The Adsorption Kinetics and Isotherms of Removing Methylene Blue Dye with Chitosan

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ABSTRACT

In this study, adsorption experiments were carried out in batch process for the removal of methylene blue (MB) using chitosan prepared from fresh river shrimp shell (Macrobrachium rosenbergii). The chitosan was confirmed by FTIR and its degree of deacetylation (DD) was 67.98%. The factors affecting the adsorption process were solution pH, contact time and initial concentration. Experiment results showed that dye uptake was a rapid process and reached equilibrium in about 5 min at pH 10. The equilibrium data were analyzed by Langmuir and Freundlich isotherm models. The better fitting isotherm model was Langmuir. The maximum adsorption capacity of chitosan obtained from the Langmuir model was 76.92 mg/g. The adsorption kinetics corresponded to the pseudo-second order model. The results in this study indicated that chitosan was a good adsorbent for removing methylene blue.

Keywords: Kinetic adsorption, Methylene blue, Chitosan, Shrimp shell

INTRODUCTION

Many industries – including textile, paper, plastics and dyestuffs – are water-intensive and use chemicals and dyes. As result, they generate colored wastewater and pollute the environment. Methylene blue (MB) is a basic dye used in the textile industry. It can cause permanent injury to human eyes and gives rise to respiratory problems, while oral ingestion produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia (Ghosh et al., 2002).

Adsorption is the most commonly used technique for decontaminating dye-containing effluents. Most commercial systems currently use activated carbons as an adsorbent because of their high adsorption capacity, large surface area and microporous structure, but they are expensive (Low et al., 2011) and activated carbons are difficult to generate (Sakkayawong et al., 2005). Considerable research in recent years has focused on finding a low-cost alternative (Bulut and Aidin, 2006; Hameed et al., 2008; Senturk et al., 2010; Santhi and Manonmani, 2011). Adsorption using agricultural waste products offers a new alternative for wastewater treatment (Ibrahim et al., 2006). Natural biodegradable waste materi-

als from industrial and agricultural operations may have potential as inexpensive adsorbents. This paper evaluates the efficiency of chitosan from river shrimp shell as an adsorbent for the removal of methylene blue dye from aqueous solutions. The experiments were performed on the batch adsorption process. In addition, the adsorption of methylene blue was studied under equilibrium conditions. Furthermore, the kinetics involved in the sorption process were evaluated.

MATERIALS AND METHODS

Preparation of chitosan

The river shrimp shell (*Macrobrachium rosenbergii*) used in the present investigation was obtained from a restaurant in Lopburi City, Thailand. The collected material was washed with tap water several times to remove all dirt particles and then dried in an oven. The dried shrimp shell was ground using a domestic mixer. The resulting shrimp shell powder was treated with 1 M HCl at room temperature for 6 h to remove minerals and then treated with 3 M NaOH (1:10 w/v) at 100°C for 3 h to remove proteins. The mixture was filtered and washed with distilled water to neutral. The obtained solid was decolorized by treating with 1% $KMnO_4$ for 1 h, and then reacted with 1% oxalic acid solution for 1 h (Chang, 1982 and Yen et al., 2009). The precipitate, chitin, was washed with distilled water to neutral pH and dried in a hot air oven at 60°C. For the purpose of deacetylation, 1 g of chitin was treated with 30 ml of 40% NaOH at 100°C for 60 min, washed with distilled water to neutral pH and dried in an oven at 60°C. The corresponding product obtained was designated as chitosan. The chitosan was characterized by FTIR (Shimadsu 8900) and its surface area was determined by methylene blue adsorption method. The chitosan used in experiments were sieved to sizes of 50 to 100 mesh and then stored in a plastic bottle for use.

Adsorbate

Methylene blue (C.I.52015, chemical formula: $C_{16}H_{18}ClN_3S.2H_2O$, molecular weight = 355.89 g mol^{-1}) (APS Ajax Finechem, Australia) was used as the adsorbate in this study. It was dried at 110°C for 2 h and kept in the desiccator for use. The stock solution was prepared by dissolving 500 mg of methylene blue in one liter of distilled water. The working solutions of desired concentrations were obtained by dilution with distilled water.

Batch adsorption

Adsorption studies were performed in batch method. The effects of the adsorption system such as pH (2−10), contact time (1−60 min) and initial dye concentration (20−200 mg/l) were studied. Adsorption experiments were carried out in 250 ml Erlenmeyer flasks with 0.1 g of chitosan and 100 ml of methylene blue solution under an isothermal shaker (30±1°C) and agitation speed 200 rpm. Kinetic studies of adsorption were carried out at two concentrations of methylene blue (50 and 100 mg/l) and the extent of adsorption was investigated as a function of time. The methylene blue solution concentration was determined by UV−Vis spectrophotometer at 662 nm

Adsorption isotherm

The Langmuir isotherm in a linear form is represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \quad \text{.....(1)}$$

where C_e (mg/l) is the equilibrium concentration, q_e (mg/g) is the amount adsorbed at equilibrium, K_L is the Langmuir constant and q_{max} (mg/g) is the maximum adsorption capacity.

The Freundlich isotherm in a linear form is represented as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{.....(2)}$$

where K_F (l/g) is the adsorption capacity and $\frac{1}{n}$ is the adsorption intensity.

Adsorption kinetics

The applied kinetics models were primarily pseudo-first order and pseudo-second order.

The pseudo first-order kinetic in a linear form is written as follows:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \text{.....(3)}$$

where k_1 (min^{-1}) is the rate constant of pseudo first-order adsorption, (mg/g) is the amount adsorbed at equilibrium and q_t (mg/g) is the amount adsorbed at any time (min).

The pseudo second-order kinetic in a linear form is written as follows:

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

where k_2 ($g.mg^{-1}.min^{-1}$) is the rate constant of pseudo second-order adsorption.

Free energy of adsorption

The thermodynamic parameter such as the Gibbs free energy change indicates the degree of spontaneity of a process and the higher negative value indicates a more energetically favorable adsorption. The Gibbs free energy change (ΔG) in the adsorption process can be expressed as follows:

$$\Delta G = -RT \ln K_c \quad \text{.....(5)}$$

where K_c is the equilibrium constant, R is the gas constant and T is the absolute temperature.

The equilibrium constant of adsorption is determined by

$$K_c = \frac{C_o - C_e}{C_e} \quad \text{.....(6)}$$

where C_e and C_o are the equilibrium and initial concentration of methylene blue in the solution.

RESULTS

Characterization of adsorbent

Figure 1 represents the FTIR spectra (400−4000 cm^{-1}) of chitosan obtained from river shrimp shell. The wide band at 3437 cm^{-1} is due to O−H stretching. The band at 2883 cm^{-1} is due to C−H stretching. The band observed at 1650 cm^{-1} corresponds to N−H stretching. The band at 1150 cm^{-1} is due to C=O stretching. The band at 1050 cm^{-1} is assigned to C−N bending. Kamari et al. (2008) reported similar observations. The degree of deacetylation (DD) of the chitosan was 67.98%.

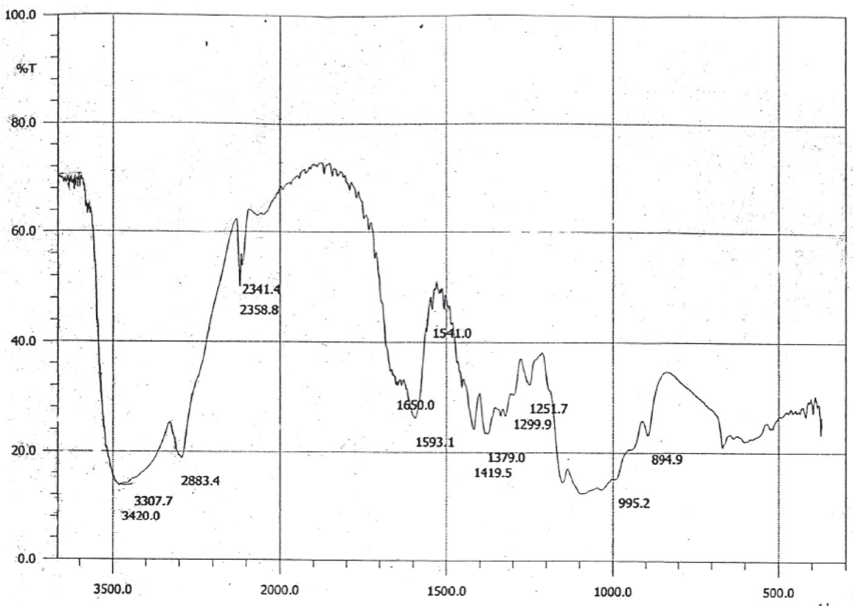

Figure 1. IR peak of chitosan.

Effect of pH

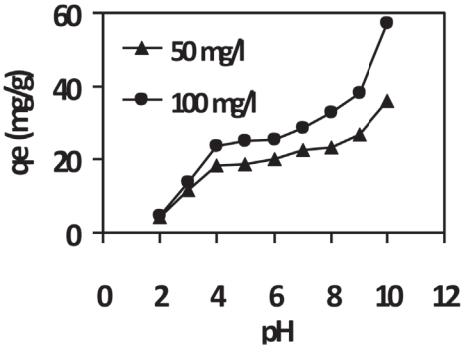

Figure 2. Effect of pH of methylene blue adsorption on chitosan.

The effect of the pH of the methylene blue solution (MB+) plays an important role in the adsorption process and on the sorption capacity. The cations are favorably adsorbed by the adsorbent at higher pH values. At high pH values, cations are adsorbed due to the negatively charged surface sites of the adsorbent. Figure 2 shows the sorption capacity of the chitosan for methylene blue at different initial pH values. As can be seen from Figure 2, the adsorption of MB^+ onto chitosan increased as the pH increased from 2 to 10. The adsorption capacity increased from 4.245 to 36.015 mg/g and 4.571 to 57.006 mg/g with an increase in the initial methylene blue concentration from 50 to 100 mg/l, respectively.

Effect of contact time and initial concentration

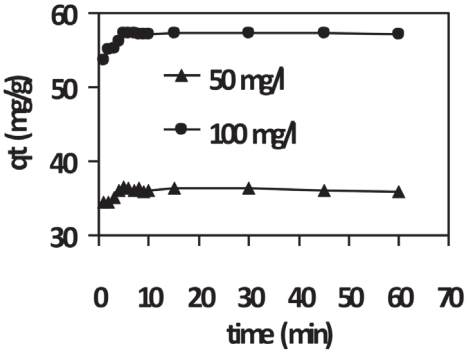

Figure 3. Effect of contact time and initial concentration of methylene blue adsorption on chitosan.

Figure 3 shows the adsorption capacity versus the adsorption time for two concentrations (50 and 100 mg/l) at pH 10. The contact time of adsorption reached equilibrium at 5 min. The adsorption capacity at equilibrium increased from 34.491 to 34.952 mg/g and 53.674 to 57.079 mg/g with an increase in the initial methylene blue concentration from 50 and 100 mg/l, respectively.

Adsorption isotherm

For the Freundlich isotherm, K_F and 1/n can be calculated from the intercept and slope of plot (Fig. 4) between log and log C_e. The value was 10.614 l/g and 1/n value was 0.414. A value of 1/n between 1−0.1 shows beneficial adsorption (Vadivelan and Kumar, 2005).

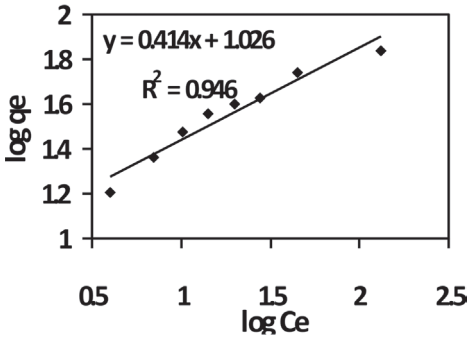

Figure 4. Freundlich isotherm for methylene blue adsorption on chitosan.

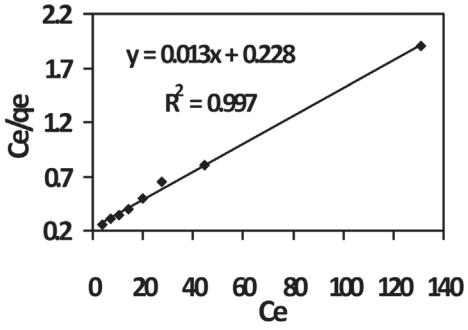

Figure 5. Langmuir isotherm for methylene blue adsorption on chitosan.

Figure 5 shows the linear plot of Langmuir isotherm for methylene blue adsorption on the chitosan. As seen in Figures 4 and 5, the equilibrium data fit the Freundlich and Langmuir equations with a correlation coefficient value of 0.946 and 0.997, respectively. The calculated isotherm constant and their corresponding correlation coefficient are given in Table 1. From Table 1, the maximum sorption capacity (q_{max}) of methylene blue on the chitosan was 76.923 mg/g.

Table 1. Langmuir and Freundlich isotherm parameters for methylene blue adsorption.

Langmuir isotherm				**Freundlich isotherm**		
K_L (l/mg)	q_{max} (mg/g)	R_L	R^2	KF (l/g)	1/n	R^2
0.057	76.923	0.081−0.467	0.997	10.614	0.414	0.946

Note: The calculated R_L values at initial dye concentration are shown in Figure 6. Values of were 0.081−0.467.

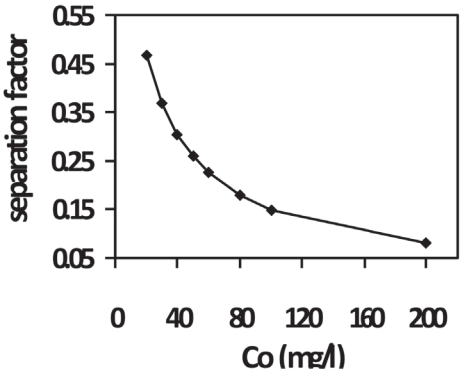

Figure 6. Separation factor of methylene blue adsorption on chitosan.

Adsorption kinetics

The pseudo-first order did not adequately describe the adsorption result (not shown). The plot of the pseudo-second order kinetic reaction is shown in Figure 7.

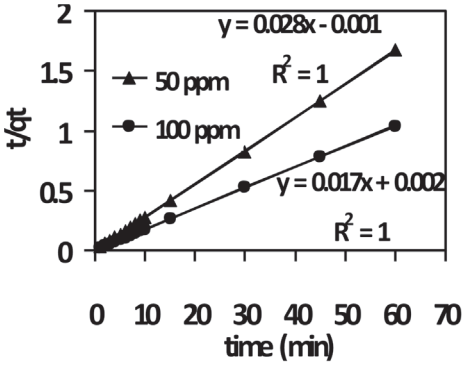

Figure 7. Pseudo-second order kinetic model for methylene blue adsorption on chitosan.

Table 2. Second-order kinetics parameters for methylene blue adsorption.

Initial concentration (mg/1)	q_e (exp) (mg-g)	q_e (cal) (mg/g)	k_2 ($g.mg^{-1}.min^{-1}$)	R^2
50	36.495	35.714	0.729	1
100	57.316	58.824	0.144	1

Note: As seen in Table 2., the adsorption of methylene blue on chitosan was best described by pseudo-second order kinetics. The value of k_2 decreased from 0.729 to 0.144 as the initial concentration increased from 50 to 100 mg/l. For the equilibrium adsorption capacity calculated from the pseudo-second order rate equation, (cal) increased from 35.714 to 58.824 mg/g as the initial concentration increased from 50 and 100 mg/l.

Free energy of adsorption

The adsorption of methylene blue on chitosan was studied at 30°C to determine free energy of adsorption (ΔG). At the initial dye concentration of 20, 30, 40, 50, 60, 80 and 100 mg/l, the Gibbs free energy changes for methylene blue adsorption were estimated to be −3.484, −2.973, −2.690, −2.353, −1.736, −1.066 and −0.535 KJ/mol, respectively. At the initial concentration of 200 mg/l, the positive value of ΔG was 1.621 KJ/mol. Moreover, q_e values (q_e,cal) calculated from the pseudo-second order model agreed well with experimental values (q_e,exp).

DISCUSSION

We studied the adsorption of methylene blue by chitosan obtained from river shrimp shell (*Macrobrachium rosenbergii*). Experimental results showed that dye uptake was a rapid process and reached equilibrium in about 5 min at pH 10. The pH of the dye solution played an important role in the adsorption of the dye, as the pH of the solution affects the surface charge of the adsorbent. The amino groups of chitosan are protonated under acidic conditions, because the pKa of chitosan's amino groups is approximately 6.3 (Chiou and Li, 2002). Thus, strong coulombic repulsions are developed between chitosan and MB^+. However, at the higher pH, the repulsive forces are weak-ended since the amino group are deprotonated, while the OH group becomes negative ($-O^-$) (Sakkayawong et al., 2005), thereby resulting in an increased adsorption of MB^+ due an increasing electrostatic attraction between the positively charged group on methylene blue and the negatively charged surface of chitosan. Several other investigations also have shown that methylene blue adsorption is higher at higher pH values (Vadivelan and Kumar, 2005; Pavan et al., 2008; and El−Sayed, 2011).

The effect of contact time could be explained by the theory that in the process of methylene blue adsorption, MB molecules have to first encounter the boundary layer and then diffuse to the porous structure of the adsorbent. The amount of methylene blue adsorption on chitosan increased with time and reached a constant value of adsorption. At this point, the amount of methylene blue desorbing from chitosan is in a state of dynamic equilibrium with the amount of methylene blue adsorbing on chitosan (Hameed et al., 2007; El−Sayed, 2011).

The best fit of the experimental data in the Langmuir isotherm indicated a homogeneous nature by the monolayer coverage on the surface and the maximum adsorption capacity value 76.923 mg/g. Similar observations were reported in the literature for monolayer adsorption of methylene blue by activated carbon (Hameed et al., 2007; Hameed et al., 2008) and rice husk (Vadivelan and Kumar, 2005). The effect of the Langmuir isotherm shape could be used to predict whether an adsorption system is favorable or unfavorable (Hall et al., 1966). The essential characteristics of a dimensionless separation factor or equilibrium parameter (R_L), the value of $0 < R_L < 1$, as in Figure 6, indicated that the adsorption of methylene blue was favorable. Adsorption kinetic studies were performed for two concentrations (50 and 100 mg/l) at varying contact time. A better correlation coefficient for the pseudo-second than the pseudo-first order indicated that the dye adsorption

process followed the pseudo-second order. Several investigations also have shown that methylene blue adsorption followed the pseudo-second order (Vadivelan and Kumar, 2005; Hameed et al., 2007; El−Sayed, 2011). The pseudo-second order model is based on the assumption that the reaction is chemisorption involving valence force or exchange of electron between adsorbent and adsorbate (Ibrahim et al., 2006; Senturk et al., 2011). The value of the pseudo-second order rate constant decreased from 0.729 to 0.144 as the initial concentration increased from 50 to 100 mg/l. Increasing methylene blue concentration in solution seems to reduce the diffusion of methylene blue in the boundary layer and to enhance the diffusion in the solid. (Abechi et al., 2011).

Thermodynamic parameters of adsorption free energy (ΔG) at initial dye concentrations of 20−100 mg/l were negative, but positive at an initial dye concentration of 200 mg/l. Negative value of ΔG indicated that the adsorption was spontaneous and positive value of ΔG indicated that the adsorption was non-spontaneous in nature. The spontaneity of the adsorption process decreased as the initial concentration increased. Spontaneous adsorption has been reported for adsorption of methylene blue on wheat shell (Bulut and Aydin, 2006) and activated carbon (Karaca et al., 2008). The Gibbs free energy changes for physical and chemical adsorption are usually in the range of 0.0 to 20 KJ/mol and 80 to 400 KJ/mol, respectively. Therefore, the adsorption of methylene blue on the chitosan can be considered physisorption.

CONCLUSION

In this study, the adsorption of methylene blue on chitosan prepared from river shrimp shell was investigated through equilibrium and kinetic processes. The adsorption confirmed that the chitosan was effective. The results indicated that the Langmuir model described the adsorption of methylene blue on the chitosan extremely well. The kinetic studies showed that the adsorption followed pseudo-second order kinetics. Thermodynamic analysis showed that the adsorption of methylene blue on the chitosan was favorable and spontaneous. From the results, we could conclude that the adsorption was a physico-chemical process.

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