Article

Mathematical Modelling of Micronutrient Recovery from Vegetable Oil by Silica-based Adsorption: Vitamin E from Palm Fatty Acid Distillate

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Abstract. Mathematical modelling on kinetics of batch adsorption of vitamin E separation from palm fatty acid distillate (PFAD) has been set-up and then applied for literature experimental data. Since the sizes of adsorbent particles used are usually relatively small, the concentration in the particles is assumed to be uniform. Hence, the adsorption rate is controlled by the rate of solute mass transfer from the bulk fluid to the surface of particles. In this model, the rate of mass transfer is assumed to be proportional to the concentration deviation from the equilibrium state. Meanwhile, the equilibrium models applied were coefficient distribution, Freundlich, and Langmuir with the values of the parameters obtained from literature data. It turned out that the model set-up can quantitatively describe the experimental kinetics data from literature. The value of mass transfer coefficient per unit adsorbent mass ($k_c a$) is obtained by curve fitting. It is also observed that the model proposed quantitatively describes the batch adsorption process well. The three equilibrium models applied are suitable for the mathematical modelling. Adjustment of the values of equilibrium isotherm parameters from literature significantly improves the accuracy of the model.

Keywords: adsorption, mathematical modeling, micronutrient, palm fatty acid distillate, vegetable oil.

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1. Introduction

Adsorption involves the mass transport of an adsorbate from a liquid or gas phase, and its accumulation on the adsorbent surface. Based on the interaction between adsorbate and adsorbent, there are two types of adsorption, which are physi-sorption and chemi-sorption (Treybal, 1981). This adsorption method is known to be a promising technique for separation due to the ease of operation, comparable low cost of application, high-quality of the treated effluents especially for well-designed sorption processes (Mahmoud, 2012).
The quantitative understanding of adsorption process is an important aspect of process design in chemical industries and regarded as a practicable separation method for purification. Adsorptive capacity is in the domain of equilibrium, while diffusional resistance is in the domain of kinetics (Do, 1998). In actual operations, maximum capacity of adsorbents cannot be fully utilized because of mass transfer effects involved in fluid-solid contacting processes. Information on adsorption equilibrium will provides maximum adsorption capacity and kinetics analysis based on rate processes is essential in order to calculate actual adsorption capacity (Suzuki, 1990).
In spite of application in waste water treatment processes, adsorption is involved in bleaching or de-colorization in the vegetable oil refining industries. It also had reported that adsorption can be applied to recover valuable components such as carotene and tocopherols (vitamin E) from vegetable oils. Experimental studies on vitamin E adsorption from palm fatty acid distillate (PFAD) in batch and its equilibrium (Chu, et.al., 2004a), its kinetics (Chu, et.al., 2004b), as well as the desorption (Chu, et.al., 2004c) have been conducted. Quantitative description of the adsorption equilibrium and kinetics of vitamin E separation needs to be further investigated for the purposes of engineering process design and operations. Hence, in this study, those literature data is further analyse to obtain quantitative description of the process as well as to approximate the values of the parameters involved. The proposed quantitative models consider the mass transfer of solute from the liquid to the surfaces of adsorbent and the adsorption equilibrium. Since the size of the adsorbent particles is relatively small, the intra particle gradient is assumed to be negligible.

2. Objective

The objectives of this study are to quantitatively describe the batch adsorption in stirred tank and to verify the results with the experimental data from the literature (Chu, et.al. 2004). The quantitative description is expected to be useful for engineering design and optimization process as well as analysis of the similar processes.

3. Theoretical Development

Adsorption takes place with suspended adsorbent particles in a vessel when adsorbate is transported from the bulk fluid phase to the adsorbent particles. The concentration in the particles is assumed to be uniform because of the sizes of adsorbent particles used are relatively small. Hence the adsorption rate is controlled by the rate of solute mass transfer from the bulk fluid to the surface of adsorbents.
Basic equations for batch adsorption in a liquid stirred vessel consist of a set of mass balance in the bulk fluid, mass balance in the adsorbent particle, and solid-fluid equilibrium correlation.
It is considered, a specific amount of adsorbent suspended in the vessel of liquid volume, V, and solute concentration, C_A. Mass balance in the bulk liquid is given by equation (1).

$$\frac{dC_A}{dt} = -\frac{k_c A_S N_b}{V}(C_A - C_A^*) \quad (1)$$

In those equation, N_b is particles number per unit of adsorbent mass and A_s is the surface area of each particle. If a is the surface area per unit of adsorbent mass, then equation (1) becomes equation (2)

$$\frac{dC_A}{dt} = -k_c a \frac{m}{V}(C_A - C_A^*) \quad (2)$$

in which $k_c a$ is the mass transfer coefficient per unit of adsorbent mass.
Mass balance of adsorbate in the adsorbent can be written as:

$$\frac{dx_A}{dt} = k_c a(C_A - C_A^*) \quad (3)$$

The equilibrium isotherms correlating the solute concentration in the bulk of fluid (C_A^*) and the solute loading on the adsorbent (x_A) are listed in Table 1 (Seader, 2011).

Table 1. Formulas of Equilibrium Isotherm Models

Model	Equation	
Langmuir	$x_A = \frac{K_L C_A^*}{1+a_L C_A^*}$	(4)
Freundlich	$x_A = K_F (c_A^*)^{\frac{1}{n_F}}$	(5)
Distribution Coefficient	$x_A = K_d C_A^*$	(6)

The proposed mathematical models are verified using the experimental data from the literature. The experimental data applied are from Chu, et.al, 2004 on vitamin E adsorption from palm fatty acid distillate (PFAD).

If $k_c a$ value and the equilibrium equation are available, the concentrations in the fluid phase and the amounts of solute adsorbed at various time can be calculated. Hence, if the experimental data of concentration in the liquid as well as in the adsorbent are available, the value of $k_c a$ as well as other parameters can be evaluated by trial and error, in such a way that the calculated results close to the experimental data.

The batch adsorption transient data from Chu, et.al, 2004 are plotted in Fig. 1.

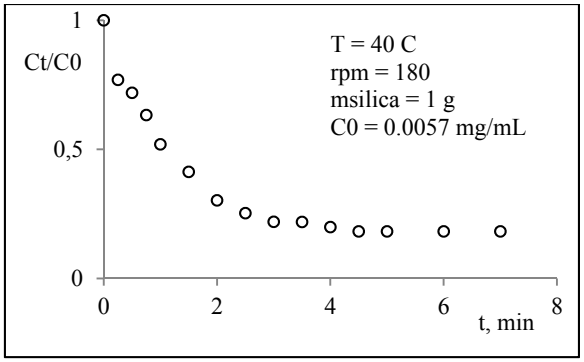

Fig. 1. Experimental Data of Batch Adsorption

The experimental equilibrium data from Chu, et.al, 2004 are presented in Table 2

Table 2. Constants of Equilibrium Isotherm for Batch Adsorption of Vitamin E from PFAD

Models	Constants
Langmuir	K_L = 9.67 mL/mg
	a_L = 170.35 mL/mg
Freundlich	K_F = 0.1019 mL/mg
	n_F = 0.24
Distribution Coefficient	K_d = 3.09

4. Results and Discussions

The validity of equation (2) and equation (3) as well as the equilibrium isotherm are verified based on the experimental data in Table 2 and Fig.1. The values of the parameters ($k_c a$) are adjusted so that the calculation results visually close to the experimental data, and listed in Table 3.

Table 3. Mass Transfer Coefficient per Unit of Adsorbent Mass (k_ca)

Equilibrium Isotherm	Kca (mL/mg/min)
Langmuir	2.5630 x 10^{-2}
Freundlich	2.2800 x 10^{-2}
Distribution Coefficient	2.2807 x 10^{-2}

The comparisons of the simulation as well as the experimental data are presented as thick line in Fig.2, Fig. 3, and Fig. 4.

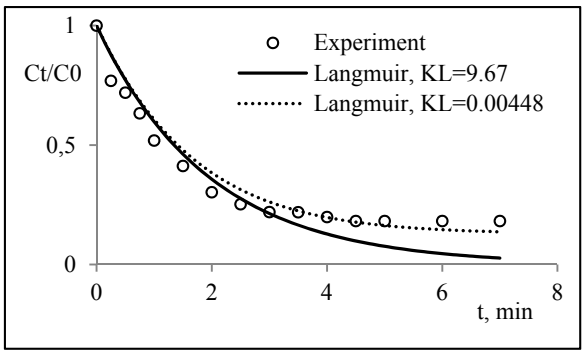

Fig. 2. Experimental Data and Simulation Result for Langmuir Isotherm Application

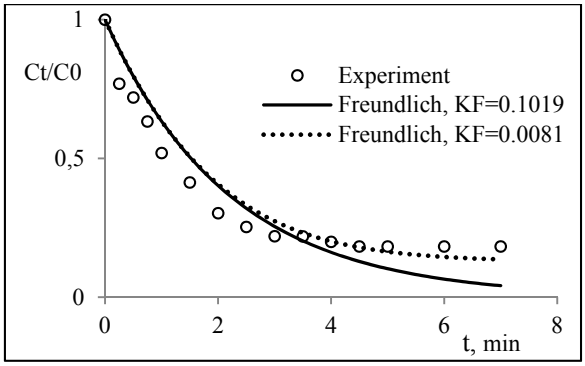

Fig. 3. Experimental Data and Simulation Result for Freundlich Isotherm Application

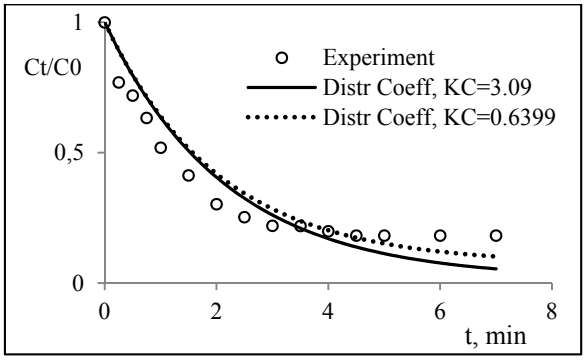

Fig. 4. Experimental Data and Simulation Result for Distribution Coefficient Isotherm Application

From those figures, it can be observed that the model proposed can quantitatively describe the batch adsorption process.
Further improvement can be obtained by adjusting also the values of the equilibrium isotherm parameters. The results are shown as dash line in Fig. 2, Fig. 3, and Fig. 4. It can be clearly seen that the model using adjustable adsorption equilibrium isotherm parameters works much better. The adjusted equilibrium isotherm parameters are listed in Table 4.

Table 4. Constants of Equilibrium Isotherm

Parameters of Equilibrium Isotherm	Literature	Simulation
Langmuir, K_L	9.67	0.00448
Freundlich, K_F	0.1019	0.00810
Distribution Coefficient, K_D	3.09	0.63990

From this simulation study, it can be concluded that the equilibrium parameters evaluated from transient data are better than the ones obtain from separated equilibrium experiments.
Even though this model quantitatively describes batch adsorption process well, further improvement can still be investigated by considering intra particle gradient, especially for larger particles. By studying this effect, the value of effective diffusivity of vitamin E in the adsorbent particles can be estimated.

5. Conclusions

This study shows that:
1. The model based on the assumption that mass transfer from the liquid to the adsorbent particles controls the rate of adsorption can quantitatively describe batch adsorption process
2. Adsorption equilibrium isotherm of Langmuir, Freundlich, and Distribution Coefficient models are suitable to be applied for mathematical modelling of batch adsorption process
3. The equilibrium isotherm parameters obtained from separated experiments (Chu, et.al., 2004) can be applied for the mathematical modelling of batch adsorption process
4. Better quantitative description can be obtained by adjusting the values of the equilibrium isotherm parameters.

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