The separation of phosphate group was carried out at a flow rate of 1.0 ml/min on Zorbax Extend-C18 column. The column temperature was set at 30°C with an auto-sampler injection volume of 25 μL . The detection wavelength of BispTM - 1100 UV/Vis detector was set at 254 nm for phosphate to be detected.

2.7. Release behaviour study on controlled-release phosphorus-fertilizer

The swelling study consists of setting the initial weight (W_o) of the beads at 5g which was immersed into 100 ml of distilled water over a fixed interval of time (1h, 2h, 4h, 6h, 1 day, 2 days, 7 days, 14 days, 21 days and 30 days) under static conditions and room temperature of 25°C. The swollen weight of the hydrogels was measured at W_{wet} and the swelling percentage was calculated using Eq. (1) as shown below:

$$\text{Swelling \%} = \frac{W_{wet} - W_o}{W_o} \times 100\% \quad (1)$$

For the dissolution study, the swollen beads were dried using oven under the same temperature of 80°C for 24 hours where the new dried weight was recorded as W_{Dry} . Thus, the dissolution was calculated using Eq. (2) as shown in the following:

$$\text{Dissolution \%} = \frac{W_o - W_{Dry}}{W_o} \times 100\% \quad (2)$$

3. Results and Discussions

3.1. Material characterization

3.1.1. Physical shape

The physical shape of the beads varies with different formulation. The variation of starch content from 3 wt% to 15 wt% as shown in Fig. 1(a) demonstrates that starch is responsible for the spherical shape of the hydrogel bead. This is because starch acts as polymer filler in this formulation. On the other hand, the variation of sodium alginate composition from 0.5 wt% to 2.5 wt% displays a significant difference in the shape. It is evident from Fig. 1(b) that viscosity increases due to higher amount of sodium alginate, thus forming tear-drop shape during sample synthesis. Figure 1(c) shows that increasing calcium chloride from 2.0M to 3.5M produces convex-shaped beads. The difference in shapes demonstrated that an appropriate balance in the formulation is necessary for a more closely packed arrangement to form uniform beads [14].

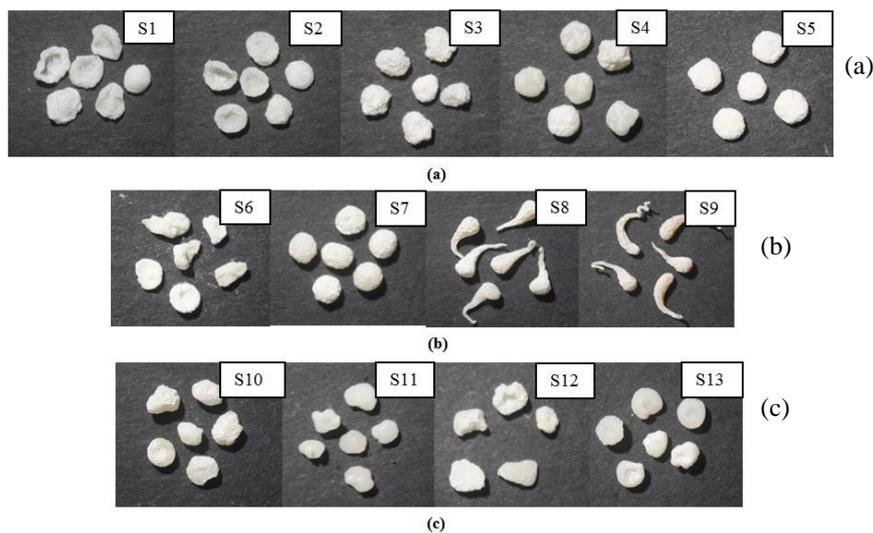


Fig. 1. Physical images of (a) starch variation, (b) sodium alginate variation, and (c) calcium chloride variation.

3.1.2. Microscopic morphology

The surface morphologies of the samples were observed using a microscope under a magnification of 40X as shown in Fig. 2. It can be seen from Fig. 2(a) that the hydrogel surface has a highly porous network with poor mechanical integrity. The porosity of the surface improves with increasing content of calcium chloride as evident from Figs. 2(b) and 2(c). This can be explained through the crosslinking effect whereby the bivalent calcium ion from the CaCl_2 is necessary for the formation of tighter cavity network. Therefore, the mesh size of the polymeric hydrogels are reduced as shown in Fig. 2(d) with highest CaCl_2 , in which in agreement with the result reported by Essawy et al. [15].

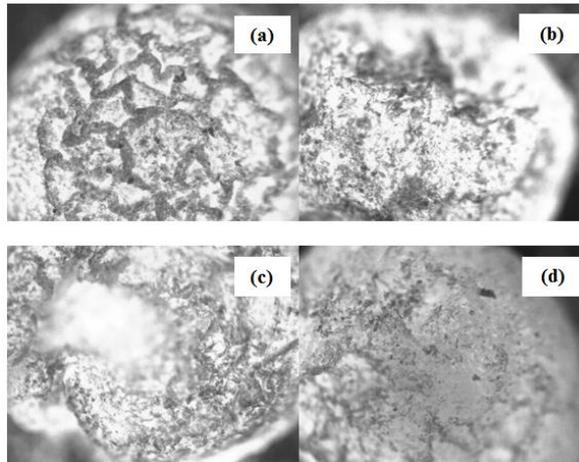


Fig. 2. Microscopic images (X40 magnification) for samples with calcium chloride variation: (a) 2.0M, S10 (b) 2.5M, S11 (c) 3.0M, S12 (d) 3.5M, S13.

3.1.3. FTIR analyses

FTIR has been used to ensure that the functional group of phosphate remains unchanged as well as to study the interactions between polymer and crosslinking agent. Figure 3(a) demonstrates the spectra of pure alginate microparticles whereby the characteristic absorption bands are found at 3430cm^{-1} due to the presence of O-H stretching vibrations, 2934cm^{-1} (C-H stretching vibrations), 1654cm^{-1} and 1464cm^{-1} (COO^- asymmetric stretching vibrations) and 1034cm^{-1} (C-O-C stretching vibration). The combination of starch and alginate caused a decrease in the wave number COO^- from 1464cm^{-1} to 1453cm^{-1} . For the phosphorous-loaded sample as shown by S4 in Fig. 3(b), the peak at 1060cm^{-1} indicates the presence of asymmetric stretching vibrations of P-O. Thus, diammonium hydrogen phosphate is present in its own form and shows successful encapsulation within hydrogel. The results are in agreement with the findings regarding the loading of fertilizer into starch-alginate which has been reported by Stoch et al. [16]. Additionally, the hydroxyl peak shifted from 3430 to 3411cm^{-1} as seen from Fig. 3(c), thus proving the interaction of St-Alg. Similar analysis has been reported by Hosseini et al. [17].

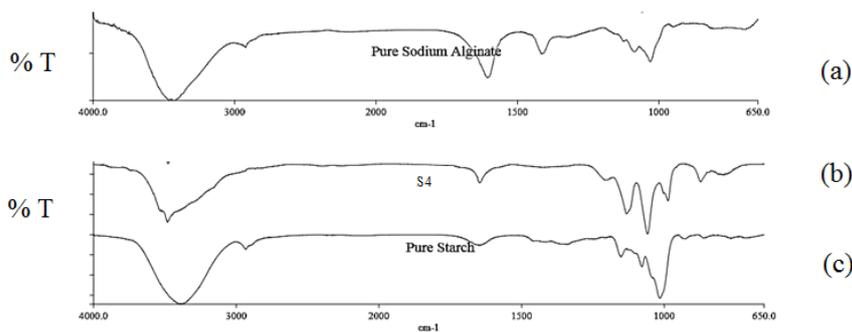


Fig. 3. FTIR spectra of (a) Sodium Alginate microparticles (b) phosphorous loaded Alg-St microparticles (c) and Starch microparticles.

Figure 4 displays the change in chemical structure of the samples with increasing CaCl_2 content. The increasing intensity of the peak at 3430cm^{-1} shows that the crosslinking has been employed effectively. This shift was considered as an additional evidence in support of the crosslinker effect between starch and alginate microparticles as reported by Nnamonu [18]. Thus, the formulation with the highest CaCl_2 should be further studied to determine the main effect of controlled-release formulation.

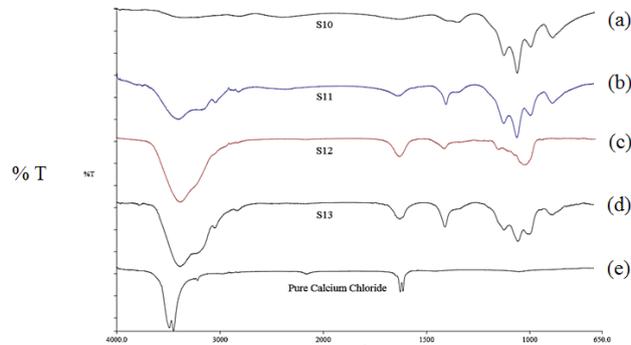


Fig. 4. FTIR spectra of sample with CaCl_2 variation: (a) 2.0M CaCl_2 (b) 2.5M CaCl_2 (c) 3.0M CaCl_2 (d) 3.5M CaCl_2 (e) pure CaCl_2 .

3.1.4. Thermogravimetric analysis (TGA)

When biomaterial is subjected to high temperature, it usually decomposes into CO , CO_2 , NO_x and H_2O . The TGA curves show a heating range of 30 to 700°C for superabsorbent material. The curve of sample S4 was used a standard for comparison as shown by Fig. 5(a) where its shape is similar to all the other curves except for Fig. 5(e). At 700°C , the thermograms of St-Alg and St-Alg- Ca^{2+} have shown 0% residual matter, indicating full degradation. The weight loss of St-Alg (Fig. 5(a)) is 45 wt% at 250°C whereas St-Alg- Ca^{2+} (Fig. 5(e)) has a greater sample loss of 60 wt% at the same temperature. This shows that the thermal stability is better with higher purity of bicomposites in St-Alg in accordance to Marie Arockianathan et al. [19]. The poor thermal stability of St-Alg- Ca^{2+} is due to higher CaCl_2 content, causing its breakdown as a whole crosslinked polymer group which no longer exists as a single component of CaCl_2 . This indicates that it is worth the current investigation to find out more about the chemical properties of sample S13 in the release behaviour study.

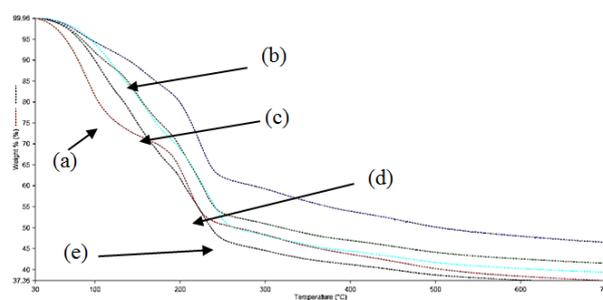


Fig. 5. TGA curves for (a) S4, (b) S10, (c) S11, (d) S12, (e) S13.

3.2. Release behaviour studies

3.2.1. Release rate of phosphorous

Figure 6 shows a common trend whereby constant release of phosphorous started after 14 days for all graphs. The maximum release is 11 wt% shown by S6 and S10 while the minimum is 4 wt% by S1. However, no conclusion can be drawn from this as further evaluation needs to be done. Figure 6(a) shows that the release rate increases with increasing starch content. Similar result was reported by Roy et al. [10] on the controlled-release of pesticide using St-Alg biocomposite whereby the same phenomena was caused by the increase in the hydrophilic nature of starch. At the same time, the non-ionic content of the hydrogel is reduced, thus the crosslinking of calcium chloride became underdeveloped. Therefore, the penetration rate of water into the hydrogel accelerated, causing a higher diffusion rate of phosphorous out of the matrix.

On a contrary, Fig. 6(b) shows that release rate decreases with increasing sodium alginate content. This is due to the greater polymer fraction which increases the encapsulation efficiency of the hydrogel bead. Thus, the path of diffusion in the matrix is increased as more COO^- from sodium alginate is able to crosslink with Ca^{2+} available in calcium chloride. Singh et al. [11] also described the same effect on testing with controlled-release thiram fungicide formulation.

Similarly, from Fig. 6(c), the observation shows that the release of phosphorous was well controlled in a sustained manner with increasing calcium chloride content. The decelerated release can be explained due to better crosslinking and tighter cavity on the superabsorbent material [10, 12]. As an overall comparison among these graphs of release rate, Fig. 6(c) shows the most stable and gradual release rate with increasing material variation while Figs. 6(a) and 6(b) shows a more unsustain release rate. It is suggested that the main controlling parameter is the amount of crosslinking agent used in the synthesis. Therefore, the formulation of S13 has the potential to be used as agrochemical to solve leaching challenges and will be further evaluated using the swelling and dissolution studies to confirm the hypothesis.

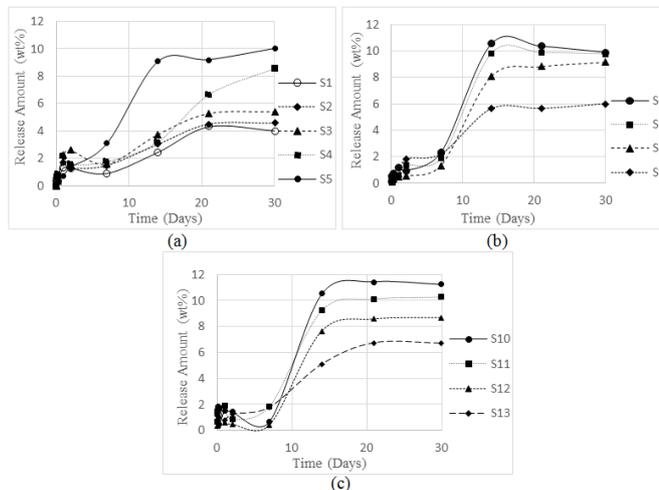


Fig. 6. Release amount of phosphorous in wt% for samples: (a) S1 - S5 with St variation, (b) S6 - S9 with Na-Alg variation, and (c) S10 - S13 with CaCl_2 variation.

3.2.2. Water absorption evaluation

Based on Fig. 7, the graphs show constant swelling over 30 days where the trend is seen to be more volatile for Figs. 7(a) and 7(b) in comparison to a more stable swelling pattern in Fig. 7(c). This is mainly due to the variation of material that affects the absorption efficiency by hydrogel beads. The swelling increases with increasing starch content as shown in Fig. 7(a). Similar to the release rate trend discussed earlier, the hydrophilic property of starch allows formation of hydrogen bonds with water molecules. This phenomena has been verified by the FTIR results showing O-H stretching alcoholic group of pure starch and S4 bead. Thus, the same observation has been reported by Roy et al. [10] proving the high water absorbency property of starch.

Increasing the sodium alginate content results in a drop of swelling as seen from Fig. 7(b), in which due to longer path of diffusion of molecules into and out of the polymeric matrix. The same reason supports the trend for the release of phosphorous previously mentioned during the study of release rate. Similar results were also justified by Wu et al. [20] on controlled-release herb encapsulated by starch-alginate.

Similar to the trend of release rate in this paper, there is a decline in water absorbency from S10 - S13 as seen from Fig. 7(c) due to the increase of CaCl_2 content up to 3.0M CaCl_2 . This causes the crosslinking density to increase, thus the network becomes more compact and reduces the penetration of water molecules into the hydrogel. This is in line with the reported results by other researchers who uses CaCl_2 as crosslinker [10, 12].

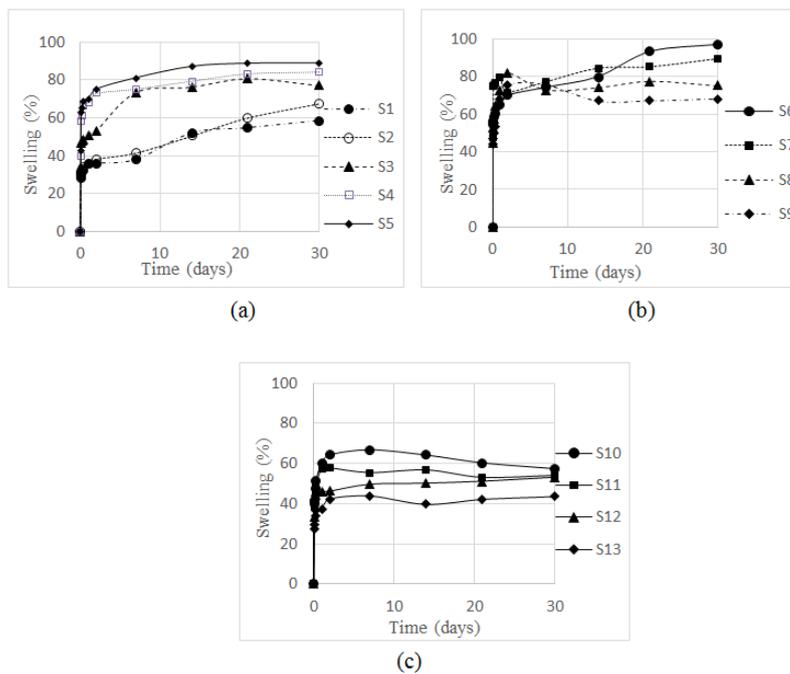


Fig. 7. Swelling percentage (%) of hydrogel for samples: (a) S1 - S5 with St variation, (b) S6 - S9 with Na-Alg variation, and (c) S10 - S13 with CaCl_2 variation.

3.2.3. Dissolution evaluation

Opposing the release rate and swelling trends of controlled-release formulation, the dissolution of phosphorous within the matrix decreases with increasing starch and sodium alginate content as shown in Figs. 8(a) and 8(b). This effect was reported by Roy et al. [10] whereby there are more intermolecular interactions between the starch and alginate molecules. With this, the polymer matrix becomes more compact, thus hindering the water penetration. There is a high tendency for the hydroxyl group from starch and the carbonyl group from sodium alginate to form strong hydrogen bonds.

On contrary, the dissolution improves with increasing calcium chloride content as shown in Fig. 8(c) due to its high solubility property. The Ca^{2+} ion readily forms bond with the O-H group from water molecules, thus increasing the interaction for dissolution to occur. This is the same effect as testified by Ahmad et al. [21]. In addition, higher amount of CaCl_2 shows a more constant dissolution at a maximum of 80% exhibited by S13 over 30 days. This shows that S13 has good dissolving property of active ingredient within the hydrogel whereby 80% of the loaded fertilizer was able to diffuse out of the polymer matrix. Therefore, formulation S13 displays one of the potential good characteristics of controlled-release fertilizer.

As an overall comparison, Figs. 8(a) and 8(b) shows unstable dissolution rate in comparison to Fig. 8(c). The same observation in the stability trend provided by the CaCl_2 can also be seen from the release rate and swelling studies. Together with the surface morphology of S13 being the best, this further supports the hypothesis whereby the main effect of controlled-release is the variation of calcium chloride.

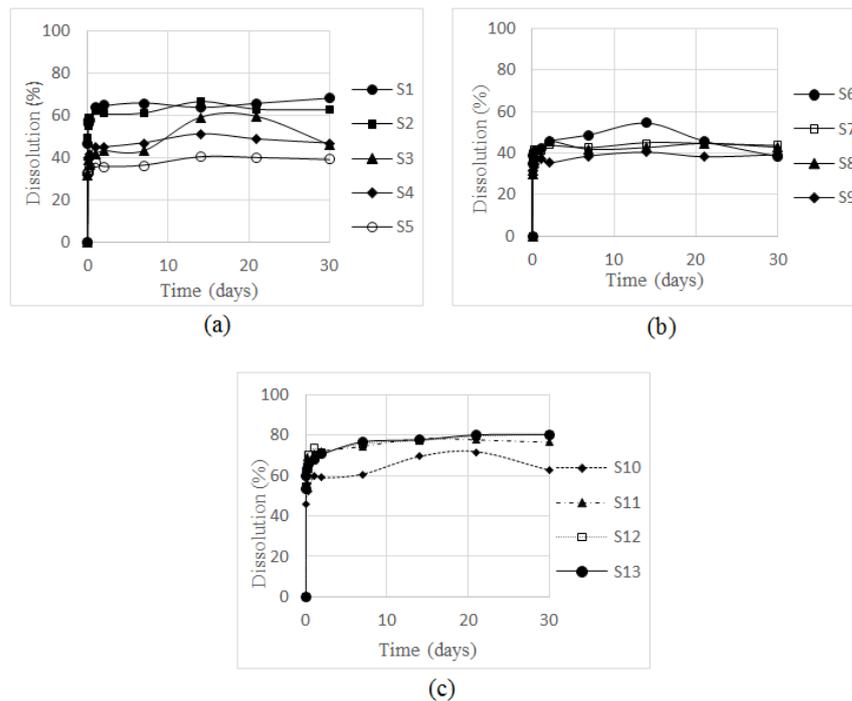


Fig. 8. Dissolution percentage (%) for samples: (a) S1 - S5 with St variation, (b) S6 - S9 with Na-Alg variation, and (c) S10 - S13 with CaCl_2 variation.

4. Conclusions

In this research, the encapsulation of phosphorous fertilizer using starch and sodium alginate has been successfully synthesized and tested for release behaviour study. The results obtained from this research proposed that there are differences in the physicochemical and morphological properties of all the 13 formulations for starch-alginate-Ca²⁺ hydrogel beads. It was found out through surface morphology analysis that CaCl₂ was responsible for the porosity of the hydrogel surface. A balanced formulation between starch and sodium alginate was important for the overall shape of the bead. The successful bonding between these functional groups were verified through TGA and FTIR. The swelling and the dissolution studies further explained the effect of each material variation on the release rate. It can be observed that the swelling characteristics of hydrogels are closely associated to the phosphorous release which is the key is determining the chemical structure of the hydrogels. The graphs of phosphorous release, swelling and dissolution rate exhibit volatile pattern for the samples with variation of starch and sodium alginate whereas it is more stable with calcium chloride variation. In conclusion, CaCl₂ is the main effect of controlled-release fertilizer whereby S13 shows stable controlled release rate with lowest swelling (40%) with highest dissolution (80%) properties. All experimental work was carried out in replicates of 3.

Future work includes the testing of controlled-release fertilizer in soil for a longer period of study. Another recommendation is to increase the concentration of CaCl₂ for a better crosslinking effect. As an alternative approach, it is also recommended to substitute the crosslinker agent with polyacrylic acid to encapsulate phosphorous-fertilizer to improve the surface morphology.

Nomenclatures

W_{dry}	Dried weight for beads, g
W_o	Initial weight for beads, g
W_{wet}	Wet weight for beads, g

Abbreviations

ATR	Attenuated Total Reflectance
CaCl ₂	Calcium Chloride
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
CRF	Controlled-release fertilizer
FTIR	Fourier Transform Infrared
H ₂ O	Water
HPLC	High Performance Liquid Chromatography
MMT	Montmorillonite
Na-Alg	Sodium Alginate
NO _x	Generic term for the nitrogen oxides, including NO, NO ₂ , etc
St	Starch
St-Alg-Ca ²⁺	Starch-Alginate-Calcium ion
TGA	Thermogravimetric Analyzer

References

1. Xiaoyu, N.; Yuejin, W.; Zhengyan, W.; Lin, W.; Guannan, Q.; and Lixiang, Y. (2013). A novel slow-release urea fertiliser: Physical and chemical analysis of its structure and study of its release mechanism. *Biosystems Engineering*, 115(3), 274-282.
2. Oertli, J.J. (1980). Controlled-release fertilizers. *Fertilizer Research*, 1(2), 103-123.
3. Han, X.; Chen, S.; and Hu, X. (2009). Controlled-release fertilizer encapsulated by starch/polyvinyl alcohol coating. *Desalination*, 240, 21-26.
4. Azeem, B.; Kushaari, K.; Man, Z.B.; Basit, A.; and Thanh, T.H. (2014). Review on materials & methods to produce controlled release coated urea fertilizer. *Journal Of Controlled Release*, 181, 11-21.
5. Chien, S.H.; Prochnow, L.I.; Tu, S.; and Snyder, C.S. (2011). Agronomic and environmental aspects of phosphate fertilizers varying in source and solubility: An update review. *Nutrient Cycling in Agroecosystems*, 89(2), 229-255.
6. Liang, R.; Yuan, H.; Xi, G.; and Zhou, Q. (2009). Synthesis of wheat straw-g-poly(acrylic acid) superabsorbent composites and release of urea from it. *Carbohydrate Polymers*, 77(2), 181-187.
7. Liu, Y.H.; Wang, T.J.; Qin, L.; and Jin, Y. (2008). Urea particle coating for controlled release by using DCPD modified sulfur. *Powder Technology*, 183(1), 88-93.
8. Rashidzadeh, A.; and Olad, A. (2014). Slow-released NPK fertilizer encapsulated by NaAlg-g-poly(AA-co-AAm)/MMT superabsorbent nano-composite. *Carbohydrate Polymers*, 114, 269-278.
9. Cao, Y.; Huang, L.; Chen, J.; Liang, J.; Long, S.; and Ly, Y. (2005). Development of a controlled release formulation based on a starch matrix system. *International journal of Pharmaceutics*, 298(1), 108-116.
10. Roy, A.; Bajpai, J.; and Bajpai, A.K. (2009). Dynamics of controlled release of chlorpyrifos from swelling and eroding biopolymeric microspheres of calcium alginate and starch. *Carbohydrate Polymers*, 76(2), 222-231.
11. Singh, B.; Sharma, D.K.; and Gupta, A. (2007). Controlled release of thiram fungicide from starch-based hydrogels. *Journal of Environmental Science and Health, Part B*, 42(6), 677-695.
12. Singh, B.; Sharma, D.K.; and Gupta, A. (2009). A study towards release dynamics of thiram fungicide from starch-alginate beads to control environmental and health hazards. *Journal of hazardous materials*, 161(1), 208-16.
13. Singh, B.; Sharma, D.K.; Kumar, R.; and Gupta, A. (2009). Controlled release of the fungicide thiram from starch-alginate-clay based formulation. *Applied Clay Science*, 45(1-2), 76-82.
14. Lozano-Vazquez, G.; Lobato-Calleros, C.; Escalona-Buendia, H.; Chavez, G.; Alvarez-Ramirez, J.; and Vernon-Carter, E. J. (2015). Effect of the weight ratio of alginate-modified tapioca starch on the physicochemical properties and release kinetics of chlorogenic acid containing beads. *Food Hydrocolloids*, 48, 301-311.
15. Essawy, H.A.; Ghazy, M.B.M.; El-Hai, F.A.; and Mohamed, M.F. (2016).

- Superabsorbent hydrogels via graft polymerization of acrylic acid from chitosan-cellulose hybrid and their potential in controlled release of soil nutrients. *International Journal of Biological Macromolecules*, 89, 144-151.
16. Stoch, P.; Stoch, A.; Ciecinska, M.; Krakowiak, I.; and Sitarz, M. (2016). Structure of phosphate and iron-phosphate glasses by DFT calculations and FTIR/Raman spectroscopy. *Journal of Non-Crystalline Solids*, 450, 48-60.
 17. Hosseini, S.M.; Hosseini, H.; Mohammadifar, M.A.; German, J.B.; Mortazavian, A.M.; Mohammadi, A.; Khaksar, R. (2014). Preparation and characterization of alginate and alginate-resistant starch microparticles containing nisin. *Carbohydrate Polymers*, 103, 573-580.
 18. Nnamonu, L.A.; Sha'ato, R.; and Onyido, I. (2012). Alginate reinforced chitosan and starch beads in slow release formulation of imazaquin herbicide-preparation and characterization. *Materials Sciences and Applications*, 3, 566-574.
 19. Marie Arockianathan, P.; Sekar, S.; Sankar, S.; Kumaran, B.; and Sastry, T.P. (2012). Evaluation of biocomposite films containing alginate and sago starch impregnated with silver nano particles. *Carbohydrate Polymers*, 90(1), 717-724.
 20. Wu, Z.; Guo, L.; Qin, S.; and Li, C. (2012). Encapsulation of *R. planticola* Rs-2 from alginate-starch-bentonite and its controlled release and swelling behavior under simulated soil conditions. *Journal of industrial microbiology & biotechnology*, 39(2), 317-27.
 21. Ahmad, S.I.; Syed, I.A.; Prasad, P.R.; and Ahmad, A. (2014). Quantitation of urea in urine by Fourier transforms infrared spectroscopy. *Der Pharma Chemica*, 6(1), 90-96.