

Palm oil mill effluent treatment using coconut shell – based activated carbon: Adsorption equilibrium and isotherm

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Abstract. The current ponding system applied for palm oil mill effluent (POME) treatment often struggle to comply with the POME discharge limit, thus it has become a major environmental concern. Batch adsorption study was conducted for reducing the Chemical Oxygen Demand (COD), Total Suspended Solids (TSS) and Color of pre-treated POME using coconut shell-based activated carbon (CS-AC). The CS-AC showed BET surface area of 744.118 m²/g, with pore volume of 0.4359 cm³/g. The adsorption uptake was studied at various contact time and POME initial concentration. The CS-AC exhibited good ability with average percentage removal of 70% for COD, TSS and Color. The adsorption uptake increased over time and attained equilibrium in 30 hours. The equilibrium data were analyzed using the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. Based on the coefficient regression and sum of squared errors, the Langmuir isotherm described the adsorption of COD satisfactorily, while best described the TSS and Color adsorption; giving the highest adsorption capacity of 10.215 mg/g, 1.435 mg/g, and 63.291 PtCo/g respectively. The CS-AC was shown to be a promising adsorbent for treating POME and was able to comply with the Environmental Quality Act (EQA) discharge limit. The outcome of treated effluent using CS-AC was shown to be cleaner than the industrial biologically treated effluent, achieved within shorter treatment time.

1 Introduction

The vast development of palm oil industry has led Malaysia to become the largest palm oil exporter to more than 100 countries [1]. Consequently, this increases the waste discharged, i.e. partly treated palm oil mill effluent (POME) into waterways. According to Malaysian Palm Oil Board (MPOB), as of December 2012, there were 429 palm oil mills nationwide; generating an average of 0.65 m³ POME from every processed ton of oil palm fresh fruit bunches (FFB). Based on annual production of 9,288,000 tons of FFB in Sarawak; this results in an estimated annual effluent generation of 6,037,200 m³.

Fresh POME is a hot (80-90°C), acidic (pH 4-5) slurry with unpleasant odor, and high colloidal suspension; which consists of mainly water, oil and total solids including suspended solids from debris of palm fruit residues [2]. POME is the result from processing of FFB mainly from physical processes such as sterilization, clarification and separation process of palm oil. Some researchers suggested that the dark, brownish color of POME could be attributed to the breakdown of lignocellulosic from the raw effluent into lignin and tannin [3, 4]. POME also contains various types of organic compounds which are mainly pigments extracted from sterilization of FFB, such as anthocyanin and carotene pigment [5].

The discharge of POME without appropriate treatment into waterways has been an environmental concern, as it affects the water quality. The high quantity of organic substance in POME has translated into high detection of Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) which has been a challenge for the treatment of this effluent. The degradation of POME in waterways can produce by-products which can be toxic to aquatic life and therefore, there is an urgency to treat POME properly before being discharged.

The typical characteristics of raw POME, biologically treated POME and the corresponding standard discharge limit of Environmental Quality Act (EQA) 1974, Department of Environment (DOE), Malaysia are shown in Table 1. The biologically treated POME characteristics showed non-compliance with the standard discharge limits. In this study, the collected POME was at pH 8, however the effluent was yet to comply with other parameters of EQA discharge limit.

In Malaysia, most of the operating palm oil mills are using the conventional ponding system for POME treatment in view of advantages such as low capital and operating cost. However, it requires large area due to the long hydraulic retention time (HRT), typically about 1–2 months. In addition, the current system has low efficiency in treating POME and sometimes could not meet the final

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discharge limit. Therefore, there is a need to upgrade the existing POME treatment system to ensure regular compliance with the stringent limit imposed by DOE Malaysia.

Various techniques have been innovated and applied by researchers for POME treatment, especially at polishing stage prior to discharge. Adsorption using activated carbon (AC) is a popular technique due to its high adsorptive capacity. Hence, broad application of AC as adsorbent can be often seen in catalysis or separation processes [6]. However, the usage of AC is not cost effective due to the utilization of costly raw material such as coal which is non-renewable. Lately, rising attention is put on the utilization of dumped biomass waste as precursor for AC such as oil palm shell [7], banana peel [4], palm kernel shell and empty fruit bunch [5]. The use of agricultural waste-based AC is much more economical as its raw material is low cost and can be easily obtained. Besides, it gives an added value to the generated waste, as this practice leads to a reduction of agricultural waste disposal, and adds functionality of the by-product.

This research explores the adsorptive potential of coconut shell-based AC (CS-AC) for reduction of COD, Total Suspended Solids (TSS) and Color from POME of different initial concentration and contact time. The equilibrium data of the adsorption process were then evaluated by fitting to four isotherm models to determine the adsorption mechanism of the pollutant molecules onto the CS-AC.

2 Experimental

2.1 Materials

2.1.1 Preparation of POME

The POME sample was supplied by a palm oil mill in Kota Samarahan, Sarawak, Malaysia from their anaerobic pond, at the end of anaerobic treatment. The samples were then cooled at a temperature of 4°C, and let to sediment for total solid removal. The supernatant was withdrawn for tests and analysis.

2.1.2 Preparation of Activated Carbon

The source of adsorbent is a commercial AC derived from coconut shell, produced via physical activation using steam, obtained from a local manufacturer. The CS-AC was sieved to sizes between 1 mm to 2 mm, and then washed 5-6 times to neutralize the pH and remove residual ash. Finally, the cleaned CS-AC was oven-dried at 110°C over night and stored in air-tight bottles. Distilled water was utilized for AC washing and preparation of reagents and solutions.

2.2 Method

2.2.1 Batch Adsorption Study

The effects of two variables were studied; contact time for adsorption and initial POME concentration. Six different POME initial concentrations were examined at a range of contact time from 0.5 to 48 hours. POME was diluted to five different ratios (50%, 60%, 70%, 80% and 90%) using distilled water. The original concentration was presented as 100%. 5.0 g of CS-AC was added to each flask containing 100 mL anaerobic treated POME (at natural pH 8) and were agitated (120 rpm at 30 ± 1 °C). The percentage removal and the adsorbed amount of COD, TSS and Color at equilibrium, q_e (mg/g) were determined using Eq. (1) and (2), respectively.

$$\text{Removal (\%)} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{(C_o - C_e) \times V}{W} \quad (2)$$

where C_o and C_e (mg/L) is POME concentration at initial and equilibrium, respectively. V (L) is the solution volume, and W (g) is the mass of CS-AC used.

Table 1. Typical POME Characteristics [8, 9, 4]

Parameter	Unit	Raw	Biologically Treated	Standard Discharge Limits
Chemical Oxygen Demand	mg/L	51000	4700	
Total Suspended Solid	mg/L	18000	1800	400
Color	PtCo/L		9900	
pH		4.2	8.4	5 - 9
Biological Oxygen Demand (BOD ₃ at 30°C)	mg/L	25000	1350	100

2.2.2 Adsorption Isotherm Model

Optimization of an adsorption system design of can be obtained through a suitable correlation for their equilibrium curves. In this study, CS-AC was used as adsorbent for anaerobic treated POME with different initial concentrations of COD, TSS and Color. The data acquired from adsorption equilibrium experiments were interpreted using four models; namely Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (DR) equations utilizing correlation method.

2.2.3 Validity of Isotherm Model

The adsorption isotherm of POME onto the CS-AC was verified at different initial concentrations. Each model validity was measured by the sum of squared errors (SSE, %) (Eq. 3).

$$SSE = \sqrt{\frac{\sum (q_{e,exp} - q_{e,cal})^2}{N}} \quad (3)$$

where N represents the number of data points. Lower SSE value indicated a better fit.

2.3 Analytical Procedure

2.3.1 Activated Carbon Characterization

The Brunauer–Emmett–Teller (BET) surface area and pore volume of the CS-AC were measured by multi-point BET from N₂ adsorption isotherms, using Automated Gas Sorption System (Quantachrome Instruments). The morphology of the CS-AC surface was determined by utilizing Scanning Electron Microscope (SEM). SEM micrographs were taken using Hitachi TM3030 with 500x magnification.

2.3.2 Analysis

Standard methods were applied for the detection of COD, TSS and Color. Method No. 8006 was used to determine COD concentration of the sample carried in COD vials by APHA potassium dichromate method (HR 20–1500 mg/L) using DR2800 HACH spectrophotometer and DRB 200 reactor. TSS was determined in conformity with the standard method No. 8000 using DR2800 HACH spectrophotometer. This Spectrophotometer was also used to detect Color according to the procedure 8025 Platinum–Cobalt standard method [1].

3 Results and Discussion

3.1 Activated Carbon Textural Characterization

From the CS-AC textural characterization results, the BET surface area was 744.118 m²/g and total pore volume was 0.436 cm³/g. These characteristics were comparable to commercial AC produced industrially which reported BET surface area between 900 to 1000 m²/g, as well as total pore volume of 0.50 and 0.60 cm³/g, respectively [10].

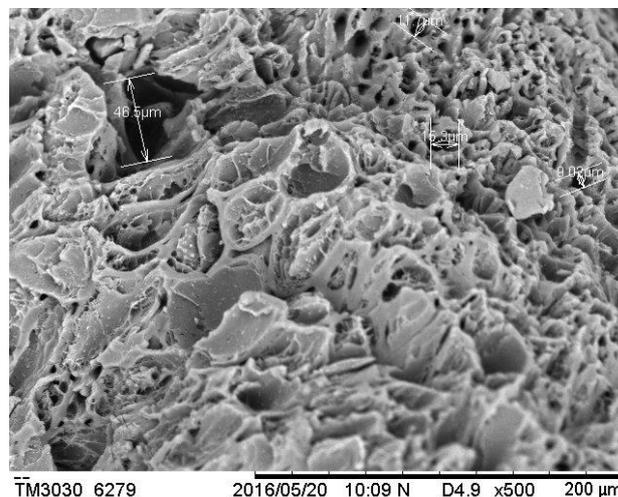


Figure 1. SEM image of CS-AC (x500)

The surface morphology of the CS-AC is shown by the SEM image in Figure 1. It was noticed that the CS-AC surface morphology reflected the common AC characteristic with the presence of various sizes pores, as reported in literature [11].

3.2 Adsorption Study

From the batch adsorption studies, about 70% removal of COD, TSS and Color was achieved from POME using CS-AC. This result was comparable with a study using palm kernel shell AC (PKS-AC) for POME pre-treatment which showed similar percentage removal about 70%. However, PKS-AC took shorter equilibrium time possibly due to the lower initial concentration of POME used [12].

3.2.1 Initial POME concentration and contact time effects on adsorption equilibrium

The adsorption uptake at time t, q_t (mg/g) at various POME concentrations is presented in Figure 2. COD, TSS and Color at all initial concentrations showed rising adsorption uptake with contact time. At early stage, the uptake increased rapidly, indicating the availability of plenty active sites. It then eventually showed a saturation curve upon reaching equilibrium, possibly due to monolayer coverage of pollutants onto the surface of the adsorbent [5]. The adsorption uptake, or the amount of pollutants adsorbed by CS-AC is utmost at equilibrium time of 30 hours (Figure 2), under the studied operating conditions [13].

The q_e values increased from 5.21 to 9.47 mg/g, 1.01 to 1.32 mg/g, and 20.80 to 39.10 PtCo/g for COD, TSS

and Color, respectively when POME concentration was increased from 50% to 100%. However, the percentage of COD, TSS and Color removal reduced with increasing POME concentration. This phenomenon indicated reduction in adsorption of pollutants due to the blocked active sites on the CS-AC for treating the concentrated POME [14], besides due to the limited capacity of CS-AC to adsorb high amount of pollutants.

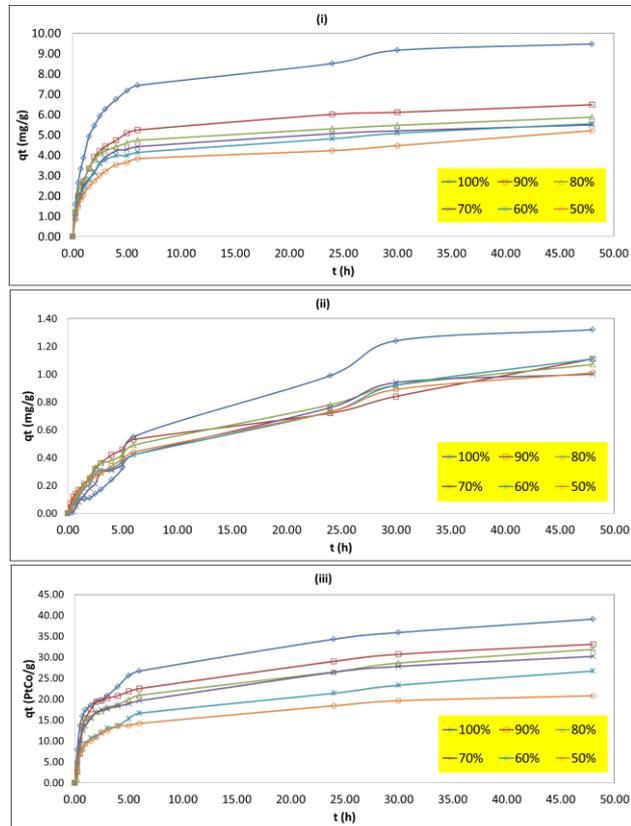


Figure 2. Adsorption uptake of: (i) COD, (ii) TSS, and (iii) Color over contact time at various POME concentration

3.3 Adsorption Isotherm

The adsorption isotherm indicates effluent distribution between the solid and solution phases at a particular temperature upon reaching the equilibrium. Isotherm data can be correlated via empirical or theoretical equations following the Langmuir, Freundlich, Temkin and DR isotherm models. The CS-AC characteristics such as adsorption capacity and surface properties can be made known from constants values obtained from each isotherm model.

3.3.1 Langmuir Isotherm

Langmuir isotherm and Freundlich isotherm [15] have been broadly applied in vast sorption processes [16]. The Langmuir isotherm equation is as shown in Eq. (4):

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e \quad (4)$$

where C_e refers to POME concentration at equilibrium (mg/L; except for Color, denoted as PtCo) and q_e is the amount of adsorbed pollutants (mg/g). Q_o (mg/g) is the adsorption capacity related to complete monolayer coverage, and Langmuir constant is denoted as b (L/g). Monolayer coverage means that each active site on the AC holds only one molecule of pollutant, which is a basic assumption for Langmuir isotherm. A linear plot between (C_e/q_e) and C_e provides the values of b and Q_o . The separation factor, R_L describes essential characteristics of Langmuir isotherm as in Eq. (5) [17]:

$$R_L = \frac{1}{(1 + bC_o)} \quad (5)$$

where C_o is the POME initial concentration (g/L). The value of R_L between 0 and 1 indicates that the isotherm is favorable. The isotherm is unfavourable if $R_L > 1$, linear if $R_L = 1$, and irreversible if $R_L = 0$ [17]. The values of R_L obtained in this study were between 0 to 1 (Table 2), which proved that the Langmuir isotherm was a favorable model to describe the adsorption of POME in terms of COD, TSS and Color, onto the CS-AC under the conditions used in this study.

Table 2. Isotherm constants and correlations for adsorption of COD, TSS and Color onto CS-AC

Isotherms	Parameter	Constants				
Langmuir		Q_o (mg/g)	b (L/g)	R_2	SSE (%)	R_L
	COD	10.215	0.011	0.686	1.103	0.11
	TSS	1.435	0.051	0.935	0.085	0.10
		Q_o (PtCo/g)	b (L/PtCo)			
	Colour	63.291	0.001	0.930	1.363	0.21
Freundlich		KF (mg/g (L/mg) ^{1/n})	$1/n$	R_2	SSE (%)	
	COD	1.280	0.317	0.524	1.037	
	TSS	1.839	0.168	0.500	2.624	
		KF (PtCo/mg (L/PtCo) ^{1/n})				
	Colour	1.149	0.532	0.937	9.962	
Temkin		A (L/g)	B	R_2	SSE (%)	
	COD	7.794	2.163	0.467	8.945	
	TSS	4.519	0.194	0.497	0.075	
		A (PtCo/g)				
	Colour	106.449	15.352	0.944	143.320	
Dubinin-Radushkevich		q_s (mg/g)	E (J/mol)	R_2	SSE (%)	
	COD	6.944	40.825	0.318	1.243	
	TSS	1.181	111.803	0.316	0.088	
		q_s (PtCo/g)				
	Colour	38.652	5.103	0.936	1.724	

This result was consistent with the work of Mohammed & Chong [4], using banana peel AC (BP-AC) for POME treatment, which reported that Langmuir isotherm was more favourable for COD, TSS and Color removal. However, the adsorption capacity, Q_o of CS-AC (10.215 mg/g, 1.435 mg/g and 63.291 PtCo/g for COD,

TSS and Color respectively) was much lower than that of BP-AC (200 mg/g, 63 mg/g and 135 PtCo/g for COD, TSS and Color respectively). This could be due to different type of raw material and carbon activation processes used to synthesize the AC. As reported by Mohammed & Chong [4], the BP-AC was a result of two-step activation, which was carbonization (physical) and chemical activation. This led to higher surface area and pore development of the AC, thus having higher capacity to adsorb pollutants. However, the usage of chemical is costly, especially when it deals with massive amount of AC preparation. Therefore, AC from single-step physical activation was implemented in this study.

The experimental data sufficiently fitted the Langmuir isotherm for both TSS and Color in accordance with the correlation coefficients $R^2 > 0.9$, except for COD. The greater values of R^2 indicated the relevance of the adsorption model for pollutants removal in POME.

Referring to Table 2, Langmuir isotherm model described the adsorption of COD satisfactorily. Yet, this model was the best in describing the adsorption equilibrium of TSS and Color, since the SSE values reported were the lowest with high correlation of $R^2 > 0.9$. These findings confirmed that the active sites were homogeneously distributed on the CS-AC surface, since the application of Langmuir equation assumed homogeneous surface of adsorbent [5].

3.3.2 Freundlich Isotherm

Freundlich isotherm model (Eq. 6) considers non-uniform heat distribution on the adsorbent surface and hence it is called as a heterogeneous adsorption [18]. Freundlich constants representing adsorption capacity and intensity are indicated as n and K_F [$\text{mg/g (L/mg)}^{1/n}$] respectively.

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (6)$$

The extent of correlation between solution concentration and adsorption depends on the adsorption intensity, n . The adsorption can be linear ($n = 1$), chemical ($n < 1$), and favorable physical process ($n > 1$) [19]. A normal Freundlich isotherm is indicated if $1/n < 1$, and indicates a cooperative adsorption if vice versa. [20]. A straight line obtained from $\log q_e$ vs $\log C_e$ plot gives the slope ($1/n$) values of 0.17-0.53 for COD, TSS and Color, which indicated their favorable adsorption onto the CS-AC at the experimental conditions studied.

Comparable adsorption intensity (K_F) between COD, TSS and Color was also observed. Although the adsorption capacity and intensity according to Freundlich isotherm showed similar results between CS-AC and BP-AC [4], however this model was found to be less favourable as a result of lower R^2 and greater SSE values.

3.3.3 Temkin Isotherm

Temkin isotherm concerns the effects of indirect adsorbent-adsorbate interactions, in which it causes the

molecules heat of adsorption to reduce with increased coverage in the layer [21]. This model is expressed by Eq. (7):

$$q_e = \left(\frac{RT}{b}\right) \ln(AC_e) \quad (7)$$

where RT/b signifies the constant B. A linear plot between q_e and $\ln C_e$ determines the values of both constants A and B. This model resulted in lower R^2 values (except for Color), thus it was not suitable to describe the overall POME adsorption onto CS-AC.

3.3.4 Dubinin–Radushkevich (DR) Isotherm

The DR equation (Eq. 8) can also be applied for the analysis of isotherm [22].

$$q_e = q_s \exp(-B\varepsilon^2) \quad (8)$$

where ε can be correlated using Eq. (9)

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (9)$$

where R represents gas constant (8.31 J/mol K) and T , the absolute temperature. The constants q_s and E can be obtained from the $\ln q_e$ versus ε^2 plot. Constant B conveys the mean free energy, E of COD, TSS and Color molecule sorption when it is transferred to the surface of the CS-AC from infinity in the effluent. The value of E can be calculated using Eq. (10). However, similar to Temkin isotherm, this model was found to be less favourable due to lower correlation for adsorption, especially for COD and TSS.

$$E = \left(\frac{1}{\sqrt{2B}}\right) \quad (10)$$

4 Conclusion

The present investigation showed CS-AC was a promising agricultural waste-based adsorbent for the reduction of COD, TSS and Color from POME over a range of 50% to 100% POME concentrations, with average percentage removal of 70% for COD, TSS and Colour after 48 hours. The BET surface area of 744.118 m^2/g and pore volume of 0.436 cm^3/g showed that the CS-AC was porous with well-developed pores. This was confirmed by the SEM image of the CS-AC. The adsorption uptake for the removal of COD, TSS and Color onto the CS-AC were 10.215mg/g, 1.435mg/g and 63.291 PtCo/g, respectively. Langmuir isotherm was proven to satisfactorily describe the overall adsorption of COD, TSS and Color in POME.

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