Indonesian Journal of Chemical Research

http://ojs3.unpatti.ac.id/index.php/ijcr Indo. J. Chem. Res., 8(3), 219-227, 2021

Characterization of Alginate-Cellulose-Kaolin Composites for Slow-Release Urea Fertilizer

Sunardi[1,2]*, Gusti Nia Faramitha[1], Uripto Trisno Santoso[1]

[1]Chemistry Study Program, Mathematics and Natural Sciences Faculty, Universitas Lambung Mangkurat, Banjarbaru, Indonesia

[2]Wetland Based Materials Research Center, Universitas Lambung Mangkurat, Banjarbaru, Indonesia

[*]*Corresponding Author: sunardi@ulm.ac.id*

Received: November 2020
Received in revised: November 2020
Accepted: December 2020
Available online: January 2021

Abstract

Research on the effect of cellulose and kaolin addition to alginate-cellulose-kaolin composites' characteristics as a slow-release agent of urea fertilizer has been done. The technique used in composites' preparation is an extrusion technique using 2% $CaCl_2$ solution as a cross-linker. The compositions of alginate-cellulose-kaolin were varied to determine their effect on composites' characteristics such as diameter, color, swelling ratio, entrapment efficiency, and release of urea. The results showed that the diameter of beads in wet condition produced ranges from 2.98 to 3.54 mm, whereas the diameter of dry beads ranges from 1.22 to 1.92 mm. The addition of cellulose and kaolin affected the color of the beads produced based on CIE Lab analysis. The value of the swelling ratio decreased with the addition of cellulose and kaolin. The entrapment efficiency of urea in beads obtained ranged from 37.25 to 45.06%. The release of urea in aqueous media showed that cellulose and kaolin's addition into the alginate affected the amount of released urea.

Keywords: Alginate, cellulose, kaolin, slow release, urea

INTRODUCTION

Urea is a nitrogen fertilizer most often used in agriculture because it has a high nitrogen content (46%) and a relatively cheap price (Wang et al., 2012). However, in application, about 40-70% of the nitrogen content in fertilizers can reduce the environment because it experiences evaporation and washing (Giroto et al., 2017). Besides, the excessive use of nitrogen fertilizers could cause serious environmental problems such as soil acidification, heavy carbon contaminants, and greenhouse gas emissions (Islam et al., 2011, Zhu and Chen, 2002). Therefore, it will lead to changes in soil structure, compaction, and decreased soil content in a long period.

The use of fertilizers with slow-release technology is considered a promising strategy to increase healthy nutrition more effectively and efficiently (Li et al., 2016a, Li et al., 2016b). Slow release fertilizers also have many benefits than conventional fertilizers, such as better fertilizer use and provide more nutritious nutritional requirements for plant needs (Nelson et al., 2009). Currently, research on slow-release fertilizer technology focuses on the use of new materials that are cheap, renewable, easily degraded, and non-toxic as materials for the development of late material in agriculture (Kumar et al., 2015, Roy et al., 2014). Alginate is a non-toxic polysaccharide that is easily degraded and has the potential to become a slow-released material because it can form cross-linked by increasing the amount of cation and forming beads (Bashan et al., 2002, Bijang et al., 2018).

However, high price gains and easy to experience high grade with a lot of monovalence when applied to agricultural land could limit its use (He et al., 2015). The addition of available materials as cheap as cellulose and clay can reduce the ability to slow down active substances production and produce higher efficiency of adsorption of active substances (Wu et al., 2014, Ningsih et al., 2019, Sekewael et al., 2015).

This study was conducted on the effect of the increase in cellulose and kaolin in alginate beads production to improve the urea slow-released composite material characteristics. Some of the parameters studied in this study are the compositional effect of alginate-cellulose-kaolin on diameter, expansion ability, beads color, the efficiency of adsorption, and the ability to release urea fertilizer on alginate beads.

METHODOLOGY

Synthesis of Alginate Beads

Synthesis of alginate beads using extrusion techniques (Wu et al., 2011). Solutions of alginate, cellulose, and kaolin mixture were prepared with various compositions as in Table 1. Alginate, cellulose, and kaolin are dissolved in 50 mL hot distilled water and stirred using a magnetic stirrer for 3 hours to make a homogeneous solution. The solution is then mixed with the urea fertilizer, prepared, and stirred slowly with a magnetic stirrer to keep it homogeneous at temperature for 60 minutes.

Table 1. Variations in alginate-cellulose-kaolin composition

Beads Code	Alginate (%w/v)	Cellulose (%w/v)	Kaolin (%w/v)
A2	2.0	0	0
A2M1	2.0	0	1.0
A2M1.5	2.0	0	1,5
A2K1	2.0	1.0	0
A2K1.5	2.0	1.0	1.0
A2M1K1	2.0	1.0	1.5
A2M1.5K1	2.0	1.5	0
A2M1K1.5	2.0	1.5	1.0
A2M1.5K1.5	2.0	1.5	1.5

The sample is then mixed and then extruded using a 10 mL syringe into 2% $CaCl_2$ solution while stirring using a magnetic stirrer for 30 minutes to form the beads. The formed beads are separated with a filtered layer of 2% $CaCl_2$ solution and washed with distilled water 2-3 times to remove $CaCl_2$ residue. The beads were dried at a temperature of 40 °C until a constant weight is obtained.

Analysis of Beads Size

The beads size was analyzed using a digital tunnel by measuring the diameter of the wet alginate-cellulose-kaolin beads that had been synthesized. A total of 15 beads in each sample with each formulation were measured in three different positions, and the mean diameter was calculated and recorded.

Analysis of Beads Color

Color measurements were carried out using the Minota C200 colorimeter by placing the sample on a white plate. The total color difference (ΔE), whiteness index (WI), and yellowness (YI) index are calculated by the Equation 1.

$$\Delta E = [\ (L_{standard} - L_{sample})^2 + (a_{standard} - a_{sample})^2 + (b_{standar} - b_{sampel})^2\ ]^{0.5} \quad (1)$$

Where a indicates a red-green color and b indicates a yellowish color, and L indicates a light-dark color.

Urea Adsorption Efficiency

The adsorption efficiency of alginate beads against urea was analyzed by calculating urea concentration in the $CaCl_2$ solution after beads formation. A total of 2.5 mL of filtrate resulting from beads' formation was added to 0.5 mL of p-dimethylamino-benzaldehyde (p-DMAB) complexing solution analyzed by using UV-Vis Spectrophotometer. The absorption efficiency can be calculated using the Equation 2.

$$\text{Adsoprtion Efficiency (\%)} = \frac{\text{No-Nu}}{\text{No}} \text{ x } 100\% \quad (2)$$

where No indicates the initial amount of urea in the alginate-cellulose-kaolin solution mixture and Nu is the amount of urea fertilizer which left in the $CaCl_2$ solution after the beads formation of the beads.

Swelling Ratio of Beads

The swelling ratio of the beads can be calculated from the amount of water that can be removed from the beads. A total of 0.05 grams of dried beads were soaked in 20 mL of distilled water. The soaked and swollen beads are separated using a filter paper and the excess water in the bead is removed by gently pressing the beads between three of the filter paper. The swollen beads are weighed and the swelling ratio can be calculated using the equation:

$$\textit{Swelling ratio}\ (\%) = \frac{\text{Ws-Wd}}{\text{Wd}} \text{ x } 100\% \quad (3)$$

where W_s is the weight of the swollen beads and W_d is the weight of the dry beads.

FTIR Analysis

Beads samples were analyzed using a Fourier Transform Infrared (FT-IR) ATR Platinum Diamond Bruker Universal spectrophotometer. This analysis was carried out to identify the beads' structure and determine the presence of free-COO or other bonds in the polymer matrix. The analysis was carried out in the range 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

The Slow Release Ability of Urea In Beads

A total of 0.05 grams of dry beads were immersed in 5 mL of distilled water in a closed beaker at room temperature and then shaken using a shaker. After 12 hours of shaking, the soaked beads were removed. The amount of nitrogen released can be determined by the colorimetric method using a UV-Vis spectrophotometer at a wavelength of 420 nm with the p-DMAB complex solution.

RESULTS AND DISCUSSION

Synthesis of Alginate-Cellulose-Kaolin Beads

The images of visual observation results of the alginate-cellulose-kaolin beads can be seen in Figure 1. In general, wet beads have a spherical shape, even though they are somewhat less regular. Almost all of the dried heads have a non-spherical shape and have a rough surface, where the morphology of the albumen is affected by the variability of composition (Li et al., 2016a). The alginate wet beads added to cellulose and kaolin (A2) in Figure 1 have the exact color. The same results were obtained from previous studies (Abdalla et al., 2015) that alginate heads synthesized without other polymers are round and semitransparent. Beads alginate-cellulose (A2-M1; A2-M1.5) were whitish and not transparent. The results obtained were the same as those of previous studies (Abdalla et al., 2015); alginate beads added with polysaccharides produced whiter beads than alginate beads. In contrast to the alginate-cellulose beads, the alginate-kaolin beads (A2-K1; A2-K1.5) have a yellowish-white color.

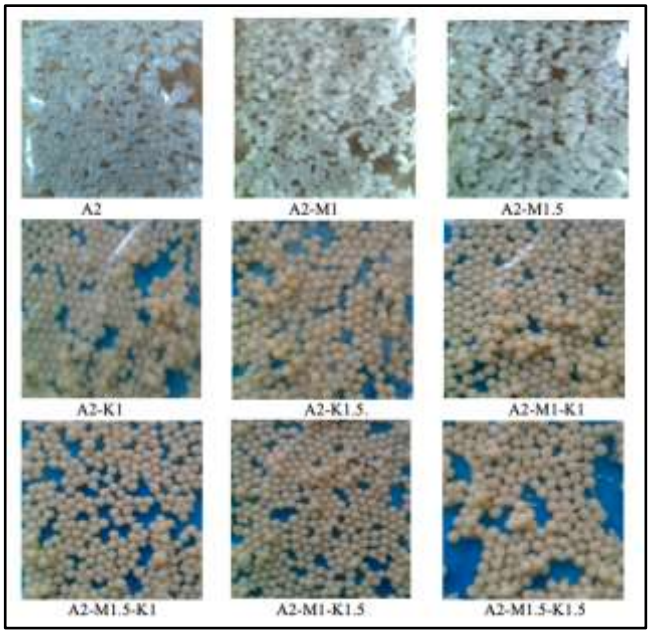

Figure 1. Images of Wet Alginate-Celulose-Kaolin Beads

The yellowish color of alginate-kaolin beads may come from the added kaolin. The color alginate-cellulose-kaolin beads (A2-M1-K1 and A2-M1.5-K1.5) also has a yellowish-white color when the cellulose and kaolin are used together. However, the alginate-cellulose-kaolin beads' yellow color was reduced when the ratio of cellulose was added (A2-M1.5-K1). A different thing also happened when the kaolin ratio was added; the color of alginate-cellulose-kaolin became yellowish.

The drying process causes shrinkage of the beads (Roger et al., 2006). It causes the size of the dry bead to become smaller than that of wet. Besides, wet tube beads that formed are not always rounded, and this is due to the variety of solution composition, which causes an increase in solvent viscosity so that the droplets that fall are not rounded. This effect is related to the increase in droplet size, which increases the size of the beads (Abdalla et al., 2015).

Analysis of the Alginate-Cellulose-Kaolin Beads Size

The size analysis was carried out in two conditions: the wet and dry bead conditions, measured using a digital caliper.

Table 2. Diameter sizes of wet and dry alginate-cellulose-kaolin beads

Formulation	Wet Beads Diameter (mm)	Dry Beads Diameter (mm)	ΔD (mm)
A2	3.23 ± 0.08^{b}	1.40 ± 0.10^{b}	1.83
A2-M1	2.98 ± 0.14^{a}	1.37 ± 0.14^{b}	1.61
A2-M1.5	2.98 ± 0.11^{a}	$1,45 \pm 0,12^{b}$	1.53
A2-K1	2.98 ± 0.16^{a}	1.22 ± 0.08^{a}	1.76
A2-K1.5	3.51 ± 0.19^{de}	1.67 ± 0.08^{c}	1.84
A2-M1-K1	3.37 ± 0.14^{bcd}	1.87 ± 0.12^{d}	1.50
A2-M1.5-K1	3.44 ± 0.13^{cde}	1.89 ± 0.12^{d}	1.55
A2-M1-K1.5	3.34 ± 0.13^{bc}	1.72 ± 0.11^{c}	1.62
A2-M1.5-K1.5	3.54 ± 0.17^{e}	1.92 ± 0.07^{d}	1.62

Note: Diameter is the average of 3 times the measurement for 15 beads. Different letters show differences based on the Tuckey HSD test.

Beads that have been oven-dried at 40 °C experience shrinkage, which causes the size of the dry beads to be smaller compared to wet beads. Table 2 shows the varied beads' sizes, and the ΔD values in Table 2 show the difference between wet and dry beads. Based on Table 2, the smallest wet bead diameters are in 3 sample formulations, namely variations in the composition of A2-M1, A2-M1.5, and A2K1, where the diameters are 2.98 ± 0.14, 2.98 ± 0.11, and 2.98 ± 0.16. However, the largest diameter is in the A2-M1.5-K1.5 formulation, which is 3.54 ± 0.17. Based on data in Table 2, the alginate beads decreased in diameter when the cellulose was added. The same thing happens when the ratio of cellulose is added; the beads' diameter decreases and has the same value as the previous cellulose ratio. The decrease that occurs is possible because the additional cellulose has low viscosity, so the mixture becomes thinner and produces smaller droplets.

Analysis of Alginate-Cellulose-Kaolin Beads Color

The color analysis was carried out on beads samples that had been dried at 40 °C. Each bead was measured on a white plate using a colorimeter. The L* value in Table 3 shows the parameters of the dark and light color of the sample, the a* value indicates a red-green color, and b indicates a yellowish blue color. The ΔE* value in Table 3 indicates the amount of color change for each sample.

The color characteristics of the dry beads samples obtained varied for all formulations, as shown in Table 3. Based on data in Table 3, the alginate beads show an increase in L* values in the addition of cellulose from 52.84 ± 0.11 to 63.14 ± 0.14. It indicates that the alginate beads sample becomes brighter or whitish after adding cellulose, as well as when the concentration of cellulose is increased, the L* value becomes more extensive, which indicates the sample become brighter. Different results occur for the a* and b* values. The addition of cellulose to the alginate beads caused a slight decrease in the a* and b* values. The decrease in the value of a* indicates that the alginate beads sample shifted to a greenish direction when cellulose was added. The same results were obtained when the ratio of cellulose was added, and the a* and b* values decreased compared to alginate beads. This decreased b* value shows the color of the beads shifting towards blue. The change from the beads' color also looks much different. Table 2 shows that cellulose's addition causes the ΔE* value to increase from 56.26 ± 0.19 to 65.46 ± 0.39 and 67.01 ± 0.41.

Table 3. Color Characteristics of Alginate-Cellulose-Kaolin Beads

Formulation	L*	a*	b*	ΔE*
A2	52.84 ± 0.11^{d}	4.95 ± 0.08^{b}	18.70 ± 0.14^{d}	56.26 ± 0.19^{d}
A2M1	63.14 ± 0.14^{h}	4.94 ± 0.19^{b}	16.54 ± 0.31^{b}	65.46 ± 0.39^{h}
A2M1.5	65.13 ± 0.21^{i}	4.00 ± 0.11^{a}	15.21 ± 0.34^{a}	67.01 ± 0.41^{i}
A2K1	49.56 ± 0.17^{a}	6.02 ± 0.22^{d}	17.35 ± 0.20^{c}	52.85 ± 0.34^{a}
A2K1.5	51.04 ± 0.12^{b}	4.83 ± 0.17^{b}	15.18 ± 0.16^{a}	53.46 ± 0.26^{b}
A2M1K1	51.81 ± 0.15^{c}	5.74 ± 0.06^{c}	16.44 ± 0.19^{b}	54.66 ± 0.25^{c}
A2M1.5K1	56.29 ± 0.20^{f}	5.52 ± 0.08^{c}	16.29 ± 0.05^{b}	58.85 ± 0.22^{f}
A2M1K1.5	55.54 ± 0.24^{e}	5.51 ± 0.11^{c}	16.41 ± 0.20^{b}	58.18 ± 0.33^{e}
A2M1.5K1.5	57.37 ± 0.10^{g}	5.50 ± 0.06^{c}	16.60 ± 0.17^{b}	59.98 ± 0.21^{g}

Note: The measurement is carried out five times and then averaged. Different letter notes indicate differences based on the Tuckey HSD test

The diameter of beads also decreased when kaolin was added to the alginate. However, when the ratio of kaolin increases, the diameter of beads also increases. It is possible because the increase in the amount of kaolin causes the mixture's viscosity to be higher and produce larger grains than the alginate beads (Wu et al., 2011).

The addition of cellulose and kaolin to alginate increases the beads' diameter, which is possible because of the high viscosity of the mixture. In the A2-M1-K1 and A2-M1-K1.5 formulations, the increase was not too high. In contrast to the formulations A2-M1.5-K1 and A2-M1.5-K1.5, the increase was relatively high. The A2-M1.5-K1.5 formulation had the largest diameter and was possible because of adding cellulose and kaolin with a large ratio and causing the mixture's viscosity to be larger.

Table 3 shows that the addition of kaolin to the alginate caused a decrease in the L* value from 52.84 ± 0.11 to 49.56 ± 0.17. It indicates that the color of the beads will become darker when kaolin is added. This result also occurs when the added kaolin ratio, the L*

value became less when the alginate was added with kaolin. Still, the kaolin ratio's addition causes the L* value to become more significant if the kaolin ratio is smaller.

An increase of a* value occurred when the addition of kaolin to alginate was carried out. An increase indicates the color of bead leads to a greenish color, but when the kaolin ratio is added, there is a decrease of a* value, which indicates that the color of heads shifts towards redness. The decrease also occurs in the b* value; when the addition of kaolin, the b* value decrease, and so when the kaolin ratio is added, the decrease is more significant. The decreasing of b* value denotes a shifting of color to head to the blue direction. The same phenomenon happened to the ΔE* value; the ΔE* value decreased when kaolin was added to the alginate. These results indicated that the sample added kaolin did not experience a sufficiently large color change as seen in the A2K1 and A2K1.5 formulations.

The mixture of alginate, cellulose, and kaolin beads experiences a decrease in L* value if compared with the alginate bead. The decrease of the L* value from 52.84 ± 0.11 to 51.81 ± 0.15 indicates the heads' color is more visible in the A2M1K1 formulation. When the cellulose ratio is added, the L* value becomes 56.29 ± 0.20, which is seen in the A2M1.5K1 formulation, the same as the A2M1K1 ratio added to the A2M1.5K1 formulation. The L* value becomes larger if it is compared with the alginate beads. The highest L* value was found in the A2-M1.5-K1.5 formulation, indicating a more extensive white or lighter weight after adding cellulose and kaolin with more excellent ratios. The L* value in this formulation is 57.37 ± 0.10, which is very far from the L* beads alginate value, namely 52.84 ± 0.11.

This result corresponds to the a* value if it is compared with an increase in the alginate amount. This result indicates that cellulose and kaolin's addition causes the color to shift in a green direction. The A2 formulation, if compared with the A2-M1-K1, A2-M1.5-K1, A2-M1-K1.5, and A2-M1.5-K1.5 formulations, differed significantly, but the addition of ratio cellulose or kaolin make a little changes for a* values.

In contrast with a* value, the value of b * decreases in proportion to alginate beads' value. The value of b* alginate from 18.70 ± 0.14 decreases to 16.29 ± 0.05 when cellulose and kaolin were added. This shows the color of the heads shifting toward a bluish direction. The ΔE* value obtained in the A2-M1-K1 formulation is smaller than the A2-beam formulation; this indicates that the change/difference in the beads' color is less. Still, in the A2-M1.5-K1, A2-M1-K1.5, and A2-M1.5-K1.5 formulations, an increase in the value of ΔE* indicates the change/difference in color heads are getting bigger.

Analysis of Alginate-Cellulose-Kaolin Beads Swelling Ratio

Swelling ratio analysis was carried out to measure the swelling ability of the sample of beads. Based on the graph obtained in Figure 2, the highest swelling was in the 2% alginate formulation, which is 67%. When the cellulose addition was carried out, a decrease in the swelling ratio's value was not much different, seen in the A2M1 formulation. The same thing was obtained when the cellulose ratio was added to the A2M1.5 formulation; the decreased swelling ratio increased. The addition of kaolin to alginate also caused a significant decrease in the welling ratio value. The same was right when the kaolin ratio was added, but the decreased swelling ratio value was not more significant than the previous ratio.

The same results were obtained when the addition of cellulose and kaolin was carried out; there was a decrease in swelling ratio value. The difference is that when the cellulose and kaolin were added, the decrease in the swelling ratio value is more significant. Based on the swelling ratio chart, three formulations have relatively the same values: A2-M1.5-K1, A2-M1-K1.5, and A2-M1.5-K1.5.

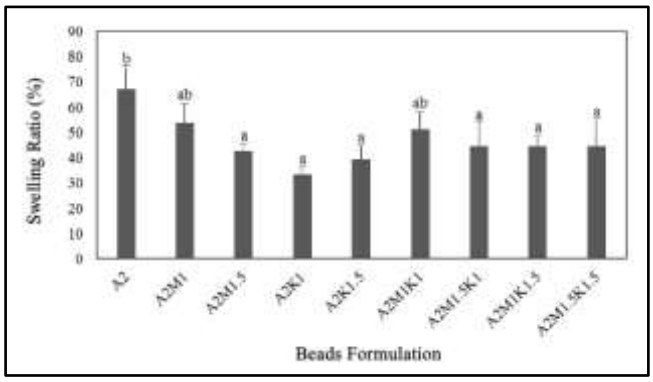

Figure 2. Value of the Swelling Ratio beads. The data displayed is the mean of three times measurements ± standard deviation. Different notations indicate different results of the Tuckey HSD Test.

The swelling ability of alginate may be due to carboxyl groups, which bind strongly to water. The decrease in welling ratios may be due to the addition of polysaccharides, which then bind with the carboxyl group in the alginate and reduce the active groups in the alginate and induce the hydrophilicity system of alginate release (Roger et al., 2006). The results

obtained in this study are similar to previous studies where there was a decrease in the value of welling ratiometric added by polysaccharide and cellulose (Li et al., 2016b). This is possible because there is an electrostatic anionic resistance of cellulose, which is hydrophilic, reducing the osmotic pressure between the tissues and the solution outside (Zhao et al., 2006).

A high swelling ratio of alginate is possible because alginate is a very ionic polymer with carboxylate and hydroxyl groups so that it can bind more hydrogen to water (Liu et al., 2013). The addition of clay in the form of kaolin to the alginate mixture is also possible to only strengthen the alginate structure and make the beads compact so that there is a decrease in the swelling value ratio. This result can be seen in Figure 5 that the lower welling ratio in A2K1 and A2K1.5.

Functional Group Analysis of Alginate-Cellulose-Kaolin Beads

FTIR analysis was carried out to determine the functional groups' changes in each bead formulation and determine the interactions that occurred. The results of the FTIR spectra in this study can be seen in Figure 3. Based on Figure 3, can be seen that the shifts in the number of wave number when the material is added to the alginate mixture. In the range 3300 cm^{-1}, which shows the O-H group, the peaks formed are more significant and broader, except for the A2K1.5 formulation where the peak peaks are not visible. Besides, all the peaks showed a sharper shape when cellulose and kaolin were added. A shift in the wavenumber indicates a change in the environment of the functional groups that occur when the addition of material is carried out.

Specific alginate absorption at 1023.583 cm^{-1} showed vibration of carboxyl and ether. The typical absorption of carbonyl groups on the alginate was shown at wavenumbers 1592.467 cm^{-1}. The absorption wave numbers 3207.364 cm^{-1} and 1404.879 cm^{-1} showed the absorption of wavenumbers for O-H vibrations. The O-H group on the alginate shows a widened band due to hydrogen-molecular binding (Asa et al., 2016). Meanwhile, C-H stretching alkyl vibration is shown in wavenumbers 2925.981 cm^{-1}.

In 2% alginate beads, there is a more excellent absorption in the OH cluster's vibrations, which is 3254.261 cm^{-1}, which is possible due to its strong interaction between the OH clusters with Ca^{2+} (Verma et al., 2013). Increased absorption also occurs when cellulose and kaolin were added, which reach 3329.705 cm^{-1} at beads formulation A2-M1-K1.5. The increase in the -OH group's absorption intensity comes from R-OH on alginate or Si-OH or Al-OH in kaolin, which indicates a hydrogen-bonding interaction between alginate and kaolin (Athaillah et al., 2018).

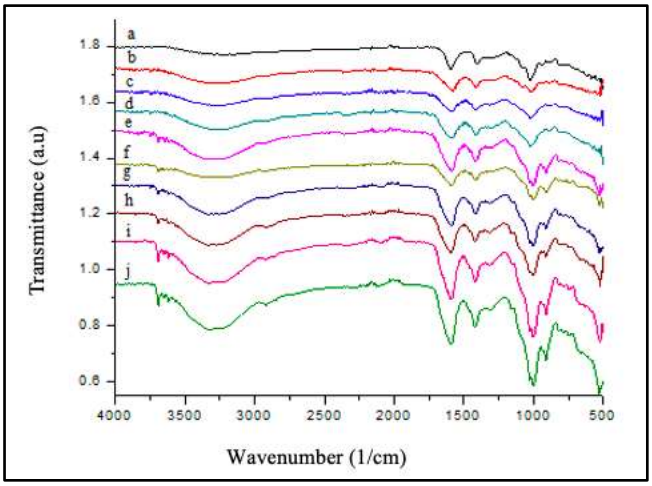

Figure 3. FTIR Spectra beads formulation. Note: (a) alginate powder (b) *beads* A2, (c) *beads* A2-M1, (d) *beads* A2-M1.5, (e) *beads* A2-K1, (f) *beads* A2-K1.5, (g) *beads* A2-M1-K1, (h) *beads* A2-M1.5-K1, (i) *beads* A2-M1-K1.5, dan (j) *beads* A2-M1.5-K1.5.

The absorption at wavenumber 694 cm-1 is the Si-O vibration, and the absorption at 949 and 3672 cm-1 is the Al-OH vibration and is a unique absorption in the kaolin spectra. The absorption obtained from the characterization of beads alginate added with kaolin was 909.399 cm^{-1}, a shift from 949 cm^{-1} from kaolin, namely Al-OH vibration, showed the presence of kaolin interaction in beads. Absorption at wavenumber 1003.193 cm^{-1} of kaolin showed symmetric Si-O-Si vibrations. The loss of absorption at 694 cm^{-1}, a Si-O vibration, and 3672 cm^{-1}, a vibration of Al-OH from kaolin, shows the formation of interactions between kaolin and alginate on the surface of Al-OH and Si-O kaolin through hydrogen bonding (Athaillah et al., 2018).

Shifting in absorption also occur in the carbonyl group, compared with the number of alginates higher when cellulose and kaolin are added. The shift that occurs between 1582.272 cm^{-1} to 1592.468 cm^{-1} wavenumbers. The shift that occurs indicates the interaction of the carbonyl alginate groups when cellulose and kaolin are added.

Besides, a shift also occurred in the carboxyl group, uptake of the alginate's wavenumber experienced an increase in intensity when added cellulose length from 1023.584 to 1025.623 cm^{-1}. When kaolin is added to the alginate beads, there is a decrease in the absorption intensity of the waves to 1001.154 cm^{-1}. Similarly, when alginate is added with

cellulose and kaolin, there is a decrease in the number of waves' absorption intensity. Sufficient reduction is possible due to strong interactions of carboxyl groups intermediate alginate, cellulose, and kaolin.

Analysis of the Alginate-Cellulose-Kaolin Beads Adsorption Efficiency

The adsorption efficiency analysis was performed to determine the ability of alginate-cellulose-kaolin beads to absorb urea. This analysis was performed by measuring the concentration of urea present in the $CaCl_2$ solution. The efficiency of adsorption efficiency of beads alginate-cellulose-kaolin is shown in Table 4.

Based on data in Table 4, there is an increase in the efficiency of alginate uptake when added polysaccharide and cellulose and when the cellulose ratio is added to increase the adsorption efficiency, but not as big as the previous ratio. The same thing was done when the addition of kaolin to alginate increased adsorption efficiency, but there was a decrease in the kaolin ratio.

Table 4. Adsorption efficiency of alginate-cellulose-kaolin beads

Beads Formulation	Adsorption Efficiency
A2	39.25
A2M1	44.83
A2M1.5	39.96
A2K1	45.06
A2K1.5	31.67
A2M1K1	42.86
A2M1.5K1	46.12
A2M1K1.5	38.08
A2M1.5K1.5	37.25

An increase in the adsorption efficiency of alginate also occurs when adding cellulose and kaolin. Increases occurred in the A2-M1-K1 and A2-M1.5-K1 beads formulations, but there was also a decrease in the A2-M1-K1.5 and A2-M1.5-K1.5 beads formulations. Based on Table 4, the value of the beads' adsorption efficiency obtained for each formulation is not much different.

Previous research (Kassem et al., 2012) stated that stirring timing is one of the most critical factors in preparing the beads. Increased stirring time can reduce adsorption efficiency due to prolonged exposure to the media resulting in the more extended release of active ingredients via alginate cross-linking. When cellulose is added, there is an increase in the adsorption efficiency of the alginate beads. The increase in trapping efficiency may be due to an increase in the prepared beads mixture's viscosity. It is also possible because the added material will cover the alginate beads' pores and prevent release from the cross-linking solubility active (Narra et al., 2012). The decrease in absorption efficiency can also be caused by an increase in the concentration of kaolin added. It can occur because the active groups that have been bound become inactivated by the active material (Kumar et al., 2009).

Slow release ability of alginate-cellulose-kaolin beads

The slow-release ability of the beads can be determined from the amount of urea release in the water. A total of 2.5 mL of the filtrate obtained was put into a cuvette and added with 0.5 mL of complexing, shaken, left for 10 minutes while analyzed using a UV-Vis spectrophotometer that the concentration of the amount of urea released was obtained. Based on the graph, the amount of urea released decreased when cellulose was added to the alginate mixture (Figure 4). When the cellulose ratio was increased, there was also a decrease in urea released, although it was not significant.

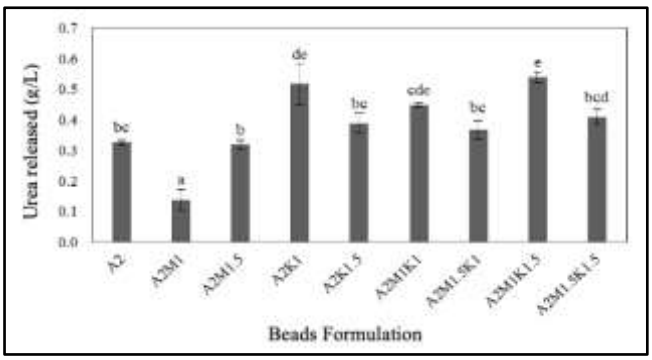

Figure 4. Graph of the amount of urea released for each bead formulation. The data shown are the mean of the two times measurements included standard deviation. Different notations indicate different results of the Tuckey HSD Test

A different thing happened when the alginate beads were added with kaolin; there was a significant increase in urea released. An increase also occurred when the kaolin ratio was added, but the increase was not significant. The same thing happened when alginate was added with cellulose and kaolin, and the highest increase was in the A2-M1-K1.5 formulation. In other formulations, the increase also occurred not much different.

Based on Figure 4, the amount of urea released decreases when cellulose as polysaccharides was added. This is following previous research (Li et al., 2016b), which states that cellulose can improve the alginate bead system by affecting the rate of release of agricultural chemicals. The increase in the amount of urea released is possible because the added material makes the structure more open or the addition of material to the alginate inhibits forming electrostatic interactions with Ca^{2+} in the beads (Li et al., 2016a). Also, the increase in urea release with additional kaolin is possible because urea is not intercalated into minerals but is retained on the surface and ends of kaolin (Barral et al., 2008). Kaolin is also known to have a neutral or slightly negative charge structure and has a weak bond so that it is unable to bind urea strongly (Reyes and Fiallo, 2011).

CONCLUSION

The addition of cellulose and kaolin to the alginate had a significant effect on alginate beads' characteristics, including wet and dry beads diameter, color, and swelling ratio but not significant to the adsorption efficiency of urea. The addition of cellulose to alginate reduced urea release while the addition of kaolin and cellulose-kaolin was small increase the release of urea in the water.

ACKNOWLEDGMENT

The authors would like to thank the Laboratory of Biomaterial Chemistry, Faculty of Mathematics and Natural Sciences, the University of Lambung Mangkurat for supporting laboratory facilities and infrastructure.

REFERENCES

Abdalla, K., Kamoun, E., and Maghraby, G., 2015. Optimization of The Entrapment Efficiency And Release Of Ambroxol Hydrochloride Alginate Beads, *J. Applied Pharmaceutical Sci.*, 013-019.

Asa, F.N.M., Sumarsih, S., and Zaidan, A.H., 2016. Komposit Kolagen Fibril-Alginat Sebagai Kandidat Membran Hidrogel Skin Substitute. *J. Biosains Pascasarjana*, 18**,** 112.

Athaillah, A., Suratman, A., and Suyanta, S., 2018. Sintesis Membran Matriks Tercampur Alginat/Zeolit Alam/Kaolin Untuk Pemisahan Gas CO_2 dan CH_4, *BIMIPA*, 25**,** 42-52.

Barral, S., Villa-García, M.A., Rendueles, M., and Díaz, M., 2008. Interactions Between Whey Proteins and Kaolinite Surfaces, *Acta Materialia*, 56**,** 2784-2790.

Bashan, Y., Hernandez, J.-P., Leyva, L., and Bacilio, M., 2002. Alginate Microbeads as Inoculant Carriers for Plant Growth-Promoting Bacteria, *Bio. and Fertility of Soils*, 35**,** 359-368.

Bijang, C.M., Tehubijuluw, H., and Kaihatu, T.G., 2018. Biosorption of Cadmium (Cd^{2+}) Metal Ion in Brown Seaweed Biosorbent (padina australis) from Liti Beach, Kisar Island. *Indo. J. Chem. Res.*, 6**,** 51-58.

Giroto, A.S., Guimarães, G.G.F., Foschini, M., and Ribeiro, C., 2017. Role of Slow-Release Nanocomposite Fertilizers on Nitrogen and Phosphate Availability in Soil, *Scientific Rep.*, 7**,** 46032-46032.

He, Y., Wu, Z., Tu, L., Han, Y., Zhang, G., and Li, C., 2015. Encapsulation and Characterization Of Slow-Release Microbial Fertilizer From The Composites Of Bentonite And Alginate, *Applied Clay Sci.*, 109-110**,** 68-75.

Islam, M.R., Mao, S., Xue, X., Eneji, A.E., Zhao, X. and Hu, Y., 2011. A Lysimeter Study Of Nitrate Leaching, Optimum Fertilisation Rate and Growth Responses Of Corn (Zea Mays l.) Following Soil Amendment With Water-Saving Super-Absorbent Polymer, *J. the Science of Food and Agriculture*, 91**,** 1990-1997.

Kassem, M.A., El Assal, M.I.a.-T., and Al-Badrawy, A.a.-S., 2012. Preparation and Evaluation of Certain Hydrophilic Drug-Loaded Microspheres. *Inter.Res. J. Pharmaceuticals*, 2**,** 82-90.

Kumar, S., Chauhan, N., Gopal, M., Kumar, R. and Dilbaghi, N., 2015. Development and Evaluation of Alginate–Chitosan Nanocapsules for Controlled Release Of Acetamiprid, *Inter. J. Biological Macromolecules*, 81**,** 631-637.

Kumar, S., Dwevedi, A., and Kayastha, A.M., 2009. Immobilization of Soybean (Glycine Max) Urease on Alginate and Chitosan Beads Showing Improved Stability: Analytical Applications, *J. Molecular Catalysis B: Enzymatic*, 58**,** 138-145.

Li, M., Tshabalala, M.A., and Buschle-Diller, G., 2016a. Formulation and Characterization Of Polysaccharide Beads for Controlled Release of Plant Growth Regulators, *J, Materials Science*, 51**,** 4609-4617.

Li, X., Li, Q., Xu, X., Su, Y., Yue, Q. and Gao, B., 2016b. Characterization, Swelling and Slow-Release Properties Of A New Controlled Release Fertilizer Based on Wheat Straw Cellulose Hydrogel, *J. the Taiwan Institute of Chemical Engineers*, 60**,** 564-572.

Liu, L., Wu, F., Ju, X.-J., Xie, R., Wang, W., Niu, C.H., and Chu, L.-Y., 2013. Preparation of Monodisperse Calcium Alginate Microcapsules Via Internal Gelation in Microfluidic-Generated Double Emulsions, *J. Colloid and Interface Sci.*, 404**,** 85-90.

Narra, K., Dhanalekshmi, U., Rangaraj, G., Raja, D., Kumar, C.S., Reddy, P.N., and Mandal, A.B., 2012. Effect of Formulation Variables on Rifampicin Loaded Alginate Beads. *Iranian J. Pharmaceutical Res.,: IJPR,* 11**,** 715.

Nelson, K.A., Paniagua, S.M., and Motavalli, P.P., 2009. Effect of Polymer Coated Urea, Irrigation, and Drainage on Nitrogen Utilization and Yield of Corn in a Claypan Soil, *Agronomy J.*, 101**,** 681-687.

Ningsih, E.P,, Ariyani, D., and Sunardi, 2019. Effects of Carboxymethyl Cellulose Addition on The Characteristics of Bioplastic from Nagara Sweet Potatoes (Ipomoea batatas L.) Starch, *Indo. J. Che. Res.*, 7**,** 77-85.

Roger, S., Talbot, D., and Bee, A., 2006. Preparation and effect of Ca^{2+} on Water Solubility, Particle Release and Swelling Properties Of Magnetic Alginate Films, *J. Magnetism and Magnetic Materials,* 305**,** 221-227.

Reyes, C.A.R., and Fiallo, L.Y.V., 2011. Application of Illite- and Kaolinite-Rich Clays in the Synthesis of Zeolites for Wastewater Treatment, *Chapter book, Earth and Environmental Sciences.* InTech.

Roy, A., Singh, S., Bajpai, J., and Bajpai, A., 2014. Controlled Pesticide Release from Biodegradable Polymers, *Open Chemistry,* 12**,** 453-469.

Sekewael, S.J., Tehubijuluw, H., and Lefmanut, I.C., 2015. Intercalation of Clay by Surfactant And Its Application as Adsorbent of Lead Ion (Pb^{2+}). *Indonesian Journal of Chemical Research,* 3**,** 231-237.

Verma, A., Sharma, M., Verma, N., and Pandit, J.K., 2013. Floating Alginate Beads: Studies on Formulation Factors for Improved Drug Entrapment Efficiency And In Vitro Release, *Farmacia,* 61**,** 143-161.

Wang, Y., Liu, M., Ni, B., and Xie, L., 2012. κ-Carrageenan–Sodium Alginate Beads and Superabsorbent Coated Nitrogen Fertilizer with Slow-Release, Water-Retention, and Anticompaction Properties, *Industrial & Engineering Chemistry Research,* 51**,** 1413-1422.

Wu, Z., Guo, L., Qin, S., and Li, C., 2011. Encapsulation of R. Planticola Rs-2 from Alginate-Starch-Bentonite And Its Controlled Release and Swelling Behavior Under Simulated Soil Conditions, *J. Industrial Microbiology & Biotechnology,* 39**,** 317-327.

Wu, Z., He, Y., Chen, L., Han, Y., and Li, C., 2014. Characterization of Raoultella Planticola Rs-2 Microcapsule Prepared With A Blend Of Alginate And Starch and Its Release Behavior, *Carbohydrate Polymers,* 110**,** 259-267.

Zhao, Y., Kang, J., and Tan, T., 2006. Salt, pH, and Temperature-Responsive Semi-Interpenetrating Polymer Network Hydrogel Based on Poly(Aspartic Acid) and Poly(Acrylic Acid), *Polymer,* 47**,** 7702-7710.

Zhu, Z.L., and Chen, D.L., 2002. Nitrogen Fertilizer Use In China-Contributions To Food Production, Impacts on The Environment and Best Management Strategies, *Nutrient Cycling in Agroecosystems,* 63**,** 117-127.