Effect of linearized expressions of Langmuir equations on the prediction of the adsorption of methylene blue on rice husk

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Abstract- In order to investigate the effect of linearized process on the adsorption equilibrium isotherms of methylene blue from solutions onto rice husk, the experimental data were fitted to the Langmuir isotherm equations by using five different types of linear expression. The adsorption equilibrium constant related to the affinity of the binding sites and energy of adsorption (K_L) and maximum adsorption capacity ($q_{\max}$) for each linear expression had been calculated. Also, values of the the amount of MB adsorbed on adsorbent at equilibrium time using the constants calculated from these five linear types of Langmuir isotherm equations were compared with the experimental data. The results indicated that the type 1 linear expressions were able to calculate the adsorption equilibrium constant and q_e for the studied system (methylene blue/rice husk) well. The results also showed that it was inappropriate to use the other four proposed alternate linear expressions (type 2 to type 5) to calculate the adsorption equilibrium constant and q_e for the studied system.

Index Terms- Langmuir; Adsorption; Isotherm

I. INTRODUCTION

Increasing concern for public health and water quality has result in the establishment of severe limits on the acceptable discharge standards of dyes. Thus, removal of dye from process or waste streams becomes a major environmental problem (Hamdaoui and Naffrechoux 2007). Liquid phase adsorption, referred to the passive uptake and physicochemical binding of dye to the adsorbate surface, is now generally known as an effective and economically feasible technique for the removal of dye pollutants from waste streams (Chowdhury and Das Saha 2011). One of the important task in the study of adsorption is to discover the adsorption mechanism, in particular the interactions which are implicated at the adsorbate / adsorbent interface. In fact, the effective description of the dynamic adsorptive separation of dye from solution onto an adsorbent depends upon an proper illustration of the equilibrium separation between these two phases. Adsorption properties and equilibrium data, normally recognized as adsorption isotherms, is established when the amount of dye being desorbed from the adsorbent is equal to the amount being adsorbed and the equilibrium solution concentration remains constant at this point (Kundu and Gupta 2006, Gimbert, Morin-Crini, et al. 2008). In order to optimize the design of an adsorption system, it is important to establish an accurate mathematical description of the equilibrium isotherms. The commonly used isotherm were the Langmuir expressions. The Langmuir isotherm eauation has been successfully applied to many dye adsorption procedures. Because the Langmuir isotherm equation as expressed in literatures is nonlinear, the non-linear regression method was applied to calculate the parameters of Langmuir isotherm equation. The calculation of Langmuir equation by using the non-linear regression technique offers a more complex calculated process for determining isotherm parameters and the researchers need to use some particular softwares or write dwown some computer programs to solve these non-linear regression equations. Due to these reasons, the rsearchers try to find a easy method to replace the non-linear regression technique to solve the Langmuir isotherm equation. A common alternative method is to use linearized forms of the Langmuir isotherm equation to replace non-linear form of the Langmuir equation to calculate the isotherm parameters. This linear regression method is often applied to estimate the Langmuir isotherm equation parameters, since this method only requires little understanding of the data fitting process, and is easily done by using Excel or similar spreadsheet softwares . However, depending on the approach of the Langmuir isotherm equation linearized, the error distribution may changes worse. Thus it will become an unsuitable substitute method to use the linearization procedure to estimate the Langmuir isotherm equation parameters.

In this study, 5 different types of linear expressions of the Langmuir equations has been used to estimate the Langmuir isotherm equation parameters and also to find the best linear type on the basis of the experiment of methylene blue adsorption from its aqueous solution onto rice husk.

II. MATERIALS AND METHODS

The experimental data used in this research was got from the literature (Shih 2012). The adsorbent used in the literature was RH (rice husk) and the dye used in the literature was methylene blue (MB). The amount of dye adsorbed at equilibrium time (q_e) (Djeribi and Hamdaoui 2008, Huang and Shih 2014):

$$\text{Amount adsorbed at equilibrium time } (q_e) = \frac{(C_i - C_e)V}{M} \quad (1)$$

where M is the weight of adsorbent used (g). C_i and C_e (mg/L) are the liquid phase concentrations of dyes initiallyand at equilibrium time, respectively. V is the volume of dye solution (L).

The Langmuir isotherm equation

The Langmuir isotherm equation derived on the basis of assumption of uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface is expressed as (Ho 2006, Hamdaoui and Naffrechoux 2007):

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (2)$$

where q_e is the amount of MB adsorbed on adsorbent at equilibrium (mg/g); C_e is the equilibrium concentration in the solution (mg/L); q_{max} is the q_e for a complete monolayer (mg/g) , a constant related to sorption capacity; and K_L is the adsorption equilibrium constant related to the affinity of the binding sites and energy of adsorption (L/mg).

The linearized forms of Langmuir equation derived on the basis of Eq. [2] is expressed as :

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \qquad \text{type1} \quad (3)$$

Eq.[3] can be rearranged to obtain another 4 different linearized types of Langmuir expressions (Hamdaoui and Naffrechoux 2007):

$$\frac{1}{q_e} = \frac{1}{K_L q_{\max}} \frac{1}{C_e} + \frac{1}{q_{\max}} \qquad \text{type2} \quad (4)$$

$$q_e = \frac{-q_e}{K_L C_e} + q_{\max} \qquad \text{type3} \quad (5)$$

$$\frac{q_e}{C_e} = -K_L q_e + K_L q_{\max} \qquad \text{type4} \quad (6)$$

$$\frac{1}{C_e} = K_L q_{\max} \frac{1}{q_e} - K_L \qquad \text{type5} \quad (7)$$

III. RESULTS AND DISCUSSION

For the current study, the experimental data for methylene blue adsorbed onto the rice husk were fitted to the 5 different linearized forms of Langmuir equations. Values of the the maximum adsorption capacity, q_{max}; the adsorption equilibrium constant, K_L by the type 1 linearized forms of Langmuir equation can be calculated from the plots of C_e/q_e versus C_e as presented in Fig. 1. In fact, the rate constant K_L and the q_{max} also can be obtained from the plot of $1/q_e$ vs. $1/C_e$ (fig.2), q_e vs. $-q_e / C_e$ (fig.3), q_e / C_e vs. q_e (fig.4) and $1/C_e$ vs. $1/q_e$ (fig.5) for the linearized expressions of type 2, type 3, type 4 and type 5 of Langmuir equations, respectively (Kumar 2006, Hamdaoui, Saoudi, et al. 2008). The predicted results of the maximum adsorption capacity, q_{max}; the adsorption equilibrium constant, K_L, and the correlation coefficient , R^2 for these 5 different linearized types of Langmuir equations were given in table 1. From Table 1, it was able to be found that the equilibrium sorption capacity of rice husk for methylene blue predicted by these five different linearized types of Langmuir isotherm equations were highly varying from 8.73 mg/g to 11.70 mg/g. Also, the K_L values and R^2 values obtained from the five linear expressions of langmuir equations were different. From table 1, It was observed that expression of type 2 and type 5 had the R^2 value higher than 0.999 for the MB adsorption on RH, the R^2 values of type 3 and type 4 expressions are higher than 0.95, and the R^2 values of type 1 expression are higher than 0.98. The comparison of R^2 values of these five different types of linearized Langmuir isotherm equations indicated that expression of type 2 and type 5 had the highest R^2 values and the type 2 and type 5 linear expressions of Langmuir equatuion may be used to represent the MB adsorption on RH. Beside the comparison of R^2 values for these five different types of linearized Langmuir isotherm equations, the expression of type 1 Langmuir isotherm was the most frequently used linear type to study the relation between the concentration of solute in the solid

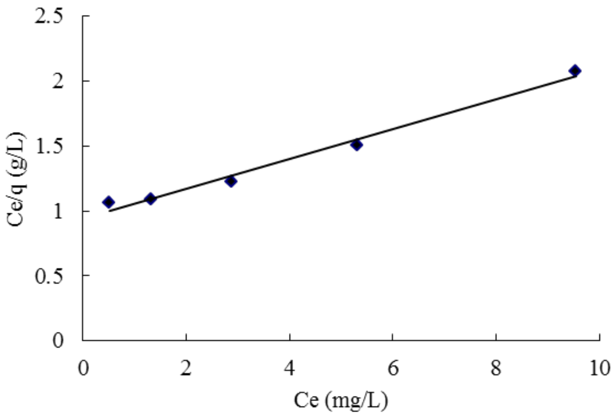

Figure 1. Type 1 Langmuir isotherm equation obtained using linear method for the sorption of methylene blue onto rice husk

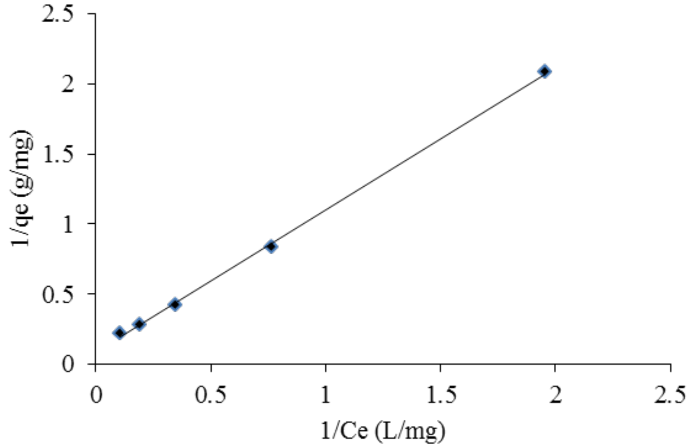

Figure 2. Type2 Langmuir isotherm equation obtained using linear method for the sorption of methylene blue onto rice husk

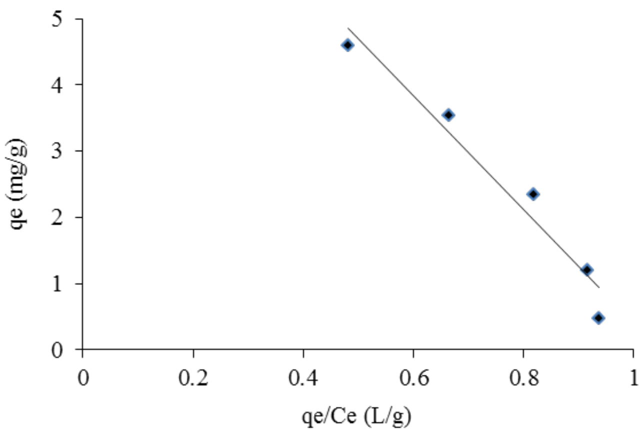

Figure 3. Type3Langmuir isotherm equation obtained using linear method for the sorption of methylene blue onto rice husk

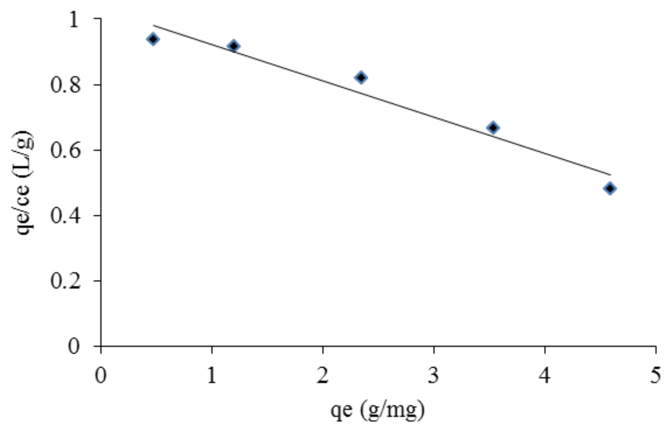

Figure 4. Type4 Langmuir isotherm equation obtained using linear method for the sorption of methylene blue onto rice husk

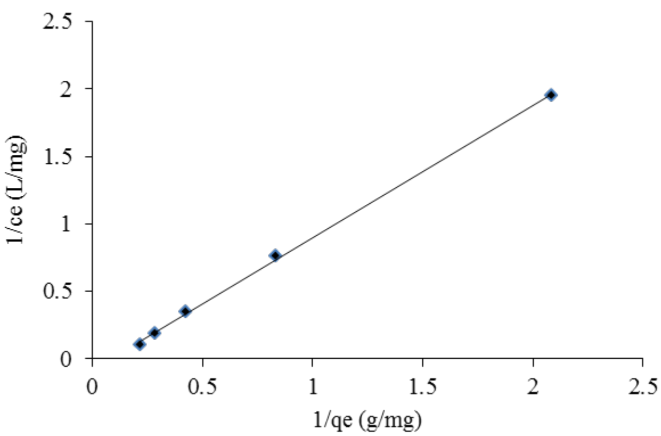

Figure 5. Type5 Langmuir isotherm equation obtained using linear method for the sorption of methylene blue onto rice husk

Linear Type	q_{max} (mgg^{-1})	K_L(Lmg^{-1})	R^2
Type1	8.73	0.12	0.985
Type2	11.63	0.08	0.999
Type3	8.99	0.12	0.955
Type4	9.29	0.11	0.955
Type5	11.7	0.084	0.999

Table 1. Isotherm parameters obtained by using linear methods for the adsorption of methylene blue onto rice husk

phase and in liquid phase at equilibrium conditions (Hamdaoui and Naffrechoux 2007, Kumar and Sivanesan 2006). In order to find the suitable linear expressions of Langmuir equatuion , the K_L values and q_{max} values obtained from these five linear expressions of Langmuir isotherm equatuion s were bring into the nonlinear form of Langmuir isotherm equatuion to calculate the q_e valuses and C_e values separately.

Comparison between the experimental points and predicted values for the adsorption of MB onto RH by these 5 linear type of Langmuir isotherm equatuions were presented in figures 6-10. From fig. 6-10, it was observed that the type 1 linear expressions of Langmuir isotherm equatuion can predict the experimental data very well.

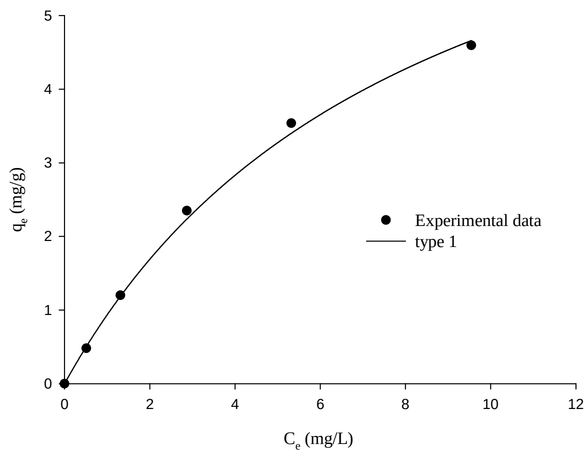

Fig. 6. Comparison between the experimental points and predicted adsorption isotherm of MB onto RH by linear type 1.

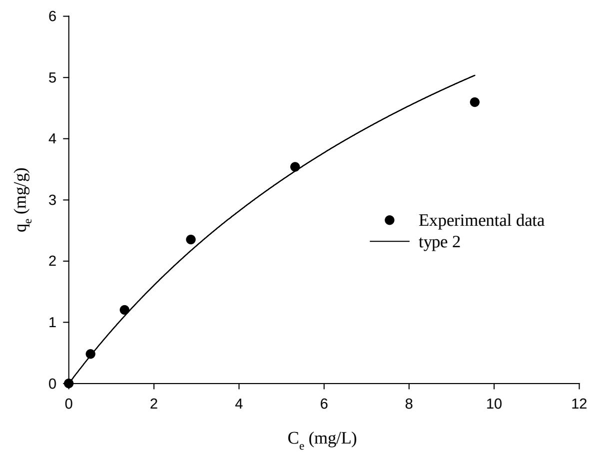

Fig. 7. Comparison between the experimental points and predicted adsorption isotherm of MB onto RH by linear type 2.

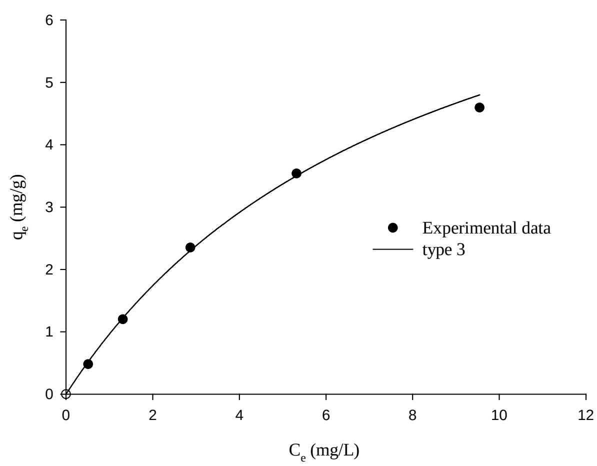

Fig. 8. Comparison between the experimental points and predicted adsorption isotherm of MB onto RH by linear type 3.

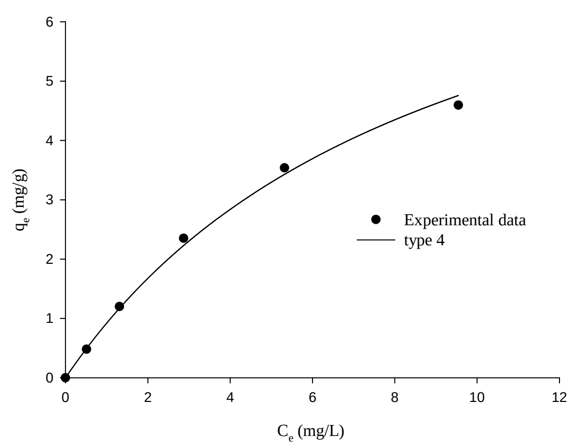

Fig. 9. Comparison between the experimental points and predicted adsorption isotherm of MB onto RH by linear type 4.

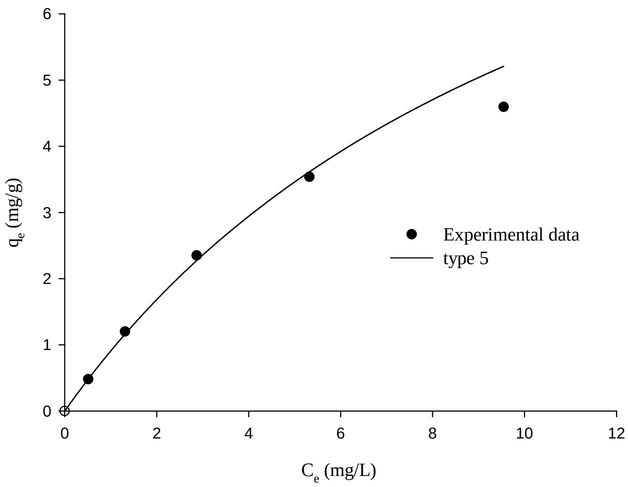

Fig. 10. Comparison between the experimental points and predicted adsorption isotherm of MB onto RH by linear type 5.

The figures 7 and 10 indicated that the type 2 and type5 linear expressions of Langmuir isotherm equatuion failed to predict the q_e valuses and C_e values for the adsorption of MB onto RH. All these results indicated that the theory behind the Langmuir isotherm equatuion was getting valid for the adsorption of methylene blue onto rice husk based on the type 1linear expression and the theory behind the Langmuir isotherm equatuion was violated by the type 2 and type5 linear expression. These results also indicated that different linear forms of the same Langmuir isotherm equatuions significantly affect calculations of the parameters. These divergent outcomes show the real complexities and problems in estimating the isotherm parameters by the linearized method. The different outcomes for different linearization form of Langmuir isotherm equatuions were produced by the variation in the error structure that would get varied upon linearizing technique of the nonlinear equation (Khambhaty, Mody, et al. 2008).

IV. CONCLUSION

The purpose of this research is to find the linear type of Langmuir isotherm equations that can describe with precision the experimental results of equilibrium isotherms, specify the parameters that can be calculated, compare the dye adsorption behavior, and determine the theoretical adsorption isotherms. The calculated results obtained from the five linear forms of Langmuir equations indicate that the q_e values and k_L values were different. Further, from the calculated results obtained from the five linear expressions of Langmuir isotherm equations, it was observed that, if the R^2 values were used to select the best-fit linear types of the same Langmuir isotherm equatuion, it can be seen that the values of R^2 of type 2 and type 5 are close to unity, which means the isotherms are approaching the type 2 and type 5 linear expressions of Langmuir isotherm equations but not the type 1, type 3 and type 4 linear expressions of Langmuir isotherm equations. The predicted q_e valuses and C_e values for the adsorption of MB onto RH by these 5 different linear expressions of Langmuir isotherm equations were used to verify the applicability of each linear type. It was observed that type 1 expressions provide relibable evaluates. However, the predicted q_e valuses and C_e values of type 2 and type 5 expression of Langmuir isotherm equations were found to be the worse fit expression of Langmuir isotherm equations. The present findings suggest that it is not appropriate to use the type 2 and type 5 expression in determining the parameters of the Langmuir isotherm equation. This inadequacy of type 2 and type 5 are primarily because transforming a nonlinear equation to a wrong linearized expression tends to alter the error distribution, and thus distort the calculated results and obtain unsuitable parameters.

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