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Utilization of Magnetic Sugarcane Baggase for Methylene Blue Dye Removal from Water: Equilibrium and Kinetic Studies

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ABSTRACT

Dyes enforces ecological and public problems due to hazardous and irretrievable properties of such pollutants on human health and the environment. Therefore, it is vital to treat this pollutant efficiently and effectively. In this study Magnetic Sugarcane Bagasse (SGB) was prepared as an alternative biosorbent for Methylene Blue (MB) dye removal from water. The Magnetic SGB characterization was performed using Fourier Transform Infrared Spectroscopy. Batch adsorption study was investigated with respect to its adsorption equilibrium, isotherm, and kinetics. The equilibrium was achieved within 75 minutes with maximum removal efficiency around 94.75%. For isotherm study, Langmuir isotherm is well fitted compared to the Freundlich isotherm. Therefore, it demonstrates that the process involved is monolayer adsorption on a homogeneous surface. In addition, the kinetic study shows that the adsorption process has the best agreement with pseudo-second-order kinetic models which describes that the process may involve chemisorption. The results show that Magnetic SGB could be used as low-cost alternative adsorbent for the removal of MB.

Keywords: *Dye removal; adsorption; biosorbent; magnetic; isotherm; kinetic*

1. INTRODUCTION

Nowadays, the discharge of wastewater containing toxic dyes from many industries has become a major environmental problem in most developing countries. Numerous industries such as textile, food, cosmetic, plastic and printing have used dyes as a coloring agent. Since they are carcinogenic and highly toxic, dyes will pose a bad impact on the environment [1].

Methylene blue (MB) dye is intensively used as the color pigment for fabric. This dye has many negative effects on people and animals such as irritation on skin, stomach, mouth and esophagus [2]. It has also been found as a non-biodegradable dye [3]. Therefore, the elimination of MB dye from wastewater is a great concern to protect the environment.

The conventional methods for dye wastewater treatment such as coagulation and flocculation, filtration, oxidation and adsorption have already been employed. Due to its excellent adsorption capability, adsorption processes using activated carbon as adsorbent has been recognized as a highly effective method for the dye removal [4]. However, the utilization of activated carbon

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has limitation due to its loss during the regeneration and high cost [5]. For this reason, it is necessary to look for an effective, convenient and inexpensive method for wastewater treatment.

Application of agriculture solid wastes for removal of dye from wastewater is one of the progressive developments in the environmental technology. According to their physicochemical characteristics and low cost, they may be good potential adsorbents [6]. A lot of alternative adsorbents have been created for the elimination of dye [7], [8], [9] and [10] and most of them were difficult to be isolated and separated from aqueous solution by common methods such as centrifugation or filtration. However, the adaptation of the magnetic separation technique to biosorption process can overcome this limitation. The magnetic materials offer exceptional adsorption ability, good mechanical properties and easy separation with the aid of magnetic field [11] and [12]. It was suitable to separate the magnetic adsorbent from aqueous solution in an external magnetic field. However, to our knowledge, slight consideration was paid on the development and utilization of the magnetic modified biosorbent using agricultural waste. It is important to create a magnetic biosorbent with great adsorption performances.

Sugarcane Bagasse (SGB) is an abundantly available material in many developing countries. In Malaysia, SGB is one of the primary agro-industrial wastes. Sugarcane is from wild species and the family name is known as *Poaceae*, while the grass family known as *Gramineae*. SGB mainly consist of cellulose 42 %, hemicellulose 25 %, and lignin 20 % while the rest is ash [13]. Due to the hydroxyl and carboxylic groups, indirectly it has advantages such as being an inexpensive, attractive and efficient dye elimination from wastewater [14]. In this work, SGB powder was converted to magnetic biosorbent through a simple process. The MB dye removal capability and biosorption characteristics in a batch mode of operations were studied. The adsorption equilibrium data were obtained to determine which isotherm and kinetic model provided the best fit for this adsorption process.

2. METHODOLOGY

2.1 Adsorbent Preparation

Sugarcane Bagasses (SGB) were obtained locally. The washed bagasses were boiled for an hour to remove the impurity and sugar residue. These steps are important as they will determine the purity of the adsorbent. It was then dried at 45 °C in an oven until it reached a constant weight. Dried SGB were ground using a grinder of the Hong Chunn Model RT-34. After that, it was size separated using the Octagon Sieve Shaker to obtain the desired particle size of 250 **µm**.

2.2 Magnetization Procedure

In order to magnetize the natural SGB powder, 20 g of SGB powder was mixed with 0.52M Fe_3O_4 solution and stirred at an agitation speed of 200 rpm for 1 hour. Then the adsorbent was filtered before being washed and rinsed with distilled water until neutral pH of the adsorbent was obtained. After the filtration process, the adsorbent was dried in an oven for 48 hours at 45˚C. Then, the adsorbent was tested with a magnet. It is clearly observed that all the magnetic SGB were attracted to the magnet, because of the magnetic behaviour of the magnetite particles.

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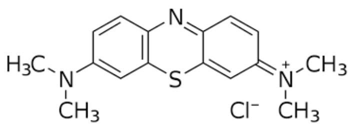
2.3 Adsorbate

The Methylene Blue (MB) dye used in this study was purchased from Merck, Germany and obtained in the solid form. Related information about tested dye is summarized in Table 1. An accurate weight of dye was dissolved in distilled water to prepare 200 mg/L of stock solution. Then it was diluted to the desired concentration for adsorption experiment.

Table 1: Chemical structure and other related information of Methylene Blue dye

Dye	Colour Index (CI) Number	Molecular Weight	Molecular Formula	Chemical Structure	Dye Class
Methylene Blue	52015	319.5	$C_{16}H_{18}N_3SCl$		Quinone-imine

2.4 Characterization of Magnetic SGB

Fourier Transform Infrared Spectroscopy (FTIR) was used on Perkin-Elmer Spectrum100 FTIR with diamond ATR to determine the functional group of the substances. The IR spectra were carried out in the wavelength ranges from 4000-400 cm^{-1}.

2.5 Adsorption experiments

Adsorption experiment in batch mode was done by mixing the magnetite SGB at a fixed amount (0.75 g) with 150 mL MB dye with varying concentrations (20-100 mg/L). Agitation speed, temperature, and particle size of adsorbent were fixed at 250 rpm, 27ºC and 250 microns respectively. The samples were collected every 10 minutes of each solution up to 2 hours. Experiments were replicated under the similar conditions and the mean values were used in calculations. The filtrate was analysed by the UV-Vis Spectrophotometer of Perkin Elmer Lambda 35 model. The uptake at equilibrium, q_e (mg/g) of dye was calculated according to equation 1:

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

where, C_o and C_e (mg/L) is the initial concentration of the solution and the concentration at equilibrium respectively. V (L) is a volume of solution and m (g) is a mass of the adsorbent used.

2.6 Data evaluation

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The adsorption results were evaluated using Langmuir and Freundlich isotherm models. Pseudo-first-order and pseudo-second-order reaction models were utilized for the determination of kinetic parameters.

3.0 RESULT AND DISCUSSION

3.1 Characterization of Magnetic SGB

The FTIR spectra of both unmodified and magnetic SGB are shown in Figure 1. The spectra display a number of absorption peaks, indicating the complex nature of SGB. From the Figure 1(a), the FTIR spectrum for unmodified SGB shows that the absorption band at 3284.90 cm^{-1} is due to O-H stretching [15]. The band at 2908.97 cm^{-1} is attributed to the stretching of the C-H groups [16]. The band at 1613.62 cm^{-1} and 1229.51 cm^{-1} corresponds to the C=O stretching of carboxyl group bends [17]. Strong C-O bands at 1016.52 cm^{-1} indicate as anhydrides functional group [18]. Based on Figure 1(b), the band which appeared at 1025.20 cm^{-1} is determined due to the formation of a hydroxyl group and vibration of Fe-OH [19]. The new peaks detected at 547.11 cm^{-1} was determined as Fe-O vibration bonds in tetrahedral site and as a typical band of spinal ferrite [20]. However, the disappeared absorption peak at 1613.62 cm^{-1} of untreated SGB might be caused by the lignocellulosic compounds, which have the ability to reduce Fe(III) to Fe(II) ions binding [21].

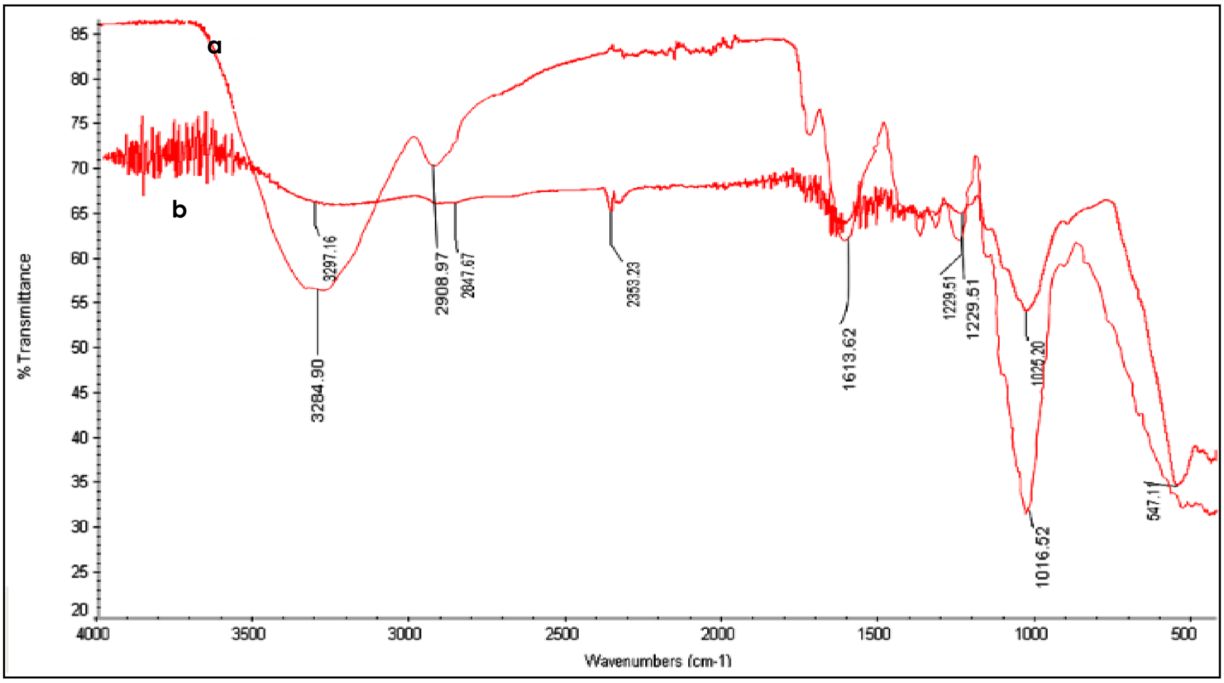

Figure 1: FTIR spectra of (a) untreated and (b) magnetic SGB

3.2 Effect of Concentration and Contact Time

The variation of MB dye concentration as a function of contact time was illustrated in Figure 2. It was observed that sudden increase of dyes uptakes onto magnetic SGB occurred at initial time intervals before gradually decreasing until equilibrium is reached at 75 min. The high number of a vacant surface is the cause of the great dyes uptake at an initial step. Then, a transitional phase takes place where the rate of removal was slow and attains equilibrium [22].

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The differences of MB removal by magnetic SGB was not substantial for an initial concentration of 20mg/L and 40mg/L. However, the removal rate decreased as increasing the initial concentration up to 100mg/l. The highest percentage removal was 94.75% for an initial concentration of 40mg/L and the lowest percentage removal that was recorded is at an initial concentration of 100mg/L which is 45.68 %. The number of active sites, available surface area and ability of adsorption sites will affect the percentage removal of MB [23].

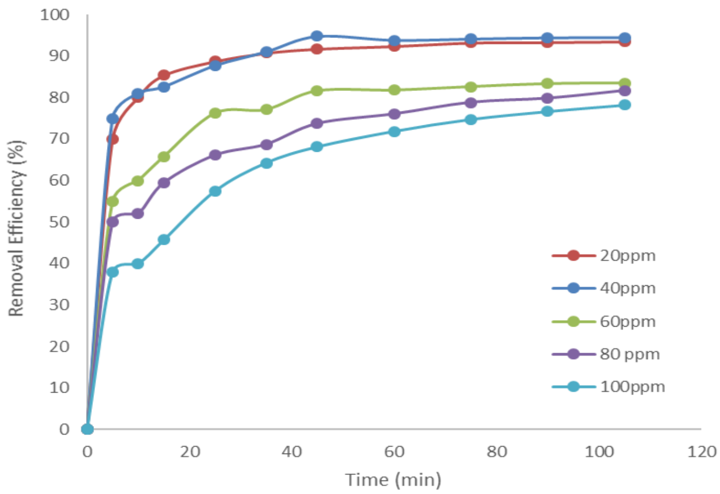

Figure 2: The effect of concentration and contact time on adsorption of MB dye onto magnetic SGB

The similar result has been reported for the adsorption process with other dyes such as Methyl Red by using adsorbent sugarcane bagasse [14]. It is found that the amount of dye being adsorbed will increase when dye concentration increase. However, the removal rate will decrease.

The experimental results indicate that all concentrations can achieve equilibrium quickly for the adsorption process to take place. A great number of available surface sites might be available(?) for adsorption at initial stages and the remaining vacant surface sites in a lapse of adsorption time were difficult to be engaged due to the repulsive forces between Basic Fuchsin dye adsorbed and solution phase [23].

3.3 Adsorption Isotherm

In order to analyze the correlation between the amounts of MB uptake by magnetic SGB and its concentration equilibrium in solution, the Langmuir and Freundlich equation were used. Langmuir model describes clearly on the adsorption procedure and does not consider the variation in adsorption energy [20]. In addition, Langmuir model is applicable for monolayer adsorption which is for the adsorption on a homogeneous surface and all sorption sites are identical and having uniform energy [21]. The isotherm is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \tag{2}$$

where, C_e (mg/L) is the equilibrium concentration of dye in solution. q_e (mg/g) is the amount of dye adsorbed at equilibrium time. q_o and *b* are Langmuir constants related to adsorption capacity and the energy of adsorption respectively.

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Figure 3a shows the plots of Ce/qe versus Ce to represent Langmuir model. The coefficient R^2 of magnetic SGB is 0.968. The maximum adsorption capacity (q_o) and the Langmuir constant were estimated as 8.467 mg/g and 0.206 L/mg respectively as summarized in Table 2.

Table 2: The isotherm constants for MB dye adsorption onto magnetic SGB

	Langmuir Isotherm			Freundlich Isotherm		
Adsorbent	b	q_o	R^2	K_F	n	R^2
Magnetic SGB	0.206	8.467	0.968	2.021	2.464	0.898

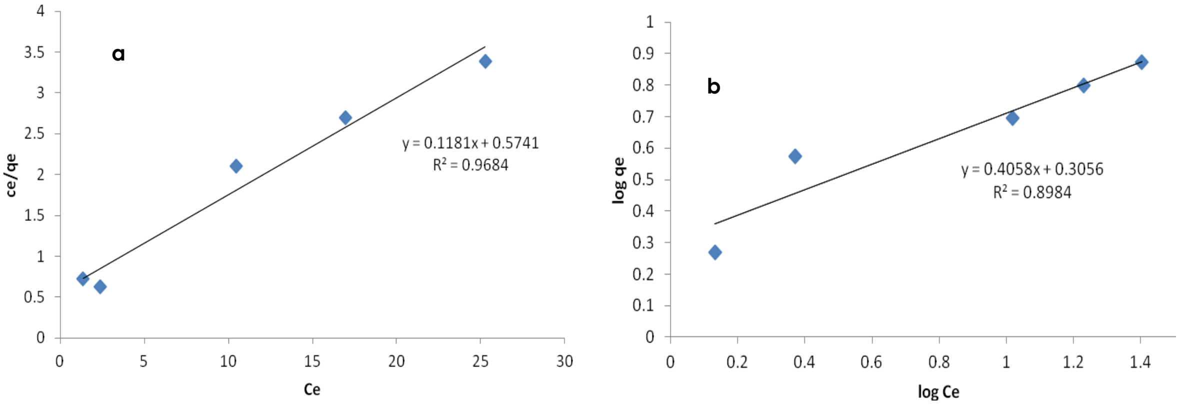

Figure 3: Isotherm models for MB dye sorption onto magnetic SGB (a) Langmuir, (b) Freundlich.

However, the equilibrium parameter, R_L is introduced to reflect the essential characteristics of Langmuir isotherm as given in the Equation 3:

$$R_L = \frac{1}{(1 + bC_o)} \tag{3}$$

If the value of R_L is $0<R_L<1$, then the adsorption is favourable. The values of R_L for this study are found to be between 0 and 1, therefore it is indicated that the adsorption of MB onto magnetic SGB is favourable.

Freundlich isotherm model is appropriate to a heterogeneous surface with multilayer adsorption as given in Equation 4:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{4}$$

where, $1/n$ is an empirical parameter relating the intensity adsorption and K_F is capacity adsorption constant. Figure 3b shows a linear graph of log qe versus log Ce with a regression of 0.8984. Constant K_F and 1/n value were measured from the graph. The calculated values were listed in Table 2. The determined value of n from Freundlich isotherm was 2.464. If the values of $n > 1$, this presents the favourability of adsorption. Thus, the adsorption of MB onto magnetic SGB is favourable.

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As seen from Table 2, the high regression of correlation coefficients R^2 was shown by Langmuir isotherm. This indicated that monolayer coverage applies on the surface of magnetic SGB by MB dye molecules. Similar results were reported for the removal of basic blue 9 dye on groundnut shell and Eichhornia [25] and the removal of CR by maghemite nanoparticles [26]. The Langmuir adsorption model is appropriate for the adsorption onto homogeneous adsorbent surfaces with constant amounts of active sites having the uniform energy and constant adsorption energy. Additionally, it is expected that this is a monolayer adsorption and the maximum adsorption will occur when adsorbed molecules form a saturated layer [27].

3.4 Kinetic Studies

The pseudo-first-order and pseudo-second-order adsorption kinetic models were used to analyse the experimental data in order to describe the adsorption mechanism in term of rate constant order. The pseudo-first-order kinetic model is followed by Equation 5:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{5}$$

where q_e and q_t are the amounts of MB adsorbed at equilibrium and time t, respectively (mg/g), and k_1 is the rate constant of first-order adsorption (min^{-1}). The value of k_1 was measured from the graph of log ($q_e - q_t$) versus t for a different initial concentration of MB dye (figure not presented). Table 3 shows the pseudo-first-order parameters. From the data, it can be concluded that the adsorption of MB onto magnetic SGB is not a first-order reaction due to the poor R^2 value gained and the experimental q_e value does not agree well with the calculated value. The data is also applied to pseudo-second-order kinetics model as expressed in equation 6:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \tag{6}$$

The pseudo- second-order rate constant q_e and k_2 can be determined from slope and intercept of linear plots t/q_t against t as presented in Figure 4. The obtained parameters for the second-order kinetic model are shown in Table 3. The Second-order kinetic model fits quite well with the experimental data with a correlation coefficient (R^2) that is almost equal to 1.0. Additionally, there is an agreement between the calculated q_e values and q_e of the experimental data. It is suggested that this model is relevant to describe the adsorption mechanism of MB onto magnetic SGB, based on the assumption that the rate-limiting step may be chemisorption related [28]. A similar result was obtained for adsorption of MB onto steam-activated carbon from date pits [29].

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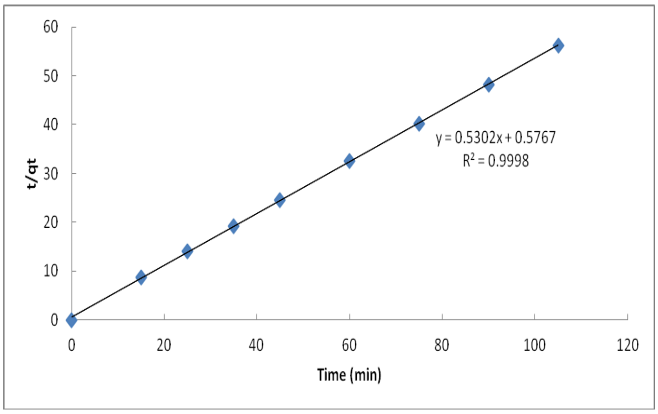

Figure 4: The linear plots of t/qt against time of pseudo-second-order for magnetic SGB.

Table 3: The kinetic constants for MB adsorption onto magnetic SB

Adsorbent	**Conc. (mg/L)**	**$q_{e(exp)}$ (mg/g)**	**Pseudo-First-Order**			**Pseudo-Second-Order**		
			k_1 (min^{-1})	**q_e (mg/g)**	**R^2**	**k_2 (min^{-1})**	**q_e (mg/g)**	**R^2**
Magnetic SGB	20	1.86	0.06	1.25	0.41	0.45	1.89	0.99
	40	3.76	0.08	1.14	0.55	0.18	3.83	0.99
	60	4.96	0.06	1.12	0.61	0.08	5.13	0.99
	80	6.30	0.03	1.24	0.86	0.03	6.76	0.99
	100	7.47	0.03	1.15	0.85	0.02	8.26	0.99

4. CONCLUSION

The magnetic SGB were synthesized and used as an efficient low-cost alternative adsorbent for the removal of MB dye in water and it may be a substitute to more pricey adsorbents such as activated carbon. The batch studies clearly showed this adsorbent exhibits maximum dye removal of 94.75% at a contact time of 75 minutes and initial concentration, 40mg/L. The adsorption isotherms were best represented by Langmuir isotherm. This indicates that the process is due to the monolayer adsorption onto adsorbent with the homogeneous surface. Furthermore, the adsorption of MB dye was well fitted by pseudo-second-order kinetic model. Therefore, the surface adsorption that might involve is chemisorptions.

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