

Evaluation of activation energy on adsorption of tenuazonic acid from fruit juice by inactivated lactic acid bacteria

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Abstract

In this work, the adsorption of tenuazonic acid (TeA) by inactivated lactic acid bacteria (LAB) published by Liu et al. (J. Food Eng. 224 (2018) 45-52) was reevaluated using deactivation kinetic model (DKM). As the result, the reaction order and the activation energies were newly calculated.

Keywords: Adsorption, Kinetics, Modeling

Liu et al. had published the paper entitled “Kinetic and isotherm studies on the adsorption of tenuazonic acid from fruit juice using inactivated LAB” (Liu et al., 2018).

Tenuazonic acid ((5S, 8S)-3-acetyl-5-sec-butyltetramic acid, TeA) is a toxic metabolite produced by *Alternaria* spp., *Phoma sorghina* and *Pyricularia oryzae* (Meronuck et al., 1972; Umetsu et al., 1972). TeA is thought to be a hybrid of an isoleucine and two acetates (Yun et al., 2015) and is considered to have the highest acute toxicity among the *Alternaria* mycotoxins (Ostry, 2008). The oral LD₅₀ of TeA was shown to be 225 mg/kg bw in mice and 100e150 mg/kg bw in *Macaca fascicularis*. The European Food Safety Authority (EFSA) evaluated the toxicological potential of TeA by following the threshold of toxicological concern (TTC) approach, yielding a TTC value of 1.5 mg TeA/kg bw per day (EFSA, 2011). TeApr

oducing fungi are ubiquitous in many biological environments and are able to infest most plant species (Gross et al., 2011).

Consequently, TeA has been detected in various food commodities, such as flour and bakery products (Janic et al., 2016; Siegel et al., 2009; Zhao et al., 2015), tomatoes and their processed products, beverages. This finding indicates a need to intensely control and reduce the presence of TeA in various food materials for health. TeA and other *Alternaria* toxins have thus attracted increasing attention in recent years.

There are many different approaches developed for mycotoxin decontamination by physical, chemical, and biological methods in recent decades.

Among these methods, biosorption, which applies certain types of inactivated microbial biomass to adsorb and remove mycotoxins from aqueous solutions, has received much attention because of its potential application. Lactic acid bacteria (LAB) and yeast, due in large part to their generally recognized as safe (GRAS) status, are of particular interest for reducing mycotoxins in the food matrix. In biosorption process, mycotoxins are transferred from aqueous medium onto the surface of the inactivated microbial cells. Thus, adsorbents with high surface reactivity, surface area and with a large number of potential mycotoxin adsorption sites are in demand. Adsorption on the cell wall surface is an interaction between the mycotoxins and functional groups of the cell surface based on physical adsorption, ion exchange and complexation

In the adsorption kinetic study (Liu et al., 2018), their experimental data were analyzed using pseudo second order kinetic model (PSO (Ho and McKay, 1999), Eq. (1)).

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (1)\text{-PSO}$$

where q and q_e are the grams of solute adsorbed per gram of adsorbent at any time (t) and at equilibrium, respectively, and k_2 is the PSO rate constant of sorption. The PSO was used in many previous studies for adsorption kinetics, the dominance of this model is simple and convenient to use. But the PSO involved the adsorbed amount which is the thermodynamic quantity and assumed reaction order. Therefore, the activation

n energy can't be accurately calculated because both the rate constant and the adsorption amount change with temperature. In some researches (Eftekhari et al., 2010; Luo et al., 2016; Choi et al., 2017) as like as the m, although the adsorption experimental data with temperature were measured and the rate constants were estimated, the activation energy could n't be calculated because PSO was used. One important purpose of kinetic research is to calculate activation energy.

In this work, the experimental data of Liu et al., 2018 was reevaluated kinetically using DKM and the activation energies were newly calculated.

The DKM (Hong et al., 2014) (Eq. (2)) is a kinetic model for heterogeneous reaction and used it for the kinetic analysis of H₂S removal over mesoporous LaFeO₃/MCM-41 sorbent during hot coal gas desulfurization in a fixed-bed reactor. The validity (Hong et al., 2017) of DKM was verified through kinetic analysis for other experimental data. DKM has not considered the detailed characteristic parameters of the solid sorbent in such a microscopic way as unreacted shrinking core model or random pore model but in a macroscopic way. The change of fractional conversion with time in solid phase was expressed as a deactivation rate, as shown in Eq. (2):

$$\frac{dX}{dt} = k_d C_A (1 - X)^\alpha \quad (2) - \text{DKM}$$

where X is the deactivation degree of adsorbent, i.e. fractional conversion of fresh adsorbent ($0 \leq X \leq 1$, dimensionless). And C_A is concentration ($\mu\text{g}\cdot\text{L}^{-1}$) of A component at any time (t), k_d is a deactivation rate constant of the adsorbent ($\text{L}\cdot\mu\text{g}^{-1}\cdot\text{h}^{-1}$), α is a reaction order of $(1-X)$. The adsorption kinetic equation used Eq. (2) in batch system is Eq. (3).

$$\begin{cases} \frac{dC_A}{dt} = -k_A C_A (1 - X) \\ \frac{dX}{dt} = k_d C_A (1 - X) \end{cases} \quad (3)$$

where k_A is the apparent adsorption rate constant of A adsorbate. Eq. (3) were solved with ODE function of MATLAB, the kinetic parameters were calculated using the nonlinear least-squares fitting of the adsorbate c

concentration obtained by solving ordinary differential equations (Eq. (3)) to the experimental data. The input data required for the nonlinear optimization were only the non-dimensionalized concentrations (C/C_0) of the adsorbates with time and X were automatically evaluated in the calculation process.

The parameters of PSO estimated by Liu et al., 2018 and kinetic parameters calculated by Eq. (3) were shown in Table. Activation energies and frequency factors were calculated from the rate constants with temperature and the Arrhenius equation. The values calculated by Eq. (1) were used as the experimental data for Eq. (3).

Table. Kinetic parameters on TeA adsorption by inactivated LAB.

Condition n*	Eq. (1) Liu et al., 2018			Eq. (3), Calculated reaction orders = 1, 2, 2, 0.5 in this work		
	k_2 g μg^{-1} h ⁻¹	q_e $\mu\text{g g}^{-1}$	R ²	k_A h ⁻¹	k_d L ^{0.5} $\mu\text{g}^{-0.5}$	R ²
0.5 (mg/L)	0.08	5.59	0.986	0.2742	0.4002	1.0000
1.0 (mg/L)	0.02	14.39	0.967	0.2229	0.2262	0.9999
1.5 (mg/L)	0.02	15.82	0.934	0.1790	0.2796	1.0000
20 (°C)	0,09	4.39	0.983	0.1860	0.3653	1.0000
30 (°C)	0.08	5.59	0.986	0.2742	0.4002	1.0000
40 (°C)	0.05	6.05	0.962	0.1970	0.2569	1.0000
*Condition: various C ₀ at 30 °C various T at 0.5 $\mu\text{g/L}$				Activation energies(kJ/mol)		
				Frequency factors		
				1.4737	-6.8988	
				0.3807	0.0235	

The following conclusions can be drawn from Table.

- The reaction orders were evaluated (Eq. (4)). If all reaction orders were equal to 1 or 2, some calculated adsorption rate constants were smaller than 0 or the correlation coefficients (R²) were smaller than 0.95.

$$\begin{cases} \frac{dC_A}{dt} = -k_A C_A (1 - X)^2 \\ \frac{dX}{dt} = k_d C_A^{0.5} (1 - X)^2 \end{cases} \quad (4)$$

- The calculated rate constants could quantitatively be compared on both adsorbate and adsorbent. As initial concentration of LAB increase, the adsorption rate constants of TeA and the deactivation rate constants of LAB become smaller except only the deactivation rate constant of LAB at $C_0=1.5$ (mg/L).

- The activation energies are newly calculated. The activation energy of TeA adsorption is 1.4737 kJ/mol, which is very small. The activation energy of LAB deactivation is -6.8988kJ/mol which is negative activation energy, i.e. the deactivation rate of LAB decreases with increasing temperature. Elementary reaction exhibiting negative activation energy are typically barrierless reactions (Mozurkewich and Benson, 1984). Therefore, increasing the temperature leads to a reduced probability of the colliding TeA capturing LAB, expressed as an absorption cross section that decreases with increasing temperature. Such a situation no longer leads itself to direct interpretations as the height of a potential barrier.

Important conclusions can be obtained from kinetic Eqs. (3 and 4) and can't be obtained from PSO, which assumes reaction order and contains the adsorbed amount. The authors think that it may be more necessary to use DKM than pseudo order models including the adsorbed amount in adsorption kinetic studies.

References

- Choi A. E. S., Roces S., Dugos N., Wan M. W., 2017. Adsorption of benzothiophene sulfone over clay mineral adsorbents in the frame of oxidative desulfurization. *Fuel*. 205,153–160
- EFSA. Panel on Contaminants in the Food Chain (CONTAM), 2011. Scientific opinion on the risks for animal and public health related to the presence of *Alternaria* toxins in feed and food. *EFSA Journal* 9, 1e9

- Eftekhari S., Habibi-Yangjeh A., Sohrabnezhad Sh., 2010. Application of AIMCM-41 for competitive adsorption of methylene blue and rhodamine B: Thermodynamic and kinetic studies. *J. Hazard. Mater.* 178, 349–355.
- Gross, M., Curtui, V., Ackermann, Y., Latif, H., Usleber, E., 2011. Enzyme immunoassay for tenuazonic acid in apple and tomato products. *J. Agric. Food Chem.* 59, 12317e12322.
- Janic, H.E., Colovic, R., Pezo, L., Orcic, D., Vukmirovic, D., Mastilovic, J., 2016. Possibility of *Alternaria* toxins reduction by extrusion processing of whole wheat flour. *Food Chem.* 213, 784e790.
- Liu B., Ge N., Peng B. Z., Pan S.Y., 2018. Kinetic and isotherm studies on the adsorption of tenuazonic acid from fruit juice using inactivated LAB. *J. Food Eng.* 224, 45-52.
- Luo Y., Li Z., Yuan Y. H., Yue T.L., 2016. Bioadsorption of patulin from kiwi fruit juice onto a superior magnetic chitosan. *J. Alloys Compd.* 667, 101-108.
- Mozurkewich M., Benson S. W., 1984. Negative activation energies and curved Arrhenius plots. 1. Theory of reactions over potential wells. *J. Phys. Chem.* 88 (25), 6429–6435.
- Ho, Y. S., McKay, G., 1999. Pseudo-second order model for sorption processes. *Process Biochem.* 34, 451–465.
- Hong, Y. S., Zhang, Z. F., Cai, Z. P., Zhao, X. H., Liu, B. S., 2014. Deactivation Kinetics Model of H₂S Removal over Mesoporous LaFeO₃ / MCM-41 Sorbent during Hot Coal Gas Desulfurization. *Energy Fuels.* 28, 16012–6018.
- Hong, Y. S., Sin, K. R., Pak, J. S., Kim, C. J., Liu, B. S., 2017. Kinetic Analysis of H₂S Removal over Mesoporous Cu–Mn Mixed Oxide/SBA-15 and La–Mn Mixed Oxide/KIT-6 Sorbents during Hot Coal Gas Desulfurization Using the Deactivation Kinetics Model. *Energy Fuels*, 31, 9874–9880.