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Comparison Of Natural Adsorbent For Emulsified Wastewater Treatment

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Abstract. Oil emulsion is often generated from machining industries, such as computer numerically controlled (CNC) machines and palm oil mill effluent (POME). The current study presents the adsorption strategy in treating the waste emulsion from CNC machines and POME using activated carbon, corncob, and rice husk. To evaluate the adsorbent performance, a jar test apparatus was used with the addition of the adsorbents for treating waste emulsion at the mixing rate of 100 rpm, mixing time of 30 min, and room temperature. The collected wastewater samples were characterised and analysed for chemical oxygen demand (COD), biological oxygen demand (BOD), oil and grease (O&G), and total suspended solids (TSS). Five dosages of activated carbon, corncob, and rice husk were used in the study (i.e., 2, 4, 6, 8, and 10 wt. %) with the control (0 wt. %). The study showed that rice husk and activated carbon managed to reduce pollutants in the emulsified wastewater. Thus, rice husk and activated carbon are suitable for treating industrial waste emulsion.

1. Introduction

Water is an essential source of life. The scarcity of clean water due to rapid industrialisation leads to the increasing demand for clean water accessibility [1]. Emulsion wastewater, such as palm oil mill effluent (POME), is a major source of water pollution [2,3]. Typically, emulsion wastewater is released or sent for treatment. However, the emulsion is insoluble and exposed to toxic chemicals and heavy metals [4].

Palm oil processing activity produces POME as wastewater. This effluent could pose environmental issues if it is discharged directly into water streams. The wastewater is frequently disposed of in transfer ponds. However, the wastewater requires the filtering of contaminants polluting groundwater and soils. Thus, it is crucial to conduct POME pretreatment before being released to the local environment [5].

In Malaysia, RM72 million is spent every year to treat 240 tons of wastewater. As large amounts of money are spent by businesses to manage wastewater, it is rational to conduct research to tackle this matter [2]. It is attainable to have a treatment facility that operates continuously on a reasonable spending plan with a high emulsion breaking framework. Despite the potential in enhancing adsorption for wastewater treatment, only several studies have utilised biomaterials as adsorbents. Economical adsorbents are favoured due to economic practicality. In this work, activated carbon, corncob, and rice husk were utilised as the biomaterials for adsorbents.



Corncob is a highly absorbent, biodegradable, and renewable material that can be used for various applications. Corncobs are mostly cellulose, which is an excellent feed additive for cattle and environmentally friendly. Corncob can be used as a carrier to dilute active ingredients safely. Meanwhile, rice husk is a biopolymer that has been recently investigated for the removal of toxic metal ions. Rice husk is the by-product of the rice milling industry, which is produced in large quantities as a waste. Rice husk mainly consists of 35% cellulose, 25% hemicelluloses, 20% lignin, 17% ash (including silica), and 3% crude protein. This composition is associated with many chelating ligands and functional groups, making rice husk suitable for metallic cation fixation. On the other hand, activated carbon with a high surface area is the most used adsorbent for treating various types of pollutants [6]. A trademark highlight is its permeable structure. Subsequently, the unique properties of activated carbon contribute to its application as an effective adsorbent to treat impurities in water and remove foul odour and toxic air pollutants. This research was conducted to assess the adsorption performance of activated carbon, corncob, and rice Husk in emulsified wastewater.

2. Materials And Methods

2.1. Experimental materials

Approximately 60 L of waste emulsion was collected from a computer numerically controlled (CNC) machine at the FTEK Laboratory in Universiti Malaysia Pahang, and the POME was collected from Kilang Sawit LCSB Lepar, Pahang, Malaysia. The samples were then refrigerated at about 4 °C to prevent bioactivities. The analysis was done within 8–24 h of collection from the plant. For the adsorbents used, rice husk was purchased from LLH Biomass Sdn. Bhd. in powder form and activated carbon was purchased from Century Chemical Works Sdn. Bhd. (CCWSB) also in powder form. Meanwhile, corncob was purchased from LC MAIZE Manufacturing Sdn. Bhd. and ground into fine powder. The properties of the adsorbents are presented in Table 1.

Table 1. Characteristics of adsorbents

No.	Adsorbent	Particle Size (d.nm)	Surface Area (m ² /g)
1	Rice Husk	297.0	42.0210
2	Corncob	604.1	4.8262
3	Activated Carbon	829.4	598.0388

2.2. Experimental procedures

The jar test was conducted using a row of six beakers, and each beaker was equipped with stirring devices for the adsorption study of emulsion wastewater. The test utilised five different dosages of adsorbents (2, 4, 6, 8, and 10 wt. %) in separate beakers at the mixing rate of 100 rpm, mixing time of 30 min, and room temperature. The sixth beaker was used as a control (0 wt. %). The study of parameters shown in Table 2 was conducted to evaluate the adsorption capacity of adsorbents for reducing the specific parameters of the collected wastewater. The analysis of the treated samples involved several parameters, such as chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended (TSS), oil and grease (O&G), and pH, which are based on the Examination Manual of Water and Wastewater [7]. The analysis was carried out at the facilities in the Central Lab, Universiti Malaysia Pahang.

Table 2. Summarised experimental analysis methods

Parameter	Test Method	Equipment
COD	ASTM D1252 - 06(2012) e1 (ASTM, 2018)	HACH Model DR/2400 and HACH reactor
BOD	ASTM D 1252 - 60 (ASTM, 2018)	Yellow Springs Model 5010 and BOD incubator
TSS	ASTM D5907-18 (ASTM, 2018)	Laboratory apparatus
O&G	ASTM D3921 (ASTM, 2018)	Laboratory apparatus
pH	ASTM D1293-18 (ASTM, 2018)	Seven Easy pH, Mettler Toledo

2.3. Characterisation of waste emulsion

The pH, TSS, COD, BOD, and O&G properties of the collected CNC and POME waste emulsion was characterised before adsorption treatment. The characteristics of the waste were compared to Standard A and Standard B water quality parameter limits set by the Department of Environmental (DOE) Malaysia.

3. Results and Discussion

Standard A and Standard B were used for the comparison of parameters analysed in this study. The results for the raw samples of CNC emulsion and POME, as well as the waste samples treated by using 10 wt. % of adsorbents are presented in Table 3. Standard A and Standard B were applied in this study as the guidelines at water catchment territories, which incorporate the regions of upstream of surface or above sub-surface of waterways, primarily for the community and human use [8].

Table 3. Treated CNC emulsion and POME using 10 wt. % rice husk, corncob, and activated carbon

	St. A ^a	St. B ^b	Raw CNC	Raw POME	CNC-RH ^c	CNC-CC ^d	CNC-AC ^e	POME-RH ^c	POME-CC ^d	POME-AC ^e
COD (mg/L)	50	100	9,000	14,450	3,440	9,090	6,400	10,100	15,500	4,290
BOD (mg/L)	20	40	170	378	74	167	133	68	180	74
TSS (mg/L)	50	100	3,475	421	72	893	915	170	437	63
O&G (mg/L)	1.0	10	523	24	8	207	100	42	11	6
pH	6.0–9.0	5.5–9.0	6.8	6.1	7.4	6.0	7.1	6.0	4.3	6.2

^aSt. A = Standard A, ^bSt. B = Standard B, ^cRH = Rice husk, ^dCC = Corncob, ^eAC = Activated carbon

Overall, the values of COD, BOD, TSS, and O&G for raw emulsion samples (CNC and POME) exceeded the acceptable limits of Standard A and Standard B, as can be seen in Table 3. These parameters are significant in determining the de-emulsification effect of emulsion waste treatment. Meanwhile, the pH recorded was 6.1 for POME and 6.8 for CNC emulsion, compared to the acceptable limits of 6.0–9.0 and 5.5–9.0 of Standard A and Standard B, respectively. For all the parameters studied, rice husk outperformed other adsorbents for CNC emulsion treatment, whereas activated carbon is more favourable towards POME in reducing COD, BOD, TSS, and O&G.

The figures below show the removal percentage of COD, BOD, TSS, and O&G by rice husk, corncob, and activated carbon for CNC emulsion and POME. The removal of COD from CNC emulsion is shown in Figure 1(a). At 10 wt. % rice husk, corncob, and activated carbon, the COD reduction obtained was 61.77%, 28.88%, and 1%, respectively. At only 2 wt. % of adsorbent dosage, the rice husk and activated carbon reduced the COD by 59.22% and 3.32%, respectively, but corncob contributed to a higher COD by 8.51%.

From Figure 1(b), at the highest adsorbent dosage (10 wt. %), corncob showed the lowest COD reduction compared to other adsorbents. Meanwhile, at the same dosage, activated carbon demonstrated the highest reduction of COD. Activated carbon achieved 70.31% of COD reduction, whereas corncob and rice husk reduced -7.27% and 30.10% of COD at the maximum dosage, respectively. At the lowest adsorbent dosage (2 wt. %), activated carbon recorded the highest COD reduction at 51.97% and rice husk achieved 14.19% of COD reduction. Meanwhile, corncob showed a negative effect on COD removal, which contributed to 33.56% of higher COD value.

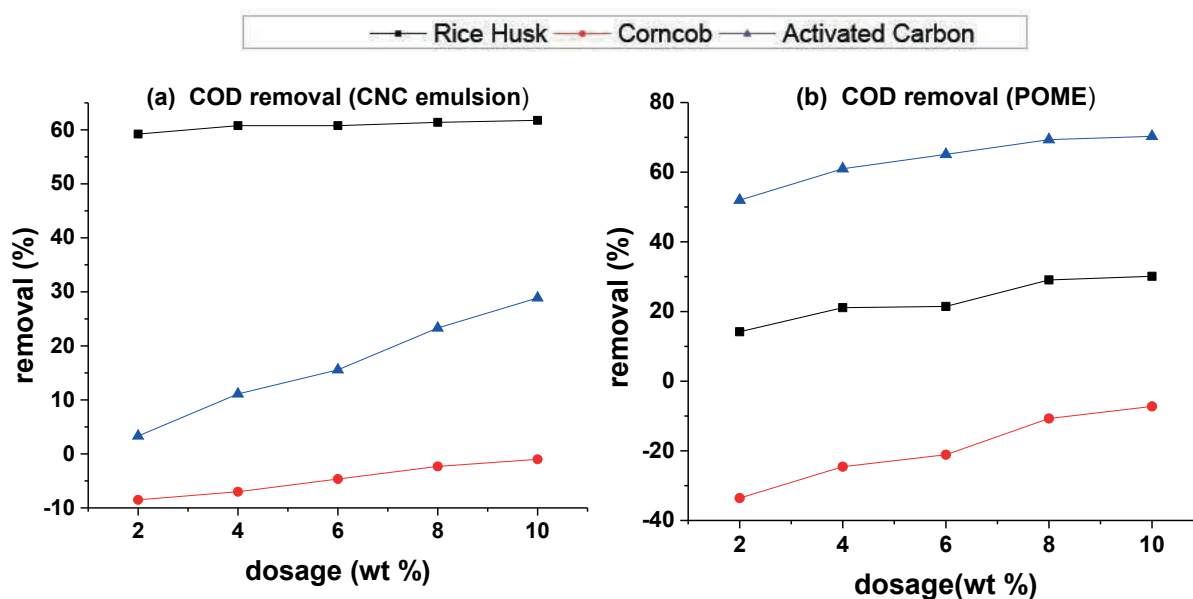


Figure 1. Effects of adsorbent dosage of rice husk, corncob, and activated carbon on the removal of (a) COD on CNC emulsion, (b) COD on POME

Figure 2(a) presents the effect of the reduction of BOD for CNC emulsion. At the highest adsorbent dosage (10 wt. %), rice husk demonstrated the highest reduction of BOD (56.47%) compared to corncob (1.76%) and activated carbon (21.76%). At the lowest adsorbent dosage (2 wt. %), rice husk also showed the highest reduction of BOD (5.29%) compared to activated carbon (2.94%). Meanwhile, at the same dosage, corncob showed the lowest reduction of BOD (-12.35%). Based on the results, rice husk proved to be the best adsorbent in reducing BOD from waste emulsion with the maximum dosage of injection. Figure 2(b) illustrates the removal of BOD for POME. At 10 wt. %, rice husk, corncob, and activated carbon achieved 82.01%, 52.38%, and 80.42% of BOD reduction, respectively. At the lowest dosage (2 wt. %), rice husk showed the highest reduction of BOD (81.75%), followed by activation carbon (79.89%) and corncob (27.51%).

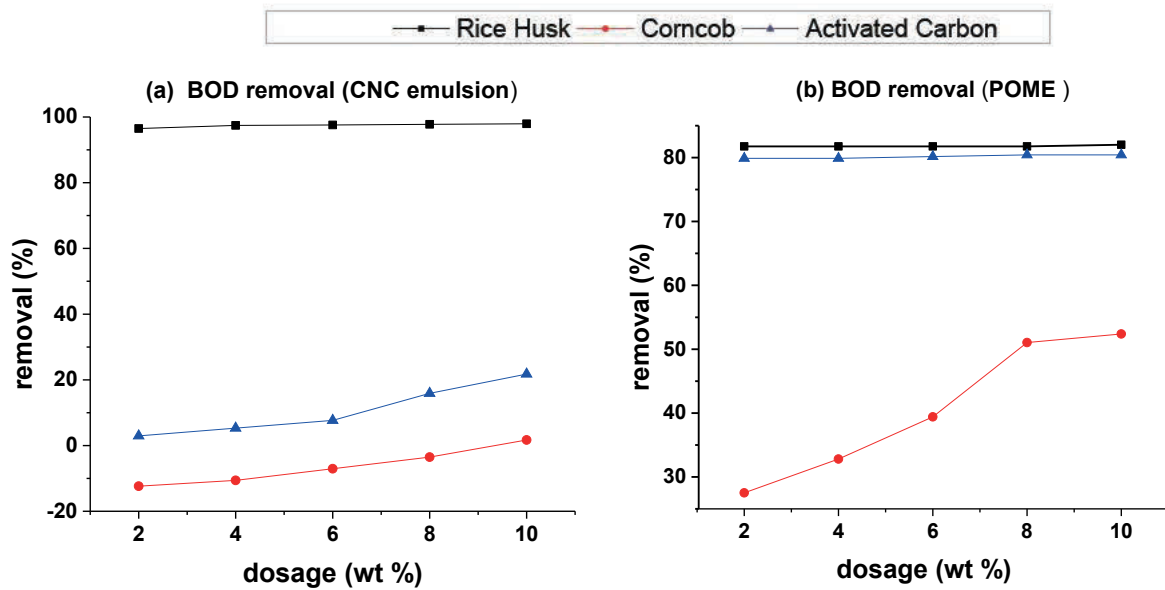


Figure 2. Effects of adsorbent dosage of rice husk, corncob, and activated carbon on the removal of (a) BOD on CNC emulsion, (b) BOD on POME

The effect of TSS reduction for CNC emulsion is shown in Figure 3(a). At the maximum dosage of 10 wt. %, rice husk, corncob, and activated carbon reduced the TSS by 97.93%, 74.30%, and 73.67%, respectively. Meanwhile, the effect of TSS reduction for POME is presented in Figure 3(b). The figure shows that at 10% wt. of adsorbents, corncob negatively affected the TSS, where the TSS value increased by 3.80%. Activated carbon demonstrated the highest reduction of TSS (85.04%), followed by rice husk (59.62%).

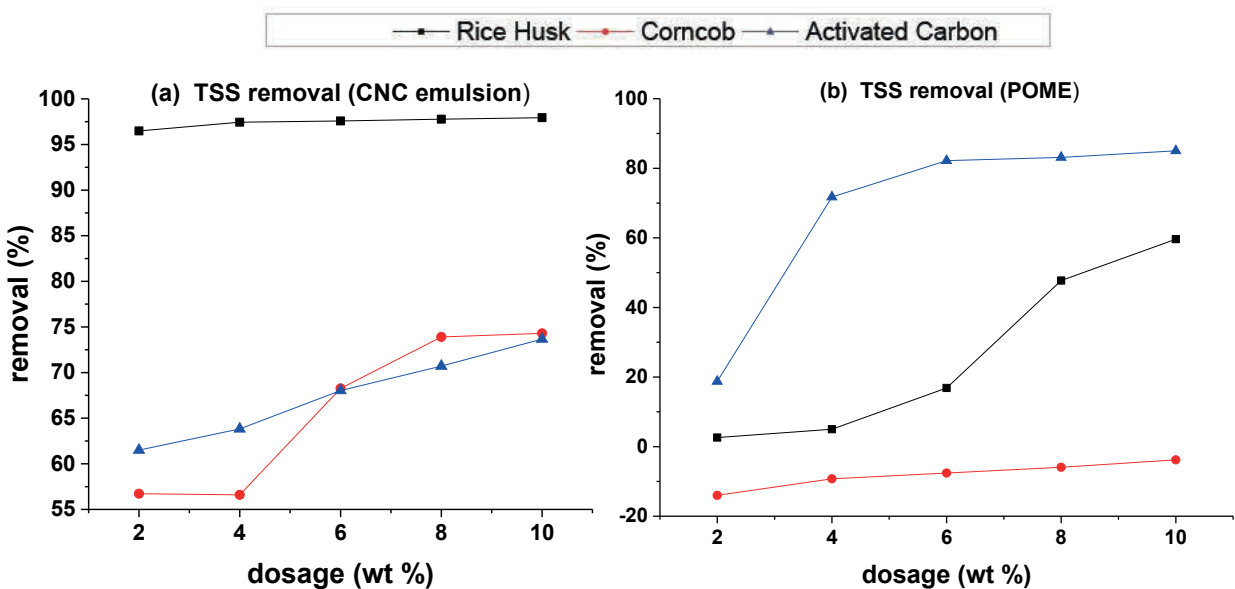


Figure 3. Effects of adsorbent dosage of rice husk, corncob, and activated carbon on the removal of (a) TSS on CNC emulsion, and (b) TSS on POME

The removal of O&G from CNC and POME samples is shown in Figure 4(a) and 4(b), respectively. By using 10 wt. % of adsorbent dosage, corncob recorded the lowest reduction of O&G compared to other adsorbents for CNC emulsion and POME. Meanwhile, rice husk demonstrated the highest reduction for CNC emulsion and POME at 98.47% and 83.33%, respectively.

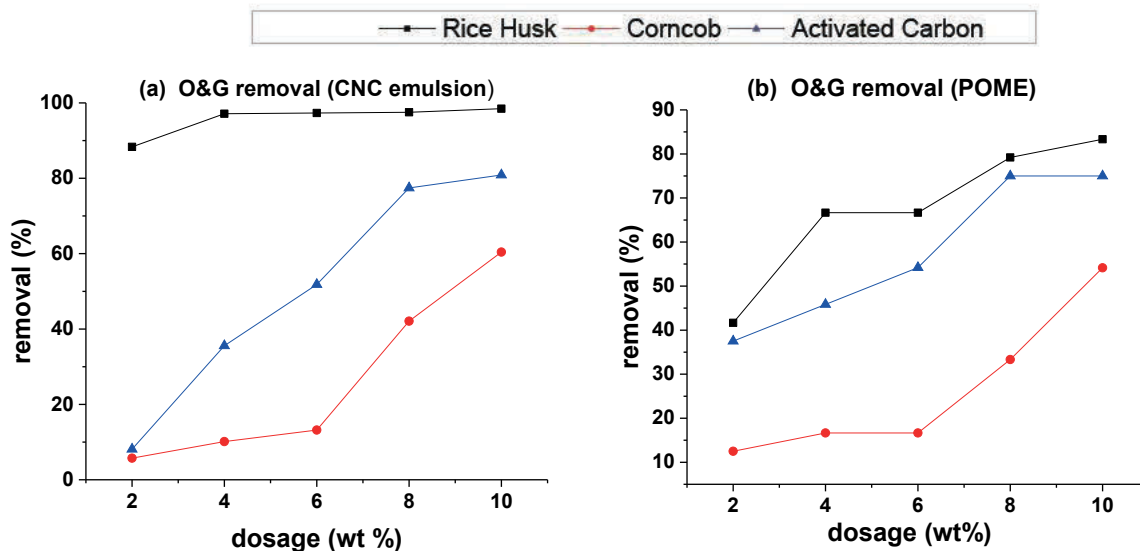


Figure 4. Effects of adsorbent dosage of rice husk, corncob, and activated carbon on the removal of (a) O&G on CNC emulsion, (b) O&G on POME

The treatment using corncob shows an increment of COD value for both CNC emulsion and POME. This could be due to the dissipation of organic compound from the corncob into the wastewaters. Thus, the corncob may not be a suitable material to reduce the COD value of emulsified wastewater as shown in this study. However, the corncob was shown to be moderately effective for TSS removal of CNC emulsion.

Activated carbon has the largest surface area of approximately $598.0388 \text{ m}^2/\text{g}$ compared to rice husk ($42.0210 \text{ m}^2/\text{g}$) and corncob ($4.8262 \text{ m}^2/\text{g}$). Therefore, this characteristic gives the advantage to activated carbon as a more effective adsorbent in treating CNC emulsion. At this point, the colloidal particles in the samples are absorbed by pores, thus reducing the TSS of wastewater. Adsorption of fine particles can be achieved by having a large surface area that helps to adsorb the suspended solids (SS) inside the waste. The fine particles dissolve and break up SS throughout the mixing time in the jar test. The TSS removal is easier, quicker, and faster for a larger surface area [9].

Better adsorption performance can be achieved using an adsorbent with a larger specific surface area. The pore volume limits the size of molecules that can be adsorbed, whereas the surface area limits the amount of materials that can be adsorbed, assuming a suitable molecular size. The adsorptive capacity of an adsorbent is related to its internal surface area and pore volume [6].

Rice husk has been proven as the best adsorbent in reducing O&G from waste emulsion with the maximum dosage of injection. The ability of rice husk to reduce O&G shows that the adsorbent can break water and oil emulsion at a higher dosage. For the O&G test in POME, the best result in O&G reduction is related to the positive charge of the adsorbent, which has a larger effect than an adsorbent with a large surface area. The dissolved solids in the oil residue in waste emulsion are absorbed by the positively-charged particles in the adsorbent. Particle size and surface area are essential factors in adsorbing oil, in which the oil will be adsorbed inside the pores of the adsorbent to demulsify water-oil emulsion [10].

Activated carbon showed the lowest reduction of TSS compared to other adsorbents. Meanwhile, at the same dosage, rice husk showed the highest reduction of TSS. Rice husk has the highest positive charge, which is approximately 0.21 ± 0.36 mV [11], followed by activated carbon (-30 ± 60 mV) [12] and corncob (-11 ± 0 mV) [13]. As the dosage increases, the more positively-charged particles can settle down the negative charged particles, where the colloidal particles in the sample are absorbed by the positively-charged particles, thus reducing the TSS of wastewater. Subsequently, the dissolved solids in the oil residue in the waste emulsion are absorbed by the positively-charged particles in the adsorbent. Therefore, the TSS removal by activated carbon and corncob increases as the dosage increases. An adsorbent with a larger surface area is more favourable in reducing the TSS for POME. At this point, the chemical compound inside the waste emulsion uses less oxygen to break organic matter because the organic matter is attracted to the positively-charged particles.

4. Conclusions

The present exploratory work demonstrated the performance of activated carbon, corncob, and rice husk for emulsion wastewater treatment by adsorption. From this study, rice husk is the best adsorbent to treat the waste from CNC machines with 97.93%, 56.47%, 61.77%, and 98.47% removal of TSS, BOD, COD, and O&G, respectively, at pH of 6.8 and a minimum dosage of 2 wt. %. Meanwhile, activated carbon is the best adsorbent to treat the waste from POME with 85.04%, 80.42%, 70.31%, and 75.01% removal of TSS, BOD, COD, and O&G, respectively, at pH of 6.1 and a maximum dosage of 10 wt. %. On the other hand, corncob showed the lowest reduction removal of 74.30%, 1.76%, -1.00%, and 60.42% for TSS, BOD, COD, and O&G, respectively, at pH of 6.0. This is because corncob has the smallest surface area compared to rice husk and activated carbon. Based on the results, the adsorption using rice husk and activated carbon managed to break the oil-water bonding from the waste emulsion. Hence, rice husk and activated carbon are suitable for treating industrial waste emulsion. Therefore, it is suggested to use rice husk and activated carbon to ensure a feasible treatment of emulsion waste.

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