

Kinetics of Methylene Blue Adsorption on Sulphuric Acid Treated Coconut (*Cocos nucifera*) Frond Powder

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Abstract In this study, coconut frond treated with sulphuric acid (SACF) was used as a low-cost adsorbent in removing methylene blue (MB) from aqueous solutions. The kinetics of methylene blue (MB) adsorption onto SACF was described by applying the pseudo-first-order and pseudo-second-order kinetic model with the latter better fitted kinetics data. FTIR analysis showed that carbonyl and hydroxyl groups were involved in the uptake of MB. Mechanisms of MB adsorption were identified as ion-exchange and complexation.

Keywords Adsorption, Coconut frond, Kinetics, Sulphuric acid

1. Introduction

Dyes are widely used in industries such as printing, textiles, plastic and cosmetic. The breakdown products of dyes may be toxic for living organisms [1]. Hence, the removal of dyes is essential before the dyes are discharged into water bodies. Removal of dyes from effluents is quite challenging due to the nature of dyes that do not degrade easily. It is also generally difficult to remove completely from wastewater by conventional wastewater treatment systems [2]. Dye removal is widely practiced by implementing physicochemical methods such as coagulation, ultrafiltration, electrochemical, and photo-oxidant [3]. One of the commonly used dyes by industries is methylene blue (MB), a heterocyclic compound with the chemical formula of $C_{16}H_{18}ClNS \cdot 3H_2O$ as shown in Figure 1.

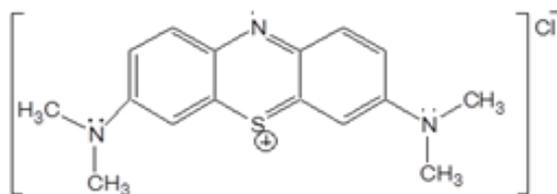


Figure 1. Structure of MB

MB is used in various industrial sectors for product finishing. Thus, without proper treatment, MB can be discharged to the environment and it will contribute to

environmental problem such as soil and water pollution. The most conventional methods which can be used to treat MB from wastewater, however, among all of the methods used, adsorption is the most preferable method because it is known to be more efficient compared to the other conventional techniques for removing dye in wastewater at low concentration [4]. Activated carbon is widely used as an adsorbent and is very effective for removing pollutants such as dyes and heavy metals from aqueous solutions. Activated carbon prepared from different precursors to remove basic dyes from aqueous solutions has been reported [5]. However, activated carbon is considered as an expensive adsorbent and the cost of producing and utilising activated carbon is still dependent on its quality. Therefore, many researchers look for other solutions by investigating a natural-plant based as an alternative material. The natural-plant based material includes chitosan/oil palm ash composite bead [6], waste material [7], almond shell [8] and dehydrated peanut hull [9]. Coconut (*Cocos nucifera*) has been called "the tree of life" because of the variety of uses it has, especially in sustaining the livelihood of millions of people in coastal regions. In this study, coconut palm frond (CF) was treated with sulphuric acid and was used as an adsorbent to remove MB from aqueous solutions. The effects of physicochemical parameters such as pH of MB solution, dosage and adsorption kinetics were also investigated.

2. Experimental

2.1. Adsorbent Preparation and Characterization

CF was obtained from Jengka, Malaysia. The frond was rinsed with water to remove dirt or impurities, and then it was rinsed with distilled water before drying in an oven at

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80 °C overnight. CF was cut into small pieces, ground and sieved to a constant size of 125µm – 250 µm. The CF powder was washed extensively with distilled water until the washing was free from colour pigments before it was dried at 110°C overnight. A volume of 450 mL (0.50 M) H₂SO₄ was heated to 110 °C and 20 g CF powder was added into the solution and heated again at 110 °C for 180 min. The sample was allowed to cool at room temperature before it was rinsed with distilled water. Then, the sample was soaked in 500 mL Na₂CO₃ solution overnight before being filtered and dried in an oven at 80 °C overnight [14]. The sample was placed in a plastic container for further use and abbreviated as SACF. The types of functional groups present in the CF and SACF were determined by using a Fourier transform infrared spectrometer (FTIR) (PerkinElmer, Spectrum 100, USA). The field emission scanning electron microscope (FESEM, JEOL, JSM7800F, Japan) coupled with energy dispersive X-ray (EDX, Microanalysis, Oxford instrument, UK) was performed to analyse the surface morphology of SACF. The percentage by mass of the element contained in the SACF was determined by using a CHNS analyser (Vario Macro CHNS, Elementar, Germany). The amount of MB adsorbed (q_e , mg g⁻¹) and removed (%) was calculated by using equations (1) and (2), respectively:

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

$$\text{Removal (\%)} = \frac{C_o - C_f}{C_o} \times 100 \quad (2)$$

where C_o and C_f are the initial and final concentration (mg L⁻¹) of MB and m is the weight of SACF (g).

2.2. Adsorption Experiments

Methylene blue was purchased from QRec, Malaysia. A stock solution of 1000 mg L⁻¹ MB was initially prepared before being diluted to the desired concentrations with deionized water. The adsorption experiments were performed by mixing 0.0100 g SACF with 50 mL (20 mg L⁻¹) MB solutions and stirred at 120 stroke per min at 298 ± 1 K for 300 min (equilibrium time). The initial pH of the MB solution was adjusted to 6 by addition of drops of 0.10 M NaOH or HCl solutions. Adsorption kinetics study was conducted using three different MB concentrations (20, 30 and 40 mg L⁻¹) at different contact times (0-300 min). After adsorption, the SACF was separated from the solution by using a centrifuge (Hermle Labortechnik Z206, Germany) at 6,000 rpm for 15 min. The final concentration of MB was determined by using a UV-Visible spectrophotometer (UV 1800, Shimadzu Corporation, Japan) at λ_{max} 665 nm.

3. Results and Discussion

3.1. Adsorbent Characterization

The result for CHNOS analysis is given in Table 1. SACF showed an increased percentage of carbon, nitrogen

and sulphur compared with raw CF. The increase of S value could come from H₂SO₄ treatment that introduced more S atoms on coconut frond powder surface.

Table 1. Comparison of elemental compositions of CF and SACF

Sample	Elements [%]				
	C	H	N	O	S
CF	38.35	6.30	0.57	54.71	0.07
SACF	45.14	6.22	1.85	46.34	0.45

The FTIR spectra of CF, SACF and SACF-MB loaded are shown in Figure 2. Various functional groups were detected on the surface of CF and SACF. The broad and strong peak at 3400 cm⁻¹ indicated -OH functional group. The weak peak at 2929 cm⁻¹ was attributed to the symmetrical stretching vibration of -CH₂ group. The strong and broad peak at 1638 cm⁻¹ indicated the present of N-H of the amine group. The peak at 1736 cm⁻¹ suggested the presence of ester group. The sharp peak at 1384 cm⁻¹ indicated the presence of the carboxylic acid. After the treatment process, the peak at 1736 cm⁻¹ of SACF disappeared, suggesting the conversion of ester to carboxylic acid. The appearance of a new peak at 1115 cm⁻¹ suggested the presence of S-O ester group. This occurrence is preceded by the reaction between the sulphuric acid with the hydroxyl groups of CF, which lead to the formation of covalent sulphate [9]. When SACF was loaded with MB, several shifts in wavenumber could be observed. The wavenumber of the hydroxyl group shifted from 3401 to 3393 cm⁻¹. It can be explained that when SACF adsorbed MB, the vibration of -OH stretching became low due to the higher molecular weight of MB molecule, which could attach to the -OH via hydrogen bond. The cationic MB could also be attached to the negatively charged -COO⁻ via electrostatic attraction, as suggested by the shift in wavenumber from 1610 to 1602 cm⁻¹. The C-O-C and S-O groups could attract the partial positive S atom of MB molecules as suggested by the shift in wavenumber from 1062 to 1057 cm⁻¹ and 1115 to 1110 cm⁻¹, respectively.

Figure 3 shows the SEM images (at 500x magnification) of CF and SACF. Before treating with H₂SO₄, the surface of the adsorbent is rough and irregular but after such treatment, the surface showed some porosity with visible hairline cracks. No significant difference was observed for SACF before and after MB adsorption. EDX spectrum of CF (Figure 4a) shows the peak of light metals such as Mg, K, Ca. After the treatment process, the EDX spectrum of SACF (Figure 4b) shows the presence of sulphur while light metals disappeared. Light metals can easily dissolve in an acid solution, leading to the disappearance of light metal peaks in EDX spectrum [10]. EDX spectrum of MB loaded SACF shows the presence of N atom (Figure 4c), which originated from MB. The peak for Na⁺ at 1.2 keV disappeared after MB adsorption, suggesting ion exchange as one of the mechanisms involved.

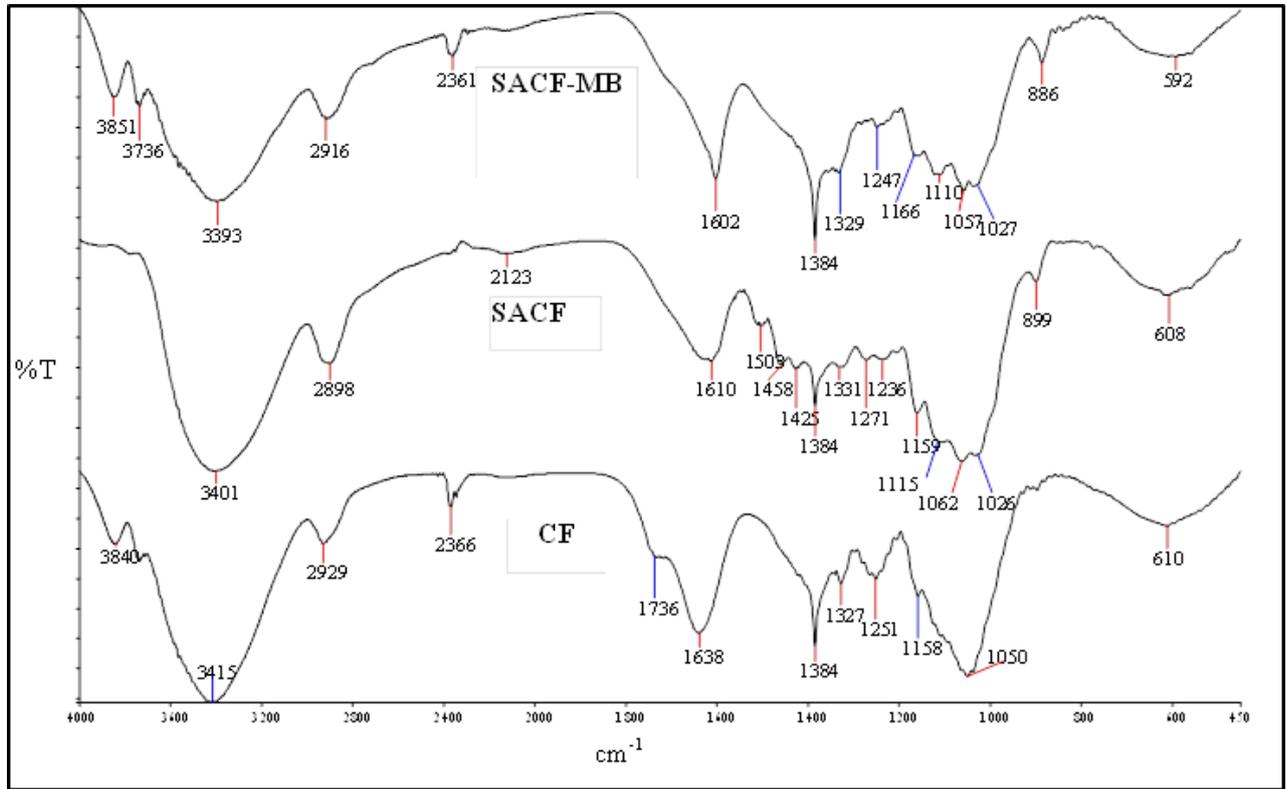


Figure 2. FTIR spectra of CF, SACF before and after MB adsorption

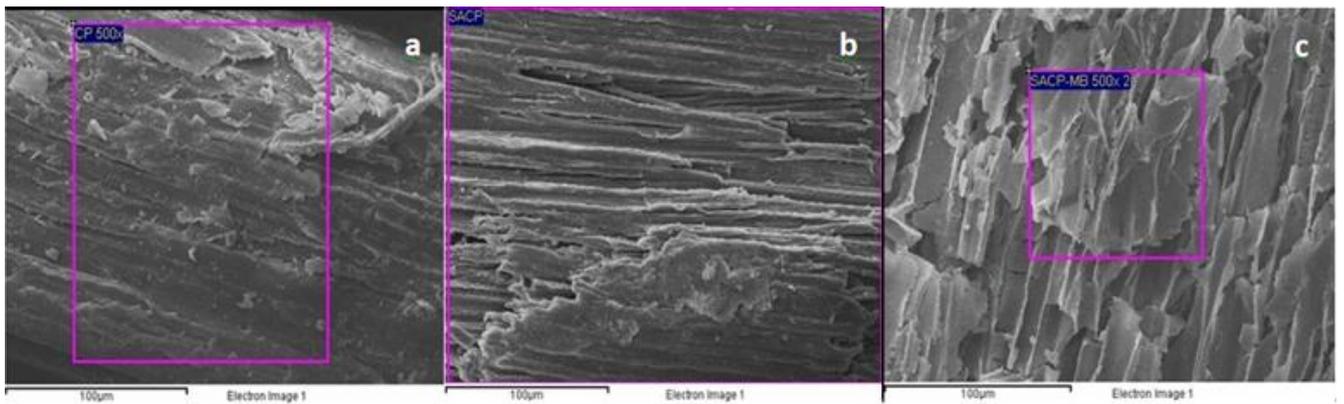


Figure 3. SEM images CF (a), SACF (b) and SACF loaded with MB (c)

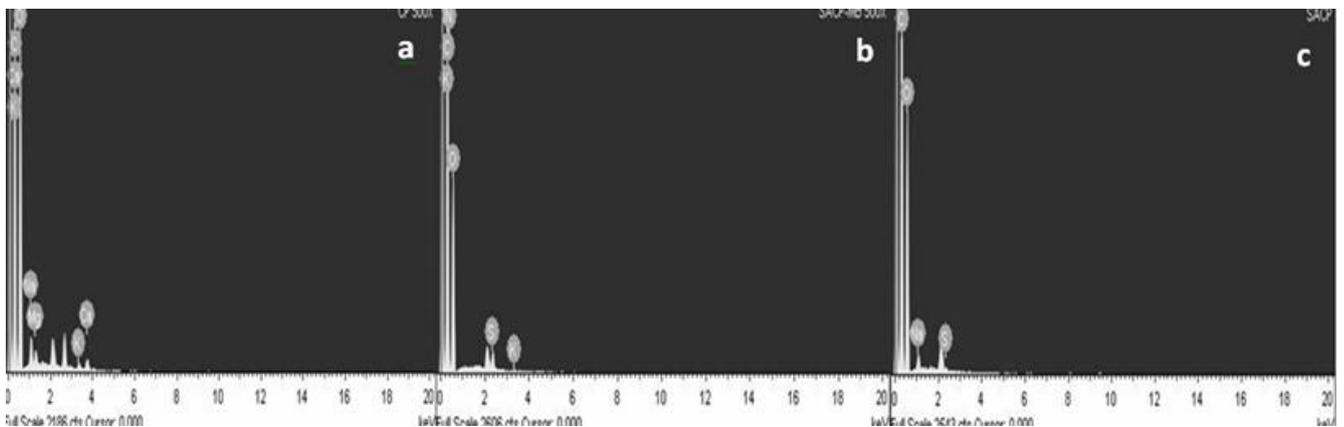


Figure 4. EDX spectrum of CF (a), SACF (b) and SACF-MB loaded (c)

3.2. Effect of pH

As shown in Figure 5, a sharp increase in the amount of MB adsorbed was observed from pH 3 to 5. At pH 3, carboxylic group would be deprotonated, exposing more negative charges and more cationic MB could be attracted. Above pH 6, the amount of MB adsorbed remained constant and this finding support by finding by [4] [14]. The lowest amount of MB adsorbed at pH 2 – 3 was due to the competition of cationic MB with H⁺ ions in an acidic solution.

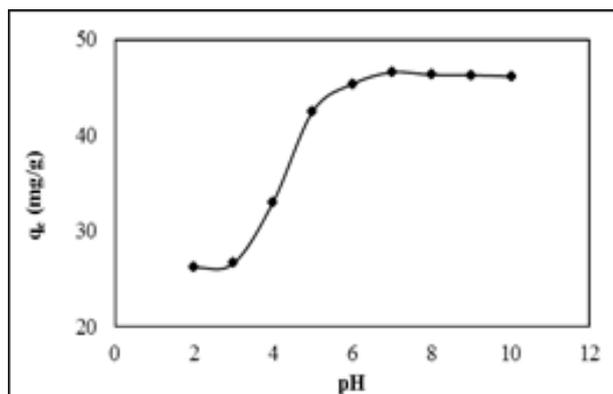


Figure 5. Effect of pH on the adsorption of MB onto SACF

3.3. Effect of Initial MB Concentration and Contact Time

Fig. 6 shows the adsorption equilibrium time was reached in 100, 150 and 200 min for MB concentrations of 20, 30, and 40 mg L⁻¹, respectively. However, experiments were continued until 300 min to ensure equilibrium was completely achieved. The amount adsorbed increased from 47.15 to 85.33 mg g⁻¹ when the concentrations of MB were increased from 20 to 40 mg L⁻¹. The maximum dye uptakes were 48.99, 73.08 and 85.83 mg g⁻¹ for MB concentrations of 20, 30 and 40 mg L⁻¹ respectively. The curves suggested that the adsorption process involved three main phases, which consist of rapid phase, slow phase and dynamic equilibrium phase. The rapid phase occurred in the first 40 min, which was related to the external surface adsorption of MB. It was followed by the slow adsorption rate within the range of 60 – 120 min. The equilibrium was reached at the last phase which is also known as dynamic equilibrium time. This process occurs when there is no more available external site, and this will lead to the diffusion into the porous structure of an adsorbent [11]. A higher amount of MB adsorbed can be

explained in term of increasing mass transfer, leading to a greater interaction between MB and SACF. More adsorption sites will be covered as more adsorbates are attached to an adsorbent surface [3].

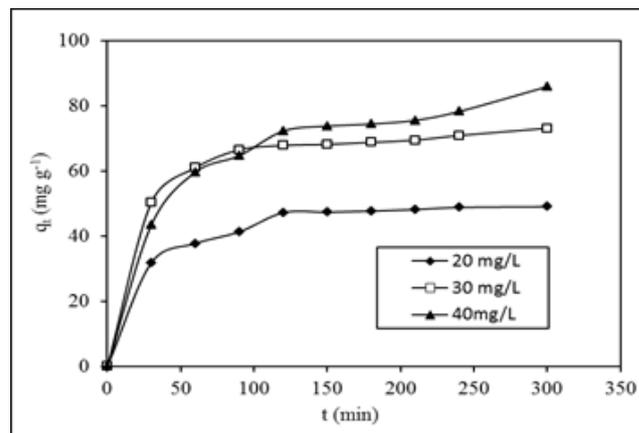


Figure 6. Effect of initial MB concentration and contact time of MB adsorption by SACF

3.4. Adsorption Kinetic

Adsorption kinetic for the adsorption of MB onto SACF was explored by applying pseudo-first-order [12] and pseudo-second-order [13] models. The models are expressed by equations (3) and (4), respectively.

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (4)$$

where q_t (mg g⁻¹) and q_e (mg g⁻¹) are the amount of MB adsorbed at time t (min) and equilibrium respectively. K_1 (min⁻¹) is the pseudo-first-order rate constant, h (mg/(g.min)) is the initial adsorption rate in pseudo-second-order equation and can be calculated as $h=K_2q_e^2$. K_2 (g/(mg.min)) is the pseudo-second-order rate constant. Pseudo-second-order plot (plot not shown) has higher linearity with R^2 close to unity compared to the pseudo first-order model (Table 2).

The calculated amount of MB adsorbed ($q_{e,calc}$) of pseudo second-order model showed values close to the experimental values ($q_{e,exp}$). Therefore, adsorption process is best fitted to pseudo-second-order model, and complexation reaction could be the rate determining step. A similar observation was reported by [14] [15].

Table 2. Adsorption kinetic parameters for MB adsorption on SACF

[MB] mg L ⁻¹	q _{e,exp} (mg g ⁻¹)	Pseudo- first-order			Pseudo-second-order			
		q _{e,calc} (mg g ⁻¹)	K ₁ (min ⁻¹)	R ²	h (mg/(g.min))	K ₂ (g/(mg.min))	q _{e,calc} (mg g ⁻¹)	R ²
20	48.99	18.32	0.014	0.765	2.59	0.0008	55.56	0.998
30	73.08	22.64	0.009	0.940	5.00	0.0008	76.92	0.999
40	85.83	62.07	0.009	0.840	2.59	0.0003	100.00	0.993

4. Conclusions

Sulphuric acid (H₂SO₄) modification can be applied to produce a biosorbent with a relatively fast uptake of MB. Based on the characterization study, a large number of carbonyl and hydroxyl groups were present on the surface of SACP. SEM images and EDX spectra of adsorbent surface, before and after adsorption showed that the adsorbent has lack of porosity and ion-exchange could be involved in the MB adsorption process. This work suggests the potential use of SACP for removal of MB from industrial wastewater.

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