Coconut Frond as Adsorbent for Removal of Methylene Blue

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In present study raw coconut frond was used as adsorbent in the removal of methylene blue dye. Adsorption using raw agricultural waste has proved to be more economical compared to other removal methods of dyes as the method of production is relatively easy. The optimum conditions for the removal of methylene blue using raw coconut frond were obtained at 0.125 mm of adsorbent size with 0.5 g adsorbent dosage at 24 h contact time. Initial dye concentration was found to work efficiently at 50 mg/L and pH 8. Adsorption isotherms were studied to understand the mechanism of dye adsorption. The experimental values obtained fitted well in the Langmuir isotherm. Maximum adsorption capacity is 18.69 mg/g with $R^2 = 1$, suggesting a monolayer adsorption mechanism. The obtained results indicate that raw coconut frond has potential in removing methylene blue.

Keywords: Coconut frond, Adsorption, Methylene blue, Wastewater treatment.

INTRODUCTION

Water pollution caused by methylene blue, especially from the textile industries has long been an issue to the environment. Malaysia is known for its 'batik' textile. The industry however pollutes the receiving water bodies and affects the marine habitants of the affected area. This is also contributed by the improper waste treatment by plants prior to waste discharge. Methylene blue is a monovalent cationic dye. It is also a heterocyclic aromatic chemical compound with a molecular formula of $C_{16}H_{18}N_3SCl$. Waste streams hold about 10 % of dye from the textile industry. Methylene blue contaminated water blocks the penetration of sunlight due to the presence of dyes, which have not yet degraded. Therefore, some marine inhabitants in the deeper side of the ocean are unable to receive sunlight. This disrupts the daily routine of those inhabitants and causes the malfunctioning of the system. This will eventually disturb the ecological chain as many marine inhabitants will suffocate and have difficulty in searching for food. On top of that, the agricultural waste dumped in landfills or eliminated through open combustion only adds to the environmental issues.

The instability and complications surrounding the breaking down process is one of the properties of dyes that are categorized as having a complex aromatic molecular structure [1]. There is a large community that still depends on sea or river water for their daily routines such as bathing, cooking, drinking and others. They tend to consume water directly from exposed water streams. The only method used before consumption is boiling the water. This is not sufficient to remove the methylene blue from the water as it only helps in killing microorganisms. Boiling water to a certain temperature, usually 100 °C, only deactivates and kills microorganisms. It does not help in the biodegradation of dye. Therefore, this may cause increases in heart beat, throwing up, shock, cyanosis, jaundice and other health problems [2]. Water pollution by methylene blue was nominated as posing a health risk at level 2 due to its carcinogenicity by the National Fire Protection Agency (NFPA). Therefore, methylene blue has to be removed from waste streams.

Existing dye removal methods such as chemical, biological and activated carbon methods are efficient but not economically feasible as they are expensive to be implemented [3]. An adsorbent is considered as a low-cost adsorbent if it utilizes a small number of procedures, is easily obtainable in the environment due to its quantity and if it is the unwanted output of a certain company [4]. Therefore, research has focused on producing adsorbents from raw agricultural waste such as coconut leaves [5], tamarind fruit shells [6], coconut husks [7] and others. Raw agricultural wastes were found to have similar potential as adsorbents as using activated carbon [8].

The current research utilizes coconut fronds as an adsorbent for the removal of methylene blue, with focus on the cushion. The fronds were obtained from a coconut farm located in Jeli, Kelantan, Malaysia. Fronds which had fallen out from trees were chosen as adsorbents. To the best of our knowledge,

the use of coconut fronds as adsorbent for methylene blue removal has yet to be reported in the literature. A few parameters such as adsorbent size and dosage, dye concentration, contact time and pH were studied in favour of verifying the coconut fronds' potential as an adsorbent. Two types of isotherms, which are Langmuir and Freundlich were exploited to determine the degree of adsorption favourability.

EXPERIMENTAL

Methylene blue was purchased from R&M. Other reagents were used for buffer preparation, *i.e.* sodium hydroxide (Merck), sodium bicarbonate (HmBG Chemicals), glycine (Merck), potassium dihydrogen phosphate (HmBG Chemicals), citric acid-1-hydrate (Bendosen), sodium citrate-2-hydrate (Bendosen) and hydrochloric acid (HmBG Chemicals). Buffer preparation was done according to http://delloyd.50megs.com/moreinfo/buffers2.html [9]. All chemicals were used without any purification.

Preparation of adsorbent: Coconut fronds were obtained from Jeli district, Kelantan, Malaysia. Leaves were removed and only the fronds were left behind. The remaining fronds were washed with distilled water and dried at room temperature for 24 h. After that, large fronds were cut into small pieces and allowed to dry further in an oven at 100 °C for another 24 h or as per requirement to be completely moisture-free. It is then grinded to powder form using a grinder. The adsorbent was then stored in an air-tight container before further use.

Preparation of stock solution and calibration curve: A stock solution of methylene blue was prepared at 1000 mg/L concentration. For the calibration curve, a few series of methylene blue concentrations were prepared in the range of 0.5-6.0 mg/L by diluting the prepared stock solution with distilled water. Then, various concentrations of methylene blue were measured using a UV-visible spectrophotometer (Thermo Scientific, Gynesis 20) at 665 nm wavelength.

Optimization of adsorption studies: The effect of adsorbent size was studied at 0.125, 0.300 and 0.710 mm. Other parameters such as dosage of adsorbent and the concentration and volume of methylene blue were fixed at 0.5 g, 100 mg/L and 200 mL, respectively. The mixture was then stirred using a glass rod for a few minutes and left undisturbed till the next 24 h. After 24 h, the supernatant was filtered using filter paper. Then, the supernatant was measured using a UV-visible spectrophotometer at 665 nm. The same procedure was used for subsequent studies.

The effect of adsorbent dosage was analyzed in the range of 0.1-3.0 g using the optimum size obtained from the previous study. Other parameters were fixed at the same rates as the previous study. To study the effect of initial dye concentration, the optimum size and dosage of adsorbent obtained from previous parameters were used. The initial methylene blue concentrations were studied in the range of 10-400 mg/L.

The effect of contact time was studied in the range of 4-24 h at 4 h intervals. Lastly, the effect of pH was studied in the range of pH 5-10. Other parameters were fixed according to the optimum conditions obtained in previous experiments.

RESULTS AND DISCUSSION

Effect of adsorbent size: Fig. 1 shows that the highest percentage removal of methylene blue was obtained at 0.125 mm adsorbent size. The removal percentage of methylene blue slightly decreased from 0.125 to 0.710 mm. A similar trend was reported by Gardazi *et al.* [10] when the smallest particle size gave the highest percentage removal of methylene blue using Melin azadarach sawdust as the adsorbent. This can be explained by the exposure of adsorbent sites. Smaller adsorbent size has more surface area exposed to the methylene blue for adsorption. Therefore, it can be concluded that a higher surface area ratio provides a higher percentage removal of dye.
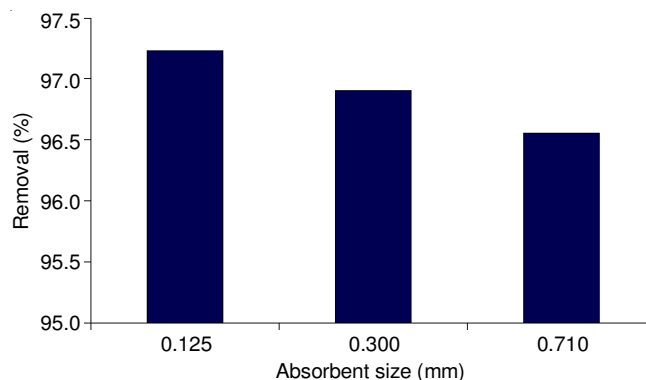

Fig. 1. Effect of adsorbent size on methylene blue removal, (dye concentration: 100 mg/L; volume: 200 mL; temperature: 25 °C; adsorbent dosage: 0.5 g; contact time: 24 h)

Effect of adsorbent dosage: Fig. 2 shows the effect of adsorbent dosage using 0.125 mm coconut fronds' measurement obtained from the previous experiment. It can be seen that the percentage of methylene blue removal increased from 96.02 to 97.36 % for an increase in coconut frond dosage from 0.1 to 0.3 g. There was very little increase in methylene blue removal (97.36 to 97.42 %; no significant difference) when the coconut frond dosage was changed from 0.3 g to 0.5 g. That shows only a difference of 0.06 %. It shows that the equilibrium has been achieved at 0.5 g coconut frond dosage and any addition of adsorbent dosage gives no significant changes on the percentage of methylene blue removal. The increase in percentage removal was due to the increase of the available sorption surface and adsorption sites [8]. A similar finding was reported for the removal of methylene blue using rejected tea [11] and lemon grass ash [12].
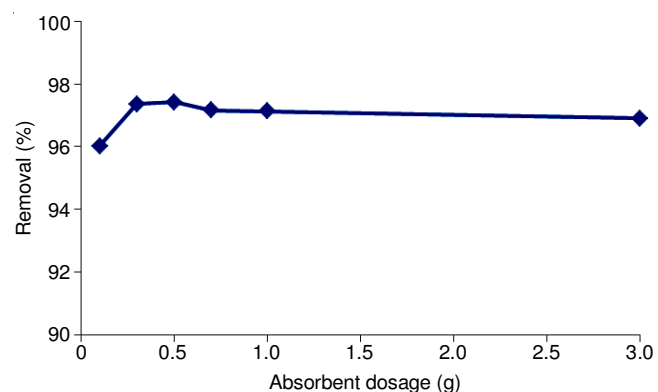

Fig. 2. Effect of adsorbent dosage on methylene blue removal (MB concentration: 100 mg/L; volume: 200 mL; temperature: 25 °C; adsorbent size: 0.125 mm; contact time: 24 h)

Effect of initial dye concentration: The effect of initial dye concentrations was studied in the range of 10-400 mg/L at fixed values of other parameters. Fig. 3 shows that the removal of percentage increases with increases of initial dye concentrations from 10-50 mg/L and then remained constant beyond 50 mg/L. The initial rapid phase may be due to an increase in the number of vacant sites available at the initial stage until it reaches saturation [8].
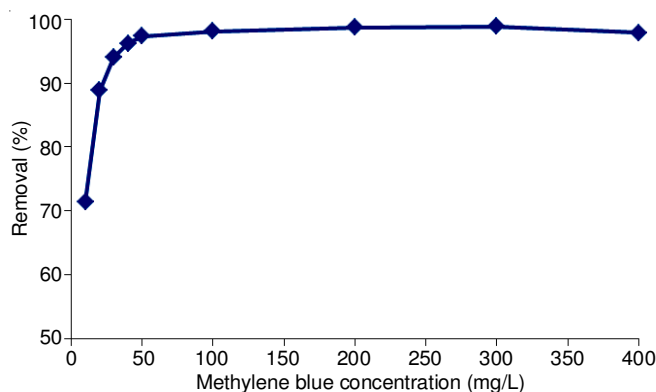

Fig. 3.   Effect of initial dye concentration on methylene blue removal (volume: 200 mL; temperature: 25 °C; adsorbent size: 0.125 mm; adsorbent dosage: 0.5 g; contact time: 24 h)

Effect of contact time: A series of adsorption experiments was carried out at different intervals of time (4, 8, 12, 16, 20, 24 h) at a constant volume of dye solution (200 mL). Other parameters such as adsorbent dosage, volume and initial methylene blue concentration were fixed at the optimum conditions obtained from previous studies. Fig. 4 shows that methylene blue adsorption slightly increases with an increase of contact time until it reaches the equilibrium state. After 18 h, very little change in the percentage of dye removal was observed. It can be concluded that it has reached a point of saturation where the entire adsorption site has reacted with most of the dyes used. So, once the saturation limit has been reached, any further reactions will not leave much impact on removal efficiency [13]. Therefore, contact time was set to 24 h.
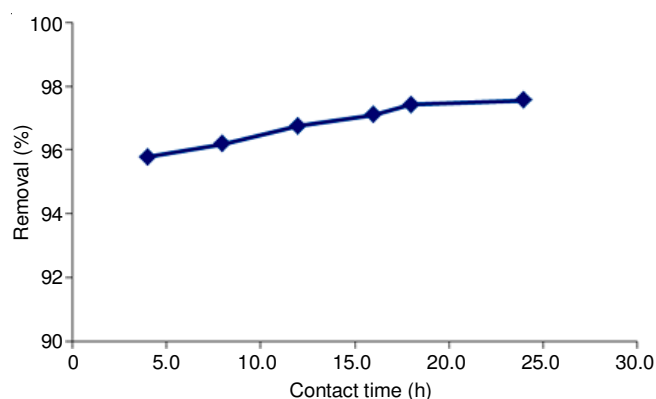

Fig. 4.   Effect of contact time on methylene blue removal (volume: 200 mL; temperature: 25 °C; adsorbent size: 0.125 mm; adsorbent dosage: 0.5 g; methylene blue concentration: 50 mg/L)

Effect of pH: pH plays a prominent role as it determines the chemistry of the solution and also the binding of reactive sites. The degree of dye ionization and surface adsorbent property is affected by the hydrogen ion concentration [14]. Methylene blue is a cationic dye. This means that it is a dye where its surface charges are positive. For an efficient adsorption to occur, charges are preferably opposite to favour electrostatic attraction.

Fig. 5 shows the increase in trend of methylene blue removal percentage using raw coconut frond from pH 5 up to 8. Then, the percentage of removal decreased as the pH increased from pH 9 to 10. In acidic buffer, presence of H^+ ions compete for the same active site as methylene blue [15]. The repulsive force is also much greater in acidic conditions due to the presence of like ions, reducing the electrostatic force of attraction. When pH is increased, the number of positive charges decreases. There will be the presence of OH^- in basic mediums, which releases anions into the solution when it dissociates. As the dyes are positively charged, the electrostatic force of attraction also increases due to the presence of opposing charges. This reduces competition for the methylene blue to fit into the active sites of the adsorbent.
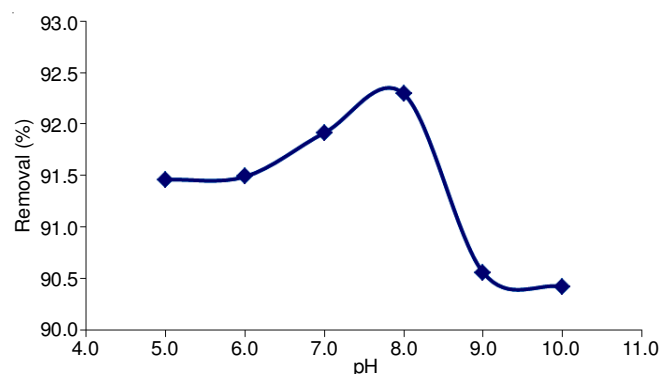

Fig. 5.   Effect of pH on methylene blue removal (volume: 200 mL; temperature: 25 °C; adsorbent size: 0.125 mm; adsorbent dosage: 0.5 g; methylene blue concentration: 50 mg/L; contact time: 24 h)

At higher pH (above pH 8) values, it can be assumed that there is an excessive presence of OH^- ions. When this happens, there will be excessive ions surrounding the surface of the adsorbent. This could block the way for an methylene blue to be adsorbed onto the active site of the adsorbent. This causes a reduction in the rate of adsorption. Another reason that may explain the lower adsorption at higher pH values is the instability of dye molecules as reported by Gecgel *et al.* [16] when using pea shells. The electrostatic force of attraction increases at higher pH values than that in basic mediums. The ionization of the adsorbent surface creates a strong bond between the adsorbent and adsorbate. When more OH^- ions exist, the particles may exert repulsion force among like ions. Therefore, the adsorption efficiency will be reduced [17].

In pH 7 and pH 8, the electrostatic force generated could have been more than sufficient for effective adsorption to take place. In other words, pH 8 is a condition with maximum negative charge [2]. From this study, it can be concluded that pH 8 was found to be the best pH for effective adsorption to take place. A similar finding was reported by Öden & Özdemir [18] for the removal of methylene blue using leech waste.

Adsorption isotherms: Two types of adsorption isotherm were used in this study, *i.e.* Langmuir and Freundlich isotherms.

Langmuir is often known as monolayer adsorption onto a surface containing a finite number of adsorption sites [19]. The Langmuir isotherm is represented by the following equation [11]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}}C_e + \frac{1}{q_{max}K_L}$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate, q_{max} is the Langmuir constant related to the maximum adsorption capacity and K_L is the Langmuir constant related to energy of adsorption. q_{max} and K_L are determined from the slope and intercept of the linear plot of C_e/q_e *versus* C_e, respectively [11].

The Freundlich isotherm is known as multilayer adsorption whereby the adsorption takes place on a heterogeneous surface or surface supporting sites of varied affinities [20]. The linear form of Freundlich is represented by the following equation [11]:

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

where K_F is the Freundlich constant related to adsorbent adsorption capacity and n is Freundlich constant related to adsorption intensity. K_F and n are determined from the intercept and slope of the linear plot of loq q_e *versus* loq C_e, respectively [11].

Based on Table-1, the adsorption inclined towards the Langmuir isotherm because it gives a higher value of correlation coefficient ($R^2 = 1$) compared to Freundlich isotherm (0.994). It can be said that the adsorption of methylene blue using coconut fronds should use the monolayer adsorption on a surface that is homogenous in adsorption affinity [8]. The adsorption capacity obtained in this study was 18.69 mg/g which is comparable with reported studies on the removal of methylene blue using *Caulerpa racemosa* var. *cylindracea* 3.423 mg/g [21], wheat shells 16.56 mg/g [22], yellow passion fruit waste 44.70 mg/g [23], luffa cylindrica fibers 47 mg/g [24] and coir pith carbon 5.87 mg/g [25]. It can be concluded that coconut fronds can be used for the removal of methylene blue from aqueous solutions.

TABLE-1
ADSORPTION ISOTHERM DATA

Langmuir isotherm		Freundlich isotherm	
K_L (L/mg)	-19.11	K_F (L/mg)	19.651
q_{max} (mg/g)	18.69	n =	-29.85
R^2	1	R^2	0.994

Conclusion

The coconut frond has the potential in removing methylene blue because the percentage of removal was more than 90 % at 0.125 mm adsorbent particle size and 0.5 g dosage. Besides, the adsorption capacity was 18.69 mg/g. The best adsorption isotherm is Langmuir isotherm which recorded $R^2 = 1$.

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