Comparison of Sodium Alginate-Based Slow-Release Beads with Varying Calcium Chloride Concentrations

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Abstract – Calcium alginate-based slow-release beads have properties which allow them to be used as fertilizer reservoirs. This study aimed to determine whether the varied concentrations of the cross-linkin agent, calcium chloride, has any effect on the slow-release rate of the beads in soil application and in water. Three concentrations at (3, 2, and 1 percent w/v) of calcium chloride were tested for UV-vis absorption and soil application, and their slow-release rates were determined. No significant difference was found among the various calcium chloride concentrations in both water and soil application, however the UV-vis spectrophotometry test showed that the 1 percent w/v calcium chloride concentration set-up had the slowest release rate in water.

Introduction. – Fertilizers also known as agrochemicals are readily available materials that provide plants the necessary elements that they need in order to grow and develop. Elements such as nitrogen, phosphorus, and potassium which are present in fertilizers help in hastening vegetative growth, increasing disease resistance, improving water intake, and stimulating root, flower, and seed development.

Despite the advantageous effects fertilizers have on plants, they can also be harmful as they may cause fertilizer burn. Fertilizer burn is caused by the overabundance of soluble salts in the soil due to excess application of fertilizer on plants [1]. It is characterized by scorching-like formations along roots or leaves, yellowish or brownish discoloration in the leaves, root damage, and stunting. Plant health such as low fruit quality, weak stem, fewer flowers, and the wilting of a plant can also be affected or influenced by fertilizer burns [1].

In addition, fertilizers can also cause harm in the environment through bioaccumulations in the food chain and contamination of various ecosystems [2]. One example of environment harm would be the occurrence of algal bloom, a result of eutrophication wherein large amounts of nutrients are accumulated in large bodies of water [3]. Despite being beneficial to the marine ecosystem for producing huge amounts of phytoplankton and cyanobacteria, intense occurrence of algal bloom can also be detrimental.

The adverse effects of fertilizers on plants and the ecosystem motivated researchers to find solutions in mitigating these effects. One solution they have developed is the use of superabsorbent polymers to control the release of fertilizer. In this way, the loss and use of fertilizers, and its adverse environmental effects can be mitigated. Slow-release fertilizers have the ability to reduce leaching, volatilization, and degradation of fertilizers. Furthermore, these materials can also cause soil compaction and prevent erosion and water run-off. These effects of slow-release fertilizers can help mitigate detrimental effects fertilizers have on the environment. These materials also improve the water-holding capacity of the soil. Moreover, ionic plant nutrients such as nitrogen, phosphorus and potassium are also stored, thus, slow-release formulations are better than conventional fertilizers.

For the development of slow-release fertilizers, polysaccharides are often being used as matrix since they are hydrophilic and biodegradable. Polysaccharides include cellulose, cyclodextrine, alginate, starch, dextran, guar gum, pectin, and chitosan. Alginate, a natural polysaccharide form algae, is one of the most commonly used materials for slow-release bead production [4]. Various studies have shown the use and application of the said polymer in the development of slow-release fertilizers.

For one project, a nanoreservoir made of alginate was designed in order to gradually release water from the bead [4]. Another study developed a similar product and it was found to have food slow-release capacity, and it was also able to improve the water-holding and water-retention capacity of the soul [5]. Furthermore, microbeads formed using sodium alginate, especially those who cross-linked with calcium chloride, are being highly studied for various medical and agricultural applications.

As shown, there is an abundance of studies which utilize sodium alginate for microbead production. This is because its viscosity and gelling, film-forming, thickening, and stabilizing properties [6]. However, there is lacking information regarding other microbead composition which can further improve its slow-release ability. Due to this, slow-release beads, with varying concentrations of its cross-linking material, calcium chloride, were made in this study in order to assess the effect of its varied concentrations on the slow-release ability of the beads.

Methods. – Calcium alginate-based slow-release beads were developed using sodium algiante and calcium chloride through the process of ionotropic gelation. These beads were varied in the calcium chloride concentration applied in order to assess which calcium chloride concentration is the most efficient in promoting the slow-release ability of the developed beads. The beads were applied and tested in water as well as in the soil. In the water setup, using UV-Vis spectroscopy, the rate of absorbance levels of the released content of the beads int he release medium was recorded and calculated. on the other hand, the rate of weight loss of the beads for seven days was determined for the soil setup.

Materials. In making the calcium chloride solution sodium alginate solution, and alginate beads, glassware such as conical tubes, beakers, and graduated cylinders were used. In addition, laboratory equipment such as the vortex mixer, UV-Vis spectrophotometer, and top-loading balance were aso utilized. Specimen cups and syringes at 1cc, 2cc, and 3cc were also utilized in this study. All laboratory glassware and equipment were available in the Philippine Science High School- Western Visayas Campus laboratory.

Preparation of calcium chloride solutions. Three varying calcium chloride concentrations were made at 1, 2, and 3 percent w/v concentrations. Calcium chloride weighing 2.5, 5.0, and 7.5 grams were separatelt mixed in distilled water in three 250mL volumetric flasks.

Preparation of sodium alginate solutions. Three percent of sodium alginate solution was made by putting 1.5 grams of sodium alginate in a 50mL conical tube. It was then initially added with a small amount of distilled water and was mixed using the vortex mixer and was diluted to mark. Continuous mixing was done after every addition of distilled water until it was fully mixed. The mixture was then left to settle overnight in order to allow it to dissolve completely.

Synthesis of calcium alginate-based beads. 3mL of the 3 percent w/v sodium alginate solution, 1mL red food coloring, and 0.15mL glycerol were mixed in a separate conical tube using a mixer. 125mL of the calcium chloride solution was placed in a beaker. The homogenous solution was then added drop-wise using a 10mL syringe with a 0.32mm needle from a height of 6cm into the calcium chloride solution, as shown in fig. 1. The dropped beads were allowed to settle in the calcium chloride solution for 40 minutes. After settling, the beads were removed from the calcium chloride solution and were washed with distilled water. The beads were then allowed to drain. After draining the beads, they were weighed and prepared for the soil and water testing.

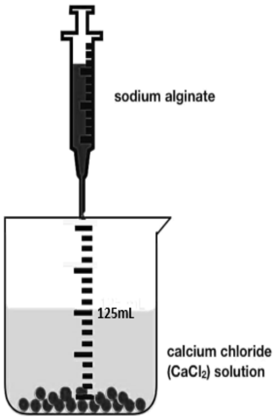

Fig. 1: Ionotropic gelation.

Testing of slow-release beads in water. 0.2 grams of the developed slow-release beads were taken from every treatment in order to be used for water testing. Three set-ups of 400mL distilled water placed in 400mL beakers were prepared to serve as the release medium. The beads were immersed in the prepared release medium. At every ten-minute interval, 5mL of the solution was taken out from the release medium in order to detect the content of the red food coloring using an ultraviolet spectrophotometer. The absorbance of the sample solution was measured.

Testing of slow-release beads in soil. For each set-up, beads weighing 0.5 grams were prepared. These beads were then placed inside a mesh and were buried into 150g of soil at a depth of 10cm from the soil surface, as shown in fig. 2. The weight of the beads were checked at a 24-hour interval. For the weighing, the beads were removed from the soil, washed with distilled water, drained for five minutes, and weighed. After weighing, the beads were placed back inside the mesh and were buried into the soil again. This was done every 24 hours for a period of seven days.

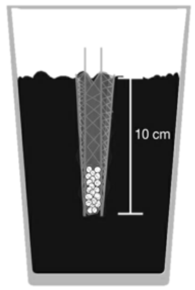

Fig. 2: Setup of slow-release beads in soil.

Results. – In terms of the weight loss of the slow-release beads over time, the beads with a three percent w/v calcium chloride concentration had he slowest rate of release, whereas those with a one percent w/v calcium chloride concentration had the fastest rate of release.
Contrary to this, the hydrogel beads which had a two percent w/v calcium chloride concentration has the highest absorbance for the wavelength range of 590 to 470nm, at all time intervals. It is followed by the slow-release beads which contain three percent w/v calcium chloride concentration. Lastly, the beads which contained a one percent w/v calcium chloride concentration had the fastest rate of release had the least absorbance at all the aforementioned wavelengths.

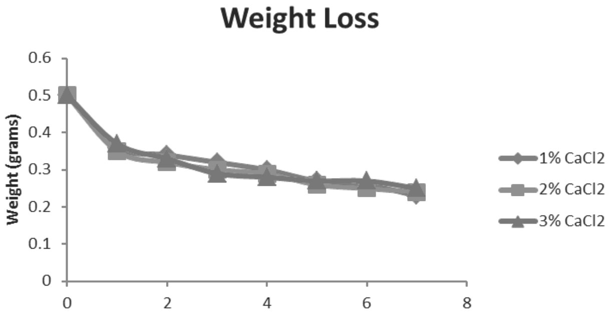

Fig. 3: Weight loss of slow-release beads for seven days.

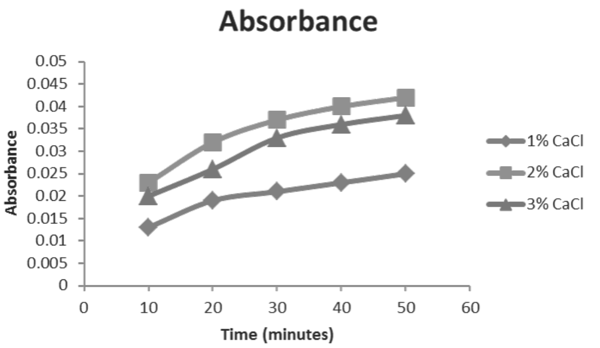

Fig. 4: Absorbance of water throughout the 50-minute duration.

The beads in the treatment which have a three percent w/v calcium chloride concentration had the slowest release rate among them. This is consistent with the study of Badwan et. al [8], where the calcium alginate beads for drug delivery that were made from the highest concentration of calcium chloride (15 percent w/v calcium chloride concentration) had the slowest rate of release. According to Badwan et. al [7], this may be attributed to the water content present in the beads. The beads with the lower concentration of water and a higher concentration of calcium chloride have resulted to a lower swelling effect on the beads, thus the slower its release. This is also similar to the study of Tavakol et. al [8] on alginate NO-carboxymethyl chitosan beads for drug delivery. The NO-carboxymethyl chitosan beads prepared from the higher concentrations of calcium chloride had a lower swelling degree due to the increased cross-linked density of the beads. Despite having the slowest release rate among the three treatments, the treatment with a three percent w/v calcium chloride concentration had no significant difference among the other two treatments at the alpha level of 0.05, having a p-value of 0.909.

Contrary to the results of the soil setup, it was the treatment with a one percent w/v calcium chloride concentration which had the slowest rate but there is also no significant difference among the three treatments. This is not consistent with previous studies on the mechanism of slow-release beads. Supposedly, it is the treatment with beads having a higher calcium chloride concentration which will have a slower release rate. There must be a difference in the behaviour of the slow-release beads in water and in soil due to the great number of impurities in the soil setup. Therefore further studies regarding the mechanism of slow-release beads in both the soil and water setups must be conducted.

Conclusion. – There is no significant difference among the treatments in both the soil and water setups. Therefore, the beads with a one percent w/v calcium chloride concentration can be used to produce slow-release beads in a large scale without utilizing huge amounts of cross-linking material for there is no significant difference on the slow-release rates of the three treatments with a varying calcium chloride concentration.

Recommendation. – Since the data for the water set-up is anomalous, further studies on the mechanism of slow-release beads should be conducted. It would also be better if the actual fertilizer material will be loaded to the bead itself to see whether there is a difference on the beads' mechanism.

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REFERENCES

[1] Miksen C., (SFGate) http://homeguides.sfgate.com/problems-overusingfertilizers-28033.html

[2] Milani C., Franca D., Balieiro A.G. and Faez R., *Polimeros*, **27** (2017) .

[3] Shukla R., Bajpai J., Bajpai A.K., Acharya S., Shrivastava R.B. and Shukla S.K., *App. Math and Comp.*, **196** (2008) 782-790.

[4] Helmiyati and Aprilliza M., *IOP Conf. Ser.: Mater. Sci. Eng.*, **69** (1969) 9691.

[5] Sharma R., Bajpai K., Bajpai A.K., Acharya S., Shrivastava R.B., and Shukla S.K., *Carbohydrate Polymers*, **102** (2014) 513-520.

[6] FMC BioPolymer (Editor), *Alginates- a world full of possibilities lies just below the surface*, Vol. **1**.

[7] Badwan A.A., Abumalooh A., Sallam E., Abukalad A. and Jawan O., *Drug Development And Industrial Pharmacy*, **11** (1985) 239-256.

[8] Tavakol M., Vasheghani-Farahani E. and Hashemi-Najafabadi S., *Progress in Biomaterials*, (2013) .