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Comparison of Thermodynamics and Kinetics of Malachite Green Adsorption onto Chitin and Chitosan†

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The adsorption of Malachite green by chitin and chitosan is investigated and compared by the adsorption method. The results shows that the Langmuir isotherm can well described the Malachite green adsorption for the chitin and chitosan. The maximum quantities of the Malachite green adsorption by the chitin and chitosan are 97.09 and 166.67 mg/g, respectively, indicating that the chitosan has more effective than the chitin two times approximately. The thermodynamic data also suggests that the chitosan is more favourable than the chitin.

Keywords: Malachite green, Chitin, Chitosan, Thermodynamics, Kinetic.

INTRODUCTION

Malachite green (MG) is the most widely used dye for colouring purposes (silk, wool, leather, paper, acrylic industry)[1]. Therefore, it results in environmental problem because it can leak to the river from many industries. The Malachite green is hazardous and can be the carcinogenic effects to mammalian cells[2]. It can irritate to the human respiration, gastrointestinal tract and other organs[3]. Treatment of wastewater from the dying industries is a huge challenge for many research groups. Many methods were suggested to remove the Malachite green but the adsorption has been presented as an economical alternative approach[4].

Chitin and chitosan, extracted from the crustacean shells (prawn, crabs and other crustaceans) are the interesting alternative adsorbents with various potential[5]. The objective of this study is to compare the ability of the chitin and chitosan for Malachite green removal from the aqueous solution. In addition, the kinetics and thermodynamics parameters were also investigated for that reason.

EXPERIMENTAL

For preparation of the adsorbate, the Malachite green solution was prepared for five concentrations (100, 200, 300, 400, 500 ppm) from 1000 ppm of stock solution.

For preparation of the adsorbent, the chitosan flake (commercial grade) with molecular weights 3.6×10^5 g/mol was obtained from A.N. Lab of Aquatic Nutrition Company in Thailand. The chitin is prepared from the shrimp shell as the conventional method[6].

For the adsorption process, the chitin and chitosan flake of 0.021 g were added to 5 mL of the Malachite green solution in the test tube for all five concentrations. Then put all sets of concentrations prepared into the shaking water bath for 15, 30, 60, 180 and 360 min at 30, 35 and 40 °C. The concentration before and after adsorption were measured by using the visible spectrophotometer (Model CE1021, Cecil Instruments). The Malachite green solution absorbs wavelength at 618 nm.

RESULTS AND DISCUSSION

Adsorption isotherm: There are interpretation of two isotherm models which are, Langmuir and Freundlich. These isotherm models can represent the character of Malachite green adsorption by chitin and chitosan. The Langmuir isotherm model represents the monolayer adsorption that occurs at the surface without lateral interaction of adsorbed. The related equation is shown in eqn. 1.

$$q_e = \frac{Q_0 b C_e}{(1 + b C_e)} \quad (1)$$

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where C_e (mg/L) and q_e (mg/g) are the Malachite green concentration in the solution at equilibrium and amount of adsorbed Malachite green per unit mass of sorbent, respectively. Q_0 is the maximum amount of Malachite green per unit mass of sorbent. b is a constant relating to the affinity of the binding regions (L/mg).

The Freundlich isotherm model represents the multilayer adsorption over the heterogeneous surface. The Freundlich model relates with the eqn. 2.

$$q_e = K_F C_e^{1/n} \quad (2)$$

The meaning of q_e and C_e are also similar to the Lanmuir equation. The K_F is the Freundlich constant (mg/g) presenting the adsorption capacity of the sorbent. While, n shows how much favourable adsorption process is (n > 1; prefer).

All parameters of these two isotherms are listed in Table-1. It appears that the character of Malachite green adsorption by chitin and chitosan is Langmuir isotherm model because the R^2 of the Langmuir approaches 1.00 which is greater than the Freundlich for the chitin (R^2 = 0.980) and the chitosan (R^2 = 0.848). The capacities of Malachite green adsorption are 97.087 and 166.67 mg/g for the chitin and chitosan, respectively, indicating that the chitosan has the higher ability of Malachite green adsorption than the chitin. In addition, it can be concluded that the Malachite green adsorptions by both of the chitin and chitosan are the monolayer model.

TABLE-1
CONSTANTS FOR LANMUIR AND FREUNDLICH ISOTHERM MODELS AND CORRELATION COEFFICIENTS FOR ADSORPTION OF MALACHITE GREEN ONTO CHITIN AND CHITOSAN AT 30 °C

Isotherm	Parameters	
	Chitin	Chitosan
Langmuir		
Q_0 (mg/g)	97.087	166.67
B (L/mg)	0.1573	0.0832
R^2	0.9802	0.848
Freundlich		
K_f (mg/g)	36.94	15.635
n	4.9383	1.4877
R^2	0.174	0.819

Adsorption kinetics: Study of adsorption kinetics are investigated in two models which are, pseudo-first-order and pseudo-second-order models, in order to obtain the rate constant and to predict the amount of Malachite green at the different concentration. The pseudo-first-order (eqn. 3) and the pseudo-second-order (eqn. 4) model can be presented as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

and

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (4)$$

where q_t is the amount of Malachite green adsorbed (mg/g) on the chitin and the chitosan at the different time (t). The q_e is the adsorption capacity (mg/g) at equilibrium. The k_1 (1/h) and k_2 (mg/g.h) are the rate constant for the pseudo-first and pseudo-second order equation, respectively. The k_1 and q_e are slope and Y-intercept obtained from the linear plot between the t and $\ln(q_e - q_t)$. As well as the k_2 and q_e are Y-intercept and slope, respectively, from the plot between t/q_t and t.

According to the kinetic results in Table-2 (chitin) and Table-3 (chitosan), it appears that the Malachite green adsorption by the chitin and chitosan follows the pseudo-second-order equation because of the greater R^2 when compare with the R^2 of the pseudo-first-order equation. Moreover, the calculated q_e values obtained from the pseudo-second-order equation close to the experiment al values for all concentration. Therefore, it can confirm that the Malachite green adsorption prefers to follow the pseudo-second-order equation.

Thermodynamics parameters of adsorption: Thermodynamic parameters can provide the information if the Malachite green adsorption process is spontaneous which can appears when the Gibb's free energy change (ΔG^o) is a negative value at a given temperature. The ΔG^o is calculated from eqn. 5 shown below.

$$\Delta G^o = -RT \ln K_c \quad (5)$$

While, the entropy (ΔS) and enthalpy (ΔH) are obtained from the plot between the ΔS and the ΔH according to the eqn. 6.

TABLE-2
KINETIC PARAMETERS FOR ADSORPTION OF MALACHITE GREEN ONTO CHITIN GEL AT 30 °C

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
		$q_{e,cql}$ (mg/g)	k_1 (1/h)	R^2	$q_{e,cql}$ (mg/g)	k_2 (g/g.h)	R^2
100	22.630	276.414	2.769	0.90	23.095	0.375	1.00
200	45.006	24.452	1.273	0.68	46.948	0.047	0.98
300	68.894	163.19	2.249	0.80	71.429	0.022	0.94
400	91.636	276.414	2.064	0.80	96.154	0.010	0.85
500	115.999	331.292	2.002	0.85	129.870	0.008	0.97

TABLE-3
KINETIC PARAMETERS FOR ADSORPTION OF MALACHITE GREEN ONTO CHITOSAN GEL AT 30 °C

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
		$q_{e,cql}$ (mg/g)	k_1 (1/h)	R^2	$q_{e,cql}$ (mg/g)	k_2 (g/g.h)	R^2
100	22.142	13.259	1.928	0.89	22.676	0.319	1.00
200	44.657	62.615	2.276	0.73	46.729	0.095	1.00
300	68.703	116.338	2.218	0.96	72.993	0.045	1.00
400	92.449	179.864	2.011	0.95	100.000	0.021	1.00
500	109.552	166.451	2.041	0.98	117.647	0.023	1.00

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} \quad (6)$$

The results show that the ΔH is positive values for the Malachite green adsorption of chitin and the chitosan indicating that the adsorption is the exothermic reaction. The ΔG^{o} of the chitosan shows that it is greater than the ΔG^{o} of the chitin for all temperatures as shown in the Table-4. This can suggest that the Malachite green adsorption process prefers the chitosan as the adsorbent.

TABLE-4
THERMODYNAMICS DATA FOR THE ADSORPTION OF MALACHITE GREEN BY CHITIN (CT) AND CHITOSAN (CS) AT DIFFERENT TEMPERATURES

T (K)	$\Delta G^{o,CT}$ (kJ/mol)	$\Delta G^{o,CS}$ (kJ/mol)
303	-2.87	-3.21
308	-2.91	-3.66
313	-3.35	-3.54

Conclusions

The adsorption of Malachite green by the chitin and chitosan are the Langmuir model and the chitosan adsorbs the Malachite green better than the chitin about two times. The ΔG also supports ability of the Malachite green adsorption of the chitosan that is more favourable than the chitin for all tempe-ratures. In addition, the thermodynamics parameters show that the Malachite green adsorptions of the chitin and chitosan are the exothermic reaction. The kinetic adsorptions of the Malachite green adsorption followed by the Pseudo-second-order equation for both of the chitin and chitosan.

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