

# Preparation of oil palm empty fruit bunch based activated carbon for adsorption of dye from aqueous solution

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**Abstract.** The objectives of this research are to determine an optimum condition for producing the activated carbon from oil palm empty fruit bunch (OPEFB) and used as an adsorbent to remove methylene blue (MB) dye from aqueous solution. Chemical activation by phosphoric acid ( $H_3PO_4$ ) was used as a procedure to modify OPEFB, in which in this study the carbonization and activation were done simultaneously. The concentrations of phosphoric acid were varied from 20-60% by weight and carbonization temperature and time were varied from 500-800°C and 30-60 minutes, respectively. It was found that among the conditions used, the best condition for producing activated carbon was obtained when using 60%  $H_3PO_4$  and carbonized at 500°C for 30 minute. The produced activated carbon had a surface area of 362.5  $m^2/g$  and average pore size of 2.94 nm. Methylene blue and Iodine numbers were 13.62 and 356.46 mg/g, respectively, which were comparable to the results of commercial activated carbon; i.e. 6.96 and 778.7 mg/g. The optimum condition for the adsorption of MB from synthetic wastewater by produced activated carbon was found at pH 8-12 with equilibrium time of 4 hours. Results demonstrated that the equilibrium data was well fitted by Freundlich isotherm model with the isotherm constants  $K_F$  of 7.75 mg/g and  $1/n$  of 0.13.

## 1 Introduction

Wastewater from tanning industry is one of the important environmental problems in Thailand. It has a wide impact especially on the communities around the plant. Reducing the toxicity of wastewater before releasing to the environment is a way to reduce the conflict between the factory and the surrounding community, and also compliance with an environmental legal standard.

Basic Dye is one of major dyes normally used in tanning industry. The dye molecule is composed of cationic ions and sometimes referred to as cationic dye. Methylene blue is an example of basic dye. Recently, there are many methods to remove dyes from wastewater such as; chemical precipitation, reverse osmosis, adsorption process, etc. Among these, adsorption by activated carbon is one of the promising processes since it is cheap, easy to operate and no chemical additional.

Oil Palm Empty Fruit Bunch (OPEFB) is waste material generated from crude palm oil extraction industry. Although, it is normally used as biomass fuel in a furnace to produce steam for palm oil production process, but many tons were generated each year and thus need to be removed. OPEFB is composed mostly of cellulose, hemicellulose and lignin with high fiber contents and large fiber size, so it has the ability to be used as a substrate for producing activated carbon [1-3].

Thus, the aim of this study was to investigate the removal of methylene blue by adsorption process using activated carbon prepared from OPEFB. 2-Level Full factorial design experiments were carried out; parameters such as concentration of activation reagent, temperature and carbonation time were varied to investigate their effect on activated carbon performance and their use for Methylene blue adsorption.

## 2 Materials and methods

### 2.1 Materials and reagents

OPEFB was obtained from Thai Taro & Oil Company, Ltd., the palm oil production company located at Surat Thani province in the South of Thailand. OPEFB was first washed, cut into 2-3 cm length size and then dried in an oven at 105°C for 12 h before use. Phosphoric acid >85% and Methylene blue used in this study were analytical grade obtained from Ajax Finechem and Merck, respectively. Nitrogen gas was from Airgas and used in high purity (>99.999%).

### 2.2 Synthesis of activated carbons from OPEFB

Dried OPEFB was chemical and physical activated by adding into 500 mL beaker containing a desired

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concentration phosphoric acid solution. The beaker was then placed on a heater stirrer and heated the mixture at 70°C for 1 h before left at room temperature for 2 h to cool down. Activated OPEFB was washed with distilled water 3-4 times until pH 7 was achieved, after that dried in an oven at 105°C for 12 h. The chemical and physical activated OPEFB was carbonized at different temperatures, under nitrogen atmosphere for different activation time. Nitrogen flow rate at 0.50 L/min and the rate of increasing temperature at 10°C/min were controlled during the carbonization. OPEFB based activated carbon was then weighed, ground and sieved to size <150 microns, and kept in a desiccator before used.

In order to find the key variables affecting % yield and the adsorption capacity of activated carbon, the two-level full factorial design experiments were carried out and the conditions used are shown in **Table 1**. Different parameters including acid concentration (20%:low and 60%:high), temperatures (500 °C:low) and 800°C:high), and activation times (30min:low and 60min:high) were selected to evaluate the performance of activated carbon produced. The total number of the experiments was 9 including one central point (average of high and low values for each parameter).

**Table 1.** 2-Level Full Factorial Design Experiments

RUN	Phosphoric acid Concentration )weight%(	Calcination Temperature (°C)	Time (min)
AC1	20	500	30
AC2	20	500	60
AC3	60	500	30
AC4	60	500	60
AC5	20	800	30
AC6	20	800	60
AC7	60	800	30
AC8	60	800	60
AC9	40	650	45

### 2.3 Methylene blue (MB) adsorption only

The applicability of OPEFB based activated carbon to remove Methylene blue dye was performed by adding 0.5 g adsorbent in a 250 mL conical flask containing 50 ml of dye solution concentration ranging from 20 to 250 mg/L at ambient temperature (28±2°C). The effect of solution pH was studied in the range of 2-12. The pH of the solution was adjusted by using HCl or NaOH. Effects of initial MB concentration (20-100 mg/L), adsorbent dosage (0.1-1.0g/50mL solution) were also investigated. All experiments were performed at 120 rpm stirring speed and done 3 times replicate to find average value. After fixed time, the sample was collected, filtered, and the concentration of dye remain in supernatant solution was determined using UV-VIS spectrometer at 663 nanometer wavelength. The adsorption capacity (mg/g) of OPEFB based activated carbon for Methylene blue was calculated from:

$$q_t = \frac{(C_o - C_f)V}{m} \quad (1)$$

where  $q_t$  is the adsorption capacity (mg/g) at time  $t$ ,  $C_o$  and  $C_f$  are the initial and final concentration (mg/L) of MB, respectively.  $V$  is the volume (L) of dye solution and  $m$  is the weight (g) of activated carbon.

### 2.4 Characterization techniques and measurement

Proximate analysis was done on raw OPEFB to calculate amount of water (moisture), ash, volatile matter, and fixed carbon contents by following ASTM standard procedures (ASTM D3173-87, D3174-93, and D3175-89) and the result is shown in **Table 2**. Low amount of ash and high content of fixed carbon indicated that OPEFB was suitable as a raw material for synthesizing activated carbon.

**Table 2** Proximate analysis of raw OPEFB

	Water (moisture)	ash	VM	FC
Raw OPEFB	17.81%	5.31%	54.47%	22.41%

A BET surface area analyzer was used to measure nitrogen adsorption isotherm at 77K, specific surface area, total pore volume, and average pore size of the activated carbon were obtained from the adsorption isotherm. The surface morphology of activated carbon was observed by Scanning Electron Microscope (SEM). Standard testing method JIS K 1470-1991 and ASTM D4607 were used to determine Methylene Blue Number and Iodine Number of the activated carbon. The point of zero charge (PZC) of the activated carbon used for adsorption experiment was determined, for this, 0.5 g of activated carbon was added to 100 ml of deionized water with varying pH from 2 to 12 (adjusted by 0.1M HCl or NaOH solution) and stirred at 120 rpm for 24 h. Difference between final pH and initial pH of the solution ( $\Delta$ pH) was plotted against the initial pH and PZC was then measured. The digital pH meter (Eutech Instrument, Model pH510) was used to measure the pH of the solution.

## 3 Results and discussion

### 3.1. Synthesis of OPEFB based activated carbon and adsorption capacity test

Prepared OPEFB was treated with two different concentrations of phosphoric acid and carbonized under nitrogen atmosphere at two different temperatures for 30 min and 1 h, and values of percentage of yield are shown in **Table 3**. Adsorption capacity experiments were carried out at ambient temperature (28±2°C) by using 10 g/L of activated carbon from RUN AC1 to AC9, 20 mg/L of methylene blue dye solution, at different contact time (0.25-24h). The removal of methylene blue and adsorption capacity values were plotted against contact

times (graphs are not shown), and values of adsorption capacity at equilibrium are also shown in Table 3.

The results from **Table 3** showed that %yield of activated carbon production decreased with an increase of calcination temperature and calcination time at both phosphoric acid concentrations. The reason can be explained on the fact that structure of OPEFB was more decomposed and released as volatile matter at higher temperature and longer calcination time. As a result, % yield of activated carbon was decreased. However, acid concentration showed a little effect on %yield of activation carbon (AC1 and AC3, AC5 and AC7).

**Table 3** also presents the values of equilibrium adsorption capacity, and it was observed that as the temperature and phosphoric acid concentration are increased, the equilibrium adsorption capacity increased. This can be attributed to greater surface area and bigger pore size of activated carbon when carbonized at higher temperature and acid concentration. However, the carbonization time showed little effect on equilibrium adsorption capacity.

**Table 3** Percentage of yield and adsorption capacity of OPEFB based activated carbon

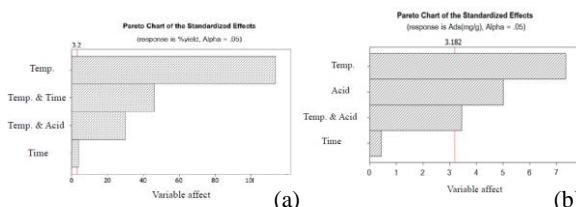
RUN	% Yield		Adsorption Capacity at equilibrium (mg/g)		MB No. (mg/g)	Iodine No. (mg/g)
	Experiment	model	experiment	model		
AC1	24.13	24.09	1.12	1.18	9.58	337.51
AC2	18.87	18.94	1.23	1.16	10.46	341.50
AC3	23.81	23.84	1.68	1.62	13.62	356.46
AC4	18.77	18.68	1.54	1.60	11.42	352.47
AC5	14.43	14.34	1.75	1.74	13.53	374.40
AC6	13.23	13.24	1.71	1.72	12.65	371.41
AC7	14.02	14.09	1.82	1.82	14.49	379.38
AC8	13.03	12.98	1.80	1.80	13.93	378.39
AC9	17.40	17.52	1.72	1.58	14.28	375.40
Com.	-	-	-	-	6.67	778.73

Analysis of variance (using Minitab program) was carried out on the basis of the experimental data in order to investigate key variables affecting on % yield and adsorption capacity (mg/g) of activated carbon, and the statistical analyses are shown in **Fig. 1**. It can be seen from **Fig. 1(a)** that the variables that influence with respect to decreasing the value of % yield followed the following order: Temp. > Temp. & Time > Temp. & Acid > Time. Whist, in **Fig. 1(b)**, the key variables that influence to lower the performance of activated carbon to remove dye are followed the following order: Temp. > Acid > Temp. & Acid > Time. Based on these analysis of variance data and linear regression analysis (p-value < 0.05 and R-sq > 95%), fitted polynomial models can be generated and are expressed in the following equations:

$$\%Yield = 52.38 - (0.046 \times Temp) - (23.816 \times Time) - (0.00643 \times H_3PO_4) + (0.027 \times Temp \times Time) \quad (2)$$

$$Adsorption\ capacity\ (mg/g) = -0.229 + (0.0024 \times Temp) + (0.0257 \times H_3PO_4) - (0.045 \times Time) - (2.958 \times 10^{-5} \times Temp \times H_3PO_4) \quad (3)$$

The models were used to predict %yield and adsorption capacity and the calculated values were shown in Table 3. From Table 3 similar values between the experiment data and those calculated by the regression model were noticed, indicating that the model can be used to predict yield and adsorption capacity at different condition. It was found that among the conditions used, RUN AC3 gave the best quality activated carbon with higher yield and acceptable adsorption capacity as shown in Table 3 and thus was chosen for subsequent Methylene blue adsorption studies.



**Figure 1** Analysis of variance effects on (a) %yield and (b) adsorption capacity of activated carbon using Minitab program

### 3.2 Methylene blue number and Iodine number

Standard testing method JIS K 1470-1991 and ASTM D4607 were used to determine Methylene Blue Number and Iodine Number of the activated carbon produced and with one selected commercial AC, values are shown in Table 2. The maximum MB No. and Iodine No. were found at RUN AC7 with equals to 14.49 and 379.39 mg/g, while for RUN AC3 values of 13.62 and 356.46 mg/g were observed, which are comparable to the results of commercial activated carbon; i.e. 6.96 and 778.7 mg/g. These results indicated that activated carbon produced in this study contained majoring mesopores while micropores were present in commercial one.

### 3.3 Methylene blue (MB) adsorption study

#### 3.3.1 Effect of initial MB concentration

Effect of pH on MB removal was examined by varying the pH of the solution from 2 to 12, with initial MB concentration of 100 mg/L, OPEFB activated carbon dosage of 0.5 g/50 mL at 28±2°C and 4 h of contact time (reached equilibrium). Adsorption Capacity of activated carbon for MB at different pH was shown in **Fig 2**. It was shown from **Fig 2(a)** that with an increasing pH from 2 to 12, the adsorption capacity of activated carbon increased (increased from 3.29 mg/g to 9.95 mg/g). The reason for this is mainly associated with abundance OH<sup>-</sup> ions at higher pH facilitated the electrostatic attractions between the positively charged dye cations and negatively charged adsorption site, thus increased the dye uptake. The similar phenomenon has been reported in other studies [4, 5]. The points of zero charges (PZC) of the activated carbons were also determined and the results were shown in **Fig 2(b)**. PZC was found at pH 5.65, indicated that above this pH of solution adsorption sites of AC produced become more negative and

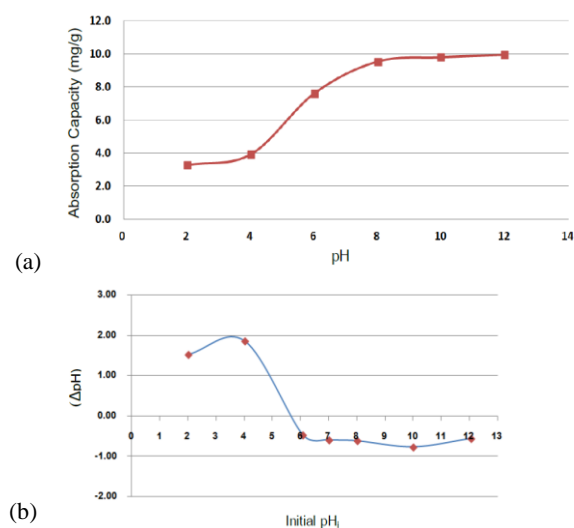
enhancing the capacity to adsorb MB positive ions, and confirmed the pH effect results mentioned earlier.

### 3.3.2 Effect of initial MB concentration

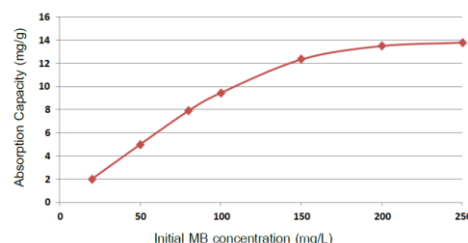
The initial concentration of dye solution provides an important driving force to overcome mass transfer limitation between liquid and solid phases. Initial MB concentration was varied from 20-100 mg/l to investigate its effect to adsorption capacity. **Fig. 3** showed the absorption capacity of activated carbon at each value of initial MB concentration, and it appeared that the capacity of activated carbon produced increased when initial concentration was increased and the maximum value was noticed at 250 mg/L. However, a further increase in concentration from 150 mg/L to 250 mg/L slightly enhanced the adsorption capacity. With increase in MB concentration, competition for the active adsorption sites increased and slow down the adsorption process.

### 3.3.3 Effect of activated carbon dosage

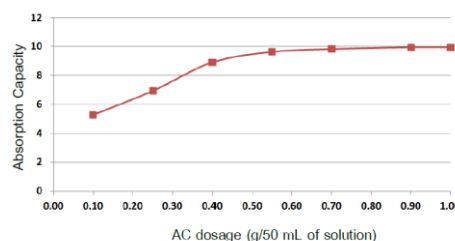
Adsorbent dosage is another important factor for MB removal by adsorption process. The activated carbon dose (varying from 0.1 to 1.0 g/50 mL of MB solution) on the capacity of activated carbon to remove MB was shown in **Fig. 4**. It was observed that MB removal increased with increasing adsorbent dose up to 0.5 g/50mL of solution and then rate of increase slow down. Initially, the capacity of activated carbon to adsorb MB increased rapidly can be attributed to greater surface area and availability of more adsorption sites. However after the certain dose, although there is abundant of adsorption sites available but there is a shortage of MB adsorbate in the solution.



**Fig. 2.** (a) Effect of pH solution on MB adsorption (AC3: 0.5g dosage/50mL of 100 mg/L MB solution, 4 h contact time)  
 (b) The point of zero charge (PZC) experiment



**Fig. 3.** Effect of initial MB initial concentration on adsorption capacity of activated carbon (AC3: 0.5g dosage/50mL solution, pH=7, 4 h contact time)



**Fig. 4.** Effect of activated carbon dosage on adsorption capacity (AC3: 100 mg/L of MB solution, pH=7, 4 h contact time)

### 3.4 Adsorption isotherms

Langmuir and Freundlich models were used to examine the adsorption behavior of activated carbon derived from OPEFB and one commercial AC used in this study, and the linear equations for each model are presented by **Eqs. (4)-(5)**, respectively.

$$1/q_e = (1/q_m b C_e) + 1/q_m \quad (4)$$

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (5)$$

where  $q_e$  (mg/g) is equilibrium adsorption capacity,  $C_e$  (mg/L) is the equilibrium MB concentration,  $q_m$  (mg/g) and  $b$  (L/mg) are Langmuir constants related to adsorption capacity and rate of adsorption,  $K_F$  and  $n$  are Freundlich constants related to a measure of adsorption intensity. The parameters evaluated from isotherm models are reported in **Table 4**.

**Table 4** Adsorption isotherm parameters

	Langmuir Isotherm model			Freundlich Isotherm model		
	$q_m$ (mg g <sup>-1</sup> )	$b$ (L mg <sup>-1</sup> )	$R^2$	$K_F$ (mg L <sup>-1</sup> )	$1/n$	$R^2$
AC3	12.59	1.53	0.8323	7.75	0.13	0.995
Com	7.07	0.726	0.999	4.48	0.103	0.928

From the correction coefficient showed in Table 3 the adsorption data of AC3 were better fitted in the Freundlich Isotherm model ( $R^2=0.995$ ), while for commercial AC were better fitted with the Langmuir Isotherm model ( $R^2=0.999$ ). This correction data suggested that a multilayer adsorption of MB occurred on the surface of our activated carbon produced, while a homogenous monolayer adsorption of dye molecules occurred at the outer surface of commercial AC. This may be due to the fact that the experimental AC has contained majority mesopores, resulting in a heterogenous absorption.

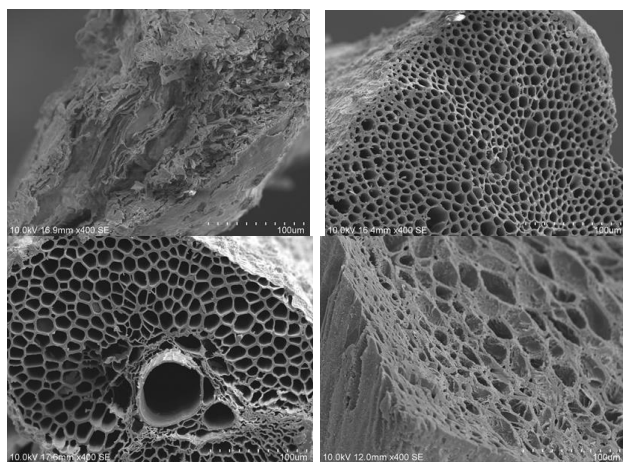
### 3.5 BET surface analysis

BET surface analyzer was used to measure surface area and average pore size of raw OPEFB, OPEFB based activated carbon, and commercial activated carbon and the data were reported in **Table 5**.

It is shown in **Table 4** that the activation by chemical and thermal treatment can improve both surface area and average pore size of raw OPEFB. BET surface area increased from 26.88 m<sup>2</sup>/g to 362.50-381.50 m<sup>2</sup>/g and pore size increased from 2.28 nm to 2.94-3.18 nm, for raw OPEFB and AC produced from OPEFB, respectively. Table 4 also shows that for commercial AC, its surface area was greater but had a smaller average pore size when compared to the AC3 and AC7. This may be the reason that can explain the monolayer adsorption behavior of the commercial AC. Due to the fact that commercial AC has smaller pore size than AC derived from OPEFB and based on its low MB No. and high Iodine No., it can be concluded that commercial AC used in this study was inferior for MB adsorption when compared to the OPEFB based AC. SEM images shown on **Fig. 5** also confirmed porosity of AC produced from OPEFB.

**Table 5.** BET surface analysis

Sample	BET surface area (m <sup>2</sup> /g)	Average pore size (nm)
Raw OPEFB	26.88	2.28
AC3	362.50	2.94
AC7	381.50	3.18
Commercial AC	814.30	2.38



**Fig. 5.** Porosity images observed by SEM of raw OPEFB (upper left), AC3 (upper right), AC7 (lower left), and commercial AC (lower right)

### 4 Conclusion

The activated carbon produced from oil palm empty fruit bunch (OPEFB) show a good adsorption capacity of Methylene blue dye. The activated carbon yield obtained ranged from 13.03-23.81% and equilibrium adsorption capacity was observed from 1.12-1.82 mg/g. It was

found that the best condition for producing activated carbon was obtained when using 60% H<sub>3</sub>PO<sub>4</sub> as an activating agent and carbonized at 500°C for 30 minute. Carbonization temperature was the most significant effect on both the yield and adsorption capacity of AC compared to acid concentration and carbonization time. The produced activated carbon had a surface area of 362.5 m<sup>2</sup>/g and average pore size of 2.94 nm. Methylene blue and Iodine numbers were 13.62 and 356.46 mg/g, respectively. The optimum condition for the adsorption of MB from aqueous solution by produced activated carbon was found at pH 8-12 with equilibrium time of 4 hours. Results demonstrated that the equilibrium data was well fitted by Freundlich isotherm model with the isotherm constants K<sub>F</sub> of 7.75 mg/g and 1/n of 0.13.

However, adsorption capacity of the experiment AC for MB adsorption was lower than the values from some researches, thus future research such as surface modification needs to be carried out.

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