A Study on the Pseudo-Second-Order Kinetic Equation for the Adsorption of Methylene Blue onto Nitric Acid-Treated Rice Husk: Comparison of Linear Methods

Yu-Ting Huang[1], Li-Chiun Lee[1], Ming-Cheng Shih[2]*

1. Department of Nutrition, I-Shou University. No.8, Yida Rd., Jiaosu Village, Yanchao District, Kaohsiung City 82445, Taiwan, R.O.C.

2. Department of Biological Science & Technology, I-Shou University. No.8, Yida Rd., Jiaosu Village, Yanchao District, Kaohsiung City 82445, Taiwan, R.O.C.

*Corresponding author.

E-mail address: mchshih@isu.edu.tw

Tel: +886-7-6151100 ext.7321.

Fax: +886-7-6577056.

Present address: Department of Biological Science & Technology, I-Shou University. No.8, Yida Rd., Jiaosu Village, Yanchao District, Kaohsiung City 82445, Taiwan, R.O.C.

DOI: 10.29322/IJSRP.8.6.2018.p7865

http://dx.doi.org/10.29322/IJSRP.8.6.2018.p7865

Abstract:

Adsorption is a feasible and environment friendly dye remediation method. The pseudo-second-order kinetic models is commonly applied to experimental data in many adsorption kinetic studies to express the adsorption mechanism of adsorbate onto the adsorbent. Six varied linear expression of pseudo-second-order kinetic equation have been examined in this research. The results showed that the R^2 values can be used to select the best-fit linear forms of the pseudo-second-order kinetic equation.In this study, the results also indicated that the linearized expression of type 6 can be used to calculate the pseudo-second-order rate constants and to predict q_t more appropriate than the other 5 expressions of pseudo-second-order equation for this studied system. .

Keywords: Linear regression; Pseudo-second-order; Nitric acid-treated rice husk; Adsorption; Methylene blue; Kinetics

1.Introduction

The chemical industries always cuased a lot of environmental pollution, such as air pollution, water pollution and soil pollution. Many researchers tried to solve these environmental pollution. Wastewater is one of the most import subject. Wastewater can found in the discharge of many industries. Synthetic dyes wastewater always can cause more attention than the other wastewater pollution due to the reducing of light penetration and its visible color. Many methods was invented to remove the dye from the wastewter. Most of the used processes for the color removal are developed based on the biological theory, physical theory and chemical theory. Some of them were not environmentfriendly method. In the recent years, environment friendly method caused a lot of attention. Therefore, recent efforts have been made to discover new environment friendly and economically feasible treatment alternatives (Hamdaoui, Saoudi et al. 2008). Among several effective methods, adsorption with natural material receive great attention due to the easy availability, ease of operation, simplicity of design and comparable low cost of application. (Karadag, Koc et al. 2007, Chowdhury and Das Saha 2011, Shih 2012). In order to investigate the adsorption mechanism to obtain a better removal efficiency, several adsorption kinetic models have been proposed to express the adsorption mechanism of adsorbate onto the adsorbent. In these adsorption kinetic models, the pseudo-second-order kinetic models is the most popular model and have been commonly applied in many adsorption kinetic studies. Numerous altered equation expression of the pseudo-second-order model were derived to simplify the calculation diffcultyduring the past few decades. Among these equation expressions, the formual derivation of Ho's equation is frequently used to investigate the correlation of the adsorption data for pseudo-second-order kinetic model due to its simplicity and its good fitting of many adsorption researchs over the past decade (Ho and McKay 1998, Ho, Ng et al. 2000, Shahwan 2014).

Among these literatures, the linear regression technique has been the most frequently used analysis method to find the best-fit kinetic models for dye removal, but linear regression is criticized since it leads to varied linearized forms. In order to find the best-fit kinetic models, six linearized types of pseudo-second-order kinetic models were used to calculatee the kinetic parameters by using the least squares method (Karadag, Koc et al. 2007). Also, the comparison of the the theoretical q_t calculated by these six inearized types of pseudo-second-order kinetic model and the experimental q_t data were used to find the best-fit kinetic model.

2. Materials and methods

The experimental data employed in this study was gained from the literature (Shih 2012). In the study of Shih (Shih 2012), many acid-treated rice husk was used as the adsorbent. The experimental data applied in this research mainly obtained from the results of the nitric acid-treated rice husk (NRH) used as the adsorbent.

The pseudo-second-order equation is generally written as below (Ho, McKay et al. 2000, Demirbas, Kobya et al. 2004, Ofomaja 2007, Sari, Tuzen et al. 2007, Neşe and T. Ennil 2008):

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad (1)$$

where q_t (mg/g) is the sorption capacity at time t (min); q_e is the sorption capacity at equilibrium (mg/g) and K_2, is the rate constant of the pseudo-second-order sorption (min^{-1}) (Djeribi and Hamdaoui 2008, Ncibi 2008, Huang and Shih 2014). Integration and rearrangment of Eq. [1] with applying border conditions t = 0 to t = t and q_t = 0 to q_t = q_t gives the non-linear form of pseudo-second-order equation as follows (Ho 2006, Huang and Shih 2014):

$$q_t = \left(\frac{K_2 q_e{}^2 t}{1 + K_2 q_e t}\right) \qquad (2)$$

Eq (2) can be rearranged to obtain a linearity forms as follows:

Type 1 pseudo second-order: $\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K_2 t$ (3)

Eq (3) is the first linearized type of pseudo-second-order equation. Eq (3) can be converted to another 5 alternative linearity forms as follows(Kumar 2006, Hamdaoui, Saoudi et al. 2008, Chowdhury and Das Saha 2011, Huang and Shih 2015, Huang and Shih 2017):

Type 2 pseudo second-order: $$\left(\frac{1}{q_t}\right) = \frac{1}{q_e} + \frac{1}{K_2 q_e^{\,2}}\frac{1}{t} \quad (4)$$

Type 3 pseudo second-order: $$q_t = q_e - \frac{1}{K_2 q_e}\frac{q_t}{t} \quad (5)$$

Type 4 pseudo second-order: $$\left(\frac{q_t}{t}\right) = K_2 q_e^{\,2} - K_2 q_e q_t \quad (6)$$

Type 5 pseudo second-order: $$\left(\frac{1}{t}\right) = -K_2 q_e + K_2 q_e^{\,2}\frac{1}{q_t} \quad (7)$$

Type 6 pseudo second-order: $$\left(\frac{t}{q_t}\right) = \frac{1}{K_2 q_e^{\,2}} + \frac{1}{q_e}(t) \quad (8)$$

3. Results and discussion

In this study, the experimental data for dye adsorbed onto the surface of NRH were fitted to the six different linearized versions of pseudo-second-order equation. The fig. 1 has 1/(qe-q_t) on the Y axis and t on the X axis for the linearized type 1. The fig. 2 has 1/q_t on the Y axis and 1/t on the X axis for the linearized type 2. The fig. 3 has q_t on the Y axis and q_t/t on the X axis for the linearized type 3. The fig. 4 has q_t/t on the Y axis and q_t on the X axis for the linearized type 4. The fig. 5 has 1/t on the Y axis and 1/ q_t on the X axis for the linearized type 5. The fig. 6 has t/ q_t on the Y axis and t on the X axis for the linearized type 6. The rate constant K_2 and the theoretical q_e for these various linearized versions of pseudo-second-order equations can be calculated from the plot of these six figures, (Kumar 2006, Hamdaoui, Saoudi et al. 2008, El-Khaiary, Malash et al. 2010, Huang and Shih 2017). All parameters for these six linearized versions of pseudo-second-order kinetic equations included theoretical q_e and the rate constant K_2 and the correlation coefficient, R^2 are shown in Table 1. From the values of parameters, it was observed that the q_e values, K_2 values and R^2 values calculated from these six linearized versionss of pseudo-second-order equations were diverse.

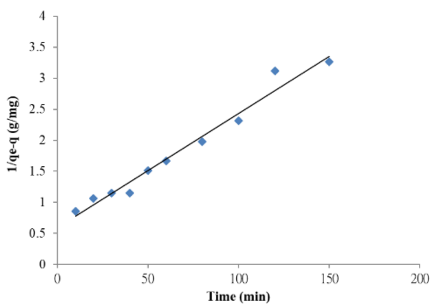

Figure 1. Type 1 linear expression of pseudo-second-order equation obtained during the adsorption of MB by using NRH

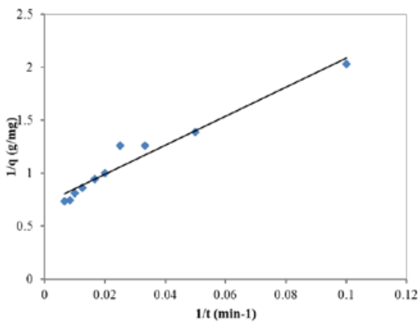

Figure 2. Type 2 linear expression of pseudo-second-order equation obtained during the adsorption of MB by using NRH

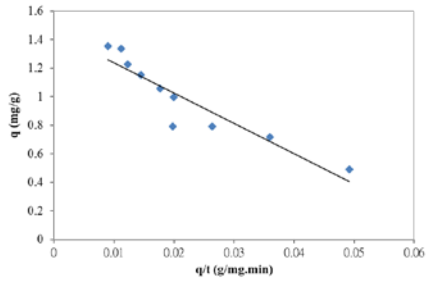

Figure 3. Type 3 linear expression of pseudo-second-order equation obtained during the adsorption of MB by using NRH

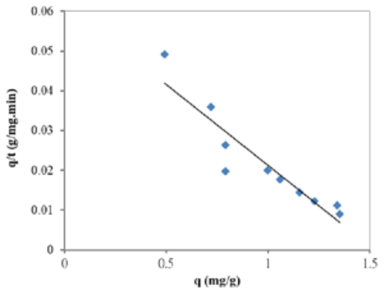

Figure 4. Type 4 linear expression of pseudo-second-order equation obtained during the adsorption of MB by using NRH

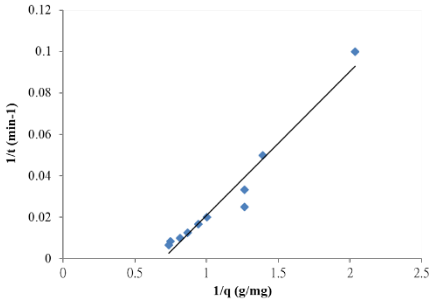

Figure 5. Type 5 linear expression of pseudo-second-order equation obtained during the adsorption of MB by using NRH

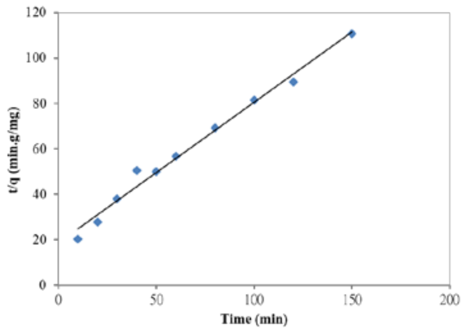

Figure 6. Type 6 linear expression of pseudo-second-order equation obtained during the adsorption of MB by using NRH

In the results of comparion of the q_e values predicted by these six linearized versions with the experimental value , the difference between the experimental value of q_e and the value of q_e obtained using linearized versions 6 is the smallest. The low difference between the experimental value of q_e and the value of q_e obtained using linearized versions 6 can not use to prove the linearized versions 6 is the bet-fit linear form of kinetic equation. From the literatures, the researchers define the best-fit linear form of kinetic equations is generally selected based on the R^2values. In the table 1, values of R^2 for types 3 and 4 were lower than 0.87, these low values of R^2 for types 3 and 4 suggested that these two linearized versions applied in the prediction of the MB adsorption onto NRH particles can not obtain a favourable results. R^2 values for types 1, 2, 5 and 6 were higher than 0.95. The high values of these 4 linear expression indicated that the calculated results will be closer to the experimental data than the types 3 and 4. We also can find the R^2 value of linearized version 6 was the highest for the MB adsorption on NRH, this high R^2 value implied that linearized version 6 of pseudo-second-order equatuion should be the best fitted kinetic exoression to represent the MB adsorption on NRH. In order to prove the correctness of the high values of R^2 can be use to find the best fitted kinetic exoression, the comparison between the plot of experimental q_t vs time with the plot of theoretical q_t calculated from these six linear pseudo-second-order kinetic kinetic models vs time were made (figure 7-12.).

Linear Type	Type 1	Type 2	Type 3	Type 4	Type 5	Type 6
q_e (mg/g)	1.68606	1.39	1.452	1.52593	1.42623	1.6176
K_2(g/mg.min)	0.0184	0.03778	0.03235	0.02654	0.03422	0.0205
R^2	0.9729	0.9536	0.8622	0.8622	0.957	0.9868

The theoretical q_t valuses of these six linear types of pseudo-second-order equations in fig 7-12 were calculated by bringing the q_e values and $k2$ valuesof each linear types of pseudo-second-order equations into the nonlinear form of pseudo-second-order equation.

From these figures, the result of figure 12 clearly indicated that the linearized version 6 is closer to the experimental data than the other 5 linearized versions.

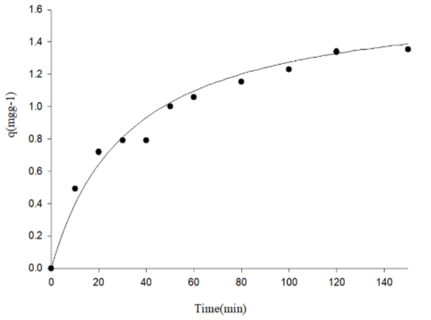

Fig. 7. Comparison of the predicted values of qt from linear type 1 with the experimental values of qt for the adsorption of MB onto NRH.

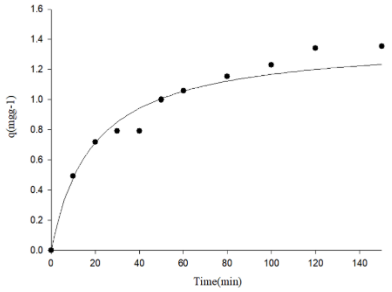

Fig. 8. Comparison of the predicted values of qt from linear type 2 with the experimental values of qt for the adsorption of MB onto NRH.

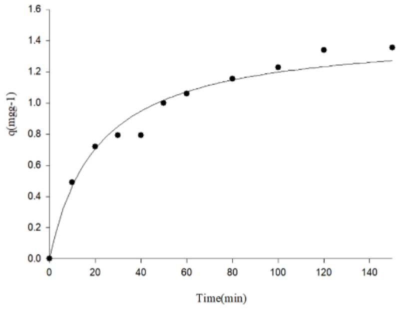

Fig. 9. Comparison of the predicted values of qt from linear type 3 with the experimental values of qt for the adsorption of MB onto NRH.

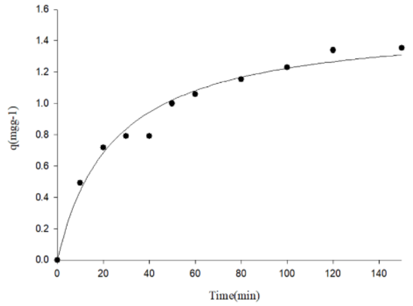

Fig. 10. Comparison of the predicted values of qt from linear type 4 with the experimental values of qt for the adsorption of MB onto NRH.

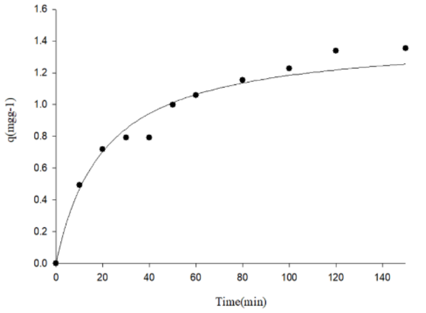

Fig. 11. Comparison of the predicted values of qt from linear type 5 with the experimental values of qt for the adsorption of MB onto NRH.

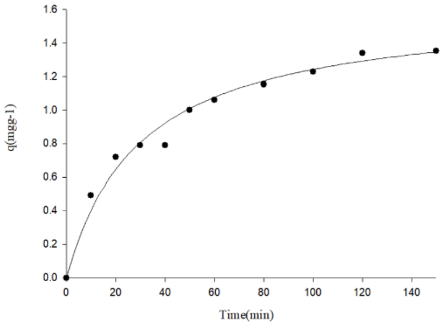

Fig. 12. Comparison of the predicted values of qt from linear type 6 with the experimental values of qt for the adsorption of MB onto NRH.

4. Conclusion

In this research, thes adsorption kinetics of experimental outcome were analyzed by using 6 different linearized expressions of pseudo-secondorder kinetic equation. The linearized transformation of the pseudo-secondorder kinetic equatuion cause the real problems and complexities in calculating the parameters of the pseudo-secondorder kinetic equatuion. The various results obtained from the various linearized expressions of pseudo-secondorder kinetic equatuion probably as a result of the variation in the error structure got varied in the linearized process of the non-linear pseudo-secondorder kinetic equatuion. Also, the different axial settings of linearized expression could affect the determination process (Khambhaty, Mody et al. 2008). In this study, six different linear expressions of pseudo-second-order equation were used for linear regression and compared using the correlation coefficient, R^2. Also, these varied linear expressions of pseudo-second-order equation were used to determine the kinetic parameters. These kinetic parameters were used to calculate the theoretical q_t and compared to evaluate the experimental q_t data. The calculated results of thses linear expressions were different. The difference of of thses linear expressions probably due to the change of the error distribution caused by the linearization technique. These results implied that it is a important issue to choose a suitable linear type to obtain the best-fitted data. In the results, it is found that the R^2 values can be used to select the best-fit linear forms of the pseudo-second-order kinetic equation.

References:

Chowdhury, S. and P. Das Saha (2011). "Comparative analysis of linear and nonlinear methods of estimating the pseudo-second-order kinetic parameters for sorption of Malachite green onto pretreated rice husk." Bioremediation Journal **15**(4): 181-188.

Demirbas, E., M. Kobya, E. Senturk and T. Ozkan (2004). "Adsorption kinetics for the removal of chromium(VI) from aqueous solutions on the activated carbons prepared from agricultural wastes." Water S. A. **30**(4): 533-540.

Djeribi, R. and O. Hamdaoui (2008). "Sorption of copper (II) from aqueous solutions by cedar sawdust and crushed brick." Desalination **225**(1-3): 95-112.

El-Khaiary, M. I., G. F. Malash and Y.-S. Ho (2010). "On the use of linearized pseudo-second-order kinetic equations for modeling adsorption systems." Desalination **257**(1-3): 93-101.

Hamdaoui, O., F. Saoudi, M. Chiha and E. Naffrechoux (2008). "Sorption of malachite green by a novel sorbent, dead leaves of plane tree: Equilibrium and kinetic modeling." Chemical engineering journal **143**(1-3): 73-84.

Hamdaoui, O., F. Saoudi, M. Chiha and E. Naffrechoux (2008). "Sorption of malachite green by a novel sorbent, dead leaves of plane tree: Equilibrium and kinetic modeling." Chemical Engineering Journal **143**: 73-84.

Ho, Y.-S. (2006). "Second-order kinetic model for the sorption of cadmium onto tree fern: a comparison of linear and non-linear methods." Water research **40**(1): 119-125.

Ho, Y. and G. McKay (1998). "A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents." Process Safety and Environmental Protection **76**(4): 332-340.

Ho, Y., J. Ng and G. McKay (2000). "Kinetics of pollutant sorption by biosorbents: review." Separation & Purification Reviews **29**(2): 189-232.

Ho, Y. S., G. McKay, D. A. J. Wase and C. F. Forster (2000). "Study of the Sorption of Divalent Metal Ions on to Peat." Adsorption Science and Technology **18**(7): 639-650.

Huang, Y.-T. and M.-C. Shih (2014). "Linear regression analysis for the adsorption kinetics of methylene blue onto acid treated rice husk."

Huang, Y.-T. and M.-C. Shih (2015). "Effect of linearized expressions of pseudo-second-order kinetic equations on the prediction of the adsorption of methylene blue on rice husk." source: International Journal of Science Commerce and Humanities: 138-145.

Huang, Y.-T. and M.-C. Shih (2017). "Comparative Analysis of Different Linearized Expressions of Estimating the Pseudo-Second-Order Kinetic Parameters for the Adsorption of Methylene Blue on Hydrochloric Acid-Treated Rice Husk." source: International Journal of Scientific and Research Publications **7**(6): 255-260.

Karadag, D., Y. Koc, M. Turan and M. Ozturk (2007). "A comparative study of linear and non-linear regression analysis for ammonium exchange by clinoptilolite zeolite." Journal of Hazardous Materials **144**(1-2): 432-437.

Khambhaty, Y., K. Mody, S. Basha and B. Jha (2008). "Pseudo-second-order kinetic models for the sorption of Hg (II) onto dead biomass of marine Aspergillus niger: comparison of linear and non-linear methods." Colloids and Surfaces A: Physicochemical and Engineering Aspects **328**(1): 40-43.

Kumar, K. V. (2006). "Linear and non-linear regression analysis for the sorption kinetics of methylene blue onto activated carbon." Journal of hazardous materials **137**(3): 1538-1544.

Ncibi, M. C. (2008). "Applicability of some statistical tools to predict optimum adsorption isotherm after linear and non-linear regression analysis." Journal of Hazardous Materials **153**(1-2): 207-212.

Neşe, O. and K. T. Ennil (2008). "A kinetic study of nitrite adsorption onto sepiolite and powdered activated carbon." Desalination **223**(1-3): 174-179.

Ofomaja, A. E. (2007). "Kinetics and mechanism of methylene blue sorption onto palm kernel fibre." Process Biochemistry **42**(1): 16-24.

Sari, A., M. Tuzen, D. Citak and M. Soylak (2007). "Equilibrium, kinetic and thermodynamic studies of adsorption of Pb (II) from aqueous solution onto Turkish kaolinite clay." Journal of Hazardous Materials **149**(2): 283-291.

Shahwan, T. (2014). "Sorption kinetics: Obtaining a pseudo-second order rate equation based on a mass balance approach." Journal of Environmental Chemical Engineering **2**(2): 1001-1006.

Shih, M.-C. (2012). "Kinetics of the batch adsorption of methylene blue from aqueous solutions onto rice husk: effect of acid-modified process and dye concentration." Desalination and Water Treatment **37**(1-3): 200-214.

ACKNOWLEDGEMENT

The authors acknowledge the effort of all students and graduates of Bioprocess Engineering and Fermentation Lab in Department of Biological Science and Technology, I-Shou University for their experiment operation.

AUTHORS

First Author –Yu-Ting Huang, assistant professor, Department of Nutrition, I-Shou University. No.8, Yida Rd., Jiaosu Village, Yanchao District, Kaohsiung City 82445, Taiwan, R.O.C., email address: ythuang@isu.edu.tw.

Second Author–Li-Chiun Lee, assistant professor, Department of Nutrition, I-Shou University. No.8, Yida Rd., Jiaosu Village, Yanchao District, Kaohsiung City 82445, Taiwan, R.O.C..

Third Author–Ming-Cheng Shih, assistant professor, Department of Biological Science & Technology, I-Shou University. No.8, Yida Rd., Jiaosu Village, Yanchao District, Kaohsiung City 82445, Taiwan, R.O.C., email address: mchshih@isu.edu.tw.

Correspondence Author –Ming-Cheng Shih, email address: mchshih@isu.edu.tw, alternate email address: mchshih@gmail.com, Tel: +886-7-6151100 ext.7321, Fax: +886-7-6577056, Present address: Department of Biological Science & Technology, I-Shou University. No.8, Yida Rd., Jiaosu Village, Yanchao District, Kaohsiung City 82445, Taiwan, R.O.C.