

RESEARCH ARTICLE | FEBRUARY 09 2018

Adsorption of saturated fatty acid in urea complexation: Kinetics and equilibrium studies

Dwi Ardiana Setyawardhani; Hary Sulisty; Wahyudi Budi Sediawan; Mohammad Fahrurrozi



AIP Conf. Proc. 1931, 030013 (2018)

<https://doi.org/10.1063/1.5024072>



CrossMark

Articles You May Be Interested In

Kinetic and equilibrium studies of stearic acid adsorption in urea complexation

AIP Conference Proceedings (April 2019)

The effect of heating surface treatment by oxy-acetylene gas on the microstructure and hardness of the UIC R42 rail

AIP Conference Proceedings (May 2023)

Development of Google Sites-based blended learning media on linier program material mathematics subjects

AIP Conference Proceedings (June 2023)

500 kHz or 8.5 GHz?
And all the ranges in between.

Lock-in Amplifiers for your periodic signal measurements



Find out more



Adsorption of Saturated Fatty Acid in Urea Complexation: Kinetics and Equilibrium Studies

Dwi Ardiana Setyawardhani^{1, 2, a)}, Hary Sulisty^{2, b)}, Wahyudi Budi Sediawan^{2, c)},
and Mohammad Fahrurrozi^{2, d)}

¹Chemical Engineering Department, Sebelas Maret University, Jl. Ir. Sutami 36A, Surakarta 57126, Indonesia
²Chemical Engineering Department, Gadjah Mada University, Jl. Grafika 2, Kampus UGM, Yogyakarta, Indonesia

^{a)} Corresponding author: dwi_ardiana@yahoo.com

^{b)} hary@ugm.ac.id

^{c)} wbsediawan@ugm.ac.id

^{d)} mfahrurrozi@ugm.ac.id

Abstract. Urea complexation is fractionation process for concentrating poly-unsaturated fatty acids (PUFAs) from vegetable oil or animal fats. For process design and optimization in commercial industries, it is necessary to provide kinetics and equilibrium data. Urea inclusion compounds (UICs) as the product is a unique complex form which one molecule (guest) is enclosed within another molecule (host). In urea complexation, the guest-host bonding exists between saturated fatty acids (SFAs) and crystalline urea. This research studied the complexation is analogous to an adsorption process. The Batch adsorption process was developed to obtain the experimental data. The ethanolic urea solution was mixed with SFA in certain compositions and adsorption times. The mixture was heated until it formed homogenous and clear solution, then it cooled very slowly until the first numerous crystal appeared. Adsorption times for the kinetic data were determined since the crystal formed. The temperature was maintained constant at room temperature. Experimental sets of data were observed with adsorption kinetics and equilibrium models. High concentration of saturated fatty acid (SFA) was used to represent adsorption kinetics and equilibrium parameters. Kinetic data were examined with pseudo first-order, pseudo second-order and intra particle diffusion models. Linier, Freundlich and Langmuir isotherm were used to study the equilibrium model of this adsorption. The experimental data showed that SFA adsorption in urea crystal followed pseudo second-order model. The compatibility of the data with Langmuir isotherm showed that urea complexation was a monolayer adsorption.

INTRODUCTION

Poly-Unsaturated Fatty Acids (PUFAs) such as omega-3, omega-6 and omega-9 are essential fatty acids that should be consumed through food. They play very important role for brain development of infants and preventing degenerative diseases, such as cancer, atherosclerosis and cardiovascular problems [1-3]. Fish oil was potential feedstock used for producing omega fatty acids. Nowadays, plant lipids are alternatively promising resource which could be developed in oleo-chemical industries.

Urea complexation is a fractionation process for splitting Saturated Fatty Acids (SFAs) from fatty acids mixtures which also contain PUFAs and mono-unsaturated fatty acids (MUFAs). To concentrate the PUFAs from plant lipids or vegetable oil, urea complexation is a process that can be considered to apply in commercial scale, due to the moderate and environmentally-friendly operation-condition, and also inexpensive renewable materials for the wetting agent [4].

Urea inclusion compounds (UICs) are guest-host bonding molecules with hexagonal channel known as clathrate. UICs is a form with two interlocking components through hydrogen and Van der Waals bonding. In this bond it is commonly known the term "host" for its crystal molecule, and "guest" for the molecule that enters into the crystal. SFAs have straight, long chain molecules with smaller diameter compared to unsaturated fatty acids whose kinked long-chain molecules and bigger diameters. Due to the limited size of the channel, only smaller molecules with diameter less than 5.8 Å could enter into the channel, forming crystalline urea inclusion compounds. Therefore, the SFAs molecules may be adsorbed into the channel, leaving the MUFAs and PUFAs molecules in the liquid phase.

Given that UICs are similar to gas hydrate in terms of host-guest molecule formation, the urea inclusion equilibrium model can also be approximated by the hydrate equilibrium model. Under equilibrium conditions, the chemical potential of the solute in the crystal phase is equal to the chemical potential of the solute in the solution phase. This is in accordance with the Van der Waals equation and it can be written as:

$$\Delta\mu_u^s(T, P) = \mu_u^\beta - \mu_u^s = \mu_u^\beta - \mu_u^l = \Delta\mu_u^l(T, P) \quad (1)$$

$$\Delta\mu_u^s(T, P) = -RT \sum_{i=1}^2 v_i \ln \left(1 - \sum_{j=1}^{N_c} \theta_{ij} \right) \quad (2)$$

where v_i represented the number of i -type cavities, the θ_{ij} was the fractional occupancy of i -type cavity with j -type guest molecule. Chemical potential of urea in the solid and liquid phase on certain pressure and temperature were presented as $\Delta\mu_u^s$ and $\Delta\mu_u^l$ respectively. This study takes the assumption that cavity types are hexagonal ($i = 1$), and guest molecules are only SFA ($j = 1$). Thus the equation (2) for hydrate becomes:

$$\Delta\mu_u^h(T, P) = -RT \ln(1 - \theta) \quad (3)$$

The relationship between the fractional occupancy fraction with the SFA fugacity at equilibrium can be written in the form of the equation:

$$\theta = \frac{C.f}{(1 + C.f)} \quad (4)$$

where C was the equilibrium constant and f was SFA fugacity in the crystal phase. Equation (4) was identical with the Langmuir isotherm equation for adsorption.

The formation process of clathrate compounds is identical with the formation of urea complex / inclusion compounds, so it was possible to predict that the complexation was the analogous process to an adsorption of solutes into the adsorbents. Urea acts as an adsorbent for the SFAs molecules in a urea complexation mixture. No previous research studied urea complexation on fatty acids separation as an adsorption mechanism. This research observed the kinetics and equilibrium model to determine the compatibility of data with this hypothesis.

MATERIALS AND METHODS

For representing SFA adsorption from fatty acids mixture, we used high purity Palmitic Acid (PA) as the single solute, instead of PA obtained from vegetable oil hydrolysis as usual. PA from Merck has $\geq 98\%$ purity was utilized without further purification. Urea pro-analyze grade with $\geq 99\%$ purity from Merck was applied as the adsorbent. For the wetting agent, commercial food grade ethanol supplied by local producers was used. Hydrochloric acid and anhydrous disodium sulphate were all from Merck used for the solute purification. Then commercial n-hexane was the extracting solvent for urea-PA separation.

The batch adsorption process was developed to obtain the experimental data. The ethanolic urea solution was made in 13.83 mole ratio of ethanol to urea. The solution was mixed with PA in certain compositions of urea/PA (1.5; 2 and 4 w/w) ratios. The mixture was heated until it formed homogenous and clear solution, then it cooled very slowly until the first numerous crystal appeared. Adsorption times for the kinetic data were determined since the crystal formed. The temperature was maintained constant at room temperature.

The urea complexation mixture consisted of two phases, namely non-urea complexed fraction (NUCF) and the urea complexed fraction (UCF), then was separated by filtration. Each phase was purified with the procedure suggested by Wanasundara & Shahidi [5]. The pure SFAs resulted from the UCF and NUCF then was weighed in analytical balance. These data were used for mass fraction calculation divided by the initial SFAs in the solution. Experimental sets of data were observed with adsorption kinetics and equilibrium models to provide the rate adsorption constants and the equilibrium parameters. Kinetic data were examined with pseudo first-order, pseudo second-order and intra particle diffusion models. Freundlich, Langmuir and Linier isotherm were used to study the equilibrium model of this adsorption.

RESULTS AND DISCUSSIONS

Batch adsorption was conducted in a solution which contained ethanolic urea and PA. For preliminary investigation, it showed that the adsorption took place very rapidly, exhibited on more than 60% removal of PA at first 15 minutes. Then it went slower until the equilibrium reached of about 150 minutes on all urea/PA ratios. It could be understood that the “adsorption” occurred spontaneously, as it was already known in urea complexation phenomenon. Adsorption rate of urea/PA ratio 2 and 4 almost have no differences. So, it was considered that the optimum urea/PA ratio was 2 and no more urea needed to be added as adsorbent.

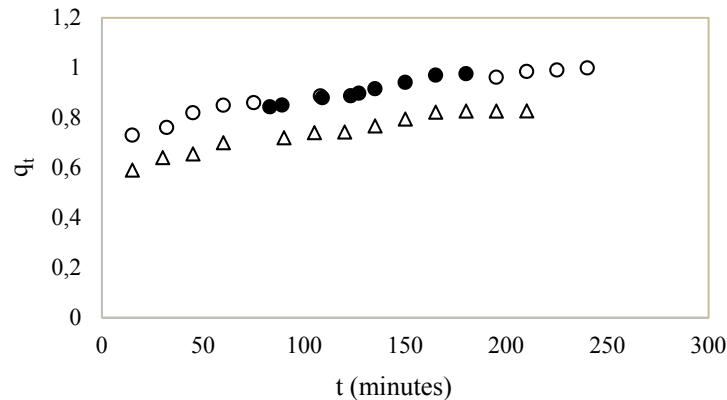


FIGURE 1. Adsorption times effect on PA removal in urea/PA ratio: 1.5 (Δ); 2 (●); 4 (○)

To determine the adsorption rate for the experiment, adsorption kinetics was investigated in three kinetic models: pseudo first-order, pseudo second-order and intra particle diffusion [6]. The models can be represented as the following equations on Table 1.

TABLE 1. Adsorption rate constants for various urea/PA ratio

Model	Equation
Pseudo first-order	$\log(q_e - q_t) = \log q_e - \frac{k_1 \cdot t}{2.303}$
Pseudo second-order	$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}$
Intra particle diffusion	$q_t = K_d \sqrt{t} + I$

Mass fraction of PA adsorbed at certain and equilibrium times represented as q_t and q_e (dimensionless). The pseudo first-order adsorption rate constant (k_1) was determined from plotting the adsorption time (t) of 15-225 minutes against $\log(q_e - q_t)$. The gradient of linear curve indicated the adsorption rate constant (k_1). The rate constants for the pseudo

second-order (k_2) and intra particle diffusion (K_d) were obtained from plotting (t/q_t) against t and q_t against \sqrt{t} , respectively.

For the various urea/PA ratio, Fig. 2 showed that more adsorbent (bigger urea/PA ratio) increased the adsorption rate constant k_1 . It means that more adsorbent provides faster adsorption. However, this model was not appropriate to describe pseudo first-order model for urea/PA ratio of 4.

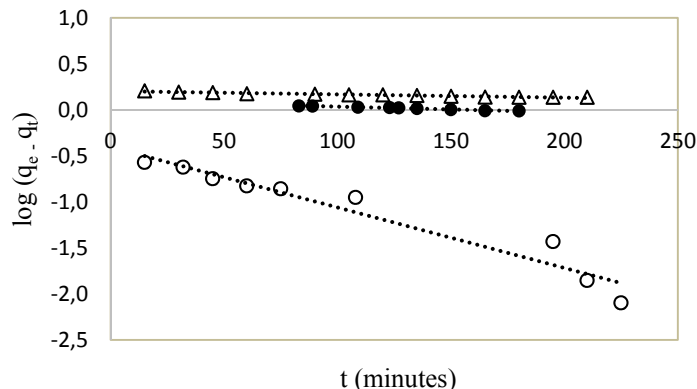


FIGURE 2. Pseudo first-order model for the fatty acid (FA) adsorption in urea/PA ratio: 1.5 (Δ); 2 (\bullet); 4 (\circ)

Compared with the first model, better compatibility was shown in Fig. 3. The plotting of t/q_t against t , as the pseudo second-order model, extremely fit the data in all urea/PA ratios ($R^2 > 0.99$). So, it indicated that urea complexation followed pseudo second-order kinetic model. This model suggested chemisorption mechanism on the adsorption process, where it involved valency forces through the exchange of electrons between adsorbent (urea) and the adsorbate (PA) [7]. The parameters of this model was listed in Table 2.

TABLE 2. Adsorption rate constants for various urea/PA ratio

Urea/P A ratio	Pseudo first-order		R^2	Pseudo second-order		R^2	Intra particle Diffusion		R^2
	k_1	q_e		k_2	q_e		K_d	I	
1.5	0.0009	1.6029	0.9610	0.0800	0.8721	0.9954	0.0230	0.5041	0.9808
2.0	0.0014	1.2505	0.9801	0.0270	1.1442	0.9950	0.0326	0.5400	0.9742
4.0	0.0152	0.3966	0.9386	0.0780	1.0372	0.9985	0.0266	0.6540	0.9834

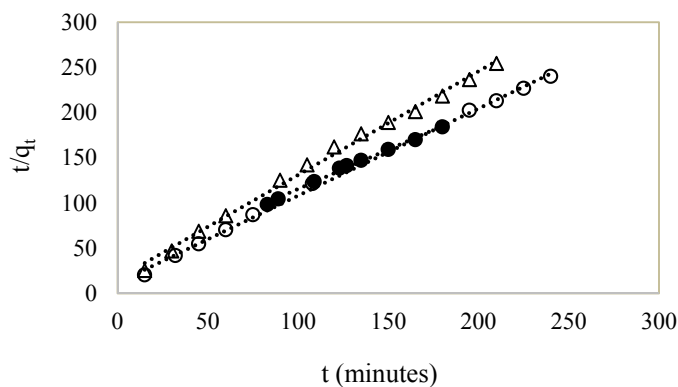


FIGURE 3. Pseudo second-order model for the fatty acid (FA) adsorption in urea/PA ratio: 1.5 (Δ); 2 (\bullet); 4 (\circ)

Figure 4 showed the plotting of q_t against \sqrt{t} for the intra particle diffusion model. It can be seen that there were almost no differences between urea/PA ratio for 2 and 4. As shown on the Table 2 on the value of R^2 , this model provide bigger discrepancies than pseudo second-order model. So, we conclude that the pseudo second-order was the most suitable for describing urea complexation as an adsorption process.

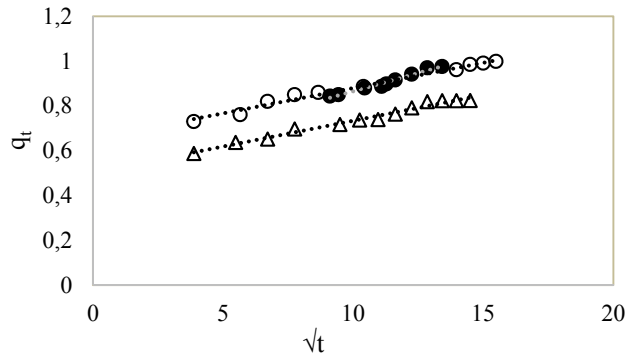


FIGURE 4. Intra particle diffusion model for the fatty acid (FA) adsorption in urea/PA ratio: 1.5 (Δ); 2 (\bullet); 4 (\circ)

The adsorption equilibrium was determined by fitting the data on adsorption isotherm. Linier, Freundlich and Langmuir model were determined to provide the most suitable isotherm, which was defined by the smallest value of R^2 . The equilibrium equations were shown on TABLE 3. Palmitic acid concentration in the liquid and solid phase are presented as C_e and Q_e respectively. Q_{\max} was the maximum concentration of PA in the solid phase. Then K_L , K_f and n indicate the Langmuir and Freundlich constants.

TABLE 3. Adsorption equilibrium equation for urea complexation

Model	Equation
Linier	$Q_e = kC_e$
Freundlich	$Q_e = k_f C_e^n$
Langmuir	$Q_e = Q_{\max} \frac{K_L C_e}{1 + K_L C_e}$

The visualization of adsorption equilibrium was shown on Fig. 5-7. Langmuir model showed the best fitting of all, represented by the smallest deviation between the data and model.

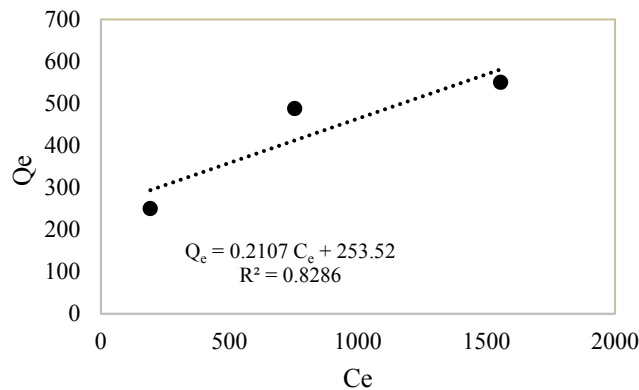


FIGURE 5. Linier isotherm for PA adsorption

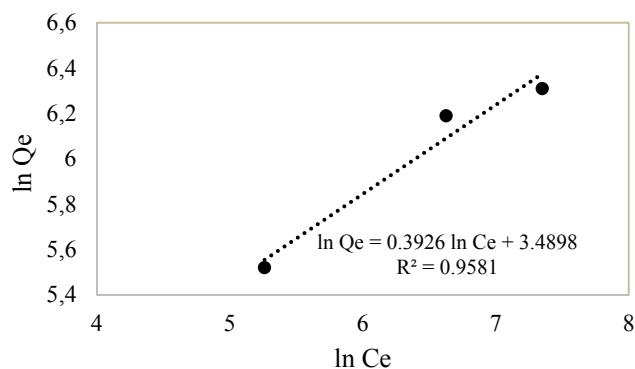


FIGURE 6. Freundlich isotherm for PA adsorption

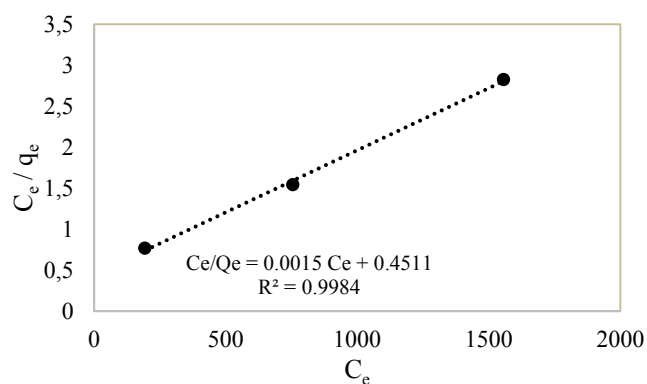


FIGURE 7. Langmuir isotherm for PA adsorption

Table 4 summarized the equilibrium parameters of the three models. Langmuir provided the best fitting for describing adsorption equilibrium of urea complexation. The suitability of Langmuir isotherm indicated that the including of PA molecules into urea channel was monolayer adsorption, wherein each site can only accommodate one molecule. This was supported by the results of earlier research. As mentioned on some previous research about urea complexation, PA builds UIC with urea in the composition of 12.6 moles urea for each mole of PA [8]. It means that every 12.6 moles of urea serve one site to be occupied by one molecule of PA.

TABLE 4. Adsorption equilibrium parameters for various urea/PA ratio

Urea/ PA ratio	Linier		Freundlich	Langmuir		Qmax mg/g	Kl L/mg	Kf	n
	Ce (mg/L)	Qe (mg/g)	Ce / Qe	ln Qe	ln Ce				
4	192.453	249.750	0.771	5.520	5.260	666.667	0.003	32.779	2.547
2	754.717	488.000	1.547	6.190	6.626				
1.5	1555.849	550.288	2.827	6.310	7.350				
R ²	0.8286		0.9951		0.9984				

CONCLUSIONS

Urea complexation could be described as an adsorption process. More urea added provided more PA adsorbed into the adsorbent. The adsorption kinetics followed pseudo second-order model and the Langmuir isotherm was the most suitable model with the adsorption equilibrium.

REFERENCES

1. I.S. Newton, "Long Chain Fatty Acids in Food and Nutrition", in [Omega -3 Fatty Acids, Chapter 2, ACS Symposium Series](#) Vol.788 (2001), pp.14-27.
2. W.S. Harris, D. Mozaffarian, E. Rimm, P.K. Etherton, L.L. Rudel, L.J. Appel, M.M. Engler, M.B. Engler and F. Sacks, American Heart Association, **119**, 902-907 (2009).
3. H. Poudyal, S.K. Panchal, V. Diwan and L. Brown, [Progress in Lipid Research](#) **50**, 372-387, 2011.
4. D.G. Hayes, 2006, "Purification of Free Fatty Acids via Urea Inclusion Compounds", in *Handbook of Functional Lipids*, edited by C.C. Akoh, (CRC Press, Taylor & Francis Group, Boca Raton, 2006), pp. 77-85.
5. U.N. Wanasundara and F. Shahidi, F., [Food Chemistry](#) **65**, 41-49 (1999).
6. D.D. Do, *Adsorption Analysis: Equilibria and Kinetics* (Imperial College Press, London, 1998), p. 211.
7. P.D. Saha, S. Chowdury, S. Datta and S.K. Sanyal, [Korean J. Chem. Eng.](#) DOI : 10.1007/s11814-011-0300-5, 1-8 (2011).
8. H. Schlenk, and R.T. Holman, "Separation and Stabilization of Fatty Acids by Urea Complexes", *Contribution from the Dept. of Biochemistry and Nutrition*, Texas Agricultural Experiment Station, Texas Agricultural and Mechanical College System, College Station, **72**, 5001-5004 (1950).