Prosiding Seminar Nasional Teknik Kimia “Kejuangan”
Pengembangan Teknologi Kimia untuk Pengolahan Sumber Daya Alam Indonesia
Yogyakarta, 18 Maret 2015

ISSN 1693-4393

Kinetic Model of Urea Desorption from a Starch-Based Controlled Release Fertilizer

Kennedy, Herry Santoso*, Judy Retti Witono, Yohanes Herjanto, dan Evan Susanto

Jurusan Teknik Kimia, Fakultas Teknologi Industri, Universitas Katolik Parahyangan
Jalan Ciumbuleuit No. 94, Bandung 40141, Indonesia

**E-mail*: hsantoso@unpar.ac.id

Abstract

The use of fertilizer has increased as the agriculture become more intensified. This increment caused a lot of environmental issue, such as water and soil pollution. It is well-known that conventional fertilizer does not have a good efficiency in practice due to fertilizer leaching or washing off problem. This problem can now be significantly minimized by using a controlled release system. There are a lot of models that have been used to study controlled release drugs, but only a few are used to describe controlled release fertilizers. In this study, we propose a simple model to represent urea desorption from a starch-based controlled release fertilizer and then use the model to predict the urea desorption characteristics of the fertilizer. The controlled release fertilizer was made from starch-based hydrogel loaded with urea. The urea desorption from the starch-based controlled release fertilizer in the water is then tested. The kinetic data collected from the urea desorption experiment is used to derive, verify, and validate the kinetic model of urea desorption from the starch-based controlled release fertilizer.

Keywords: *starch-based hydrogel, controlled release fertilizer, kinetic model, urea desorption.*

Introduction

Fertilizer is any material, solid or liquid, which is added to soil to supply one or more nutrients essential for the proper development and growth of a plant (Gowariker, et al, 2009). Lack or excess in nutrient is not good for the plant. One of the common fertilizers is urea in granular form. Urea is an odorless and colorless crystal with 45-46% nitrogen (Lingga and Marsono, 2008). However, only 30-50% of nitrogen can be absorbed by the plants. The excess is washed into the groundwater and rivers, which causes water and soil pollution. Further pollution can cause degradation in soil quality such as decrement in microorganism and worm quantity (. For that, a solution is needed to increase the efficiency in the use of urea fertilizer (Martodireso and Suryanto, 2007).

Controlled release is a method that release or deliver a compound in a response of time (Jamnongkan and Kaewpirom, 2010). This method firstly practiced in medical field to optimize the dosage, to minimize the cost and toxic effect, and to increase the drugs overall efficiency. In agriculture field, this method is used to make a controlled release fertilizer. The advantages in this method are (1) to minimize the effect of excess fertilizer, (2) to decrease the operational cost, (3) to release the fertilizer directly to the root of the plants, (4) to decrease the fertilizer loss, and (5) to decrease water and soil pollution (Han, et al, 2008).

Hydrogel is a three dimensional macromolecule polymer matrix which has a hydrophilic character. It can absorb water multiple times from its dry weight and its volume can expand significantly. A common hydrogel is made from a natural material, e.g. starch, so it can be biologically degraded. A good hydrogel has some criteria: (1) it can hold fertilizer in large amount, (2) it can release the fertilizer periodically, (3) it can hold the fertilizer for a long time, and (4) it can keep the soil moisture and control soil erosion (Bortolin, et al, 2011).

Modeling is a process to make a model that represents a set of experimental data, so that the model can describe the system’s characteristics (Bender, 2000). From an existing model, we expect to know the characteristic of the same system in different variation without doing the experimental procedure. Modeling nowadays is greatly demanded to reduce the experimental cost. There are a lot of model to describe the controlled release systems in medical field, but only a few describe the controlled release fertilizer.

In this paper, an urea controlled release fertilizer will be made from starch hydrogel and the urea release data will be collected from desorption experiment. A simple mathematical model is then developed to represent the controlled release fertilizer system.

Methodology

Experimental

The experiment has three main stages: (1) hydrogel synthesis, (2) fertilizer adsorption, and (3) fertilizer release. Hydrogel is synthesized by grafting reaction, using 10%-weight starch in 1 kg of mixture, heated to 70^{o}C in aquadest while stirred for 25 minutes in no-oxygen reactor. The mixture is then cooled to 40^{o}C before 37.2 ml acrilic acid is added. After 5 minutes, 0.585 g of Ferro Ammonium Sulfate (FAS) is added, followed by 0.51 g of H_2O_2 2 minutes later. The reaction occurs for 2 hours before a variety of methylenbisacrilamide (MBAm) is added. After 20 minutes, 2 ml of NaOH is added, followed by 2 ml of 0.1 M hydroquinone 20 minutes later. The reaction is finished 10 minutes later (Witono, et al, 2012).

The formed copolymer is then washed using 80% acetone, with the amount of 4 times of copolymer’s weight. The washing process is done 3 times, then the copolymer is dried using an oven at 60^{o}C until the weight is constant. The dried copolymer is then crushed to -60+80 mesh (Witono, et al, 2012).

The adsorption process is done by soaking the hydrogel in 1 L urea solution (10,000 ; 15,000 ; 20,000 ; 30,000 ppm). The solution concentration is analyzed at a particular time interval by spectrophotometry method using Ehrlich reagent. The hydrogel is then dried until the weight is constant (Liang, et al, 2008) .

The release process is done by soaking the urea-containing hydrogel in 1 L of water. The solution concentration is then analyzed at a particular time interval by spectrophotometry method using Ehrlich reagent until the concentration is constant (Wijaya, 2014).

Model

Desorption is the inverse of adsorption, the release of a molecule, ion, or particle, which was adsorbed by the adsorbent from a solvent. In equilibrium state, the desorption rate is equal to adsorption rate. Desorption kinetics can be approached by adsorption kinetics, for example by using pseudo first-order model. This kinetic model was the first invented model to describe solid-liquid adsorption kinetic. The pseudo first order model can be written as equation 1.

$$\frac{dq_t}{dt} = k_{p1}\,(q_e - q_t) \qquad (1)$$

where:

- q_e is the adsorption capacity in equilibrium (mg/g).
- q_t is the adsorption capacity at time t (mg/g).
- t is the time (minute).
- k_{p1} is the pseudo first order model parameter.

The model parameter estimation is done to estimate the value of the unknown parameter in the model equation. The unknown parameter in this equation is k_{p1}. The k_{p1} parameter is estimated using 2 sets of data from the experimental result. The appropriate value of k_{p1} is obtained by minimizing the sum of square of the error between the experimental data of q_t and the value of q_t estimated by the model using a particular value of k_{p1}. This optimization problem can be solved easily using any numerical optimization solver (e.g. in MATLAB we can use ‘fminseach’ command). The value of q_t estimated by the model using the model using a particular value of k_{p1} can be calculated by solving Equation (1) using any numerical ordinary differential equation solver (e.g. in MATLAB we can use ‘ode23s’ command).

The model validation is done by substituting the value of k_{p1} calculated above into Equation (1) and then solving it using any numerical ordinary differential equation solver. The value of q_t estimated by the model using the value of k_{p1} is then checked against the other 2 sets of experiment data in order to determine whether the model is valid or not.

Result and Discussion

The experiment is done by varying the initial solution concentration in adsorption process, i.e. 10,000; 15,000; 20,000; 30,000 ppm, and the cross-linker (MBAm) fraction, i.e. 1.5% and 2.5%. The corresponding urea release data from the desorption experiment is shown in **Table 1** and **Table 2**. The solution concentrations keep increasing because the urea is moving from the hydrogel to the solution.

Table 1. Concentration of solution with 1.5% cross-linker and various initial adsorption concentrations.

Time (s)	Solution Concentration (ppm)			
	10,000 ppm	**15,000 ppm**	**20,000 ppm**	**30,000 ppm**
0	0	0	0	0
25	467.3810	394.8224	384.5001	436.2195
55	519.5352	529.9991	436.2195	529.9991
80	498.6406	550.9599	519.5352	550.9599
110	509.0824	561.4569	593.0147	582.4843
200	519.5352	550.9599	582.4843	571.9650
920	519.5352	561.4569	571.9650	571.9650

Table 2. Concentration of solution with 2.5% cross-linker and various initial adsorption concentrations.

Time (s)	Solution Concentration (ppm)			
	10,000 ppm	**15,000 ppm**	**20,000 ppm**	**30,000 ppm**
0	0	0	0	0
25	241.1033	292.0789	261.4621	281.8628
55	322.7904	415.4993	456.9829	509.0824
80	488.2098	540.4739	436.2194	593.0147
110	529.9990	593.0147	446.5957	582.4842
200	593.0147	602.5563	593.0147	614.1091
920	582.4842	582.4242	603.5563	624.6732

Figure 1 shows the comparison between the experimental data and the model estimation. There are 2 sets of data in each cross-linker variation used to estimate the k_{p1} parameter, i.e. for the 1.5% cross-linker, the initial concentration of 10,000 ; 15,000 ppm. From **Figure 1**, it can be seen that the experimental data and the model estimation are close to each other. The value of k_{p1} for the model is -0.0627.

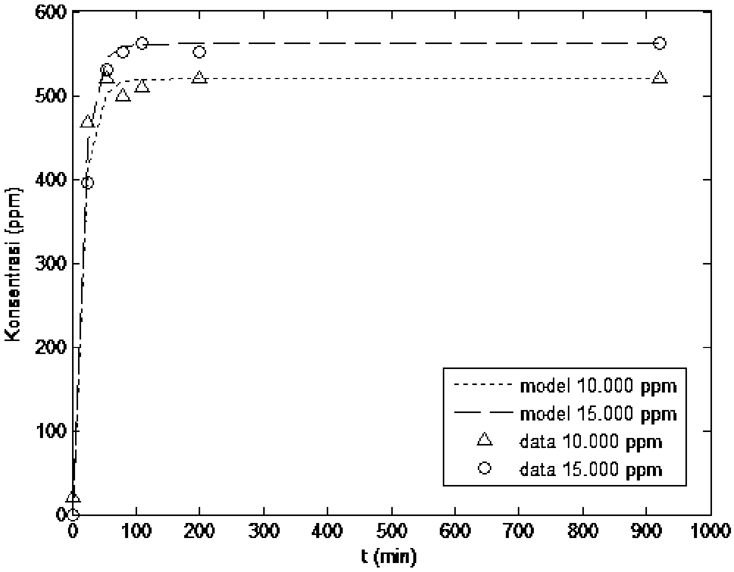

Figure 1. Parameter k_{p1} estimation for initial concentration of 10,000 and 20,000 ppm with 1.5% cross-linker

The k_{p1} value of -0.0627 is validated using the other 2 sets of data, i.e. for the 1.5% cross-linker, the initial concentration of 20,000 ; 30,000 ppm. **Figure 2** shows the comparison between the experimental data and the model estimation using the k_{p1} value of -0.0627. From **Figure 2**, the data and the model is alike. This means the k_{p1} value can represent all the concentration variations in the 1.5% cross-linker experiment. Thus, we can say that the value of k_{p1} is not a function of the initial urea concentration.

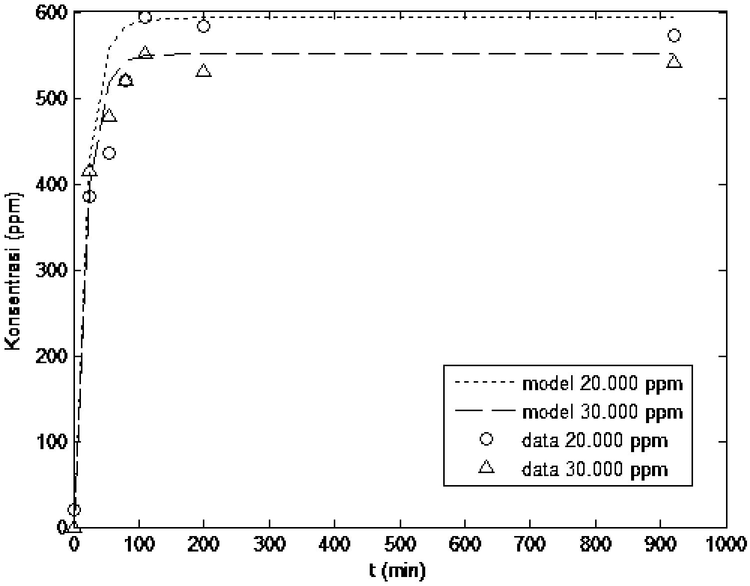

Figure 2. Parameter k_{p1} (-0.0627) validation for initial concentration of 20,000 and 30,000 ppm with 1.5% cross-linker

The k_{p1} value of -0.0627 is also tested against the 2.5% cross-linker experiment data. The result is shown in **Figure 3**. From **Figure 3**, it can be seen that the model prediction is tend to deviate from the experiment data. This means the k_{p1} value estimated from the 1.5% cross-linker experiment cannot represent the data in 2.5% cross-linker experiment. The k_{p1} value estimated from the 1.5% cross-linker experiment is significantly larger than the actual k_{p1} value for 2.5% cross-linker experiment.

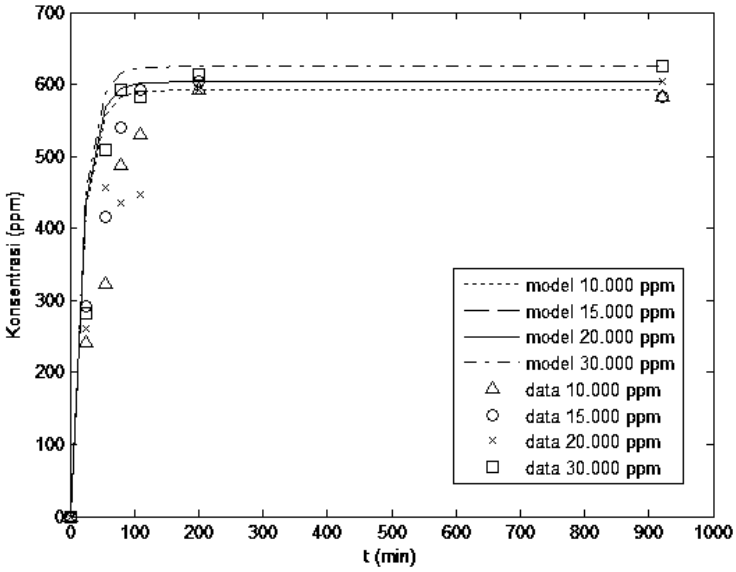

Figure 3. Parameter k_{p1} (-0.0627) validation for initial concentration of 10,000; 15,000; 20,000; and 30,000 ppm with 2.5% cross-linker

The parameter estimation for the 2.5% cross-linker is done using 2 sets of data from the the 2.5% cross-linker desorption experiment, i.e. with the initial concentration of 10,000 and 15,000 ppm. **Figure 4** shows that the experimental data and model is alike. As expected, the value of k_{p1} is -0.0216, which is smaller than the value of k_{p1} obtained from the 1.5% cross-linker desorption experiment.

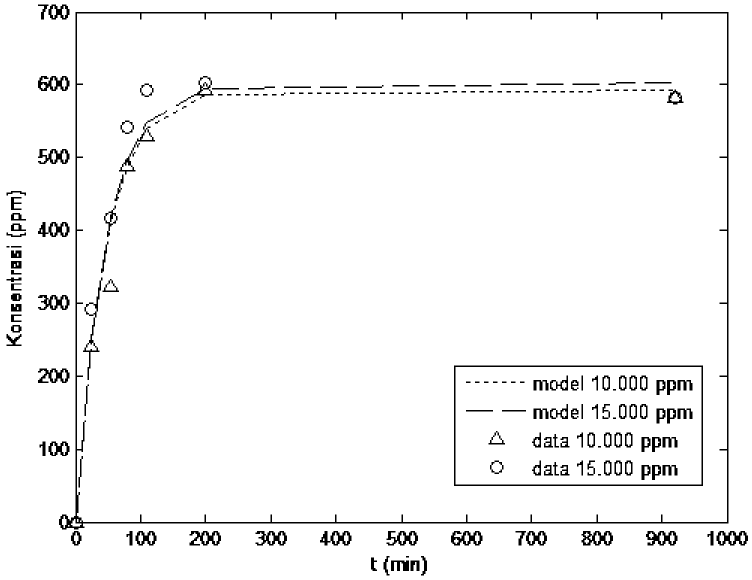

Figure 4. Parameter k_{p1} estimation for initial concentration of 10,000 and 15,000 ppm with 2.5% cross-linker

The k_{p1} value of -0.0216 is then validated using the other 2 sets of data, i.e. for the 2.5% cross-linker, the initial concentration of 20,000 and 30,000 ppm. **Figure 5** shows the comparison between the experimental data and model estimation using k_{p1} value of -0.0216.

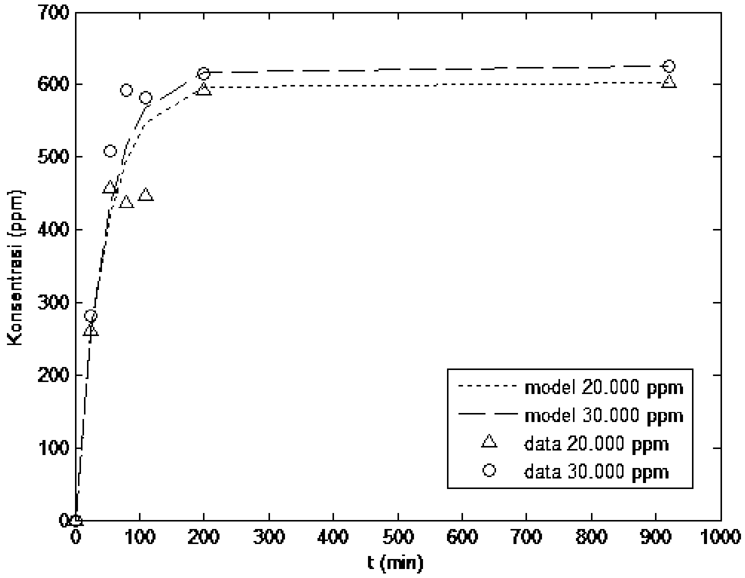

Figure 5. Parameter k_{p1} (-0.0216) validation for initial concentration of 20,000 and 30,000 with 2.5% cross-linker

The k_{p1} value for 1.5% cross-linker is -0.0627, and for 2.5%cross-linker is -0.216. These show that k_{p1} is a function of cross-linker percentage, where the more cross-linker in a hydrogel, the more effective the hydrogel ability to retain or hold the urea entrapped in it, thus the longer time is needed for the urea to be released to the environment.

Conclusion

The controlled release fertilizer modeling can be done using a pseudo first order kinetics model. The parameter k_{p1} in this experiment is not a function of concentration, but a function of cross-linker percentage. The value of k_{p1} for 1.5% cross-linker is -0.0627 and for 2.5% cross-linker is -0.0216. In general, the pseudo first order model is able to describe the controlled release fertilizer’s desorption characteristic. The more cross-linker in the hydrogel, the more ability the hydrogel has to retain or hold the urea entrapped in it. This property might be desired in order to increase the efficiency of using a controlled release fertilizer.

Reference

Bender, E. A., 2000, *An Introduction to Mathematical Modeling*, Dover Publication, New York.

Bortolin, A., et al, 2011, Application of Polysacchatide Hydrogels in Adsorption and Controlled-Extended Release of Fertilizer Processes, *J. of Applied Polymer Sci., 123, 2291-2298.*

Gowariker, V., et al, 2009, *The Fertilizer Encyclopedia*, John Wiley & Sons, New Jersey.

Han, X., et al, 2008, Controlled-release Fertilizer Encapsulated by Starch/Polyvinyl Alcohol Coating, *j. Desalination*, 240, 21-26.

Jamnongkan, T. and Kaewpirom, S., 2010, Controlled-Release Fertilizer Based on Chitosan Hydrogel: Phosphorus Release Kinetics, *Sci. J. UBU, 1, 43-50.*

Liang, R., 2008, Synthesis of Wheat Straw-g-poly(acrylic acid) Superabsorbent Composites and Release Urea from it, *Carbohydrate Polymers*,77, 181-187.

Lingga, P., and Marsono, 2008, *Petunjuk Penggunaan Pupuk*, Penebar Swadaya, Jakarta.

Martodireso, S., 2007, *Terobosan Teknologi Pemupukan dalam Era Pertanian Organik*, 6th ed., Kanisius, Yogyakarta.

Wijaya, L., 2014, Pengembangan Controlled-Release Fertilizer Berbasis Pati Ganyong, *Bachelor Essay*, Universitas Katolik Parahyangan, Bandung, Indonesia.

Witono, J., R., 2012, Graft Copolymerization of Acrylic Acid to Cassava Starch-Evaluation of the Influences of Process Parameters by An Experimental Design Method, *Carbohydrate Polymer*, 90, 1522-1529.

Lembar Tanya Jawab

Moderator : Didi Dwi Anggoro (Universitas Diponegoro Semarang)
Notulen : Susanti Rina Nugraheni (UPN "Veteran" Yogyakarta)

1. Penanya : Didi Dwi Anggoro (Teknik Kimia Universitas Diponegoro Semarang)

Pertanyaan :
- Disini bagian mana yang dimodelkan?
- Kenapa ada konstanta bernilai (-) ?

Jawaban :
- Saat air menggenang (saat pengairan berhenti)
- Pada saat adsorpsi dqt/dt=kp1(qe-qt) saat desorpsi jangan mengubah persamaan (persamaan jangan dibalik)