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DRIED LEAVES AS POTENTIAL ADSORBENT FOR REMOVAL OF METHYLENE BLUE

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Abstract— Dyes are an important class of coloured synthetic organic compound that used and applied in various industries, especially in textile industry. In this work, the aim was to remove cationic dye (Methylene Blue) from aqueous solution using a low-cost and eco-friendly adsorbent, dried leaves (DLs). Dried leaves (DLs) are agricultural waste largely available in Malaysia. The main objective was to investigate the removal efficiency and the effects of operational parameters on Methylene Blue (MB) removal efficiency under batch adsorption method. The batch experiments were carried out to study the effects of the following variables included the adsorbent dosage (0.05-2.0 g), initial methylene blue concentration (20-200mg/L), temperature (30-60°C) and initial pH solution (2-11). Adsorption experiments

using DL resulted in higher methylene blue (MB) removal efficiency ranging from 85 to 98% for 0.05-2.0 g of adsorbent dosage. From the experiments result, it was found that MB adsorption increased with increasing the adsorbent dosage. However, methylene blue adsorption decreased with increasing the initial methylene blue concentration, temperature and initial solution pH. The methylene blue removal using 0.3 g of adsorbent was 98.25%. This dosage (0.3 g) was considered as optimum dosage to remove MB from the aqueous solutions.

I. Introduction

Dye are widely used and applied in various industries such as plastic, textile, dyestuffs, paper, rubber, food, leather, cosmetics, carpet, and printing. There have different types of dye that used in textile industry depended on fabrics manufactured such as reactive dyes, direct dyes, naphthalol dyes and indigo dyes [1]. Wastewaters are generated from the following processes of textile production which is slashing/sizing, desizing, scouring, bleaching, mercerising, dyeing, printing, and finishing [2]. Methylene blue dyes solution is basic dyes, commonly used as substance for dying cotton, wood and silk. However, it also caused harmful effect to environment and human health such as eye burns which may be responsible for permanent injury to the eyes of human and animals. There are several conventional treatment process has been applied for removal of dye from wastewater such as chemical coagulation, activated sludge, trickling filter, photocatalytic degradation, electrochemical degradation and adsorption. However, among

these, adsorption is one of the most effective methods to treat dye from wastewater. Activated carbon are widely used as an adsorbent for removal of dye from the wastewater solution using adsorption process due to its more effective and high adsorption capacity, however, conventional activated carbon has high operating cost. In addition to that, activated carbon have to go through regeneration process which will increased the operating cost after adsorption with dye [3]. Therefore, there is a need for the low cost raw adsorbents of the dyes solutions in order to utilize activated carbon in treating the wastewater [4]. In Malaysia, agricultural industry has been produced largest amount of by-products each year. Agricultural by-product is cheap and renewable resources and conversions of these agricultural waste into activated carbon will reduce the cost of activated carbon production and also assist in solving the waste disposal problem. Several agricultural waste and residues have been investigated for the adsorption of dyes with varying success includes *Magnoliaceae* fallen leaves [5], tea leaves [6], sumac leaves [3], pineapple leaves [7], fallen leaves of Platanus [8] and guava leaf [9]. Dried leaves (DL) is used as new-conventional and low-cost adsorbent for removal of methylene blue adsorption in batch process at 30°C. Dried leaves are abundantly available and inexpensive. Dried leaves are waste of agriculture that can impact into environment pollution. Hence, used of dried leaves as adsorbent to remove dyes can positively reduce amount of waste. Earlier, several studies related to the dried leaves as potential adsorbent has been reported namely *Thypha* stem and leaves [10], *Magnoliaceae* leaves [5], *Aegle Marmelos* leaves [11], powdered palm tree flower [12] and *Salix babylonica* (Weeping willow) leaves powder [13]. Hence this work is dedicated to use fallen dried leaves as adsorbent for removal of methylene blue. The effect of variable parameter such as adsorbent dosage, initial methylene blue concentration,

temperature and initial pH solution were studied. This work focus on the performance of dried leaves as low-cost and abundant adsorbent that potentially could be an alternative for the removal of methylene blue.

II. Materials and Methods

A. Preparation of Dried Leaves

The dried leaves were collected from Universiti Sains Malaysia Engineering Campus, Nibong Tebal, Penang. The sample were washed repeatedly with distilled water to remove dust until the filtered water was cleared and dried in an oven at 65°C for overnight. The sample were crushed and sieved to obtain a smaller size with approximate size between 0.5 and 1.0 mm. The sample was stored in an airtight container or plastic bottle for further use.

B. Preparation of Methylene Blue Solutions

Dye solution used for this study was methylene blue (MB). A stock of methylene blue solutions was prepared by dissolving the required amount of methylene blue in distilled water. Concentration of Methylene Blue was determined by using UV-visible spectrometer (Cary 60, Agilent Technologies, USA) at the characteristic wavelength (λ_{max} = 668 nm). In addition, a series of standard solutions were prepared with concentration varied from 0-12 mg/L to obtain the calibration curve for the determination of the dye concentration of unknown solutions.

C. Batch Adsorption Studies

The adsorption study was conducted to analyse the effect of adsorbent dosage (0.05-2.0 g), pH (2-11), methylene blue concentration (20-200 mg/L) and temperature (30-60 °C) on the removal of methylene blue using dried leaves. In batch adsorption experiment was carried out by agitating the number of 250 mL stoppered glass Erlenmeyer flasks containing a 200 mL methylene blue solution and placed in thermostatic water bath shaker at required temperature. The flask

was shaken at speed 120 rpm for 180 min in water bath shaker. After that, dried leaves were separated from the solution and analysed the dye in the solution using the UV-vis. The amount of methylene blue adsorbed at equilibrium, q_e and the percentage removal efficiency (%R) were calculated using Eq. (1) and Eq. (2).

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

$$\% R = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

where,

C_o= Liquid-phase dye concentrations at initial stage (mg/L),

C_e = Liquid-phase concentrations of dye at equilibrium stage (mg/L),

V = Volume of dye solution (L),

W = Mass of adsorbent used (g).

D. Effect of Adsorbent Dosage

The effect of the DL dosage on the amount of methylene blue was studied at the different amount (0.05, 0.1, 0.3, 0.6, 0.9, 1.2, 1.5 and 2.0 g). Varied range of dried leaves dosage were added into a number of 250 mL stoppered glass Erlenmeyer flasks containing a 200 mL of fixed initial concentration (60 mg/L) of dye solution with constant solution pH and temperature 30°C. The Erlenmeyer flask are then sealed and placed in the thermostatic water bath shaker with agitation speed of 120 rpm for 180 min.

E. Effect of Initial pH

The effect of pH on the adsorption of methylene blue was investigated with mixed the 0.30 g of dried leaves and 200 mL of dye solution of 60 mg/L initial concentration over the pH range value (2 to 11) at constant temperature 30 °C. The pH value was adjusted with 0.1N NaOH and 0.1N HCl solution and measured by using a pH meter. The sample was agitated with speed of 120 rpm for 180 min. The concentration of methylene blue was measured by a double beam UV-vis spectrometer (Cary 60, Agilent Technologies, USA).

F. Effect of Methylene Blue Concentration

Effect of Methylene Blue concentration on the adsorption

was investigated by added a fixed amount of dried leaves into a number of 250 mL stoppered glass Erlenmeyer flasks containing a 200 mL of different concentration (20 - 200 mg/L) of dye solution. The other parameter such as solution pH and temperature were kept constant. The solutions were placed in the thermostatic water bath shaker with agitation speed of 120 rpm for 180 min until the equilibrium stage is reached.

G. Effect of Temperature

To study the effect of temperature, adsorption was carried out at different solution temperatures ranging from 30 to 60 ºC with 10 ºC interval at constant initial dye concentration of 60 mg/L. The other variables namely dosage of dried leaves, volume of dye solution speed and pH were remained the same.

III. Result and Discussions

A. Effect of Adsorbent Dosage

The amount of adsorbent on the removal methylene blue is major factor in determining the efficiency of adsorption dyes. Figure 1 shows that the adsorbent dosage was strongly affected by the amount of methylene blue adsorbed. It is clear that further addition of dried leaves dosage from 0.30 to 2.00 g show no significant change in the removal percentage of 98% as the adsorption process reach its equilibrium. This result is parallel to previous work reported by Hameed et al. which studied tea leaves as adsorbent for dye removal from aqueous solution and found that the removal percentage of methylene blue increased with increase in adsorbent dosage [6]. This result further strengthens by the change of solution colour from the dark blue to green colour (Figure 1).

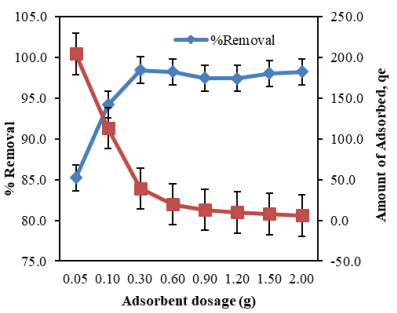

Figure 1: Effect of adsorbent dosage on the adsorption of methylene blue at 60 ppm

(a)

(b)

Figure 2: Colour of methylene blue solution at different of adsorbent dosage ranging from 0.05 to 2.00 g (A-H) respectively

Figure 2 also showed that removal efficiency was increased sharply with increasing amount of dried leaves up to 0.3 g. After that there was a slight increment in percent removal of methylene blue dye. The increased in adsorption efficiency due to more availability of adsorption sites or surface area. On other hand, the value of q_e decreased from 204.54 to 5.90 mg/g. Han et. al., (2007) reported that the primary factor of amount of methylene blue adsorbed at equilibrium, q_e decreased with increase of adsorbent dosage is the adsorption sites remain unsaturated during the adsorption reaction, whereas number of sites available for adsorption sites increase with increase of adsorbent dosage [14]. Therefore, 0.3 g was found effective and it reached 98% of methylene blue adsorption in 60 ppm in 180 minutes.

B. Effect of Initial Concentration of Methylene Blue

The effect of initial concentration on the removal of methylene blue is shown in Figure 4. The removal efficiency is however less affected by the initial concentration of adsorbate solution. As illustrated in the figure, removal percentage almost stagnant with varied concentration of solution. This finding denotes that methylene blue can easily remove from the wastewater even at lowest initial concentration as low as 20 ppm. The effect of initial concentration of methylene blue

on the sorption of this dye onto the dried leaves was carried out in the concentration range from 20 to 200 mg/L. While varying the dye concentration, pH, adsorbent dose, temperature and agitation speed were kept constant.

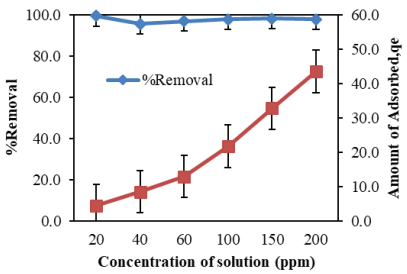

Figure 3: Effect of initial concentration at 200 ml solution on the adsorption of methylene blue

Meanwhile, Figure 3 shows that the percentages of removal decreased with increases of initial concentration of methylene blue. However, amount of methylene blue adsorbed per unit mass adsorbent increased gradually with an increase in the initial concentration of solution. The amount of methylene blue adsorbed at equilibrium (q_e) increased from 4.43 to 43.53 mg/g as the initial concentration increased from 20 to 200 mg/L. This is due to increase in the driving force from the concentration gradient. On top of that, concentration provides an important driving force to overcome the mass transfer resistance of the methylene blue between the aqueous and solid phase. This results in parallel with the previous finding [3].

C. Effect of Temperature

The effect of temperature on the percentages of removal efficiency of methylene blue was shown in Figure 4. The percentages of methylene blue removal onto dried leaves shows slight decrement from 97.47 to 95.21% as the temperature increased from 30 to 60 °C at 60 ppm. This finding shows that removal of methylene blue using dried leaves is not affected by reaction temperature. Percentages of removal was found to be marginally superior at lower temperature because all methylene blue dye ions present in solution could interact with the bindings sites effectively. Previous work done by Khodabandehloo, et al., (2017) reported similar pattern suggesting that removal of

methylene blue using dried leaves is exothermic in nature [13].

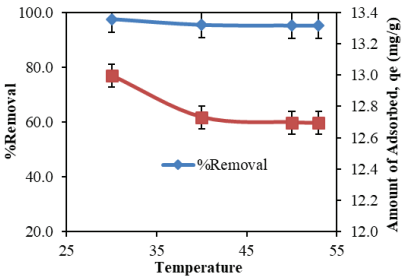

Figure 4: Effect of temperature on the adsorption of methylene blue

D. Effect of pH Solution

The pH of the solution is an important factor that influences the adsorption of methylene blue using dried leaves. Effect of initial pH of solution on the adsorption of methylene blue using the dried leaves was carried out in range of pH from 2 to 11 using 60 mg/L concentration of methylene blue at 30 °C with agitation speed at 120 rpm and then the mixture stirred for 180 minutes. The attained results are shown in Figure 5, where the pH of solution was controlled by using 0.5 M NaOH and 0.5 M HCl. From the figure, it is obvious to noted that the adsorption of methylene blue somewhat rises with increase in the pH solution from pH 2 to 3 which illustrated by enhancement in the amount of adsorbed, q_e. After that, methylene blue adsorption was slightly decrement from pH 3 to 11. Figure 6 shows that the higher adsorption of methylene blue at pH = 3 which is due to increased protonation by neutralization of the negative charges at the surface of adsorbent [15]. Lower adsorption of methylene blue at acidic pH is probably due to presence of excess H^+ ions competing with the cation groups on the dye for adsorption sites [6]. At higher pH the surface of DL may be negatively charged which enhances the positively charged methylene blue cations through electrostatic force at attraction [3].

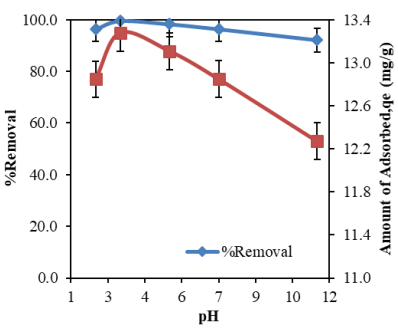

Figure 5: Effect of pH solution on the adsorption of methylene blue

IV. Conclusion

Potential of dried leaves as an adsorbent for removal of methylene blue from the aqueous solutions was investigated. The results obtained show that the dried leaves which are abundantly available as waste can be used for the removal of methylene blue from the aqueous solution. Adsorption of methylene blue using dried leaves was found to be dependent on initial concentration of methylene blue, initial of pH solution, adsorbent dosage, and temperature. Hence, it can be concluded that the dried leaves powder can be effectively used an adsorbent to treat industrial effluent. In addition to that, the dried leaves used is abundantly available and require none pretreatment for the removal of methylene blue. Therefore, dried leaves can be economically feasible for removal of methylene blue from aqueous solutions.

V. Acknowledgement

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