



Adsorption thermodynamics of Methylene Blue onto bentonite

Song Hong^a, Cheng Wen^a, Jing He^a, Fuxing Gan^a, Yuh-Shan Ho^{b,c,*}

^a School of Resource and Environmental Science, Wuhan University, Wuhan 430079, People's Republic of China

^b Department of Biotechnology, College of Health Science, Asia University, Taichung 41354, Taiwan

^c Department of Biological Science and Technology, College of Life Sciences, China Medical University, Taichung 40402, Taiwan

ARTICLE INFO

Article history:

Received 21 October 2008

Received in revised form 2 January 2009

Accepted 6 January 2009

Available online 16 January 2009

Keywords:

Sorption

Thermodynamics

Trial-and-error method

Temperature

Bentonite

ABSTRACT

The effect of temperature on the equilibrium adsorption of Methylene Blue dye from aqueous solution using bentonite was investigated. The equilibrium adsorption data were analyzed using three widely applied isotherms: Langmuir, Freundlich, and Redlich–Peterson. A non-linear method was used for comparing the best fit of the isotherms. Best fit was found to be Redlich–Peterson isotherm. Thermodynamic parameters, such as ΔG° , ΔH° , and ΔS° were calculated using adsorption equilibrium constant obtained from the Langmuir isotherm. Results suggested that the Methylene Blue adsorption on bentonite was a spontaneous and endothermic process.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Two important physicochemical aspects for the evaluation of adsorption processes as a unit operation are the adsorption equilibria and the adsorption kinetics. Adsorption equilibrium is established when the concentration of adsorbate in the bulk solution is in dynamic balance with that of the interface concentration. Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium. Adsorption thermodynamic parameters can be obtained from adsorption equilibrium constants with temperatures [1,2]. Linear regression is frequently used to determine the best-fitting isotherm. The linear least-squares method with linearly transformed isotherms has also been widely applied to confirm experimental data and isotherms using coefficients of determination. In recent years, several error analysis methods, such as the coefficient of determination, the sum of the errors squared, a hybrid error function, Marquardt's percent standard deviation, the average relative error, the sum of the absolute errors, and Chi-square, have been used to determine the best-fitting isotherm equation [3,4]. In general, the accuracy of the fit of an isotherm model to experimental equilibrium data is typically assessed based on the magnitude of the coefficient of determination for the lin-

ear regression. The isotherm giving a coefficient of determination value closest to unity is deemed to provide the best fitting. Such transformations of non-linear isotherms to linear forms implicitly alter their error structure and may also violate the error variance and normality assumptions of standard least squares [5,6]. It has been reported that bias results from deriving isotherm parameters from linear forms of isotherms, for example, Freundlich isotherms tend to fit experimental data better at low concentrations and Langmuir isotherms tend to fit the data better at higher concentrations [7]. Moreover, it has been also presented that using the linear regression method for comparing the best-fitting isotherms is not appropriate [8]. Non-linear optimization provides a more complex mathematical method for determining isotherm parameter values [9–12]. An error function assessment is required in order to evaluate the fit of the isotherm to the experimental results [3]. In addition, non-linear optimization techniques were reported earlier to determine isotherm parameters [10]. The advantage of using the non-linear method is that there is no problem with transformations of non-linear isotherms to linear forms, and also they had the same error structures when the best-fitting isotherms are compared [6].

In this study, a non-linear method of three widely used isotherms, Langmuir, Freundlich, and Redlich–Peterson, were compared in an experiment examining Methylene Blue adsorption onto bentonite. A trial-and-error procedure was used for the non-linear method using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel [6,12]. The temperature effect on the equilibrium adsorption of Methylene Blue onto bentonite was examined. Thermodynamic parameters were also calculated.

* Corresponding author at: Department of Biotechnology, College of Health Science, Asia University, Taichung 41354, Taiwan.

E-mail address: ysho@asia.edu.tw (Y.-S. Ho).

Table 1
Main chemical compositions of bentonite.

Composition	Percent (%)	Composition	Percent (%)
SiO ₂	77.0	TiO ₂	0.123
Al ₂ O ₃	15.7	MnO	0.0626
MgO	2.63	SO ₃	0.0436
Fe ₂ O ₃	1.98	Cl	0.0369
CaO	1.81	BaO	0.0257
K ₂ O	0.378	ZrO ₂	0.0169
Na ₂ O	0.192	SrO	0.0146

2. Materials and methods

2.1. Materials

Bentonite used in this study was a commercial product from the Shangtianti nonmetallic ore deposit in Xinyang, Henan Province, China. It was stored in desiccator with silica gel and dried in oven at 150 °C for 2 h before experiments.

The basic dye, Methylene Blue, was used without further purification. A stock solution of 2000 mg/L was prepared by dissolving a weighed amount of Methylene Blue in 1000 mL distilled water. The experimental solution was prepared by diluting the stock solution with distilled water when necessary.

2.2. Methods

The particle size distribution of bentonite powder was determined by using laser diffraction particle size analyzer, Malvern ZetaSizer 3000, and the X-Ray fluorescence spectrometer, Bruker AXS S4 Pioneer was used for chemical composition analysis.

A volume of 50 mL of Methylene Blue solution with a concentration ranging from 200 to 380 mg/L was placed into five 150 mL conical flasks. A weighed amount (0.1 g) of bentonite was added to the solution. The conical flasks were then shaken at a constant speed of 150 rpm in a shaking water bath with temperatures 283, 293, 303, and 308 K, respectively. After shaking the flasks for 4.5 h, the bentonite was separated by centrifugation. The solution was analyzed for the remaining Methylene Blue concentration by a spectrophotometer ($\lambda_{\text{max}} = 664 \text{ nm}$).

The amount of Methylene Blue adsorbed onto bentonite was calculated by using the following expression:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q_e is the equilibrium adsorption capacity of Methylene Blue adsorbed on unit mass of bentonite (mg/g), C_0 and C_e the initial Methylene Blue concentration (mg/L) and Methylene Blue concentration (mg/L) at equilibrium, respectively, V the volume of the Methylene Blue solution (L), and m is the weight of bentonite (g).

3. Results and discussion

3.1. Properties of bentonite

The particle size distribution of bentonite was 618–707 nm (61.9%), 707–806 nm (38.1%), and the average size was 698.4 nm. The result of XRF analysis was showed in Table 1.

3.2. Effect of temperature on equilibrium isotherm

The analysis of the isotherm data is important to develop an equation which accurately represents the results and could be used for design purposes. In order to investigate the adsorption isotherm, three equilibrium isotherms were analyzed: Langmuir, Freundlich, and Redlich–Peterson. The Langmuir adsorption isotherm is per-

haps the best known of all isotherms describing adsorption [13]. The theoretical Langmuir isotherm is often used to describe adsorption of a solute from a liquid solution as [13,14]

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (2)$$

where q_e is the equilibrium adsorption capacity (mg/g), C_e the equilibrium liquid phase concentration (mg/L), q_m the maximum adsorption capacity (mg/g), and K_a is the adsorption equilibrium constant (L/mg).

The Freundlich isotherm is the earliest known relationship describing the adsorption isotherm [15]. This fairly satisfactory empirical isotherm can be used in adsorption from dilute solutions. The ordinary adsorption isotherm is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where C_e is the equilibrium concentration in the solution (mg/L), q_e the equilibrium adsorption capacity (mg/g), and K_F and $1/n$ are empirical constants.

The Redlich–Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms [16]. It can be described as follows:

$$q_e = \frac{A C_e}{1 + B C_e^g} \quad (4)$$

It has three isotherm constants, namely, A , B , and g ($0 < g < 1$).

It has been presented that the non-linear method is a better way to obtain the isotherm parameters [8]. A trial-and-error procedure, which is applicable to computer operation, was used to compare the best fit of the three isotherms using an optimization routine to maximize the coefficient of determination r^2 , between the experimental data and isotherms in the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel [2,6]. The coefficient of determination r^2 was

$$r^2 = \frac{\sum (q_m - \bar{q}_e)^2}{\sum (q_m - \bar{q}_e)^2 + \sum (q_m - q_e)^2} \quad (5)$$

where q_m is the equilibrium capacity obtained from the isotherm model, q_e the equilibrium capacity obtained from experiment, and \bar{q}_e is the average of q_e .

In order to assess different isotherms and their ability to correlate with experimental results, the theoretical plots from

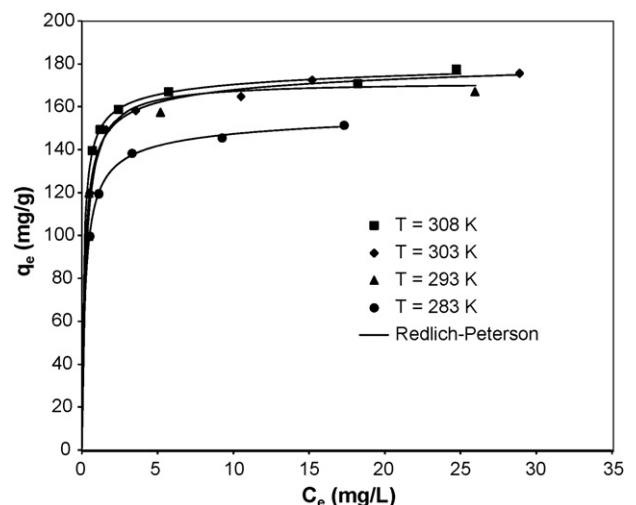


Fig. 1. Redlich–Peterson isotherms obtained using the non-linear method for the adsorption of Methylene Blue onto bentonite at different temperatures.

Table 2
Isotherm parameters obtained using the non-linear method for the adsorption of Methylene Blue onto bentonite at different temperatures.

Isotherm		T (K)			
		283	293	303	308
Langmuir	q_m (mg/g)	151	172	173	175
	K_a (L/mg)	3.65	3.81	4.08	5.25
	ΔG° (kJ/mol)	-17.0	-17.7	-18.5	-19.4
	r^2	0.991	0.907	0.974	0.955
Freundlich	$1/n$	0.115	0.120	0.0918	0.0621
	K_F ((mg/g)(L/mg) ^{1/n})	114	124	134	147
	r^2	0.925	0.811	0.905	0.942
Redlich-Peterson	g	0.974	1.00	0.972	0.976
	B (L/mg) ^g	4.91	3.81	6.22	8.76
	A (L/g)	695	655	996	1430
	r^2	0.998	0.907	0.991	0.985

each isotherm have been fitted with the experimental data for adsorption of Methylene Blue on bentonite. Fig. 1 shows the Redlich-Peterson isotherm with experimental data at the various temperatures. The graph is plotted in the form of Methylene Blue adsorbed per unit mass of bentonite, q_e , against the concentration of Methylene Blue remaining in solution, C_e . A comparison of coefficient of determination for three isotherms has been made and listed in Table 2. Redlich-Peterson isotherm was most suitable for the data followed by Langmuir and then Freundlich isotherm. The Langmuir and the Redlich-Peterson isotherms had been well fitted the adsorption of Methylene Blue onto bentonite at various temperatures but Redlich-Peterson might be better fitting isotherm because of its higher r^2 value. However in the temperature of 293 K, the coefficients of determination of Redlich-Peterson and Langmuir isotherms were the same ($r^2 = 0.907$). Fig. 2 shows the plots comparing the theoretical Langmuir, empirical Freundlich, and the Redlich-Peterson isotherm with the experimental data for the adsorption of Methylene Blue onto bentonite at a temperature of 293 K. The Redlich-Peterson and Langmuir isotherms overlapped and seemed to be the best-fitting isotherms for the experiment results. By using non-linear method there was no problem with transformation of non-linear isotherm equation to linear forms, and also they had the same error structures [8]. The adsorption capacity of Methylene Blue increases with temperature which is

typical for the adsorption of most dyes from their solution. When the system is in a state of equilibrium, the distribution of Methylene Blue between the bentonite and the Methylene Blue solution is of fundamental importance in determining the maximum adsorption capacity of bentonite for the Methylene Blue from the isotherm. The Langmuir, Redlich-Peterson, and Freundlich isotherms constants are shown in Table 2. The maximum adsorption capacity, q_m , and the adsorption constant, K_a , were found to increase from 151 to 175 mg/g and 3.65 to 5.25 L/mg for an increase in the solution temperatures from 283 to 308 K, respectively. The increase in K_a values with temperature indicates a higher heat of adsorption with increasing temperature. It might be that stronger bonds are formed at higher temperatures supporting the fact that adsorption is endothermic. In addition, the values of g were close to unity (>0.972), which means that the isotherms are approaching the Langmuir form and not the Freundlich isotherm.

3.3. Thermodynamic studies

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, ΔG° , is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. Reactions occur spontaneously at a given temperature if ΔG° is a negative quantity. The free energy of an adsorption, considering the adsorption equilibrium constant K_a is given by the following equation:

$$\Delta G^\circ = -RT \ln K_a \quad (6)$$

where ΔG° is the standard free energy change (J/mol), R the universal gas constant (8.314 J/mol K), and T is the absolute temperature (K). Considering the relationship between ΔG° and K_a , change in equilibrium constant with temperature can be obtained in the differential form as follows [1,17]:

$$\frac{d \ln K_a}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (7)$$

After integration, the integrated form of Eq. (7) becomes:

$$\ln K_a = -\frac{\Delta H^\circ}{RT} + Y \quad (8)$$

where Y is a constant. Eq. (8) can be rearranged to obtain

$$-RT \ln K_a = \Delta H^\circ - TRY \quad (9)$$

Let

$$\Delta S^\circ = RY \quad (10)$$

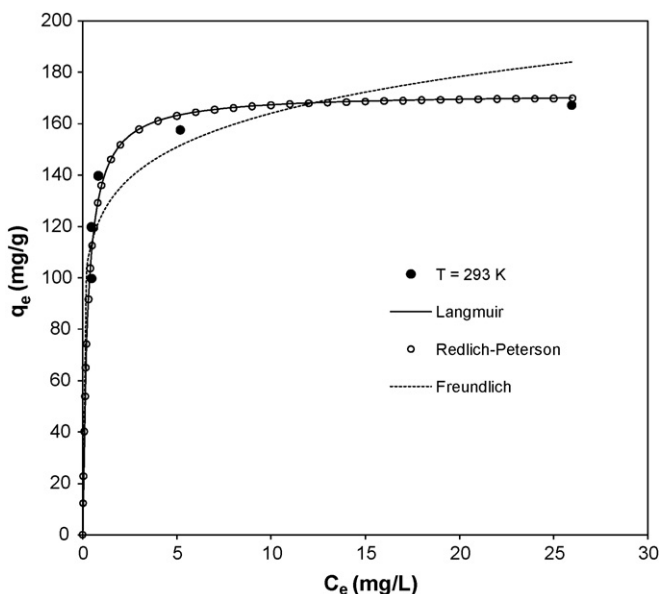


Fig. 2. Isotherms obtained using the non-linear method for the adsorption of Methylene Blue onto bentonite at a temperature 293 K.

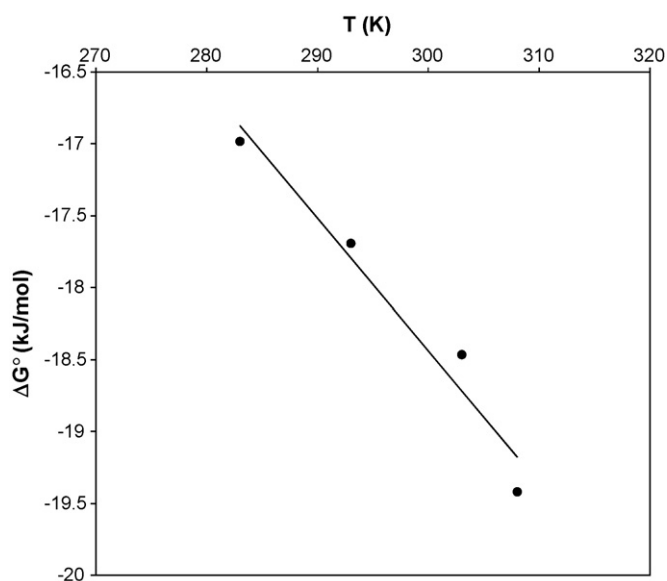


Fig. 3. Plot of Gibbs free energy change, ΔG° versus temperature, T .

Substituting Eqs. (9) and (10), ΔG° , can be represented as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

The adsorption equilibrium constant, K_a , obtained from non-linear method was analyzed using Eqs. (2) and (11). A plot of ΔG° versus temperature, T , will be linear and the values of ΔH° and ΔS° are determined from the slope and intercept of the plot (Fig. 3). The parameter ΔG° for the adsorption process using the K_a from the Langmuir isotherm is shown in Table 2. The values of ΔG° calculated using the K_a were negative for the adsorption of Methylene Blue onto bentonite at all temperatures. The negative values confirm the feasibility of the process and the spontaneous nature of the adsorption.

The values of ΔG° , were found to decrease -17.0 to -19.4 kJ/mol using the equilibrium constant, K_a . The decrease in the negative value of ΔG° with an increase in temperature indicates that the adsorption process of Methylene Blue on bentonite becomes more favorable at higher temperatures [18]. The values of ΔH° and ΔS° calculated from the plot of ΔG° versus T were given as 9.21 kJ/mol and 92.2 J/mol K, respectively. The value of ΔH° was positive, indicating that the adsorption reaction was endothermic. The positive value of ΔS° reflects the affinity of the bentonite for the Methylene Blue and suggests some structural changes in dye and bentonite [19]. Spontaneous and endothermic adsorption have also been reported for the system of basic dyes on tree fern [1], wheat shell [20], and mansonia wood sawdust [21].

4. Conclusion

Bentonite is able to adsorb Methylene Blue dye from aqueous solutions. The removal of Methylene Blue using bentonite was a function of temperature. The adsorption capacity increased with

increasing temperature. It is successful to use the coefficient of determination of the non-linear method for comparing the best fit of the Langmuir, Freundlich, and Redlich-Peterson isotherms. The Redlich-Peterson and the Langmuir isotherms had higher coefficients of determination than that of Freundlich isotherm but Redlich-Peterson might be the best-fitting isotherm. Thermodynamic parameter, ΔG° could be calculated from adsorption equilibrium constant obtained from Langmuir isotherm. The value of ΔH° and ΔS° could be obtained from the slope and intercept of the relationship between ΔG° and reaction temperature. The negative values of ΔG° indicate the spontaneous nature of adsorption with a high preference of Methylene Blue onto bentonite. The value of ΔH° was positive, indicated that the adsorption reaction was endothermic. The positive value of ΔS° shows that increasing randomness at the solid/liquid interface during the adsorption of Methylene Blue on bentonite.

References

- [1] Y.S. Ho, T.H. Chiang, Y.M. Hsueh, Removal of basic dye from aqueous solution using tree fern as a biosorbent, *Process Biochem.* 40 (2005) 119–124.
- [2] Y.S. Ho, A.E. Ofomaja, Kinetics and thermodynamics of lead ion sorption on palm kernel fibre from aqueous solution, *Process Biochem.* 40 (2005) 3455–3461.
- [3] Y.S. Ho, J.F. Porter, G. McKay, Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems, *Water Air Soil Pollut.* 141 (2002) 1–33.
- [4] S.J. Allen, Q. Gan, R. Matthews, P.A. Johnson, Comparison of optimised isotherm models for basic dye adsorption by kudzu, *Bioresour. Technol.* 88 (2003) 143–152.
- [5] D.A. Ratkowsky, *Handbook of Nonlinear Regression Models*, Marcel Dekker, Inc., New York, 1990.
- [6] Y.S. Ho, Isotherms for the sorption of lead onto peat: comparison of linear and non-linear methods, *Pol. J. Environ. Stud.* 15 (2006) 81–86.
- [7] E. Richter, W. Schutz, A.L. Myers, Effect of adsorption equation on prediction of multicomponent adsorption equilibria by the ideal adsorbed solution theories, *Chem. Eng. Sci.* 44 (1989) 1609–1616.
- [8] Y.S. Ho, Selection of optimum sorption isotherm, *Carbon* 42 (2004) 2115–2116.
- [9] K. Stamberg, J. Cabicar, L. Havlicek, Ion-exchange kinetics in systems with non-linear equilibrium isotherms: sorption of uranium(VI) on strong acid cation exchangers, *J. Chromatogr. A* 201 (1984) 113–120.
- [10] A. Seidel, D. Gelbin, On applying the ideal adsorbed solution theory to multicomponent adsorption equilibria of dissolved organic components on activated carbon, *Chem. Eng. Sci.* 43 (1988) 79–89.
- [11] C. Huang, C.P. Huang, A.L. Morehart, Proton competition in Cu(II) adsorption by fungal mycelia, *Water Res.* 25 (1991) 1365–1375.
- [12] Y.S. Ho, W.T. Chiu, C.C. Wang, Regression analysis for the sorption isotherms of basic dyes on sugarcane dust, *Bioresour. Technol.* 96 (2005) 1285–1291.
- [13] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [14] Y.S. Ho, C.T. Huang, H.W. Huang, Equilibrium sorption isotherm for metal ions on tree fern, *Process Biochem.* 37 (2002) 1421–1430.
- [15] H.M.F. Freundlich, Über die adsorption in lösungen, *Z. Phys. Chem.* 57A (1906) 385–470.
- [16] O. Redlich, D.L. Peterson, A useful adsorption isotherm, *J. Phys. Chem.* 63 (1959) 1024.
- [17] Y.S. Ho, Removal of copper ions from aqueous solution by tree fern, *Water Res.* 37 (2003) 2323–2330.
- [18] A.B. Zaki, M.Y. El-Sheikh, J. Evans, S.A. El-Safy, Kinetics and mechanism of the sorption of some aromatic amines onto amberlite IRA-904 anion-exchange resin, *J. Colloid Interf. Sci.* 221 (2000) 58–63.
- [19] V.K. Gupta, Equilibrium uptake, sorption dynamics, process development, and column operations for the removal of copper and nickel from aqueous solution and wastewater using activated slag, a low-cost adsorbent, *Ind. Eng. Chem. Res.* 37 (1998) 192–202.
- [20] Y. Bulut, H. Aydin, A kinetics and thermodynamics study of Methylene Blue adsorption on wheat shells, *Desalination* 194 (2006) 259–267.
- [21] A.E. Ofomaja, Y.S. Ho, Effect of temperatures and pH on Methyl violet biosorption by mansonia wood sawdust, *Bioresour. Technol.* 99 (2008) 5411–5417.