Adsorption kinetics of colour removal from palm oil mill effluent using wastewater sludge carbon in column studies

S.R.M. Kutty [*], N.M.Y. Almahbashi, A.A.M. Nazrin, M.A. Malek, A. Noor, L. Baloo, A.A.S. Ghaleb

Department of Civil and Environmental Engineering, Universiti Teknologi PETRONAS, 32610 Perak, Malaysia

ABSTRACT

Treated palm oil mill effluents (POME) is of great concern as it still has colour from its dissolved organics which may pollute receiving water bodies. In this study, the removal of colour from treated palm oil mill effluent were investigated through adsorption studies using carbon derived from wastewater sludge (WSC). Sludge from activated sludge plants were dried and processed to produce WSC. In this study, three different bed depths of WSC were used: 5 cm, 10 cm, and 15 cm. For each bed depth, the flowrate was varied at three different values: 100 mL/hr, 50 mL/hr and 25 mL/hr. It was found that at bed depth of 5 cm, the breakthrough curves were occurred at 360 min, 150 min and 15 min for flowrates of 25, 50 and 100 mL/hr respectively. It was observed that at a particular depth the exhaustion time for column reduced as flow rate increases. Kinetic models, Adams-Bohart and Yoon-Nelson were used to analyze the performance of the adsorption. It was found that rate constant for Adams Bohart model decreased with the increase in bed depth. Adsorption capacity obtained from Adams-Bohart model ranged from 2676.19 mg/L up to 8938.78 mg/L. The maximum adsorption capacity increases with smaller bed depth. For Yoon-Nelson model, the rate constant decreases with increase in bed depth. The required time for 50% breakthrough obtained from the models ranged from 17.01 to 104.17 minutes for all three bed depths. The reduction of colour was found to be effective at all bed depths. The experimental data was best described by both models as with higher values of correlation coefficient (R^2).

1. Introduction

Production of Palm Oil Mill in Malaysia is one of the world largest palm oil exporters. It produces 39% and exports 44% [1]. POME is brown in colour and it contains high soluble organic loads that is devastating to nature [2]. Existence of colour in POME effluent hinders the photosynthetic process and has a toxic impact [3], many techniques and methods have been applied to remove the colour, but the cost of these physical and chemical methods is high [4]. Hence, the need for low cost treatment methods are of major concern [5]. Currently, there are about 3.0 million hectares of land cultivated for palm oil plantation and processing the fresh fruit bunches (FFB) [6]. The milling of crude palm oil (CPO) will requires large amount of fresh water. This leads to a large volume of effluent that will be produced at the end of the process which later discharged into water bodies. The conversion process of the crude palm oil to refined oil involves activities in removal of the products of hydrolysis and oxidation. After the refining process, the oil can be separated into both liquid and solid phases. FFB will be sterilized and this process is the first contributor in the production of the palm oil mill effluent (POME).

Sewage sludge are produced as a result of wastewater treatment activity. The production is expected to increase by time due to growing population and environmental necessity to comply with the legal requirements for the treatment of wastewater. Using incorrect or inefficient disposal methods leads to major environmental problem such as contamination of land and groundwater table and emission of greenhouse gases [7]. There are several techniques for sludge management which may include recycling and reuse as a fertilizer [8].

Adsorption is one of the physical-chemical treatment processes which is effective in removal of colour from aqueous solution using low cost materials. Most commonly used adsorbents are fox nutshell [9], ash derived from bagasse, wood, sawdust [10] and tea leaves [11]. The type of adsorbent is determined by their adsorption capacity, characteristic, and the physical properties of the produced activated carbon. Sewage sludge can be used as adsorbent material due to its carbonaceous property and has been reported to efficiently removed colour in wastewater effluent by adsorbing up to 139.4 mg/g of methylene blue and 1358.5 mg/g of iodine [12]. Sewage sludge can be converted from waste materials into a cheap, and easy to obtain activated carbon material.

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* Corresponding author.
E-mail address: shamsulrahman@utp.edu.my (S.R.M. Kutty).

Consequently, producing activated carbon from sewage sludge has dual advantages: potentially low cost adsorbent for treatment of wastewater as well as minimizing sludge disposal costs [13]. Recent studies used WSC in colour removals but not in the treatment of POME. The objective of this study was to reuse WSC in adsorption of colour from treated POME through column studies and to determine the appropriate kinetic models for the adsorption.

2. Materials and methods

2.1. Preparation of adsorbent

For the study, sewage sludge was collected from Universiti Teknologi PETRONAS Sewage Treatment Plant (STP) and the POME was collected from Nasaruddin Palm Oil Mill in Bota, Perak. Raw sludge was first dried in an oven at 110 °C for about 24 hrs. Then, the dried sludge was grinded and sieved into smaller particles within diameter range of 300–425 nm. The dried sludge was carbonized in muffle furnace at 700 °C for one hour, a method with some modifications based on Wen-Hong Li et al. [14]. POME was initially filtered using Whatman filter paper 0.45 microns to remove the suspended solids using laboratory vacuum filtration system to obtain the soluble fraction.

2.2. Kinetic models

2.2.1. Adams-Bohart model

Adams and Bohart model was developed in 1920 for the adsorption of chlorine from air on activated carbon used gas masks [15] focused on maximum adsorption capacity (N_0) and kinetic constant (k_{AB}). The linearized form of Adams-Bohart model is expressed in Eq. (1). This model was applied to check the dynamic behavior of adsorption column. The model was applied to experimental data and used to describe the initial part of the breakthrough curve as reported by Chu et al. [16].

$$\ln\left(\frac{C_t}{C_0}\right) = k_{AB}C_0 t - k_{AB}N_0\left(\frac{Z}{U_0}\right) \qquad (1)$$

where k_{AB} (L/mg. min) is the kinetic constant, Z (cm) is the bed depth, N_0 (mg/L) is the maximum adsorption capacity and U_0 (cm/min) is the linear velocity of the solution. A plot of ln (C_t/C_0) versus t gives the value of correlation coefficients (R^2), k_{AB}, and N_0.

2.2.2. Yoon-Nelson model

Yoon-Nelson model is a simple theoretical model which was applied to explore the colour breakthrough through the adsorbents. In this model, it is assumed that the probability of adsorbate molecule is related to the adsorbate breakthrough and its adsorption [17]. The values of the constant k_{YN} and τ can be found using nonlinear regressive analysis from Eq. (2).

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{YN}t - \tau k_{YN} \qquad (2)$$

where k_{YN} (L/min) is the rate of constant and τ (min) is the time required for 50% adsorbate breakthrough.

2.3. Experimental setup

The experimental setup used for the column study is as shown in Fig. 1. Three glass tubes columns with diameter of 20 mm and height of 20 cm were used for adsorption studies. The columns were filled with WSC at varying heights of 5 cm, 10 cm and 15 cm, respectively. The columns were initially filled with distilled water to unclog pores of WSC and then POME was fed into the columns using a peristaltic pump at various flow rates of 25, 50 and 100 mL/hr. The pH of raw POME was
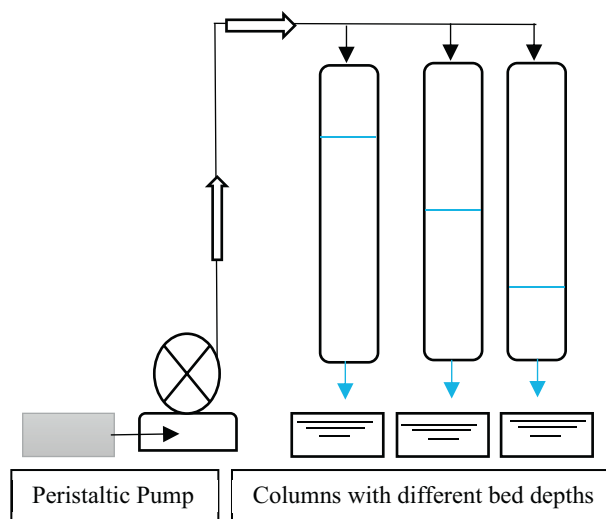

Fig. 1. Schematic diagram of column setup.

recorded at pH 8.4. Sampling of effluents from the columns were collecting at intervals of 15 mints. The colour of each sample was measured using spectrophotometer at wavelengths range between 380 nm to 780 nm until the column achieved breakthrough.

3. Results and discussions

3.1. Production of adsorbents

Wastewater sludge carbon (WSC) was prepared at 700 °C and 500 °C with one hour and three hours dwelling time respectively. At 500 °C and three hours contact time, the surface of produced WSC was brownish and the lower surface was grey, by increasing contact time to 4 hours whole WSC became almost brownish, whereas by increasing the heating temperature to 700 °C the beneath surface layer become black. The difference in colour might be attributed to uneven burning of the sample. As the burning period was increased to four hours, the uneven colour of WSC decreased.

3.2. Adsorbent characteristics

3.2.1. Scanning electron microscope (SEM)

The morphologies of the adsorbent was analyzed under SEM as shown in Fig. 2. The material exhibit porous characteristics and fibrous in nature. In SEM, sample is coated with the provided thin layer of gold using sputter coater, then it placed in the testing unit under 20 kV [18]. Fig. 2 image A, shows 1000x magnified SEM photo of raw material where the surface is smooth with small pores. However, image B shows better homogeneity in structure with semi-spherical shapes and no obvious pores. SEM imaging of both raw wastewater sludge (RWS) and wastewater sludge carbon (WSC) indicates high possibility of the presence of large porous structure. Adsorbent with large pore size has a good adsorption capacity.

3.2.2. Energy dispersive X-Ray analysis (EDX)

Table 1 shows the elemental analysis corresponding to the sewage sludge used as materials for production of the activated carbon. The EDX test shows that the RWS contains high carbon percentage but it reduced after activation in the muffle furnace.

3.3. Fourier Transform Infrared Spectroscopy (FTIR) analysis

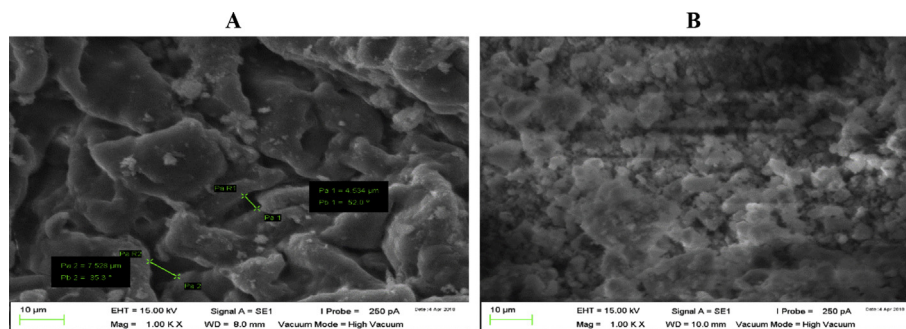Prepared activated carbon surface hosted some functional groups

Fig. 2. Scanning electron microscope imaging; porous size differences **(A)** RWS **(B)** WSC.

Table 1
Elements characterization of RWS and WSC.

Sample	Elements (wt. %)							
	C	O	Fe	Si	Al	P	Ca	K
RWS	53.3	34.5	4.9	4.1	2.6	-	0.5	-
WSC	17.0	40.4	12.8	12.8	10.5	3.6	2.0	0.8

such as hydroxyl and carboxylic groups as shown in Fig. 3. Peaks at 3697.0 cm^{-1} is a weak sharp represents isolated O–H groups. At 3621.24 cm^{-1} weak sharp can be attributed to the O–H stretching of hydroxyl groups. Weak peak at 3436.78 cm^{-1} ascribed to O–H stretching groups.Whereas weak splayed peak at 1631.28 cm^{-1} is related to C–C vibrations in aromatic rings [19]. Peak at 1034.98 cm^{-1} is strong board and might be assigned to the alcoholic C–O stretching vibration [20].

FTIR shows the surface chemistry of the materials. In Fig. 3, there is no obvious change in the functional groups between the raw sludge (RS) and the wastewater sludge carbon (WSC), this is because no chemicals were added during activation process.

3.4. Effect of bed depth on breakthrough curve

The breakthrough point is the time taken for the concentration to reach its allowable solute concentration in the effluent fluid. As breakthrough continues, the concentration of effluent increases gradually up to the feed. The allowable value is usually 5–10% of the initial value. When this happen, no more adsorption can take place in the bed. The time when bed is fully saturated is known as exhaustion point which occurs when the concentration of effluent is 90–95% of its initial concentration.

Treated POME was passed through the columns with different bed depth of 5, 10 and 15 cm with flow rate varying from 25, 50 and 100 mL/hr. At a particular flowrate, the colour intensity in effluents of the columns were reduced as the POME was passed through the bed. As the flowrate were increased for a particular bed depth, the reduction in colour was observed at a shorter exhaustion time. These reasoning coincide to results which achieved by M.M. Bello et al. [17].

It was observed that the breakthrough time varied with different bed depth with bed depth of 15 cm having the longest breakthrough time at 60, 420 and 720 mints for flowrates of 100, 50 and 25 mL/hr respectively. This can be attributed to the longer contact time between the adsorbate and adsorbent and the increasing in surface area and porosity of the adsorbent which enhance the adsorption capacity of adsorbent [21]. Once the fluid enters the bed, it will come in contact with the first few layers of adsorbents. The exhaustion points for all 3 bed depths also differ according to the depth, wherein the shorter bed depth of 5 cm have shorter exhaustion time at 1800, 2460 and 7020 mints for flowrates of 100, 50 and 25 mL/hr. respectively. Therefore, it has smaller adsorption
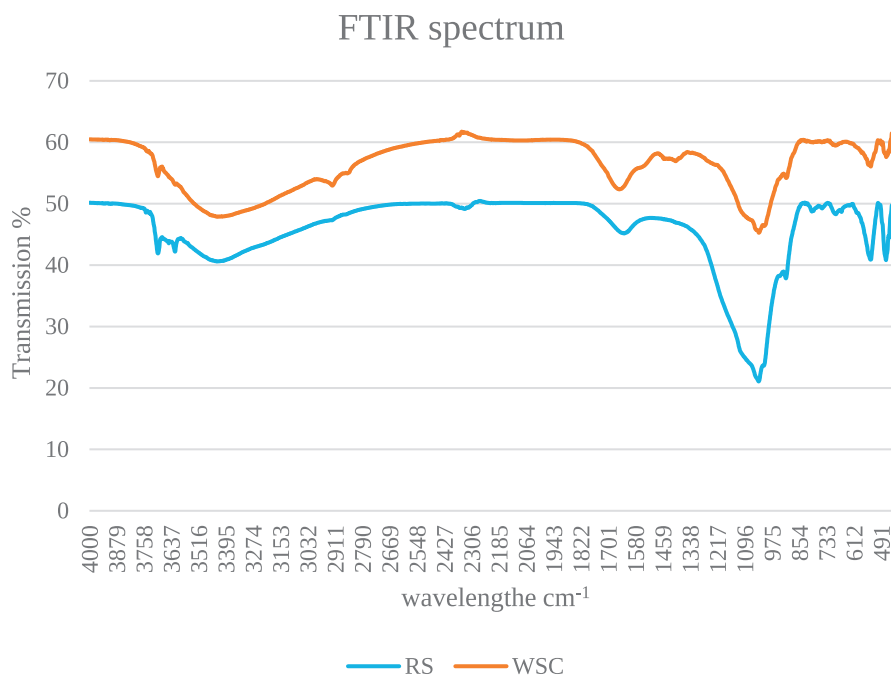

Fig. 3. Fourier Transform Infrared Spectroscopy (FTIR) spectrum.

capacity. The breakthrough curve indicated similar results for the three different flow rates showing that longer breakthrough point and exhaustion was achieved with bed depth of 15 cm. However, the longest exhaustion time for the column bed was observed when the slowest flow rate of 25 mL/hr was used that ensured more contact time. It can be inferred that slower flow rates yielded longer breakthrough and exhaustion time compared to faster flow rates as shown in Table 2.

Faster breakthrough curve of 15 cm bed depth was achieved by using the flow rate of 100 mL/hr, 50 mL/hr and 25 mL/hr respectively. This showed that slower flow rate exhibits longer breakthrough time. The maximum exhaustion time of about 9660 minutes was obtained by the minimum flow rate of 25 mL/hr. At particular depth of 15 cm, 90% of adsorption capacity was achieved at 2460, 3240 and 3960 min for flowrate of 100 mL/hr, 50 mL/hr and 25 mL/hr respectively. For bed depth of 10 cm, the breakthrough time for all the flow rates differs by 45, 360 and 600 minutes when flowrate differs by 100 mL/hr, 50 mL/hr and 25 mL/hr respectively. The exhaustion time was maximum for flow rate 25 mL/hr while for 100 mL/hr and 50 mL/hr, the exhaustion time occurred before 3960 minutes. The breakthrough showed similar results for bed depth of 5 cm, with similar trend of breakthrough and exhaustion points were observed for all three bed depths.

3.5. Evaluation of kinetic models

3.5.1. Adams-Bohart model

The data was fitted to the adsorption model by Adam-Bohart for all the flow rates for different bed depths. The models provide an accurate prediction of the breakthrough curve with most coefficient of correlation (R^2) value between 0.90-0.98. Table 3 indicated that the adsorption capacity of the adsorbent (N_0) increased as the flow rate increased and decrease as the bed depth increases. Meanwhile, kinetic constant of the model k_{AB} decreased with increased in bed depth and decreased when having slower flow rate.

3.5.2. Yoon Nelson model

The data was fitted to the Yoon Nelson adsorption model and the results were tabulated as in Table 4. It was observed that the rate constant k_{YN} and time required for 50% adsorbate breakthrough (τ) decreased and increased respectively with increase of bed depth. Also, it was found that the rate constant for a particular depth increases with increment of flow rate from 0.0303 L/min to 0.3121 L/min. Due to less residence time of the adsorbate in the bed, time required for 50% breakthrough decreased with increasing flowrate. It can be concluded that both models are appropriate to describe the fixed bed operation.

From the study, it showed that the column achieved a significant breakthrough curve and higher removal of colour at bed depth of 15 cm and flowrate of 25 mL/hr was achieved as more contact time between the solute in the effluent and adsorbents. Both variables have shown the longest breakthrough and exhaustion period. In addition to that, the Adams-Bohart and Yoon-Nelson kinetics models were studied to describe the column adsorption kinetics. The experimental data was found to be best described by Adams-Bohart model as it shows higher range of R^2

Table 2
Breakthrough and exhaustion time with varying flow rates and bed depth.

Flow rate (mL/hr)	Bed depth (cm)	Breakthrough time (min)	Exhaustion time (min)
100	5	15	1800
	10	45	2150
	15	60	2340
50	5	150	2460
	10	360	3240
	15	420	3960
25	5	360	7020
	10	600	8400
	15	720	9660

Table 3
Adams-Bohart kinetics.

Flow rate	Z	k_{AB}	N_o	R^2
mL/hr	cm	L/mg.min $\times 10^{-5}$	mg/L	
100	5	13.14	8938.78	0.9814
	10	10.98	5818.95	0.9458
	15	10.80	4193.16	0.9422
50	5	13.39	5108.01	0.9343
	10	13.11	3333.68	0.9354
	15	10.90	2676.19	0.9556
25	5	9.05	7484.81	0.9277
	10	9.04	6146.23	0.9478
	15	8.39	6002.74	0.9017

Table 4
Yoon-Nelson kinetics.

Flow rate	Z	k_{YN}	τ	R^2
ml/hr	cm	l/min	min	
100	5	0.3121	17.01	0.9289
	10	0.2006	23.46	0.9208
	15	0.2086	25.26	0.9084
50	5	0.1111	27.77	0.8616
	10	0.0984	37.78	0.9123
	15	0.087	44.06	0.9344
25	5	0.0401	58.24	0.8512
	10	0.0378	79.72	0.8929
	15	0.0303	104.17	0.8494

values. The rate constant, adsorption capacity and time for the 50% adsorbate breakthrough were dependent on the bed depth where longer time τ means it has greater adsorbing capacity. Results showed that with increasing flow rate 25, 50 and 100 mL/hr and bed depth 5 cm, 10 cm, 15 cm, adsorption capacity of the adsorbent has increased in Adams-Bohart model while the 50% adsorbate breakthrough and rate constant decreased and increased respectively, in the Yoon-Nelson model.

4. Conclusion

It can be concluded that the removal of colour through adsorption by the WSC as indicated by the adsorption capacity. The determined column parameters can be scaled up for the design of fixed bed column. The use of sludge which is a waste material as an adsorbent material for removal of colour was proven in this research and can be further investigated for other removal of contaminants.

Declarations

Additional information

No additional information is available for this paper.

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