Alkali Treatment on Rice Husk in POME Treatment

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Abstract - **Palm oil industry is one of the world's most expanding and significant contributing towards the economic growth among the South East Asian countries such as Malaysia and Indonesia. However, along with the increasing production of palm oil, it also has high contaminant in the wastes production which is in palm oil mill effluent (POME). There are several treatment technologies were introduced to reduce the pollution concentration in wastewater but they are very expensive for cost installation. Adsorption treatment by using activated carbon can be more effective method to treat POME but activated carbon is an expensive materials. Therefore, recent study is more focused on using low cost adsorbent by using natural fibre, rice husk. However, the past studies found that by using unmodified of natural fibre exhibited poor efficiency for oil removal due to lower hydrophobicity and low oil adsorption capacity. The modification of rice husk was by using alkali treatment of sodium hydroxide (NaOH) with different concentrations (0.5 M, 1.0 M, 1.5 M, 2.0 M) and different volumes (60 mL, 80 mL, 100 mL). The oil adsorption capacity will be obtained by using n-hexane solvent extraction method. Based on results, it showed that the usage of 2.0 M and 100 mL of NaOH used to modify the rice husk was found to be the optimum condition for the modification where it gave the highest reading of oil adsorption capacity. The oil adsorption capacity of modified rice husk was higher compared to the unmodified rice husk which was at 0.4737 g/g and 0.0579 g/g, respectively. Therefore, the modified rice husk was proven to be used as adsorbent in POME treatment compared to the unmodified rice husk.**

Keywords: Palm Oil Mill Effluent (POME), Adsorption, Rice Husk, Alkali Treatment, Sodium hydroxide (NaOH), Oil Adsorption Capacity.

I. INTRODUCTION

Palm oil industry is one of the world's most expanding and significant contributing towards the economic growth among the South East Asian countries. Malaysia and Indonesia are the two countries of largest producing palm oil (Tabassum, et. al., 2015). However, along with the increasing production of palm oil, it also has contaminant in the wastes production which is in palm oil mill effluent (POME). Normally, from the palm oil industry, there were two types of waste discharged which are liquid and solid wastes. POME is a liquid wastes were produced from palm oil industry. It released from the sterilization process, crude oil clarification process and cracked mixture separation process in the production of crude oil. POME has contributed environmental pollution when discharged into water bodies without treatment so it can contaminate drinking water for human and animal communities. It can also be harmful to aquatic life by creating highly acidic to environments (Alhaji, et. al., 2016).

Treatment of POME is necessary conducted in order to prevent the environment pollution. There are several treatment technologies were introduced to reduce the pollution concentration in wastewater such as membrane separation, liquid extraction, coagulation, crystallization, electron-precipitation, ion exchange, chemical oxidation and reduction, ultrafiltration and adsorption. These treatments have their own advantages and disadvantages. Among of these technologies, it had been found that membrane separation is the most efficient method of high removal efficiency of COD but it is very expensive for cost installation (Mohammed and Chong, 2013). However, adsorption treatment by using activated carbon also can be more effective method to treat POME but activated carbon is an expensive materials. Therefore, recent study more focused on using low cost adsorbent by using natural fibre.

Natural fibres like coconut husk, wheat straw, banana peel, barley straw, rice husk and agriculture waste are eco-friendly materials with low cost adsorbents and less production of by products in wastewater treatment (Mohammed and Chong, 2013). Agriculture materials have varied greatly ability to remove metals from solution. In the recent years, there are many studies were focused and investigated the removal of heavy metals from the wastewater by using low cost materials as adsorbent in adsorption techniques. Several materials had been proved their abilities in wastewater treatment such as rice husk, banana peels, wheat straw, kapok fibre and other different agriculture by-products were used (Pehlivan, et. al., 2012). Rice husk also is one of agriculture was introduced and investigated for wastewater treatment as adsorbents. Table 1.1 shows the physicochemical of the rice husk.

Table 1.1: The physicochemical characteristic of the Rice husk (Kumar, et. al., 2010)

Characteristics	**Unit**	**Value**
Bulk density	g/mL	0.79
Solid density	gm/L	1.48
Moisture content	%	5.98
Ash content	%	48.81
Particle size	mesh	200-40
Surface area	$m^{2/}g$	320.9
Surface acidity	meq/gm	0.15
Surface basicity	meq/gm	0.55

Adsorption using natural fibre has been considered as an alternative method to treat POME due to simple of processes and low cost of adsorbents, rice husk is selected as an adsorbent to use in POME treatment. The adsorption properties are controlled by porous structure and the chemical nature of the surface. Chemical compositions that have been existed on rice husk surface mainly consist of lignin, cellulose and hemicellulose which the former two components are hydrophilic and others are hydrophobic (Xiao, et. al., 2001). Table 1.2 shows the typical composition of rice husk.

However, using raw material of natural fibre as adsorbent has been found exhibit poor oil adsorption capacity due to lower hydrophobicity and inadequate buoyancy.

Table 1.2: The typical composition of rice husk (Kumar, et. al., 2010)

Composition	Percentage (%)
Cellulose	31.12
Hemicellulose	22.48
Lignin	22.34
Mineral ash	13.87
Water	7.86
Extractives	2.33

Therefore, the modification of natural fibre is needed for better application in adsorption. Alkaline treatment is introduced to modify the rice husk. The treatment will improve and reinforce the functional group potential and increasing the number of active sites on the surface of fibre (Hokkanen, et. al., 2016). Sodium hydroxide, (NaOH) which is strong alkali is used for interrupt the covalent association between lignocellulose, depolymerizing lignin and hydrolyzing hemicellulose to improvement of adsorption capacity of the modified rice husk as adsorbent in POME treatment. Hence, NaOH is suitable reagent that can change the surface structure of fibre through alkaline treatment through the hydrogen bonds existed between the fibre broke down and formed reactive hydrogen bonds among the cellulose molecular chain which successfully removed the hydrophilic hydroxyl group and increased the moisture content of fibre surface (Kabir, et. al., 2013).

In this study, the rice husk is modified by using sodium hydroxide, NaOH. The purpose of modification of rice husk is to increase the hydrophobicity and adsorption capacity of rice husk as oil adsorbent. The rice husk was modified by using different concentrations (0.5 M, 1.0 M, 1.5 M, 2.0 M) and different volumes added (60 mL, 80 mL, 100 mL) of NaOH in order to determine the optimum (highest) oil adsorption capacity. In order to determine the effect of alkali modification on rice husk, the oil adsorption capacity of optimum condition obtained was compared to the oil adsorption capacity of unmodified rice husk.

II. MATERIALS AND METHODS

A. Adsorbents Preparation

A rice husk was repeatedly washed with distilled water in order to remove other impurities and dust. The rice husk was dried in an oven at 65°C for 48 hours to achieve a constant weight and then grounded by using Cutting Mill in Polymer laboratory with mesh size of 100 μm. The sample was separated into two containers and labeled as unmodified rice husk and modified rice husk. The modification of the surface characteristic of rice husk was achieved by using alkali treatment. The alkali treatment was prepared by using Sodium Hydroxide, NaOH which is strong alkali. Firstly, the preparation of adsorbent was carried out by soaking 10 g of rice husk with 0.5 M sodium hydroxide (NaOH) solution with different volumes of NaOH which were 60 mL, 80 mL and 100 mL. Then, the suspended solutions were shaken by using orbital shaker for 2 hours at room temperature with speed of 170 rpm. The modified rice husks then were rinsed with distilled water three times in order to allow the absorbed alkali to drain from the husk. The modified rice husks were dried again in an oven at 65°C for overnight (Ibrahim, et. al., 2009). The experiment was repeated by soaked the rice husk with NaOH solution using different concentrations which are 1.0 M, 1.5 M and 2.0 M.

B. Oil Adsorption Test

The batch adsorption experiment was carried out at room temperature by testing using modified adsorbent and unmodified adsorbent of rice husk on raw POME. Before being filtered, the raw POME and rice husk adsorbents were mixed and the mixture was stirred using magnetic stirrer for 30 min with stirring scale 130 rpm. The mixture was stirred at minimum speed in order to get uniform mixing of mixture. The filtration process was conducted to analyse for oil adsorption content. The n-hexane solvent extraction method was used for adsorption of oil content in POME. 20 mL sample of mixture was poured into separatory funnel. Prior for addition 3 mL of hexane, the sample must pH $\leqslant$ 2 by adding 9 drops of water and HCl with ratio 1:1. Then, the separatory funnel was shaken vigorously for 2 min and left until formation of two layers of sample. The oil layer was obtained by using gravity filtration apparatus. After that, the oil sample was dried in oven for 15 min at 103°C and then cooled at room temperature before weighed. The weight of sample was recorded and labeled as oil and grease content value (Wahi, et. al., 2014). Therefore, the oil adsorption capacity was obtained by following equation:

Oil adsorption capacity = Mass of oil removed (g) / Mass of adsorbent used (g) …………………….. (1)

III. RESULTS AND DISCUSSION

1. Effect of Molarity of Sodium Hydroxide Added

The study of modification of rice husk is to increase the hydrophobicity and adsorption capacity of rice husk as oil adsorbent. It is expected that the modified rice husk will increase the oil adsorption capacity. The difference concentrations of sodium hydroxide (NaOH) were studied in modification of rice husk in order to determine the highest oil adsorption capacity. Figure 1.1 shows the oil adsorption of rice husk treated with the 0.5 M of NaOH.

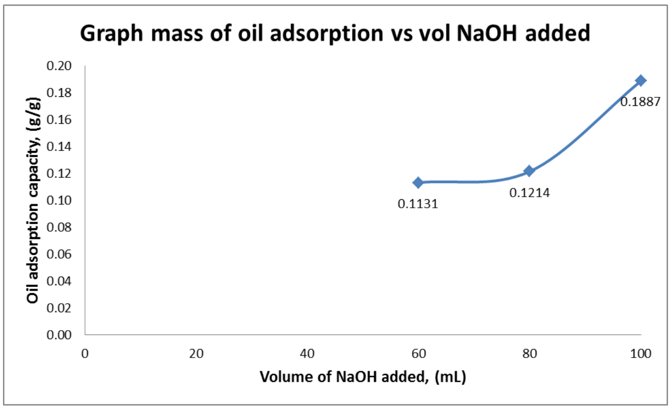

Figure 1.1: Oil Adsorption of POME at 0.5 M of NaOH

Figure 1.1 shows that the oil adsorption capacities of modified rice husk with 0.5 M of NaOH. The trend showed that the oil adsorption capacity of POME at 60 mL of NaOH added was obtained at 0.1131 g/g and when the volume of NaOH was increased to 80 mL, the oil adsorption capacity was slightly increased which was 0.1214 g/g. Meanwhile, at 100 mL of NaOH added, the oil adsorption started to increase sharply with the value of 0.1887 g/g. It can be concluded that the oil adsorption capacities of modified rice husk increased with the increasing of volume of NaOH.

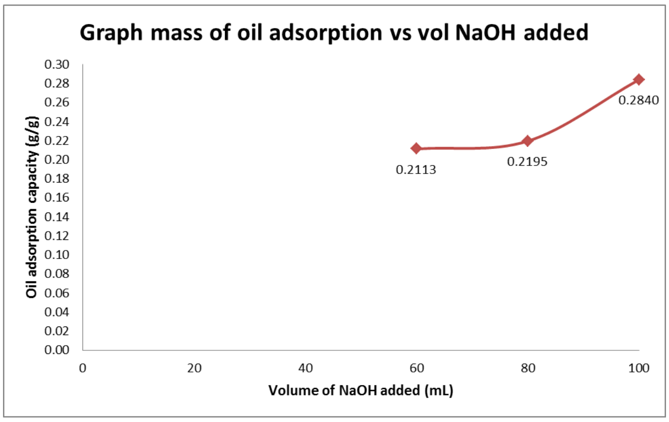

Figure 1.2: Oil Adsorption of POME at 1.0 M of NaOH

The oil adsorption capacity of rice husk with the 1.0 M of NaOH was shown in Figure 1.2. It illustrated the oil adsorption capacities of modified rice husk had same trend as Figure 1.1. However, by using 60 mL of NaOH, it exhibits slightly higher in oil adsorption capacity compared to 60 mL of NaOH at 0.5 M concentration which was 0.2113 g/g. The graph started to increase slightly to 0.2195 g/g when the volume of NaOH increased to 80 mL. There was a significant increased in the oil adsorption capacity which about 0.2480 g/g due to the increasing of NaOH at 100 mL. It can be concluded that the oil adsorption capacity of POME is directly proportional to the volume of NaOH added. This is supported by Min et. al. (2004), the study showed when the increasing the concentration of NaOH enhanced the increment the amount of carboxylates which the maximum adsorption capacity of cadmium ions up to three times which to 0.26 g/g.

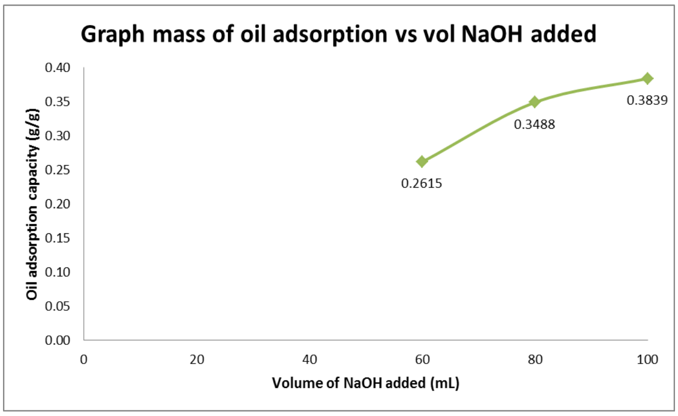

Figure 1.3: Oil Adsorption of POME at 1.5 M of NaOH

Figure 1.3 demonstrated that the oil adsorption capacities of modified rice husk with 1.5 M of NaOH. The result showed that the oil adsorption capacity of POME went up when using the volume of NaOH was 60 mL which obtained at 0.2615 g/g. It showed that the value of oil adsorption capacity for 1.5 M is higher compare to 0.5 M and 1.0 M concentrations of NaOH. Then, the graph started to increase sharply when the volume of NaOH increased to 80 mL and exhibited at 0.3488 g/g. It was continued increased when using 100 mL of volume NaOH which was 0.3839 g/g. Therefore, it can be concluded that the oil adsorption capacities of modified rice husk increases with increasing the volume of NaOH.

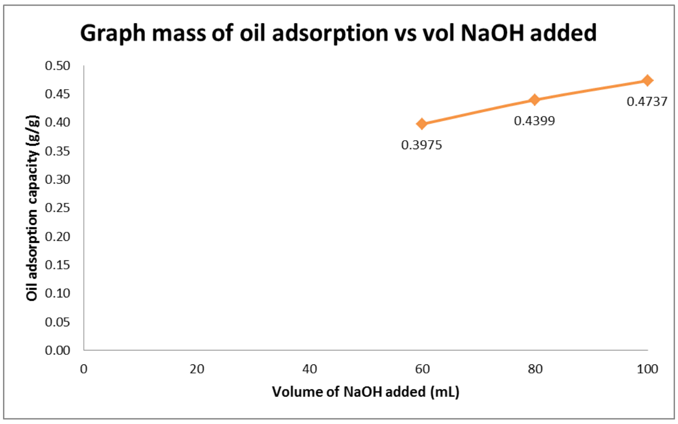

Figure 1.4: Oil Adsorption of POME at 2.0 M of NaOH

On the other hand, the Figure 1.4 showed and proved that the oil adsorption capacities of modified rice husk with 2.0 M of NaOH exhibit the highest value of oil adsorption capacities when the volume of NaOH added to 60 mL, 80 mL and 100 mL which were 0.3975 g/g, 0.4399 g/g and 0.4737 g/g respectively. The trend showed that the oil sorption capacity of POME at 60 mL of NaOH was rises to 0.3975 g/g and continued increased sharply when the volume of NaOH added to 80 mL and 100 mL at 0.4399 g/g and 0.4737 g/g.

Based on Figure 1.1, Figure 1.2, Figure 1.3 and Figure 1.4, showed that the effect of the difference concentration of NaOH in oil adsorption capacity of POME. Hence, the modified rice husk with higher concentration of NaOH exhibits higher oil adsorption capacity. It can be concluded that rice husk modified with 2.0 M of NaOH exhibits the highest oil adsorption capacity. From the result showed that the modified rice husk exhibits higher oil adsorption capacity which was The similar result has been reported in the study of effect of kapok fiber treated with various solvents on oil absorbency (Wang, et. al., 2012). The oil absorbency of the treated kapok fibre increases when the concentrations of sodium hydroxide increase. However, the oil absorbency was going down when the further treatment by increasing treatment concentration up to 3%.

It is proven that through the alkali treatment, the external surface of fibre becomes rougher due to removal some of hemicellulose and lignin wax. The hydrogen bonds existed between the fibre broke down and formed reactive hydrogen bonds among the cellulose molecular chain which successfully removed the hydrophilic hydroxyl group and increased the moisture content of fibre surface (Kabir, et. al., 2013). Some studies showed that the unmodified fibre will have smoother surface compared to the modified fibre. Meanwhile, Wahi, et. al. (2014), reported that the modified sagu bark obtained rougher surface with formation of pores. It also showed that, the rougher surface of sorbent will enhance lower BET surface area while higher hydrophobicity of sorbents. However, it showed that the raw fibers have smooth and homogeneous surface with higher porosity of sorbent while through chemical treatment (acid or alkali), there has no changes or effect on the sorbent's surface.

2. Effect of Volume Added of Sodium Hydroxide

The difference volumes of sodium hydroxide (NaOH) were studied in modification of rice husk in order to determine the effect of volume added of NaOH on oil adsorption capacity of POME. The oil adsorption capacity of modified rice husk after treated with different volume of sodium hydroxide is shown in Figure 1.4. The previous results showed that the rice husk modified with 2.0 M of NaOH concentration exhibit the highest oil adsorption capacity. The result demonstrates that the oil adsorption capacities were increased gradually when the volume of NaOH also increased. When using 100 mL of volume NaOH, it exhibits the highest oil adsorption capacity which was 0.4737 g/g. It is proven that the volume of NaOH also gave a significant impact to the oil adsorption capacity of POME. Therefore, the modified rice husk using sodium hydroxide as alkali treatment will obtain higher oil adsorption capacity and can produced modified rice husk as a new development technology for POME treatment which is more environmental friendly. The sodium hydroxide is commonly used in chemical treatment of natural fibre due to NaOH treatment can eliminated any waxy substances, pectin and natural oil that presence at external surface of fibre which can obtained a rough surface. Therefore rough surface will increase the hydrophobic interaction between the sorbent and the sorbate. The sorbent have the capabilities to float on oil surface and allow the rice husk to work effectively as an oil adsorbing material for oil mixtures (Wang, et. al., 2012).

Therefore, the usage of 2.0M and 100 mL of NaOH used to modify the rice husk was found to be the optimum condition for the modification where it gave the highest reading of oil adsorption capacity. It can be concluded that the higher the concentration of rice husk, the higher the adsorption capacity. Furthermore, as the volume of alkali used for treatment increase the higher is the oil adsorption capacity. Then, the oil adsorption capacity of optimum condition obtained was compared to the oil adsorption capacity of unmodified rice husk in order to determine the effect of alkali modification on rice husk. Figure 1.5 and Figure 1.6 showed the comparison of oil adsorption of unmodified rice husk and modified rice husk.

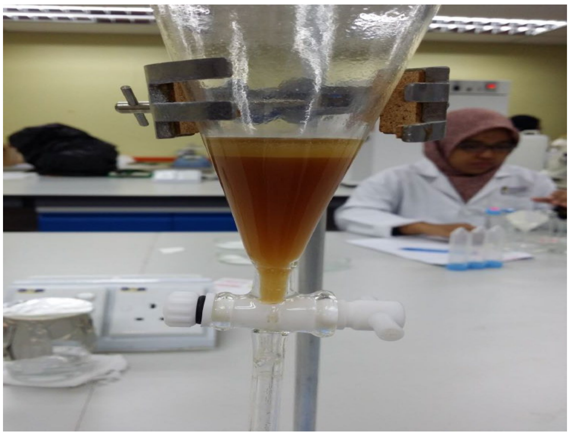

Figure 1.5: The oil adsorption of unmodified rice husk

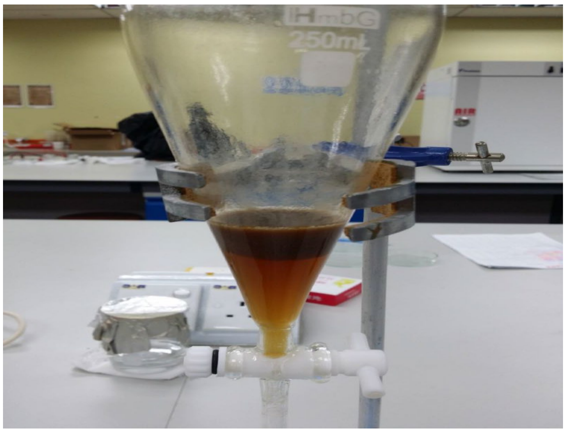

Figure 1.6: The oil adsorption of modified rice husk with 2.0 M of NaOH

Based on the Figure 4.5 and Figure 4.6, showed that the oil adsorption capacity of modified rice husk was higher compared to the oil adsorption capacity of unmodified rice husk. The oil adsorption capacity of modified rice husk and unmodified rice husk was obtained at 0.4737 g/g and 0.0579 g/g respectively. There were significant different between the oil adsorption capacity of modified and unmodified rise husk. The results shows that when the rice husk was treated with alkali, NaOH the oil adsorption capacity was higher compared to unmodified rice husk. It had been proven that the modification of rice husk by using alkali treatment can be used as adsorbents in POME treatment.

IV. CONCLUSION

In conclusion, the results obtained from this study had showed the capability of rice husk to be used as a medium to adsorb oil contained in POME. However, in order to overcome the limitation of rice husk as natural adsorbent to adsorb oil, it was modified with alkali treatment. The results showed that when the rice husk was treated with alkali, Sodium hydroxide (NaOH), the oil adsorption capacity was higher compared to unmodified rice husk. The usage of 2.0M and 100 mL of NaOH used to modify the rice husk was found to be the optimum condition for the modification where it gave the highest reading of oil adsorption capacity. Thus, it can be concluded that the higher the concentration of rice husk, the higher the oil adsorption capacity. A high hydrophobicity and high buoyancy of modified rice husk contributes to high oil adsorption capacity. Furthermore, as the volume of alkali used for treatment increased, the oil adsorption capacity became higher. Therefore, the modified rice husk by using sodium hydroxide as alkali treatment can be used as a new development technology for POME treatment which is more environmental friendly.

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