Full Length Research Paper

Equilibrium studies for the removal of basic dye by sunflower seed husk (*Helianthus annuus*)

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The sorption characteristics of sunflower (*Helianthus annuus*) seed husk (SSH) to remove Methylene Blue (MB) from aqueous solution under batch conditions have been investigated. Sorption of MB was found to be pH, concentration and agitation dependent. The kinetics of sorption was rapid with 80% sorption taking place within the first 60 min regardless of its initial concentration. The fast attainment of equilibrium implying the biosorbent could be suitable for continuous flow system. Using the pseudo-second order kinetics model, the predictive model for MB sorbed at time t (q_t) with the initial concentration of (C_o) is given by $q_t = C_o t/[0.0607C_o + 2.0762 + (0.0012C_o + 5.1949)t]$. Results indicated that the predicted uptakes of MB agreed closely with experimental values obtained. The experimental data fitted well to Langmuir isotherm model with the correlation coefficient of 0.9860 and maximum monolayer sorption capacity of 45.25 mg/g.

Key words: Sunflower seed husk, sorption, basic dye, methylene blue, kinetics, modelling.

INTRODUCTION

The demand for synthetic dyes has experienced phenolmenal growth in the past several decades and it was reported that more than 7×10^5 metric tons of various dyes are produced worldwide annually (Pearce, 2003). The usage of these dyes has continuously increased in many industries such as textile, paper, plastics and cosmetics. However, most of the dyes are difficult to degrade, as they are generally stable to light and oxidizing agents and are resistant to aerobic digestion. As such, the environmental issues surrounding the removal of these pollutants are gaining much more attention now.

Conventional technologies employed for removing dye from industrial effluents include coagulation, chemical oxidation, biological treatment and adsorption. Amongst all, the adsorption process by activated carbon is one of the most efficient techniques. Despite the versatility of activated carbon as an adsorbent in wastewater treatment, drawback such as high capital and problems with the spent carbon limits its large-scale application. Thus, extensive research has been directed to the investigation of low cost materials as viable substitutes for activated carbon. These materials, including sugarcane bagasse, castor seed shell, rice hull and spent tea leaves that have the advantage of being inexpensive and readily available (Ong et al., 2010; Oladoja et al., 2008; Ong et al., 2009a; Hameed et al., 2009).

Because of their proven capability and economic considerations, therefore, in our continued effort to use low-cost materials for the removal of dye, the potential of sunflower (*Helianthus annuus*) seed husk (SSH) was explored. Basic dyes, which are predominantly used in

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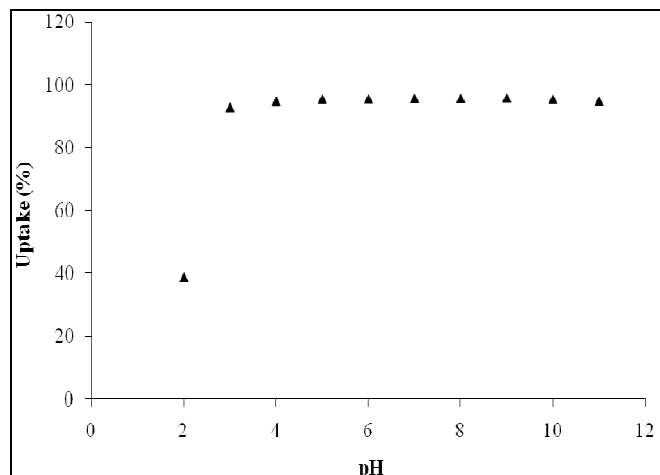**Abbreviations: SSH,** Sunflower seed husk; **MB,** Methylene Blue.

Figure 1. Effect of pH on the uptake of MB by SSH.

colouring acrylic fiber, are generally more toxic than other classes of dyes (Hunger, 2003). Thus, the removal of basic dyes, such as Methylene Blue (MB) from the environmental is worthwhile noting. In this present study, we report the effectiveness of SSH to remove MB under equilibrium conditions which can provide useful information on the sorption process before extending it to commercial systems.

MATERIALS AND METHODS

Preparation of sunflower seed husk

Sunflower seeds were purchased from a local market and dehusked. The sunflower seed husks (SSH) were washed thoroughly with distilled water for several times to remove the surface adhered particles. The washed materials were then oven-dried at 60°C for 48 h. The dried materials were ground in the grinder through 3.0 mm-sieve. The samples were then stored in a plastic bottle for further use. No other physical or chemical treatments were used prior to adsorption experiments.

Batch experiments

The batch studies were carried out at room temperature (25 ± 2°C) by mixing 0.1 g of sorbent with 20.0 mL MB solution in a centrifuge tube and shaken on an orbital shaker at 150 revolutions per minute (rpm) for four hours unless otherwise stated. The reaction mixture was then centrifuged at 3000 rpm for phase separation. All the batch experiments were carried out in duplicate and the results given are the means with a relative standard deviation (RSD) of less than 5%. Control experiments without sorbent was carried out to ascertain that the sorption was by the sorbent and not the wall of the container. The supernatant was analyzed for its dye concentration using a Perkin Elmer Lambda 35 UV-vis spectro-photometer. All measurements were made at the wavelength corresponding to maximum absorption; for MB, λ_{max} = 665 nm and dilutions were

carried out when measurement exceeded the linearity of the calibration curve.

To study the effect of pH, a series of 100 mg/L dye solutions of MB in the pH range of 2 - 11 were prepared. The pH adjustment was achieved by adding HCl or NaOH with the concentration ranging from 0.1 to 2.0 M. Time course experiments were investigated by shaking the sorption mixture at various predetermined intervals and analyzing the dye concentration at the end of the contact time. The effect of agitation rate was investigated by varying the agitation rates from 50 to 250 rpm. For sorption isotherm, the dye concentrations were varied from 50 to 200 mg/L. The effect of temperature on the sorption of dyes was studied in the temperature range of 30 to 80°C. The percentage of dye uptake (% uptake) was calculated using the following equation:

$$\% \text{ Uptake} = \frac{C_o - C_t}{C_o} \times 100 \tag{1}$$

Where C_o is the initial dye concentration and C_t is the dye concentration (mg/L) at any time.

RESULTS AND DISCUSSION

Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process. The influence of pH on the adsorption capacity of MB by SSH was studied and result indicated that adsorption process was more favourable at the pH range from 4.0 to 11.0. From Figure 1, the percentage dye uptake increased from 38 to 95% when the pH value increased from 2 to 4. Thereafter, the maximum dye uptake remains in the pH range of 4 to 11. The MB adsorption rate on SSH was minimum at low pH and this might be due to the positively-charged surface of the sorbent. The presence of excess H^+ ions will most likely prevent and compete with the MB cation for the binding sites of the biosorbent. As the pH of the system increased, SSH might become negatively charged and therefore lead to a higher uptake of positively charged dye cations through the electrostatic forces of attraction (Hameed et al., 2007).

Similar trend was observed in the previous work for the removal of Malachite Green onto the activated carbon prepared from Tuncbilek lignite (Onal et al., 2006), the removal of three cationic dyes: MB, Neutral Red (NR) and Acridine Orange (AO) by using granular kohlrabi peel (Gong et al., 2007) and the removal of Basic Blue 3 by ethylenediamine rice husk (Ong et al., 2009b).

Effect of initial concentration and sorption kinetics

Figure 2 illustrated the adsorption of MB for different initial concentration of MB at room temperature as a function of contact time. The curves show rapid initial rate of sorption and reached equilibrium in less than 240 min regardless of initial concentration. Relatively short contact time for the sorption process would indicate that
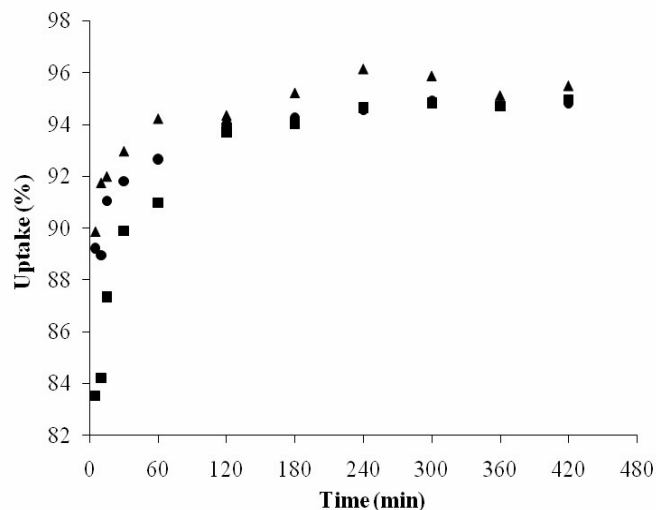
Figure 2. Effect of initial concentration and contact time on the uptake of MB by SSH (▲, ●, ■ -25, 50 and 100 mg/L of MB).

chemisorption is probably important. The fast uptake at the beginning may be attributed to the rapid attachment of the dye molecules to the surface of the sorbent, followed by slower sorption due to the intraparticle diffusion (Hameed et al., 2007; Banat et al., 2003). Sorption kinetic studies can be considered as vital as it provides some important insight about the mechanism of sorption. The modelling of the kinetics of adsorption MB onto the SSH were investigated by two common model, namely pseudo-first (Langergren, 1898) and pseudo-second-order kinetic models (Ho and McKay, 1999). It may be represented in the following form:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad \text{(Pseudo-first order)} \quad (2)$$

And

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \qquad \text{(Pseudo-second order)} \quad (3)$$

Where q_e = the amount of MB sorbed at equilibrium (mg/g), q_t = the amount of MB sorbed at time t (mg/g^{-1}), k_1 = the rate constant of pseudo-first-order kinetics (1/min), h $(k_2 q_e^2)$ = the initial sorption rate (mg/ g min) and k_2 = the rate constant of pseudo-second order kinetics (g/mg min).

The various rate parameters associated with MB at various concentrations are shown in Table 1. It was found that application of pseudo-second order kinetics provides better correlation of the experimental data than the pseudo-first order model for the different systems studied. In addition, the equilibrium sorption capacities determined from the first order kinetic model were lower than those

determined experimentally. It thus appears that the system under study is more appropriately described by the pseudo-second order model which was based on the assumption that the rate limiting step may be chemical sorption or chemisorptions involving valency forces through sharing or exchange of electron between sorbent and sorbate (Ho and McKay, 2000).

A similar kinetic result was reported for the adsorption of Methylene Blue and Methyl Violet onto mansonia (*Mansonia altissima*) wood sawdust (Ofomaja, 2008) and the adsorption of MB onto wheat shells (Bullut et al., 2006). The values of q_e, k_2 and h against C_0 in the corresponding linear plots of the pseudo-second order equation were then regressed to obtain expressions for these values in terms of the initial dye concentration.

The generalized predictive models for MB sorbed at any contact time and initial concentration within the given range with relationship of q_t, C_o and t can be represented by substituting the following equation:

$$q_t = \frac{C_o t}{A_h C_o + B_h + (A_q C_o + B_q)t} \quad (4)$$

By substituting the constant values into equation 4.9, the theoretical model for MB-SSH system can be represented as:

$$q_t = \frac{C_o t}{0.0607 C_o + 2.0762 + (0.0012 C_o + 5.1949)t} \quad (5)$$

The theoretical model derived for MB sorption by SSH can be used to derive the sorption capacity, q_t at any given C_o and t. A comparison of the experimental data and the predicted theoretical values by equation 5 is shown in Figure 3. The theoretically generated curves were obviously agreed well with the experimental data for adsorption of MB dye by SSH.

Effect of agitation rate

Figure 4 shows the results of the effect of agitation rate on the percentage uptake of MB onto SSH. It is evident that the percentage dye uptake increased when the agitation rate was increased. Increasing agitation rate decreases the film resistance to mass transfer surrounding the sorbent particles thus increasing sorption of dye molecules. At 250 rpm, the percentage uptake of dye was the highest followed by 150 and 50 rpm. For the first 10 min, the percentage uptakes were 78.24, 84.21 and 87.11% for the agitation rate of 50, 150 and 250 rpm, respectively. At the 120th minute, the percentage uptakes increased to 92.90, 93.71 and 94.35% for the agitation rate of 50, 150 and 250 rpm, respectively. Thereafter, the different in percentage uptakes for the three agitation rates was minimal. Similar trend has been reported by Tsai et al. (2008) on the removal of Basic Blue 9 and Acid

Table 1. Pseudo-first and pseudo-second-order kinetic model parameters for different initial MB concentrations.

Initial MB concentration (mg/L)	$q_{e,\,exp}$ (mg/g)	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model			
		$q_{e,\,cal}$ (mg/g)	k_1 (1/min)	R^2		$q_{e,\,cal}$ (mg/g)	k_2 (g/mg min)	h (mg/mg min)	R^2
25	4.757	0.208	4.6×10^{-3}	0.306		4.737	3.33×10^{-1}	7.536	1.000
50	6.564	0.094	5.0×10^{-4}	0.0004		6.592	1.67×10^{-1}	7.184	1.000
100	23.196	1.208	-1.6×10^{-3}	0.077		23.364	2.62×10^{-2}	14.085	1.000
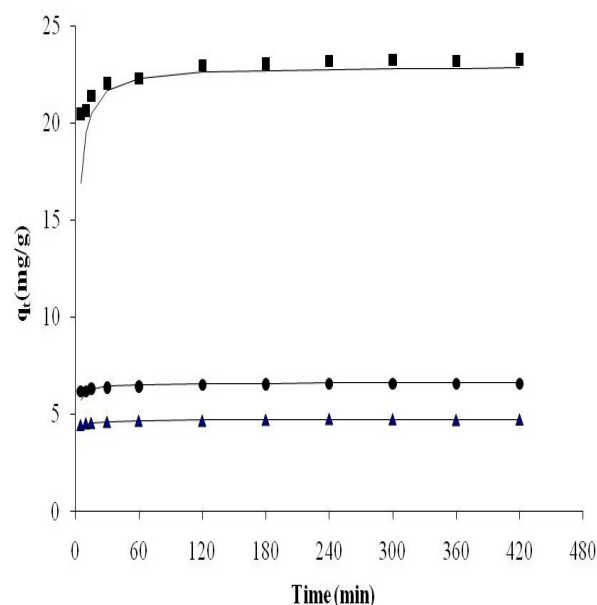
Figure 3. Comparison between the measured and pseudo-second order modelled time profiles for MB sorption by SSH (▲, ●, ■ -25, 50 and 100 mg/L of MB).

Orange 51 onto ground eggshell waste. They found that the beneficial effect of increasing agitation could attribute to the increase in turbulence and the decrease in boundary layer thickness around the adsorbent particles.

Sorption isotherm

The adsorption isotherms indicate how the adsorption molecules distribute between the solid phase and the liquid phase when the adsorption process reaches an equilibrium state. The analysis of the adsorption data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose (Hameed et al., 2007). Langmuir (1918) and Freundlich (1906) isotherms were tested in order to establish the most appropriate correlations for the equilibrium data in the design of adsorption system. The linear form of Langmuir isotherm can be expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_a q_m} \tag{6}$$

Whereas the linear form of Freundlich can be represented as:

$$\log q_e = \log K_f + (1/n) \log C_e \tag{7}$$

where C_e = concentration of MB solution at equilibrium (mg/L), q_e = amount of MB adsorbed at equilibrium (mg/g), q_m = maximum adsorption capacity of sunflower seed husk (mg/g), K_a = adsorption equilibrium constant (L/mg), K_f = Freundlich equilibrium constant and n = Freundlich

Freundlich exponent.

Figure 5 shows the Langmuir plots of MB onto SSH. The maximum adsorption capacity, q_e, was calculated to be 45.25 mg/g for the uptake of MB from aqueous using sunflower seed husk with the correlation coefficient, R^2, of 0.9860. The value K_a was determined to be 0.1436 L/mg suggested that there was no further adsorption process can be occurred at an occupied site once a dye molecule occupied that particular site.

The essential characteristics of Langmuir isotherm can be expressed in the term of dimension-less constant separation factor R_L (which is also known as equilibrium parameter) as given by the equation below:

$$R_L = \frac{1}{1 + K_a C_o} \tag{8}$$

Where: K_a = Langmuir constant (L/mg), C_o = Highest initial concentration of sunflower seed husk (mg/L).

The parameter R_L indicated the nature of shape of the isotherm according to Table 2 and the R_L value for MB was determined to be a favourable sorption ($0 < R_L < 1$).

The plot of Freundlich isotherm was shown in Figure 6. By comparing both Langmuir and Freundlich isotherms, the experimental data fitted well to Langmuir equation. The best equilibrium
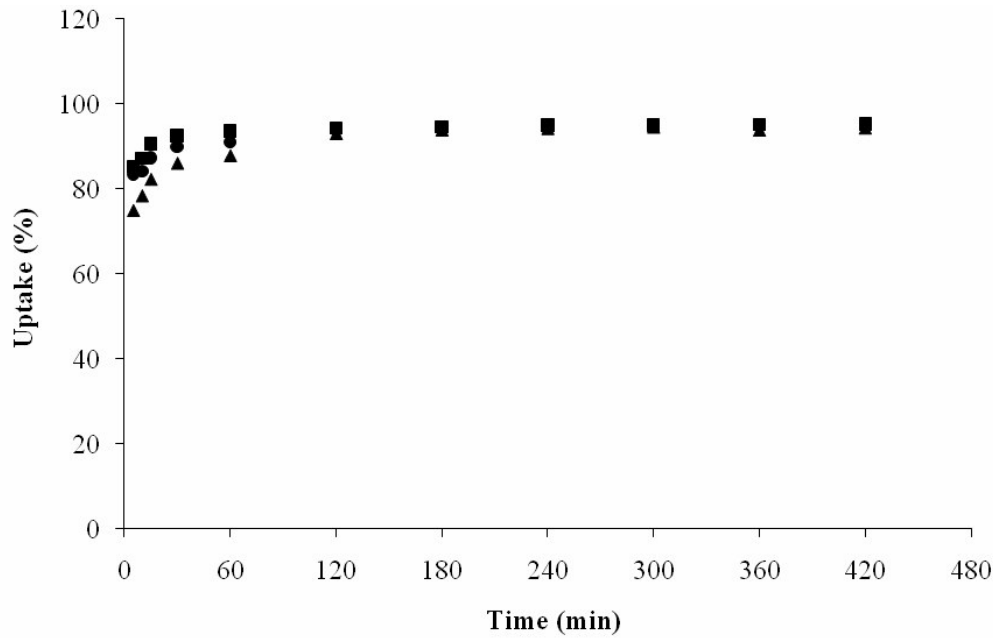
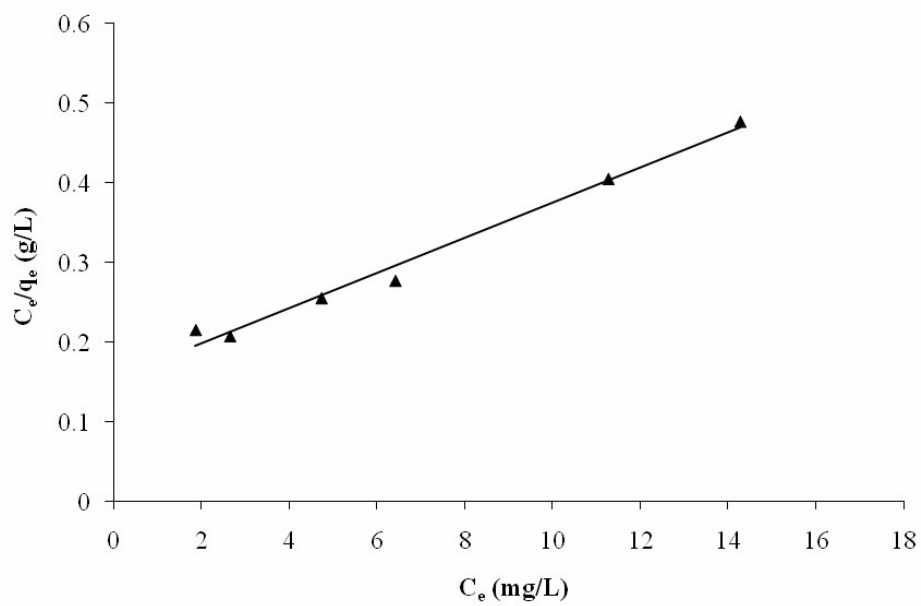**Figure 4.** Effect of agitation rate on the uptake of MB by SSH. (▲, ●, ■, - 50, 150 and 250 rpm).

Figure 5. Langmuir isotherm of MB on SSH.

Table 2. Shape of isotherm.

R_L value	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

Table 3. Comparative between Langmuir and Freundlich isotherm.

Langmuir				Freundlich		
q_e (mg/g)	K_a (L/mg)	R^2	R_L	K_F	n	R^2
45.25	0.1436	0.9860	0.0423	0.04764	0.6172	0.9562
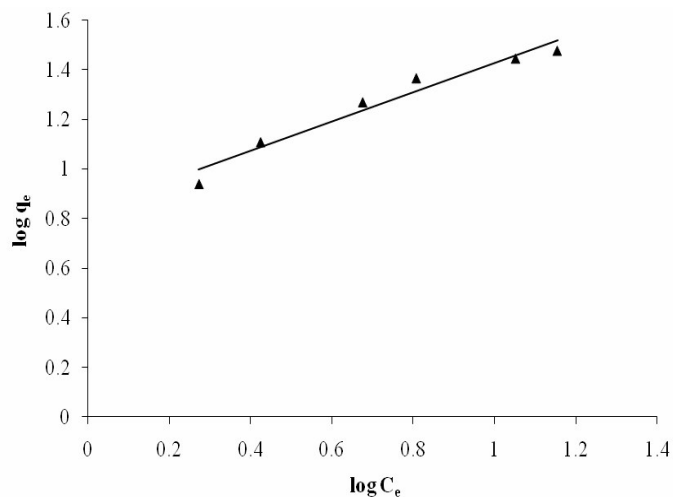
Figure 6. Freundlich isotherm of MB on SSH.

Figure 7. Effect of temperature on the uptake of MB by SSH.

model was determined based on the linear square regression correlation coefficient, R^2 (Table 3). The best fit isotherm expressions confirm the monolayer coverage process of MB onto SSH.
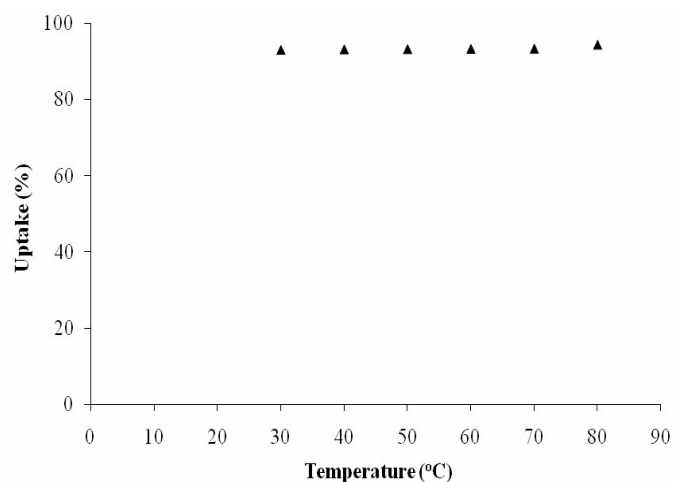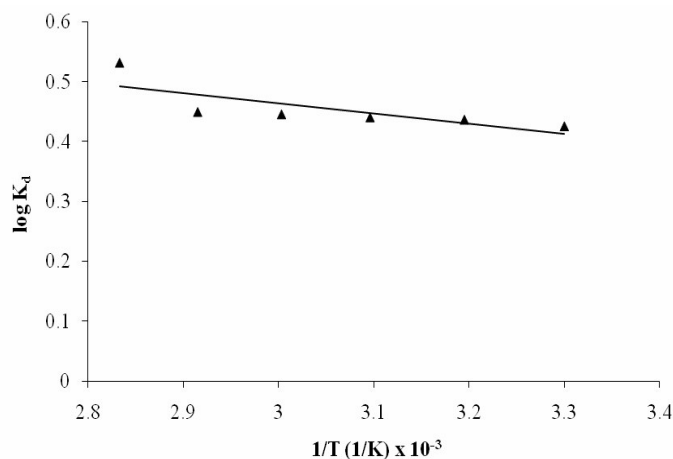
Effect of temperature

In this parameter, a series of experiments were conducted at different temperature to investigate the effect of temperature to the sorption of MB dyes on SSH.

As seen from Figure 7, the effect of temperature on the equilibrium dye uptake was minimal. An increase in temperature from 30 to 70°C leads to a slightly increase in percentage uptake from 93.0 to 93.4%. When the temperature was further increased to 80°C, equilibrium uptake value was detected as 94.4%. The variations in adsorption capacity values due to temperatures were assumed negligible because the dye uptake changed insignificantly by the temperature. Similar trend was reported by Cengiz et al. (2008) on the removal of MB by using invasine marine seaweed, *Caulerpa race-mosa* var. *cylindracea* and Tunc et al. (2008) on the removal of Remazol Black B onto the cotton plant wastes.

Nevertheless, the effect of temperature on sorption is further analysed by using the Van't Hoff equation (Atkins and Paula, 2006):

$$\log K_d = \Delta S^o/2.303R - \Delta H^o/2.303RT \qquad (9)$$

Figure 8. Van't Hoff equation plots for the uptake of MB by SSH.

where $K_d = q_e/C_e$ = distribution coefficient (L/g), R = universal gas constant (8.314 J/mol.K), ΔH^o = the enthalpy change (kJ/mol), ΔS^o = the entropy change (kJ/mol), T = temperature of dye solution (K).

The values of ΔH^o and ΔS^o obtained from the Van't Hoff plot (Figure 8) are 3.274 and 0.0187 kJ/mol, respectively. The positive value of enthalpy confirming the sorption process was endothermic in nature.

Conclusion

In this study, SSH has demonstrated its potential to be an economical and efficient sorbent for the removal of MB from aqueous solutions. Sorption was pH dependent and the optimal pH for the removal of MB is in the range of 4 – 11. The rapid uptake and fast attainment in the equilibrium suggest that SSH is a very attractive alternative sorbent material. Sorption kinetics obeyed preferably the pseudo-second-order kinetics and the sorption profiles generated based on the pseudo-second-order kinetic model showed good agreement with the experimental curves. Besides, the percentage of MB uptake increased with increasing agitation rate and the thermo-dynamics data showed that the sorption was an endothermic process.

ACKNOWLEDGEMENTS

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