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Slow- Release Fertilizer Formulation Using Acrylic and Chitosan Coating

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ABSTRACT

The low-efficiency problem in fertilizer application can be overcome by controlling fertilizer solubility, *i.e.* by rendering the fertilizer to be released gradually; such material is also known as slow-release fertilizer (SRF). This research was aimed to formulate SRF by coating technique using acrylic and chitosan as the coating material, and to evaluate fertilizer resistance to too fast disintegration, and rate of nutrient release method. The results demonstrated that fertilizer formulation containing N, P, K, Fe, Cu, and Zn with granulation technique yielded 74% of granules with 2-5 mm in diameter. The SRFs (formulated fertilizer with acrylic or chitosan coating) were more resistant to water pounding than non-SRF. Furthermore, shaking test with distilled water or 2% citric acid, or by percolation test with distilled water showed that the SRFs had lower nutrient solubility than the non-SRFs. The results of shaking test also specifically indicated that coating with acrylic made the fertilizer more resistant to the citric acid, suggesting that this coating material would be more suitable in acidic soils. The SRFs formulated with the addition of chitosan during blending of micronutrients prior to mixing with macronutrients, granulation, and final coating exhibited lower nutrient solubility than the SRFs without the pre-coating chitosan addition.

Keywords: Coating technique, nutrient solubility, percolation test, shaking test

INTRODUCTION

It is noteworthy that, to this day, continuing fertilizer technology development and application have not really addressed in full the problem of low fertilizer efficiency. This concern, among other issues, has been brought to the fore by many researchers, including Tomaszewka and Jarosiewics (2002), who underscored the fact that a large proportion of essential nutrients from applied fertilizers have been lost into the environment meaning, they could not be taken in by plants nitrogen (40-70%), phosphorous (80-90%), and potassium (50-70%). The practice of multiple or repetitive fertilization with the aim of increasing efficiency is not considered an economic alternative since, among other offsetting factors, labor cost can be exceedingly prohibitive thereby only cancelling out any incremental benefit.

The concept in such phased application of nutrients has been adopted in the development of a fertilizer formulation, which is more commonly referred to as Slow-Release Fertilizer (SRF). SRF can more efficiently dispense nutrients by means of measured and gradual release of nutrient elements so that they are more likely to be fully taken in and utilized by plants. At the same time, SRF can solve another fertilization problem, which is related to the release of certain micro-elements, and which can otherwise become toxic to plants when rendered at one time in large amounts. The slow and gradual release of nutrients in SRF are done in several ways, such as by regulating nutrient element solubility in water (through the use of semi-permeable coating, occlusion, protein substances, polymers, or other forms of chemical elements); by delayed hydrolysis, or by other methods (UNIDO and IFDC 1998).

There have been many researches on the formulation and application of SRF in many countries. Chatzsoudis and Rigas (1998), for example, employed polyalkene applied with talcum powder and metal oxide as fertilizer mixing and delaying agent. Tomaszewska and Jarosiewicz (2002) developed a polysulfonemix to serve as a coating material to granular NPK fertilizer. In another study, Fernandez *et al.* (2004) used active bentonite in making SRF that was formulated from atrazine in alginate, and produced in the form of grains in order to simulate SRF. However, in Indonesia, there has been limited research undertaking in this subject. Some trials have focused on the use of various additives such as active carbon,

bentonite, and zeolite as mixing or coating agent to produce SRF.

Among the potential coating materials for SRF are acrylic and chitosan, but which have not been investigated thoroughly. Acrylic is made from fossil oil and gas, and can also be derived from elemental synthesis of organic materials, or more specifically, glycerin aldehyde. On the other hand, chitosan is the second most common glucosamine after cellulose which is non-toxic, bio-compatible, and biodegradable and thus, safe to use (Huacai *et al.* 2006). One potential source of raw material for making chitosan is waste shrimp skin which has not yet been much utilized.

An SRF product is likely to be acceptable and marketable if it is environment-friendly, and has been adequately proven, in practical terms, to increase fertilizer efficiency which implies that it releases nutrients as desired, as assessed in both technical and economical parameters. In this view, SRF products need to be evaluated of its nutrient release capacity.

Thus, this study was aimed to formulate and produce SRF that contains macro- and micro-nutrients through coating technique with acrylic and chitosan. Another objective of this study was to establish the rate of nutrient release from SRF produced as described above, through solubility and percolation testing.

MATERIALS AND METHODS

To produce SRF in this study, the required materials were acrylic, chitosan, chemical elements to supply macro-nutrients (urea, ZA, H₃PO₄ and K₂SO₄), as well as source of micro-nutrients (FeSO₄7H₂O, CuSO₄5H₂O, ZnSO₄.7H₂O, and Na₂B₄O₇.10H₂O), and other necessary things. Commercial liquid acrylic, which is easily available in the market, was used while chitosan was selfproduced from waste shrimp skin by means of a method modified from Suptijah (2012). To assess solubility, distilled water and 2% citric acid were utilized as extracting agent while for percolation test, peat soil media was employed. SRF analysis made use of commonly-used laboratory chemicals. Equipment used to make SRF consisted of a granulator, sprayer, and dryer. Laboratory measurements were conducted using Atomic Absorption Spectrophotometer (AAS), Flame Photometer, and Spectrofotometer UV Vis.

SRF Formulation

The formulation of SRF in this study was done in two stages: first, production of fertilizer compound

and second, coating of the fertilizer granules. Fertilizer compound (PM) was made by means of blending i.e. mixing chemical elements used as sources of macro- and micro-nutrients which involved mechanical stirring until a homogeneous mixture had been formed. Then, granulation was done by means of a granulator machine and yielded two types of fertilizer compounds, PM1 and PM2. PM1 resulted from blending of raw material sources of macro- and micronutrients. PM2 was produced in the same way, however during the blending of micro-elements, chitosan amounting to 0.50% of overall fertilizer weight then, added with the mixture was of macronutrient elements. This blending process yielded a paste material which was then granulated with the granulator and dried with a dryer and oven.

The coating stage was done on the fertilizer granules by applying acrylic on PM1 and PM2 to produce PM1A and PM2A, and by applying chitosan (K) on PM1 and PM2 to form PM1K and PM2K, respectively. Coating was carried out with the use of granulator machine and sprayer: acrylic or chitosan was put into the sprayer and sprayed into the surface of PM1 or PM2, and dried with a dryer.

Testing SRF disintegration and capacity to release nutrient elements

Fertilizer durability (or resistance to disintegration or dissolution) was assessed by applying drops of water from a burette placed at a height of 20 cm onto the fertilizer thereby pounding the fertilizer until it was fully disintegrated. The test for nutrient element release was done in two ways: by shaking and by percolation. Shaking method was done with distilled water as extracting agent, and with 2% citric acid at shaking time durations of 0, 15, 30, 45, and 60 min. This was followed by measurement of the dissolved nutrient. The percolation method was applied over a period of one month, in which water was applied weekly in conformity with average rainfall, and the dissolved nutrient in the percolate was then measured.

RESULTS AND DISCUSSION

Fertilizer Characteristics

Size of Granules

The size of the fertilizer grains was obtained from the paste-like fertilizer resulting from the blending process, which came in rough texture and was rather moist, and which were then granulated

Eastilians	N	P	K	Fe	Cu	Zn
Fertilizer		%			mg kg-	1
PM1	28.09	5.80	9.46	52.17	14.47	14.55
PM1A	26.95	5.50	9.35	48.03	12.50	13.51
PM1K	27.89	5.12	9.44	49.50	13.09	13.03
PM2	28.32	5.24	9.30	65.79	15.28	19.40
PM2A	26.70	5.13	8.93	56.31	15.98	16.38
PM2K	26.97	5.10	9.16	60.91	14.45	16.72

Table 1.Result of analysis on fertilizer nutrient content.

by trial-and-error method, based on rotation speed of the machine and its slope, fertilizer dampness, and similar factors until the desired fertilizer grains had been achieved. Figure 1 shows the comparative sizes of the resulting fertilizer granules, and it can be seen that granules less than 2 mm constituted 4%, 2-5 mm made up 74%, more than 5 mm was 20%, while left-over granules in the granulating machine amounted to 2%. Fertilizer granules of size 2-5 mm were taken as the chosen final product, consistent with the typical size of fertilizer granules in the market.

Physical Characteristics

The qualitative description of the fertilizer without coating (non-SRF) and with coating (SRF) is illustrated in Figure 2. The resulting fertilizer was

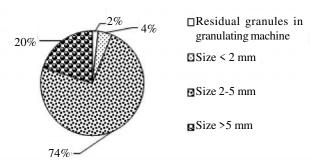


Figure 1. Percentage composition of the fertilizer granule sizes after granulation.

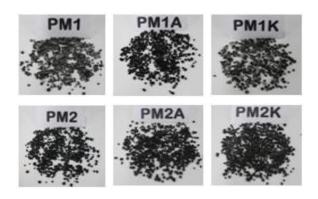


Figure 2. Result of fertilizer formulation with coating (SRF), and without coating (non-SRF).

generally in granular form and grayish to blackish in color. Also, the coated fertilizer appeared to be more shiny than the product without coating. And the chitosan-coated fertilizer displayed opaque shine, while the acrylic-coated one shined more clearly.

Nutrient Element Content

The nutrient element content of the fertilizer is summarized in Table 1. As shown, N content of the fertilizer ranged 26.70 - 28.32%, deliberately formulated so, to reach a high level considering that plant seedlings to be fertilized would generally require a higher dosage of N nutrient.

It can be seen from Table 1 that the nutrient element content of the fertilizer formulation SRF did not significantly differ from that of non-SRF. This implies that coating of the fertilizer granules did not really affect the nutrient content of the fertilizer.

Nutrient Element Release in SRF

Resistance to water drop pounding

The results on the test on resistance of the fertilizer to pounding with water drops are depicted in Figure 3. Resistance was measured in terms of

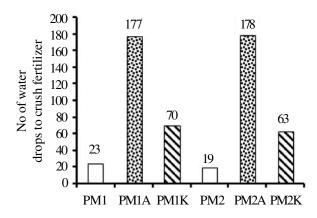


Figure 3. Resistance of fertilizer to water drop pounding use until full dissolution. PM 1, 2 refers to types of fertilizer compound, A denotes acrylic coating, K indicates chitosan coating.

the total number of water drops it took to break the fertilizer granules into pieces. As shown, SRF with acrylic coating exhibited higher resistance to water pounding by 6-7 times compared to non-SRF while SRF with chitosan coating demonstrated 3-4 times higher resistance.

Release of macronutrient (N, P, K) through shaking in distilled water and 2% citric acid

Figure 4, 5, and 6 display the results of the test on release of macronutrients N, P, and K.

As pictured in Figure 4 (a) and (b), shaking of the fertilizer compound up to the 30th minute produced more dissolved N from the non-SRF (fertilizer) compared to the SRF, suggesting that in the fertilizer without coating N disintegrated or dissolved easier and faster. The same phenomenon was observed for macronutrients P and K, as portrayed in Figure 5 (a) and (b), and Figure 6 (a) and (b).

Comparison of PM1A, PM1K, PM2A, and PM2K shaking in distilled water did not show a clear difference between acrylic and chitosan coating. Nevertheless, shaking with 2% citric acid showed

a relatively higher dissolution of nutrient element from the fertilizer with chitosan coating compared to acrylic coating. This could have been due to the natural property of chitosan to dissolve in weak acid while acrylic does not. This implies that using fertilizer with acrylic coating is more suitable for the generally acidic soils in Indonesia.

Release of micronutrient elements (Fe, Cu, and Zn) through shaking in distilled water and 2% citric acid

The results of measurement on micronutrient elements dissolved by shaking in distilled water and 2% citric acid are summarized in Tables 2 to 7. As shown, the release of the micronutrients by the two extracting agents exhibited a similar trend as in dissolved macronutrients which was that dissolved micronutrient in non-SRF fertilizer was higher than in the SRF. However, the dissolution of Fe with distilled water in PM1 and PM2 resulted differently, as depicted in Table 2.

Table 2 demonstrates that dissolution of Fe by distilled water from PM2, in both SRF and non-SRF fertilizer coated with acrylic or chitosan was

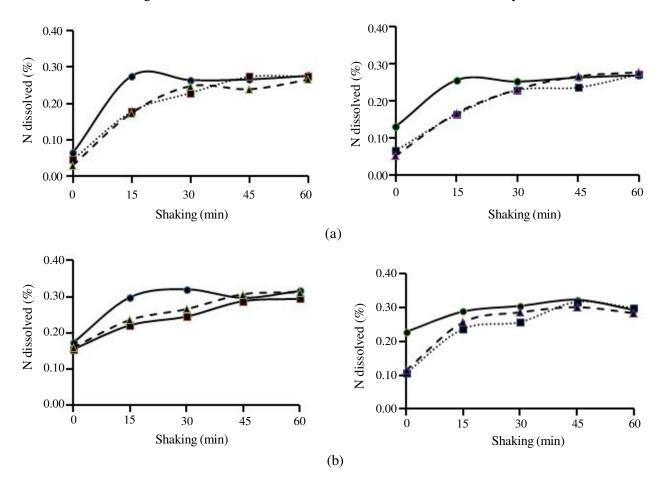


Figure 4. N dissolved in distilled water (a) and 2% citric acid (b). PM 1, 2 refers to types of fertilizer compound, A denotes acrylic coating, K indicates chitosan coating. PM1: ———, PM1A: ———, PM1K: ———, PM2A: ————, PM2K: ————.

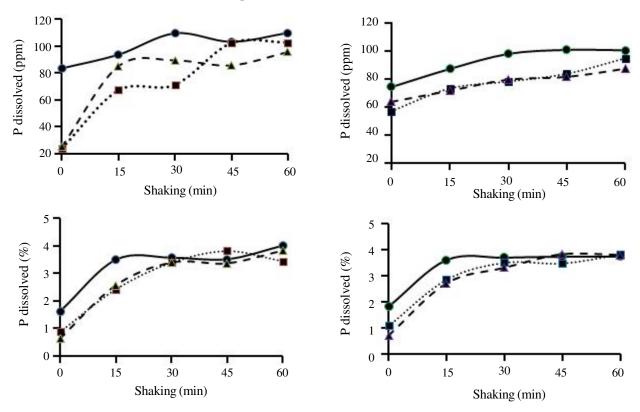


Figure 5. P dissolved in distilled water (a), and in 2% citric acid (b). PM1, 2 refers to types of fertilizer compound, A denotes acrylic coating, K indicates chitosan coating. PM1: ———, PM1A: ———, PM1A: ———, PM2K: ———, PM2K: ———.

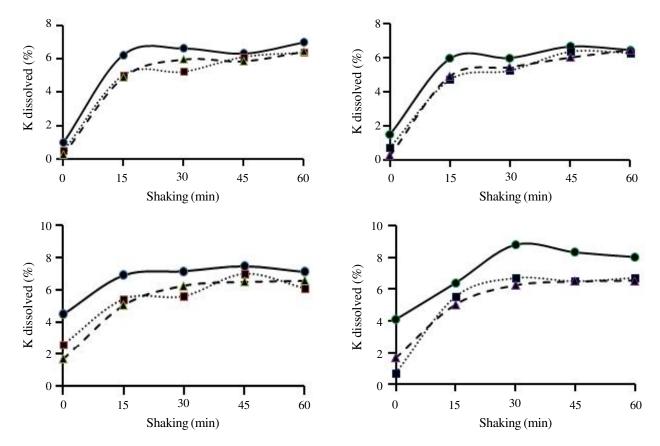


Figure 6. K dissolved in distilled water (a), and in 2% citric acid (b). PM 1, 2 refers to types of fertilizer compound, A denotes acrylic coating, K indicates chitosan coating. PM1: ———, PM1A: ———, PM1A: ———, PM2K: ———, PM2K: ————, PM2K: ————.

Table 2. Amount of extracted Fe from the fertilizer using distilled water

Fertilizer -	Amo	unt of Fe (g	Total Fe Amount			
reiunzei –	0	15	30	45	60	$(g kg^{-1})$
PM1	1.82	5.96	6.11	6.28	5.55	52.17
PM1A	1.14	5.78	6.49	5.72	5.90	48.03
PM1K	0.72	5.54	7.22	6.76	6.50	49.50
PM2	0.36	0.50	0.86	1.45	2.26	65.79
PM2A	0.26	0.74	0.67	0.96	1.12	56.31
PM2K	0.17	0.55	0.84	0.94	1.44	60.91

PM1, 2 refers to types of fertilizer compound, A denotes acrylic coating, K indicates chitosan coating

Table 3. Amount of extracted Cu from the fertilizer using distilled water

Eastilians	Amou	int of Cu (th minute	Total Cu		
Fertilizer –	0	15	30	45	60	Amount (g kg ⁻¹)
PM1	2.40	3.63	3.76	3.89	3.07	14.47
PM1A	2.90	2.75	2.67	2.69	2.89	12.50
PM1K	1.10	2.48	2.70	2.65	2.66	13.09
PM2	0.10	0.11	0.22	0.23	0.20	15.28
PM2A	0.07	0.08	0.13	0.11	0.16	15.98
PM2K	0.07	0.08	0.13	0.12	0.19	14.45

PM1, 2 refers to types of fertilizer compound, A denotes acrylic coating, K indicates chitosan coating

Table 4. Amount of extracted Zn from the fertilizer using distilled water

Fertilizer –	Amo	Total Zn				
refullzer –	0	15	30	45	60	Amount (g kg ⁻¹)
PM1	5.95	6.86	9.54	10.48	10.97	14.55
PM1A	4.84	6.50	6.39	6.24	7.23	13.51
PM1K	3.03	6.31	6.80	6.89	6.93	13.03
PM2	2.53	3.20	3.79	4.40	4.03	19.40
PM2A	3.03	3.31	3.44	4.11	4.04	16.38
PM2K	3.03	3.75	3.38	3.80	3.32	16.72

PM1, 2 refers to types of fertilizercompound, A denotes acrylic coating, K indicates chitosan coating

significantly lower than from PM1 up to the 60th minute of stirring. The same pattern was observed in the case of Cu and Zn which can be seen in Tables 3 and 4. The application of chitosan by as much as 0.5% of the gross fertilizer weight at the time of *blending* actually formed another *coating* such that *double coating* occurred for micronutrient in PM2A and PM2K. Thus, this mechanism caused a longer delay in the dissolution of the micronutrient.

The release of micronutrient elements by the 2% citric acid extraction can be seen in Tables 5, 6, and 7. At the fertilizer formulation PM1, PM1A, PM1K, PM2, PM2A, and PM2K the rates of nutrient element extraction were quite comparable. This could be attributed to the capacity of the citric

acid to disssolve chitosan such that Fe, Cu, and Zn were released and joined the citric acid solution.

An interesting occurrence was noted in this part of the study, as can be deduced from Tables 6 and 7, particularly for micronutrient elements Cu and Zn that were extracted with 2% citric acid that is, the amount of extracted Cu and Zn approached the total quantity of such nutrients in the fertilizer. In reality however, this does not happen in the plant root environment as the concentration of organic acid does no treach the level corresponding to 2% citric acid. This implies that the available micronutrient elements in the root surroundings is lesser than that dissolved by 2% citric acid. But this trend did not happen in the case of Fe.

Table 5. Amount of extracted Fe from the fertilizer using 2% citric acid

Fertilizer	Amou	nt of Fe (g	Total Fe			
1 Crumzer	0	15	30	45	60	Amount (g kg ⁻¹)
PM1	6.26	9.54	12.31	10.66	9.20	52.17
PM1A	6.22	8.52	10.44	9.23	10.22	48.03
PM1K	6.23	8.93	9.22	9.58	10.54	49.50
PM2	6.14	9.66	9.84	9.54	10.89	65.79
PM2A	2.26	9.44	9.49	9.48	10.23	56.31
PM2K	3.45	10.62	10.68	9.84	9.84	60.91

PM1, 2 refers to types of fertilizer compound, A denotes acrylic coating, K indicates chitosan coating

Table 6. Amount of extracted Cu from the fertilizer using 2% citric acid

Fertilizer	Amoun	t of Cu (g k	g ⁻¹) by stir	ring at th	minute	Total Cu
-	0	15	30	45	60	Amount (g kg ⁻¹)
PM1	6.70	10.90	11.50	11.50	12.80	14.47
PM1A	4.50	9.40	9.90	11.20	10.10	12.50
PM1K	4.30	6.90	9.40	12.80	10.30	13.09
PM2	5.10	8.40	9.10	10.60	10.70	15.28
PM2A	1.70	7.30	9.10	9.80	10.80	15.98
PM2K	2.90	7.20	8.00	9.40	10.90	14.45

PM1, 2 refers to types of fertilizer compound, A denotes acrylic coating, K indicates chitosan coating

Tabel 7. Amount of extracted Zn from the fertilizer using 2% citric acid

Fertilizer -	Amou	nt of Zn (g	Total Zn			
rerunzer -	0	15	30	45	60	Amount (g kg ⁻¹)
PM1	9.36	12.54	13.91	12.58	12.58	14.55
PM1A	8.77	10.53	12.74	11.62	11.61	13.51
PM1K	8.77	10.04	10.14	11.81	10.33	13.03
PM2	9.98	13.25	16.38	18.47	17.09	19.40
PM2A	5.42	9.58	15.22	15.80	15.58	16.38
PM2K	6.77	10.29	14.27	15.63	15.80	16.72

PM1, 2 refers to types of fertilizer compound, A denotes acrylic coating, K indicates chitosan coating

Release of macronutrient elements (N, P, and K) through percolation

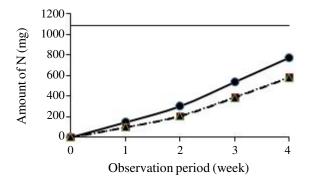
The results of data analysis on the release of macronutrient elements (N, P, and K) using percolation method can be seen in Figure 7 to 9.

Based on Figure 7, it is clearly demonstrated that leaching (washing off) of macronutrient element N from SRF was slower than from non-SRF, this was apparent from the first up to the 4th week. The same pattern was observed in the case of macronutrient elements P and K. Further, it can be seen that at the 4th week, washing off of N already reached 71.03% of the total macronutrient amount in PM1, 53.67% of PM1A, 53.27% of PM1K, 72.33% of PM2, 54.93% of PM2A, and 51.32% of

PM2K. In other words, up to the 4th week, there still remained around half of the total amount of macronutrient elements in the fertilizer.

The macronutrient element P likewise exhibited a delayed release trend until the 4^{th} week. Figure 8 shows that percolation on the 4^{th} week already washed off as much as 75.61% of PM1, 51.13% of PM1A, 48.95% of PM1K, 68.64% of PM2, 52.04% of PM2A, and 51.04% of PM2K of the total amounts of the respective macronutrient elements.

The same observation was attained on macronutrient element K. From Figure 9, it can be seen that in the 4th week, already 83.05% was washed off in PM1, 52.26% in PM1A, 41.93% in PM1K, 77.94% in PM2, 53.54% in PM2A, and 52.09% in PM2K of the respective total macronutrient amounts in the fertilizer.



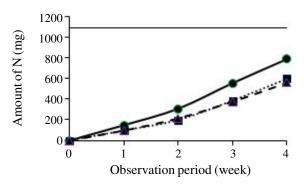
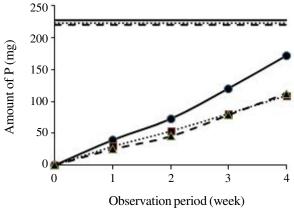
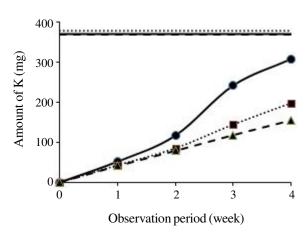
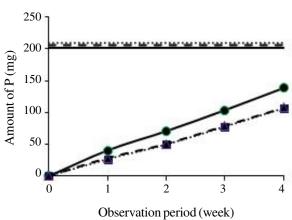


Figure 7. Leached N from percolation testPM1, PM1A, PM1K (left) PM2, PM2A, PM2K (right). PM 1, 2 refers to types of fertilizer compound, A denotes acrylic coating, K indicates chitosan coating. PM1: ———, PM1A: ———, PM1K: – ——, Total N PM1: ———, Total N PM1A:, Total N PM2A:, Total N PM2K: – —.







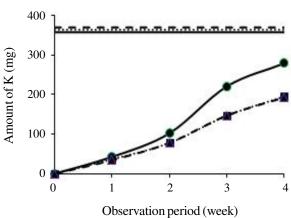


Figure 8. Leached P from percolation test PM1, PM1A, PM1K (left) PM2, PM2A, PM2K (right). PM 1, 2 refers to types of fertilizer compound, A denotes acrylic coating, K indicates chitosan coating. PM1: ———, PM1A: ———, PM1K: ————, Total N PM1A: ————, Total N PM1A: ————, PM2A: ————, PM2K: ————, Total N PM2: ————.

Figure 9. Leached K from percolation test PM1, PM1A, PM1K (left) PM2, PM2A, PM2K (right). PM 1, 2 refers to types of fertilizer compound, A denotes acrylic coating, K indicates chitosan coating. PM1: ———, PM1A: ————, PM1K: ————, Total N PM1A: ————, Total N PM1A: ————, PM2A: ————, PM2K: ————, Total N PM2: ————, Total N PM2: ————, Total N PM2A: ————, Total N PM2A: ————,

CONCLUSIONS

The results of this study have conclusively demonstrated that efficiency in the use of fertilizer, as measured in terms of the amount of nutrient element contained in the fertilizer that is made economically available in the soil for absorption by plant roots to boost initial growth, can be effectively increased through the use of slow-release fertilizer (SRF) which, in this study, was formulated by means of fertilizer compound preparation, granulation, and coating with acrylic (easily available in the market) and chitosan (made from waste shrimp skin) material. The resulting SRF, particularly the one coated with acrylic, is especially suitable to the generally acidic soils in Indonesia which are planted to economic farm or plantation crops.

At least 74% of the SRF produced were of size 2.5 mm (diameter), which is the same as the common granule size in the fertilizer market. The other 20% were bigger than 5 mm, 4% were smaller in size while the rest (2%) remained as residue in the granulating machine. SRF (fertilizer granules coated with acrylic or chitosan) clearly rendered the fertilizer to release nutrient element in a slow and gradual rate compared to non-SRF (not coated). Even after 4 weeks of treatment, about half of the nutrient content of the fertilizer still remained.

SRF with acrylic *coating* exhibited higher macronutrient (N, P, K) and micronutrient element

(Fe, Cu, Zn) preservation, *i.e.* more resistant to disintegration (by water pounding) and dissolution (by shaking in distilled water and 2% citric acid, or leaching by percolation with distilled water). The release of micronutrient elements can be slowed down by *double coating* with chitosan during granulation and *blending* of macro- and micronutrients with the fertilizer compound.

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