

## **PREPARATION OF ACTIVATED CARBON FROM TEA WASTE AND APPLICATION FOR REMOVAL OF METHYLEN BLUE**

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### **TÓM TẮT**

#### **CHẾ TẠO VẬT LIỆU THAN HOẠT TÍNH TỪ BÃ CHÈ VÀ ỨNG DỤNG HẤP PHỤ METHYLEN XANH TRONG MÔI TRƯỜNG NƯỚC**

*Trong bài báo này, bã chè hoạt hóa  $H_2SO_4$  thành than hoạt tính (ký hiệu là AC8) đã được sử dụng làm chất hấp phụ màu metylen xanh trong môi trường nước. Đặc điểm bề mặt, tính chất vật lý, cấu trúc của AC8 được nghiên cứu bởi các phép đo phổ SEM, Raman, XRD. Một số yếu tố ảnh hưởng đến quá trình hấp phụ metylen xanh của AC8 đã được nghiên cứu như: pH dung dịch (2-10), thời gian tiếp xúc (30 - 240 phút), lượng chất hấp phụ (0,01 - 0,08g) và nồng độ ban đầu (15 mg /L đến 400 mg /L )... Kết quả cho thấy quá trình hấp phụ metylen xanh của AC8 tuân theo mô hình hấp phụ đẳng nhiệt Langmuir, dung lượng hấp phụ cực đại là 208,33 mg/g.*

**Keywords:** *Hấp phụ; than hoạt tính; Metylen xanh; mô hình hấp phụ đẳng nhiệt; Langmuir.*

### **1. INTRODUCTION**

Water pollution by dyes is a worldwide problem particularly in textile industry where large quantities of dye effluents are discharged from the dyeing processes. Considering both volume and composition, effluent from the textile industry was declared as one of the major sources of wastewater in the world [10]. Dyes are also widely used in many industries such as rubber, paper, plastic, cosmetic etc. There are more than 10.000 commercially available dyes with over  $7 \times 10^5$  tons of dyestuff being produced annually across the world. The total dye consumption of the textile industry

worldwide is more than  $10^7$  kg/year with about 90% ending up on fabrics. Dye producers and consumers are interested in the stability and fastness of dyes and consequently, are producing dyestuffs which are more difficult to degrade after being used. It is estimated that 10-15% of the dye is lost during the dyeing process and released with the effluent [8]. Methylene blue (MB), one of the colored organic compounds, is the most commonly used substance for dyeing cotton, wood and silk. However, it can cause permanent burns to the eyes of human and animals, nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [2]. Therefore, the removal of MB is considered as one of the environmental challenges in the recent years [4, 9]. Currently, the sorption technique is proved to be an effective and attractive process for the treatment of dye containing wastewater. Also, this method will become inexpensive if the sorbent material used has cheaper cost and does not require any expensive additional pretreatment step.

On the other hand, tea waste is a household waste abundant in Thai Nguyen Province (Vietnam). It is an oxygen demanding pollutant and takes a long time for biodegradation. Therefore, the use of tea waste for removal of MB appears to be a sustainable solution for controlling of these two wastes at very low cost. When the tea waste is saturated after adsorption of MB, it is just dried under the sun and burned for energy recovery. The waste tea ash obtained by incineration would not a pollutant and can be use as fertilizer in agriculture or adsorbent for other water treatment processes.

In this study, activated carbon was prepared from tea waste by  $H_2SO_4$  activation and used as adsorbent for removal of MB in its aqueous solution. The effects of initial MB concentration, tea waste mass, pH and contact time on the amount of color removal was investigated. The  $pH_{pzc}$  of the adsorbent was determined by titration method. Equilibrium isotherm data were fitted to Langmuir and Freundlich equations and the constants of isotherm equations were determined. Furthermore, the kinetics involved in the sorption process was evaluated at different initial MB concentrations.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Tea waste was washed with distilled water at  $100^\circ C$  to remove all the dirty particles, then reacted with concentrate sulfuric acid (98%) (tea waste:  $H_2SO_4$  ratio = 1:1.5,w/v) at the temperature  $90^\circ C$  for 4 h. The product cooled down to room temperature was filtrated and washed several times with distilled water, then neutralized by sodium bicarbonate solution (1%) to remove excess acid. The materials was further washed several times with distilled water and dried at  $800^\circ C$  for 24 h in the oven. The black material obtained was finally crushed in a mortar to the size of about 180 - 300  $\mu m$  and stored in a desiccator. This material is named as AC8 and used for further experiments.

## 2.2. Adsorbate

The basic dye, methylene blue (C.I. 52015, S.D. Fine Chemicals, 85% dye content, chemical formula  $C_{16}H_{18}N_3SCl$ , FW 319.86, nature basic blue, and  $\lambda_{max}$  665 nm) was used in this study. The MB was chosen in this study because of its well-known strong adsorption onto solids. The solution of this nature is blue in an oxidizing environment, but turns to colorless if exposed to a reducing agent. Methylene blue has been used as an indicator to analyze a number of elements in the kinematic method (Figure 1).

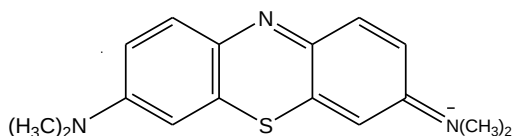


Fig 1. Structure of methylene blue dye

## 2.3 Adsorption studies

### 2.3.1 Effect of contact time

Contact time is one of the most important parameters for the assessment of practical application of adsorption process. In this experiment, 30 ml of the working solution with concentration of 30 mg/L was put in each different conical flasks. An adsorbent dose of 0.05 g/30 mL and an initial pH of 8 were used. The flasks were put in at shaker at 25°C for a predetermined time period ranging from 30 to 180 minutes with a 30 minutes interval while other parameters were kept at constant conditions. The flasks were then taken out and the absorbance of the solutions was measured. The percentage of dye adsorbed (% H) was plotted again the contact time.

### 2.3.2 Effect of initial pH

In this experiment, 30 ml of the 50 ppm methylene blue dye solution was put in different conical flasks. The optimum adsorbent dose as obtained from the above study (0.05 g) was put in each flask. The pH of each flask was adjusted in the range of 2 - 10 with dilute  $HNO_3$  (0.1 M) and NaOH (0.1 M) solution using a pH meter. Then, all the flasks were kept inside the shaker at 200 rpm and 25°C for 120 min. After that, the flasks were withdrawn and absorbance of the solutions was measured. A graph was plotted with % H vs. initial pH.

### 2.3.3 Effect of adsorbent dose

In this test, 30 ml of the working solution was put in each different conical flasks. Then, different adsorbent doses from 20 to 80 mg was added in each flask while other parameters are constant. And all the flasks were kept inside the shaker at 200 rpm and 25°C for 120 min. After that, the flasks were withdrawn from the shaker and the dye solutions were separated from adsorbents. The absorbance of all the solutions was then measured. A graph was plotted with percent removal (%H) vs. adsorbent dose.

### 2.3.4 Effect of temperature

This effect was investigated at temperature range from 298 to 328 K. The solution

was preheated on the magnetic stirrer and heater with a time of 120 min, shaking speed of 200 rpm at the respective temperatures while other parameters were kept constant. The flasks were then withdrawn from the shaker and the absorbance of the solutions was measured. A graph was plotted with % H vs. temperature.

### 2.3.5 Effect of adsorbate concentration

In this test, 30 ml of the methylene blue dye solution with concentration ranging from 15.31 mg/L, 25.54 mg/L, 46.15 mg/L, 98.92 mg/L, 172.20 mg/L, 205.28 mg/L, 257.28 mg/L, 302.07 mg/L, 343.58 mg/L, and 396.83 mg/L was put in each different conical flasks. The optimum contact time, adsorbent dose and pH obtained from the above studies was applied for this test. Then, all the flasks were kept inside the shaker at 200 rpm and 25°C. After that, flasks were withdrawn and the absorbance of the solutions was measured. A graph was plotted with %H vs. adsorbate concentration.

## 2.4 Data analysis

The data obtained were analyzed by using Microsoft Excel to get the mean, standard deviation, and linear regression values.

A graph was plotted with percent removal (%H) vs. adsorbent dose. %H is expressed as,

$$\%H = \frac{(C_0 - C_e)100}{C_0}$$

Where, %H=percentage of dye adsorbed,  $C_0$ =initial dye concentration (mg/L).  $C_e$  = equilibrium time solution. concentration (mg/L). The adsorption capacity was calculated as:

$$q = \frac{(C_0 - C_{cb})V}{M}$$

Where: V: the volume of the solution (L), M: the adsorbent amount (g),  $C_0$ : the initial concentration (mg/L),  $C_{cb}$ : the equilibrium concentration (mg/L), q: the adsorption capacity at equilibrium time (mg/g).

In the present investigation, the equilibrium data were analyzed using the Freundlich and Langmuir isotherm expressions given by the following equations, respectively,

$$\text{Freundlich : } q_e = K_f \cdot C_e^{\frac{1}{n}}$$

$$\text{Langmuir : } q_e = \frac{q_0 b C_e}{1 + b C_e}$$

where  $K_f$  and  $n$  are Freundlich constants related to sorption capacity and sorption intensity of adsorbents. The value of  $n$  falling in the range of 1–10 indicates favorable sorption.  $q_e$  is the adsorption density at equilibrium of MB,  $C_e$  is the equilibrium concentration of the dye in solution,  $q_0$  is the monolayer adsorption capacity, and  $b$  is the Langmuir constant related to the free energy of adsorption

### 3. RESULTS AND DISCUSSION

#### 3.1 Material synthesis and characterization

The Raman spectrum (Fig 2a) indicates two characteristic peaks at  $1340\text{ cm}^{-1}$  and  $1590\text{ cm}^{-1}$ , corresponding to D and G bands of carbon, respectively. Here, G and D bands infer the in-plane vibration of  $\text{sp}^2$  carbons and structural disorder mode. In addition, the XRD pattern (Fig. 2b) shows two broad diffraction peaks at  $24.121$  and  $43.51$ , corresponding to the (002) and (101) planes, respectively, which reveals the amorphous behavior of AC8.[3]

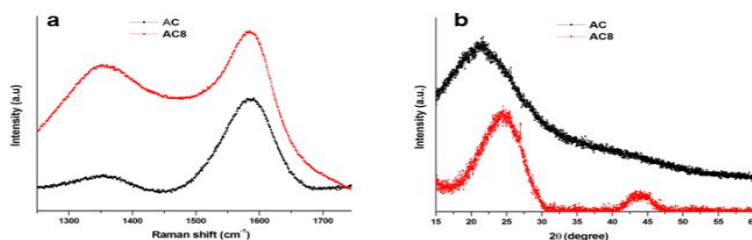


Fig 2.(a) Raman spectra, (b) XRD pattern of AC8

SEM analyses were applied for tea waste and AC8 in order to explore the surface texture and morphology of the adsorbent. The AC8 surface exhibited porous structure and a predominately microporous character which was responsible of the high surface area and adsorption capacity of this material (Figure 3)

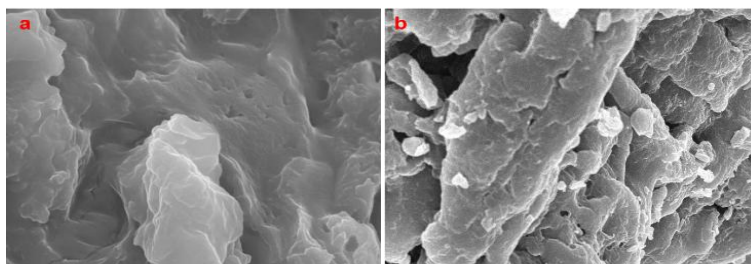


Fig 3. SEM image of (a) tea waste, (b) AC8

#### 3.2 The effect of contact time on the removal of MB dye

The effect of contact time on the removal of MB dye by AC8 at different equilibration times is given in Figure 4. It indicates that the rate of color removal increased depending on the contact time. For the first 90 min, the percentage removal for MB dye by the adsorbent was very fast. After that, it proceeded at a slower rate and finally attained saturation at different contact times for different initial concentrations of the dye.

The rate of removal of the adsorbate was higher in the beginning due to the large surface area of the adsorbent available for the adsorption of dye ions [6]. After a certain period, only a very low increase in the dye uptake was observed because there were few active sites on the surface of sorbent. From the contact time studied, it was revealed that 120 minutes of agitation time was sufficient to reach the equilibrium condition when 50 mg/L of dyes concentration was employed. Therefore, equilibrium time of 2 hours was selected for further adsorption studies.

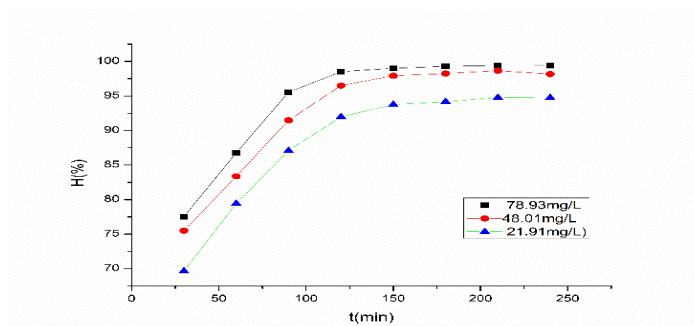


Fig 4. The effect of contact time on the removal of MB dye by AC8

### 3.3 Effect of initial pH

The effect of initial pH on adsorption percentage of MB dye was examined over a range of pH values from 2 to 10 and the results are presented in Figure 5. The dye removal was minimum at the initial pH 2. The dye adsorbed increased as the pH was increased from pH 2 to 7. Incremental dye removal was not significant beyond pH 8. For this reason, pH 8 was selected for future equilibrium studies.

After adsorption experiments, it was found that at low pH, the dyes become protonated. Therefore, the electrostatic repulsion between the protonated dyes and positively charged adsorbent sites resulted in decreased adsorption. Higher adsorption at increased pH may be due to increased protonation by the neutralization of the negative charges at the surface of the adsorbent. Hence, it facilitates the diffusion process and provides more active sites for the adsorbent. These findings obtained are in line with the results reported in the literature [5].

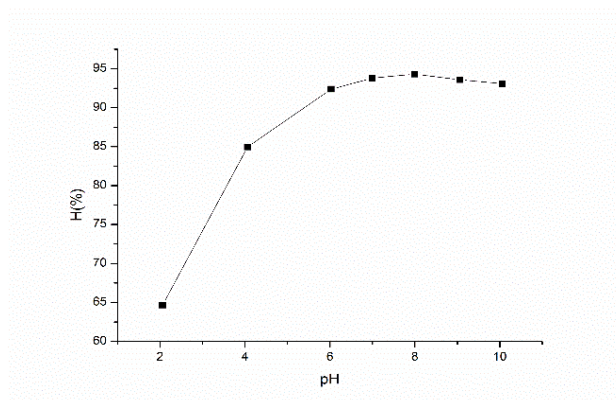


Fig 5. The effect pH on the removal of MB dye by AC8

### 3.4 Effect of adsorbent dosage

An attempt to enhance MB dye removal was evaluated by examining the effect of adsorbent dosage. This was conducted by varying the adsorbent dose from 20 mg to 80 mg at a dye concentration of 35.66 mg/L. As shown in Figure 6, it is apparent that the removal percentage of MB dye increased as the adsorbent amount increased and then became constant. The removal increased with increased amount of adsorbent dose up to a maximum efficiency (>90%). After that, an increase in adsorbent dosage did not

further improve the dye removal, implying that a complete dye removal could not be achieved even when large amount of adsorbent was used. From these results, an adsorbent dose of 50 mg was selected for subsequent equilibrium studies.

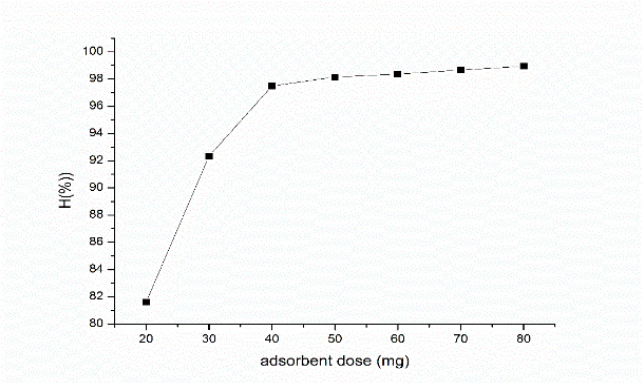


Figure 6. Effect of adsorbent dosage on bio adsorption of MB by AC8

### 3.7. Effect of temperature.

It is well known that temperature plays an important role in the sorption process [1]. The sorption of MB on AC8 was investigated in the temperature range of 298 - 328 K. As can be seen from Figure 7, an increase in temperature lead to a decrease in the removal efficiency. The percentage of dye removal decreased from 99.36 % to 97.93% with the increasing of temperature from 298 to 328 K. However, the data is very small and can be negligible. The amount of dye adsorbed decreased with the increase in temperature indicates that this system was an exothermic process.

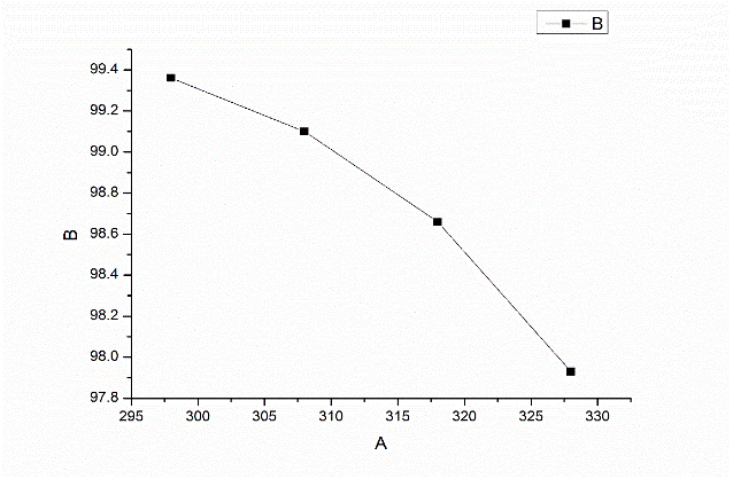


Fig 7. Effect of temperature

### 3.8 Effect of adsorbate concentration

The adsorption of MB on AC8 was studied by varying the MB concentration (15.31 – 396.83 mg/L) and the results are shown in Table 1. As seen from Table 1, the increasing concentration of MB resulted in the decrease of adsorption efficiency but increased the adsorption capacity.

Table 1: The dependence of MB adsorption on the MB concentration

| $C_o(\text{mg/L})$ | $C_e(\text{mg/L})$ | $H(\%)$ | $q(\text{mg/g})$ |
|--------------------|--------------------|---------|------------------|
| 15.31              | 0.20               | 98.69   | 9.07             |
| 25.54              | 0.38               | 98.51   | 15.10            |
| 46.15              | 0.73               | 98.42   | 27.25            |
| 98.92              | 2.56               | 97.41   | 57.82            |
| 172.20             | 6.28               | 96.35   | 99.55            |
| 205.28             | 9.34               | 95.45   | 117.57           |
| 257.28             | 18.00              | 93.00   | 143.57           |
| 302.07             | 21.73              | 92.81   | 168.20           |
| 343.58             | 42.11              | 87.74   | 180.88           |
| 396.83             | 75.16              | 81.06   | 193.00           |

### 3.9 Adsorption isotherm

The adsorption results in Table 2 showed that the Langmuir adsorption was the best model describing the adsorption of MB using AC8. Based on this model, the maximum adsorption amount ( $Q_{\max}$ ) was identified as 208.33 mg/g and the constant  $b = 0.169$ . Therefore, it could be concluded that the adsorption of MB followed the Langmuir model [7].

Table 2. Adsorption isotherm constants for the adsorption of MB by the AC8.

| Model      | Parameters        | MB     |
|------------|-------------------|--------|
| Langmuir   | $q_{\max}$ (mg/g) | 208.33 |
|            | $B$               | 0.169  |
|            | $R^2$             | 0.9976 |
| Freundlich | $N$               | 0.557  |
|            | $K_f$             | 0.0026 |
|            | $R^2$             | 0.9570 |

## 4. CONCLUSIONS

This study confirmed that AC8 could effectively remove MB from an aqueous solution. The amount of MB dye adsorbed was found to be dependent on solution pH, adsorbent concentration, initial dye concentration, and contact time. The basic MB dye adsorption decreased at low pH values in accordance with a presupposed ion-exchange mechanism of the adsorption. The optimal condition for favorable adsorption of dye was at pH 8. The adsorbent dose had an effect on the adsorption of MB dye with the equilibrium condition reached in ca. 2 h. From this study, the adsorption equilibrium data fitted the Langmuir isotherm equation. With the experimental data obtained in this study, it is possible to design and optimize an economical treatment process for the dye removal from industrial effluents by AC8. The results will form the basis for research oriented to the application of AC8 for waste water treatment.

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