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Tertiary Treatment of Biologically Treated POME in fixed-bedC: Color and COD removal

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ABSTRACT

Color and COD are two of the major constituents of palm oil mill effluent [POME] which make it highly pollutant and difficult to treat. Conventional treatments are inadequate in removing the color and the treated POME still contains appreciable residual color. Therefore there is a need to further treat the conventionally treated POME to remove the residual color and COD. A fixed-bed column adsorption was carried out to investigate color and chemical oxygen demand [COD] removal from conventionally treated palm oil mill effluent [POME] using resin [TULSION A-72 MP] as adsorbent. Biologically treated POME from final discharge point with a color above 500 ADMI and 534 mg COD/L was used in the study. A preliminary analysis showed that all the parameters are within the discharge regulation, except the color. A fixed-bed column with 3.5 cm internal diameter and 40 cm height was used. Experiments were performed at known bed heights [BH] and hydraulic loading rates [HLR]. Breakthrough curves were developed from the experimental results in order to analyze the adsorption process. The resin shows a high adsorption capacity by removing more than 98 % of the initial color of the POME. The adsorption capacity for COD removal was not as much as that for color as only 88 % of the initial COD was removed. Column elution was carried out using a solution of NaOH and NaCl. The adsorbent is also suitable for repeated use without much loss of capacity.

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INTRODUCTION

Malaysia has become the largest producer as well as exporter of palm oil in the world, having overtaken Nigeria as the world's largest producer, some four decades ago [1]. Malaysia accounts for about 51% of world palm oil production and about 62% of world exports [2]. Although this is economically positive, there is an intrinsic environmental problem associated with the processing of crude palm oil into finished products. The processing of palm oil involves many stages which generate large amount of wastewater in the form of Palm oil mill effluent [POME]. It is estimated that for any ton of crude palm oil processed, a corresponding 5 to 7.5 tons of water are required [3] and unfortunately more than 50% of this water ended up as a wastewater [4] which has to be treated prior to being discharged. This POME has been identified as one of the major sources of water pollution in Malaysia [5].

The major issue with this POME is its high biochemical oxygen demand [BOD], chemical oxygen demand [COD] and total solid [TS]. On the average, POME contains 25,000 mg / L BOD, 53,630 mg / L COD and 43,635 mg / L TS [6]. Table 1 shows typical characteristics of POME and the discharge limits set by the Malaysian Department of Environment [DOE].

Various technologies have been employed to reduce these pollutants from the POME, with anaerobic digestion being the most common treatment method employed by the palm oil mills[7]. Of recent, however, the problem of color of the POME has been receiving attention [8]. The presence of color in POME gives it an unpleasant sight which is aesthetically offensive. This unsightly condition would be impacted onto the receiving water body once discharged. The problem with this color is mostly aesthetic but it can also reduce the amount of light penetration into the water and thereby affecting the aquatic lives [9]. Color may also hinder water reuse, pose problem to treatment processes, and contribute to the appearance of plumes in the receiving water bodies [10].

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Table 1: Characteristic of raw POME and DOE discharge limits

Parameters	POME range	POME mean	DOE Discharge limits
Temperature ^oC	80 -90	85	45
pH	3.4 – 5.2	4.2	5.0 – 9.0
Oil and grease [mg/L]	130 – 18,000	6000	50
BOD[mg/L]	10,250 – 43, 750	25, 000	100
COD[mg/L]	15, 000 – 100,000	51,000	1000
TS[mg/L]	11,500 – 79, 000	40,0000	1500
SS[mg/L]	5000 – 54,000	18,000	400
TVS[mg/L]	9000 – 72, 000	34,000	-
Total nitrogen[mg/L]	180 -1400	750	200
Color [ADMI]	>500	-	200

Despite the problems of this color, the final discharge POME from most Malaysian palm oil mills has color above 200 ADMI, the regulation for color in industrial discharge as outlined in the Fifth Schedule Paragraph 11[1][a] Environmental Quality [Industrial Effluents]Regulations 2009 [11]. However, the palm oil mill industries are exempted from this regulation and therefore discharge their POME with the color above this standard. Most of the current researches focus on the removal of BOD, COD and TS [e.g. [5,7,12,13,14], and though this result in color reduction, the effluent POME still contains an appreciable amount of color and ended up being discharged as it is. However, the removal of color is also becoming important in the POME treatment [8]. Also COD is not among the regulated parameters and as such, the final discharge POME contains appreciable amount of COD.

Resin is a synthetic compound that have found various applications as an adsorbent especially in textile industries where it is used for dye removal from the effluent wastewater [15,16,17]. Resin has a highly developed structure of pores on the surface and can be easily modified to suite a particular application. The ability of resin to be easily regenerated with a common salt [NaCl] is one of its properties that make it a suitable adsorbent [18].

Therefore this study was carried out to investigate the potential and effectiveness of a commercial resin as adsorbent for color removal from POME. Experiments were carried out in a fixed-bed column. Breakthrough curves were developed and the adsorptive capacity of the resin was for color removal was determined. The influence of column bed height on the color removal was also investigated.

MATERIALS AND METHODS

Experimental Materials:

POME sample was collected from the final discharge point of SertingHilir Oil Palm Mill in Negeri Sembilan, Malaysia. This POME has undergone all the treatments normally adopted by the oil mill which include anaerobic as well as aerobic treatment using ponds. The sample was analyzed for BOD, COD, color, metals, and nutrients prior to the experiment and stored under 4 ^{0} C throughout the study.

The resin used was a commercial resin [TULSION A-72 MP]and was supplied by Thermax Limited, India. This resin is a robust polymeric adsorbent which is insoluble in all common solvents. It is in a form of moist spherical beads with a mesh size 16 to 50 and particle size 0.3 to 1.2 mm. Table 2 listed the physicochemical properties of the resin. The Resin was transferred into the glass column using distilled water. It was then thoroughly washed with distilled water.

Table 2: Characteristics of the Resin

Matrix structure	Polystyrene copolymer
Functional group	Quaternary ammonium type 1
Physical form	Moist spherical beads
Screen size US mesh [wet]	16 – 50
Particle size [95 % min]	0.3 to 1.2 mm
Moisture	60 ± 3 %
Specific gravity of beads	1.02 to 1.05 g/ml
Surface area of dry beads	550 m^2/g [BET]
Porosity of dry beads	0.4 ml/ml of bead
Bulk density	43 – 47 lb/cft
Maximum operating temperature	80 ^oC
Suitable pH range	0 – 14
Solubility	Insoluble in all common solvents

Experimental Set-up:

The experimental set-up consists of a glass column, 40 cm height and 3.5 cm internal diameter, mounted vertically and filled with the resin[fig. 1]. Glass wool was placed at the bottom of the column to act as supporting material and also serve the purpose of filtration of the adsorbent particles [19]. A control valve was fixed to regulate the flow rate [20]. The POME sample was introduced at the top of the column using peristaltic pump at known flow rates, initial color value and COD and effluent samples were collected at regular intervals of time. The residual level of color was then determined using a HACH Spectrophotometer [DR 2500]in the unit mg [Pt/Co]/L. According to the DOE guidelines, the color was also measured based on the ADMI Weight Ordinate Method. The COD was determined using digestion method as described in the Standard Method for Water and Wastewater Analysis. The experiments were carried out at room temperature. The effect of column bed height was investigated at three different bed heights 0.1, 0.2 and 0.3 m. The effect of initial sample pH was also observed

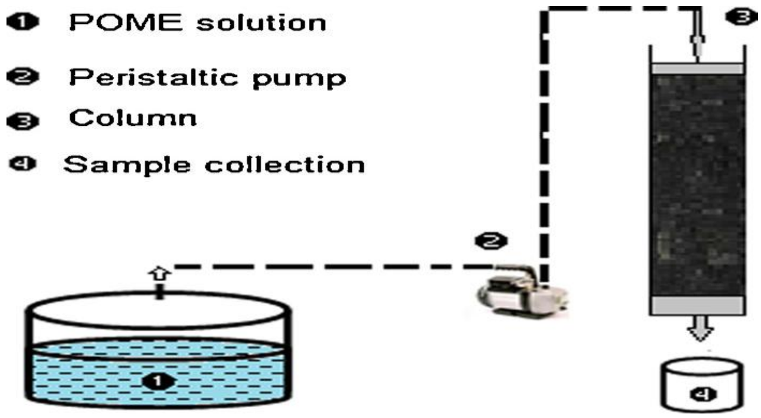

Fig. 1: Schematic diagram of the column adsorption

Column Elution:

Resin life is considered as one of the important parameter for industrial application. At the exhaustion, that is when there was very little or no further color removal; column elution was performed using a solution of 1 % Sodium Hydroxide [NaOH] and 10 % Sodium Chloride [NaCl]. The resin was first washed with 1 bed volume of distilled water within 15-20 minutes. The resin was then washed with 5 bed volumes of the regenerant[1 % NaOH and 10 % NaCl] within 45 minutes. Twenty bed volumes of distilled water were then passed down the column within 1 hour.

RESULTS AND DISCUSSION

Characteristics of the POME:

Table 3 shows the characteristics of the POME sample from the final discharge point. The pretreatment analysis revealed that all the parameters are within the discharge limit, with exception of the color which was above 500 ADMI. The COD is still relatively high, albeit within the discharge limit. Heavy metals were also within the standard regulations. Although the suspended solids are quite low, the color was still high and as such could not be wholly due to the suspended solids as suggested by [21]. Also the oil and grease are quite low, indicating that the color may not have been due to them.

Table 3: Characteristics of the POME

S/N	Parameter	Before treatment	After Treatment	Standard
1	pH value	5.0	-	5.5 – 9.0
2	BOD[mg/L]	47	-	100
3	COD [mg/L]	534	151*	1000
4	Suspended Solids [mg/L]	60		400
5	TKN[mg/L]	23.8		200
6	Phosphorous [mg/L]	22.5		-
7	Color [ADMI]	> 500	180*	200
8	Oil & Grease [mg/L]	1	ND	50
9	Total heavy metals [mg/L]	0.01	<0.01	-

*****parameter considered under this study

Color Removal:

The adsorption capacity of the columnis the maximum amount of color that can be removed at the *breakthrough*. Normally the breakthrough point would be point when the effluent color reached the discharge standard or some pre-set value. Here the breakthrough point was defined as that point at which the effluent color reached 10 % of the initial sample color.

Fig 2 shows the breakthrough curve for the color removal at a bed height of 0.3 m and hydraulic loading rate of 0.24 $m^3/h\ m^2$. The breakthrough curve was developed for the ratio of the effluent color[C_e] to the influent color[C_i] and the adsorption time. It can be seen that the effluent color is very low at the beginning of the process as the resin pore spaces are still empty and the color is effectively adsorbed as the POME travels down the column. The resin was able to remove more than 98 % of the initial color of the POME for nearly 50 minutes of the process. The breakthrough point occurs at nearly 150 minutes of the process.Although the breakthrough occurred at this point, the adsorption process continued for a long time without reaching the exhaustion point. In fact based on the trend of the curve, it may take a very long time to reach the column *exhaustion*. Since in practice the process should be stopped once the breakthrough is reached, the process here was not continued much beyond the breakthrough point. Even after reaching the breakthrough, the resin continued to remove the color, albeit less effectively. After two hours of running the process, more than 90% of the color was still removed from the POME. Therefore, the resin can be said to have a high adsorption capacity for the color removal.

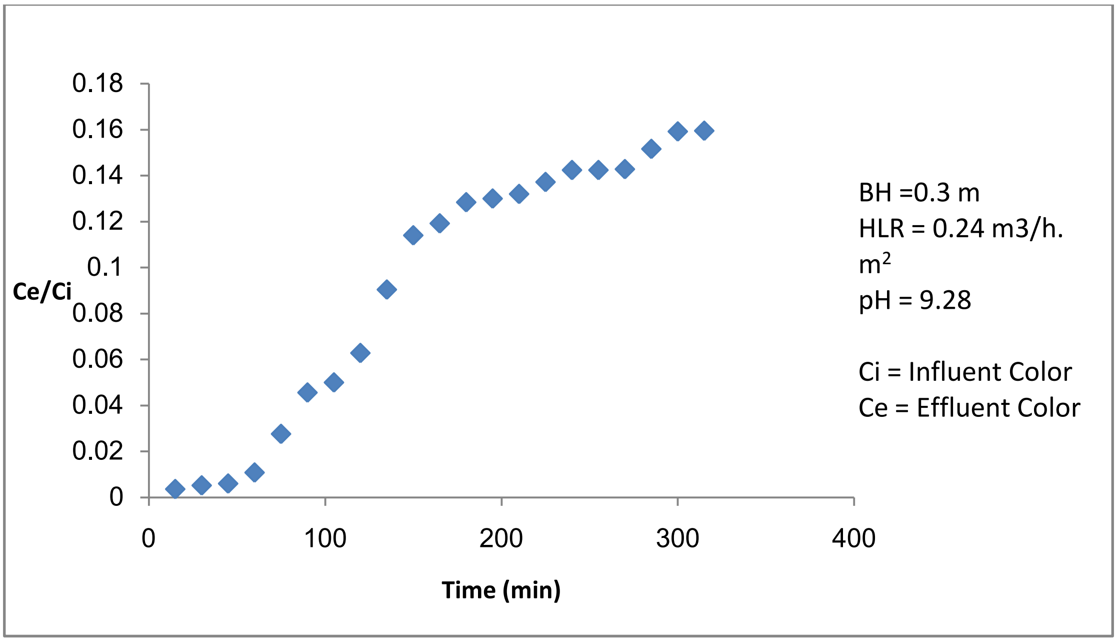

Fig. 2: Breakthrough curve for color removal

COD removal:

Since the sample COD was relatively high, the adsorption process was also studied for the removal of COD from the POME. Column study was performed at a hydraulic loading rate of 0.24 $m^3/\ m^2$ h and a bed height of 0.3 m. Fig 3 shows the experimental results for the removal of COD. It is developed from the ratio of the effluent COD [COD_f] to the influent COD [COD_{in}] and the process time. It can be seen from the figure that about 12 % of the initial COD escapes the column at the start, and this remain constant for about 50 minutes. Thereafter, the effluent COD then raises steadily and approaches the influent COD. As the sample flows down the column, the COD is absorbed by the resin, and little COD escapes the column [about 10 %]. As the flow continues however, the adsorptive capacity of the resin decreases as the pore spaces are filled by the COD. Thus, more COD escapes the column. After about 180 minutes, the effluent COD reached 80 % of the initial COD. Also the resin has a high capacity for COD removal by removing more than 88 % of the initial COD, it is easily exhausted and thus frequent regeneration is required. However, the resin can be easily regenerated by simple solution of NaCl and NaOH.

Effect of Bed Height:

Breakthrough experiments were carried out at different bed height [0.1 m, 0.2 m and 0.3 m] in order to evaluate its effect on the breakthrough time and adsorptive capacity. The hydraulic loading rate was kept constant at 0.24 $m^3/h\ m^2$. Fig 4 below shows the experimental results for the three bed height. It can be seen from fig. 4 that the breakthrough time increases with an increase in bed height. Also the minimum outlet color value decreases with the bed height. The reverse is the case for lower bed height. For example, just an hour after starting the process, the effluent color was about 27 PtCo, 225 PtCo, and 355 PtCo for 0.3 m, 0.2 m, and 0.1 m respectively. Also the breakthrough occurs at about 140 min, 80 min and 15 min for the 0.3 m, 0.2 m and 0.1 m respectively. Thus it can be seen that both the adsorptive capacity as well as the breakthrough time increase with increase in bed height.

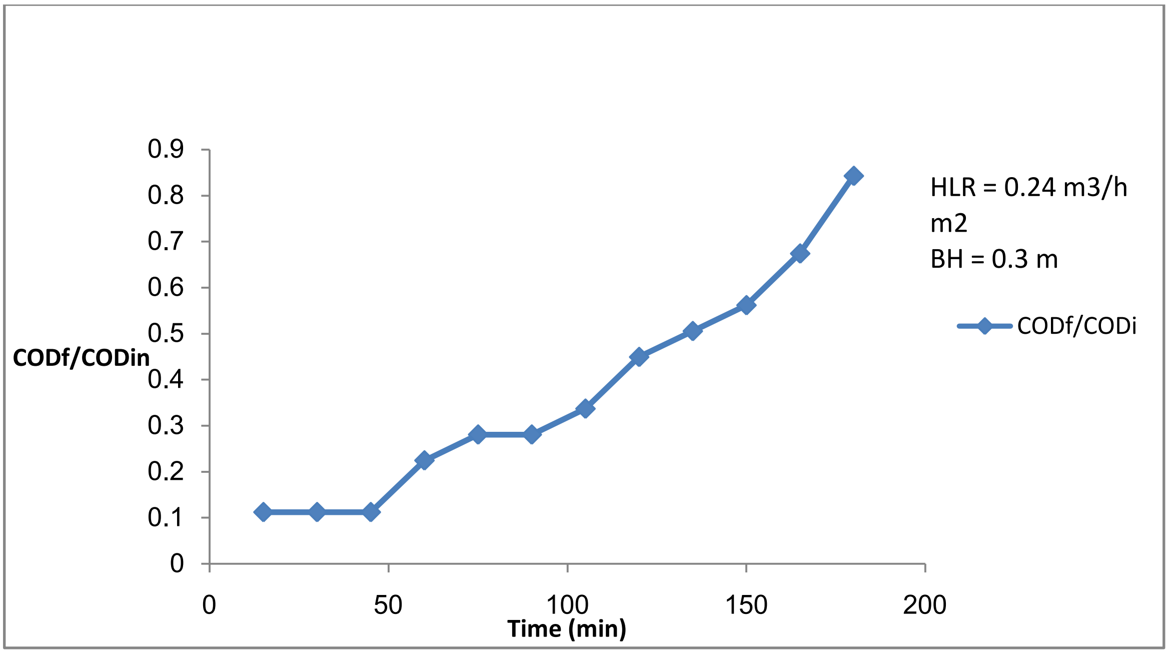

Fig. 3: breakthrough curve for COD

This effect can be explained from theoretical perspectives either using mass transfer or the concept of hydraulic retention time.For mass transfer, as the height of the adsorption bed increases, more adsorbent surfaces are provided for the adsorbate, and thus more adsorption occurs. Enough surfaces are provided and the adsorbates only escape when the surfaces are filled. When the bed height is low, fewer surfaces are provided and the adsorbate easily escapes. Thus as the bed height increases, more color is removed as a result of more availability of adsorption surfaces.

In terms of hydraulic retention time [HRT], as the bed height increases, so does the hydraulic retention time provided that the hydraulic loading rate remains constant. This is the time taken for a particular sample to exist the adsorption column after introducing it from the top of the column. Therefore, the longer the retention time, the longer the sample stay in contact with the adsorbent and hence the higher the chances for adsorption to occur.Higher bed height means longer retention time and consequent effective adsorption.The results are similar to reported literature [20]

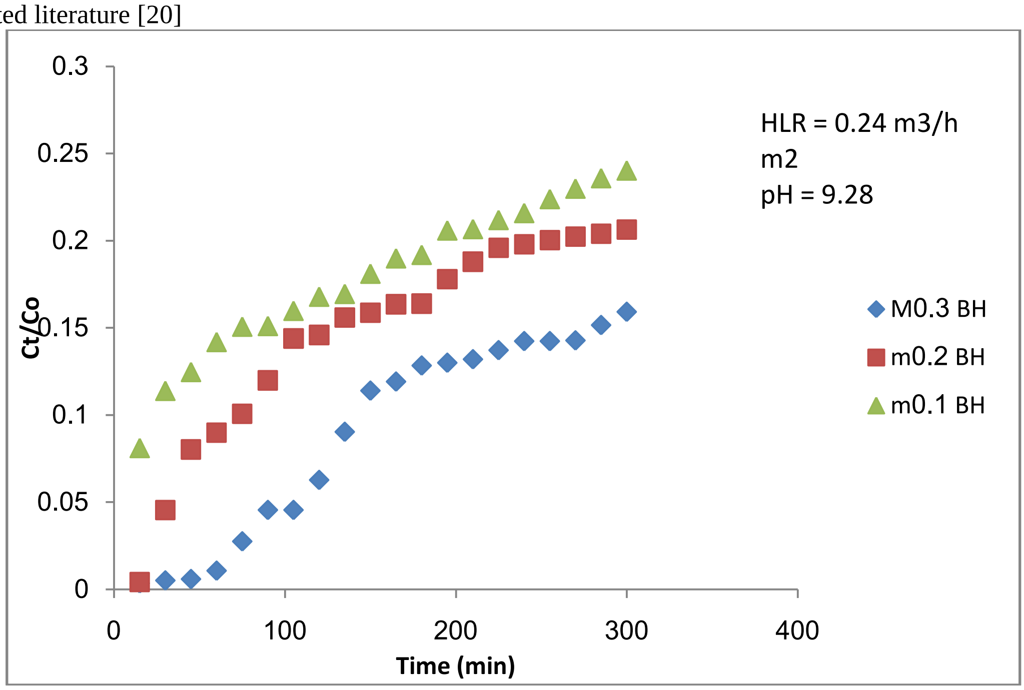

Fig. 4: Effect of Bed Height

Conclusions:

In this study, the suitability of using resin to remove color and COD from final discharge POME was investigated. Breakthrough curves were developed and the resin was found to have high adsorption capacity for color removal. However, the COD removal is not as effective as the color removal and the resin capacity is easily exhausted in the case of COD. The ability of the resin to be used repeatedly without much loss of capacity is advantageous.

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