Acid Treatment on Rice Husk in POME Treatment

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Abstract*— Palm oil industry is an important industry in Malaysia as it is one of the biggest contributors to Malaysia's economy. With the expansion of oil palm industry, the pollution caused by the industry also increase. The main problem with oil palm plantation is its mill effluent known as POME. There are many treatments available to treat the effluent but the problem is it is not environmental friendly. The most efficient way available to treat the effluent is by adsorption treatment. Adsorption treatment usually uses activated carbon as its adsorbent. However, usage of activated carbon has many drawbacks such as regeneration problem. Thus, this research is focusing on environmental friendly alternative to the usage of activated carbon which is agricultural waste, rice husk. Rice husk exists abundantly throughout the world at low price. It can be used as replacement to activated carbon but it needs to be treated first to overcome its drawback such as low adsorption capacity and low hydrophobicity. The fibre is treated with strong acid, sulphuric acid to increase its hydrophobicity and sorption capacity. The mass of rice husk used for modification was varied from 5g, 10g and 15g. The rice husk was modified by using 0.5M, 1.0M, 1.5M, and 2.0M of sulphuric acid. The oil adsorption capacity of the rice husk was determined by using n-hexane extraction method. The optimum condition of oil adsorption capacity was obtained when 5g of rice husk was modified with 0.5M sulphuric acid. The percentage of oil removed by 5g unmodified adsorbent was 42.67% while for 5g adsorbent modified with 0.5M was 72.91%. Thus, it can be concluded that the sorption capacity can be improved when the adsorbent undergo acid treatment.

***Keywords*— Palm oil mill effluent (POME), Adsorption, Rice Husk, Acid Treatment, Sulphuric Acid**

I. INTRODUCTION

In year 2013, Malaysia had accounts for 39% of world palm oil production and 44% world export. There had been 3.0% increment in year 2011 in oil palm planted area which is from 4.85 million hectares to 5 million hectares comparing to year 2010 (Mohammed & Chong, 2014). Increasing palm oil production is good for economy but it also means increasing of environmental pollution. Crude palm oil production process will generate large amount of waste in the forms of empty fruit bunch, mesocarp fibre, shell and palm oil mill effluent (POME). POME can be described as a highly viscous liquid, discharge at temperature between 80° to 90°C and appear as brownish colour liquid. It causes a major environmental problem because it is extremely poisonous with very low pH, high chemical and biological oxygen demand, high suspended solids and high salt content (Alhaji et al., 2016). POME if discharge directly into rivers without prior treatment will pollutes the environment as it is a highly polluted wastewater.

Treatment process of POME can be classified into two categories which is pre-treatment of raw POME and physiochemical treatment. Pre-treatment of raw POME include mechanical and physiochemical treatment. The pre-treatment process of POME consists of three stages which is coagulation-flocculation, then sedimentation followed by filtration. This method is commonly used to treat POME before it is being released into the river. The setback of using this method is mainly due to the high cost used to import chemical needed for the wastewater treatment. Other method that can be used was aerobic and anaerobic treatment but the drawbacks of these methods are it requires long retention time and in order to place the reactor large surface area is needed. Membrane technology is treatment of POME by using adsorption principal combined with biological treatment. Main advantages that can be obtain by using this process is that the water recovered is of high quality. However the disadvantages of using this process are the cost to set-up, installation along with its maintenance cost is very high (Alhaji et. al., 2016).

Adsorption process is an adhesion process of dissolved solid to a surface where it will create a film of adsorbate on the surface of adsorbent. This method of POME treatment is preferable compare to other methods due to its high treatment efficiency and the most important is this treatment is low cost (Mohammed & Chong, 2014). Based on test conducted by Jahi et. al. (2015), the oil adsorption process from the POME can be divided into three steps. The first step is involving diffusion process where molecules of oil diffuse on the sorbent surface. The second step is oil molecule is trapped in the sorbent structure with capillary interaction. The last step is the step where the oil that had been trapped will experience agglomeration on the pores and at the rough sorbent material. The surface where the adhesion takes place is known as adsorbent. Mohammed & Chong (2014) states that despite the types of adsorbent used, the percentage of removal will increase rapidly as the amount of adsorbent increase. This is due to the facts that there will be more surface area available for adsorption to occur. Contact time of the adsorbent and the contaminant also plays an important role. As the contact time increase, the percentage of removal will also keep on increasing until it reach certain equilibrium.

Currently, the activated carbon is widely used as an adsorbent but unfortunately it has major drawback such as expensive price and has regeneration problem (Mohammed & Chong, 2014). As a replacement of activated carbon, natural fibre had been introduced as an adsorbent. There is a lot of natural fibre that can be readily used as adsorbent such as pearl millet husk, barley straw, coconut husk, wheat straw, banana peel and rice husk.

Rice husk is the outer part of paddy used to cover it. Rice husk is the residue obtained from rice milling process where it is responsible for approximately 23% of the total weight of rice. Based on the world gross rice production of 545 million metric ton, rice husk takes part about one fifth of the total amount. It is made up of mainly silica and has high ash content with low nutritional value (Priscilla & Furlong, 2016). Rice husk is made up of 32.34% cellulose, 21.34% hemicelluloses, 21.44% lignin, 8.11% water, 15.05% mineral ash and 1.82% extractives. The mineral ash is found out to be silica dioxide with percentage of 94.5% to 96.34% (Masoud et. al.,2012). Rice husk also have high potential to be used as adsorbent due to the functional group present in it which is carboxyl and amidogen group (Masoumi et. al., 2016).

The adsorptive properties of natural fibre depend on factors such as its physical and porous structure and most importantly the chemical nature of the fibre surface. Various surface functional groups had been found to exist on the fibre surface like ketones, quinones, phenol, lactones and carboxyls. The functional groups will determine the character of the carbon either it is basic or acidic. The type of functional group present on the surface fibre depends on the activation process and the surface treatment (Chand et. al., 2009). Even though natural fibre is environmental friendly and inexpensive adsorbent its major problem as adsorbent is that it exhibit low sorption capacity. In order to overcome this problem, natural fibre needs to undergo chemical treatment as it will increase the sorption capacity together with its surface area (Ibrahim et al., 2009). There are various fibre treatment available such as alkaline treatment, esterification, benzoylation treatment and acid treatment.

Acid treatment was used on the natural fibre to improve its chemical and physical characteristic. After the surface treatment, it is found that pores within adsorbent particles become highly heterogeneous. This will increase the possibility of contaminant to be adsorbed and trapped. The average of the pores diameter also shows a mesoporous structure. Mesopores structure is important to increase adsorption capacity of adsorbent. There is also an increment in oxygen and hydrogen content that shows more activated site available for adsorption (Mahmoud et. al., 2012). The treatment of fibre with acid will cause the surface to become more negatively charged and also cause the removal of impurities. Strong acid which is sulphuric acid is chosen in this research to treat the rice husk to create a condition where excess hydrogen ion is present. This will cause a condition where the cation is attracted to the negatively charged sites, OH- of the adsorbent surface. Treatment with acid is believed to accelerate the removal of the contaminant. This is because as the surface had become positively charged it will attract more contaminant which is negatively charged due to electrostatic attraction between them. This will increase the rate of adsorption (Kabir et. al., 2012).

In this study, the rice husk was modified by using acid treatment. Acid used for the treatment was strong diprotic acid which is sulphuric acid, H_2SO_4. The effect of mass of rice husk and molarity of acid used for modification on oil removal efficiency were investigated. The mass of rice husk used was varied from 5g, 10g and 15g whereas the molarity of acid used were 0.5M, 1.0M, 1.5M and 2.0M. The optimum result on oil removal efficiency was compared with result of unmodified rice husk.

II. MATERIALS AND METHODS

A. *Preparation of adsorbent*

Rice husk that acts as an adsorbent was obtained from company that supplies it in Malaysia. The adsorbent was then repeatedly washed with water to remove dust and soluble impurities. Then it was crushed in cutting mill for about 15 minutes. The crushed rice husk was later washed again with distilled water and it was left overnight for drying at 65°C in oven. After it had been dried, it was placed in glass container and labelled as raw rice husk. For acid treated rice husk, the weight of raw rice husk was varied to be 5 gram, 10 gram and 15 gram and it was then treated with 50 mL sulphuric acid by soaking the rice husk in the acid with different molarity. The molarity of acid used was 0.5M, 1.0M, 1.5M and 2M (Pehlivan et. al., 2012). The suspension of rice husk and the sulphuric acid was then shaken for 24 hours in orbital shaker with speed of 170 rpm at room temperature. Treated rice husk was separated from the liquid and washed with distilled water for several times to remove any trace of sulphuric acid attached to its surface. The modified rice husk was lastly dried in an oven at temperature of 60°C overnight. After it was taken out from the oven, it was placed in airtight container that was labelled as modified rice husk (Oei et. al., 2009).

B. *Oil Removal Test*

Method used to conduct the oil removal test was n-hexane solvent extraction method. To determine the amount of oil adsorbed by the modified rice husk, 0.35 gram of the modified rice husk was added to 20 mL raw POME at room temperature. The mixture was then stirred on magnetic stirrer for 30 minutes at 125 rpm. Then, the mixture was filtered. The filtrate was tested for oil content. For the oil content test, 20 mL of the sample was first transferred into separatory funnel. To obtain pH of POME less than 2, 9 drops of 1:1 mixture of hydrochloric and water was added into the sample before the addition of 3 mL hexane. The separatory funnel was then vigorously shaken for 2 minutes. After the vigorous shaking, the separatory funnel was left for 10 minutes in order for the solution to form two layers. Oil sample was then dried at 103°C in oven for 15 minutes. The sample was left to cool to room temperature and later weighed. The weight measured was regard as oil and grease content value. The oil removal efficiency was determined by using equation (Wahi et. al., 2013):

$$\text{Oil removal efficiency (\%)} = [(Co- C)/Co] \times 100\% \quad \ldots\ldots\ldots\ldots(1)$$

Where:

Co is the initial oil concentration (mg/L) in POME

C is the oil concentration in the filtrate (mg/L)

III. RESULTS AND DISCUSSION

A. *The effect of mass on the percentage efficiency of oil removal*

The effect of mass on the efficiency of oil removal in terms of percentage was calculated based on the average mass of oil collected. The relationship between mass of rice husk used and percentage efficiency of oil removal were presented in graphs.

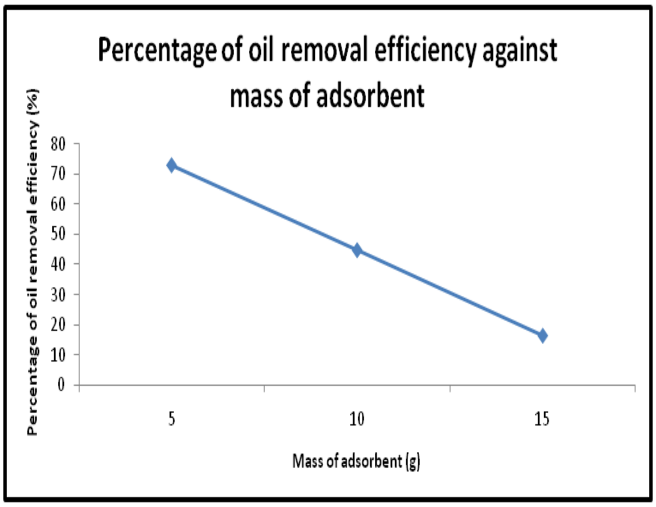

Figure 1: Plots of percentage of oil removal efficiency of modified adsorbent with 0.5M sulphuric acid

Based on Figure 1, there was a sharp declined in the percentage of oil removal efficiency as the mass of adsorbent increase. When the mass of modified adsorbent is only 5g, the percentage of oil removed was 72.91% and as the mass increased to 10g, the percentage of oil removed decreased to 44.81%. As the mass of modified adsorbent kept on increased to 15g, there was also a further decrease in the amount of percentage of oil removed. The percentage of oil removed was only 16.55%. The most efficient mass of adsorbent was 5g when the molarity of sulphuric acid used was 0.5M.

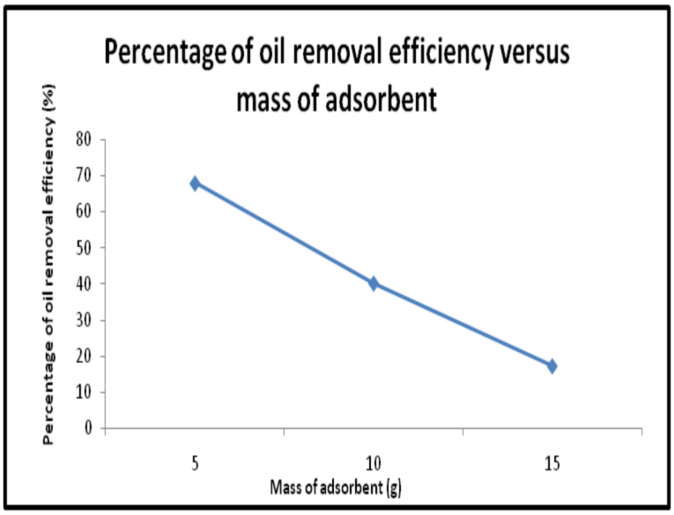

Figure 2: Plots of percentage of oil removal efficiency of modified adsorbent with 1.0M sulphuric acid

Figure 2 show the relationship of mass of modified adsorbent on the percentage of oil removal efficiency when the 1.0M of sulphuric acid was used. The percentage of oil removed was 67.91% when 5g of adsorbent was used for the adsorption process. As the mass of adsorbent increased to 10g and 15g, the percentage of oil removal efficiency was decreased to 40.1% and 17.09%, respectively. From the trend of the plotted graph, it can be concluded that the percentage of oil removal efficiency dramatically decrease when the mass of adsorbent increased from 5g to 10g and 15g. The conclusion that can be drawn from the graph was the best mass of modified adsorbent that should be used for oil removal process was 5g. This was because it can adsorb the most amounts of oil originally presented in POME.

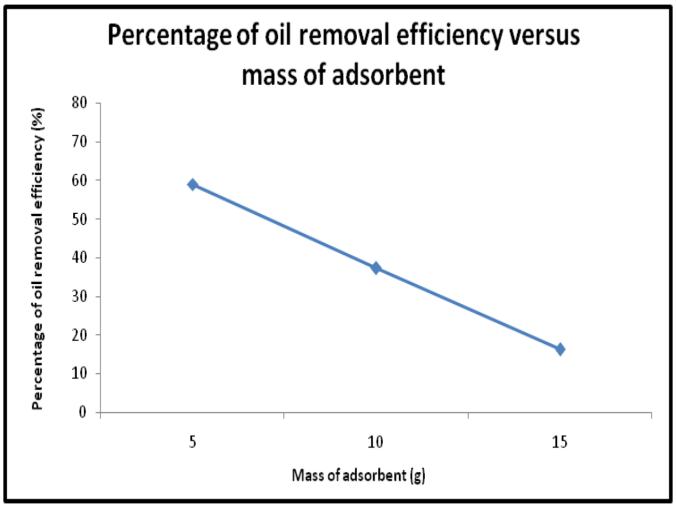

Figure 3: Plots of percentage of oil removal efficiency of modified adsorbent with 1.5M sulphuric acid

Based on Figure 3, the graph was steeply decreased when the mass of adsorbent increased as compared to the percentage of oil removal efficiency. The reading of percentage oil removed when 5g of adsorbent used was 59.04%, while for 10g and 15g of adsorbent the percentage oil removed was 37.28% and 16.31% respectively. Based on the graph, the most efficient mass of modified adsorbent for the removal of oil from POME was 5g.

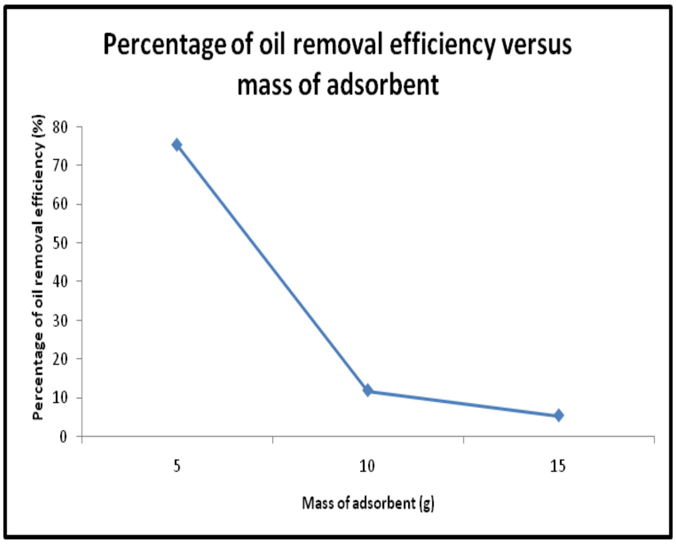

Figure 4: Plots of percentage of oil removal efficiency of modified adsorbent with 2.0M sulphuric acid

Figure 4 represents the percentage of oil removal efficiency when the mass of modified adsorbent is varied from 5g, 10g and 15g. The adsorbent had been modified beforehand with 2.0M sulphuric acid. The percentage of oil removal for 5g of modified adsorbent was 75.44%. From the graph, there was a sudden decrease when the mass of modified adsorbent was increased to 10g where the oil removal percentage was only 11.94%. The graph kept on decreasing steadily to 5.44% when the mass of modified rice husk used for adsorption increased to 15g. Figure 4.4 clearly showed that the most suitable mass of adsorbent that should be used for adsorption of oil in POME treatment was 5g.

Based on Figure 1, Figure 2, Figure 3 and Figure 4, the most suitable mass of modified rice husk for the adsorption of oil from POME was 5g. It had the highest percentage of oil removed for all molarity of acid used. Ibrahim et. al. (2017) had stated that addition in mass of adsorbent might not increase the effective adsorption capacity when it is above the maximum dosage as there is overlapping of adsorption site. Mor et. al. (2016), had also reported that increase in adsorbent dosage will increase the percentage of substance removal until it reach its equilibrium as it provides more free sites causing increment in net surface area of adsorbent. However, addition of adsorbent dosage above its maximum point will cause aggregation of adsorbent which in turn will result in decrease of available adsorption site. Research conducted by Mohammed & Chong (2014) had showed that there were many parameters that affect the adsorption efficiency such as amount of adsorbent used, size particle of adsorbent and contact time between the contaminant and the adsorbent. They had stated that the percentage of removal will increase as the amount of adsorbent increase for all types of adsorbent. The adsorption will increase until it reaches a certain limit where the addition of adsorbent did not increase the adsorption performance due to the overlapping of adsorption sites caused by overcrowding of adsorption particles.

B. The effect of molarity on the percentage efficiency of oil removal

The effect of molarity on the percentage of oil removal was investigated based on the most efficient mass of rice husk used for adsorption which is 5g. The relationship between the molarity of acid used for modification of rice husk and the percentage efficiency of oil removal was presented in Figure 5.

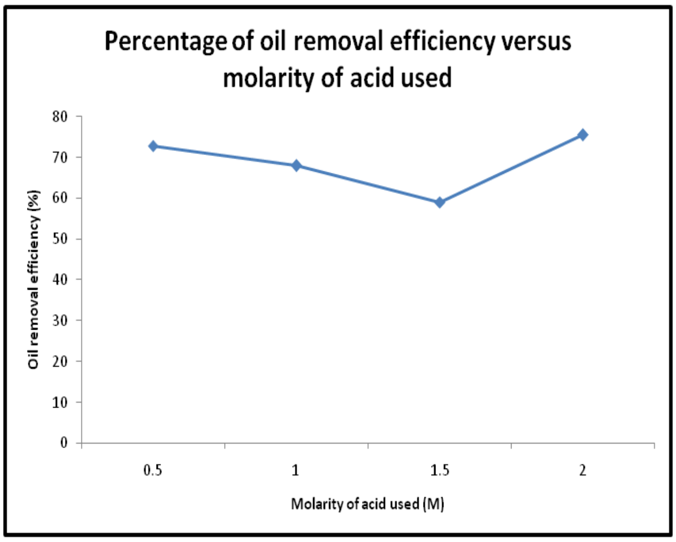

Figure 5: Plot of percentage of oil removal against molarity of sulphuric acid used to modified 5g of adsorbent.

Figure 5 represents the relationship between the molarity of sulphuric acid used for modification with its respected oil removal efficiency when using 5g of adsorbent. When 0.5M of acid used, the percentage of oil removed was 72.91%. As the molarity increased to 1.0M and 1.5M, the oil removal efficiency reduced gradually to 67.91% and 59.04% respectively. When the molarity of acid used was further increased to 2.0M, there was slight increase in percentage of oil removed which is 75.44%. This might be due to error while conducting the experiment. The overall trend of the graph was the increase in molarity will reduce the efficiency of oil removed. The most efficient molarity to obtain the most oil removed from POME was 0.5M.

Based on research conducted by Abdelwahab et. al. (2017), the acid treatment is originally used to improve the mechanical properties of the adsorbent surface. It can be improve by the removal of compounds such as lignin, pectin and wax which is the material the cover the outer layer of the fibre. Interaction between oil and inner surface of the fibre will be influenced by the rough surface of exposed inner fibre when it is acidly treated. There is an exception to the case where the oil removal is reduced when it is treated by using acid as the waxy coating that covers the outer surface of the fibre is removed. Functional group of the fibre which in the case of rice husk, carboxyl will become disappears or reduced from the outer surface of the fibre causing the reduction in efficiency of oil adsorption of the adsorbent.

Therefore, the highest efficiency of oil removal was obtained by using 5g of rice husk in the acid modification. The molarity of sulphuric acid that gives the most efficient oil adsorption of oil contained in POME was 0.5M. Thus, the most efficient way to adsorb oil from POME was to use 5g of rice husk modified with 0.5M of sulphuric acid. The results obtained from the most efficient condition of adsorption were used to make comparisons with the unmodified rice husk.

C. Comparison between Modified & Unmodified Rice Husk by using Acid Treatment

In order to investigate the effect of acid modification on adsorbent, graph on oil removal efficiency and mass of adsorbent had been plotted and showed in Figure 6:

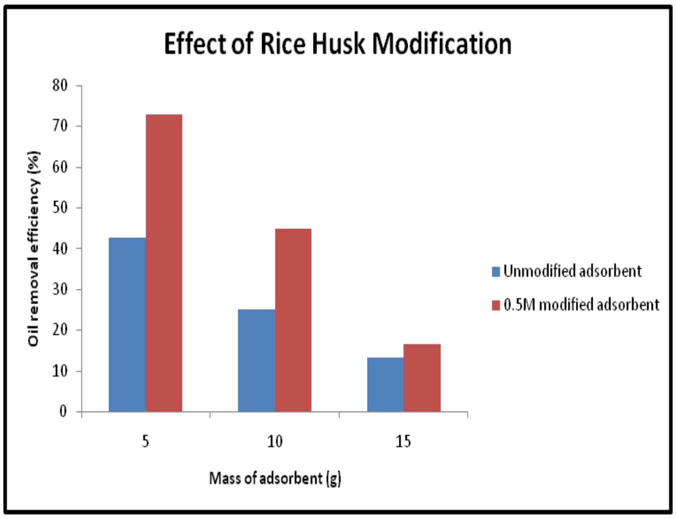

Figure 6: Graph on oil removal efficiency versus mass of adsorbent

The oil removal efficiency when the mass of adsorbent used 5g was 42.67% for unmodified adsorbent and 72.91% for modified adsorbent. There was about 30% difference between the unmodified and modified adsorbent in oil removal efficiency. When 10g of adsorbent was used the oil removal efficiency for both unmodified and modified rice husk reduced to 44.81% and 25% respectively. The difference between the oil removal efficiency for unmodified and modified adsorbent also reduced to about 20%. For 15g of rice husk, the oil removal efficiency was 13.3% for the unmodified adsorbent and 16.55% for modified adsorbent. The difference between in oil removal efficiency also reduced to only 3.25%. Based on the Figure 4.8, it can be concluded that modification of adsorbent will improve the adsorption ability of adsorbent and thus will increase the percentage of oil removal efficiency in POME.

Research by Mahmoud et. al. (2012) had found that after adsorbent was treated with acid, the pores inside the adsorbent particles will become highly heterogeneous. It is important to increase the possibility of contaminant which in this case oil to be trapped and adsorbed. Mesoporous structure was also observed on the average pore diameter which is important to improve the adsorption capacity of adsorbent. Other than that, after acid treatment on adsorbent it was found that there was an increase in concentration of oxygen and hydrogen that shows more active site available for adsorption. This showed that efficiency of rice husk increase when it undergo acid treatment.

IV. CONCLUSION

From this study it can be concluded that rice husk is suitable to be used as adsorbent for POME treatment. It is also suitable to be used as environmental friendly replacement of activated carbon. This is shown with its ability to adsorb oil contained in POME. Even so, in order to increase its oil adsorption efficiency the rice husk should be modified by using acid treatment. Sulphuric acid is proven to be suitable to modify the rice husk. This is because when the rice husk was treated by using sulphuric acid, its ability to adsorb oil also increased. This is shown by the increase in percentage efficiency of oil collected. The optimum result was obtained when 5g of mass of modified adsorbent was used with the molarity of sulphuric acid of 0.5M. The results obtained were consistent with previous research where as the molarity of acid used for modification increased, the adsorption capacity will be reduced. The adsorption capacity was also reduced when mass of rice husk increased.

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