

# Adsorption of Methylene Blue by NaOH-modified Dead Leaves of Plane Trees

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## ABSTRACT

NaOH-modified dead leaves of plane trees were used as bioadsorbent to remove methylene blue (MB) from aqueous solution. Variable influencing factors, including contact time, temperature, initial MB concentration and pH were studied through single-factor experiments. The results showed that the initial concentration 100 mg/L, bioadsorbent of 2.5 g/L, pH of 7, room temperature were the best adsorption conditions. The NaOH-modified bioadsorbent had a high adsorption capacity for MB, and its saturated extent of adsorption was 203.28 mg/g, which was higher than the un-modified dead leaves (145.62 mg/g) and some other bioadsorbents. Finally, adsorption kinetics and isotherms were discussed, suggesting that the Langmuir isotherm model and Pseudo-second order kinetics were fitted well with the adsorption process.

**Keywords:** Modified; Bioadsorbent; Methylene Blue; Kinetics; Adsorption Isotherm

## 1. Introduction

Dyes are extensively used in many industries such as leather, paper, textiles, printing and cosmetics. Low or high concentration of dye wastes can be often detected in the effluents arising from these industries. However, dye wastes are difficult to be removed from the effluents due to their complex composition and bad biodegradation [1]. Therefore, removal of dyes is an essential procedure of wastewater treatment before discharge.

The methods to treat dyeing wastewater can be classified into two types: physical and chemical processes. Among all these methods, activated carbon is the most popular used as solid adsorbent because of its high adsorption capability [2,3]. However, widely utilized activated carbon in commerce is vastly limited with its initial cost and the high expense of regeneration after exhausted. For these reasons, many researchers are aiming at developing cheaper substitutes to replace activated carbon, such as fly ash [4], cellulose-based waste [5], rice husk [6], tea waste [7], dehydrated wheat bran [8], bagasse fly ash [9], etc.

In many areas, plane trees with dense leaves and fast-growing character are often planted as urban greening tree species. Lots of plane tree leaves can be available in autumn when they fall, so they are obtained easily and low-cost. So in the present study, dead leaves of plane trees have been used as bioadsorbent for the removal of MB from aqueous solution, and relatively simple pretreatment with NaOH was used to modify the properties

of them. The purpose of this study is to find the feasibility of plane tree leaves as a bioadsorbent.

## 2. Materials and Methods

### 2.1. Preparation of Adsorbents

The dead leaves used in the study were collected from Qingdao University of Science and Technology in autumn. The collected leaves were washed with deionized water several times to remove the dust and other water-soluble materials. The process couldn't stop until the washing water was colorless. The washed leaves were dried at 333K in a hot air oven for one day, and then shattered and sieved to get different geometrical sizes (0.45 - 0.9 mm). The sieved particles were washed repeatedly with deionized water till the UV absorbency of washing water was close to zero, and the final pH kept constant. The washed materials were then dried at 333K in the hot air oven for one day. Finally, the obtained particles were modified with NaOH (0.5 mol/L) [10] that was the bioadsorbent the experiments needed.

### 2.2. Adsorbate

The stock solution (1 g/L) of MB (methylene blue,  $C_{16}H_{18}ClN_3S \cdot 3H_2O$ , 82% pure, a molecular weight of 373.9, supplied by Shanghai reagent Co., Ltd), was prepared in distilled water. Calibration curve for MB was prepared by measuring the absorbance of different concentrations of MB at 665 nm (UV-VIS spectrophotome-

ter, TU-1901, Beijing PGENERAL Co., Ltd).

### 2.3. Sorption Experiments

The experiments were conducted in 250 mL Erlenmeyer flasks containing different amount of bioadsorbent and 200 mL of MB solution at desired concentrations. The flasks were agitated in a Water Baths Shaker at constant shaking rate. Samples were pipetted from the mixed solution in flasks at prearranged time intervals to determine the residual MB concentration. The samples were centrifuged and the supernatant liquid was determined its absorbance after dilution. For isotherm studies, a series of flasks containing 200 mL MB solution in the range of 100 - 500 mg/L were prepared. Bioadsorbent of 0.5 g was added to each flask and then the mixtures were agitated at 293.15K.

The adsorption amount of MB adsorbed onto the bioadsorbent at equilibrium was calculated with the following equation:

$$q_{eq} = \frac{(C_0 - C_{eq}) V}{X} \quad (1)$$

where  $C_0$ (mg/L) and  $C_{eq}$  (mg/L) are the initial and equilibrium concentration of MB,  $V$ (L) is the volume of solution,  $X$ (g) is the weight of adsorbent in one container,  $C$ (mg/L) is the solution concentration after reaction for a period of time.

### 2.4. Sorption Kinetics

For kinetic studies, the effect of initial MB concentration on the kinetics of MB adsorption was studied. Three adsorption kinetic models are used in this study to describe the adsorption characteristics.

The Pseudo-first order equation can be expressed in Equation (2):

$$\frac{dq}{dt} = K_1 (q_e - q) \quad (2)$$

where  $K_1$ (min<sup>-1</sup>) is the rate constant of the pseudo-first order adsorption,  $q_e$ (mg/g) is the amount of equilibrium adsorption,  $q$ (mg/g) is the amount of dye adsorbed at any time.

Equation (2) can be integrated to the following form by applying the initial conditions  $q = 0$  at  $t = 0$ :

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

The value of  $K_1$  can be determined by the slope of plot of  $\log(q_e - q)$  versus  $t$  in Equation (3).

The Pseudo-second order equation can be expressed in Equation (4):

$$\frac{dq}{dt} = K_2 (q_e - q)^2 \quad (4)$$

where  $K_2$ (g·mg<sup>-1</sup>·min<sup>-1</sup>) is the rate constant pseudo-second

order,  $q_e$  and  $q$  are the same with Equation (2).

Considering that  $q = 0$  when  $t = 0$  and that  $q = q$  when  $t = t$ , integrating Equation (5), result is as follows:

$$\frac{1}{q_e - q} = \frac{1}{q_e} + K_2 t \quad (5)$$

The value of  $K_2$  can be determined by the slope and intercept of the plot  $1/(q_e - q)$  versus  $t$  or by  $t/q$  versus  $t$ .

Intraparticle diffusion process can be expressed in Equation (6):

$$q = K_i t^{0.5} + C \quad (6)$$

where  $K_i$  (mg·g<sup>-1</sup>·min<sup>0.5</sup>) is the Intraparticle diffusion constant,  $C$  is the intercept.

Among the three steps—film diffusion, pore diffusion and intraparticle transport, of the adsorption mechanism, the slowest step usually controls the whole rate of the process. However, in a batch reactor, the intraparticle diffusion is often a rate-limiting step. Therefore, the rate constant of intraparticle transport ( $K_i$ ) is estimated from the slope of the linear portion of the plot  $q$  against square root of  $t$ . Values of  $C$  represent the thickness of boundary layer, and that they are positive correlation [11,12].

### 2.5. Sorption Equilibrium Isotherm Models

The Langmuir adsorption model [13] is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The Langmuir equation may be written as

$$1/q_e = 1/q_m C_{eq} b + 1/q_m \quad (7)$$

where  $q_e$ (mg/g) is the amount of per unit weight of adsorbent,  $q_m$ (mg/g) is the monolayer adsorption capacity,  $b$ (L/mg) is the constant related to the free energy of adsorption,  $C_{eq}$ (mg/L) is the equilibrium concentration of the solute in the bulk solution.

The Freundlich model [14] is an empirical equation that assumes heterogeneous adsorption due to the diversity adsorption sites. Its equation may be written as:

$$q_e = K_F \cdot C_{eq}^{1/n} \quad (8)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln \rho_e \quad (9)$$

where  $q_e$  and  $C_{eq}$  are the same with the Langmuir's,  $\rho_e$  (mg/L) is the equilibrium concentration of the solute in the bulk solution,  $K_F$  (mg<sup>1-1/n</sup>L<sup>1/n</sup>/g) is a constant indicative of the relative adsorption capacity of the adsorbent,  $n$  is a constant indicative of the intensity of the adsorption.

## 3. Results and Discussion

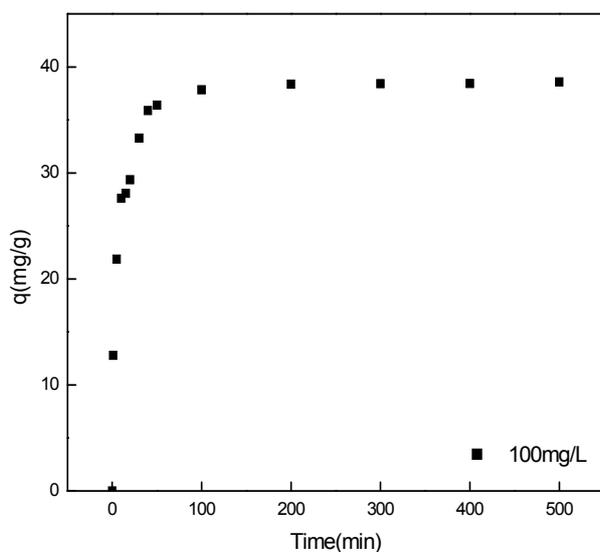
### 3.1. Effect of Contact Time

The effect of contact time on the sorption of MB was

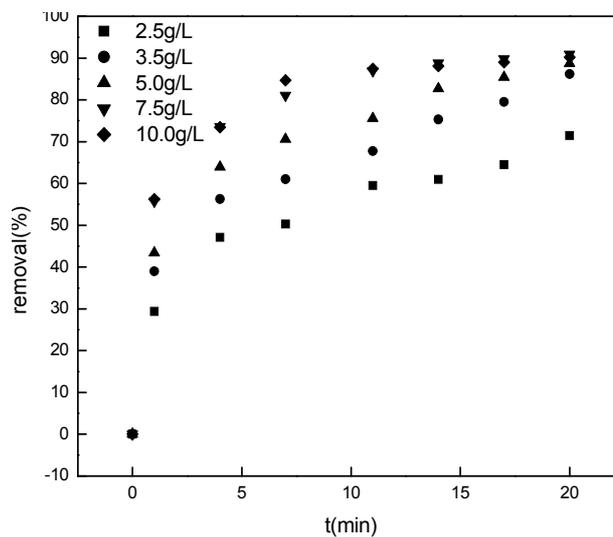
studied for an initial MB concentration of 100 mg/L. The result is shown in **Figure 1**. The obtained result reveals that the speed of MB uptake onto bioadsorbent is fast at the initial stage (before 50 min), and then it decreases gradually and becomes near the equilibrium in about 150min. This is obvious from the fact that there are abundant vacant surface sites available for adsorption during the initial stage, and with the lapse of time, the remaining vacant surface sites are difficult to be occupied as a result of repulsive forces between the dye molecules on the solid and bulk phases [15]. Besides, at the beginning, the dye ions are adsorbed onto the exterior surface of the bioadsorbent till reaching saturation at a fast rate, and after that, the dye ions enters the pores of the bioadsorbent and are adsorbed by the interior surface of the particles, which carries on at a relatively slow rate[16,17].

### 3.2. Effect of Adsorbent Dosage

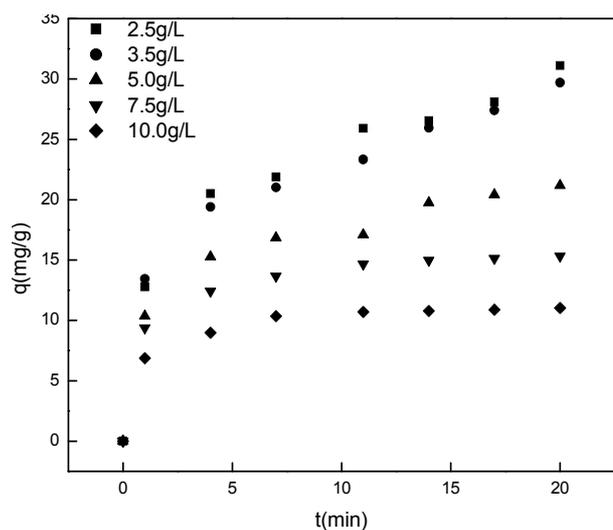
To determine the effect of adsorbent dosage on the sorption of MB, the bioadsorbent concentration was set from 2.5 to 10.0 g/L. As shown in **Figure 2**, the percentage of MB uptake increases with increasing adsorbent dosage at the same initial MB concentration. As observed from **Figure 2(a)**, the removal rate increases from 71.5% (2.5 g/L) to 90.2%(10.0 g/L) due to the increased available surface area and more sorption sites. Though the range of particle size is constant, the surface area will enlarge along with the increase of the adsorbent dosage in the solution. However, as seen from **Figure 2(b)**, the more the adsorbent dosage, the lesser the adsorption capacity (from 42.09 mg/g to 11.87 mg/g), which could be explained with the reduction of the effective surface area.



**Figure 1.** Effect of contact time on the sorption of MB onto dead leaves.



(a)



(b)

**Figure 2.** Effect of adsorbent dosage on the sorption of MB onto dead leaves.

### 3.3. Effect of Initial MB Concentration

The effect of different initial MB concentration ranging from 100 to 500 mg/L at 298.15K on dye adsorption is shown in **Figure 3**, which is shown that the initial MB concentration influences the contact time necessary to reach equilibrium: the shorter the contact time, the lower the initial MB concentration. 100 minutes are sufficient to reach the adsorption equilibrium in the range of 100 to 300 mg/L, whereas the equilibrium time for 500 mg/L increases to 400 min. It is reported that the adsorption spectrum shape of MB is dependent on its concentration. Higher concentration causes a decrease of the monomer band (Here MB has a long-wavelength maximum-665 nm) and an increase of the more energetic band (Here MB has a short wavelength shoulder-608 nm). In lower

concentration, of about  $1 \times 10^{-5}$  mol/L, MB doesn't display obvious dimerization or aggregation. So the longer equilibrium time for the higher initial concentration can be accounted for the obvious dimerization or aggregation because of the lower intraparticle diffusion rate of aggregate forms[4]. It also can be seen that the saturated extent of adsorption of the adsorbent increases for the higher initial MB concentration (44.44 to 203.28 mg/g) as a result of stronger driving force. And that, the saturated extent of adsorption of un-modified adsorbent is only 145.62 mg/g in the same condition. This result is also obtained by other authors for the adsorption of dyes on various adsorbents [1,18].

### 3.4. Effect of Temperature

Figure 4 illustrates the effect of temperature on MB

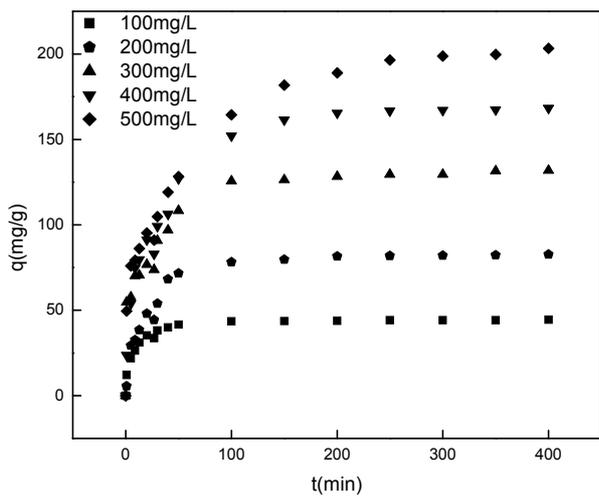


Figure 3. Effect of initial MB concentration on the sorption of MB onto dead leaves.

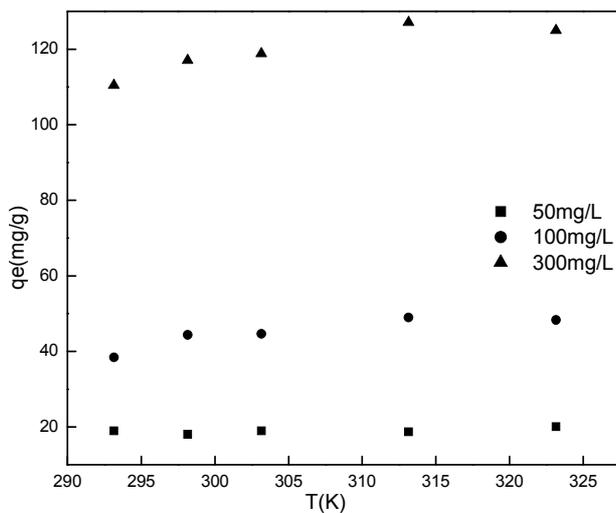


Figure 4. Effect of temperature on the sorption of MB onto dead leaves.

adsorption for different initial MB concentrations. It is shown that higher temperature can help the adsorbent acquire higher adsorption capacity for the same concentration, especially for higher initial concentration. This reveals that the adsorption of MB onto the bioadsorbent is an endothermic process. The temperature has several effects on the adsorption process: i) High temperature increases the rate of diffusion of MB molecules across the external boundary layer and into the internal pores of the adsorbent particles; ii) Rising temperature may increase the deaggregate tendency and the uptake of monomers of MB[4]; iii) High temperature could enlarge the pore size or create some new active sites on the adsorbent surface due to rupture of bond[19].

### 3.5. Effect of pH

To determine the effect of initial pH on MB adsorption, the pH of MB solution is varied from 3 to 13. As seen from Figure 5, the adsorption capacity of bioadsorbent increases from 12.8 mg/g to 25.8 mg/g in 1min at pH 13, which is obviously higher than other pH values. MB belongs to one of cationic dyes, which exists in aqueous solution in form of positively charged ions. Therefore, higher pH value leads to more electrostatic forces of attraction. In addition, at lower pH,  $H^+$  could fight for the vacant adsorption sites with the positively charged MB cations, which also causes lower adsorption capacity.

However, the adsorption capacity of dead leaves at pH 7 comes to be close to that pH 13 after 30 minutes, so pH 7 is fine for the adsorption in the practical wastewater treatment.

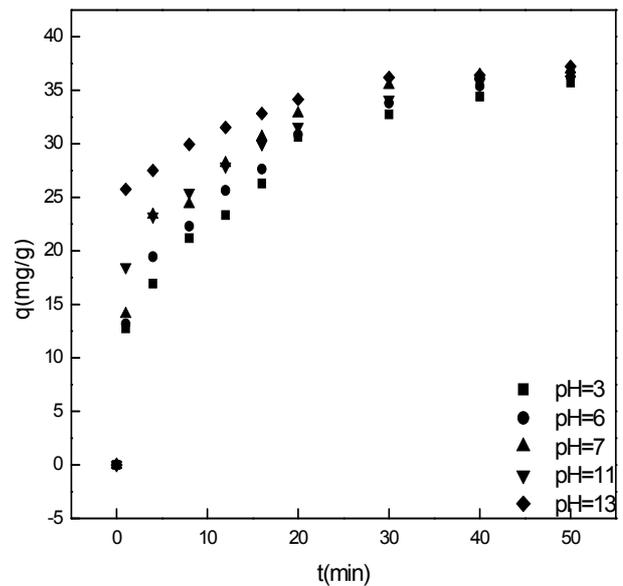


Figure 5 Effect of pH on the sorption of MB onto dead leaves.

### 3.6. Sorption Kinetic Models

The sorption kinetics could provide valuable insights into the reaction pathways and the mechanism of a sorption reaction, so they are worth paying attention to. The constants and correlation coefficient of three kinetics models are summarized in **Table 1**. The value of  $R^2$  of pseudo-second order model is proved to be best among the three models. In addition, its calculated  $q_{e(\text{calc.})}$  is very close to the experimental  $q_{e(\text{exp.})}$ . In the view of the result, it indicates that the sorption of MB onto adsorbent is more appropriate for the pseudo-second order model in contrast to the pseudo-first order model and intraparticle diffusion model, suggesting that the adsorption process is controlled by chemisorption [20,21]. A similar result is obtained for the adsorption of MB from aqueous solution onto spent tea leaves [22].

From **Table 1**, the value of  $C$  increases with higher initial MB concentration, leading to a greater boundary layer effect. when  $C = 0$ , the intraparticle diffusion is thought to be the rate limiting step; If  $C > 0$ , both intraparticle diffusion and external mass transfer are considered as rate limiting steps[23]. Therefore, the adsorption of MB onto dead leaves is controlled by both external mass transfer and intraparticle diffusion.

### 3.7. Equilibrium Isotherms

Adsorption isotherms are necessary to design adsorption systems. Here Langmuir and Freundlich equations are used to model the adsorption data. To determine the equilibrium isotherms for each equation, initial MB concentrations are designed from 50 to 800 mg/L while the adsorbent concentration was kept constant (2.5 g/L) at 293.15K. The isotherm constants and correlation coefficients are shown in **Table 2**. The Langmuir isotherm is represented by equation (7). The Freundlich isotherm is represented by equation (9). As seen from **Table 2**, the

$R^2$  of Langmuir model is better than the Freundlich model's, illustrating that the adsorption equilibrium can be best represented by the Langmuir isotherm model, with maximum monolayer adsorption capacity of 243.902 mg/g onto the adsorbent at 293.15K.

The characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor  $R_L$  that is given by equation(10) [24]:

$$R_L = \frac{1}{1 + bC_0} \quad (10)$$

where  $C_0$  (mg/L) is the highest initial concentration of adsorbate and  $b$  is Langmuir constant. The parameter  $R_L$  indicates the nature of the shape of the isotherm accordingly: unfavorable adsorption of  $R_L > 1$ , favorable adsorption of  $0 < R_L < 1$ , irreversible adsorption of  $R_L = 0$ , linear adsorption of  $R_L = 1$ .

The value of  $R_L$  in this study found to be 0.025 shows that the adsorption of MB onto adsorbent is favorable. And in the Freundlich model,  $1/n$  is the adsorption intensity. It also gives an indication of the favorability of adsorption. Value of  $n > 1$  means favorable adsorption conditions [25].

## 4. Conclusions

The results obtained show that the dead leaves of plane trees can be used for the removal of MB from aqueous solution. Kinetic data were tested using the pseudo-first, pseudo-second and intraparticle diffusion kinetic models. The kinetics of the adsorption process was found to follow the pseudo-second order kinetic model, suggesting that the adsorption process was controlled by chemisorption. The plots of intraparticle diffusion didn't pass the origin, implying that there were other processes affected the adsorption except intraparticle diffusion. The equilibrium data were fitted to models of Langmuir and Freundlich,

**Table 1. The constants and  $R^2$  of three kinetic models for the adsorption of mb onto dead leaves.**

MB concentration (mg/L)	$q_{e(\text{exp.})}$	Pseudo-first order model			Pseudo-second order model			Intraparticle diffusion model		
		$q_{e(\text{calc.})}$	$k_1$	$R^2$	$q_{e(\text{calc.})}$	$k_2$	$R^2$	$C$	$k_i$	$R^2$
100	44.38	27.38	4.72	0.9889	45.44	0.0059	0.9953	10.83	4.69	0.9664
200	82.61	72.86	3.77	0.9886	83.26	0.0015	0.9934	11.11	8.54	0.9744
300	131.77	82.20	2.33	0.9880	132.83	0.0006	0.9963	19.70	10.02	0.9695
400	168.35	126.01	2.11	0.9846	165.56	0.0003	0.9999	41.26	11.63	0.9617
500	203.28	142.45	1.31	0.9836	199.45	0.0002	0.9994	42.50	14.63	0.9717

$q_e = \text{mg/g}$ ;  $k_1 = \times 10^{-2} \text{ min}^{-1}$ ;  $k_2 = \text{g mg}^{-1} \text{ min}^{-1}$ ;  $k_i = \text{mg} \cdot \text{g}^{-1} \text{ min}^{-0.5}$

**Table 2. Langmuir and freundlich isotherm constants and correlation coefficients.**

Isotherm	Langmuir			Freundlich		
	$q_m$ (mg/g)	$b$ (L/mg)	$R^2$	$K_F$	$n$	$R^2$
Values	243.902	0.046	0.996	16.592	1.677	0.963

and the adsorption equilibrium can be best represented by the Langmuir isotherm model, with maximum monolayer adsorption capacity of 243.902 mg/g of the adsorbent at 293.15K. The dead leaves of plane trees used to be adsorbent in this study are freely and abundantly available, and have high adsorption capacity for MB. Therefore, the prospect of dead leaves of plane trees used as adsorbent for removal of MB dye from aqueous solution is very promising.

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