Encapsulation Of Eugenol In Urea-Membranes Formaldehyde As A Slow Realese Pesticides

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ABSTRACT

In agriculture, managing pests by applying pesticides to protect crops is one of the most crucial aspects. However, less than 1% of these pesticides actually come in direct contact with or are consumed by target pests. controlled-release was approaches of pest management that have been developed to target the needs of these different environments. In this study, the natural pesticide (Eugenol) was encapsulated in a Urea-Formaldehyde membrane using PVA surfactant. The encapsulation method used was the emulsification method using a stirrer speed from 500-1000 rpm with a PVA concentration of 0.5 - 1 gram and a Resorchinol concentration of 0.5 - 1 gram. Base on FTIR Result, Eugenol can be encapsulated in Urea-Formaldehyde granules. The average diameter microcapsule was 0.44 µm. The maximum concentration of eugenol in water was 642.479 ppm within 8 hours.

Keywords: Emulsification, Eugenol, Microencapsulation, and Urea-Formadehyde

1. Introduction

Urea is one of the main sources of N used due to its high concentration (46% N) which allows concentrated formulations at a lower cost compared to other sources [1]. However this fertilizer shows lower efficiency than other nitrogen sources for a large number of plants in different soils and climates, due to different causes, such as evaporation of NH_3 and its toxic effects on plants early in the vegetative period [2-3].

These factors not only contribute to the reduction of the efficiency of urea, biomass products, and economic cultivation, but also an important source of environmental pollution. One alternative to reduce such losses is to reduce the hydrophility of urea, allowing its application as a slow-release fertilizer. Slow release of urea fertilizer can be done by making granules by reacting urea with formaldehyde [4].In agroindustry, Urea-Formaldehyde as a slow-release fertilizer, can act as a superabsorbent [5] and also slow-release control of pesticides [6]. Slow-release control of pesticides is carried out by encapsulating pesticide compounds in urea-formaldehyde [7], In this research, factors that influence the formation of urea formaldehyde were studied, such as temperature, microcapsule formation time and stirring time. but some of the microcapsules produced were agglomerated. To produce urea formaldehyde microcapsules that did not agglomerate in this study, the stirrer speed factor in the formation of microcapsules was studied, the stirring speed could influence the agglomeration of urea formaldehyde microcapsules [8]. In addition, the addition of surfactant was studied for its effect on the agglomeration of urea formaldehyde microcapsules. To prevent agglomeration, surfactants such as Gum Arabic [9], Tween 40 [10] and Polyvinyl Alcohol (PVA) [11 & 12] can be used.

2. Material and Methods

Equipment

Equipment used in this study is the Overhead stirrer RW 20 Digital IKA, Impeller, Thermometer, microscope, filter paper, Mantel Heater, and three-necked flask. Microcapsule characterization using a digital camera koppace industrial microscope, Fourier transform infrared (FTIR**) (**FTIR Alpha II-Bruker)**,** Scanning Electron Microscope (SEM) (Hitachi SU-3500).

Materials

The materials used in this study include Urea (Pupuk Indonesia), Formaldehyde (Technical Grade, CV. Chemical Indonesia Multi Sentosa), Eugenol oil (Giri Wangi), Resorcinol (Merck), Ammonium Chloride (Merck), Polyvinyl Alcohol (PVA) (Merck), and Aquadest.

Method

Aquades as much as 137 mL mixed with 10% PVA weighing 0.75 grams into a three-necked flask at a reaction temperature of 55 ºC at a speed of 300 rpm, stirring was carried out for 10 minutes. Urea 5 grams, resorcinol 0.5-1 grams, and ammonium chloride 0.5-1 grams was poured into a three-neck flask, stirring was carried out for 15 minutes. Eugenol oil 20 ml was introduced into the three-neck flask slowly. Stirring was carried out for 15 minutes. A total of 14 mL of formaldehyde was inserted into a three-necked flask. Stirring was carried out for 150 minutes. The encapsulation results was separated using a centrifugation device for 20 minutes at 4000 rpm. The results of the encapsulation that have been separated was rinsed using aquades as much as 8 repetitions to remove surfactants with pH 7 before drying at room temperature. Repeat steps for stirring speeds of 500 rpm and 800 rpm. The dry microcapsules was then tested for diameter size using a microscope and SEM, tested for functional groups using FTIR,.

For Analysis of the size of the resulting microcapsule was carried out using a microscope. Diameter size testing followed Anggi et al in [13]. The diameter of the microcapsule was determined by observing 30 droplets to calculate the average diameter.

3. Results and Discussions

FTIR testing was used to see the success of encapsulation Eugenol Oil in urea-formaldehyde based on the functional groups. Based on Figure 1, where in the microcapsule there is an -OH group (peak 3517.20 cm^{-1}) and which is a group contained in eugenol peak (3326.9 cm^{-1}) and which is the group contained in Eugenol Peak (3326.9 cm^{-1}). This shift in peak values indicates that there is an interaction between eugenol and urea-formaldehyde. The same interaction also occurs in another research where eugenol encapsulation by chitosan where the interaction between eugenol and chitosan causes a shift in peak values [14]. Based on Figure 1, the blue line is a microcapsule without eugenol, the red line is a microcapsule with eugenol and the black one is only eugenol. This proves that microcapsules with eugenol are well encapsulated because there is an -OH group where the group is also present in eugenol.

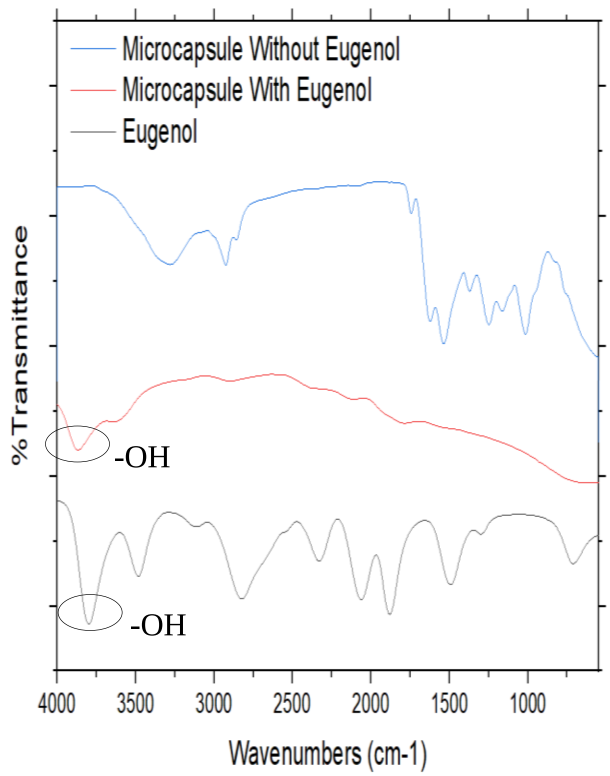


Figure 1. Microcapsule FTIR Result

4.

The stirring speed affects the size of the eugenol oil during the emulsification process. In the research conducted by Maria et al in [8], the results of the average diameter of the microcapsules can be seen in Table 1. This suggests that there is an influence of mixing speed on the average diameter of the microcapsules from the encapsulation of eugenol oil in urea formaldehyde. The mixing speed of 300 rpm has a smaller average microcapsule diameter, 1.65µm. The decrease in the average diameter of microcapsules is in accordance with previous, which states that encapsulation with a mixing speed of 800 rpm results in a smaller microcapsule diameter, which is 0.44 µm. However, in order to obtain better self-healing performance, it is necessary to optimize the microcapsule diameter size of <50 µm which can be produced with higher mixing speeds or change the mass ratio of urea and formaldehyde used, and pH during the encapsulation process [8].

Table 1. Microcapsule Average Diameter

Strirring speed (rpm)	Average Diameter (µm)
800	0,44
500	1,57
300	1,65

The slow release function of microcapsules was tested by immersing 1 gr of microcapsule granules in water, where the graph can be seen in Figure 2. The slow release rate of eugeol oil increases over time until 8 hours where the rate stop. This is happened because the eugenol oil in the water is saturated where the concentration of eugenol oil within 8 hours is equal to the concentration of eugenol oil in 24 hours. Research conducted by resercher in [14], showed the rate of release of eugenol oil from chitosan granules stopped in less than 50 minutes. Anggi et al in [13], showed that the rate of eugenol release from PVA granules stopped in less than 40 hours.

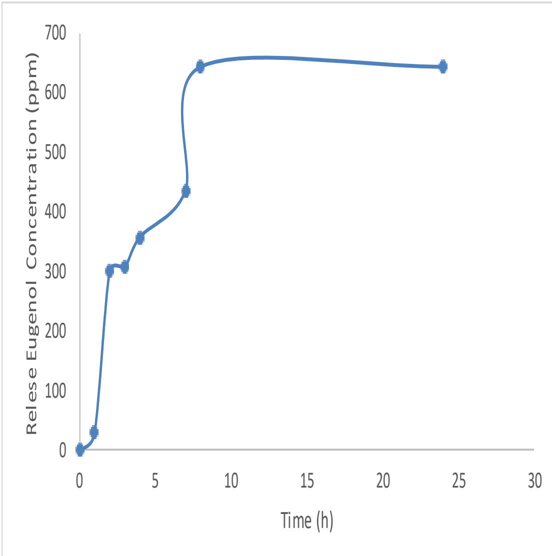
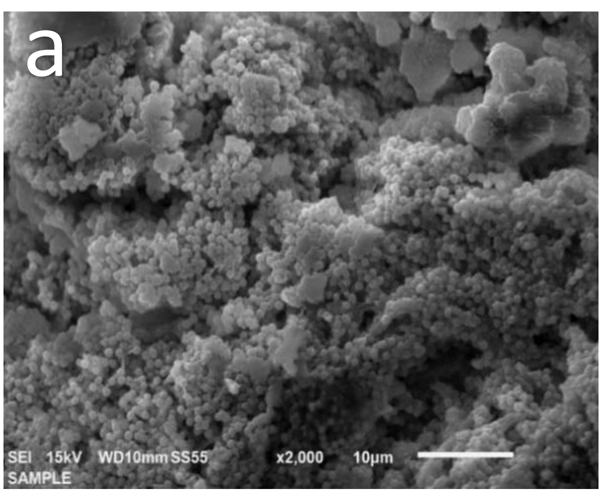


Figure 2. Slow Release Eugenol in Water

PVA concentration has no effect on agglomeration, when PVA concentration is increased, agglomeration still occurs as shown in figure 3. This is different from the research conducted by [15] to encapsulate walnut oil by urea formaldehyde, where the greater the PVA concentration, the agglomeration process does not occur. Similarly, the effect of resorchinol concentration, where when the concentration of resorchinol is increased, the microcapsule is not formed as shown in Figure 4.



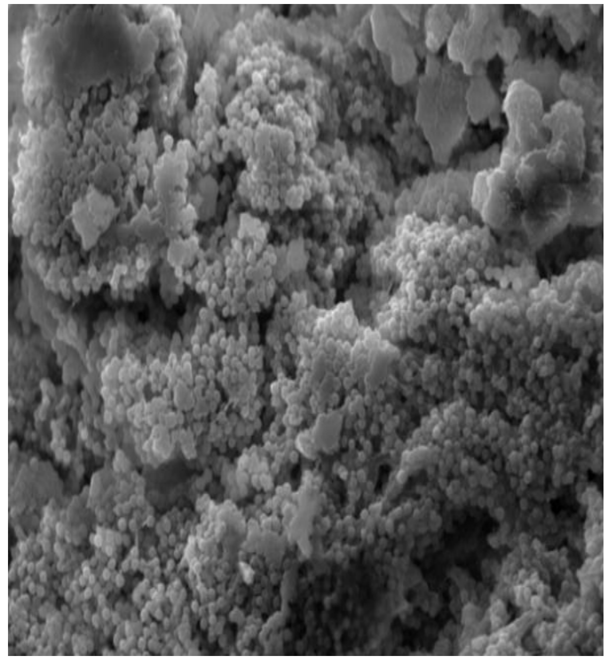
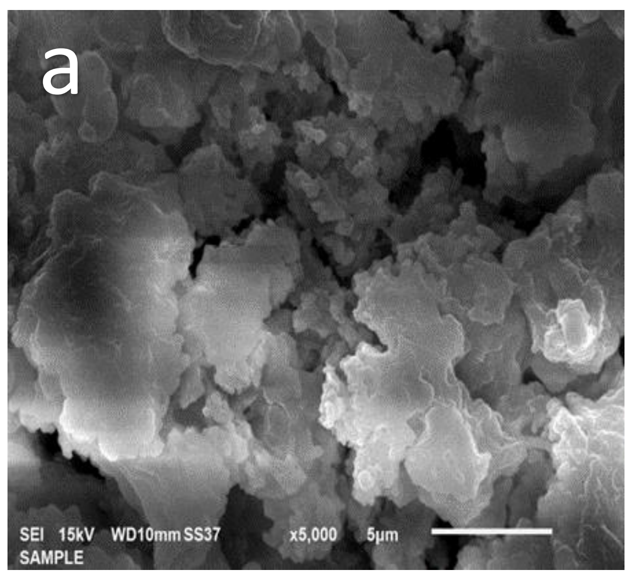


Figure 3. Microcapsule observation results, a. concentration 0.5% PVA, b. concentration 0.5% resorchinol



b

b

Figure 4. Observation of microcapsules with SEM, a. concentration of 1% PVA, b. concentration of 1% resorchinol

5. Conclusion

In this study, base on FTIR and SEM Analisys eugenol can be encapsulated in urea formaldehyde granules wich diameter microcapsule is 0,44 µm. Concentration PVA and Resorchinol influence size microcapsule. The maximum concentration of eugenol in water of 642.479 ppm and constant at 8 hours.

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References

[1] Cabezas, W. A. R. L., Korndorfer, G. H., & Motta, S. A. . Volatilização de N-NH3 na cultura de milho:: II. avaliação de fontes sólidas e fluidas em sistema de plantio direto e convencional. *Revista Brasileira de Ciência Do Solo*, 1997, *21*(3), 489–496. https://doi.org/10.1590/s0100-06831997000300019

[2] Melo Júnior, H. B.; Duarte, I. N.; Silva, A. A.; Lana, R. M. Q. Uso De Fontes Revestidas Com Polímeros De Liberação Gradual E Uréia Convencional. *Enciclopédia Biosfera*, 2010 *6*(11), 1–12. http://www.ncbi.nlm.nih.gov/pubmed/15003161%5Cnhttp://cid.oxfordjournals.org/lookup/doi/10.1093/cid/cir991%5Cnhttp://www.scielo.cl/pdf/udecada/v15n26/art06.pdf%5Cnhttp://www.scopus.com/inward/record.url?eid=2-s2.0-84861150233&partnerID=tZOtx3y1

[3] Suherman, Widayat, & Djaeni, M.. Producing Sulfur Coated Urea by Fluid Bed Wet Coating Method : Drying Kinetics and Product Quality. *International Review of Chemical Engineering*, 2010, *2*(January 2011), 707–712.

[4] Erceg, T., Vukić, N., Šovljanski, O., Teofilović, V., Porobić, S., Baloš, S., Kojić, S., Terek, P., Banjanin, B., & Rakić, S.. Preparation and characterization of biodegradable cellulose acetate-based films with novel plasticizer obtained by polyethylene terephthalate glycolysis intended for active packaging. *Cellulose*, 2023, *30*(9), 5825–5844. https://doi.org/10.1007/s10570-023-05240-6

[5] Giroto, A. S., Guimarães, G. G. F., & Ribeiro, C.. A Novel, Simple Route to Produce Urea:Urea–Formaldehyde Composites for Controlled Release of Fertilizers. *Journal of Polymers and the Environment*, 2018, *26*(6), 2448–2458. https://doi.org/10.1007/s10924-017-1141-z

[6] Kumbar, S. G., Kulkarni, A. R., Dave, A. M., & Aminabhavi, T. M. Encapsulation efficiency and release kinetics of solid and

liquid pesticides through urea formaldehyde crosslinked starch, guar gum, and starch + guar gum matrices. *Journal of Applied Polymer Science*, 2001, *82*(11), 2863–2866. https://doi.org/10.1002/app.2141

[7] Rochmadi, Prasetya, A., & Hasokowati, W. (2010). Mechanism of microencapsulation with Urea-Formaldehyde polymer. *American Journal of Applied Sciences*, *7*(6), 739–745. https://doi.org/10.3844/ajassp.2010.739.745

[8] Kosarli, M., Bekas, D. G., Tsirka, K., Baltzis, D., Vaimakis-Tsogkas, D., Orfanidis, S., Papavassiliou, G., & Paipetis, A. S. Microcapsule-based self-healing materials: Healing efficiency and toughness reduction vs. capsule size. *Composites Part B: Engineering*, 2019,*171*, 78–86. https://doi.org/10.1016/j.compositesb.2019.04.030

[9] Fan, C., & Zhou, X. Effect of emulsifier on poly(urea-formaldehyde) microencapsulation of tetrachloroethylene. *Polymer Bulletin*, 2011 *67*(1), 15–27. https://doi.org/10.1007/s00289-010-0355-1

[10] Lubis, M. A. R., Park, B. D., & Lee, S. M. Microencapsulation of polymeric isocyanate for the modification of urea-formaldehyde resins. *International Journal of Adhesion and Adhesives*, 2020, *100*, 102599. https://doi.org/10.1016/j.ijadhadh.2020.102599

[11] Liu, X., Le, J. K., & Kessler, M. R. Microencapsulation of self-healing agents with melamine-urea-formaldehyde by the Shirasu porous glass (SPG) emulsification technique. *Macromolecular Research*, 2011, *19*(10), 1056–1061. https://doi.org/10.1007/s13233-011-1009-3

[12] Kurt Çömlekçi, G., & Ulutan, S.. Encapsulation of linseed oil and linseed oil based alkyd resin by urea formaldehyde shell for self-healing systems. *Progress in Organic Coatings*, 2018, *121*(April), 190–200. https://doi.org/10.1016/j.porgcoat.2018.04.027

[13] Wahyuningsi , A., Rochmadi, & Perdana, I. Mikroenkapsulasi Eugenol dengan Penyalut Polyvinyl alcohol Sebagai Pestisida Nabati dengan Metode Emulsifikasi dan Spray drying. *Seminar Nasional Teknik Kimia Indonesia*, 2015, (pp. 1-8). Yogyakarta: UGM.

[14] Cahyono, B., A'yun, Q., Suzery, M., & Hadiyanto. Characteristics of eugenol loaded chitosan-tripolyphosphate particles as affected by initial content of eugenol and their in-vitro release characteristic. *Joint Conference on Chemistry*, 2016, (pp. 1-6). Semarang: IOP.

[15] Suyatmo, Reviana Inda Dwi; Topandi, Abdussalam; Sari, Lathiefah Oktriananda; Nulhakim, L.. Pengaruh Penambahan Poli Vinil Alkohol (PVA) pada Enkapsulasi Minyak Kacang Kenari dalam Urea-Formaldehid untuk Aplikasi Self-Healing Coating. *Jurnal Teknologi*, 2023 *Vol 10, No 2*. http://jurnalftijayabaya.ac.id/index.php/JTek/article/view/226/pdf