

FORMULATION OF SLOW-RELEASE NPK DOUBLE- COATED GRANULES USING BIOBLEND POLYMER BY SPRAY

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ABSTRACT

The slow-release NPK double-coated granules obtained was evaluated in term of chemical interaction, surface morphology, and release rate of phosphate by Fourier Transform Infra Red spectrophotometer, Scanning Electron Microscope, and Visible spectrophotometer. Results showed that the FTIR spectrum of granules showed that no chemical interaction was observed between NPK granules and coating polymers during the coating process. The bioblend polymer used was effective as a coating material for the slow-release double-coated NPK. The SEM micrograph showed the clearly different part between core and coating polymers. The percentage of phosphate released after 48 hours through the slow-release double and one coated NPK granules were 21.89, and 39.13%, respectively. While through un-coated NPK granules was 93.60%. The release profile of phosphate through slow release double coated NPK granules was following the Langenbuecher kinetics ($r = 0.9015$).

Keywords: polystyrene, polycaprolactone, polyhydroxybutyrate-hydroxyvalerate

دجمان واخرون

مجلة العلوم الزراعية العراقية - 2018: 49(6): 1032-1040

تصنيع حبيبات NPK بطيئة التحرر ثنائية الغلاف باستعمال خليط البوليمرات بطريقة الرذاذ في التغليف

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المستخلص:

صنعت حبيبات NPK بطيئة التحرر باستعمال خليط من مركبات البوليمرية شملت Polycaprolacton و poly hydroxyb utyruite و hydroxylvalerate كطبقات داخلية وخارجية في تغليف الحبيبات وبطريقة الرذاذ وبنسبة 1:1:4 للمركبات البوليمرية على التوالي. أختيرت حبيبات NPK المصنعة من خلال التفاعل الكيميائي والمظهر الخارجي لسطح الحبيبات ومعدل تحرر الفوسفات باستخدام تحويل فوريير (fourier) للمطياف الضوئي للاشعة تحت الحمراء والمجهر الإلكتروني الماسح والمطياف الضوئي للاشعة المرئية. اظهرت النتائج ان جهاز تحويل فوريير (FTIR) للمطياف الضوئي للاشعة تحت الحمراء بعدم وجود تفاعل كيميائي بين حبيبات NPK وخليط المركبات البوليمرية خلال عملية التغليف وان حبيبات NPK المغلفة بخليط البوليمرات ثنائية الطبقة بطيئة التحرر. اظهرت الاشكال البيانية الدقيقة من المجهر الإلكتروني الماسح وجو اختلافات واضحة بين حبيبات NPK غير مغلفة والحبيبات المغلفة. بلغت نسبة الفوسفات المتحرره بعد 48 ساعة 21.89 و 39.13 و 93.60 % لكل من حبيبات NPK ثنائية الغلاف واحادية الغلاف وغير المغلفة على التوالي. ان معادلة Lngae- bueher كانت الافضل في وصف حركيات تحرر الفوسفات من حبيبات NPK ثنائية الغلاف بطيئة التحرر

*Received:27/3/2018, Accepted:7/6/2018

INTRODUCTION

The implementation of slow or controlled release formulation technology is not only suitable for medicine but also can be used for pesticides, fertilizers or other substances. It also enables the release of active ingredients to the target at a controlled level, to maintain its concentration in the system to the optimum limit over a period of time. In the other hand, it is also able to minimize the side effects and optimize the effectiveness of the active ingredients (6). The application of slow-release fertilizers (SRF) in the agricultural field of study is one of the methods to improve the efficiency of nutritional consumption, minimize the environmental pollution, and nutrient loss due to uncontrolled leaching. The rate of the nutrient release can be controlled by coating the fertilizer granules using coating materials (1,2,9). Slow-release or controlled-release fertilizers is physically prepared by coating the conventional fertilizer granules using various materials that able to reduce the dissolution rate of the fertilizers. The most commonly used materials as coatings are sulfur, wax, polyethylene, polyolefins, polyacrylamide, polysulfone, polystyrene or PS, and pine craft lignin (4,7). The use of conventional polymers as coating materials is usually associated with high costs and the accumulation of unwanted residual synthesis in the soil. Recently, a number of studies have focused on the use of biodegradable polymers as a promising coating agent for fertilizers (1). Bioblend polymers could be biodegraded like natural polymers event have excellent water resistant properties that owned by most synthetic polymers (8). Poly (3-hydroxybutyrate-co-hydroxyvalerate) or P(3HB-HV) is the most famous polyhydroxyalkanoate, PHA, group. However, this polyester has attractive advantages, not only environmentally friendly but also can be used in various fields of agriculture, industry, and medical (3,10). Based on the description above, the study rate of phosphate release through the slow release NPK fertilizer (SRF) formulated by double coating technique using PS, polycaprolactone or PCL, and P(3HB-HV) polymers. The last polymer is a non-biodegradable synthetic polymer but will be biodegraded in a bioblend mixture.

MATERIALS AND METHODS

Materials used in this study were PS, PCL (Sigma-Aldrich), P(3HB-HV), NPK granules with diameter around 2 mm, chloroform (Merck), alcohol (Merck), Molybdate reagent, potassium antimonyl tartrate, ascorbic acid, H₂SO₄(p), distilled water.

Preparation and characterization of double coating slow-release NPK

preparation of coating solution: PS and PCL bioblend as an inner coating were used at a ratio of 4: 1. The mixture of 2 grams PS and 0.5 grams PCL was dissolved in 50 mL chloroform and stirred using a magnetic stirrer at 380 rpm for 10 minutes. P(3HB-HV) copolymer was used for outer coating. 0.5 grams of the copolymer was dissolved in 50 ml of chloroform.

Preparation of slow-release NPK granules

The coating process is carried out using a pan-coating method. A total of 25 grams of NPK granules were placed into the coating pan. The first coating solution was poured into the solution container in the spray gun. The NPK granules were sprayed with coating solution into rotated coating pan at speed of 70 RPM, and the temperature of 60 to 70°C. The first coated NPK granules obtained was dried using an oven at 70 to 80°C for 1 hour to ensure the solvent evaporated completely. It was then coated with the second coating polymer solution. The treatment was similar to the previous coating process.

Granules surface morphology characterization using SEM

Characterization of a cross-sectional morphology of the double-coated slow-release NPK was performed in order to evaluate the characteristics and compatibility between the coating polymer and the NPK granules using JEOL-JSM-6510LV scanning electron microscopy (SEM).

FTIR Analysis

FTIR analysis was conducted to determine the possible chemical interaction between the components of the coating material with the NPK granules using a PerkinElmer, ATR Universal type FTIR. The grinded sample was compressed into a KBr pellet. Each spectrum was created with a total of 16 scans at a resolution of 2 cm⁻¹.

Release rate of phosphate in aqueous media

The rate of phosphate releases through the double-coated slow-release NPK granules was carried out in aqueous media. A total of 0.5 grams of the double-coated slow-release NPK granules were tied in a stainless wire sleeve, placed into a container containing 100 mL of distilled water at 25-30°C. Around of five mL sample solutions were withdrawn after 5, 15, and 30 minutes; 1, 4, 12, 36, and 48 hours. Five mL of fresh distilled water at the similar temperature was added to maintain the sink condition after each sampling. Filtered sample solutions were added with 5 mL of dye reagent. The absorbance of the final solution was measured using a UV-Visible spectrophotometer at a wavelength of 716.5 nm.

RESULTS AND DISCUSSION

This study has demonstrated the effectiveness of using a mixture of non-biodegradable synthetic polymers with biodegradable synthetic polymers into bioblend polymers expected not to pollute the environment for long periods of time. In addition, the two-layer coating technique used in the slow-release NPK granules were formulated in order to slow release the rate of nutrient release to be absorbed by the plant and minimized unexpected effects.

Double-coated slow-release NPK granules surface morphology characterization

Cross-section SEM micrograph of the single and double coating slow-release NPK granules shown in Figure 1. Cross-section SEM of the double-coated slow-release was shown a three-layer structure (Fig. 1.b). The outer layer is P(3HB-HV). The middle layer is a PS-PCL bioblend, which can reduce the rate of water diffusion into the core and the release of nutrients outside the core. The center core is a NPK granules that have water soluble properties. Thus, once the core of the fertilizer dissolves by water, this solution will pass through two layers, the PS-PCL bioblend layer, and P(3HB-HV) layer, to be released into the soil. In short, the outermost layer has a water retention, while the middle layer has the slow-release properties (15). SEM micrograph of double-coated slow-release NPK granules shown in Fig. 1.b depicted the thickness of the coating polymer. The thickness of the inner

layer was 52.2 μm. This was due to the amount of inner coating polymers which are a mixture of non-biodegradable synthetic polymers with biodegradable synthesis polymers. The amount of PS:PCL (4:1) was increased the outer coating polymers, P(3HB-HV). This caused the inner coating was thicker than the outer coating.

FTIR Analysis

FTIR is electromagnetic radiation in the range from 400 to 4000 cm⁻¹, by passing the sample and absorbed by the molecular bonds in a sample so that the molecule stretches or bends. The length of the absorbed radiation is a characteristic of the bond which absorbs it (Watson, 2005). Results of FTIR spectrum of double-coated slow-release NPK granules showed the presence of 4 major peaks at 827, 1082, 1372, and 3026 cm⁻¹ wave numbers represented aromatic C-C bonds, C-O bonds, C-H group, and C-H group, respectively (Figure 2.a). Likewise, the single-coated slow-release NPK on the 825, 1090, 1349, and 3026 cm⁻¹ wave number represented aromatic C-C bond, C-O bond, C-H group, and C-H group (Figure 2 .b). These peaks did not differ significantly with the FTIR spectrum of NPK granules at 884, 1072, 1343, and 3045 cm⁻¹ wave numbers represented aromatic C-C bonds, C-O bonds, C-H group, and C-H group (Figure 2.c). The similarity of FTIR spectrum of slow-release NPK, both of double- and single-coated with non-coated FTIR spectrum proved that the formulated of slow-release NPK granules using PS-PCL-P(3HB-HV) coatings did not show significant interactions between NPK granules and coating polymers (11,14).

Release rate of phosphate in aqueous media

The release phosphate estimated as P₂O₅ from double-coated slow-release NPK granules per unit time was performed in aqueous media. From the graphic, it can be seen that the release rate of the double-coated slow-release NPK granules is slower than single-coated (p<0.5). After 48th hours, the release of phosphate from double- and single-coated slow-release NPK granules were 21.89, and 39.13%, respectively, while from uncoated granules was 93.60% (Figure 3). It was assumed that the mechanism of phosphate release from coated NPK granules was

occurred in three steps: penetration of water into coating pores, dissolution of fertilizers, and the solute will be diffused through the coating. In this case, the diffusion was controlled by the concentration difference through the coatings (12,13).

Release profile of phosphate in aqueous media

The kinetics of release profile of P_2O_5 from single- and double-coated slow-release NPK granules in aqueous media was followed the Langenbucher release kinetics ($R=0.9015$, and 0.912 , respectively) (Figure 4). While for non-coated NPK granules was followed the Korsmeyer-Peppas release kinetics model ($R=0.9563$) (Figure 4). The release kinetic of Langenbucher kinetics model means that mechanism of release was occurred by diffusion and erosion and then the accumulation existed in the soluble fraction and no lag time. While the release of phosphate from the non-coating NPK granules was followed the Korsmeyer-Peppas kinetics model. It means that the release was based on the Fickian diffusion mechanism (5). Based on this Langenbucher equation, it can be considered that the release time of active compound from NPK granules was retarded. The release of active ingredient from

single-coated slow-release NPK granules could be achieved 99% within 4 months. While 99% of active substances release from the double-coated slow-release NPK granules was reached in 9.6 months. Double-coated slow-release NPK granules using of polymer PS-PCL-P(3HB-HV) as a coating material had been conducted. The coated granules obtained were characterized using FTIR and SEM. The release rate of phosphate as P_2O_5 was analyzed using a UV-Visible spectrophotometer. The percentage of phosphate released within 48 hours from uncoated NPK granules, single- and double-coated slow-release NPK granules were 93.60, 39.13, and 21.89%, respectively. It was found that as the amount of coating layers increases, the rate of release will be slower. Double-coated slow-release NPK granules was effective to control the rate of active substance release.

ACKNOWLEDGMENT

The authors would like to thank the Ministry of Research and Higher Education, Republic of Indonesia, as the research is funded through the Grant Research Scheme Graduate Team 2018, with Contract Number: 050/SP2H/LT/DPRM/2018, University of Andalas, Padang, Indonesia.

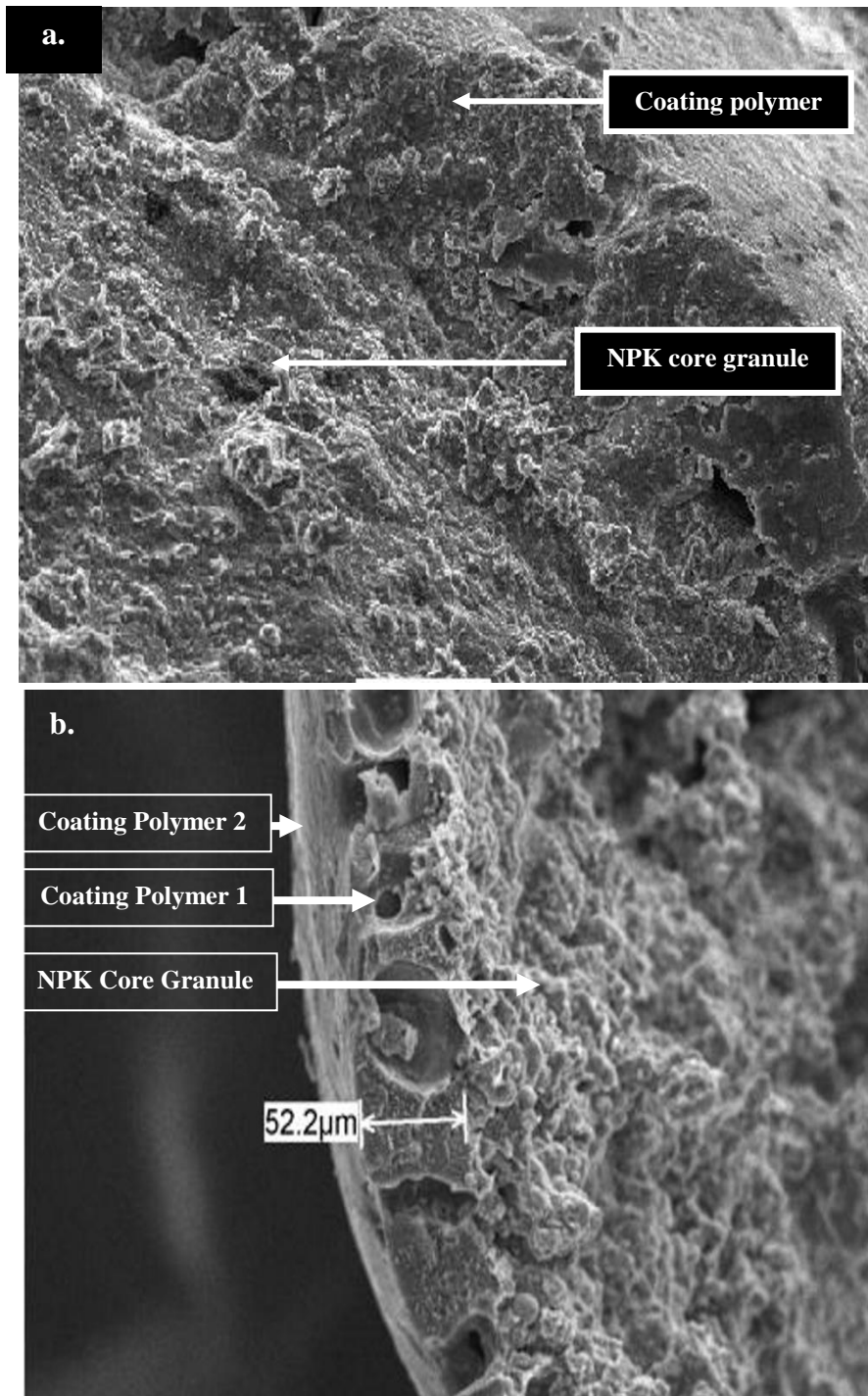


Figure 1. SEM of Slow-Release NPK granules at 300x magnification, (a). SEM of Single-coated Slow-release NPK granules; (b). SEM of Double-coated Slow-release NPK granules.

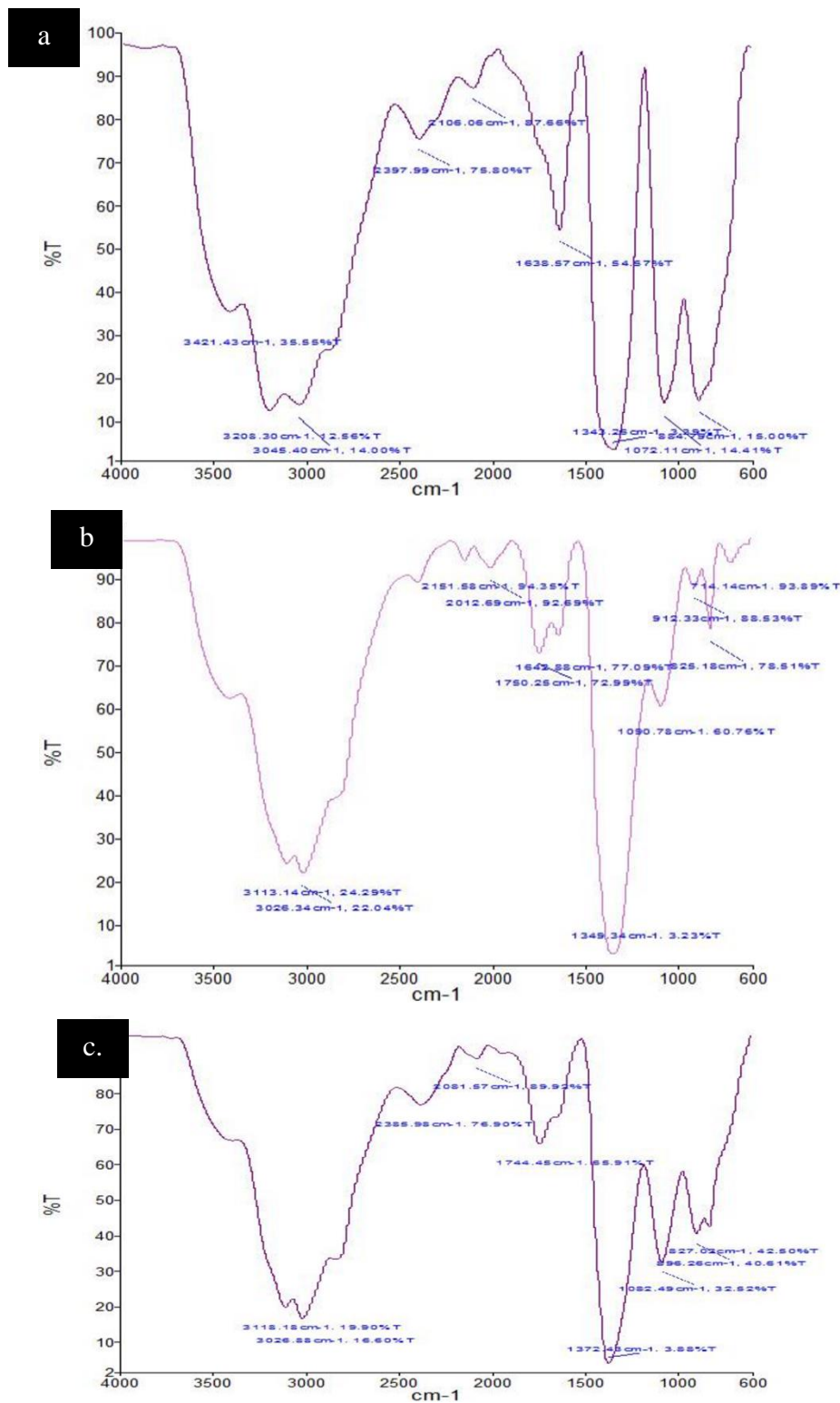


Figure 2. (a.) FTIR Spectrum of uncoated NPK granules; (b.) FTIR of Single-coated Slow-release NPK granules; (c.) FTIR of Double-coated Slow-release NPK granules.

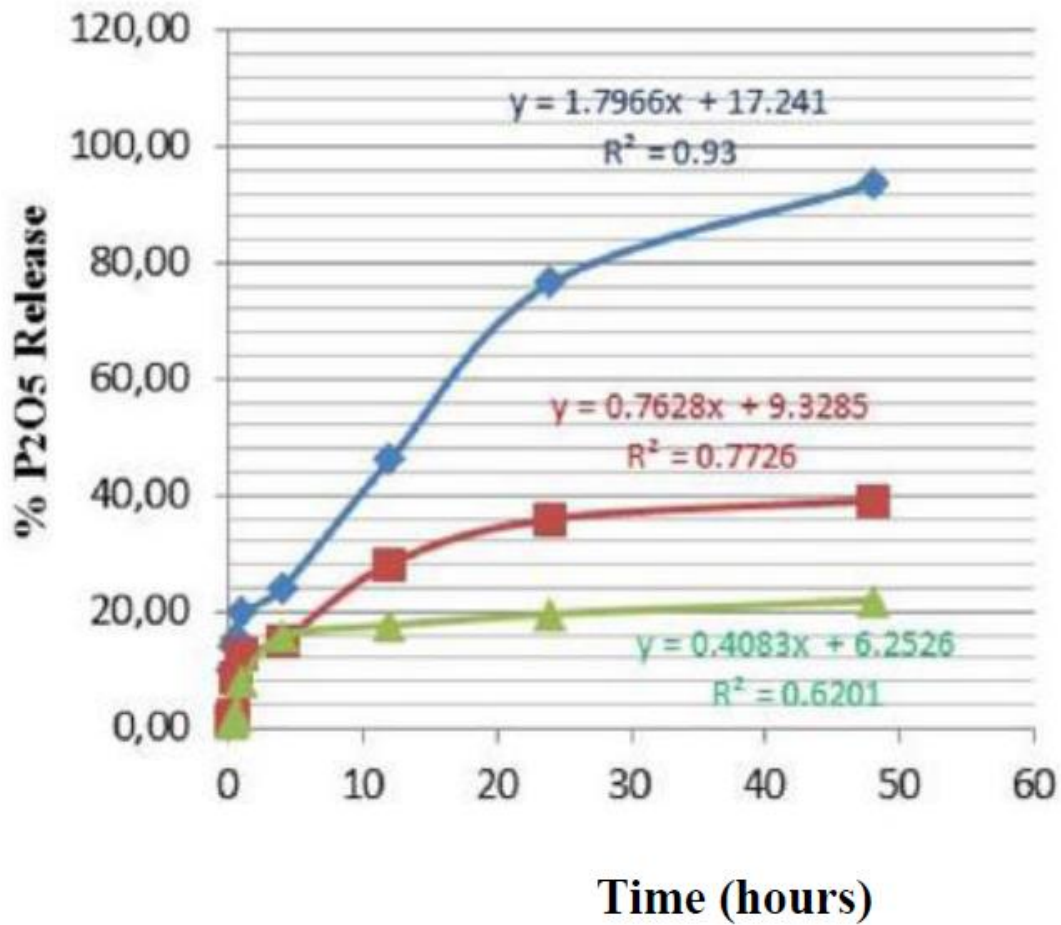
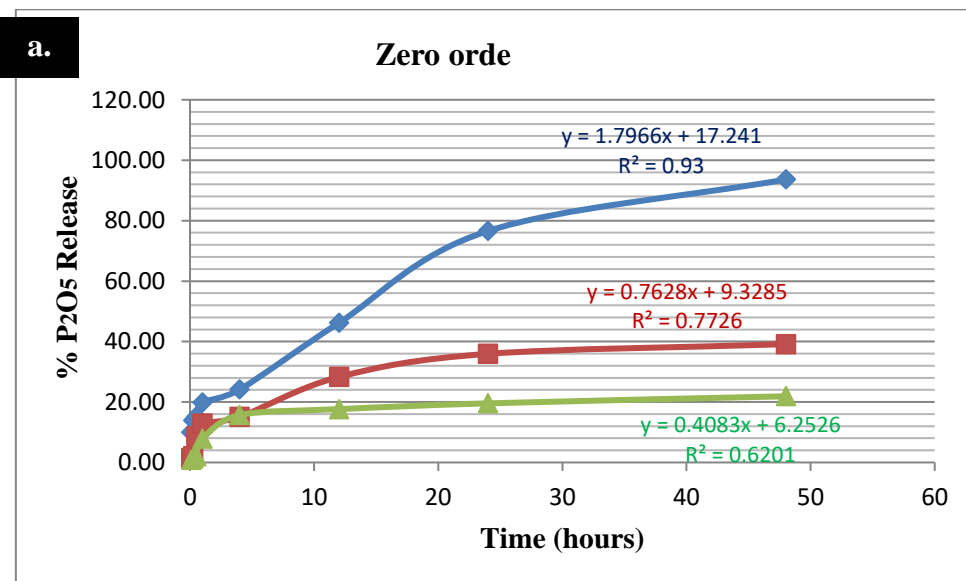
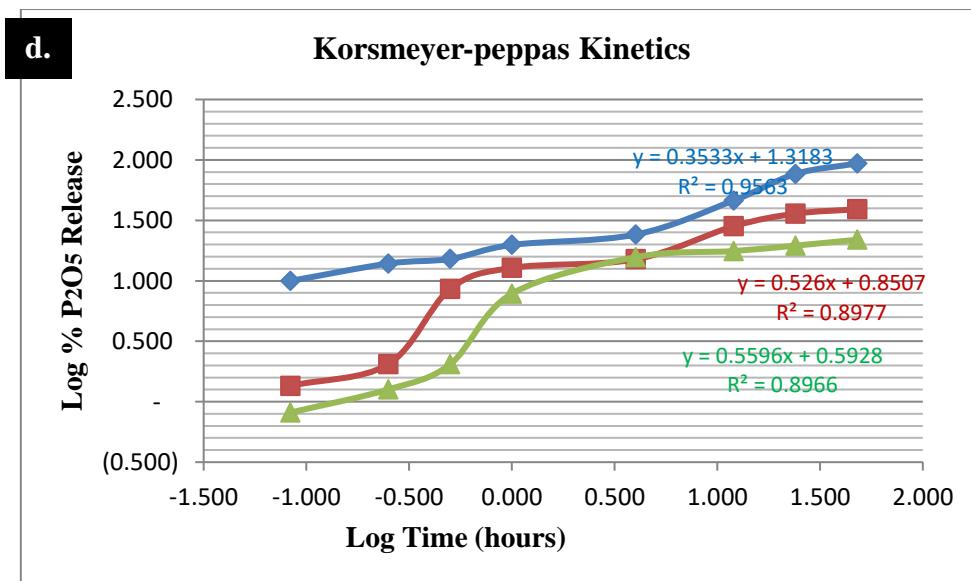
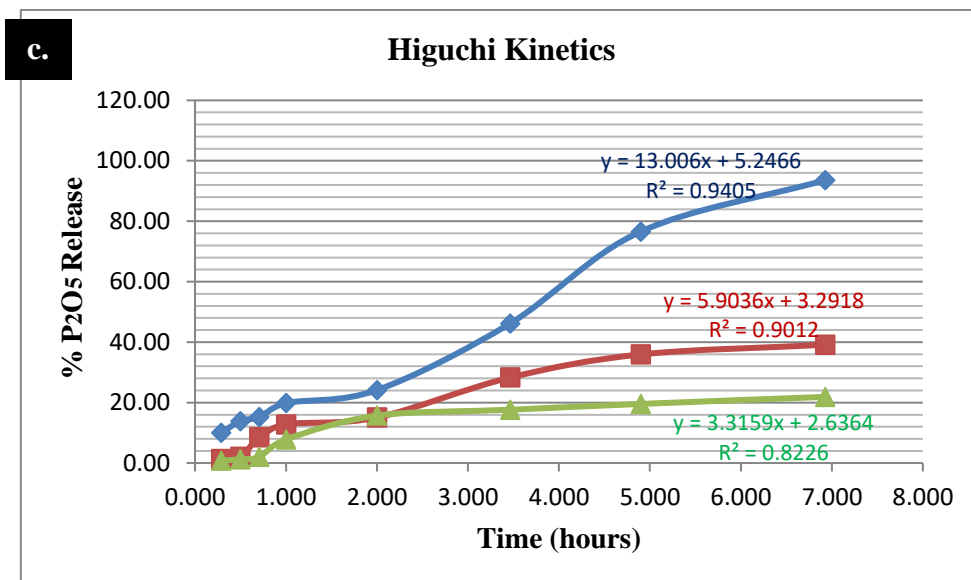
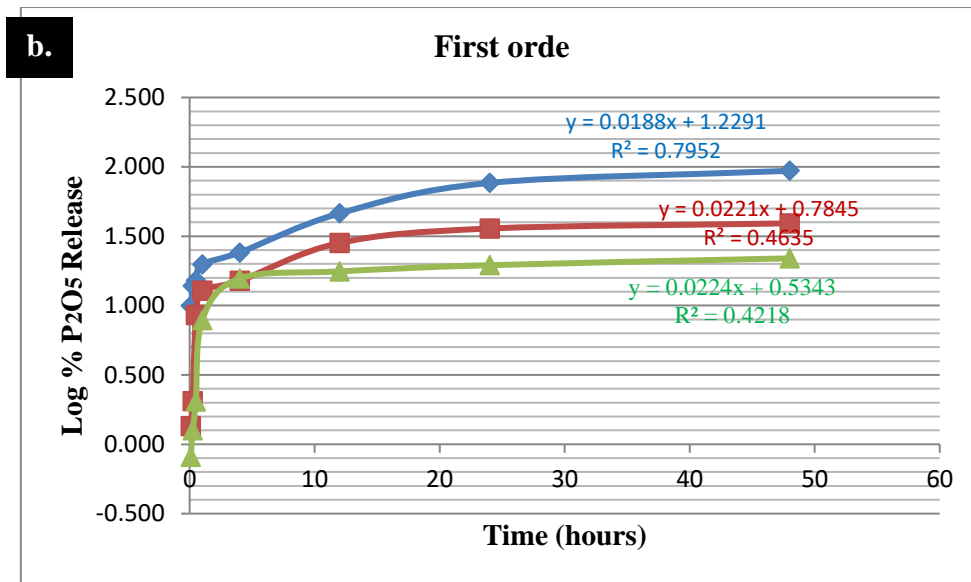


Figure 3. The release profile of phosphate as P₂O₅ from double-coated slow-release NPK granules. (—◆—) uncoated, (—■—) single-coated, (—▲—) double-coated.





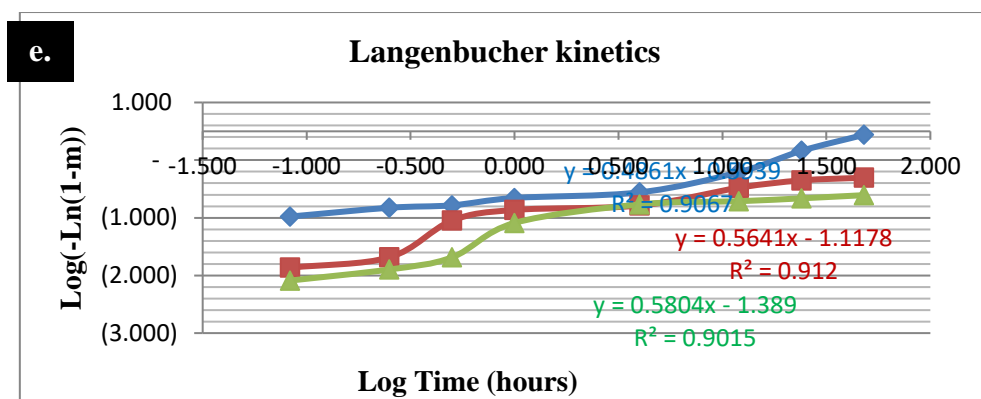


Figure 4. Profile of phosphate release kinetics (P_2O_5) in aqueous media; a. Zero order kinetics; b. First order kinetics; c. Higuchi kinetics; d. Korsmeyer-peppas kinetics; e. Langenbuche kinetics. (—◆—) uncoated, (—■—) single-coated, (—▲—) double-coated.

REFERENCES

- Ahmad N N R, W. J. N. Fernando and M H. Uzir 2015. Parametric evaluation using mechanistic model for release rate of phosphate ions from chitosan-coated phosphorus fertilizer pellets. *Biosystems Engineering*; 129: 78-86.
- Akmal D., R Monica, P D, Asiska M, Suardi E .S . Ben and Z. Erizal 2015. The Use of biopolymer of Poly(3-hydroxybutyrate) as matrix of urea slow release fertilizer. *J. Chem. Pharm. Res.*7(7): 558-563.
- Bonartsev A P. 2007. Biosynthesis, Biodegradation, and Application of Poly(3-hydroxybutyrate) and its Copolymers, Natural Polyesters Produced by Diazotrophic Bacteria. *Communicating Current Research and Educational Topics and Trends in Applied Microbiology*. A. Méndez-Vilas (Ed.).
- Cong Z, S. Yazhen, D, Changwen Z, Jianmin W. Huoyan and C. Xiaoqin 2010. Evaluation of waterborne coating for controlled release fertilizer using wurster fluidized bed. *Ind. Eng. Chem. Res.*; 49(20): 9644–9647.
- Costa P, and L. J .M. Sousa 2001. Modeling and Comparison of Dissolution Profiles. *Europ. J. Pharm. Sci.*13(2): 123–133
- Fernandez-Perez M, F J, Garrido-Herrera E, Gonzalez-Pradas M. Villafranca-Sánchez and F. Flores-Céspedes 2008. Lignin and Ethylcellulose as polymers in controlled release formulations of urea. *J. Appl. Polymer Sci.*108(6): 3796–3803
- Jarosiewicz A and M. Tomaszewska 2003 .Controlled-Release NPK Fertilizer encapsulated by polymeric membranes. *J. Agric. Food Chem.*51(2): 413-417
- Mohanty A K, M. Misra and G. Hinrichsen 2000. Biofibres, biodegradable polymers, and biocomposites: An overview. *Macromol. Mat. Eng.* 276-277(1): 1–24.
- Muslim S, L, Salman Fitriani, N, Suharti Erizal, Febriyenti, Aldi and D,Akmal 2015. Use of bioblend polystyrene/starch for coating urea granules as slow release fertilizer. *J. Chem. Pharm. Res.* 7(11): 478-484
- Sudesh K, H. Abe and Y. Doi 2000. Synthesis and structure properties of polyhydroxyalkanoates: biological polyesters. *progress in polymer Sci.* 25: 1503-1555
- Suharti N, S, Sulaiman Febriyenti, E, Zaini M, Suardi ESB Sahlan, and A. Djamaan 2016. Coating of urea granule for slow fertilizer using bioblend polystyrene/polycaprolactone. *Res. J. Pharm. Biol. Chem. Sci.* 7(1): 1691-1699
- Tomaszewska M. 2003. Controlled Release NPK Fertilizer Formulation Using Polyacrylonitrile. XVIIIth ARS Scriptoria. 186-189
- Tomaszewska M and Jarosiewicz A. 2004. Polysulfone coating with starch addition in CRF Formulation. *Desalination.*163(1–3): 247–252.
- Watson D G. 2005. *Pharmaceutical Analysis: A Text Book for Pharmacy Students and Pharmaceutical Chemists* 2nd ed. Oxford. United Kingdom: Elsevier Limited
- Wu L, Liu M. & Liang R. 2008. Preparation and properties of a double-coated slow-release NPK compound fertilizer with super absorbent and water-retention. *Biores. Tech.*99: 547-554.