Adsorption Studies of Methylene Blue and Methylene Red on Activated Carbon Derived from Agricultural waste: Rubber (*Havea brasiliensis*) Seed Powder

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ABSTRACT

Activated carbon prepared from rubber (*Havea brasiliensis*) seeds was used to remove methylene blue and methyl red from aqueous solutions. Adsorption studies were conducted to evaluate the effect of contact time and amount of carbon active on the removal of methylene blue and methyl red at temperature of 25^{o}C. The equilibrium adsorption data of methylene blue and methyl red on activated carbon were analyzed by Freundlich and Langmuir isotherm model. The absorption kinetic models were predicted by pseudo-first-order and pseudo-second-order. The pseudo-second-order kinetic model was the best fitting equilibrium adsorption data. The results of adsorption methylene blue and methyl red on aqueous solutions shown that rubber seeds as carbon active can be used as material for adsorption.

Keyword: Activated carbon, Rubber seed, Methylene blue, Methyl Red

1. Introduction

Methylene blue (MB) and methyl red (MR), which is classified as a basic dye is widely used in the silk, wool, cotton, leather and paper industries for coloring purposes. The industrial effluent wastewater may contain chemicals that exhibit toxic effects toward microbial populations and can be toxic and carcinogenic to animals [1]. Over 10,000 dyes with a total yearly production over 7×10^7MT worldwide are commercially available and 5 – 10% of dyestuffs are lost in the industrial effluents [2-4]. This dye-bearing wastewater exhibit high colour and high chemical and biochemical oxygen demands (COD and BOD) [3]. A very small amount of dye in water is highly visible. The discharge of these dyes effluents in the environment is worrying for both toxicological and aesthetical reasons [5]. MB is a cationic dye used for dyeing cotton and silk. It can cause irritation in humans and animals, such as methemoglobinemia, cyanosis and convulsions [6]. MR, an anionic azo dye, has been used in paper printing and textile dyeing [7]. Similar to MB, it causes irritation of the eye, skin and digestive tract if inhaled/swallowed [8].

Therefore, an increased interest has been focused on removing of such dyes for minimized the damage to the environment and also decolorize the water from the wastewater.

There are several dye removal techniques from wastewaters, including adsorption, biosorption coagulation/flocculation, advanced oxidation, ozonation, membrane filtration and liquid-liquid extraction. All processes have their own limitations.

The removal of dyes in an economic way remains an important problem although a number of systems have been developed with adsorption technique. Adsorption is an effective and important means of controlling the extent of pollution due to basic dye in industrial effluent. A number of reports are available on the removal of MB and MR from wastewater using activated carbon as an adsorbent [1, 2, 9-11].

Therefore, the present study is aimed to study a convenient and economic method for MB and MR removal form water by adsorption. This work is the production of new adsorptive materials form adsorption on a low cost and an abundantly available adsorbent such as rubber seed powder. The kinetic data and equilibrium data of adsorption studies were processed to understand the adsorption mechanism of MB and MR onto the prepared activated carbon.

2. Material and methods

2.1 Adsorbent

Rubber seed were obtained from a rubber plantation estate in Muara Enim, Sumatera Selatan, Indonesia and was used as adsorbent for the preparation of activated carbon in this work. The rubber seeds were washed repeatedly with distilled water to remove adhering dirt and soluble impurities. The seeds were dried in an oven at 600^{O}C for 2 h and crushed. The dried biomass was ground in a mortar to a fine powder and passed through British Standard Sieves (BSS) of 35 MESH. The powdered biomass was stored in an airtight plastic container and used for analysis as well as for adsorption experiments. Acid modified rubber seed powder adsorbent was prepared by mixing 10 g of raw rubber seed powder with 100 ml of 0.1 M HCL solution. The whole reaction mixture was stirred in a shaker batch for a period of 24 h and then the powder was filtered and repeatedly washed with distilled water until the pH of the washing solution reached 6–7. The washed powder was then oven dried overnight at 50^{0}C. The activated product was then cooled to room temperature and used for adsorption and characterisation.

2.2 Adsorbate

MB and MR was purchased from Sigma Aldrich and used without purification. A stock solution of 50 mg/l was prepared by dissolving the appropriate amount (50 mg) of MB and MR in a litre of distillate water. The working solutions were prepared by diluting the stock solution with distillate water to give the appropriate concentration of the working solutions. All sample bottles and glassware were cleaned, and then rinsed with distillate water and oven dried at 60^{O}C.
The UV/VIS Spectrophotometer (Shimadzu UV Mini 1240) was used to determine the concentrations of MB and MR in solution. Calibration curve was plotted between absorbance and concentration of the dye solution to obtain absorbance-concentration profile.

2.3 Batch kinetic studies

Adsorption measurement was determined by batch experiments of known amount of the adsorbent with 100 ml of aqueous dye solutions of known concentration in a series of 250 ml conical flasks. The mixture was shaken at a constant temperature at 120 rpm, 25^{0}C and 120 min.
At predetermined time, the bottles were withdrawn from the shaker and the residual dye concentration in the reaction mixture was analysed by measuring the absorbance of the supernatant at the wavelength that correspond to the maximum absorbance of the sample using an UV/VIS Spectrophotometer at 660 nm and 419 nm for MB and MR, respectively. Dye concentration in the reaction mixture was calculated from the calibration curve. Adsorption experiments were conducted by varying adsorbent dose under the aspect of adsorption kinetics and adsorption isotherm study. The amount of adsorbate adsorbed at equilibrium, qe (mg/g), was calculated by

$$q_e = \frac{(C_0 - C_t)V}{W} \qquad (1)$$

And dye removal efficiency i.e. % of adsorption was calculated as

$$\%\ adsroption = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (2)$$

where C_0 and C_t (mg/L) are the liquid-phase concentrations of dye at initial and time, t, respectively. V is the volume of the solution (L) and W is the mass of dry adsorbent used (g).

3. Results and discussion

3.1 Effect of dyes on activated carbon

Study of the effect of dyes on activated carbon gives an idea of the effectiveness of an adsorbent and the ability of a dye to be adsorbed onto rubber seed carbon. The adsorption curves for both dyes reached equilibrium after a certain time, which differed among them. It is observed on Fig. 1 that the equilibrium time reached 25 mins for both dyes. [12].

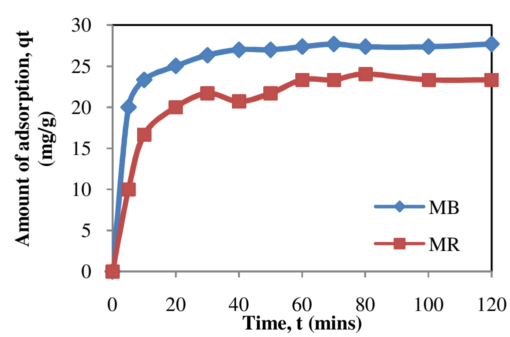
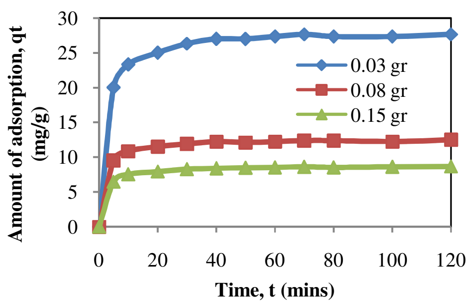


Fig. 1 Effect of dyes on activated carbon at 25^{O}C. Volume of dye solution = 100 ml; intial dye concentration = 20 ppm; shaker speed = 120 rpm

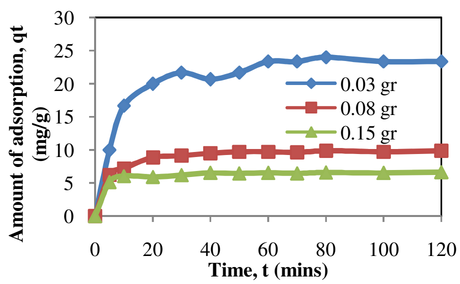
From Fig. 1, it was found that the amount of two dyes adsorbed 27.7 mg/g and 23.3 mg/g for MB and MR, respectively. It was also found that at equilibrium the percentage dye removal was 41.5% and 35.0% for MB and MR, respectively. Comparing the adsorption of the two dyes by rubber seed powder, it is observed that MB showed a greater affinity than MR. The lower-rate adsorption of MR was caused by charged ion groups. MR have ion negative groups and they repelled by the negatively charged activated carbon surface leading to relatively low adsorption capacity

3.2 Effect of adsorbent dosage on MB and MR adsorption kinetics

The dependence of adsorption of MB and MR on the dosage of activated carbon is shown in Fig. 2. The amount of both dyes removal decreased with increase in adsorbent dosage. It was found from Fig. 2(a) that the increase in adsorbent dosage from 0.03 to 0.15 gr resulted in decreased of amount of adsorbed MB from 27.7 to 8.7 mg/g. Similarly, the removal MR form solution decreased from 23.3 to 8.7 mg/g with increase in adsorbent dosage.



(a)



(b)

Fig. 2 Effect of adsorbent dosages on dyes at 25^{O}C, Intial concentration of 20 ppm, shaker speed of 120 rpm. (a) MB; (b) MR

It was also found that at equilibrium the percentage MB removal was increased from 41.5% to 65.0% with the increase of adsorbent mass from 0.03 g to 0.15 g for which plots are not presented here. The percentage MR removal was also increased from 35.0% to 50.0% with the increase of adsorbent mass. This is due to the availability of more binding sites as the dosage of adsorbent increased. However, the amount of both dyes adsorbed (mg/g) was found to decrease with increasing adsorbent dosage. According to Shukla et al. [13], the decrease in adsorption capacity (mg/g) with increase in adsorbent dosage is due to the high number of unsaturated adsorption sites.

3.3 Adsorption isotherm

The adsorption isotherm is important for the description of how the adsorbate will interact with the adsorbent and gives an idea of the adsorption capacity of the adsorbent [14].
To simulate the adsorption isotherm, two commonly used models, the Freundlich [15] and Langmuir [16] were selected to explicate dye-seed rubber activated carbon interaction.
The Freundlich adsorption isotherm, which assumes that adsorption takes place on heterogeneous surfaces, can be expressed as

$$\ln q_e = \ln K_f + \frac{1}{n}(\ln C_e) \qquad (3)$$

where K_F is maximum adsorption capacity (mg/g) i.e. the greater K_F value, the greater adsorption capacity. The other Freundlich constant n is related to adsorption intensity. According to Mohanty et al. [17] if the value of n is greater than 1, it indicates favourable adsorption of dyes on the surface of adsorbent and a physical process. Further, n below unity indicates that adsorption is a chemical process, whereas, n is equal to unity, the adsorption is linear [2, 18, 19]. Fig. 3 gives results on Freundlich isotherm fittings for MB and MR with linear correlation coefficient (R^2) of 0.96 and 0.94, respectively. The value of n determined from Freundlich isotherm was 1.92 and 2.14 for MB and MR, respectively. The n value of MB and MR is higher than 1 which indicates the favourable nature of adsorption and a physical process. Adsorption capacity (K_F) are 7.54 and 6.05 mg/g for MB and MR, respectively.

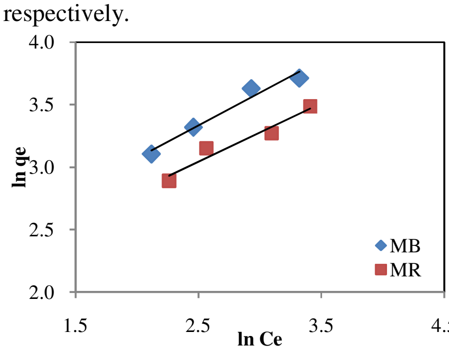


Fig. 3 Freundlich plot: amount of adsorbent (rubber seed) added = 0.03 gr; Initial concentration = 15, 20, 30, 40 ppm; Temperature = 25^{O}C; Shaker Speed = 120 rpm

The linearized form of Langmuir can be written as:

$$\frac{C_e}{q_e} = \left(\frac{1}{K_a q_m}\right) + \frac{C_e}{q_m} \quad (4)$$

The Langmuir constants, qm (maximum adsorption capacity) (mg/g) and K_a (values for Langmuir constant related to the energy of adsorption (l/mg)) are predicted from the plot between C_e/q_e versus C_e.

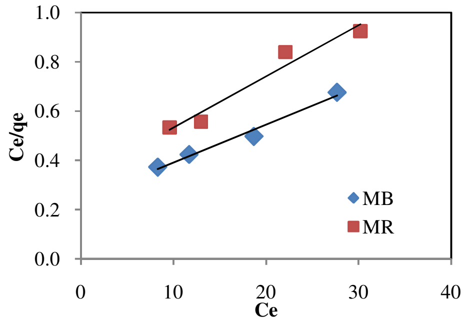


Fig. 4 Langmuir plot: amount of adsorbent (rubber seed) added = 0.03 gr; Initial concentration = 15, 20, 30, 40 ppm; Temperature = 25°C; Shaker Speed = 120 rpm

Fig. 4 gives results on Langmuir isotherm fitting for rubber seed activated carbon. The maximum monolayer adsorption capacity of rubber seed activated carbon, q_m, and constant related to the binding energy of the sorption system, K_a is calculated from Fig. 4 which are 64.9 mg/g and 0.06 respectively for MB. The q_m and K_a value of MR are 48.1 mg/g and 0.06, respectively.

3.4 Adsorption kinetics

In order to investigate the mechanism of adsorption, particularly potential rate-controlling step, the transient behaviour of the SDS adsorption process was analysed using the pseudo-first-order and pseudo-second-order.

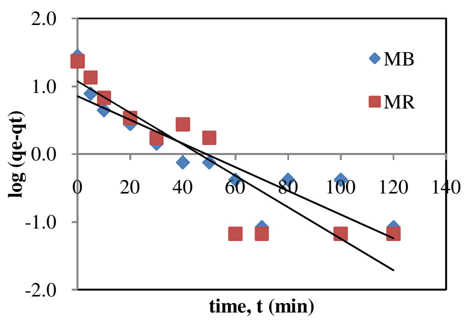


Fig. 5 Pseudo-first-order kinetic model of MB and MR adsorption by rubber seed activated carbon.

The pseudo-first-order kinetic equation is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

where qt and qe are the amount of copper adsorbed (mg/g) at time t (min) and at equilibrium, and k_1 is the rate constant of the pseudo-first-order adsorption process (/min).

A plot of $\log(q_e - q_t)$ versus t gives a straight line with poor linear regression coefficient (R^2) in the range of 0.79 to 0.82 at different dyes (Fig. 5).

The pseudo-second-order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (6)$$

A plot between t/qt versus t gives the value of the constants k_2 (g/mg h) and also qe (mg/g) can be calculated. The constant k_2 is used to calculate the initial sorption rate h, at $t \to 0$, as follows:

$$h = k_2 q_e^2 \quad (7)$$

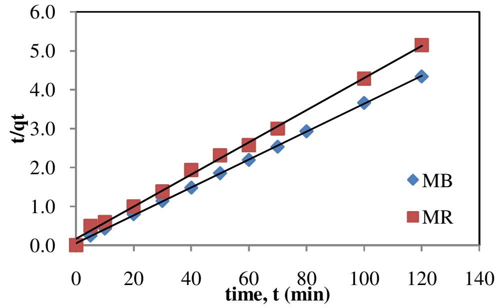


Fig. 6 Pseudo-first-order kinetic model of MB and MR adsorption by rubber seed activated carbon.

Better linearity was obtained for these plots as shown in Fig. 6 with regression coefficient greater than 0.99 and the pseudo-second-order rate constant, k_2 having value 0.02 and 0.01 g/mg.min for MB and MR, respectively.

Both facts suggest that the adsorption of MB and MR by rubber seed activated carbon follows pseudo-second-order model.

4. Conclusion

This study demonstrated that the rubber seed activated carbon could be used as an effective adsorbent for the treatment of wastewater containing MB and MR. The isotherm study indicates that adsorption data correlated well with Freundlich and Langmuir isotherm models. The kinetic data showed that the pseudo-second-order kinetic model was obeyed better than pseudo-first-order kinetic model.

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