Release Dynamic study for Controlled-released-fertilizer by Starch-derivative-alginate based formulation

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Abstract
Controlled release fertilizer had been developed to minimize harmfulness to environment and increase delivering efficiency by controlling the release rate of fertilizer. However, conventional Controlled release fertilizer will acidify or left residue in soil which affect the growth of agricultural crops. This research is to synthesis Controlled release fertilizer with sodium alginate and cassava starch with performs of release dynamic studies to overcome the drawbacks of conventional type of Controlled release fertilizer. The synthesis of starch derivative alginate fertilizer is by crosslinking starch, alginate and urea mixture with calcium chloride solution and this Controlled release fertilizer is further used to undergo release studies. Release dynamic study is carry out in static condition by immersing Controlled release fertilizer in distilled water for duration of one month with measuring amount of urea released according to absorbance value obtained from UV-Vis Spectrophotometer under wavelength of 210nm. Starch derivative alginate fertilizer provide significant decrement in release rate where conventional fertilizer is fully release to water in two days but Starch derivative alginate fertilizer spent twenty one days to have full release; besides that, through data analysis the release rate can be reduced through high level (0.2667g/ml) of sodium alginate, high level (1M) of Crosslinker concentration and low level (0.1g/ml) of urea content.

Keywords: Controlled-release-fertilizers, starch-alginate formulation, release dynamic study.

1. Introduction

The growth of worldwide population outdistances global agricultural production and this lead to shortage of food supply; achieving higher agricultural yield is necessary to overcome the problem. Therefore, agricultural chemicals and fertilizers are introduced to control pests and supply nutrients to agricultural crops and increases the production of crops [1]. In the real life phenomena, only 30% of agrochemical and fertilizer applied on the agricultural crops reach the target region and produce desired biological responses. The reason of having low delivering efficiency is due to excess application, leaching due to rainfall and irrigation water, and degradation of active ingredients[2-4]. Besides that, improper application of agricultural chemicals and fertilizers is causing environment pollution and water pollution which affected the natural, animals as well as human life [5]. Furthermore, overdose of urea fertilizer will having reaction with bio-enzyme in soil which accounting 24% of global annual emission of N_2O and NH_3 [6,7].

To overcome leaching of fertilizer and increase the efficiency of delivering nutrients towards target, Controlled Release Formulations (CRF) is introduced to assure the delivering [7,8]. Controlled release formulation has been applied in many region such as pharmaceutical, biotechnology and agricultural region. Coating active ingredients with material that reduces the release rate of active ingredients (medicine, agrochemical or tissue) is the basic principles of CRF. Efficiency of delivering active ingredients to the target area will increase as controlled release formulation applied ensures the utilization of active ingredients by agricultural crops with reduction of leaching percentage. The primary standards for choosing coating material are low cost, having good coating property and degrade in soil without forming harmful toxic substances [5,9].

As Controlled Release fertilizer to the market and research still on-going to further improve the delivering mechanism and reduce the leaching of fertilizer. The coating material for Controlled Release fertilizer can be classified to three types that included organic, inorganic compound and polymer or matrix of polymer[10, 11].Moreover, the most widely applied controlled release fertilizer; sulfur coated fertilizer and polymer encapsulated fertilizer caused pollution to the soil where sulfur coated acidified the soil and polymer only degraded after a long period of time [10].

Starch derivative alginate based controlled release formulation is biodegradable and preparing through natural resources that showed a potential to be applied on controlled release fertilizer. Besides that, few researches have been done on pesticide, herbicide and fungicide; the release rate of starch derivative alginate formulation on these agrochemical is showed in Figure 1 which support the applicability of this formulation on fertilizer[5,12-13].

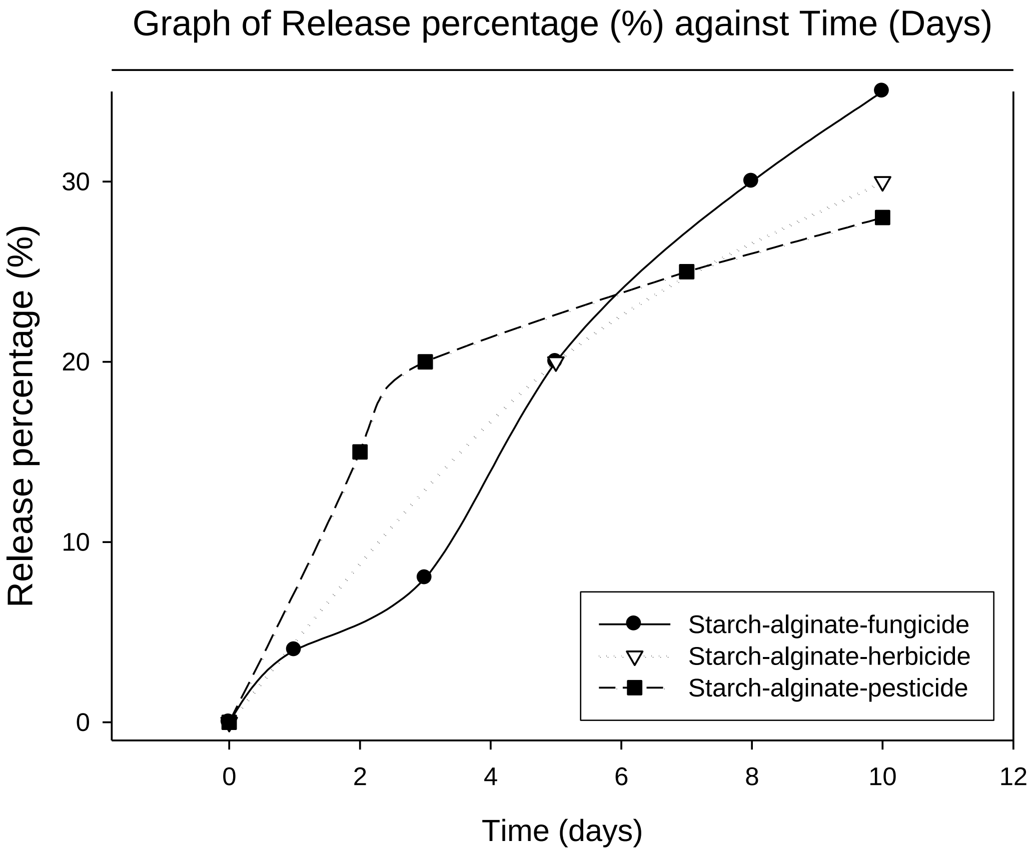
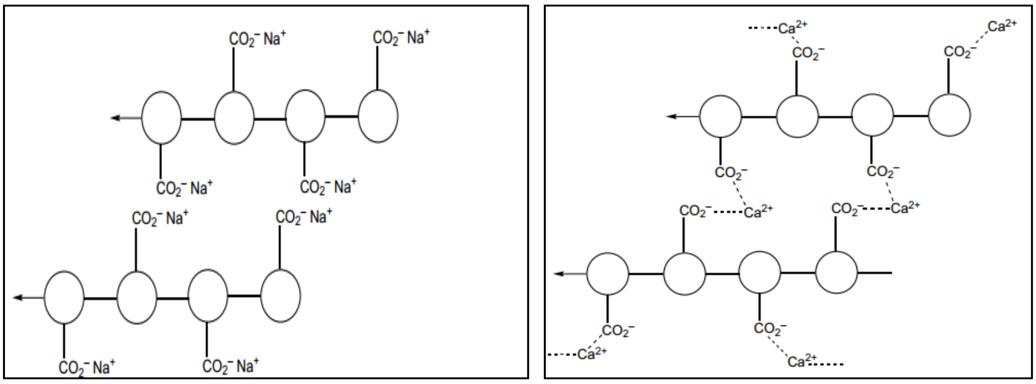


Figure 1.Graph of Release Percentage(%) against Time (days)

Alginate, an unbranched binary copolymer consists of 1,4 linked α-L-guluronic acid and β–D-mannuronic acid obtain from brown sea weeds that with non-toxic, fast gelling and simple handling properties [14]. The release of active ingredient encapsulated by alginate occurs after swelling of alginate granule as alginate is hydrophilic. Alginate beads that encapsulated with active ingredients can easily formed by dropping alginate-active ingredient solution to divalent ion solution as alginate will crosslink with divalent ion (refer to Figure 2) [15]. The drawback of alginate coating is due to macrospores presence in alginate molecular which enhances the diffusion of hydrophilic molecules and reduces physical stability of alginate beads to environment condition. Other polysaccharides is then applied on alginate formulation to improvise the physical properties and release dynamics of alginate [16,17]



(A) (B)

Figure 2**1.**Crosslinking Sodium alginate solution with Calcium Chloride (A) Before crosslinking (B) After Crosslinking [15].

Starch, a natural polysaccharide that consists of repeating 1,4-α-D-gulucopyranosyl unit with naturally discrete granules. In compared with other carbohydrate, starch discrete granules are relative dense, immiscible and lightly hydrate in cold water which enforced the reduce in release rate [13]. Besides that, starch is easily found from crops and biodegradable by microorganism.

This research is to conduct release dynamic study of starch derivative alginate based fertilizer by first synthesis the controlled release fertilizer with three levels of 4 parameters- Starch, Sodium alginate, Crosslinker ($CaCl_2$) concentration and Urea content. With the controlled release fertilizer, release dynamic experiment is undergo to evaluate the encapsulation efficiency of controlled release fertilizer and the effect of each parameter to the release rate of urea to water.

2. Research Methodology

2.1 Materials

Sodium alginate (R&M) the gelation material for controlled release formulation was obtained from Evergreen Engineering & Resources Sdn.Bhd. Cassava starch or tapioca starch as filler for alginate formulation to improve the mechanical and physical properties of Controlled release formulation was obtained from Thye Huat Chan Sdn.Bhd. Urea (Duchefa, Netherlands) the active ingredient to be encapsulated in controlled release formulation was obtained from Saintifik Sdn.Bhd. Calcium Chloride anhydrous (Alpha) was purchased from Saintifik Sdn.Bhd. and used as crosslinking agent for starch-alginate-urea mixtures for synthesis of Controlled release fertilizer.

2.2 Design of Experiment

The experiment is conducted on three levels four parameter design; with application of Taguchi method, L9 arrays are applied to evaluate the effect and interaction of each parameter and 9 samples are required for the different parameter and level involved. The four parameters are cassava starch, sodium alginate, calcium chloride and urea content in the formulation. Three levels for cassava starch and sodium alginate are 0.0067, 0.2000 and 0.2667g/ml respectively for determination the interaction of different levels. For concentration of crosslinking agent- calcium chloride solution, three levels are 0.2M, 0.5M and 1.0M. Lastly, for active ingredient- urea, the low, medium and high are 0.1, 0.1667 and 0.2333g/ml respectively. The formulation using Taguchi method was tabulated in Table 1.

Table 1. Composition and Crosslinker concentration for controlled release fertilizer

Experiment	Starch (g/ml)	Alginate (g/ml)	Calcium Chloride concentration (M)	Urea (g/ml)
1	0.0067	0.0067	0.200	0.1000
2	0.0067	0.2000	0.500	0.1667
3	0.0067	0.2667	1.000	0.2333
4	0.2000	0.0067	0.500	0.2333
5	0.2000	0.2000	0.200	0.1000
6	0.2000	0.2667	0.500	0.1667
7	0.2667	0.0067	0.500	0.1667
8	0.2667	0.2000	1.000	0.2333
9	0.2667	0.2667	0.200	0.1000

2.3 Synthesis of Controlled Release Fertilizer

Synthesis of starch-derivative-alginate based fertilizers is based on gelation properties of sodium alginate. Different formulation is prepared by mixing sodium alginate, starch and urea in distilled water according to concentration shown in Table 1. These mixtures are then stirred until homogeneous mixture formed. This alginate mixture is then dropped wisely into different concentration of Calcium Chloride solution by using syringe with needle size of 1.2mm diameter. Sodium alginate mixture will then crosslinked with Ca^{2+} ion to produced beads [18,19]. The beads are left inside the $CaCl_2$ solution to ensure completed gelation. Beads are then removed from the solution and rinsed with distilled water to remove CaCl2 content. Beads are dried at room temperature and further dried in oven operating at 50ºC until constant weight achieved [20]. The dried beads are then use to carry out release dynamics experiment. The resulted formulation is label sample 1-9 according to Table 1.

2.4 Calibration curve for pure urea

A calibration curve of pure urea is prepared for determination of amount of urea release to water in release dynamics studies; the calibration curve is done by first dissolving 5mg to 2g of urea in 100ml of distilled water. Absorbance of these pure urea solution is then measured with Thermo Scientific™ GENESYS 10S UV-Vis Spectrophotometer with wavelength of 210nm and a curve of absorbance value against concentration of urea solution is plotted for further release dynamic experiment.

2.5 Release dynamic study of Controlled Release Fertilizer

Release dynamic study is to evaluate the effect of parameter to release rate of urea and conclude the interaction between these parameters. The release dynamic study is carry out in water; dry controlled release fertilizer is added to 100ml of distilled water. At different time interval, 3.5ml of sample is removed for determination of urea by using Thermo Scientific™ GENESYS 10S UV-Vis Spectrophotometer under wavelength of 210nm which follows the literature review done [21]. 3.5ml of distilled water is then added to the beaker to maintain constant level.

Determination of urea concentration is done with absorbance value obtained by referring to predetermined calibration curve.

3.0 Results and discussion

3.1 Release study of urea

Release dynamics study is the key experiment of this research; it was done by measuring amount of urea release to water over a period of 28 days by using UV-Vis Spectrophotometer. A sample of pure urea was also performed as a comparison to starch-alginate controlled release fertilizer. Figure 3 shown the amount of urea release of sample 1 to 9 and also a reference of pure urea; from Figure 3 can observed that the release rate of sample 1 to 9 were respectively lower than pure urea where the urea was totally release to water within 2days and sample 1 to 9 showed a reduction in release rate.

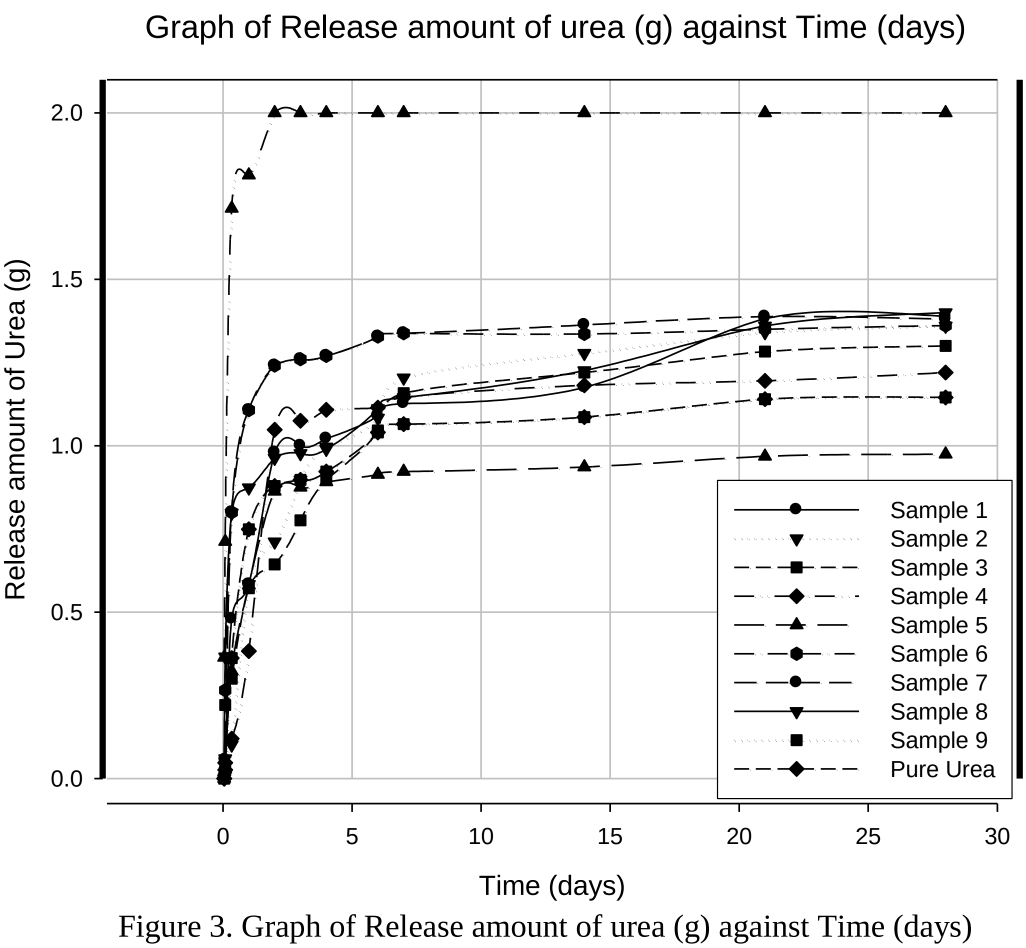


Figure 3. Graph of Release amount of urea (g) against Time (days)

3.2 Main effect of parameter to release rate of urea

Based on the main effect plot obtain from Minitab 17 with using Taguchi L9 array; the effect of each parameter to release of urea was showed as Figure 4.

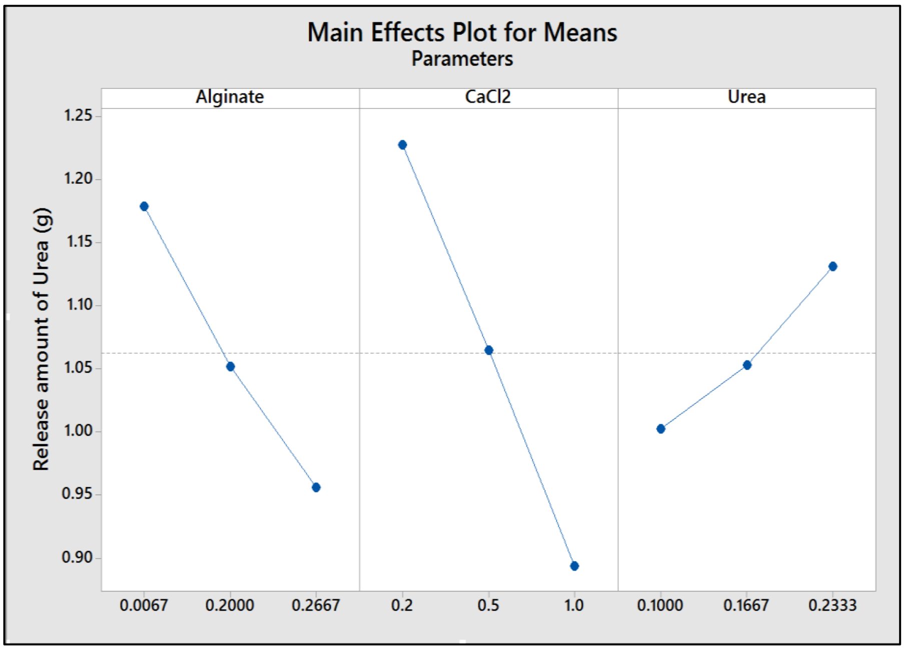


Figure 4. Main Effect of Alginate, CaCl2 and Urea concentration to Release rate

3.2.1 Effect of Sodium Alginate to Release Rate of Urea

From Figure 4, when sodium alginate concentration increased from 0.0067g/ml to 0.2267g/ml in alginate mixture for synthesis of controlled release fertilizers, the release rate of urea to water decreased. The same effect was also described by Baljit et al. on encapsulated thiram fungicide by using starch derivative alginate based controlled release formulation [12]. The effect of sodium alginate to release rate of urea can be explained as increase of sodium alginate content resulting in higher polymer compound was developed to encapsulate urea which increased the path of diffusing [12]. The effect can further describe by Figure 5, where the average release rate of controlled release fertilizer prepared with low, medium and high level of sodium alginate content was showed with respect with time.

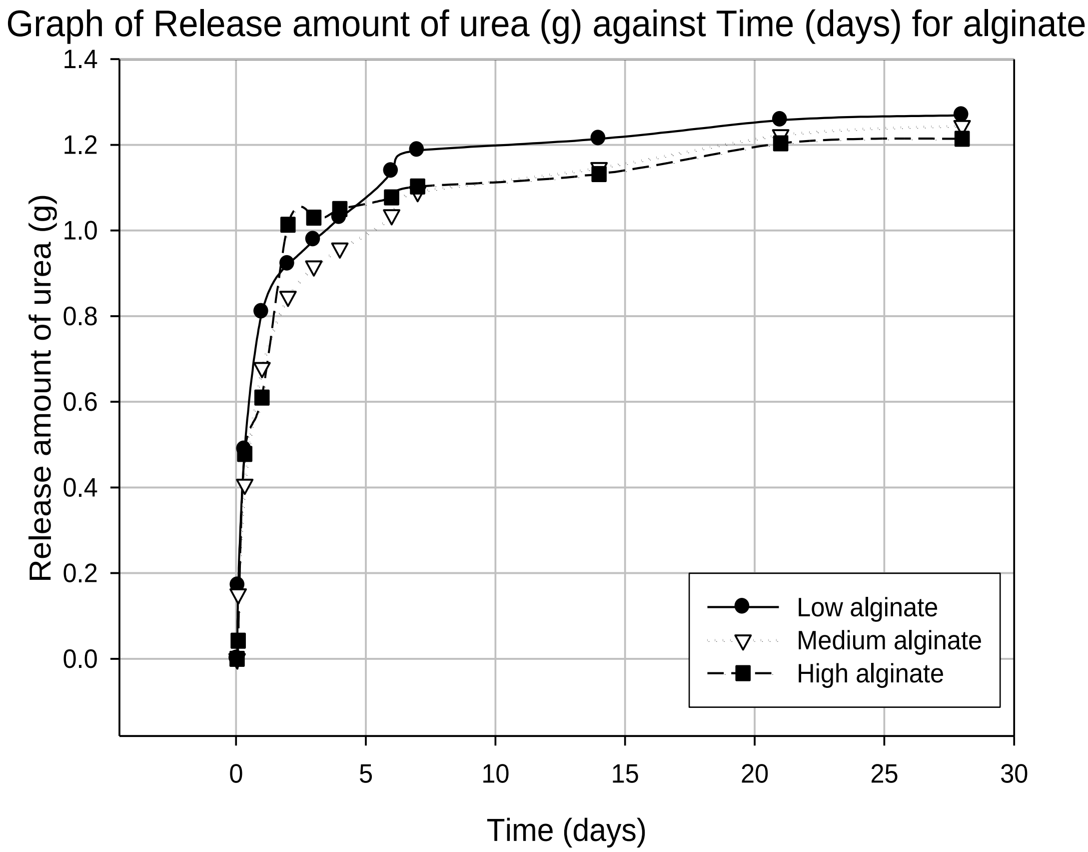


Figure 5.Graph of Release amount of urea (g) against Time (days) for alginate

3.2.2 Effect of $CaCl_2$ concentration to Release Rate of Urea

Crosslinking agent ($CaCl_2$ solution) showed a large effect towards the release rate of urea to water. The effect of $CaCl_2$ solution was done by varying the concentration from 0.2M to 1M when preparing the controlled release fertilizer. Effect of $CaCl_2$ solution is showed in Figure 4 where increased of concentration resulting in reduction in release rate of urea to water; Pepperman et al. and Roy et al. on alginate based controlled release formulation showed the same effect which supported the finding of this research[13,22]. This phenomenon can be explained as crosslinking agent $CaCl_2$ increase the crosslink between sodium alginate with calcium ion which strengthen the structure of the polymer and reduced the distance between each bonding and reduced the diffusion rate of water into controlled release fertilizer. Figure 6 showed the release of urea on low, medium and high level of $CaCl_2$ solution over time.

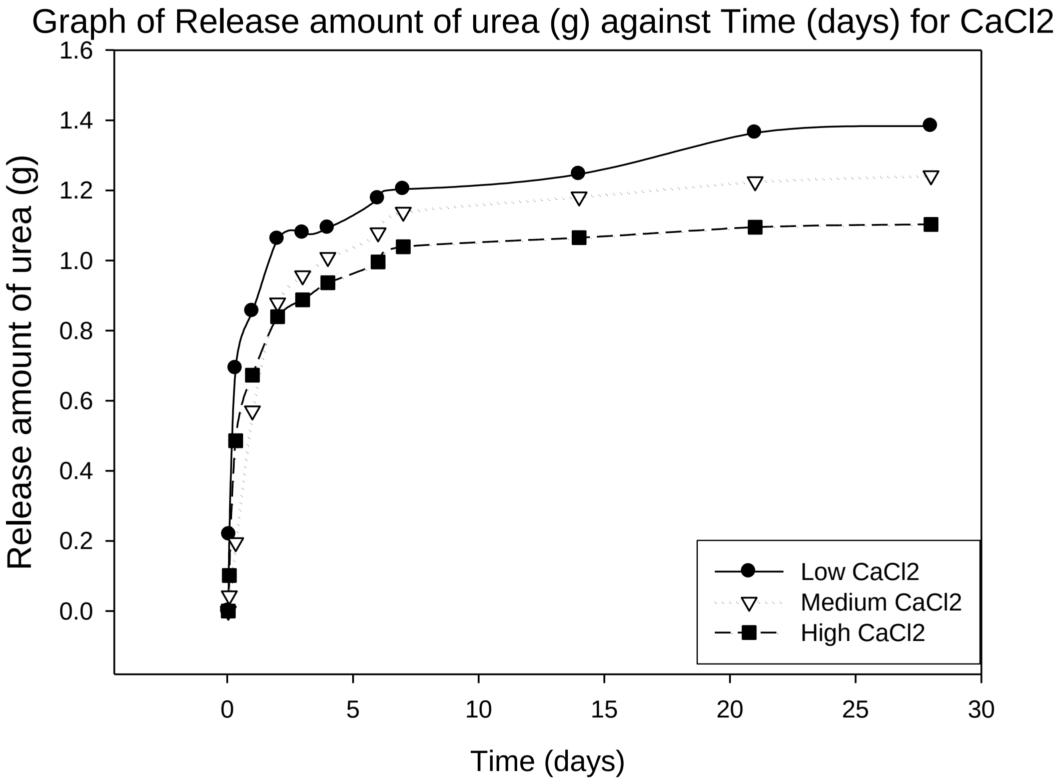


Figure 6.Graph of Release amount of urea (g) against Time (days) for $CaCl_2$

3.2.3 Effect of Urea to Release Rate of Urea

Urea the active ingredient which encapsulated in starch derivative controlled release formulation showed effect to release rate. Based on Figure 4, the increased of urea content increased the release of urea; from Roy et al. research, the loading of active ingredient also gave the same phenomenon which support the result of this research [13]. Increased in active ingredient concentration resulting in higher content encapsulated which increase the gradient of diffusion between controlled release fertilizer with water and resulting in increase in release rate. Figure 7 showed the effect of three level of urea to release rate over period of 28days.

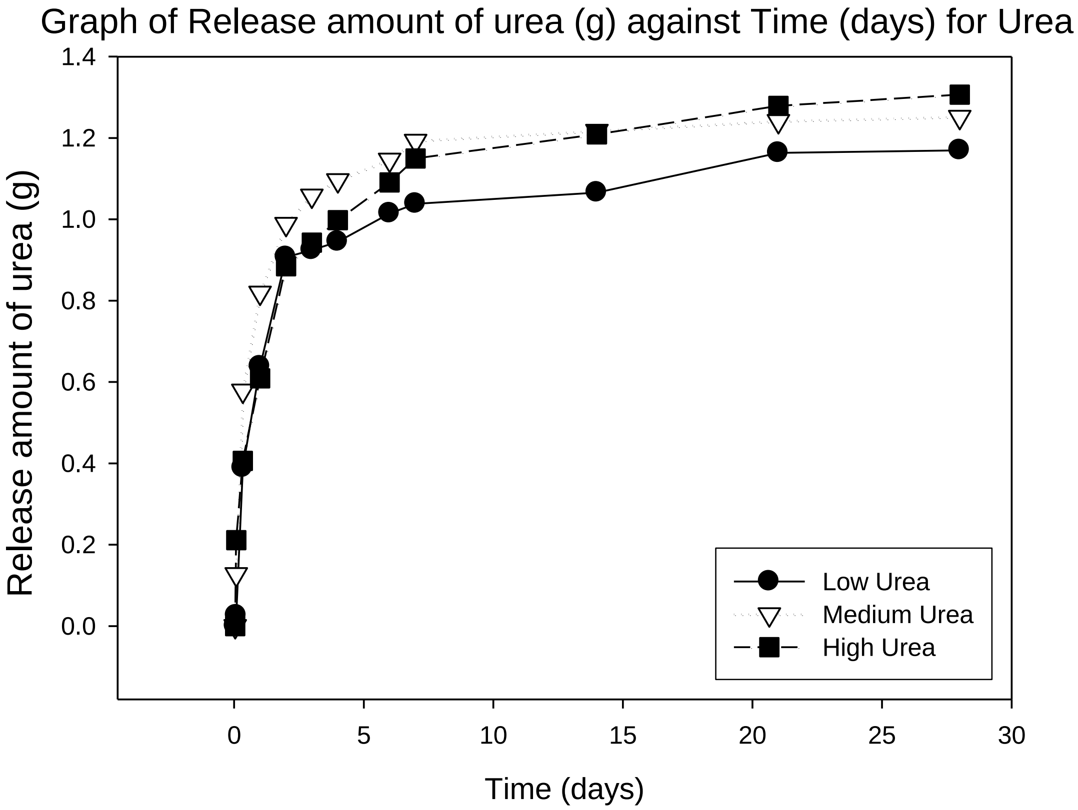


Figure 7.Graph of Release amount of urea (g) against Time (days) for urea

4.0 Conclusions

In the conclusion, this research successfully demonstrated the new Controlled Release Formulation on Fertilizer. Release dynamic of starch derivative alginate based fertilizer is done in water and results are analysed. Parameters- alginate, Crosslinker ($CaCl_2$ solution) and urea concentration showed effect to release rate of urea where increase in sodium alginate and crosslinker concentration reduced the release rate of urea but in opposite situation, increase in urea concentration in formulation increase the release rate of urea. With the results from this research, different combination of fertilizer can be prepared for usage in different region and benefit to agricultural field and reduce pollution towards environment. Further work such as analysis of release under different region, temperature and also biodegradability study can also proceed to identify applicability of this formulation.

References

[1] E. R. Kenawy, D. C. Sherrington, and A. Akelah, "Controlled release of agrochemical molecules chemically bound to polymers," *Eur. Polym. J.*, vol. 28, no. 8, pp. 841–862, Aug. 1992.

[2] N. Xiaoyu, W. Yuejin, W. Zhengyan, W. Lin, Q. Guannan, and Y. Lixiang, "A novel slow-release urea fertiliser: Physical and chemical analysis of its structure and study of its release mechanism," *Biosyst. Eng.*, vol. 115, no. 3, pp. 274–282, Jul. 2013.

[3] Y. Cao, L. Huang, J. Chen, J. Liang, S. Long, and Y. Lu, "Development of a controlled release formulation based on a starch matrix system.," *Int. J. Pharm.*, vol. 298, no. 1, pp. 108–16, Jul. 2005.

[4] F. Flores Céspedes, S. Pérez García, M. Villafranca Sánchez, and M. Fernández Pérez, "Bentonite and anthracite in alginate-based controlled release formulations to reduce leaching of chloridazon and metribuzin in a calcareous soil.," *Chemosphere*, vol. 92, no. 8, pp. 918–24, Aug. 2013.

[5] A. Pepperman and J. Kuan, "Controlled release formulations of alachlor based on calcium alginate," *J. Control. Release*, vol. 34, pp. 17–23, 1995.

[6] H. Akiyama, H. Tsuruta, and T. Watanabe, "N 2 O and NO emissions from soils after the application of di € erent chemical fertilizers," vol. 2, pp. 313–320, 2000.

[7] Y. Ji, G. Liu, J. Ma, G.-B. Zhang, and H. Xu, "Effects of Urea and Controlled Release Urea Fertilizers on Methane Emission from Paddy Fields: A Multi-Year Field Study," *Pedosphere*, vol. 24, no. 5, pp. 662–673, Oct. 2014.

[8] M. Mogul, H. Akin, and N. Hasirci, "Controlled release of biologically active agents for purposes of agricultural crop management," *Resour. Conserv. …*, vol. 16, pp. 289–320, 1996.

[9] X. Han, S. Chen, and X. Hu, "Controlled-release fertilizer encapsulated by starch/polyvinyl alcohol coating," *Desalination*, vol. 240, no. 1–3, pp. 21–26, May 2009.

[10] M. Trenkel and I. F. I. Association, *Controlled-release and stabilized fertilizers in agriculture*. Paris, France: International Fertilizer Industry Association, 1997.

[11] B. Azeem, K. KuShaari, Z. B. Man, A. Basit, and T. H. Thanh, "Review on materials & methods to produce controlled release coated urea fertilizer.," *J. Control. Release*, vol. 181, pp. 11–21, May 2014.

[12] B. Singh, D. K. Sharma, and A. Gupta, "A study towards release dynamics of thiram fungicide from starch-alginate beads to control environmental and health hazards.," *J. Hazard. Mater.*, vol. 161, no. 1, pp. 208–16, Jan. 2009.

[13] A. Roy, J. Bajpai, and A. K. Bajpai, "Dynamics of controlled release of chlorpyrifos from swelling and eroding biopolymeric microspheres of calcium alginate and starch," *Carbohydr. Polym.*, vol. 76, no. 2, pp. 222–231, Mar. 2009.

[14] Z. Wu, Y. He, L. Chen, Y. Han, and C. Li, "Characterization of Raoultella planticola Rs-2 microcapsule prepared with a blend of alginate and starch and its release behavior.," *Carbohydr. Polym.*, vol. 110, pp. 259–67, Sep. 2014.

[15] K. I. Drageta, K. Steinsv, E. Ons, and O. Smidsr, "Na- and K-alginate ; effect on Ca2 + -gelation," vol. 35, pp. 6–11, 1998.

[16] H. S. Samanta and S. K. Ray, "Synthesis, characterization, swelling and drug release behavior of semi-interpenetrating network hydrogels of sodium alginate and polyacrylamide.," *Carbohydr. Polym.*, vol. 99, pp. 666–78, Jan. 2014.

[17] A. López Córdoba, L. Deladino, and M. Martino, "Effect of starch filler on calcium-alginate hydrogels loaded with yerba mate antioxidants.," *Carbohydr. Polym.*, vol. 95, no. 1, pp. 315–23, Jun. 2013.

[18] R. Liang, M. Liu, and L. Wu, "Controlled release NPK compound fertilizer with the function of water retention," *React. Funct. Polym.*, vol. 67, no. 9, pp. 769–779, Sep. 2007.

[19] E. Ivanova, E. Teunou, and D. Poncelet, "Alginate based macrocapsules as inoculants carriers for production of nitrogen biofertilizers," *... Balk. Conf. Biol.*, vol. 9, 2005.

[20] F. Flores Céspedes, M. Villafranca Sánchez, S. Pérez García, and M. Fernández Pérez, "Modifying sorbents in controlled release formulations to prevent herbicides pollution.," *Chemosphere*, vol. 69, no. 5, pp. 785–94, Oct. 2007.

[21] T. H. Trinh, K. Kushaari, A. S. Shuib, L. Ismail, and B. Azeem, "Modelling the release of nitrogen from controlled release fertiliser: Constant and decay release," *Biosyst. Eng.*, vol. 130, pp. 34–42, Feb. 2015.

[22] R. M.Johnson and Armand B.Pepperman, "Leaching of Alachor from Alginate-encapsulated Controlled-release Formulations." pp. 157–164, 1996.