



Research Article

# Kinetic of Adsorption Process of Sulfonated Carbon-derived from *Eichhornia crassipes* in the Adsorption of Methylene Blue Dye from Aqueous Solution

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## Abstract

The evaluation of kinetic adsorption process of sulfonated carbon-derived from *Eichhornia crassipes* in the adsorption of methylene blue dye from aqueous solution has been carried out. The sulfonated carbon-derived from *E. crassipes* (EGS-600) was prepared by carbonation of *E. crassipes* powder at 600 °C for 1 h, followed by sulfonation with concentrated sulfuric acid for 3 h. The physical properties of the adsorbents were characterized by using Fourier transform infrared spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and nitrogen adsorption-desorption studies. Adsorption study using methylene blue dye was carried out by varying the contact time and initial dye concentration for investigated kinetics adsorption models. The effect of varying temperature was used to determine the thermodynamic parameter value of  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$ . The results showed that the equilibrium adsorption capacity was 98% when EGS-600 is used as an adsorbent. The methylene blue dye adsorption onto adsorbent takes place spontaneity and follows a pseudo-second-order adsorption kinetic model. Copyright © 2019 BCREC Group. All rights reserved

**Keywords:** *Eichhornia crassipes* (water hyacinth); methylene blue; adsorption; sulfonation; carbon

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## 1. Introduction

Every year, more than 100,000 kinds of synthetic dyestuff from textile, paper, rubber, plastic, leather, cosmetic, pharmaceutical and food industries are discharged as liquid waste in

large volumes. Methylene blue dye is a type of synthetic dye, which is widely used in coloring papers, as temporary hair colorant, and for dyeing cotton and wool [1]. The disposal of liquid dye waste from industry to environment (river and lake) can cause serious ramifications on the environment and the health of living beings. The colored wastewater in the environment can cause infertility of the soil, increased amount of chemical oxygen demand (COD) in water, and

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reduced light penetrability that can influence the photosynthetic processes of aquatic plants [2,3]. Apart from that, studies have also shown that many synthetic dyestuff are harmful and even carcinogenic, which can pose serious hazards to the health of living beings, such as heartbeat increase, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis in human [2,4].

Many researchers have investigated the usage of different methods in removing synthetic dyestuff from wastewater to reduce their impact on the environment. Among the methods that have been used to discharge synthetic dyestuff in wastewater treatment are physicochemical, chemical, and biological methods, such as: coagulation and flocculation [5-7], adsorption [8-10], ozonation [11], electrochemical [5], fungal decolorization [12], microbiological or enzymatic decomposition [13].

Adsorption is a physicochemical method of treating aqueous effluent that is rapidly gaining prominence due to its proven efficiency and great potential as means of producing quality effluent [14]. Activated carbon is an example of an adsorbent, which is effective and widely used to dispose of synthetic dyestuff in wastewater treatment [15,16]. However, the cost of its commercial application is still very high [15]. This has prompted many researchers to try out cheaper and more efficient alternative materials, such as: agricultural residues [4], clay minerals [1,7], cashew nut shell [3], fly ash [17], peat [10], yellow passion fruit peel [9], fish bones [18], wood powder and lignin [16,19].

*E. crassipes* (water hyacinth) is a weed plant with a high growth rate that can damage the aquatic environment, such as: in many tropical lake and river [20]. Its existence can disrupt fisheries, transportation and hydroelectric power production [14]. Many researchers have attempted to looking for low cost adsorbent from *E. crassipes* for adsorption dye, such as: adsorption of congo red dye from aqueous solutions using roots of *E. crassipes* [14], biosorption of basic dyes by *E. crassipes* root [21], removal of azo and anthraquinone dye from aqueous solutions by *E. crassipes* [20], and activated carbon prepared from *E. crassipes* as an ad-

sorbent for the removal of dye from aqueous solution [15]. Nevertheless, adsorbents used by previous researches consist of powder with varying particle sizes and activated carbon that was thermally activated.

In the present study, we have prepared adsorbent from *E. crassipes* which is activated not only by thermal activation but also chemical activation by using concentrated sulfuric acid. Thermal activation or carbonation process was carried out to transform the *E. crassipes* powder to carbon. The activation by concentrated sulfuric acid or sulfonation process was to enhance the number of oxygen functional groups that can serve as the adsorption sites, while increasing hydrophilicity [22]. In this research, the effect of contact time and initial concentration of methylene blue were used to determine equilibrium adsorption capacity and to investigate the kinetic process in the adsorption by Lagergren and Svenska equation. The effect of temperature was used to study the parameter of thermodynamic of methylene blue dye adsorption process by Van't Hoff's plots. In this research the effects of pH of solution and dosage of adsorbent were also investigated.

## 2. Materials and Method

### 2.1 Carbonation Process

The fresh *E. crassipes* trunks were collected from a pool around Mulawarman University and washed with tap water to remove impurities. Then, it was cut and dried in the oven at 110 °C overnight. The dry trunks were blended to form powder which was labeled as EG. Subsequently, the powder was carbonated by heating in a furnace at 600 °C for 1 h.

### 2.2 Sulfonation Process

The carbon obtained from *E. crassipes* was sulfonated by using 6 mL of concentrated sulfuric acid (98%, JT Baker) per gram sample. The mixture was stirred at room temperature for 3 h. Any loosely-bound acid were removed from the sample by washing with distilled water. The sample was then dried overnight in an oven at 110 °C [23-25]. The sulfonated carbon from *E. crassipes* was labeled as EGS-600. The

**Table 1.** Codes and treatments done to the samples

Samples	Type of treatment	Time of sulfonation (h)	Temperature of carbonation (°C)	Time of carbonation (h)
EG	-	-	-	-
EGS-600	Sulfonation	3	600	1

codes of the adsorbents are given in Table 1.

### 2.3 Samples Characterization

The properties of sulfonated carbon from *E. crassipes* were determined by using Fourier transform infrared spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and nitrogen adsorption-desorption studies. The functional groups in the sulfonated carbon were determined by FTIR spectroscopy using a Prestige 21 Shimadzu. Crystallinity and phase content of the samples were determined by X-ray diffractometer (XRD) using a Phillips PANalytical X'Pert PRO type, with the Cu-K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation. The surface morphology was investigated by SEM images obtained using a JEOL JSM-6510. Data from a Quantachrome nova 1200e instrument were used as the base to determine nitrogen adsorption-desorption isotherms, surface area, micropore area and pore size distribution.

### 2.4 Adsorption Test

The adsorption ability of the samples was carried out by mixing the samples (0.125 g) with 25 mL of methylene blue dye solution ( $C_{16}H_{18}ClN_3S$ ;  $100 \text{ mg.L}^{-1}$ ) in a 100 mL beaker glass at room temperature for the durations of 5, 10, 15, 20, 25, 30, 60, 120, 240, 480, and 720 min. After the adsorption test, the solid adsorbent was separated from the filtrate by centrifugation technique. The residual dye was analyzed by using a UV-Vis spectrophotometer by monitoring the changes in absorbance of solu-

tion at 660 nm. The effect of sorbate to sorbent ratio for the percentage and unit dye sorbate sorption capacity of the sulfonated carbon from *E. crassipes* was investigated by varying the dose of sorbent between 0.0625-0.125 g. The effect of pH on the dye sorption by sulfonated carbon from *E. crassipes* was evaluated in the pH range of 1.0-12.0. The initial pH of dye solution was fixed by the mixing 0.1 M HCl and 0.1 M NaOH. Apart from that, different initial dye concentrations ( $80, 100, \text{ and } 120 \text{ mg.L}^{-1}$ ) were also investigated in this the study. Powder and carbon from *E. crassipes* were also tested as comparison.

The adsorption efficiency of the adsorbent was calculated using this equation:

$$\text{Adsorption efficiency}(\%) = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (1)$$

where,  $C_0$  and  $C_t$  are the initial and the dye concentration after adsorption time  $t$  ( $\text{mg.L}^{-1}$ ) in the solution, respectively. The adsorption capacity  $q_t$  of *E. crassipes* adsorbent as milligram per gram of adsorbent ( $\text{mg/g}$ ) was determined with this equation:

$$q_t = (C_0 - C_t) \frac{V}{W} \quad (2)$$

where  $V$  is the volume of dye solution (mL) and  $W$  is weight adsorbent (g).

## 3. Results and Discussion

### 3.1 Physical Properties

The FTIR spectra for EG and EGS-600 are shown in Figure 1. The broad band at 3416

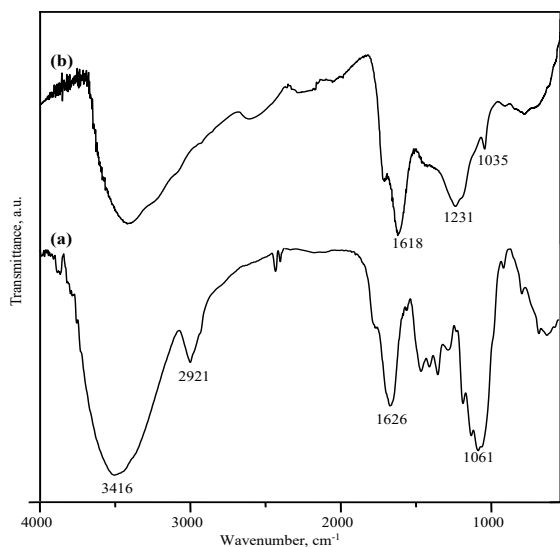


Figure 1. FTIR spectra of (a) EG and (b) EGS-600

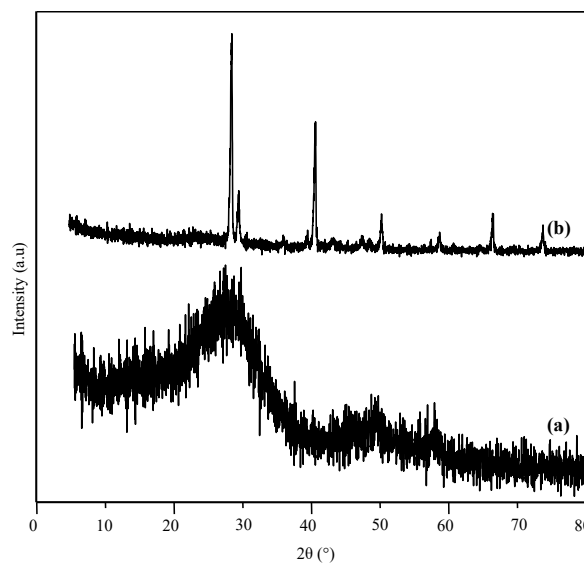


Figure 2. XRD pattern of (a) EG and (b) EGS-600

cm<sup>-1</sup> that was detected in all of the FTIR spectra, is assigned to the O–H stretching mode of the –COOH and phenolic -OH groups [23]. The amount of -OH groups in the samples decreases when the powder of *Eichhornia crassipes* (water hyacinth) was carbonated and sulfonated. The adsorption peaks at 2919 cm<sup>-1</sup> is attributed to C–H (aliphatic) stretching vibration. This adsorption peak of C–H disappeared when the adsorbent was carbonated and sulfonated. The effect of sulfonation process on the adsorbent can also be proven by the attachment of –SO<sub>3</sub>H groups. This was indicated by the adsorption band at 1034 cm<sup>-1</sup>, S=O stretching and 1231 cm<sup>-1</sup>, stretching in –SO<sub>3</sub>H [26]. The increasing of amount of S=O, –SO<sub>3</sub>H functional groups and releasing of C–H onto EGS-600 surface can increase its polarity properties. The adsorption peak of aromatic C=C stretching mode in polyaromatics is indicated by the vibration band at 1626 cm<sup>-1</sup>.

The XRD pattern in Figure 2a shows that *E. crassipes* powder (EG) has low crystallinity. Amorphous carbon, which is composed of aromatic carbon sheets, can be observed in *E. crassipes* powder by the broad peak at 2θ value of 10-30° (C (200)) [27]. After carbonation and sulfonation, the crystallinity of *E. crassipes* increased significantly, as can be seen by the XRD pattern at Figure 2b. Both XRD patterns showed a sharp crystalline peaks at 2θ value of 28.6°, 40.8°, 50.3°, 66.7°, and 74.1°, which can be assigned to calcite [28].

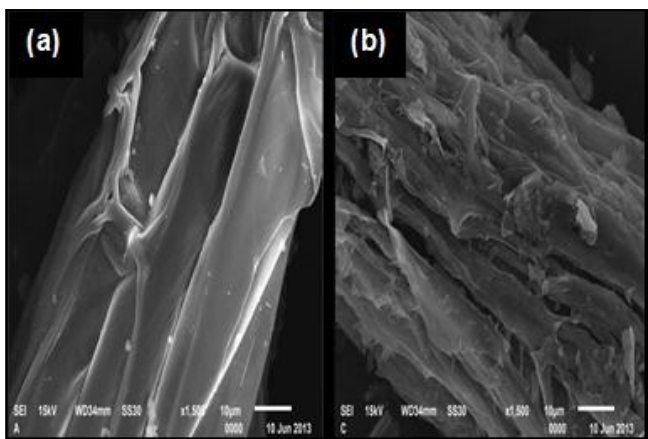


Figure 3. SEM Image of (a) EG and (b) EGS-600

Table 2. Physical properties of EG and EGS-600

Samples	BET surface area (m <sup>2</sup> .g <sup>-1</sup> )	Pore Volume (cm <sup>3</sup> .g <sup>-1</sup> )	Mean pore size (nm)	Micropore Area (m <sup>2</sup> .g <sup>-1</sup> )
EG	123.79	14.22	22.97	57.54
EGS-600	70.31	13.34	37,95	14.56

The SEM images of EG and EGS-600 are shown in Figure 3. The SEM images show that the EG and EGS-600 are in the fiber form, which are arranged as fibrils. Hollow spaces started to appear after the *E. crassipes* was carbonated and sulfonated. The surface morphology of *E. crassipes* powder (EG) is smooth, but turned rough after being carbonated and sulfonated (EGS-600).

The N<sub>2</sub> adsorption-desorption isotherms for EG and EGS-600 are shown in the Figure 4. All the isotherms are of type III and can be attributed to the relatively weak adsorbent-adsorbate interaction. The adsorbed molecules are clustered around the most favorable sites. The other physical properties of EG and EGS-600 obtained from this analysis, such as BET surface area, pore volume, mean pore size, and

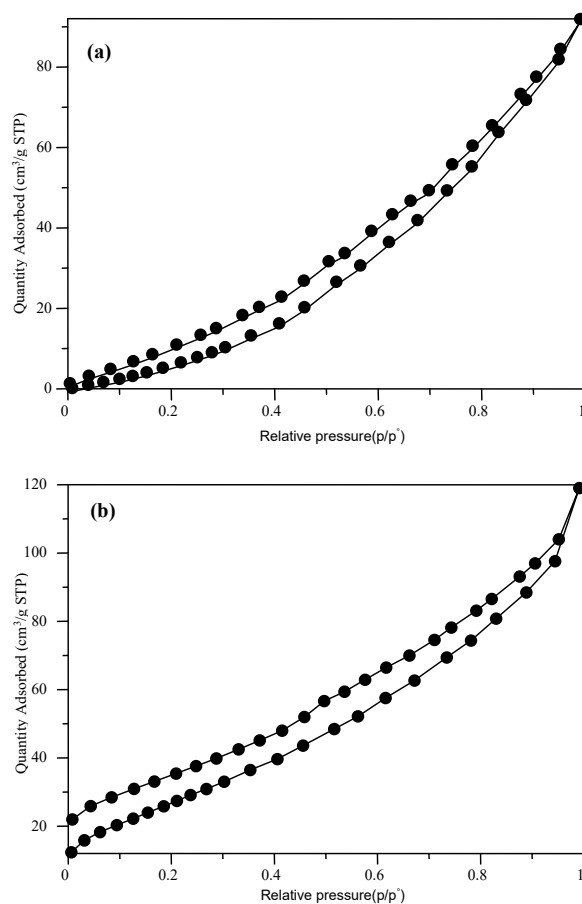
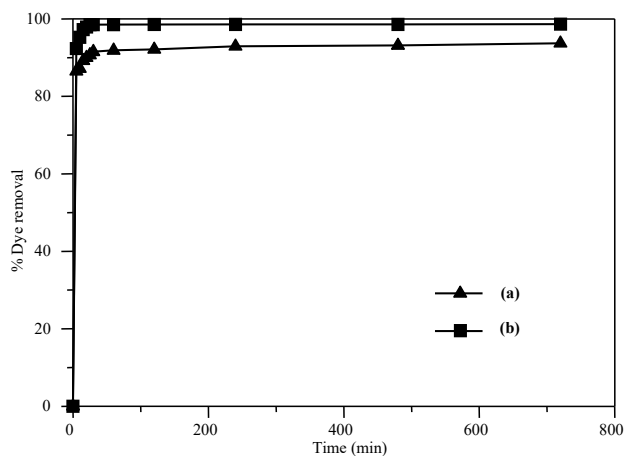


Figure 4. N<sub>2</sub> adsorption-desorption isotherms of (a) EG and (b) EGS-600

micropore area, are given in Table 2. The BET surface area, pore volume, mean pore size and micropore area of EG and EGS-600 showed the following values; 123.79 m<sup>2</sup>.g<sup>-1</sup>, 14.22 cm<sup>3</sup>.g<sup>-1</sup>, 22.97 nm, 57.544 m<sup>2</sup>.g<sup>-1</sup> and 70.31 m<sup>2</sup>.g<sup>-1</sup>, 13.34 cm<sup>3</sup>.g<sup>-1</sup>, 37.95 nm, 14.56 m<sup>2</sup>.g<sup>-1</sup>, respectively. It can be seen that the BET surface area and micropore area decreased slightly when *E. crassipes* powder was carbonated and sulfonated.

### 3.2 Effect of Contact Time

Figure 5 shows the effect of contact time on the adsorption of methylene blue on EG and EGS-600 adsorbents. These results indicate that the equilibrium adsorption was reached within 20 min by both adsorbents and dye removal percentage increased with increasing contact time. Both adsorbents rapidly adsorbed methylene blue within the first 5 min of contact time with adsorption capacity of 86% for EG and 92% for EGS-600. After 5 min, the changes in adsorption capacity increased gradually until the equilibrium was achieved within 20 min, with adsorption percentage of 90% for EG and 98% for EGS-600. The percentage of dye removal for EG was lower than EGS-600. This phenomenon was probably caused by the physical properties of EG on the surface, which was dominated by micropores. The small sizes of the pores may have hindered the effective adsorption of the methylene blue dye on the adsorbent surface. And also the increase of the amount of -OH, -COOH, S=O, -SO<sub>3</sub>H functional groups onto EGS-600 surface which can become active site when adsorption of methylene blue dye in aqueous solution was done.



**Figure 5.** Effect of contact time on % Methylene Blue dye removal on (a) EG and (b) EGS-600 Conditions: (pH: 6.9, MB: 100 mg.L<sup>-1</sup>, weight of adsorbent: 125 mg, at 25°C)

Comparison of the adsorption process onto EG and EGS-600 can be illustrated in Figure 6.

### 3.3 Adsorption Kinetics

In removing dyes from coloured wastewater, it is important to evaluate the adsorption mechanism and potential rate control measures that control the adsorption rate. To investigate the controlling rate of adsorption mechanism process, mass transfer and two kinetic models were tested out.

The adsorption kinetic of dye adsorption by powder and sulfonated carbon-derived from *E. crassipes* was investigated by pseudo-first-order and pseudo-second-order kinetic equation which were introduced by Lagergren and Svesnska [2,14]. The pseudo-first-order equation can be expressed as follows:

$$\frac{dq}{dt} = k_{1,ad}(q_e - q) \quad (3)$$

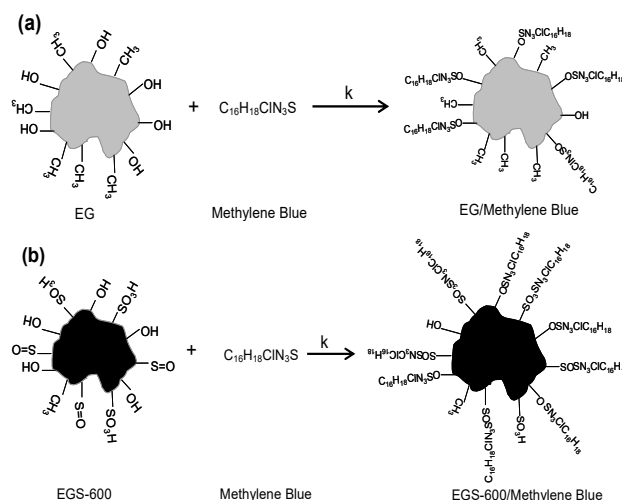
after integration with boundary condition  $t = 0$  to  $t = t$  and  $q = 0$  to  $q = q_t$ , it obtained the integrated form as:

$$\log(q_e - q_t) = \log q_{e,cal} - \frac{k_{1,ad}}{2.303} t \quad (4)$$

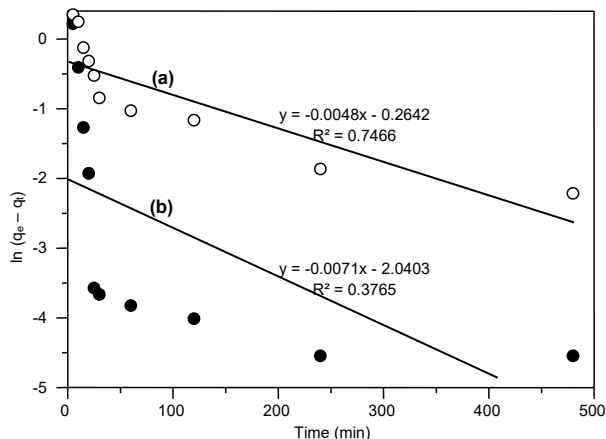
where  $k_1$  (g.mg<sup>-1</sup>.h<sup>-1</sup>) is the rate constant for the pseudo-first-order adsorption,  $q_e$  and  $q_t$  are the amounts of dye adsorbed per gram of adsorbent (mg/g) at equilibrium and any time  $t$ . The plot of  $t$  versus  $\log(q_e - q_t)$  was used to calculate  $q_{e,cal}$  from slope and  $k_1$  from intercept.

The pseudo-second-order can be expressed as equation:

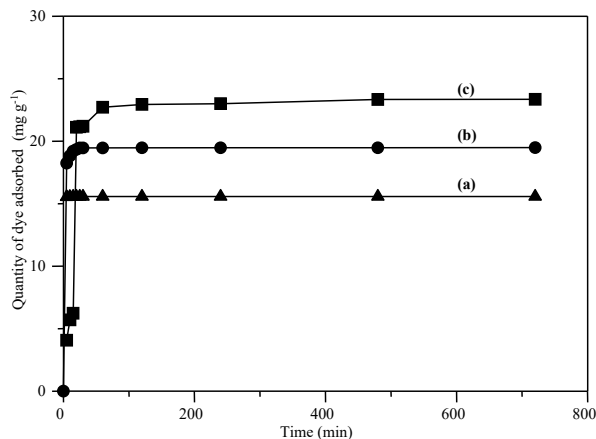
$$\frac{dq}{dt} = k_{2,ad}(q_e - q) \quad (5)$$



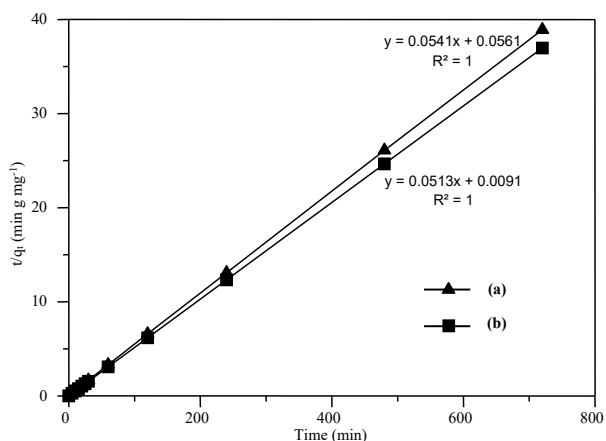
**Figure 6.** The illustration of methylene blue adsorption process onto (a) EG and (b) EGS-600 adsorbent



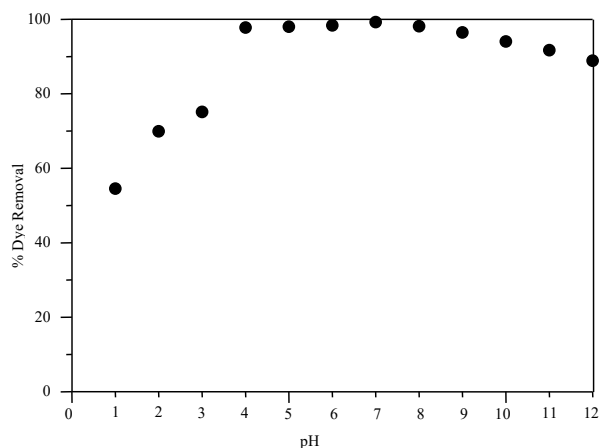
**Figure 7.** Pseudo-first-order kinetics plot for the adsorption of methylene blue dye onto (a) EG and (b) EGS-600 adsorbent. Conditions: (pH: 6.9, MB: 100 mg.L<sup>-1</sup>, weight adsorbent: 125 mg, at 25°C)



**Figure 9.** Effect of initial dye concentration on sorption of Methylene blue. Conditions: (pH: 6.9, MB: (a) 80 mg.L<sup>-1</sup>, (b) 100 mg.L<sup>-1</sup> (c) 120 mg.L<sup>-1</sup>, weight adsorbent: 125 mg, at 25°C)



**Figure 8.** Pseudo-second-order kinetics plot for the adsorption of methylene blue dye onto (a) EG and (b) EGS-600 adsorbent. Conditions: (pH: 6.9, MB: 100 mg.L<sup>-1</sup>, weight adsorbent: 125 mg, at 25°C)



**Figure 10.** Effect of pH on % Methylene Blue dye removal on EGS-600, Conditions: (MB: 100 mg.L<sup>-1</sup>, weight adsorbent: 125 mg, at 25°C)

**Table 3.** Kinetic parameter of the pseudo-first-order and pseudo-second-order models for adsorption of Methylene blue dye of EG and EGS-600

<i>Eichhornia crassipes</i> Adsorbent	Pseudo-first-order				Pseudo-second-order			
	$q_e$ Calculation (mg.g <sup>-1</sup> )	$q_e$ experiment (mg.g <sup>-1</sup> )	$k_1$ (g.mg <sup>-1</sup> .min <sup>-1</sup> )	R <sup>2</sup>	$q_e$ Calculation (mg.g <sup>-1</sup> )	$q_e$ experiment (mg.g <sup>-1</sup> )	$k_2$ (g.mg <sup>-1</sup> .min <sup>-1</sup> )	R <sup>2</sup>
EG	0.769	18.982	0.0048	0.746	18.484	18.517	0.0521	1.000
EGS-600	0.129	19.480	0.0071	0.376	19.493	19.480	0.2891	1.000

after integration with boundary condition  $t = 0$  to  $t = t$  and  $q = 0$  to  $q = q_t$ , the new equation form can be written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e,cal}^2} + \frac{t}{q_{e,cal}} \quad (6)$$

where,  $k_2$  ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{h}^{-1}$ ) is the rate constant for the pseudo-second-order adsorption. The plot  $t$  versus  $t/q_t$  was used to calculate  $q_{e,cal}$  from slope and  $k_2$  from intercept.

The Freundlich isotherm equation was used to determine the adsorption isotherm of powder and sulfonated carbon-derived from *E. crassipes*. The Freundlich equation is followed as:

$$q_e = K_F C_e^{1/n} \quad (7)$$

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (8)$$

Based on the intercept and slope of the plot of  $\ln q_e$  vs  $\ln C_e$ , the  $K_F$  and  $n$  can be calculated. In this relation,  $K_F$  ( $\text{mg} \cdot \text{g}^{-1}$ )( $\text{L} \cdot \text{mg}^{-1}$ ) $^{1/n}$ , which indicate a measure of adsorption capacity and  $1/n$  indicate the favorability of adsorption. If the value of  $n > 1$ , it characterizes favorable adsorption condition.

The pseudo-first-order and pseudo-second-order kinetics plots of both EG and EGS-600 as adsorbent of methylene blue dye are shown in Figures 7 and 8, respectively. The rate constant ( $k$ ), equilibrium sorption calculated ( $q_{e,cal}$ ) were determined by slope and intercept of the plots. The value of rate constant ( $k$ ), equilibrium sorption calculated ( $q_{e,cal}$ ), equilibrium sorption experiment ( $q_{e,exp}$ ) and the correlation coefficient

( $R^2$ ) were listed in Table 3. The value of the correlation coefficient ( $R^2$ ) for pseudo-first-order of EG and EGS-600 as 0.746 and 0.376 were lower compared with the value for pseudo-second-order of both adsorbent as 1.000 which seen to be more accurate. This phenomenon is in line with result of Ho and McKay [29], that concluded the first order equation of Lagergren is not suitable well with the whole range of contact time and is generally applicable over the initial stage of the adsorption process in many cases. The result of this research showed that the adsorption of methylene blue onto EG and EGS-600 adsorbents were not following the pseudo-first-order kinetic.

On the other hand, the value of rate constant ( $k$ ), equilibrium sorption calculated ( $q_{e,cal}$ ), equilibrium sorption experiment ( $q_{e,exp}$ ) and the correlation coefficients ( $R^2$ ) for pseudo-second-order of EG and EGS-600 showed the following values; 0.0521  $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ , 1.000, 18.484  $\text{mg} \cdot \text{g}^{-1}$ , 18.517  $\text{mg} \cdot \text{g}^{-1}$  for EG and 0.2891  $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ , 1.000, 19.493  $\text{mg} \cdot \text{g}^{-1}$ , 19.480  $\text{mg} \cdot \text{g}^{-1}$  for EGS-600, respectively. It can be seen that the correlation coefficients for pseudo-second-order models for both EG and EGS-600 were very high ( $R^2 \sim 1.000$ ) and the difference in calculated equilibrium adsorption capacity,  $q_{e,cal}$  with experimental equilibrium adsorption capacity,  $q_{e,exp}$  for both adsorbents in pseudo-second-order were lower compared to pseudo-first-order. Therefore, it can be concluded that the adsorption of methylene blue dye onto both EG and EGS-600 adsorbents follow the pseudo-second-order adsorption mechanism model.

The heterogeneous adsorption process on the surface of both powder (EG) and sulfonated carbon (EGS-600) from *E. crassipes*, which was done through a multi-layer adsorption mechanism, can be described by using the Freundlich Isotherm model. The constant of Freundlich isotherm ( $K_F$ ) and  $n$  value are presented in Table 4. The values of  $n$  are more than 1, which indicates a favorable adsorption of methylene blue dye on both of the adsorbents.

**Table 4.** Freundlich isotherm constants for adsorption of Methylene blue dye on EG and EGS-600 adsorbent

<i>Eichhornia crassipes</i> Adsorbent	$K_F$	$n$	$R^2$
EG	0.2101	1.011	0.9996
EGS-600	0.2471	1.049	0.9935

**Table 5** Pseudo-second-order models parameter for adsorption of Methylene blue dye of EGS-600 on different initial concentration

Initial Concentration of Methylene Blue ( $\text{mg} \cdot \text{L}^{-1}$ )	$q_e$ calculation ( $\text{mg} \cdot \text{g}^{-1}$ )	$q_e$ experiment ( $\text{mg} \cdot \text{g}^{-1}$ )	$k_2$ ( $\text{g} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$ )	$R^2$
120	23.981	23.348	0.0028	0.9967
100	19.493	19.480	0.2892	1.0000
80	15.576	15.566	13.738	1.0000

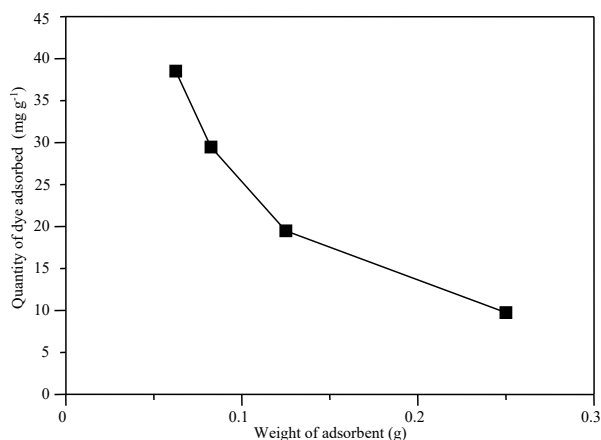
### 3.4 Effect of Initial Concentration

Figure 9 shows the effect of different initial methylene blue dye concentrations on the adsorption. The adsorption amount of methylene blue increased when the initial concentration of methylene blue increased. At equilibrium, the amount methylene blue adsorbed increased from 15.57 to 23.35 when the initial concentration of methylene blue increased from 80 to 120 mg.L<sup>-1</sup>. It is hypothesized that the increasing concentration acted as an increasing driving force to overcome all mass transfer resistances of the methylene blue dye molecules between the aqueous and solid phase, leading to an increasing equilibrium sorption until saturation was achieved. A similar trend was also reported with methylene blue onto roots, stems and leaves with methylene blue concentrations of 0.80 to 8.0 mg.L<sup>-1</sup> [2].

As another evident that adsorption process of methylene blue onto sulfonated carbon-derived from *E. crassipes* take pseudo-second-order kinetic models were done the effect of initial concentration. The data show that the differences in calculated equilibrium adsorption capacity,  $q_{e,cal}$  with experimental equilibrium adsorption capacity,  $q_{e,exp}$  are low and the values of the correlation coefficients ( $R^2$ ) are 0.9967 to 1.000 when used initial concentration 80 mg.L<sup>-1</sup> to 120 mg.L<sup>-1</sup>. The complete data were listed in Table 5.

### 3.5 Effect of pH

Figure 10 displays the effect of pH on the methylene blue adsorption on EGS-600 adsorbent. The adsorption of methylene blue dye was unaffected in the pH range of 4-8. Adsorption



**Figure 11.** Effect of adsorbent dose on quantity of Methylene Blue dye adsorbed (mg g<sup>-1</sup>). Conditions: (pH: 6.9, MB: 100 mg L<sup>-1</sup>, weight adsorbent: 62.5; 82.5; 125 and 250 mg, at 25°C)

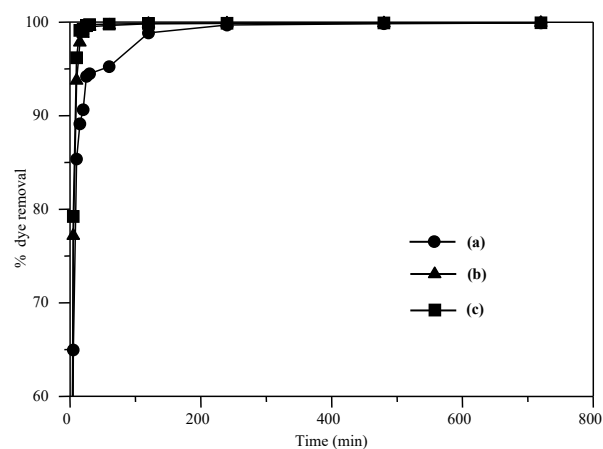
at pH less than 3 was not beneficial as the excess hydrogen ions (H<sup>+</sup>) may have caused competition in absorption between the positive charge sites of methylene blue dye with hydrogen ions (H<sup>+</sup>) [3,9]. At pH value of dye solution more than 9, the adsorption of methylene blue dye tends to decrease due to the excess number of negative charged sites of hydroxide ions (OH<sup>-</sup>) [9].

### 3.6 Effect of Adsorbent Dosage

Figure 11 shows the effect of adsorbent dosage on the quantity of methylene blue dye adsorbed (mg.g<sup>-1</sup>). The adsorbent quantity used in the adsorption is important to determine the quantity of dye adsorbed per unit weight of adsorbent in the system. The quantity of dye adsorbed per unit weight of adsorbent decreased when the dosage of adsorbent increased. This phenomenon shows that the active sites of the adsorbent were more effective at low ratio of adsorbent/adsorbate. If the ratio of the adsorbent/adsorbate is high, this will cause many of the remaining active sites to be covered by the adsorbate, thus causing sorption of specific dye to be low. This result shows a similar tendency with a previous work that investigated the adsorption of methylene blue onto roots, stems and leaves of *E. crassipes* [2].

### 3.5 Effect of Temperature

Figure 12 shows the effect of temperature on the removal percentage of methylene blue dye. The removal percentage of methylene blue dye at varying temperatures increased from 64.94% to 99.90% (at room temperature), 77.16% to 99.92% (at 40°C) and 79.21% to



**Figure 12.** Effect of temperature on methylene blue dye sorption (%). Conditions: (pH: 6.9, MB: 100 mg L<sup>-1</sup>, temperature (a) 25°C, (b) 40°C and (c) 50°C)



99.92% (at 50 °C). It can be clearly seen that by increasing the temperature, the removal percentage of methylene blue dye also slowly increased and reached optimum at almost 99.92%. As the adsorption capacity increased with adsorption temperature, this shows that the adsorption of methylene blue dye by sulfonated carbon from *E. crassipes* was endothermic in nature.

Parameters of thermodynamic were determined by the experiments carried out at different temperatures. The value changes of free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) of adsorption were determined with the equation:

$$\log K_C = \frac{\Delta S}{2.303R} + \frac{\Delta H}{2.303RT} \quad (9)$$

$$\Delta G = \Delta H - T \Delta S \quad (10)$$

where  $\Delta S$  and  $\Delta H$  are the changes in entropy and enthalpy of adsorption. A plot of  $\log K_C$  vs.  $1000/T$  is linear with  $K_C$  was calculated by the equation:

$$K_C = \frac{C_1}{C_2} \quad (11)$$

where  $T$  is temperature (K);  $R$  is the gas constant ( $8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$ );  $K_C$  is the equilibrium constant;  $C_1$  is the quantity of methylene blue dye adsorbed per unit mass of adsorbent, and  $C_2$  is the concentration of methylene blue dye in aqueous phase. Values of  $\Delta S$  and  $\Delta H$  are calculated from the slope and intercept of Van't Hoff's plots. Negative value of  $\Delta G$  at each temperature indicates the feasibility and spontaneity of ongoing adsorption. The positive value of  $\Delta S$  indicates the increase in randomness of ongoing process. The positive value of  $\Delta H$  indicates that the adsorption process is endothermic in nature.

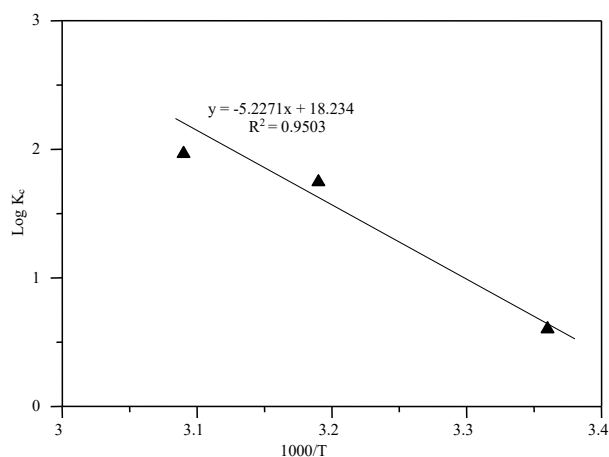


Figure 13. Van't Hoff's plots,  $\log K_c$  vs.  $1000/T$

The thermodynamic parameters of  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  are calculated based on the slope and intercept of Van't Hoff's plots, as shown in Figure 13. The values of  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  were  $-109.38 \text{ kJ.mol}^{-1}$ ,  $-100.08 \text{ J.mol}^{-1}$ , and  $+349.13 \text{ J.K}^{-1}.\text{mol}^{-1}$ , respectively. Negative value of free energy ( $\Delta G$ ) indicates that the feasibility and spontaneity of ongoing methylene blue dye adsorption onto sulfonated carbon of *E. crassipes* as the adsorbent. The positive value of enthalpy ( $\Delta H$ ) indicates that the adsorption process of methylene blue dye by sulfonated carbon of *E. crassipes* as the adsorbent is endothermic in nature. The positive value of entropy ( $\Delta S$ ) indicates that the increase in degree of system irregularities.

#### 4. Conclusions

*E. crassipes* (water hyacinth), a tropical plant can be used as the resources of low-cost adsorbent. The *E. crassipes* that was modified by carbonation followed sulfonated can be obtained good and low-cost adsorbent for methylene blue adsorption in aqueous solution. The ability of EG and EGS-600 adsorbent were investigated in batch system at methylene blue dye initial concentration of  $100 \text{ mg.L}^{-1}$  at room temperature. The sorption capacity of EGS-600 was better than EG adsorbent which can be proven of the value of equilibrium sorption experiment ( $q_{e,exp}$ ) of both adsorbent was  $18.517 \text{ mg.g}^{-1}$  (EG) and  $19.480 \text{ mg.g}^{-1}$  (EGS-600). Adsorption processes of both adsorbent for methylene blue dye adsorption in aqueous solution follow pseudo-second-order kinetics models with the rate constant  $0.0521 \text{ g.mg}^{-1}.\text{min}^{-1}$  (EG) and  $0.2891 \text{ g.mg}^{-1}.\text{min}^{-1}$  (EGS-600). The adsorption process onto both adsorbents took place through a multi-layer adsorption mechanism that were illustrated well by Freundlich isotherm model with correlation coefficient,  $R^2$ , of 0.9996 (EG) and 0.9935 (EGS-600). The free energy thermodynamic parameters showed a negative value ( $-109.38 \text{ kJ.mol}^{-1}$ ), which indicates that the adsorption process of methylene blue dye on EGS-600 was spontaneous.

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