

# Decolorisation of Biologically Treated Palm Oil Mill Effluent (POME) Using Adsorption Technique

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**Abstract:-** An experimental study was conducted on the adsorption of color from biologically treated POME using palm kernel shell (PKS) and empty fruit bunches (EFB) as natural biosorbents, and activated carbon prepared from them by microwave and chemical activation with potassium hydroxide (KOH). BET surface area of all sorbents was determined and  $1252 \text{ m}^2 \cdot \text{g}^{-1}$  was recorded for activated carbon prepared from PKS by chemical and microwave method (PKSCM). Adsorption performance was investigated as a function of contact time, adsorbent concentration, and pH. The adsorbents studied exhibit high efficiency for color adsorption. Adsorption increased with increasing contact time and the equilibrium states could be achieved in 12 hr. Optimum dose of adsorbents was found at 5g/100ml. The maximum uptake of color by all adsorbents occurred at pH of 2. A maximum percentage of color removal of 100% was obtained at the optimum conditions for PKSCM. Results were analyzed by the Langmuir and Freundlich isotherm models. Based on regression coefficient equilibrium, the data was found to fit well to the Langmuir equilibrium model. Pseudo-first order, pseudo-second order, and second order kinetic models were used to test the adsorption kinetics. Evaluation of experimental data indicated that the surface adsorption of color follows the pseudo-second order equation.

**Keywords:-** adsorption, color removal, empty fruit bunch, microwave, palm kernel shell, palm oil mill effluent POME.

## I. INTRODUCTION

Oil palm currently occupies the largest acreage of farmed land in Malaysia. Palm oil mill industries are large industrial consumers of water as well as producers of wastewater. The effluent discharged from an oil mill is still objectionable whereas the situation in many countries is quite different where much attention has been given to the subject of effective disposal [1].

Palm oil mill effluent (POME) is a colloidal suspension of 95 - 96% water, 0.6 - 0.7% oil and 4 - 5% total solids including 2 - 4% suspended solids originating from the mixing of stabilizer condensate, separator sludge and hydro cyclone wastewater that are mostly debris from palm fruit mesocarp [2]. The quantity of POME produced is about 60% for every ton of fresh fruit bunches (FFB) processed. The color of the effluent is derived from plant constituents such as lignin and phenolic compounds as well as repolymerization of coloring compounds after anaerobic treatment [3]. Color in the effluent from industry inhibits the growth of the desirable aquatic biota necessary for self purification by reducing the penetration of sunlight with a consequent reduction in photosynthetic process activity [4, 5]. In addition, the color reduces dissolved oxygen which can be hazardous to micro and macro-aquatic life [5, 6]

The oil palm mills generate many byproducts and wastes besides the liquid wastes mentioned above, that may have a significant impact on the environment if they are not properly dealt with. The most common among these byproducts is the empty fruit bunch (EFB) and the palm kernel shell (PKS). The empty bunch is a solid waste product of the oil palm milling process and has a high moisture content of approximately 55 - 56% and high silica content starting from 25% of the total palm fruit bunch [7]. The common way of disposal of these unwanted byproducts is by burning in simple incinerators, burning in the open, putting in landfills, or leaving to rot in massive piles, all of which pose environmental problems. These cause major pollution which poses a serious problem for the country.

Physical pretreatment of POME consists of stages such as screening, sedimentation, and oil removal prior to the secondary treatment in biological treatment systems. However this treatment process is still inefficient which may lead to several environmental pollution issues. This is largely due to the high BOD load and low pH of POME, together with the colloidal nature of the suspended solids, which renders POME treatments by environmental methods difficult [8]. Several researchers have used the composting technology for managing the liquid waste coming from agro-industries.

Today, many industries commonly use activated carbon as adsorbent agent for dye removal. Adsorption by activated carbon has advantages over other methods due to availability, profitability, efficiency and the simple and sludge free design [9]. The high cost of activated carbon has encouraged research in order to

find alternative low cost adsorbents. Nowadays, there are many low cost, commercially available adsorbents which are being used for dye removal [10-11]. However, as the adsorption capacities of the above adsorbents are not very large, new adsorbents that are more economical, easily available and highly effective are still needed. Producing inexpensive AC is one of the main challenges in commercial manufacturing. To this end, new production techniques and the use of inexpensive raw materials have been studied [12], including the use of agricultural waste as an inexpensive precursor with high carbon content and low inorganic content [13,14]. Several studies were initiated to utilize EFB and PKS as the crude material for activated carbon and it is reported that a good quality product can be obtained, especially from PKS, because of its granular structure, insolubility in water, chemical stability, and high mechanical strength [15, 16]

Activated carbon is usually prepared by conventional carbonization, where samples are heated externally. However, this method of carbonization takes a long time leading to inefficient energy use. To overcome this problem, microwave pyrolysis has been proposed as an alternative to conventional activated carbon preparation technique. Microwave radiation heats materials internally making it an ideal solution for carbonizing samples faster. The low electricity consumption and size of material being heated was also shown to be inversely proportional [17], giving microwave pyrolysis an advantage over conventional carbonization. In view of maximizing waste utilization, an adsorption method using solid waste from palm oil industry to treat the POME may need to be introduced. Therefore, in this study, we investigate the use of EFB and PKS as a natural biosorbent and the activated carbons produced from them for the reduction of color from POME.

## II. MATERIALS AND METHODS

**2.1 Palm kernel shell:** PKS samples were collected at Dengkil, Selangor, Malaysia. The samples were washed, dried and grinded to particle size range of 0.5-1.0 mm. Microwave heating was conducted in a 2.45 GHz commercial microwave oven. The oven has a power controller to select different power levels and a timer for various exposure times at a set microwave power level. Activation was performed in a reactor fixed in the chamber of the microwave oven at a power level of 1000 W and 8 min of exposure time. Nitrogen gas at a pre-set flow rate of (300 cm<sup>3</sup>/min) was used to purge air in the reactor before the start of microwave heating and it continued to flow during the activation stage. This sample was labeled as (PKSM). Another sample was produced by chemical activation of the natural PKS by soaking in potassium hydroxide (KOH) solution with an impregnation (PKS: KOH) ratio of 1:1.75 (wt%) for 48 hours. This sample was then placed in the microwave as above. The microwave power and irradiation time was selected based on preliminary runs. The activated product was then washed with deionized water and hydrochloric acid of 0.1M until the pH of the washing solution reached 6–7. This sample was labeled as (PKSCM).

**2.2 Empty fruit bunches** The EFBs were collected from the Nottingham University Malaysia campus, in plastic bags and stored in the laboratory cold room at 4°C for later use. The EFB samples were dried at 105°C for 24 h in the oven to remove the moisture content until constant weight was obtained. The sample was then grounded using Ultra Centrifugal Mill ZM 200 with a mesh size of 0.2mm, and were sieved using an ELE international laboratory sieve with a size of 125 micron. Microwave and chemical activations were done as above. Samples were labeled as EFBM and EFBM for microwave activation, and chemical followed by microwave activation respectively.

### 2.3 POME preparation

The effluent was collected from the final pond effluent of a palm oil mill in Dengkil, Selangor, Malaysia, in plastic containers. The containers were properly washed and rinsed with the effluent before collection to avoid contamination and dilution. Containers were then brought back to laboratory and stored in refrigerator at temperature of 4°C for tests and analysis. The final treated effluent concentration of color is 9900 PtCo. unit. It was observed that the biologically treated POME was still objectionable and the color concentration was still extremely high. POME pH was (8.4) which indicated that the biologically treated POME was alkaline.

### 2.4 Instrumentation and analyses of various parameters

The color analysis was carried out by following platinum-cobalt standard method 8025 and the color was detected at a wavelength of 455 nm using HACH spectrophotometer (DR 2800, Loveland, CO). (Memmert Universal hot air oven Model UFE 600 - Germany) was used for drying. The materials were grounded by using Retsch Cutting Mill SM 100 (Germany) with mesh size 0.2, and screened using ELE international laboratory sieve shaker (USA) with required mesh size. In the adsorption experiments, all solutions were thermally set and stirred by using digital orbital shaker (Heidolph unimax 1010, Germany). Microwave heating was conducted in a 2.45 GHz modified commercial microwave oven Panasonic (NN-CD997SMPQ). The oven has a power controller to select different power levels (550, 700 and 1000 W) and a timer for various exposure times (2, 5, 8, 12 min). Scanning electron microscopy (SEM) (JSM-6390LV (JEOL Ltd., Japan) Scanning Electron Microscope) was used to identify the surface physical morphology.

A Micromeritics ASAP-2020 instrument was used for the adsorption isotherms of N<sub>2</sub> at -196 °C to clarify textural properties of produced ACs. Prior to measurement, the samples were degassed under vacuum at 350 °C and 10–5 Torr for 10 h. Approximately 0.15 g of the degassed samples was used in each adsorption experiment. By analyzing the N<sub>2</sub> adsorption profile, the BET surface area was obtained.

**2.5 Chemical characterization:** To test the moisture content, the activated carbon prepared was weighed, oven dried (100 °C, 24 h), and reweighed. The ash content was determined by igniting the moisture free activated carbon in furnace (500 °C, 1 h) followed by second ignition (700 °C, 4 h), and weighing.

**2.6 Adsorption study:** (a) Effect of adsorbent dosage: Five different adsorbent dosages (1, 2, 3, 4, and 5 g) were mixed with 100 ml of biologically treated POME in an (250 ml) Erlenmeyer flask. The flasks were then shaken in an isothermal shaker at 120 rpm at 30°C for 14 hrs to reach equilibrium. (b) Effect of contact time: Seven different contact time durations (0.5, 1, 2, 4, 7, 10, and 14 hrs) were examined. 4.0 g of adsorbent at pH 8.4 was added to each flask and agitated on rotary shaker (120 rpm at 30°C). Prior to the analysis, all samples were filtered to prevent interference from adsorbent fines.

The amount of color adsorbed per unit mass of adsorbent at equilibrium conditions,  $q_e$  (mg/g), was calculated by [18],

$$q_e = \frac{(C_o - C_t) \times V}{m} \quad (1)$$

where  $C_o$  (mg L<sup>-1</sup>) is the initial concentration of color,  $C_t$  (mg L<sup>-1</sup>) is the residual color concentration in solution at time  $t$ ,  $V(L)$  is the volume of the solution, and  $m$  (g) is the mass of adsorbent. The measurement of each sample was replicated twice and averaged. To calculate the color adsorption efficiency by prepared adsorbents, the following equation was used:

$$(\%) \text{Removal} = \frac{(C_o - C_t)}{C_o} \times 100 \quad (2)$$

### III. RESULTS AND DISCUSSION

#### 3.1 Physical characterization

The results of the physical characterization of the raw materials are summarized in Table 1. Palm shell is suitable for adsorption due to its ability to be modified, thus becoming high porosity carbon. From the elemental analysis, weight percentage of the carbon is the highest. Other elements can be removed in high temperature, due to the gaseous composition, therefore increasing the carbon content. Apart from that, high lignin content and low cellulose content makes activation on palm shell in short time due to less fibrous structure [19]. However, upon carbonization, palm shell undergoes high weight loss of approximately 50%. The low ash content indicates that palm kernel shell is a suitable precursor for preparation of activated carbon. The ash content is a measure of the minerals as impurities in carbons, mainly derived from the carbon precursor. Ash consists mainly of minerals such as silica, aluminum, iron, magnesium and calcium which are not desired [20]. The BET surface area (SBET), total pore volume ( $V_{tot}$ ), and average pore size of natural and activated adsorbents were determined from the physical adsorption data of N<sub>2</sub> at 77 K and the values are shown in Table 2.

#### 3.2 Microwave and chemical activation

Conventional heating is one of the most applicable preparation methods for producing AC. In this method, heat is transferred to the samples by conduction, convection, and radiation mechanisms. The surface of the particles is heated before their interiors, inducing a thermal gradient between the surface and core of each particle. This thermal gradient leads to an inhomogeneous microstructure for high heating rates. As an alternative heating method, microwave irradiation has produced promising results over the last several years in the production of low-cost and homogeneous AC with high energy savings. These results are related to the direct heating of the particle interior by microwave radiation, which induces rapid volumetric heating [21].

It can be seen from Table 2 that the microwave activated carbons have the highest surface area and total pore volume. Inside the microwave oven a high temperature could be reached in comparatively shorter periods of time resulting in dissipation of huge amounts of energy at the molecular level. Consequently, the roughness of the pore walls may also be increased due to rapid heating with the formation of additional active sites. Besides, rapid heating could accelerate the release of tar or volatile matter from the pore interior which results into higher pore volume [22]. Microwave treatment enhances the basic properties of the activated carbons at the expense of the acidic properties. Acidic surface oxygen functional groups are more weakly attached to the carbon surface than basic ones. During microwave treatment, acidic surface oxygen functional groups are released as CO<sub>2</sub> and CO [23]. Activated carbons were prepared from palm kernel shell and empty fruit bunch as a precursor with chemical activation using potassium hydroxide as activating agent. Potassium hydroxide is a common activating agent in activated carbon manufacturing industries. This chemical was chosen in this work due to its cleaner production technology compared to the use of ZnCl<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub> and other chemical agents that are frequently used. The function of the dehydrating chemical agent is to inhibit the formation of tar and other undesired products during the carbonization process. It is important for activated carbon to have high

surface area. Commercial activated carbons have specific areas between 600 and 1200m<sup>2</sup>/g. From previous studies, Jumasih et al. [24] produced surface area of 1088m<sup>2</sup>/g from palm kernel shell activated carbon, Adinata et al. [25] produced 1170m<sup>2</sup>/g surface area by chemical activation with K<sub>2</sub>CO<sub>3</sub> from palm shell. 1141m<sup>2</sup>/g surface area was obtained from empty fruit bunch by Hameed et al. [26].

**Table 1: Physical properties of raw material (dry basis)**

Biosorbent	Moisture content	Ash content	Volatile material	Fixed carbon
PKS	4.78	2.26	74.11	18.85
EFB	5.91	5.13	69.24	19.72

**Table 2: Textural characteristics of studied adsorbents**

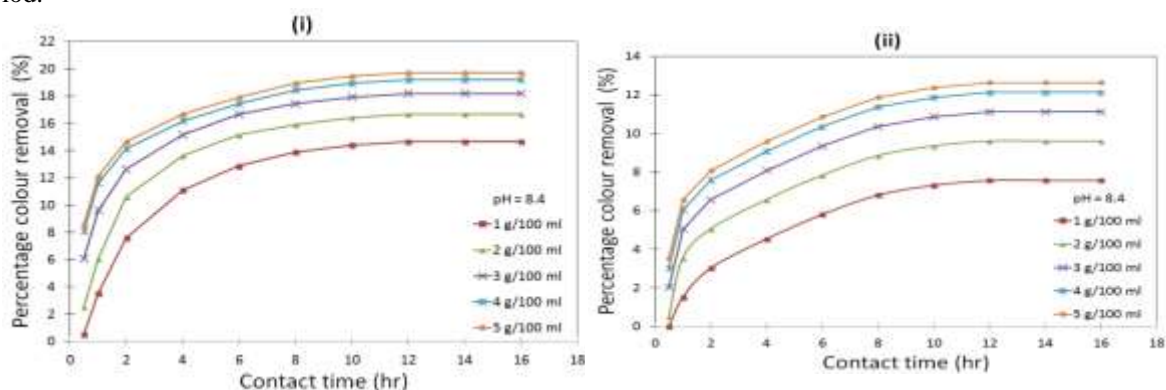
Adsorbent	BET surface area (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Pore size width (Å)
PKSN	13.187	0.017516	8.925
EFBN	4.392	0.016801	5.446
PKSM	1065.903	0.6124	24.275
EFBM	879.811	0.5809	21.898
PKSCM	1252.741	0.7233	27.456
EFBCM	1137.85	0.6541	25.089

### 3.3 Performance Study

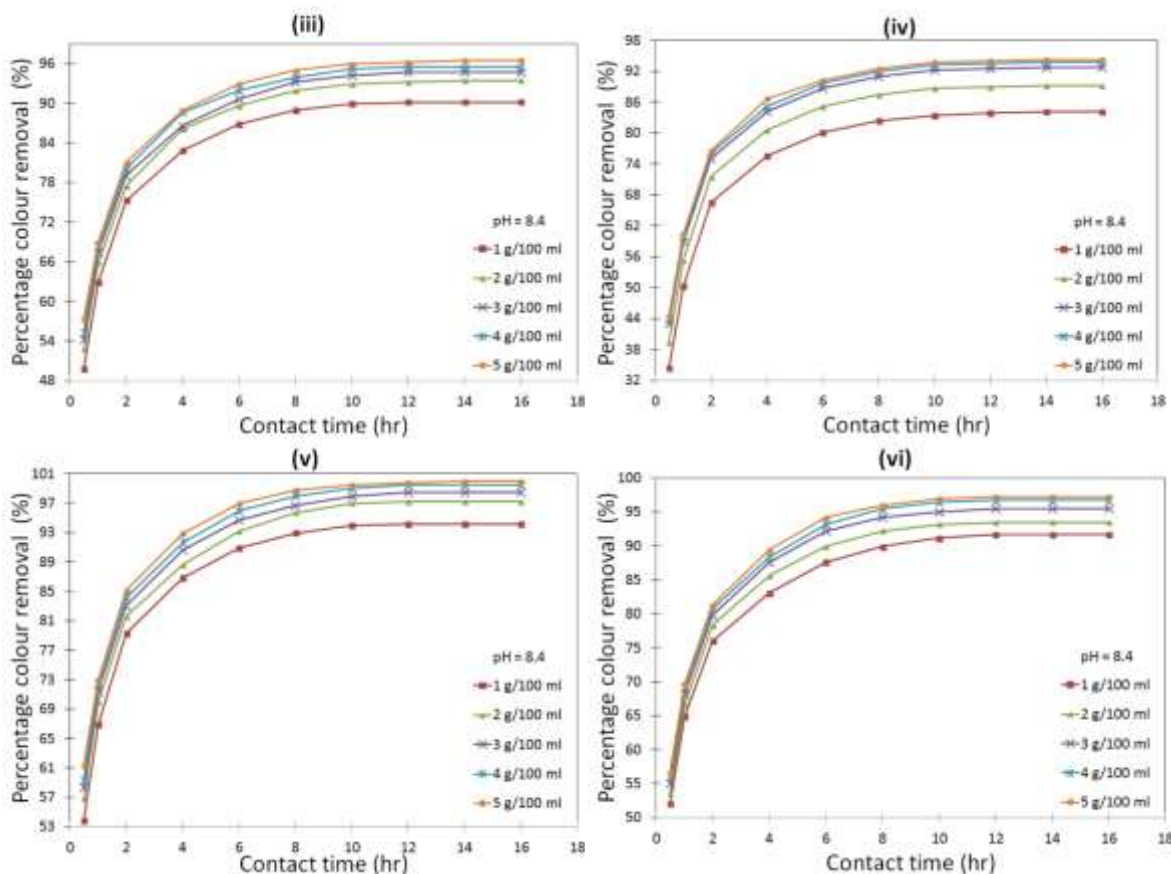
PKS, EFB and activated carbons prepared from them were used for removal of highly colored effluent of biologically treated POME and nearly 100% removal of color was observed. The dark brown color of palm oil mill effluent consisted of many organic compounds such as anthrocyanin and carotene pigment that was extracted from fresh fruit bunches in the sterilization process. Moreover, it included polyphenol compounds, tannin, polyalcohol and melanoidin [27]. Removal of color depends on,

**3.3.1 Contact time** — the curve adsorption uptake, qt as a function of time, t is presented in Fig.1. Adsorption uptake and dye removal efficiency increased with prolonged contact time. The adsorption process increased sharply at the initial stage (Fig.1) indicating availability of readily accessible sites. The process gradually slowed down as the equilibrium approached. The time profile of dye uptake is a single, smooth and continuous curve leading to saturation, suggesting possible monolayer coverage of color onto the surface of adsorbent. It is observed from the figure that color removal is maximum at a contact time of 16 hr and as the contact time is increased the efficiency of color removal is increased.

**3.3.2 Dosage of adsorbent** — Adsorption rate depends on driving power per area unit. In this case, that is true as long as the initial concentration of the solution and other variables of the system remain constant. Several adsorbent concentrations were used to determine the efficiency of color removal and choice of the best adsorbent concentration in the adsorption process of the color at 25°C (Fig.1). The adsorbent dosage was varied from 1 to 5 g/100 ml. It was observed that increasing the adsorbent dosage increased the removal efficiency. The results clearly indicate that the removal efficiency increases to an optimum value at adsorbent dosage of 4 g above which further increase in adsorbent dosage has no significant effect on it, but the value remains constant. This could be explained by the fact that adsorption equilibrium has been reached between the adsorbent/POME, thereby, preventing further color removal by the excess adsorbent dosage. In Fig.1, it was observed that efficiencies are greater than 94.19% with 10 g L<sup>-1</sup> of adsorbent, reaching up to 100%, for 50 g L<sup>-1</sup>, in a 12-hour period.







**Fig.1. Effect of contact time and adsorbent dose on adsorption of color on: (i) PKS<sub>N</sub>, (ii) EFB<sub>N</sub>, (iii) PKS<sub>M</sub>, (iv) EFB<sub>M</sub>, (v) PKS<sub>CM</sub>, and (vi) EFB<sub>CM</sub>.**

**3.3.3 pH of POME** — Fig. 2 illustrates the profile of pH effect on the percentage removal of color.

It is well known that adsorption processes depend highly on pH because of the high sensitivity of functional groups of the adsorbate. Activated carbons are materials with amphoteric character; thus, depending on the pH, their surfaces might be positively or negatively charged, which has a direct influence regarding the interactions of electrostatic nature. Alterations in environment pH can lead to changes in adsorbent surface load and affect the degree of color attraction. Solution pH affects adsorption by regulating the adsorbent's surface charge as well as degree of ionization of adsorbates present in the solution [28]. The activity of an adsorbent is due to the presence of different functional groups: carboxylic ( $-\text{COOH}$ ), sulfonyl ( $-\text{S}-\text{O}$ ), amine ( $-\text{NH}_2$ ), hydroxyl ( $-\text{OH}$ ), etc. At higher pH (basic pH), these groups become anionic in nature (carboxylate,  $\text{COO}^-$ ) and are not suitable for the adsorption of negatively charged color causative molecules due to interionic repulsion between similarly charged particles. The adsorption of an anionic dye generally decreases with an increase in pH, and this phenomenon is associated not only with the negative charge on the surface of the adsorbent but also with excess  $\text{OH}^-$  ions in the solution that compete for the adsorption sites [29]. It is obvious that the color removal increased with decrease in pH values and as the pH was increased from 2 to 8.4, the color removal efficiency was decreased by about 40%. This may be attributed to the degree of the protonation of the active groups of the adsorbent surface. Because the materials responsible for POME color are characterized by the presence of hydroxyl groups, these anionic functions are attracted by protonated groups of the surface. Thus, the protonation of the surface active groups was necessary for the attraction of hydroxyl groups, which led to the color removal. The effect of pH was studied by varying the pH of POME solutions from 2 to 12 with an initial concentration of 9900 PtCo/L, as shown in Fig. 2. The decrease in pH caused a significant enhancement of the adsorption capacity of color. Yet, the effect of pH value on the quantity of color adsorbed was diversified. In this work, increasing pH value from 2.0 to 8.4 was observed to diminish the adsorption capacity of PKS<sub>N</sub> and EFB<sub>N</sub>. Whereas it was observed that the successive increase in pH value up to 12.0 no longer had a significant effect on the adsorption capacity (Fig. 2). During adsorption onto prepared activated carbons, as in the case of PKS<sub>N</sub> and EFB<sub>N</sub>, the pH value also affected the effectiveness of the sorption process. Also, increasing the pH value from 2.0 to 12.0 evoked a successive decrease in the quantity of the color adsorbed. Analogous results, pointing to the influence of the pH value on the quantity of dye adsorbed, were reported in other works of, among others: Chiou and Li [30], Wen et al. [31], Muhammad et al. [32],

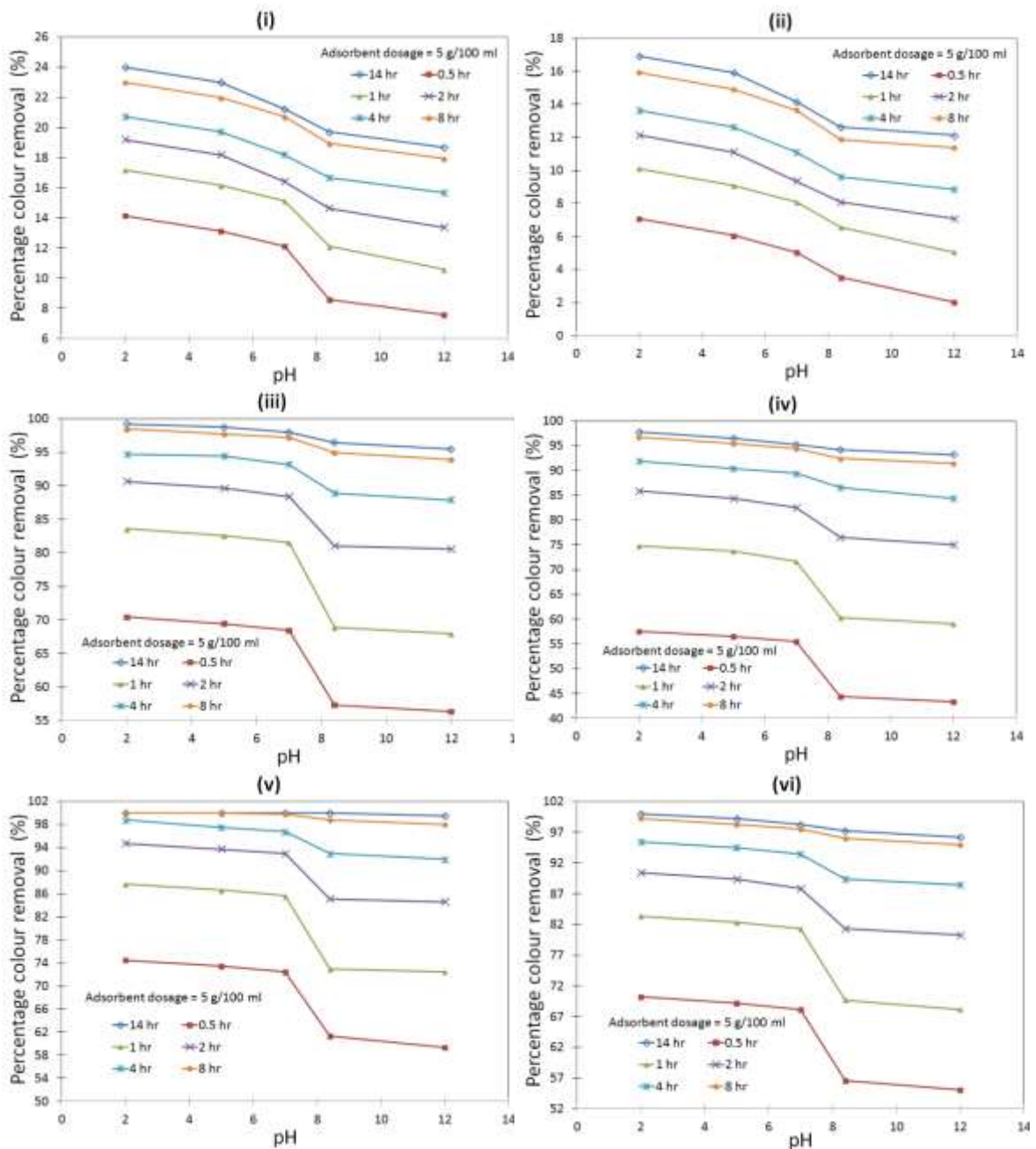


Fig.2. Effect of pH and contact time on adsorption of color on: (i) PKS, (ii) EFB, (iii) PKS, (iv)

EFB, (v) PKSC, and (vi) EFB.

### 3.4 Sorption isotherm

When an adsorbent is in contact with the surrounding fluid of a certain composition, adsorption takes place and, after a sufficiently long time, the adsorbent and the surrounding fluid reach equilibrium. Generally, an adsorption isotherm is an expression or diagram, which provides information about the fraction of a surface that is covered by adsorbed molecules in equilibrium at constant temperature as a function of pressure or concentration [33]. Adsorption isotherms are described in many mathematical forms, some of which are based on a simplified physical picture of adsorption and desorption, while others are purely empirical relationships intended to correlate the experimental data in simple equations with two or at most three empirical parameters, the more the number of empirical parameters the better the fit between experimental data [34]. Two isotherms; Freundlich and Langmuir isotherms were chosen to analyze the adsorption process. The Freundlich and Langmuir isotherms are the earliest and simplest known relationships. The relative coefficients of these models are calculated using linear least-square fitting. The Langmuir model assumes that uptake of color occurs on a

homogenous surface by monolayer adsorption without any interaction between adsorbed materials [35] and can be written in linear form as:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + 1/(Q_m b) \tag{3}$$

where  $q_e$  and  $C_e$  are color equilibrium concentration in adsorbed and liquid phase in mg/g and PtCo/L, respectively.  $Q_m$  and  $b$  are Langmuir constants representing the sorption capacity (in mg/g) and energy of sorption, respectively. These constants can be calculated from the intercept and slope of the linear plot,

$$\frac{C_e}{q_e} \text{ vs } C_e \tag{4}$$

The essential characteristics of the Langmuir isotherm can be expressed in terms of either a dimensionless constant separation factor or equilibrium parameter,  $R_L$

$$R_L = 1/(1 + b C_o) \tag{5}$$

where  $R_L$  is a dimensionless separation factor,  $C_o$  is the initial dye concentration (PtCo/L) and  $b$  is the Langmuir constant (L/PtCo). The parameter  $R_L$  indicates the shape of isotherm, as follows:  $R_L > 1$  unfavorable,  $R_L = 1$  linear,  $0 < R_L < 1$  favorable,  $R_L = 0$  irreversible.

The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface [35] and can be written in the linear form as;

$$\log q_e = \log K_F + \frac{1}{n} C_e \tag{6}$$

where  $K_F$  and  $n$  are indicators of sorption capacity (in mg/g) and intensity respectively. These Freundlich constants can be calculated from the slope and intercept of linear plot, with

$$\log q_e \text{ vs. } \log C_e \tag{7}$$

The validity of the models was verified by root-mean-square deviation (RMSD), the commonly used statistical tool measuring the predictive power of a model derived as:

$$RMSD = \sqrt{\frac{\sum_{n=1}^n (q_{exp} - q_p)^2}{n-1}} \tag{8}$$

where  $q_{exp}$  (mg/g) and  $q_p$  (mg/g) are the experimental and theoretical adsorption capacity, respectively.

A comparison between the experimental data points and the theoretical isotherms plot is displayed in Fig.3. The detailed parameters of these different forms of isotherm equations are listed in Table 3. The Langmuir isotherm model was satisfactory in describing the adsorption equilibrium, as the lowest RMSD values and  $R^2$  were higher than 0.99. The applicability of the Langmuir isotherm model suggests that the adsorption process occurred at a monolayer with each molecule having equal enthalpies and activation energy. The results also demonstrate no interaction and transmigration of color in the plane of the neighboring surface. As well as, the higher the adsorption, the greater the value of the sorbent binding capacity ( $Q_m$ ). The fact that the Langmuir isotherm fits the experimental data very well may be due to the homogeneous distribution of active sites on the adsorbent surface because application of the Langmuir equation involves the assumption that the surface is homogeneous.

The results show that the values of  $R_L$  are between zero and one, indicating the favorable adsorption of color onto all studied adsorbents (Table 4) [36].

Table 4 lists the maximum monolayer adsorption capacities of various activated carbons derived from different precursors. The activated carbon prepared in this study showed a comparatively high adsorption capacity of 208.33 mg/g. Thus, it is noteworthy that considerable changes in the surface properties were achieved within a short time, which may be attributable to the distinct mechanism of microwave heating. This irradiation promoted the release of volatiles from the char surface widening the porosity in the original carbon network. Moreover, microwave heating (internal and volumetric heating) has assisted the penetration of the KOH within the char matrix, and created a more orderly porous structure by opening of previously inaccessible pores and formation of new pores [37].

**Table 4: Adsorption isotherm constant parameters**

Adsorbent	Langmuir Isotherm					Freundlich Isotherm			
	$Q_m$ (PtCo/g)	$b$ (L/PtCo)	$R_L$	$R^2$	RMSD	$K_F$ [(PtCo/g)(PtCo/L)] <sup>n</sup>	1/n	$R^2$	RMSD
PKSN	40	$6.32 \times 10^{-3}$	0.0157	0.9997	0.813	5.839	0.2299	0.915	1.557
EFBN	27.933	$1.16 \times 10^{-3}$	0.0804	0.9962	0.425	1.1051	0.3608	0.934	0.852
PKSM	200	$4.77 \times 10^{-3}$	0.0207	0.9993	2.412	9.445	0.3896	0.878	13.291
EFBM	188.679	$8.43 \times 10^{-3}$	0.01184	0.9995	3.125	17.314	0.3065	0.941	9.88
PKSCM	208.333	$4.83 \times 10^{-3}$	0.02048	0.9991	3.179	9.784	0.3914	0.861	13.91
EFBCM	196.078	$9.42 \times 10^{-3}$	0.01061	0.9993	4.203	19.387	0.298	0.939	9.476

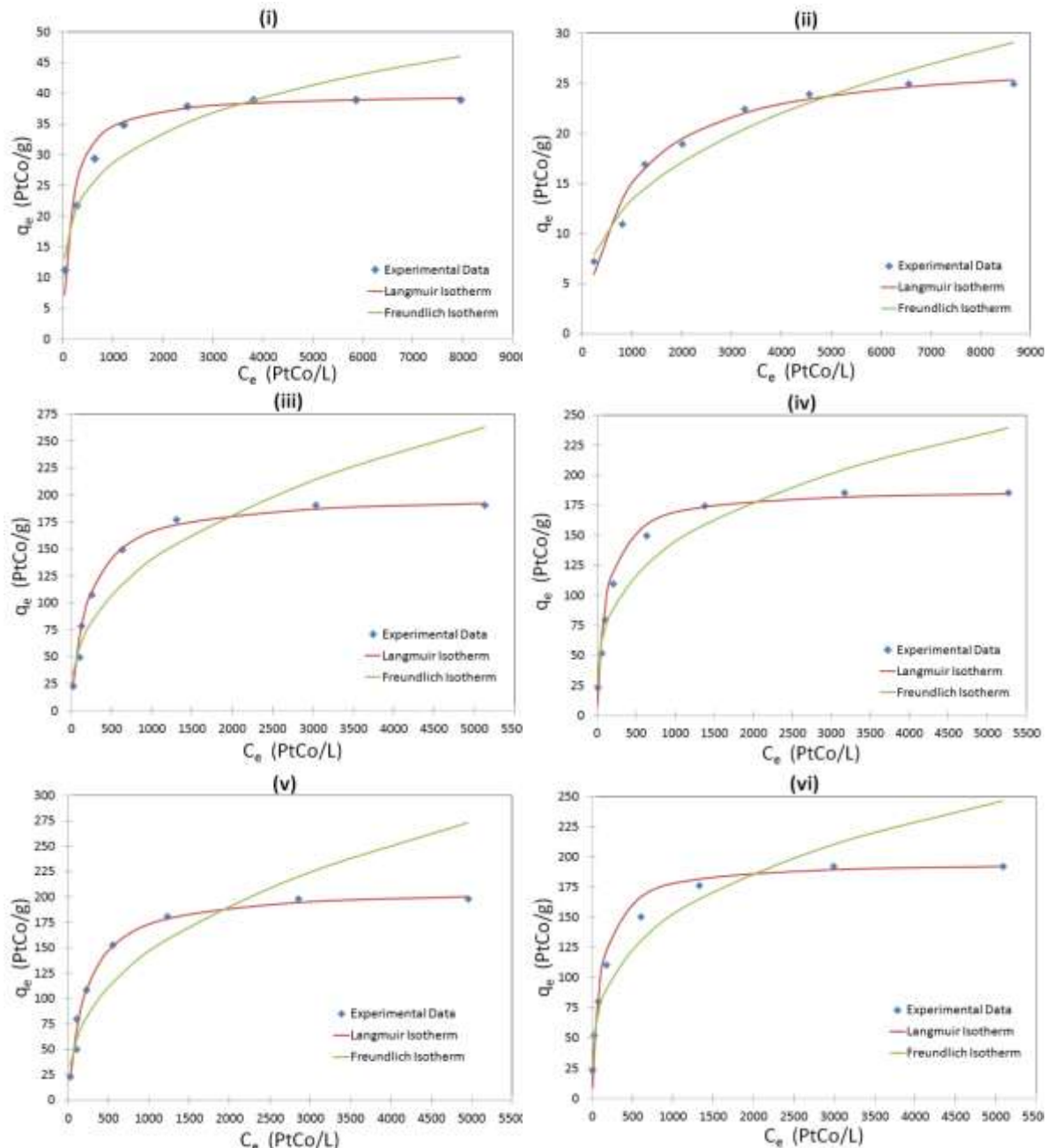


Fig.3. Adsorption isotherm of color on: (i) PKS N, (ii) EFB N, (iii) PKS M, (iv) EFB M, (v) PKS CM, and (vi) EFB CM.

### 3.6 Adsorption kinetics

The study of adsorption kinetics describes the solute uptake rate and evidently these rates control the residence time of adsorbate uptake at the solid–solution interface including the diffusion process. Adsorption kinetics were tested with several kinetic models in order to describe the adsorptive interaction between the color and the adsorbent. The kinetic models used in the analysis of the data are as follows: Pseudo-first order, pseudo-second order, and second order kinetic equations. The respective linear forms of the equations are as given below:

$$\ln \left( 1 - \frac{q_e}{q_t} \right) = -K_1 t \tag{9}$$

$$\frac{t}{q_e} = \left( \frac{1}{K_2 q_e^2} \right) + \frac{1}{q_e} t \tag{10}$$

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K t \tag{11}$$

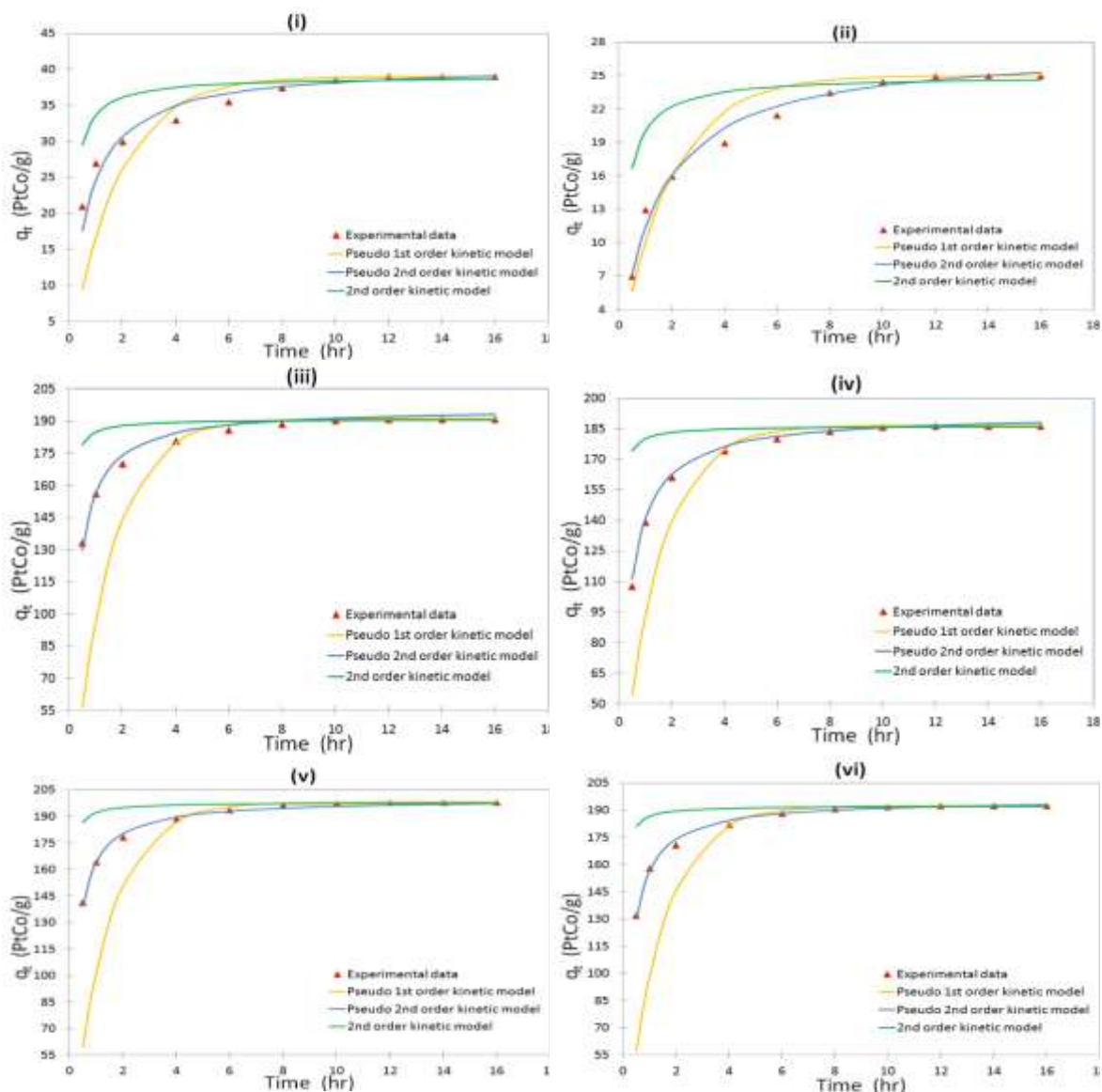
The associated kinetic parameters were evaluated from the slopes and intercepts of the respective linear plots of the kinetic equations, and the values are shown in Table 2. Comparison of the analyzed data based on the linear regression coefficient ( $R^2$ ) values as shown in the table; show that the experimental data is best described by the



pseudo-second order equation (Eq. 10), which has the most linear fit with correlation coefficient  $R^2 > 0.999$ . The values of experimental  $q_t$  and calculated  $q_t$  were close in agreement showing the applicability of pseudo second order kinetic model Fig. 4. The transfer of the dyes from the solution phase into the pores of the adsorbent may also be considered as the rate controlling stage in the batch experiments under the rapid stirring condition [38].

**Table 8. Parameters and correlation coefficient of kinetic models obtained by using the linear methods for adsorption of color on prepared adsorbents**

Adsorbent	$q_e(\text{exp.})$ (mg/g)	Pseudo first-order model		Pseudo second-order model		Second-order model	
		$K_1$ (1/hr)	$R^2$	$K_2$ (g/mg/hr)	$R^2$	K (g/mg/hr)	$R^2$
PKSN	39	0.5538	0.8889	0.0374	0.9992	0.1592	0.7104
EFBN	25	0.5082	0.8794	0.0253	0.9998	0.1601	0.7351
PKSM	191	0.6992	0.9171	0.0211	1	0.168	0.657
EFBM	186.5	0.6888	0.9291	0.0142	1		
PKSCM	198	0.7103	0.9202	0.0227	1	0.165	0.7204
EFBCM	192.5	0.7058	0.9275	0.02	1	0.1653	0.7196



**Fig.4. Comparison of different kinetic models for color adsorption on: (i) PKSN, (ii) EFBN, (iii) PKSM, (iv) EFBM, (v) PKSCM, and (vi) EFBCM.**

#### IV. CONCLUSION

- Palm kernel shell, empty fruit bunches, and activated carbons prepared from them showed considerable potential for the removal of color from biologically treated POME.
- PKS and EFB can be effectively converted to activated carbon through microwave pyrolysis or impregnation in KOH activating agent followed by microwave pyrolysis.
- Since PKS and EFB are freely, abundantly and locally available, they can be used as an economical sorbent and may be considered a good precursor for preparation of a low cost activated carbon for the real industrial effluent.
- The use of microwave pyrolysis in carbonization of PKS and EFB was found to be an effective and time saving alternative compared to the time and energy consumed by conventional carbonization.
- The optimum conditions of sorption were found to be: a sorbent dose of 5 g in 100 ml of POME, contact time of 12 hr, pH 2 for the color.
- The results gained from this study were well described by the theoretical Langmuir with a characteristic correlation coefficient of 0.999.
- The kinetic data indicated that the adsorption process was controlled by pseudo-second order equation.

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