Size diameter prediction of urea fertilizer microcapsules using dimensionless numbers: The influence of chitosan solution concentration and stirring speed

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Size Diameter Prediction of Urea Fertilizer Microcapsules Using Dimensionless Numbers: The Influence of Chitosan Solution Concentration and Stirring Speed

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Abstract. The aim of this study is to compose empirical equation of Reynold (Re) and Weber (We) numbers predicting the size of urea fertilizer microcapsules based on concentration of chitosan solution and stirring speed. Urea fertilizer microcapsules are prepared by applying emulsion cross-linking method using chitosan solution as a wall material and glutaraldehyde saturated toluene (GST) as a crosslinking agent. The diameter of microcapsules that are formed is analyzed using digital microscope. To predict the size of urea fertilizer microcapsules, this study uses correlation of empirical equation of dimensionless numbers proposed by Reynold (Re) and Weber (We) number, then the size of the calculated microcapsules compared with the results of research. The obtained equation is used to calculate microcapsules diameter and compare it to research data. The result is it has a small % error for parameters, the influence of chitosan solution concentration and stirring speed is 0,58% and 1,29%.

INTRODUCTION

Urea fertilizer is one of the most important nitrogen nutrient resources for plant growth. The weakness of conventional urea fertilizers is highly soluble in water, while plants only absorb 30-35% nutrients [1,2]. The residue run over the environment and will be lost due to the leaching by rainfall, irrigation, and water flow. Absorption and coating of urea fertilizer using biodegradable material (fertilizer microcapsules) can reduce or control the excessive of nitrogen release. Besides, it can increase the efficiency of nutrients consumption by the plants [3].

Microcapsules forming process or encapsulation consist of physical and chemical method. Physical method (mechanical) is applied by spray drying, freeze drying, spray chilling, extrusion, and fluidised bed. For chemical method, such as simple coacervation, complex coacervation, molecular inclusion, and emulsion cross-linking [4]. This study employs encapsulation method is emulsion cross-linking using chitosan as a wall material and glutaraldehyde saturated toluene (GST) as a crosslinking agent. This method involves crosslinking reaction between functional group of aldehyde from GST and amino functional group from chitosan [5]. Emulsion cross-linking is a simple method that

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can be used for highly soluble and unsoluble substances, liquid, and solid. This method is able to produce perfectly spherical geometry microcapsules [5,6,7].

Encapsulation products using emulsion cross-linking method change liquid phase to be solid phase through through the solidification process of the droplet emulsion by crosslinking reaction. The size of emulsion droplets may have the same size with microcapsules. The factors that influence microcapsules size are the concentration of chitosan solution and the stirring speed. The increasing concentration of chitosan solution can increase viscosity that will produce rough emulsions production with large droplets and will lead to form micro particles in large [8]. Size of microcapsules can also be affected by the stirring speed because it influences the interfacial tension [9].

Microcapsules size can be calculated by using dimensionless numbers, such as numbers of Weber (We) and Ohnesorge (Oh) related to interfacial tension. Meanwhile, Reynold (Re) numbers are related to inertia force and viscosity [10]. Size prediction of red ginger oleoresin microcapsules uses Ohnesorge (Oh) and Reynold (Re) numbers had reported by Jayanudin, et al[9]. Dalmoro, et al [10] had also reported the prediction of droplet size in microencapsulation process applying ultrasonic atomization method using dimensionless numbers of Reynold (Re), Weber (We), and Ohnesorge (Oh). Empirical equation composed from dimensionless numbers is able to predict the size of urea fertilizer microcapsules produced based on the changes of chitosan concentration and the stirring speed. This study aims to compose the empirical equation to predict the size of urea fertilizer microcapsules. This study use Reynold (Re) and Weber (We) dimensionless numbers and compare the size of urea fertilizer microcapsules gained in this study.

MATERIALS AND METHODS

Materials

This study used urea fertilizer from PT. Pupuk Sriwijaya, 25% glutaraldehyde solution from Merck, 96% technical toluene from CV. Tri Jaya Dinamika, chitosan from PT. Biotech Surindo with degree of deacetylation (DD) = 87.2% and viscosity 37.10 cps, vegetable oil produced by PT. Sarwana Nusantara, 100% glacial acetic acid from Merck, technical petroleum ether and technical n-hexane from CV. Labora. The research equipment used was IKAWerk Ultra-Turrax homogenizer, Kirin Oven model KBO-90M, and Dino-Lite digital microscope.

Urea Fertilizer Microcapsules Preparation

Urea fertilizer microcapsules are produced by emulsion cross-linking method with chitosan as a wall material and glutaraldehyde saturated toluene (GST) as a crosslinking agent. This method refers to the research conducted by Jayanudin, et al [8]. This method consists of four stages. First, 5 g urea fertilizer is dissolved with 2%, 3%, and 4% (w/v) chitosan solution. Chitosan is dissolved with 1% (v/v) glacial acetat acid. Second, to form the emulsions, put the mixture of urea fertilizer and chitosan solution in vegetable oil and stirred with homogenizer Daihan at 10,000 rpm, 15,000 rpm, and 20,000 rpm for 1 hour. Third, the formed emulsions are dripped with 20 ml GST gradually. GST is formed by mixing 25% (v/v) glutaraldehyde and toluene in 1:1 volume ratio. After that, the mixture is stirred for 3 hours at speed of 500 rpm and let them stand for overnight. The fusion is then separated by taking the upper layer as GST. Next, the addition of GST is continued with adding 2 ml of 25% (v/v) glutaraldehyde solution and keep stirring for 2 hours. Fourth, separating the formed microcapsules is conducted by filtering and washing them using petroleum ether and hexane. The formed urea fertilizer microcapsules is dried in oven at 65^{o}C. Then, the particle size is analyzed using digital microscope.

Analysis of Raw Material

This analysis is aimed to find out the components used to calculate Reynold (Re) and Weber (We) numbers, that are viscosity and density of chitosan solution using viscometer Ostwald and picnometer. Interfacial tension analysis of vegetable oil and chitosan solution is measured by tensionmeter.

Determining the Size of Urea Fertilizer Microcapsules

The size of urea fertilizer microcapsules is analyzed by using Dino-Lite digital microscope with magnification of 500x. Diameter of urea fertilizer microcapsules is measured then multiplied with the result correction factors from digital microscope calibration. This calibration is conducted by comparing the diameter size of wire fibers measured with digital microscope and the real size. This study measured 100 urea fertilizer microcapsules and calculated the average of their diameter. Equation 1 is used to find out the average of diameter.

$$\bar{d} = \sum_{i=n}^{n} \frac{d_i}{N} \qquad (1)$$

d_i is diameter of each microcapsule, N is total number of microcapsules, and $\bar{d}$ is the average of microcapsules diameter.

Empirical Equation Model for Predicting the Size of Urea Fertilizer Microcapsules

To predict the size of urea fertilizer microcapsules, this study used equation model that is modification of equation reported by Jayanudin, et al [9]. Dimensionless numbers used in this study is Reynold (Re) and Weber (We) numbers. The correlation can be seen empirically in equation 2-4.

$$d_{avg} = K(We)^m (Re)^n \qquad (2)$$

$$Re = \frac{\rho .v.d_p}{\mu} \qquad (3)$$

$$We = \frac{\rho .v^2.\ d_p}{\sigma} \qquad (4)$$

The number of K, m and n in equation 2 is determined by using the smallest square (*least squares*). Below is the method used to find out constant number in equation 1.

$$d_{avg} = K(We)^m (Re)^n \qquad (2)$$

$$\log d_{avg} = \log K + m \log(We) + n \log(Re) \qquad (5)$$

By simplifying equation 5 to be:

$$Y = a + b.X + c.Z \qquad (6)$$

To find out the number of a, b, and c is as follows:

$$N.a + b\sum X_i + c\sum Z_i = \sum Y_i \qquad (7)$$

$$N\sum X_i + b\sum X_i^2 + c\sum Z_i X_i = \sum X_i Y_i$$

$$N\sum Z_i + b\sum Z_i X_i + c\sum Z_i^2 = \sum Z_i Y_i$$

Number of *a* = *K*, *b* = *m*, and *c* = *n* can be found by using matrix.

Microcapsules size that is found from calculation results using equation 2 is compared with the size of urea fertilizer microcapsules from reasearch data. The data of calculation results in this study will also be compared with the equation reported by Jayanudin, et al [9] as follows.

$$d_{avg} = 422,06(Oh)^{0,37}(Re)^{-0,18} \qquad (8)$$

Where:

d_{avg} = average diameter of microcapsules (μm)
ρ = mass density of chitosan (kg/m^3)
μ = viscosity of chitosan solution (N.s/m^2)
σ = interfacial tension of chitosan solution with oil phase (corn oil) (N/m)
v = stirring speed (m/s)
d_p, = diameter of the mixer (homogenizer) (m)
Re = Reynold numbers
We = Weber numbers
Oh = Ohnesorge numbers
K = Constant
m and *n* = rank value of dimensionless numbers

RESULTS AND DISCUSSION

The Influence of Chitosan Solution Concentration and Stirring Speed Towards the Size of Urea Microcapsules

The microcapsules size of urea fertilizer is analyzed by using digital microscope based on the concentration changes of chitosan solution and stirring speed shown in Fig. 1.

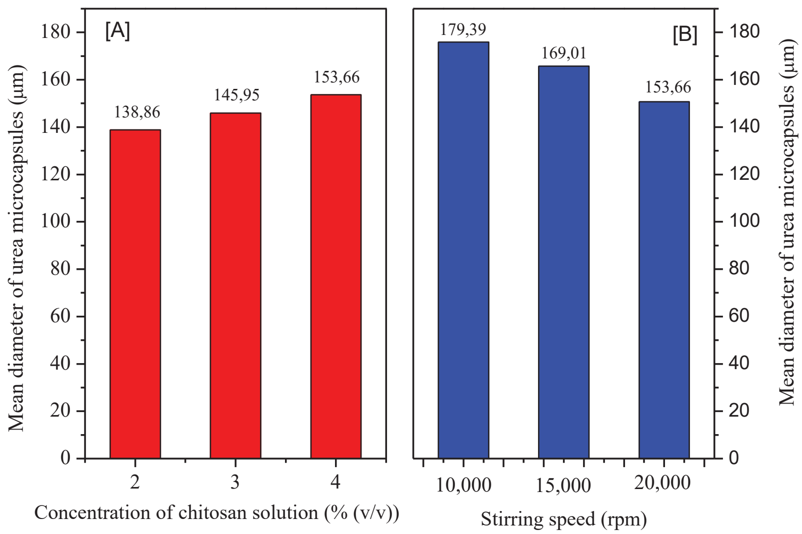

FIGURE 1. The influence of [A] chitosan solution concentration and [B] stirring speed towards the size of urea fertilizer microcapsules. For [A] using a stirring speed of 20,000 rpm, while [B] using 4% (w/v) concentration of chitosan solution

The average of microcapsules diameter found in this study is started from 138.86 μm to 179.39 μm. The concentration changes of chitosan solution did not give significant differences. The lowest diameter of urea microcapsules gained from 2% chitosan solution is 138.86 μm. For 4% (v/v) chitosan solution, the average diameter that is produced is around 153.66 μm. The increase of the chitosan solution concentration causes the increase of polymer viscosity in internal phase and it can form emulsions with large droplets. This droplet size influences the size of urea fertilizer microcapsules directly [8,11]. The same phenomenon is also reported by Jayanudin, et al [9] and Patel and Patel [12]. It shows that the increase of chitosan solution concentration influence the increase of microcapsules diameter.

The study conducted by Jayanudin, et al [8] found the size of microcapsules that is smaller than what is found in this study. For instance, in 4% (v/v) chitosan solution, stirred at 10,000 rpm, and 20 mL GST produce microcapsules in 161.42 μm. Meanwhile, this study got microcapsules in 179.39 μm. The difference is found because the continuous phase (oil) used in this study is 400 mL, that is higher than the previous study conducted by Jayanudin, et al [8], that is only 150 mL. Volume increasing in the continuous phase can make the diameter of microcapsules increase too because the higher volume of the continuous phase cause the faster polymer solidification process and irregular sedimentation process [13].

Stirring speed influences the stages of forming emulsions, mixed of urea fertilizer and chitosan in vegetable oil. The increasing of stirring speed makes emulsion droplets smaller because of the decreasing interfacial tension between chitosan solution and oil. Fig. 1 shows that at speed of 20,000 rpm produces smaller urea microcapsules diameter than at speed of 15,000 rpm and 10,000 rpm. The speed of 20.000 rpm produces the smallest microcapsules size than the speed of 15,000 rpm and 10,000 rpm, that is 153.66 μm.

Size Prediction of Urea Fertilizer Microcapsules

Microcapsules size is related to the large area for urea releasing process to environment. The size of microcapsules can be predicted by using empirical equation composed from dimensionless numbers. Parameters that influence microcapsules size are stirring speed, coating concentration (chitosan solution), interfacial tension, mixer diameter, etc. Those parameters can be found in Reynold (Re) and Weber (We) dimensionless numbers. Objects analysis data such as viscosity, density, and interfacial tensions are obtained from the study conducted by Jayanudin, et al [9]. It is because the previous study used the same parameters, while the different data is in stirring speed and mixer diameter. Table 1 shows that the data used to determine the empirical equation of dimensionless numbers.

To determine Weber numbers, the data needed here is interfacial tension between chitosan solution and oil. Interfacial tenson is related to emulsions stability. The increasing of interfacial tension can increase the emulsions stability as well. The other data that are needed is density of chitosan solution. This data is needed to determine Weber (We) and Reynold (Re) dimensionless numbers. Reynold (Re) numbers are related to the stirring speed, the increasing of stirring speed can increase Reynold (Re) numbers and size comminution of emulsion droplets [14].

TABLE 1. Data for determining empirical equation of dimensionless numbers

No	Strirring speed and concentration of chitosan solution (% v/v)	Density (ρ) (kg/m^3)	Viscosity (μ) (Ns/m^2)	Interfacial tension (σ) (N/m)	diameter of the stirrer (m)	Stirring speed (m/s)	Average diameter of microcapsules (d_{avg}) (μm)
1	kitosan 2%	998.3	0.111795	0.000580	0.012	12.56	138.864
2	kitosan 3%	1003.2	0.132951	0.000553	0.012	12.56	145.949
3	kitosan 4%	1004.6	0.141078	0.000333	0.012	12.56	153.658
4	10.000 rpm	1004.6	0.141078	0.000333	0.012	6.28	179.393
5	15.000 rpm	1004.6	0.141078	0.000333	0.012	9.42	169.011
6	20.000 rpm	1004.6	0.141078	0.000333	0.012	12.56	153.658

Data in Table 1 is used to determine empirical equation of dimensionless numbers for predicting diameter of microcapsules. Equation 2-7 is used to determine constant numbers of equation 2, that are the value of K, n, and m. Those constant can be determined by using least squares method (Equation 7). Calculation results show the value of K = 688.94, m = 0.059, and n = -0,346. Based on those contant numbers, equation 2 becomes:

$$d_{avg} = 688.94(We)^{0.059}(Re)^{-0.346} \quad (9)$$

Equation 8 is used to compare microcapsules size from this study findings with calculation based on concentration changes of chitosan solution and stirring speed that are shown on Fig. 2 and Fig. 3.

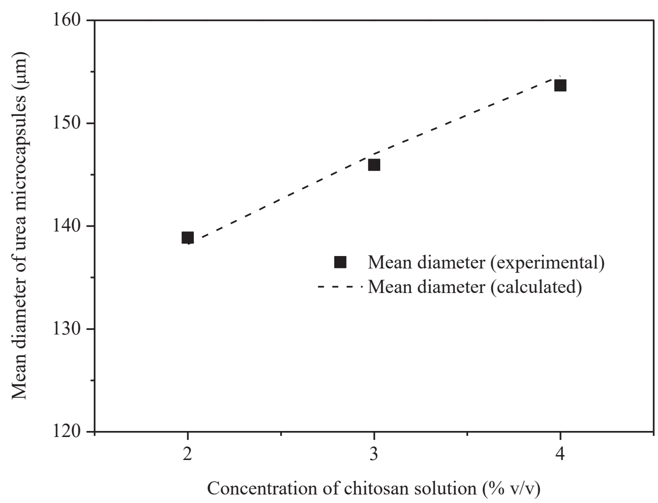

FIGURE 2. Comparation of the calculated average of microcapsules diameter ($d_{avg\ calculated}$) and experimental data ($d_{avg\ data}$) based on concentration changes of chitosan solution

Fig. 2 shows calculated diameter of urea fertilizer microcapsules using equation 9 and then be compared to the research data. Fig. 2 shows that calculated diameter for 3% (w/v) and 4% (w/v) chitosan solution is bigger, while in

2% (v/v) chitosan solution is smaller than what is found in reasearch findings. Nonetheless, the contrast is relatively small with the average of percent error is 0.58%. Fig. 2 shows that a good fitting between calculation result (Equation 9) and analysis of microcapsules diameter based on concentration changes of chitosan solution has been reached.

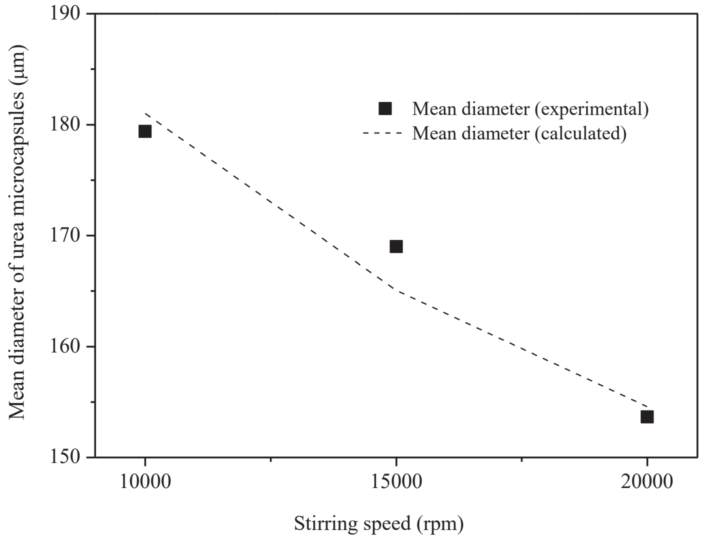

FIGURE 3. The calculation average of microcapsules diameter ($d_{avg\ calculated}$) compared to experimental data ($d_{avg\ data}$) based on changes of stirring speed

Fig. 3 shows the comparation of calculated diameter of urea fertilizer microcapsules using equation 9 with research data. The average deviation (% error) of Fig. 3 is relatively small, only 1.29%. The difference between calculated data and analysis of stirring speed at 10,000 rpm and 20,000 rpm is sufficiently small, 0.89% and 0.59%. Meanwhile, there is a bigger deviation for stirring speed at 15,000 rpm that is 2.4%.

Equation 9 shows that Reynold (Re) numbers have negative grade so that the increase of Reynold (Re) numbers can reduce microcapsules diameter. The increase of Reynold (Re) numbers is influenced by the increase of stirring speed. The speed also influences Weber (We) numbers, the more the speed increased the more Weber (We) numbers increased.

Empirical equation in this study is compared to the equation reported by Jayanudin, et al [9]. The comparation is applied to get the differences of diameter of urea fertilizer microcapsules based on concentration changes of chitosan solution as shown in Fig. 4.

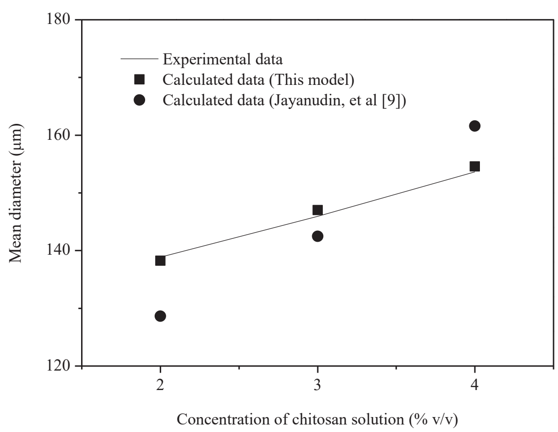

FIGURE 4. Comparation of empirical equation of dimentionless numbers that is conducted to predict diameter of microcapsules from this study with the result that is reported by Jayanudin, et al [9]

The equation 9 found in this study is then compared to the equation reported by Jayanudin, et al [9] to determine diameter of microcapsules based on concentration changes of chitosan solution. Picture 4 shows that the equation of this study indicates the goodness of fit than the model from Jayanudin, et al (2018). Percent error of this study is smaller at 0.58%, than the study conducted by Jayanudin, et al [9], that was 4% (w/v).

CONCLUSION

Empirical equations composed from Weber and Reynold dimensionless numbers are used to predict the size of urea fertilizer microcapsules. These equations focus on the influence of concentration changes of chitosan solution and the stirring speed. The diameter of urea fertilizer microcapsules taken from the calculation results of this method is then compared to research findings of microcapsules diameter in this study. The average of percent error (% error) is relatively low, only 0.58% for the influence of concentration changes of chitosan solution, whereas the changes of stirring speed is 1,29%. In short, this model is already good to predict the diameter size of urea fertilizer microcapsules.

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