JURNAL REKAYASA PROSES

Research article / Vol. 14, No. 2, 2020, pp. 189-197

Journal homepage: http://journal.ugm.ac.id/jrekpros

Simulation of Nitrogen Release from Chitosan/Local Organic Fertilizer Composite as Slow-Release Fertilizer

Alit Istiani[1,*], Yuni Kusumastuti[2,3*], dan Rochmadi[2]

[1]Department of Chemical Engineering, Faculty of Industrial Engineering, Universitas Pembangunan Nasional Veteran Yogyakarta
Jl. Ring Road Utara No.104, Yogyakarta, Indonesia 55283

[2]Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada
Jl Grafika No. 2 Kampus UGM, Yogyakarta, Indonesia 55281

[3]Bioresource Engineering Group, Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada,
Jl Grafika No. 2 Kampus UGM, Yogyakarta, Indonesia 55281

*Corresponding author: alit.istiani@upnyk.ac.id (A.I.) dan yuni_kusumastuti@ugm.ac.id (Y.K.)

(Submission: 3 October 2019; Revision: 30 August 2020; Acceptance: 1 September 2020)

A B S T R A C T

The application of conventional fertilizer, especially for inorganic fertilizer, has low efficiency due to the fast release of its nutrients into the environment. Also, it has a high operating cost caused by multiple fertilization processes in one of the planting periods. One of the possibilities to overcome this limitation is applying organic fertilizer as a slow-release fertilizer (SRF). The objective of this research is to prepare SRF by modifying the formulation of local organic fertilizer with chitosan as a binder. The rate of the nitrogen release was studied and simulated with MATLAB. The result shows that the nitrogen loss by water leaching decreased up to 85% in chitosan/organic fertilizer rather than the fertilizer without chitosan. By MATLAB simulation, the release of nitrogen has followed the proposed mathematical model in which the mass transfer occurred dominated by diffusion mechanism with the diffusivity coefficient of 1.61×10^{-5} cm^2/s.

Keywords: chitosan; organic fertilizer; slow-release fertilizer

A B S T R A K

Penggunaan pupuk anorganik masih memiliki efisiensi rendah yang disebabkan oleh cepatnya pelepasan nutrisi pupuk ke lingkungan sehingga nutrisi tersebut tidak dapat terserap baik oleh tanaman. Selain itu, aplikasi pupuk anorganik yang berulang dalam satu periode tanam berdampak pada peningkatan biaya operasional. Salah satu metode untuk mengatasi permasalahan tersebut adalah dengan menggunakan pupuk lepas lambat (slow-release fertilizer) atau dengan menggunakan pupuk organik. Tujuan pada penelitian ini adalah dengan

DOI: 10.22146/jrekpros.50341

Published online: 31 December 2020
e-ISSN 2549-1490 p-ISSN 1978-287X

mengombinasikan dua metode tersebut yaitu dengan memodifikasi formulasi dari pupuk organik lokal dengan penambahan kitosan sehingga dapat diperoleh pupuk organik yang memiliki sifat lepas lambat. Laju pelepasan nitrogen dari pupuk yang dihasilkan kemudian dianalisis dan disimulasikan dengan software MATLAB. Hasil penelitian menunjukkan bahwa nitrogen yang hilang pada komposit pupuk organik-kitosan melalui water leaching menurun hingga 85% jika dibandingkan dengan komposit pupuk organik tanpa kitosan. Hasil simulasi MATLAB juga menunjukkan bahwa laju pelepasan nitrogen pada pupuk mengikuti model matematika yang diusulkan yaitu dengan mekanisme difusi, nilai koefisien difusivitas yang diperoleh adalah sebesar $1{,}61\times10^{-5}$ *cm*^{2}*/s.*

Kata kunci: *kitosan; pupuk lepas lambat; pupuk organik*

1. Introduction

The extensive use of inorganic fertilizer has a side effect on the environment due to the fast release of its nutrients. Some researchers state that inorganic fertilizer has a low nitrogen use efficiency and high nitrogen loss (Zhang et al., 2018). In addition, the nitrogen which is absorbed by the plant is only about 0-50%, and the rest is leached out and accumulated into the environment (Mózner et al., 2012; Wang et al., 2018). Consequently, it decreases the soil quality, increases the greenhouse gas emission, causes eutrophication and water contamination which affect to the human health (Chen et al., 2010; Liu et al., 2013; Smith and Siciliano, 2015; Uphoff and Dazzo, 2016; Zhang et al., 2017). Furthermore, the application of inorganic fertilizer needs high-cost labor due to several times of fertilization usage in one cycle of planting periods (Zhang et al., 2018).

Increasing interest on the environmental issue due to the fast release of inorganic fertilizer, enhances researchers develop the advance sustainable technologies such as controlled-release fertilizer, crop rotation or intercropping, organic-inorganic fertilizer, organic fertilizer, and recycled agriculture (França et al., 2018; Jannoura et al., 2014; Kusumastuti et al., 2019; Wang et al., 2018; Zhao et al., 2016). The sustainable environment could be created through the usage of organic fertilizer because it releases nutrition slower than conventional fertilizer (Fairhurst, 2012). Furthermore, it could improve the soil fertility, increase the organic matter availability in soil and reduce the crop residue (Hui et al., 2017; Khaliq et al., 2006; Wang et al., 2018).

Organic fertilizer can be categorized as slow-release fertilizer (SRF). This condition is in accordance with the definition of SRF by the Association of American Plant Food Control Officials (AAPFCO). Slow-release fertilizer can provide the nutrient longer than conventional fertilizer; thus, the fertilization process can be conducted only once at the beginning of the planting period and can reduce the operation cost (Trenkel, 2010). There are some methods to produce slow-release fertilizer, such as adding a chemical compound, coating with inert material, and formulating with matrix material (Trinh and Kushaari, 2016). From all the methods, formulating with a matrix is the most natural technique and has low production costs (Al-Zahrani, 1999; Purnomo et al., 2018). Instead of the matrix, a binder is a component which affects nutrient release. The binder can hold other material and decrease the pores of the composite thus retaining the nutrient release (Al-Zahrani, 1999; Purnomo et al., 2018). Some materials can be used as fertilizer binders such as either organic or inorganic. Apart from that, chitosan is an organic material that has a potential as a binder. Some studies said that chitosan as a coating material on NPK fertilizer was able to decrease the nitrogen release and improve its mechanical strength (Kusumastuti et al., 2019). Chitosan is a polysaccharide which consists of glucosamine and N-acetyl glucosamine with β1-4 glycosidic bonding (Mardyaningsih et al., 2014; Rinaudo, 2006). It is available abundantly in nature and can be produced from deacetylated chitin. Moreover, chitosan is a non-toxic material and can be degraded in the environment (Akmaz et al., 2013).

The objective of this research is to prepare chitosan/local organic fertilizer composite as a slow-release fertilizer and then compare the nutrient release for both organic and chitosan/local organic fertilizer with chitosan solution as a binder. The mechanisms of the nitrogen release from SRF fertilizer will be investigated with the diffusion approach and the result will be compared to some empirical equation to obtain the suitable mathematical model for the nitrogen release.

2. Research Methodology

2.1 Materials

A simple mixture of manure and organic compost which obtained from local fertilizer production (Solo, Indonesia) was used as a raw material for organic fertilizer. Local Indonesian chitosan powder (>90% degree of deacetylation, 10-500 cps, <1.5% ash content, <0,5% protein content) was purchased from PT. Biotech Surindo (Cirebon, Indonesia). Glacial acetic acid was purchased from Merck (Germany). The Kjeldahl analysis used potassium sulfate (K_2SO_4), cuprum (II) sulfate ($CuSO_4$), sulphuric acid (H_2SO_4), sodium hydroxide (NaOH) and chloric acid which purchased from Merck (Germany). Local commercial organic SRF "Vedagro" was used with specifications: the average diameter of 3.36–4.0 mm with composition 10-12% Nitrogen, 2-3% P_2O_5 and 3-3.5% K_2O, respectively.

2.1 Procedures

A simple mixture of manure, organic compost, and limestone was added into a pan granulator with the addition of 1% chitosan solution with a ratio of 30:1 (w/v). The chitosan solution was used as a binder while the limestone as a matrix. The resulting fertilizer was sieved with 5-6 mesh, thus obtained the average diameter of 3.36–4.0 mm. The nitrogen release test was conducted by immersing 1 gram of fertilizer in 100 mL aquadest for 5 hours. The accumulative nitrogen release in water was analyzed every hour by the Kjeldahl method. The release kinetics was approached with a diffusion mechanism and simulated with MATLAB software to obtain the diffusion coefficient. The sample identification is shown in Table 1.

Table 1. Sample Identification

Sample ID	Preparation method
S1	Organic fertilizer with chitosan binder
S2	Organic fertilizer without chitosan binder
S3	Local commercial organic SRF "Vedagro"

2.2 Mathematical Modelling

The kinetic of nitrogen release from the fertilizer composites is approached by the diffusion mechanism, where it is considered as diffusion in a solid particle. The nitrogen mass transfer is occurred by diffusion in a radial direction. With the arrangement of the mass balance equation in the volume element of fertilizer as shown in Figure 1, the mathematical model of nitrogen release can be proposed as shown in Equation (1).

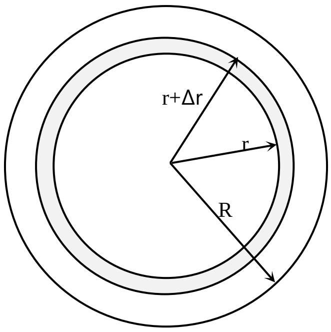

Figure 1. Volume element of solid fertilizer

$$\frac{\partial Ca}{\partial t} = De\left(\frac{\partial^2 Ca}{\partial r^2} + \frac{2}{r}\frac{\partial Ca}{\partial r}\right) \quad (1)$$

with the boundary condition as follows:

$t=0$	$t=t$	$t=t$
$r=r$	$r=0$	$r=R$
$Ca = Cas$		

The maximum nitrogen concentration ($\frac{\partial Ca}{\partial r} = 0$)

$De\frac{\partial Ca}{\partial r}|_R = k(\frac{Ca|_R}{H} - Cal)$

where Ca is the nitrogen concentration in the fertilizer granules (gram/cm^3), C_{as} is the initial nitrogen concentration in fertilizer granules (gram/cm^3), C_{al} is the nitrogen concentration in aquadest (gram/cm^3), De is the diffusion coefficient (cm^2/s), t is the time (s), and r is the particle radius (cm).

Cal is a function of time and can be correlated with the mass total of nitrogen which correspond to number of particle (N_b), volume of solution (W), and volume of one granular fertilizer (V_b) as shown in Equation (2). With the resulting data from the experiment, all equations are solved and simulated by the MATLAB program.

$$Cal = \frac{N_b}{W}(Cas.V_b - 4\pi\int_0^R Ca\, r^2\, dr) \quad (2)$$

To obtain the suitable model of nitrogen release, the proposed mathematical model was also compared with some empirical equation for nutrients release behavior of fertilizer such as:

a. Zero order kinetics model (Sempeho et al., 2014).
   In this model, the nutrients release is assumed constant by the time and there is no equilibrium. The model has been useful for the release of nutrients from the matrix that do not disaggregate and release the nutrient slowly. This model is expressed as Equation (3).

$$Qo\text{-}Qt = Ko\ t \quad (3)$$

   Qo is initial nutrient concentration in the solution, Qt is the nutrient concentration in solution at any time, Ko is the zero order release constant, t is the time.

b. Diffusion-relaxation model (Bi et al., 2020; Saigusa and Ombodi, 2014; Upadrashta et al., 1993).
   This model is expressed as Equation (4).

$$\frac{M_t}{Mload} = k_1\, t^m + k_2\, t^{2m} \quad (4)$$

   where M_t is the release nitrogen at time t, M_{load} is the loading nitrogen in fertilizer, m is the diffusional exponent of 0.5 (for spherical shape), k_1 is associated with diffusion, and k_2 is associated with relaxation.

c. Diffusion-erosion model (Bi et al., 2020; Saigusa and Ombodi, 2014; Upadrashta et al., 1993).
   This model is expressed as Equation (5).

$$\frac{M_t}{Mload} = a\, t^{0.5} + b\, t + c\, t^2 + d\, t^3 \quad (5)$$

   where M_t is the release nitrogen at time t, M_{load} is the loading nitrogen in fertilizer, a is associated with diffusion, b, c, and d is associated with erosion.

3. Results and Discussion

In this research, the release of nitrogen as one of the main fertilizer contents were observed. Due to its wide application in the agriculture area, nitrogen becomes the yield-limiting nutrient release of fertilizer (Fageria, 2014). The result of nitrogen release test which was carried out in 100 mL aquadest is shown in Figure 2.

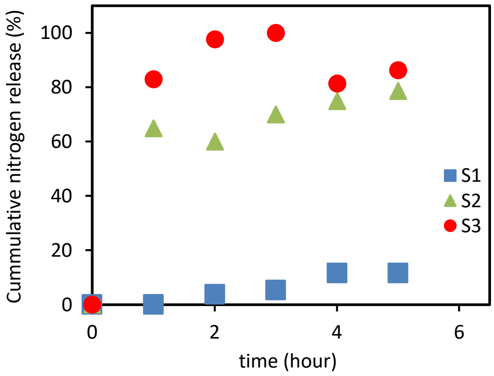

Figure 2. Effect of chitosan matrix on the release of nitrogen

It shows that among all the samples, chitosan/organic fertilizer (S1) has the slowest release of nitrogen. In the first three hours, the amount difference of the nitrogen release is significant where the S1 fertilizer released only 5% of the total nitrogen in the fertilizer, while the S2 and S3 release 70% and 100%, respectively. Macro-images of S1 fertilizer during the immersion in aquadest were presented in Figure 3. It showed that the longer the immersion time, the color of the solution was darker than the initial one, which represented the addition of nitrogen content in the aquadest. Also, the results showed that chitosan addition as a binder decreased 85% of nitrogen loss due to the existing intramolecular hydrogen bonding between the chitosan molecules. Thus, the pores of fertilizer became smaller, and it might retain the nutrient release (Lee et al., 2013; Mati-baouche et al., 2014).

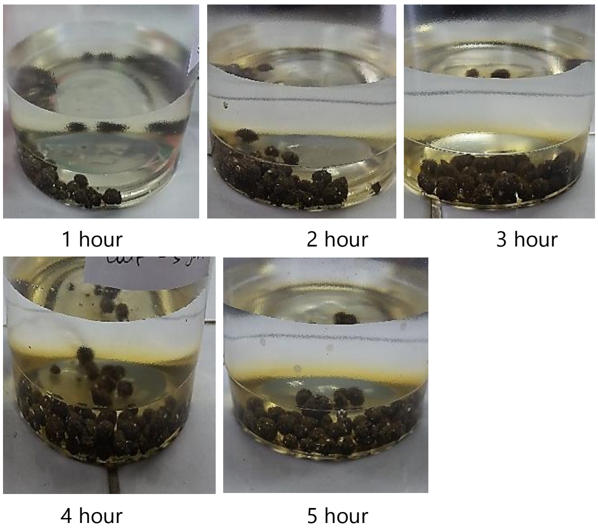

Figure 3. The appearance of nitrogen release test on chitosan/organic fertilizer (S1) during the water immersion

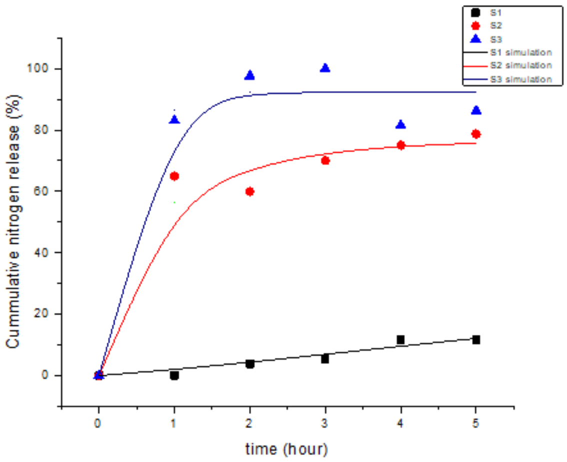

Figure 4. MATLAB simulation of nitrogen release with proposed mathematical model

The mathematical model of nitrogen release was simulated using MATLAB software. Diffusion model for nitrogen through the solid is assumed to diffuse radially. The result of the simulation in Figure 4 shows that the proposed mathematical model follows the experimental data. Therefore, it can be concluded that the nitrogen release of the prepared fertilizer followed the diffusion mechanism with the value of diffusion coefficient (*De*) obtained are shown in Table 2.

Table 2. Calculated diffusion coefficient from the MATLAB simulation

	S1	S2	S3
De [cm^2/s]	1.61x10^{-5}	2.88x10^{-3}	1.13x10^{-2}
Sum square error (SSE)	1.91x10^{-15}	4.46x10^{-16}	6.97x10^{-23}

Diffusion coefficient (*De*) value describes how fast the nitrogen could diffuse in the fertilizer. The smaller of *De* value, the slower the rate of diffusion will be. Therefore, it can be concluded that chitosan as binder was able to decrease the nitrogen release rate of the prepared fertilizer. This result can also be compared to a previous experiment reported by Kusumastuti et al. (2019) which conducted a layer-by-layer method of chitosan coating in NPK fertilizer and obtained the *De* value of 4.5747×10^{-6} cm^2/s, similar to the obtained *De* in this research. Comparing with the *De* values in the solid (1×10^{-7} cm^2/s or smaller) and liquid phase (1×10^{-5} cm^2/s), the obtained diffusion coefficient value in S1 fertilizer is still out of the range from the diffusion coefficient in the solid phase. It might be due to the less homogenous chitosan distribution in fertilizer granule.

The simulation result of nitrogen release with some empirical equation is shown in Figure 5 where the constant value is shown in Table 3. From Figure 5 a, b and c, the nitrogen release data follow the diffusion-relaxation and diffusion-erosion model rather than zero order kinetic model. The constant value of S1 in the diffusion-relaxation model shows that k_1 (associated with diffusion) is smaller than k_2 (associated with relaxation). Thus, chitosan addition contributes to the relaxation release mechanism. Here, the mass transfer occurred could be associated with stresses and state transition in hydrophilic-glassy polymer which can swell in the water (Peppas and Sahlin, 1989; Upadrashta et al., 1993).

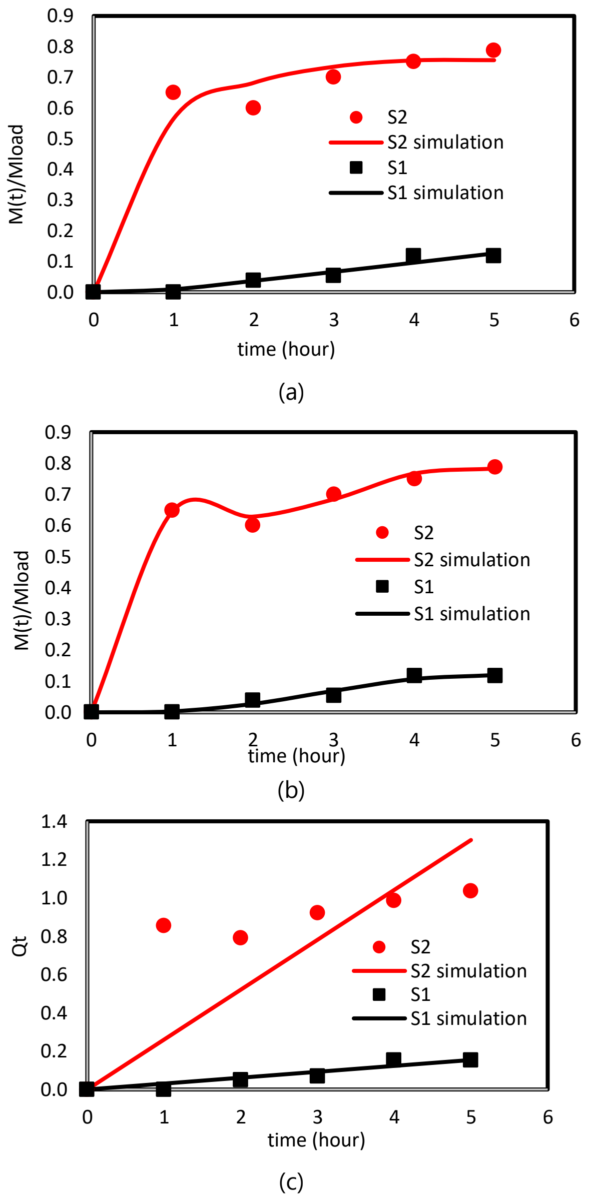

Figure 5. MATLAB simulation of nitrogen release with model of (a) Diffusion-relaxation (b) Diffusion-erosion (c) Zero order kinetic

Table 3. Simulation result of diffusion-relaxation model, diffusion-erosion model and zero order kinetics model

Model	Diffusion-Relaxation			Diffusion-Erosion					Zero Order	
Sample	k_1	k_2	SSE	*a*	*b*	*c*	*d*	SSE	*Ko*	SSE
S1	-0.036	0.0456	6.95×10^{-4}	0.0402	-0.0669	0.0337	-0.0038	4.77×10^{-4}	0.0308	0.0025
S2	0.7529	-0.1871	0.0137	1.746	-1.3258	0.2444	-0.0208	0.0013	0.2604	0.518

In the diffusion-erosion model, constant a is associated with diffusion where *b, c* and *d* are associated with the erosion. Comparing the constant value, the erosion constant is much smaller than the diffusion constant; thus, the nutrient release is dominated by the diffusion mechanism. The SSE value of the proposed mathematical model also confirmed that the nitrogen release also followed the diffusion mechanism.

4. Conclusions

Adding chitosan as a binder in the organic fertilizer formulation was able to decrease the release of nitrogen by water leaching thus the nitrogen loss decreased up to 85%. In addition, the simulation of proposed mathematical model and empirical model shows that nitrogen release from composite fertilizer is dominated by diffusion mechanism. The obtained diffusion coefficient from the proposed model is 1.61×10^{-5} cm^2/s.

Acknowledgements

The authors gratefully acknowledge the financial support provided by the International Foundation for Science (IFS) Grantee number J-3-F-6014-1 belongs to Dr Yuni Kusumastuti as a grantee.

References

Akmaz, S., Dilaver, E., Ad, J., Yasar, M. and Erguven, O., 2013, The effect of Ag content of the chitosan-silver nanoparticle composite material on the structure and antibacterial activity, Adv. Mater. Sci. Eng., 2013, 12–18.

Al-Zahrani, S.M., 1999, Controlled-release of fertilizers: modelling and simulation, Int. J. Eng. Sci., 37, 1299–1307.

Bi, S., Barinelli, V. and Sobkowicz, M.J., 2020, Degradable controlled release fertilizer composite prepared via extrusion: Fabrication, characterization, and release mechanisms, Polymers, 12, 301.

Chen, X., Wo, F., Chen, C. and Fang, K., 2010, Seasonal changes in the concentrations of nitrogen and phosphorus in farmland drainage and groundwater of the Taihu Lake region of China, Environ. Monit. Assess., 169, 159–168.

Fairhurst, T., 2012, Handbook for Integrated Soil Fertility Management, Africa Soil Health Consortium, Nairobi.

França, D., Fracon, Â., Luiz, L. and Souza, C.F., 2018, Chitosan spray-dried microcapsule and microsphere as fertilizer host for swellable−controlled release materials, Carbohydr. Polym., 196, 47–55.

Hui, L.I., Wen-ting, F., Xin-hua, H.E., Ping, Z.H.U., Hong-jun, G.A.O., Nan, S.U.N. and Ming-gang, X.U., 2017, Chemical fertilizers could be completely replaced by manure to maintain high maize yield and soil organic carbon (SOC) when SOC reaches a threshold in the Northeast China Plain, J. Integr. Agric., 16 (4), 937–946.

Jannoura, R., Georg, R. and Bruns, C., 2014, Organic fertilizer effects on growth, crop yield, and soil microbial biomass indices in sole and intercropped peas and oats under organic farming conditions, Eur. J. Agron., 52, 259–270.

Khaliq, A., Abbasi, M.K. and Hussain, T., 2006, Effects of integrated use of organic and inorganic nutrient sources with effective microorganisms (EM) on seed cotton yield in Pakistan, Bioresour Technol., 97, 967–972.

Kusumastuti, Y., Istiani, A. and Purnomo, C.W., 2019, Chitosan-based polyion multilayer coating on NPK fertilizer as controlled release fertilizer, Adv. Mater. Sci. Eng., 2019, 2958021

Lee, D.W., Lim, C., Israelachvili, J.N. and Hwang, D.S., 2013, Strong adhesion and cohesion of chitosan in aqueous solutions, Langmuir, 29 (46) 14222–14229

Liu, C., Li, F., Zhou, L., Zhang, R., Lin, S., Wang, L., Siddique, K.H.M., et al., 2013, Effect of organic manure and fertilizer on soil water and crop yields in newly-built terraces with loess soils in a semi-arid environment, Agric. Water Manag., 117, 123–132.

Mardyaningsih, M., Leki, A. and Rerung, O.D., 2014, Pembuatan kitosan dari kulit dan kepala udang laut perairan kupang sebagai pengawet ikan teri segar, Jurnal Rekayasa Proses, 8 (2), 69–75.

Mati-baouche, N., Elchinger, P., Baynast, H. De, Pierre, G., Delattre, C. and Michaud, P., 2014, Chitosan as an adhesive, Eur. Polym. J., 60, 198–213.

Mózner, Z., Tabi, A. and Csutora, M., 2012, Modifying the yield factor based on more efficient use of fertilizer — The environmental impacts of intensive and extensive agricultural practices, Ecol. Indic., 16, 58–66.

Peppas, N. and Sahlin, J., 1989, A simple equation for the description of solute release. III. Coupling of diffusion and relaxation, International J. Pharm., 57, 169–172.

Purnomo, C.W., Respito, A., Sitanggang, E.P. and Mulyono, P., 2018, Slow-release fertilizer preparation from sugarcane industrial waste, Environ. Technol. Innov., 10, 275–280.

Rinaudo, M., 2006, Chitin and chitosan: Properties and applications, Prog. Polym. Sci., 31, 603–632.

Saigusa, M. and Ombodi, A., 2020, Broadcast application versus band application of polyolefin-coated fertilizer on green peppers grown on andisol, J. Plant Nutr., 23 (10), 1485-1493

Sempeho, S.I., Kim, H.T., Mubofu, E. and Hilonga, A., 2014, Meticulous overview on the controlled release fertilizers, Advances in Chemistry, 2014, 363071

Smith, L.E.D. and Siciliano, G., 2015, A comprehensive review of constraints to improved management of fertilizers in China and mitigation of diffuse water pollution from agriculture, Agriculture, Ecosyst. Environ., 209, 15-25

Trenkel, M.E., 2010, Slow- and Controlled-Release and Stabilized Fertilizers: An Option for Enhancing Nutrient Use Efficiency in Agriculture, 2nd ed., International Fertilizer Industry Association (IFA), Paris, France.

Trinh, T.H. and Kushaari, K., 2016, Dynamic of water absorption in controlled release fertilizer and its relationship with the release of nutrient, Procedia Eng., 148, 319–326.

Upadrashta, S.M., Katikaneni, P.R., Hileman, G.A. and Keshary, P.R., 1993, Direct compression-controlled release tablets using ethyl cellulose matrices, Drug Dev. Ind. Pharm., 19 (4), 449–460.

Uphoff, N. and Dazzo, F.B., 2016, Making rice production more environmentally friendly, Environments, 3 (2), 12.

Wang, Y., Zhu, Y., Zhang, S. and Wang, Y., 2018, What could promote farmers to replace chemical fertilizers with organic fertilizers?, J. Clean. Prod., 199, 882–890.

Zhang, M., Tian, Y., Zhao, M., Yin, B. and Zhu, Z., 2017, The assessment of nitrate leaching in a rice – wheat rotation system using an improved agronomic practice aimed to increase rice crop yields, Agriculture, Ecosyst. Environ., 241, 100–109.

Zhang, M., Yao, Y., Tian, Y., Ceng, K., Zhao, M., Zhao, M. and Yin, B., 2018, Field crops research increasing yield and N use efficiency with organic fertilizer in Chinese intensive rice cropping systems, F. Crop. Res., 227 102–109.

Zhao, J., Ni, T., Li, J., Lu, Q., Fang, Z. and Huang, Q., 2016, Effects of organic – inorganic compound fertilizer with reduced chemical fertilizer application on crop yields, soil biological activity and bacterial community structure in a rice – wheat cropping system, Appl. Soil Ecol., 99, 1–12.