Letter to the Editor

Comments on "Adsorption of acid dye onto organobentonite"

An adsorption isotherm relates the amount of solute adsorbed onto the solid adsorbent and the left out solution concentration at equilibrium condition. Linear regression was frequently used to determine the most fitted isotherm and the method of least squares has been used for determining the parameters involved in the isotherms. Currently, non-linear method was proved to be a more appropriate method in determining the isotherm parameters [1]. Irrespective of the technique, either the linear method or the non-linear method, the availability of the experimental equilibrium data should be sufficient enough to represent a complete isotherm. In general, a complete isotherm should represent the region of Henry, Freundlich and Langmuir isotherm. Recently, Baskaralingam et al. [2] had published a paper entitled above. In Section 3.6, the equilibrium data were fitted to the Freundlich and Langmuir isotherm by linear regression method. The Freundlich and Langmuir plots in the paper by Baskaralingam et al. [2] does not help much to identify the region (region of Henry, Freundlich and Langmuir) where the experimental equilibrium data are actually located. The experimental equilibrium data points located in the Henry, Freundlich and the Langmuir isotherm may well represent the Henry (linear isotherm), Freundlich and Langmuir isotherms, respectively. However, from design point of view, it is a must to predict the best-fit isotherm that well represents the experimental equilibrium data of a complete isotherm. In addition, the monolayer formation is not evident in the Langmuir plot, which makes the problem more complex. I would like to suggest the authors to show the experimental equilibrium data and the predicted isotherms represented by a plot of q_e versus C_e. A plot of q_e versus C_e representing an equilibrium isotherm will be helpful to identify the region where the experimental equilibrium data are located.

In 1966, Hall et al. [3], reported four idealized types of equilibrium behaviour, each of which is approached by many experimental systems:

1. irreversible equilibrium;
2. favorable equilibrium;
3. linear equilibrium;
4. unfavorable equilibrium.

In order to explain the different idealized equilibrium behaviour Hall et al. reported the separation factor, R_L based on the shape of the isotherm, which is given by:

$$R_L = \frac{1}{1 + KC_0} \tag{1}$$

where K is a Langmuir constant and C_0 is the initial dye concentration. The increasing R_L values with decreasing initial dye concentration favours the adsorption at lower dye concentrations and vice versa. In the paper by Baskaralingam et al. [2], the Table 2 reports the R_L value as 0.024 and 0.00118 for CBDA-bentonite and CP-bentonite, respectively, based on a generalized Langmuir isotherm. I would like to point out that it is not possible to obtain R_L values from the generalized Langmuir isotherm as presented by the authors [2]. So I would like to suggest the authors to calculate the R_L values at different range of initial dye concentrations studied and to report the variation in shape of isotherm for varying initial dye concentration.

In 1906, Freundlich [4] presented the semi-empirical relation to represent the equilibrium sorption system, which is given by:

$$q_e = K_F C_e^{1/n} \tag{2}$$

The value of n in the range of 0–10 will suggest the favorable adsorption. In the paper by Baskaralingam et al. [1], the authors too agree with the assumption behind the Freundlich isotherm in Section 4. The author pointed out the calculated n values were more than the favorable range as per the theory of adsorption. However, I would like to point out that it is not practically possible to get the value of $n > 10$. I think there is some problem while calculating the constants. If the experimental equilibrium data does not lie in the Henry region, then the linear regression method will just check the hypothesis instead of verifying the theory behind the Freundlich model. In addition, there is no meaning in using the Freundlich isotherm unless the equilibrium data represents the complete isotherm [5]. Thus, I would like to suggest the authors to show the experimental equilibrium data

and the predicted isotherms in a plot of q_e versus C_e. A plot of q_e versus C_e will show where the experimental equilibrium data actually lie in the complete isotherm. The plot of q_e versus C_e is suggested because it will be useful to identify is there worthwhile in applying the theoretical isotherms in the experimental equilibrium data.

In Section 5, the authors had wrongly reported the integrated expression of Lagergren pseudo first-order kinetics. The integrated form of Lagergren pseudo first-order kinetics is given by [6]:

$$\log(q_e - q) = \log(q_e) - \frac{K_1 t}{2.303} \tag{3}$$

However, the authors had wrongly reported the Lagergren pseudo first-order kinetic expression, which may lead to wrong predictions of kinetic constants. Thus, I would like to suggest the authors to recalculate the kinetic constants based on the correct integrated form of pseudo first-order kinetic expression. Further the authors had wrongly cited the paper by Namasivayam and Ranganathan [7] for pseudo first-order kinetic expression. However, the pseudo first-order kinetic expression was firstly reported by Lagergren [6]. The correct reference citing the original Lagergren paper was first presented by Ho and McKay [8]. A citation review of the Lagergren's first-order rate equation for adsorption reactions as presented by Ho [9] reports that Lagergren's equation has been widely cited but with lots of second hand references with more mistakes made in the reference section of a paper than anywhere else, such as author, journal title, year, volume and page number. It has been suggested that an accurate citation allow the reader to retrieve the cited reference readily [10]. Thus, I would like to suggest the authors to cite the original paper by Lagergren for pseudo first-order kinetics.

Further the authors concluded the best fit of experimental kinetic data in pseudo second-order kinetics suggests the chemisorption, which may involve valency forces through shar-

ing of electrons between dye anion and adsorbent. I feel there is no validation for this statement. If any there, then I would like to suggest the authors to represent the exchange or sharing of ions through a reaction equation or some other expression which would represent the pseudo second-order kinetic process.

Acknowledgment

References

[1] K.V. Kumar, S. Sivanesan, J. Hazard. Mater. B123 (2005) 288–292.
[2] P. Baskaralingam, M. Pulikesi, D. Elango, V. Ramamurthi, S. Sivanesan, J. Hazard. Mater. B128 (2006) 138–144.
[3] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Ind. Eng. Chem. Fund. 5 (2) (1966) 212–223.
[4] H.M.F. Freundlich, Zeitschrift fur Physikalische Chemie (Leipzig) 57A (1906) 385–470.
[5] K.V. Kumar, S. Sivanesan, J. Hazard. Mater., doi:10.1016/j.jhazmat.2005.11.002.
[6] S. Lagergren, Kungliga Svenska Vetenskapsakademiens, Handlingar 24 (4) (1898) 1–39.
[7] C. Namasivayam, K. Ranganathan, Waste Manage. 14 (1994) 709–716.
[8] Y.S. Ho, G. McKay, Process Saf. Environ. Protect. 76 (B4) (1998) 332–340.
[9] Y.S. Ho, Scientometrics 59 (1) (2004) 171–177.
[10] Y.S. Ho, Biochem. Eng. J. 23 (2005) 291–292.

K. Vasanth Kumar
Department of Chemical Engineering, AC Tech, Anna University, Chennai 600 025, TN, India

E-mail address: vasanth_vit@yahoo.com

27 March 2006

Available online 7 April 2006