Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2017, 9(11):81-86

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Slow Release Fertilizer: Production of Urea Microcapsules using Polycaprolactone as a Coating Material

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ABSTRACT

Urea is a most widely used fertilizer in agriculture due to high nitrogen content, low cost, and commercial availability, but there are some finites related with in-effective used of the fertilizer, and environmental pollution. This study aim was to produce urea slow-release microcapsules using polycaprolactone as coating material by solvent evaporation method. The ratio of urea-PCL were 1:1, 1:2, and 1:3. Microcapsules obtained were characterized by Fourier Transform Infra-Red (FTIR), Scanning Electron Microscopy (SEM), particle size distribution, amount of urea entrapped in microcapsules, and release kinetics profile. There was no chemical interaction between urea and polycaprolactone. The result of SEM showed that microcapsules were spheric in shape with the rough surface and aggregate formed. Particle size distribution of coated urea microcapsules was in the range of 20-240 μm, influenced by the concentration of PCL. Encapsulation efficiency of urea microcapsules in formula 1, 2, and 3 were 80.28 ± 0.81, 82.65 ± 1.22, and 79.64 ± 0.65%, respectively. The percentage of release efficiency from formula 1, 2, and 3 were 58.85 ± 1.72, 26.76 ± 0.76, and 40.42 ± 2.39%, respectively. In conclusion, PCL could be used in microencapsulation formulation of urea slow release. The release kinetics of urea from microcapsules followed Langenbucher equation related with diffusion and erosion mechanism. PCl affected the release efficiency significantly ($p<0.05$).

Keywords: Urea; Microencapsulation; Polycaprolactone; Slow release

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INTRODUCTION

Fertilizer plays an important role in providing nutrients to plants to improve or maintain the optimal yields of the crop. Thus, increasing the efficiency of fertilizer used to fulfill nutrient intake that useful for crops and affect crop yields are essential for fertilizer producers and farmers [1]. The most widely used of the fertilizer in agriculture is urea due to its high nitrogen content (45 to 46%), low cost and commercial availability [2-4]. Nitrogen is a very important nutrient for plants because it works to promote plants growth, nourish leaf growth, and enhance protein levels in plants [5]. The limitations in using urea as fertilizer are not complete absorption. 20 to 70% of urea used to pollute the environment due to the leaching and evaporation process as a source of pollution and eutrophication, and can then cause the green house effect. Only 30 to 50% of urea is absorbed by the plants, it will increase costs due to more frequently used of fertilizers [6].

A possible alternative to minimize the problems related to contamination of fertilizers on the environment is a development of a slow-release fertilizer (SRF) or controlled release fertilizer (CRF) [6]. In the application of CRF or SRF, the active substance is released slowly and in a long period of time. It will reduce the toxicity compared to

conventional fertilizers [7]. SRF/CRF nutrients are available over a longer period and their assimilation is gradual to avoid potential losses and providing more time for plant uptake. It will reduce the frequency of applications of nutrients and therefore serve positive effect on the cost concepts and environmental benefits [8,9]. Microencapsulation is the process where the solid, liquid or even gas materials are encapsulated at microscopic particle size by forming a coating wall around the core material [10,11]. The benefit of microencapsulation in agriculture is limited the release of fertilizer by reducing the leaching process into the groundwater [12].

One method used in microencapsulation is the solvent evaporation method. In this method, the polymer as a coating material is dissolved in a volatile solvent mixed with the carrier fluid phase. The core material to be microencapsulated is dissolved or dispersed in a polymer solution [13]. The method chosen because of the polymer used soluble in volatile solvents such as dichloromethane, easy and efficient in its processing, takes a short time and low cost [14]. The coating material used in this study is polycaprolactone (PCL). It is one of the biodegradable polymers, have good thermal stability and elasticity, and not toxic characteristics. PCL is degraded slower than other polyester groups, it reaches 1 year, so it is considered to use in slow release application [15-17].

Based on the reason above, the urea slow release fertilizer microcapsules were prepared using PCL as a coating material by solvent evaporation method.

EXPERIMENTAL SECTION

Equipments and Materials

Equipment used in the study were Fourier Transform Infrared Spectrophotometer (Perkin Elmer FT-IR Spectrophotometer Frontier), Scanning Electron Microscope (JEOL, Japan), UV-Vis Spectrophotometer (*Shimadzu UV-1700*), analytical balance (*Shimadzu AUX 220*, Japan), Microscope and Optilap viewer, *Heating Magnetic Stirrer (IKA,Germany)*, and other glass wares usual used in laboratory. Materials used were urea (PT. Pupuk Sriwijaya, Indonesia), urea (Merck, Jerman), biopolymer polycaprolactone (Aldrich Chemical), Span 80 (PT. Brataco, Indonesia), liquid paraffin (PT.Brataco, Indonesia), dichloromethane, *n*-hexane, distilled water, etc.

Methods

Preparation of urea microcapsules:

Urea slow-release microcapsules were prepared following the formulas are shown in Table 1 below. Add the mixture of PCL solution in dichloromethane and urea slowly into the dispersion of Span 80 in liquid paraffin, stirred at a rate of 700 rpm until dichloromethane completely evaporated. The microcapsules formed were collected by decantation and washed with n-hexane until free from paraffin and Span 80, then filtered and dried at room temperature.

Table 1: Formula of microcapsules

Materials	Formula				
	Urea	**F0**	**F1**	**F2**	**F3**
Urea (mg)	500	-	500	500	500
Polycaprolactone (mg)	-	500	500	1000	1500
Dichloromethane (mL)	-	20	20	20	20
Span 80 (mL)	-	1	1	1	1
Liquid Paraffin (mL)	-	100	100	100	100

Evaluation of Microcapsules

IR spectroscopy analysis:

The spectrum of the powdered microcapsules was observed using a Fourier Transform Infrared (FTIR) spectrophotometer at the wave number of 400-4000 cm^{-1}.

Particle size distribution:

The particles size of microcapsules obtained were determined using a microscope and Optilab viewer. Particles were observed and displayed on the computer screen and around 300 counted [18].

Determination of amount of urea in the microcapsules:
50 mg of microcapsules obtained was grinded and dissolved in distilled water using a 25 mL measuring flask, shaken, and added 1 mL Erlich reagent. The absorbance of solutions were measured at the maximum absorption wavelength of urea using a UV-Vis spectrophotometer (n=3) [19].

Determination of fertilizer loading, encapsulation efficiency and, amount microcapsules obtained [20]:
The percentage of fertilizer loading in the microcapsules obtained was calculated using the following equation:

% Fertilizer Loading = weight of active substance in microcapsules/weight of microcapsules × 100%

The percentage of the microcapsules produced was calculated using the formula below:

Microcapsules produced (%) = weight of microcapsules/(initial weight of active substance + polymer) × 100%

Entrapment Efficiency = (amount of measurable active substances/amount of theoretically active substances) × 100%

SEM (Scanning Electron Microscopy)
The sample was attached to the sample holder and observed at a various magnification of SEM (Phenom pro-X, Netherlands). The equipment was set at 15 kV and 12 mA.

Release Profile Test
A certain amount of microcapsules equivalent to 100 mg urea were placed into the container containing 50 mL of distilled water. After 10, 20, 30, 45, 60, 120, 240, and 360 minutes 5 mL of the sample solutions were withdrawn. After each sampling, the medium solution in the container was replaced by the fresh medium at the same temperature. The absorbance of sample solutions were measured using a UV-Vis spectrophotometer at maximum absorption wavelength (n=3) [16,19,21].

RESULTS AND DISCUSSION

FTIR Spectroscopy Analysis
FTIR spectra of urea microcapsules shown that the valleys depict the functional groups of urea and polycaprolactone (Figure 1). No new functional group formed. This proves that urea and polycaprolactone used are compatible, only physical interaction occurs but no chemical interaction [22-24].

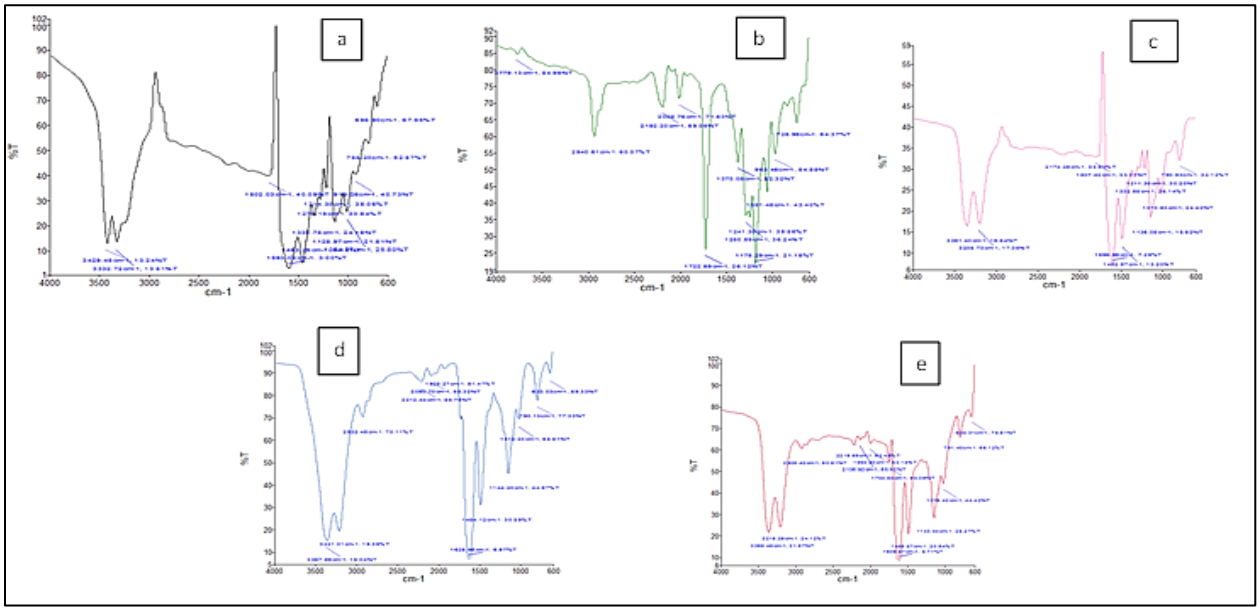

Figure 1: FTIR spectra of (a) urea, (b) PCL, (c) formula 1, (d) formula 2, and (e) formula 3

Scanning Electron Microscopy (SEM)

The placebo and urea microcapsules were evaluated by SEM is shown in Figure 2. The placebo microcapsules or microcapsules without active substance showed irregular spheric in shape and have the rough surface. While urea microcapsules were more spheric with a rough surface and formed aggregate caused by the incomplete drying process. Urea microcapsules have a rough surface caused by the presence of urea on microcapsules surface [18].

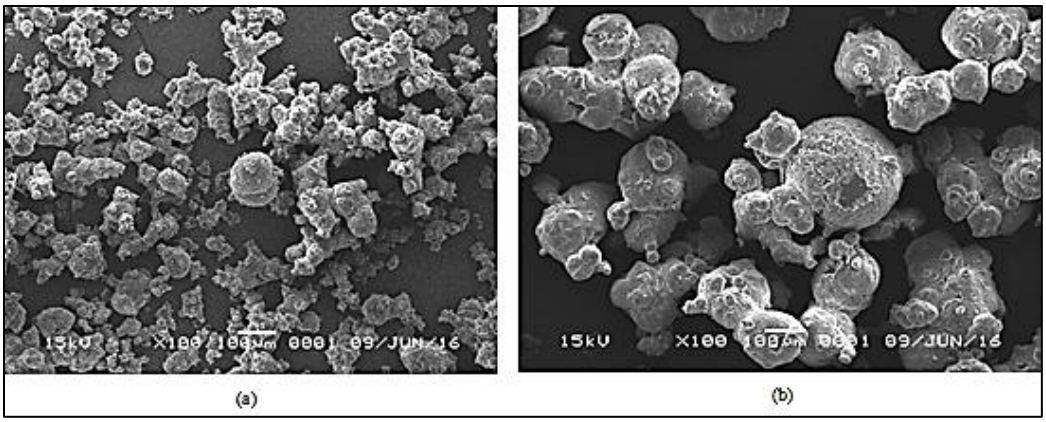

Figure 2: Scanning electron microscopy (a) placebo microcapsules and (b) urea microcapsules at 100x magnification, at 15 kV and 12 mA

Particle Size Distribution

Particles size distribution determined by using microscope and optilab viewer as shown in Figure 3. Microcapsules were counted as 300 particles at 10x magnification. The particle size in a range of 20-240 µm. Most particle size in Formula 1 and 2 were in the range of 20.1-40 and 40.1-60 µm. The frequency of Formula 1, 2, and 3 were 57.33, 25.67%, and 19.33%, respectively. Microcapsules particle size by solvent evaporation methods usually is in the range of 5-5000 µm [25]. Increasing of particle size with increasing polymer concentration may be occurred due to the higher viscosity of polymer solution leading to an increase in the emulsion droplet size and caused a bigger microcapsules size. In addition, the particle size will be also bigger with an increase in the amount of the coating caused by an increase in thickness of the microcapsules walls formed [20,24,26].

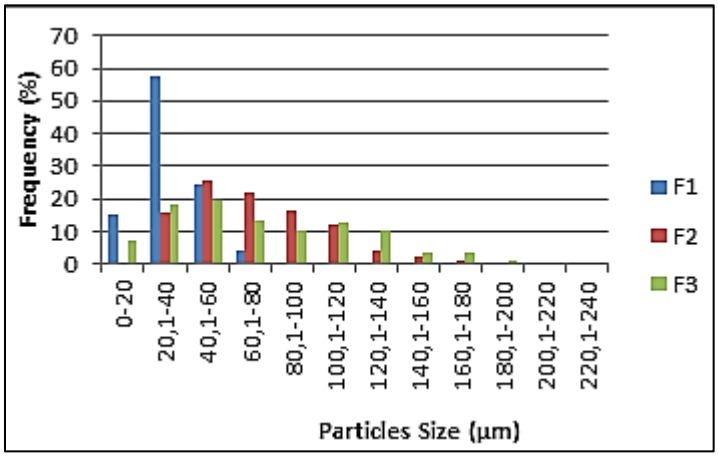

Figure 3: Particle size distribution of urea microcapsules

Determination the Amount in Urea in Microcapsules

The wavelength of maximum absorption (λ_{max}) of urea in distilled water obtained was at a wavelength of 417.5 nm. Calibration curve equation obtained was y=5.364x-0.0006.

The amounts of urea microcapsules obtained in Formula 1, 2, and 3 were 78.53, 82.74, and 85.67%, respectively (Table 2). The amount of urea microcapsules were less than 100% because the microcapsules were carried away during filtration and washing process by using *n*-hexane. The microcapsules were also stuck and left on the surface of sieve paper. Encapsulation efficiency of urea in microcapsules in Formula 1, 2 and 3 were 80.28 ± 0.81, 82.65 ± 1.22%, and 79.64 ± 0.65% (Table 2). Urea encapsulated were less than 100%. It caused by incomplete coating of

urea during sedimentation process. The un-encapsulated urea were stuck on the surface of microcapsules and will be carried away with paraffin when washing process by *n*-hexane [27].

Table 2: The characteristics of microcapsules produced

Microcapsules formula	Amount of microcapsules produced (%)	Amount of urea in microcapsules (mg)	Fertilizer loading(%)	Encapsulation efficiency(%)
F1	78.53	20.07 ± 0.20	40.14 ± 0.41	80.28 ± 0.81
F2	82.74	13.78 ± 0.20	27.55 ± 0,41	82.65 ± 1.22
F3	85.67	10.00 ± 0.08	19.91 ± 0.16	79.64 ± 0.65

Release Profile Studies

The release profile of uncoating urea and urea microcapsules in distilled water medium are shown in Figure 4. The release of uncoating urea is very significantly faster compared to urea microcapsules. It is caused by the very soluble characteristic of plain or uncoating urea in distilled water leading to the very fast release of urea. Urea microcapsules were coated with PCL that has hydrophobicity characteristic. It is hard for the liquid to penetrate and to diffuse leading to the longer time needed and small amount liquid could penetrate into the core of microcapsules. However, the time needed by urea to release from microcapsules are longer [16]. The percentage of urea released from microcapsules Formula 2 after 6 hours were lower than Formula 1 and 3. The percentage of urea released from microcapsules Formula 1, 2, and 3 were 68.79 ± 3.67, 31.84 ± 6.70, and 47.16 ± 3.16%, respectively. The increasing of polymer concentration will reduce the release rate of urea from microcapsules. The higher the polymer concentrations, the thicker the microcapsules wall [26]. In Formula 3, particle size distribution graphic shown that the distribution of particles of Formula 3 microcapsules shown on the graph was uneven, where much amount of particles in a small range leading to the fast release of urea from the microcapsules [20].

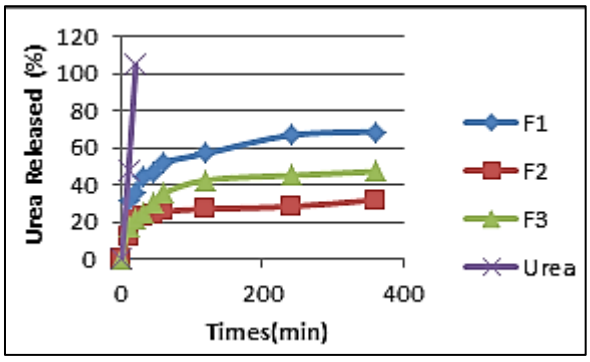

Figure 4: Release profile of urea from microcapsules in distilled water medium

The release efficiency of urea from Formula 1, 2, and 3 were 58.85 ± 1.72, 26.76 ± 0.76, and 40.42 ± 2.39, respectively ($p<0.05$). Polycaprolactone used as coating polymer affect the release rate significantly. Post hoc test also shown the significant difference among of formulas. There was a significant influence of variation of polymer concentrations used. Release kinetics profile of urea from microcapsules was fitted with zero- and first-order kinetics. It was also fitted with Higuchi, Korsmeyer-Peppas, and Langenbucher equation. The release kinetics profiles of urea from Formula 1, 2, and 3 followed the Langenbucher equation. It means that the release mechanism occurs by diffusion and erosion process.

CONCLUSION

The percentage of urea released from PCL microcapsules with urea-PCL ratio of 1:1, 1:2 and 1:3 after 6 hours were 68.79 ± 3.67, 31.84 ± 6.70, and 47.16 ± 3.16%, respectively. Results indicated that polymer concentrations affect the release rate of urea. The release kinetics profile of urea from microcapsules followed Langenbucher equation. It means that the release of urea occurs by diffusion and erosion process. Biopolymer polycaprolactone can be used as a coating material in the formulation of urea slow release fertilizer microcapsules.

ACKNOWLEDGMENT

The authors would like to thank to the Rector of Andalas University, because of a part of this research data was funded by Cluster Research Grant Research Professor of Andalas University 2017, with Contract Number: 17/UN.16.17PP.HGB/LPPM/2017 (Prof. Elfi Sahlan Ben).

REFERENCES

[1] SH Chien; L Prochnow; H Cantarella. *Adv Agronomy*. **2009**, 102, 267-322.
[2] Suherman; DD Anggoro. *Int J Eng Technol.* **2011**, 11(6), 62-66.
[3] N Xiaoyu; W Yuejin; W Zhengyan; W Lin; Q Guannan; Y Lixiang. *Biosyst Eng*. **2013**, 115(3), 274-282.
[4] TH Trinh; K KuShaari; A Basit; B Azeem; A Shuib. *APCBEE Procedia*. **2014**, 8, 146-150.
[5] MM Sutedjo. Pupuk dan Cara Pemupukan. Jakarta: Rineka Cipta, **1987**.
[6] MM Costa; C Albuquerque; EC Alves; TL Pinto; RL Fialho. *J Agr Food Chem*. **2013**, 61(42), 9984-9991.
[7] ME Trenkel. Slow and Controlled-Release and Stabilized Fertilizer: An Option for Enchancing Nutrient Use Efficiency in Agriculture. Paris: International Fertilizer Industry Association. **2010**.
[8] M González, M Arces, E Cuesta, P Corredera, C Sardina, J Rieumont, B Guenther. FERLENT® A Controlled Release Fertilizer Produced From A Polymer Material, **2011**.
[9] G Liu; L Zotarelli; Y Li; D Dinkins; Q Wang; OM Hampton. *UF/IFAS Extension*. **2014**, 1-7.
[10] HC Ansel. Pengantar Bentuk Sediaan Farmasi. Terjemahan oleh Farida Ibrahim, Edisi Keempat, Jakarta: UI Press, **2008**.
[11] M Jadupati; D Tanmay; G Souvik. *Int Res J Pharm*. **2012**, 3(4), 8-13.
[12] J Sri; A Seethadevi; KS Prabha; P Muthuprasanna; P Pavitra. *Int J Pharm Bio Sc*. **2012**, 3(1), 509-531.
[13] K Sailaja; M Jyothika. *CIB Tech J Pharm Sci*. **2015**, 4(2), 26-33.
[14] S Tiwari; P Verma. *Int J Pharm Life Sc*. **2011**, 2(8), 998-1005.
[15] MA Woodruff; DW Hutmacher. *Progress Pol Sc.* **2010**, 35(10), 1217-1256.
[16] MR Hussain; RR Devi; TK Maji. *Iranian Pol J.* **2012**, 21(8), 473-479.
[17] S Panda. *Asian J Pharm Clin Res.* **2013**, 6(3).
[18] A Martin, J Swabrick, A Cammarata. Farmasi Fisik Dasar-Dasar Kimia Fisika Dalam Ilmu Farmasetik (Edisi 3). Jakarta: Universitas Indonesia Press, **1993**.
[19] A Djamaan; R Monica; PD Asiska; M Suardi; ES Ben; Z Erizal. *J Chem Pharm Res.* **2015**, 7(7), 558-563.
[20] PK Gaur; S Mishra; M Bajpai. *J Food Uurea Analysis*. **2014**, 22(4), 542-548.
[21] L Chen; Z Xie; X Zhuang; X Chen; X Jing. *Carbohydr Pol*. **2008**, 72(2), 342-348.
[22] SJ Park; KS Kim. *Colloids Surfaces B: Biointerfaces*. **2005**, 43(3), 138-142.
[23] A Tadudari; K Thadkala; KR Devara; J Aukunuru. *Int J Pharm Tech Res*. **2014**, 6(4), 1170-1179.
[24] A Djamaan; DL Afrina; L Fitriani; PD Asiska; S Netty; S Muslim; ESB Ben; Z Erizal. *J Chem Pharm Res*. **2015**, 7(8), 683-689.
[25] L Lachman, AL Herbert, JL Kanig. Lachman's theory and practice of pharmaceutical industry. Jakarta: UI Press. **1994**.
[26] BC Behera. SK Sahoo; S Dhal; BB Barik; BK Gupta. *Trop J Pharm Res*. **2008**, 7(1), 879-885.
[27] S Dehghan. R Aboofazeli. M Avadi; R Khaksar. *Afr J Pharm Pharm*. **2010**, 4(6), 346-354.