ADSORPTION OF METHYLENE BLUE ON WASTES FROM LEMONGRASS LEAVES AFTER ESSENTIAL OIL EXTRACTION

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ABSTRACT

In this study, a biosorbent from lemongrass leaf after the distillation of essential oil was prepared by the alkali treatment with NaOH 10%. The removal of Methylene blue (MB) was tested under the following conditions: adsorbent dose (0.02-0.4 mg), pH (2-10), and dye concentration (20 and 100 mg/L). When the adsorbent dose and pH were raised, the percentage removal and adsorption capacity of dye increased. The kinetic studies revealed that the MB adsorption process complied with the pseudo-second-order model with a 30-min adsorption equilibrium. The percentage removal and adsorption capacity of MB at a concentration of 20 mg/L were 90.9% and 6.30 mg/g at the adsorbent dose of 0.1g in 30 min. According to the findings, alkali-treated lemongrass waste is an inexpensive and effective biosorbent in treating dye wastewater.

Keywords: Biosorbent, lemongrass, adsorption, methylene blue.

1. INTRODUCTION

The textile and garment industry is a core industry in many economies, accounting for 7% of global export trade, worth $1400-1550 billion USD, and employing over 35 million people worldwide [1]. Nevertheless, the textile industry also contributes significantly to environmental pollution. Textile dyeing procedures use a lot of water throughout the manufacturing process, and the wastewater generated varies between 12 and 300 m^3/ton of cloth. Textile dyes are now available in over 10,000 types [1]. Methylene Blue (MB) is a popular cationic dye that has been identified as being more harmful than other anionic dyes [2]. This is a synthetic dye that dissolves in water to produce a blue solution that is difficult to remove. According to previous reports, dye-containing wastewater can block light and impede photosynthesis, increase chemical and biological oxidation demands, impede organism growth and reproduction, and have a negative impact on photosynthesis. Methylene blue can cause skin allergies, nausea, and breathing problems [2, 3]. As a result, water pollution from dye-containing wastewater and dye adsorption for wastewater treatment has gotten a lot of attention.

Many techniques have been employed to remove these contaminants, including nanofiltration, reverse osmosis, electrolytic deoxidation, aerobic treatment, and adsorption. Adsorption, one of the most effective dye removal processes, has several advantages over other methods, including a lower cost, a simpler process, and complete dye removal [4]. Agricultural wastes such as bagasse, corn cobs, orange peels, and coconut shells are commonly utilized as adsorbents to remove dyes due to their inexpensive cost, abundance, high adsorption capacity and speed, and selectivity [4-6].

In the last two years, Coronavirus disease (COVID-19) has emerged as a global health threat. Lemongrass (*Cymbopogon citratus*) contains 1-2% essential oil, 39.5% cellulose, 22.6% hemicellulose, and 28.5% lignin [7]. Lemongrass essential oil, which is a mixture of volatile compounds, has antibacterial, antifungal, and antiviral properties. Due to its benefits, lemongrass oil is used as a COVID prevention method, resulting in a significant amount of lignocellulose-containing waste after distillation. The functional groups in cellulose fibers, such as hydroxyl and carboxyl, participate in the formation of covalent bonds with the chromogenic groups of dye molecules. Therefore, MB molecules were kept on the cellulose surface. As a result of the good adsorption characteristics of cellulose materials, lemongrass leaves are a viable choice for dye adsorption. Previous studies focused on MB adsorption by activated carbon from lemongrass leaves using a 500 ^{o}C - 600 ^{o}C thermal treatment [8, 9]. However, this method necessitates a complex treatment process, resulting in a high price for activated carbon. Furthermore, it is difficult to separate activated carbon from the water after dye adsorption, posing a risk to many living organisms. In this study, cellulose-containing lemongrass waste was chemically treated with a caustic soda solution to investigate methylene blue adsorption in water. The goal is to introduce a simpler and more effective method of treating biosorbents used in dye adsorption. This helps to reduce treatment time and increase the reuse of agricultural waste. This alkali treatment of lemongrass leaves has been rarely used, particularly in terms of methylene blue adsorption [8]. Furthermore, SEM and XRD measurements were used to evaluate the surface properties and identify the crystallinity of cellulose. To determine the adsorption mechanism, the adsorption kinetics and factors such as adsorbent dosage, pH, and dye concentration were investigated.

2. MATERIALS AND METHODS

2.1. Adsorbent preparation

Lemongrass is cultivated on a farm in Taiwan's Tainan province. After distillation, lemongrass leaves were dried overnight at 60^{o}C to make the adsorbent. These lemongrass leaves were alkali-treated to eliminate lignin. The elimination of lignin aids in increasing cellulose concentration and improving the material's surface characteristics for improved pigment adsorption [10]. The preparation steps of the biosorbent were described as follows. Lemongrass leaves after distillation were powdered, milled, and sieved to obtain sizes ranging from 250 µm to 1000 µm. Lemongrass leaves were stirred for 2 hours at 90^{o}C in a vessel containing a 10% NaOH solution. The ratio of lemongrass mass to the volume of NaOH solution was kept constant at 1:25 (w/v). After alkalinizing, the lemongrass leaves were rinsed many times with deionized water until the pH was neutral, then dried for 24 hours at 60^{o}C. Lemongrass leaves after alkali treatment were named TLG.

2.2. Absorbent characterization

The characteristics of TLG material before and after dye adsorption were examined using a scanning electron microscopic (SEM) analysis and X-ray spectroscopy (XRD). The surface morphology of absorbents was investigated by scanning electron microscopy (SEM) (Hitachi SU8010). A small amount of adsorbent was placed on the specimen stub and coated with a thin gold layer by a DC sputter coater (AGAR B7340, Agar Scientific, Stansted, UK). The adsorbent was then imaged at a 110KV accelerating voltage with a 10 mm working distance and magnifications of ×2500 were applied. XRD measurements were carried out with an Ultima IV diffractometer (Rigaku Americas Corp., USA) equipped with a Cu-target tube at wavelength λ = 0.1540 nm. Diffractograms were collected at 2θ ranging from 5^{o} to 65^{o} with a scan step of 0.02^{o}. The crystallinity index (CrI %) of TLG was determined by Eq. (1) [11].

$$CrI(\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad \text{(Eq. 1)}$$

where I_{002} is the maximum intensity of the crystalline peak ($(22^{\circ} < 2\theta < 23^{\circ})$ and I_{am} is the scattered intensity of the amorphous peak ($18^{\circ} < 2\theta < 19^{\circ}$) of the sample.

2.3. Preparation of MB adsorbate

The appropriate quantity of methylene blue (analytical grade, Sigma Aldrich 46465224) was dissolved in distilled water to make a stock solution (1000 mg/L). Solutions of various concentrations (1, 2, 4, 8, and 10 mg/L) were prepared by a serial dilution process of the initial stock solution. For all experiments, the MB concentration was determined by a UV-visible spectrophotometer (CT-2200 spectrophotometer, Germany) at a wavelength of 665 nm.

2.4. The influence of adsorbent dose and pH

The following steps were used to test the effect of the adsorbent dose. In Erlenmeyer flasks containing 40 mL of 20 mg/L MB solution, different amounts of TLG adsorbent (0.02, 0.06, 0.1, 0.2, 0.3, and 0.4 gram) were added. The sample was shaken at 25 ^{o}C at 150 rpm and then put into a thermostatic shaker. Aqueous solutions were obtained after two hours of adsorption. The percentage removal H (%) and the adsorbed amount Q (mg/g) of MB on TLG were calculated following Eqs. (2)-(4) [8, 9].

$$H(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad \text{(Eq. 2)}$$

$$Q_t(mg/g) = \frac{C_0 - C_t}{m} \times V \quad \text{(Eq. 3)}$$

$$Q_e(mg/g) = \frac{C_0 - C_e}{m} \times V \quad \text{(Eq. 4)}$$

where C_o, C_t and C_e (mg/L) are the liquid-phase concentrations of MB at the initial time, time t, and the equilibrium state, respectively. V (mL) is the volume of the MB solution, and m is the weight of the adsorbent (g). Q_e and Q_t (mg/g) are the amounts of MB adsorbed per weight of TLG at the equilibrium state and at time t, respectively.

On the other hand, pH changes the charge on the surface of the adsorbent and thus affects its dye adsorption capacity. The adsorption of 20 mg/L MB solution with pH values ranging from 2.5 to 10.5 by TLG was investigated. The pH of the MB solution was adjusted using sodium hydroxide (NaOH) and hydrochloric acid (HCl), both from Labscan (Thailand). A properly weighed amount of TLG (0.1 g) was added to an Erlenmeyer holding 40 mL of MB (20 mg/L) at the appropriate pH. The adsorption procedure was followed in the same way as the experiment to determine the adsorbent dose. All experiments were performed in triplicate.

2.5. Kinetic studies

A fixed amount of TLG (0.1 g) was added to twelve Erlenmeyer flasks containing 40 mL of dye. The effect of dye concentration on adsorption kinetics was investigated at 20 mg/L and 100 mg/L of MB. The Erlenmeyer flasks were firmly covered and held at a constant temperature of 25 ^{o}C in a thermostatic shaker with 150 rpm. The absorbance of the MB solution in Erlenmeyer was then measured between 0 and 180 min. The rate constants and other parameters for the kinetic data were calculated using the kinetic equations of the first and second-order reactions, as demonstrated in Eqs. (5) & (6) [12]:

$$ln\,(Q_e - Q_t) = lnQ_e - k_1 t \quad \text{(Eq. 5)}$$

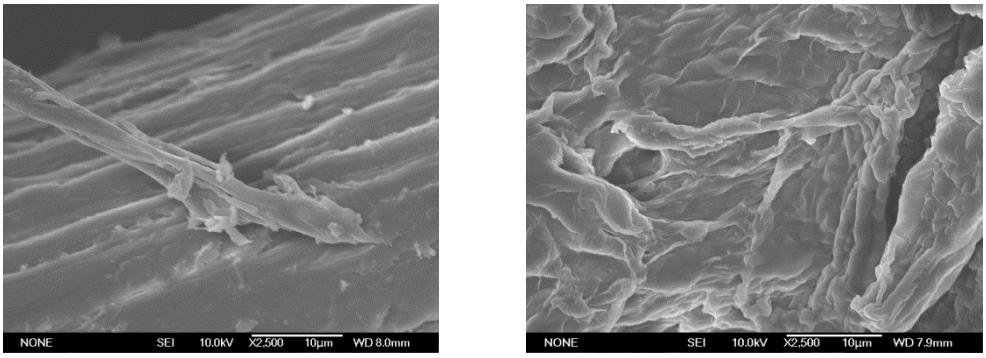
$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad \text{(Eq. 6)}$$

where k_1 (min^{-1}) and k_2 (g $mg^{-1}min^{-1}$) were respectively the adsorption rate constant of the pseudo-first order and pseudo-second order models.

3. RESULTS AND DISCUSSION

3.1. Characterization of absorbents

The surface shape of TLG before and after MB adsorption can be seen in Figure 1. Before adsorption, the surface of the alkali-treated lemongrass leaves (TLG) was rough fibers with cellulose-like characteristics. This observed behavior was similar to the findings of Putri *et al*. [4]. These fibers formed thin layers by stacking them up in a disorderly manner. The irregular rough structure and pores play an important role in dye adsorption [13]. After MB adsorption, the surface morphology of TLG became rougher than before, and there was an aggregation of MB particles on the surface of the material.



(a) TLG before adsorption (b) TLG after adsorption

Figure 1. SEM images of adsorbent (a) before and (b) after MB adsorption.

The X-ray diffractograms for TLG are shown in Figure 2. The diffraction peaks of TLG at 2θ values of 15.9° (101), 22.5° (002), and 34.9° (040) are similar to cellulose characteristic peaks [4]. From equation 2-1, TLG has a crystallinity index of 78%.

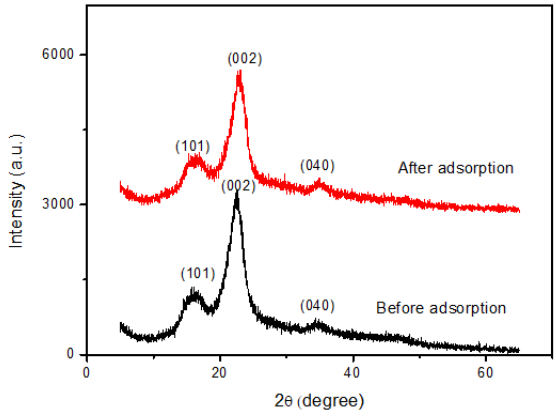


Figure 2. XRD patterns of TLG before and after adsorption

3.2. Effect of adsorbent dose and pH on adsorption

The adsorbent dose has a direct impact on the adsorbent's surface area and the number of active adsorption sites. Figure 3 shows the effect of TLG doses ranging from 0.02 to 0.4 g on MB adsorption at a concentration of 20 mg/L. As the adsorbent dose increased from 0.02 to 0.3g, the amount of MB removed increased. This is because more active adsorption sites become available as the adsorbent's mass increases. The percentage removal of MB was nearly unchanged with a dose increase from 0.3g to 0.4g at MB 20 mg/L, owing to the fact that the number of free binding sites exceeded the number of MB molecules. The formation of hydrogen bonds between the hydroxyl group of cellulose and the nitrogen atom of the MB seems to contribute to the adsorption capacity. According to this finding, as the dose of TLG was increased, the percentage removal increased and the adsorption capacity decreased.

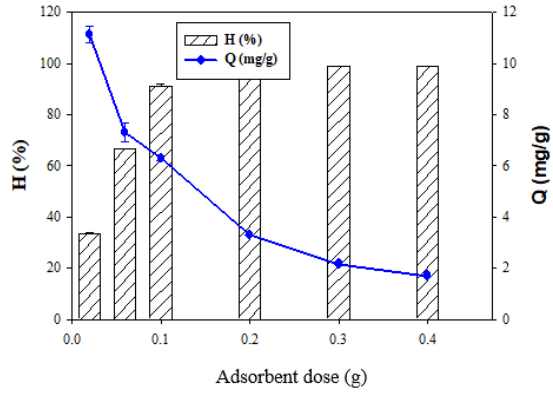


Figure 3. Effect of adsorbent dose on the percentage removal and adsorption capacity.

The pH changed the surface charge of the adsorbent, causing changes in the adsorption capacity of MB. Fig. 4 shows the adsorption capacity of the TLG toward MB at various pH values (2.5, 3.5, 5.0, 6.5, 8.5, 9.5, and 10.5). A significant increase in MB sorption was observed as the pH increased from 2.5 to 6.5, while further increasing the pH value from 6.5 to 10 resulted in a slight change in sorption. As illustrated in Fig. 4, the lowest removal percentage was observed at pH 2.5 (9.30%) and the highest percentage of removal was 92.4% at pH 10.5. The removal of MB dye from TLG was found to be pH-dependent, which is consistent with previous studies [4, 8]. As the pH increased, the active adsorbent sites deprotonated, promoting electrostatic interaction between the positively charged cationic methylene blue molecules and the negatively charged surface of the adsorbent. In this study, pH 6.5 was selected because it was the pH of the MB solution that did not need to be modified. As a result, all subsequent adsorption studies were carried out at pH 6.5.

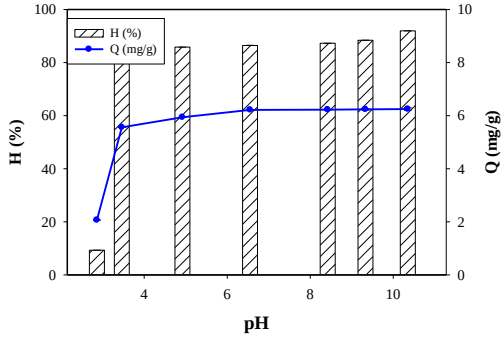


Figure 4. Effect of pH on the percentage removal and adsorption capacity.

3.3. Adsorption kinetics

The effect of contact time on the adsorption of MB is shown in Figure 5. During the first 30 min, at both MB concentrations tested, adsorption increased swiftly and gradually. The adsorption capacity achieved equilibrium after 30 min. The huge number of active sites on the material surface caused a quick increase in the rate of adsorption at the first stage, resulting in a high adsorption capacity. However, as the number of active sites decreased and the adsorbent lost its ability to adsorb MB, the adsorption capacity was nearly unchanged, reaching 6.3 mg/g and 18.6 mg/L, respectively, for MB concentrations of 20 and 100 mg/L. As the MB concentration increased, the amount of MB adsorbed increased until the maximum adsorption capacity of the biosorbent was reached.

Pseudo-first-order and second-order models were demonstrated in these plots in Fig. 6 and values of Q_e and rate constants were presented in Table 1. The computed findings revealed that the coefficient of determination (R^2> 0.995) in the second-order model was higher than that in the pseudo-first-order model at all MB concentrations. Furthermore, the Q_e values calculated from equation 6 were closer to the experimental Q_e value. Hence, pseudo-second-order kinetic was the best way to describe the adsorption process. The chemical sorption occurred due to the formation of hydrogen bonding between the hydroxyl group on the cellulose surface and the nitrogen of MB [13]. Furthermore, the insignificant difference in the adsorption rate constant at both MB concentrations in the pseudo-second-order models (k_2) pointed out that the adsorption rate depended on the number of adsorption sites available on the TLG surface rather than the quantity of MB dye molecules adsorbed.

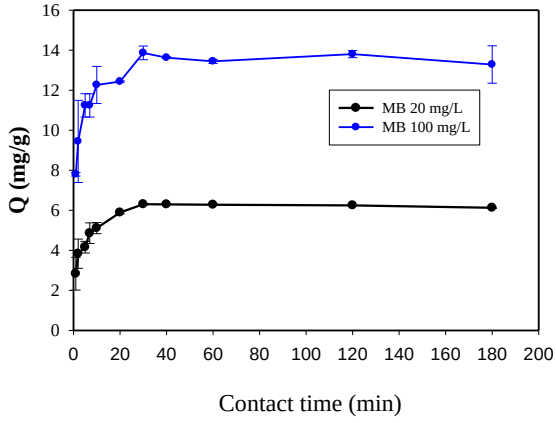


Figure 5. Effect of contact time on MB dye adsorption capacity

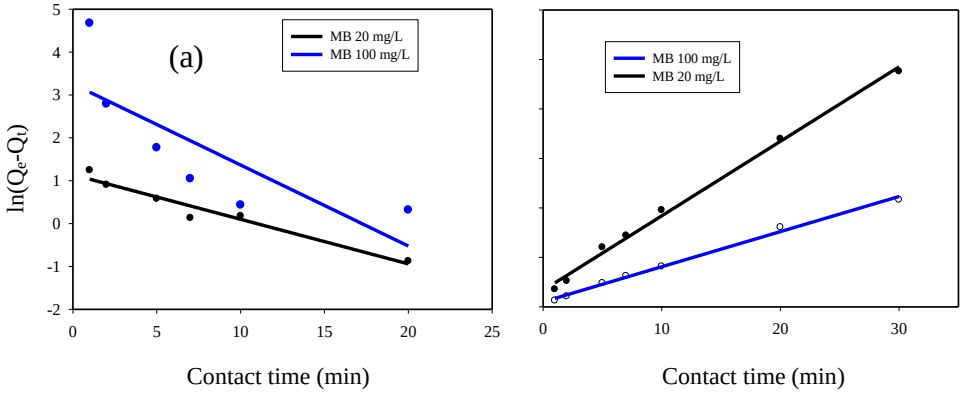


Figure 6. Kinetic plots for MB adsorption (a) pseudo-first order, (b) pseudo-second order model.

Table 1. Kinetic parameters of MB adsorption onto TLG

Model	Parameter	C_{MB}(mg/L)	
		20	100
Experiment	Q_e (mg/g)	6.3047	13.8643
Pseudo-first-order	Q_e (mg/g)	3.1267	25.9196
	k_1 (min^{-1})	0.1039	0.1889
	R^2	0.9511	0.6217
Pseudo-second-order	Q_e (mg/g)	6.6401	14.084
	k_2 ($g.mg^{-1}min^{-1}$)	0.007	0.005
	R^2	0.9954	0.9952

In comparing the Q_e value in this study to Ahmad's study [9], we recognized that, while the Q_e of the TLG biosorbent was low (13.864 mg/g at MB 100 mg/g), the adsorption equilibration time was short, lasting only 30 minutes. In contrast, in Ahmad's study, the adsorption of MB 100 mg/L on lemongrass activated carbon reached equilibrium with Q_e at 43.931 mg/g after 24 hours [9].

4. CONCLUSION

A new biosorbent was successfully prepared from lemongrass waste after distillation of essential oil. Lemongrass leaves are stirred for 2 hours at 90 ^oC in a vessel containing a 10% NaOH solution. SEM and XRD results indicated that the functional groups of cellulose and irregular rough surface of fibers contributed to the adsorption process. The removal of dye from cellulose-containing lemongrass waste was 90.9%. The adsorption capacity is 6.30 mg/g, which corresponds to the experimental conditions of pH 6.5, 0.1 g adsorbent dose, and 30-min quick equilibrium time. The results show that alkali treatment with NaOH for lignocellulose-derived materials is a simple method that requires no complicated equipment, has a short fabrication time, and has a low adsorbent dose. Lemongrass waste has the potential to be a low-cost, abundant and effective biosorbent source in environmental treatment.

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TÓM TẮT

NGHIÊN CỨU KHẢ NĂNG HẤP PHỤ METHYLEN BLUE BẰNG VẬT LIỆU SINH HỌC TỪ BÃ LÁ SẢ SAU KHI CHƯNG CẤT TINH DẦU

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Trong nghiên cứu này, một vật liệu sinh học chuẩn bị từ lá sả sau khi chưng cất tinh dầu được điều chế bằng phương pháp xử lý kiềm với NaOH 10%. Hiệu suất hấp phụ metylen xanh (MB) được khảo sát trong các điều kiện sau: liều lượng chất hấp phụ (0,02-0,4 mg), pH (2-10), và nồng độ MB (20 và 100 mg/L). Khi liều lượng chất hấp phụ và pH tăng lên, hiệu suất hấp phụ màu tăng lên. Các nghiên cứu động học cho thấy rằng quá trình hấp phụ MB tuân theo phương trình động học bậc hai với cân bằng hấp phụ sau 30 phút. Hiệu suất và dung lượng hấp phụ tại MB có nồng độ 20 mg/L là 90,9% và 6,30 mg/g khi sử dụng 0,1 g chất hấp phụ trong 30 phút. Kết quả nghiên cứu cho thấy bã lá sả sau khi xử lý kiềm là một vật liệu sinh học rẻ tiền và hiệu quả trong xử lý nước thải nhuộm.

Từ khoá: chất hấp phụ sinh học, lá sả, sự hấp phụ, methylene blue.