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ADSORPTION OF RESIDUAL OIL FROM PALM OIL MILL EFFLUENT USING RUBBER POWDER

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Abstract - A synthetic rubber powder was used to adsorb the residual oil in palm oil mill effluent (POME). POME is the wastewater produced by the palm oil industry. It is a colloidal suspension which is 95-96% water, 0.6-0.7% oil and 4-5% total solids including 2-4% suspended solids originating in the mixing of sterilizer condensate, separator sludge and hydrocyclone wastewater. POME contains 4,000 mg dm^{-3} of oil and grease, which is relatively high compared to the limit of only 50 mg dm^{-3} set by the Malaysian Department of Environment. A bench-scale study of the adsorption of residual oil in POME using synthetic rubber powder was conducted using a jar test apparatus. The adsorption process was studied by varying parameters affecting the process. The parameters were adsorbent dosage, mixing speed, mixing time and pH. The optimum values of the parameters were obtained. It was found that almost 88% removal of residual oil was obtained with an adsorbent dosage of 30 mg dm^{-3} and mixing speed of 150 rpm for 3 hr at a pH 7. Adsorption equilibrium was also studied, and it was found that the adsorption process on the synthetic rubber powder fit the Freundlich isotherm model.

Keywords: Rubber powder; Palm oil mill effluent; Adsorption; Adsorbent; residual oil.

INTRODUCTION

Over the last three decades, the Malaysian palm oil industry has grown to become an important agriculture-based industry. Malaysian palm oil accounted for about 52% of the world palm oil output and this industry generated RM 13 billion in export earnings for the country. With increased cultivation and production of palm oil in the region, the disposal of the processing waste is becoming a major problem that must be appropriately addressed.

Palm oil mill effluent (POME) is a colloidal suspension of 95-96% water, 0.6-0.7% oil and 4-5% total solids including 2-4% suspended solids originating in the mixing of sterilizer condensate, separator sludge and hydrocyclone wastewater that are mostly debris from palm fruit mesocarp. It is acidic (pH 4-5), hot (80-90 ^{0}C), and nontoxic (no chemicals are added during oil extraction). One of the major problems with POME is its residual oil content. Residual oil has to be removed in order to comply with the Malaysian Department of Environment's discharge limits and to prevent it from interfering with downstream treatment. Numerous techniques to remove residual oil from POME, such as the solvent extraction method (Ahmad et al., 2003), chemical-biological (Rivas et al., 2001), sedimentation, flocculation and coagulation methods (Ahmad et al., 2003; Qiu Zunan et al., 1995; Kamal Al-Malah et al., 2000) have been reported. The removal of residual

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*To whom correspondence should be addressed oil by adsorption using adsorbents is very promising and requires further study.

Adsorbents have been developed for a wide range of separations. Commercial materials are usually used in the form of pellets, granules or beads, although powder is occasionally used. The adsorbent can be used once and discarded, or as is more common, it can be employed on a regenerative basis and used for a number of cycles. Commercial adsorbents are divided into five major classes: molecular-sieve zeolites, activated alumina, silica gel, synthetic polymers or resins and activated carbon (Keller et al., 1987; Geankoplis, 1995). Since adsorption is a surface-related phenomenon, the useful adsorbents are all characterized by a large surface area per unit of weight (Smith et al., 1996). However there is no research reported in the literature on adsorption of residual oil using synthetic rubber powder as the adsorbent. However, rubber has been used for other adsorption processes, such as adsorption of organic compounds, i.e., dye and phenol (Ariyadejwanich et al., 2003; San Miguel, 2002). Even in these cases rubber as such was not used. It was converted into activated carbon before being used as an adsorbent. The activated carbon was fairly mesoporous with mesopore volumes and BET surface areas up to 1.09 cm^3/g and 737 m^2/g, respectively (Ariyadejwanich et al., 2003). Scrap rubber was also used to adsorb metal ions such as copper, cadmium and zinc (Zarraa, 1998), and results showed that adsorption capacity for the single-component metals was in the following order: Cd>Cu>Zn. Rubber by itself has not been used as an adsorbent, but rubber seed coat (RSCS) was used to adsorb phenol and removal was 2.25 times more efficient than that with commercial activated carbon (CAC) based on a column adsorption study (Rengaraj et al., 2002).

There are a number of natural adsorbents used to adsorb residual oil. Ahmad et al., (2004) applied chitosan, a biopolymer, to adsorb residual oil from POME. Fibrous sorbents prepared from natural plants, such as milkweed floss, kenaf, kapok, straw, corn cob or ear, wood fibers, sawdust, bark and cotton, have been reported as potential adsorbents (Shukla et al., 2002; Setti et al., 1999; Haussard et al., 2003; Inagaki et al., 2002). Satisfactory results were obtained using these natural adsorbents.

Therefore in the current study the use of synthetic rubber powder to adsorb and remove residual oil from POME as the pretreatment was explored.

The main objective of this research is to remove the residual oil from POME using synthetic rubber powder as the adsorbent. This removal is necessary in order to meet the requirement set by the Department of Environment of Malaysia. The effect of process variables, such as adsorbent dosage, mixing speed, mixing rate and pH, on removal of residual oil was studied in order to determine the optimum process conditions. The adsorption equilibrium data were obtained to discover which isotherm model provided the best fit for this adsorption process.

MATERIALS AND METHODS

Materials

A novel sample of synthetic rubber powder developed at the School of Industrial Technology, Universiti Sains Malaysia, Penang, Malaysia was used. The properties of this synthetic rubber powder are presented in Table 1. The POME samples were obtained from United Oil Co., Malaysia and cooled in a refrigerator at temperatures of 90°C to 0°C before the corresponding adsorption tests were conducted. Each sample was collected one day prior to the experiment. Samples varied depending on the production capacity and any amount of fresh fruit being processed on any particular day. Composition and residual oil content of the POME might also vary throughout the day, depending on the weather and time of sample collection. Hence the initial concentration of residual oil for each sample might vary due to these factors.

Procedure

Each sample of POME was diluted with distilled water and a known quantity of alum was added in the flocculation step. The supernatant liquid produced after several minutes of the sedimentation was collected and used as feed for adsorption process. Six beakers, each containing 100 ml of this supernatant were used. A known amount of rubber powder was added to each beaker.

The averaged value of five different samples was plotted in parameter graphs. The contents of all the beakers were mixed in a flocculator (Stuart Science Flocculator model (SW1)) for a specified time and speed. After mixing, the contents were allowed to sediment and separated by filtration.

Table 1: Properties of synthetic rubber powder

Property		Result	ISO Specification
Total solid content	% (m/m)	61.60	61.5 min
Dry rubber content	% (m/m)	60.20	60.0 min
Non-rubber solid	% (m/m)	1.40	2.0 max
Alkalinity (as NH_3)	% (m/m) on latex	0.660	HA 0.6 min/ LA 0.29 max
	% (m/m) on water	1.650	HA 1.6 min/ LA 0.75 max
Mechanical stability	Second tested	980	650 min
KOH no.		0.582	1.0 max
Volatility fatty acid no.		0.022	0.2 max
Coagulum content	% (m/m)	-	0.05 max
Sludge content	% (m/m)	-	0.10 max
Copper content	mg/kg of total solids	2	8 max
Manganese content	mg/kg of total solids	1	8 max
pH		10.56	
Viscosity	Brookfield LVF spindle 1@ 60 rpm cps [TS 60%)]	58	
Color	Visual inspection	WHITE	
Odor	No putrefaction	Smell	
Density	g/ml	0.9396	
Surface area	m^2/g	15.98	

Oil and Grease Extraction

The original and treated POME samples were transferred to a separating funnel. Thirty ml of petroleum ether were introduced into the separating funnel. The contents were shaken vigorously for 2 min and allowed to separate into layers for 5 min. The aqueous layer was drip drained into a sample holder. Extraction was repeated twice with two more portions of 30 ml petroleum ether. Then, the solvent layer was drained through a funnel containing filter paper and 2g of anhydrous sodium sulphate, both of which had been solvent-rinsed, into a sample holder. The sample of extracted residual oil with petroleum ether was used for the analysis.

Analysis

The concentration of residual oil extracted with petroleum ether was then measured using a spectrometer Cecil 1000 series, Cambridge, England with an absorbance wavelength of 444 nm. A calibration with different concentrations of residual oil versus absorbance was done. Hence, using this calibration curve the concentrations of residual oil before and after adsorption were calculated. Figure 1 shows the calibration curve. The experiments were repeated five times and the averaged data were used to plot the resultant graphs with a standard error of ±10%.

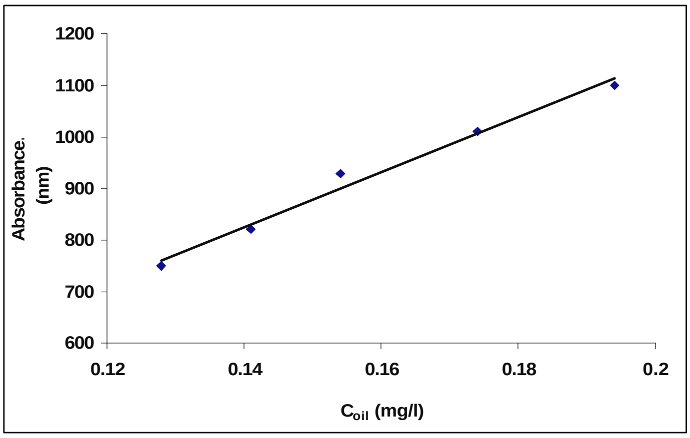

Figure 1: Calibration Curve

RESULTS AND DISCUSSION

Effect of Adsorbent Loading

Different quantities of adsorbent were added to the POME sample. It was found that as the dosage of adsorbent was increased, the percentage of residual oil removal also increased, as shown in Figure 2. Adsorption is a surface-related phenomenon, and the surface selectivity can be broadly classified as hydrophilic or hydrophobic (Keller et al., 1987). Rubber powder has a hydrophobic surface that can strongly adsorb oil and grease. On the other hand, the internal porosity of the rubber also creates adsorption forces (Frederick, 1990) as well as an adsorption-surface area. These forces cause large and small molecules of dissolved organic molecules to be deposited and adsorbed from the solution onto the molecule-sized pores. At equilibrium, most of the oil and grease molecules in the solution were adsorbed on the surface and in the intermolecular pores of the rubber powder. The quantity of oil adsorbed on an adsorbent varied within an error of ± 10%. It takes about 30 mg dm^{-3} of rubber powder to reduce the initial residual oil concentration of about 850 mg dm^{-3} to a final concentration of 200 mg dm^{-3}.

Effect of Mixing Speed

Figure 3 shows the effect of mixing speed on the adsorption of residual oil on synthetic rubber latex powder. Lin and Liu (2000) reported that the mass transfer rate increases with the increase in stirring speed. The increase in stirring speed results in a reduction in surface film resistance, thereby allowing residual oil to reach the particle surface more easily. Surface film resistance slowed the rate of adsorption. The rate of oil adsorption increased with an increase in mixing speed. Figure 3 illustrates this phenomenon, showing that with the increase in mixing speed, oil removal was increased. Figure 3 shows that by increasing the mixing speed up to 150rpm and above residual oil was reduced to 150 mg dm^{-3}.

Effect of Mixing Time

The influence of contact time on residual oil removal using synthetic rubber powder as the absorbent is shown in Figure 4. By increasing contact time, the residual oil molecules have a longer residence time for adsorption on the rubber powder surface area. At equilibrium, the surface of the rubber powder was covered with oil molecules; therefore a longer mixing time does not increase residual oil removal from POME. Figure 4 shows that when mixing time was increased from 1 hr to 3 hr, for 1 hr of mixing the final reduction value was 200 mg dm^{-3} and for 3.0 hr of mixing the reduction was up to 150 mg dm^{-3}. These values prove that contact time increases the capacity of rubber to adsorb residual oil from POME.

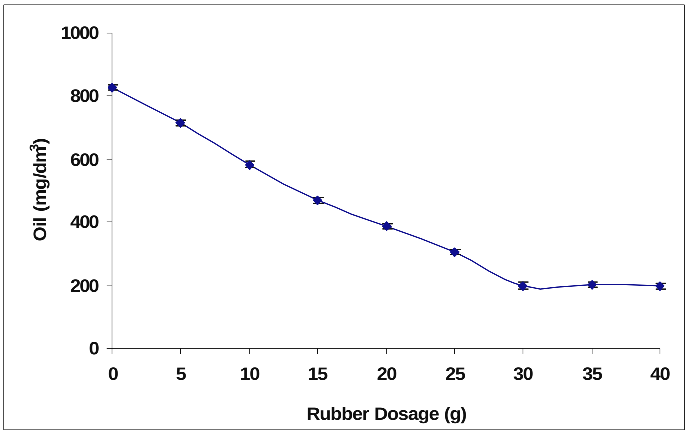

Figure 2: The influence of amount of synthetic rubber powder on the reduction of residual oil at 27°C (room temperature), a mixing time of 1 hr, a mixing speed of 100 rpm and pH 4.

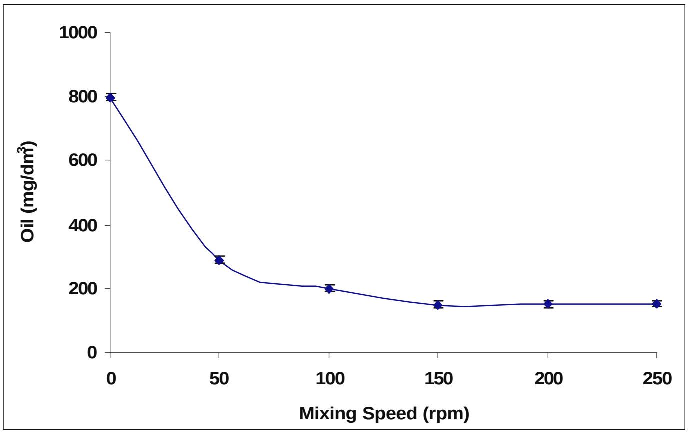

Figure 3: The influence of mixing rate on the reduction of residual oil at 27^{o}C (room temperature) with 30 grams of synthetic rubber powder, a mixing time of 1 hr and pH 4.

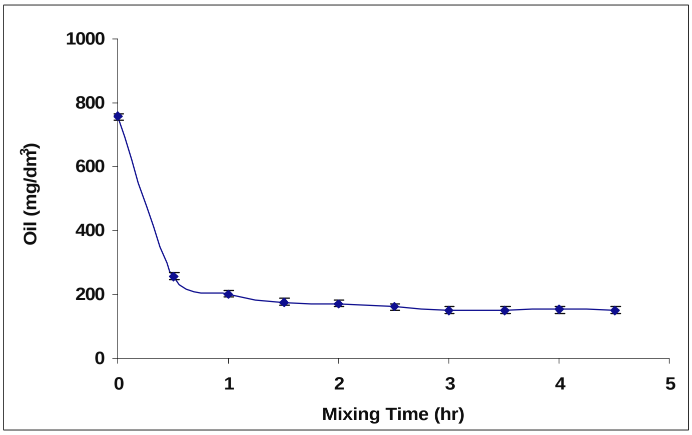

Figure 4: The influence of mixing time on the reduction of residual oil at 27^{o}C (room temperature) with 30 grams of synthetic rubber powder, a mixing rate of 100 rpm and pH 4.

Effect of pH

The effect of pH on residual oil removal is shown in Figure 5. The final values of residual oil in the sample were averaged and are shown in this figure. There was a slight increase in residual oil removal when the pH was increased. For example, at pH 4, the concentration of residual oil was about 150 mg dm^{-3}, but at pH 9, this value was reduced to about 105 mg dm^{-3}. However, this does not mean that residual oil adsorption is effective at pH 9 because, when studying the effect of pH, NaOH was added to POME to increase the pH. The addition of NaOH results in saponification, which means that the residual oil reacts or undergoes hydrolysis with sodium hydroxide to produce glycerol and fatty acid salts called soap, which is more soluble in water than in petroleum ether (Ahmad et al., 2003). Therefore, when determining the oil concentration in the treated sample using petroleum ether, the oil concentration was to be less at pH 9.0 since the oil was hydrolyzed inside the POME and was not being extracted to the solvent. Thus, as shown in Figure 5, the optimum pH for the adsorption of residual oil was 7. The final value of residual oil at this pH is 120 mg dm^{-3}. Hence this gives an advantage to the treatment process whereby the final discharge after adsorption will have a neutral pH. For this reason, no further adjustment of pH would be required after this adsorption before the effluent could be discharged.

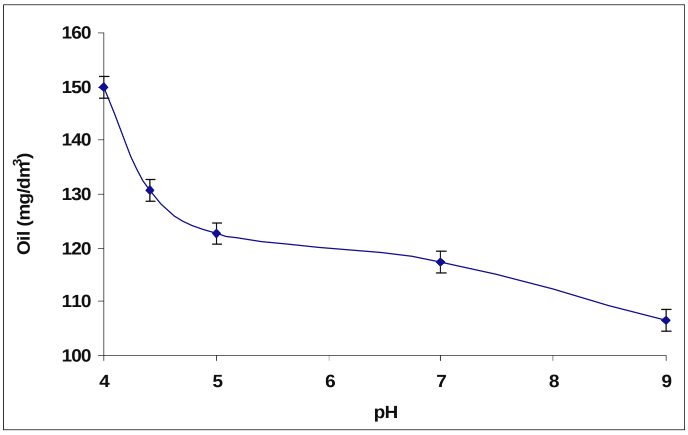

Figure 5: The influence of pH on the reduction of residual oil at 27^{o}C (room temperature) with 30 grams of synthetic rubber powder, a mixing rate of 150 rpm, a mixing time of 3 hr and pH 4.

Adsorption Equilibrium

Adsorption equilibrium studies were conducted using the optimum conditions obtained in the previous sections. Adsorption equilibrium was determined at different initial concentrations of residual oil with the optimum conditions studied in the previous section. Figure 6 shows the plot of equilibrium values of q_e versus c_e for residual oil adsorption using synthetic rubber powder. It can be seen that adsorption capacity increases until an equilibrium concentration is obtained. This confirms a favorable adsorption system.

The isotherm of the residual oil adsorption by synthetic rubber powder was represented by applying the Langmuir and Freundlich adsorption models.

The Freundlich isotherm is expressed as

$$q_e = K_f C_{oil}^{1/n} \tag{1}$$

This isotherm is usually used in special cases for heterogeneous surface energy where it is characterized by the heterogeneity factor 1/n, where, q_e is the equilibrium value of oil adsorbed per unit weight of synthetic rubber powder, C_{oil} is the liquid-phase sorbate concentration at equilibrium, K_f is the Freundlich constant and 1/n is the heterogeneity factor. The Freundlich equation was linearized by taking logarithms on each side of the equation. Figure 7 shows the Freundlich plot and gives a straight line.

$$\ln q_e = \ln K_f + n \ln C_{oil} \tag{2}$$

The Langmuir isotherm is expressed as

$$q_e = \frac{q_o c_{oil}}{K_L + c_{oil}} \tag{3}$$

Equation (3) is rearranged as

$$C_{oil}/q_e = (1/K_L q_o) + (1/q_o)C_{oil} \tag{4}$$

where q_o is the maximum amount of adsorption corresponding to complete monolayer coverage and K_L is the Langmuir constant. A linearized plot of (C_{oil}/q_e) vs C_{oil} is shown in Figure 8.

In Figure 7 it is clearly shown that the Freundlich isotherm model fits the analyzed data well with its correlation coefficient (R^2) value of 0.9721; therefore the isotherm at 300 K is represented as

$$q_e = 2.6x10^{-6} C_{oil}^{0.3422} \tag{5}$$

The Freundlich model assumes that the uptake of any adsorbate occurs on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration. From these assumptions it can be concluded that synthetic rubber powder takes up residual oil on a heterogeneous surface by multilayer adsorption.

The heterogeneity factor 1/*n* was calculated. The calculated value was 0.3422 and the *n* value was 2.92. It is known that when the *n* value is greater than 1.0, conditions are favorable to adsorption. Hence it is clearly proved that residual oil adsorption by synthetic rubber powder agrees well with the Freundlich adsorption model.

It was found that in Figure 8, the Langmuir constant did not fit the data with its correlation coefficient (R^2). The correlation coefficient (R^2) was much lower than 1.0 throughout the experimental range of oil concentrations studied.

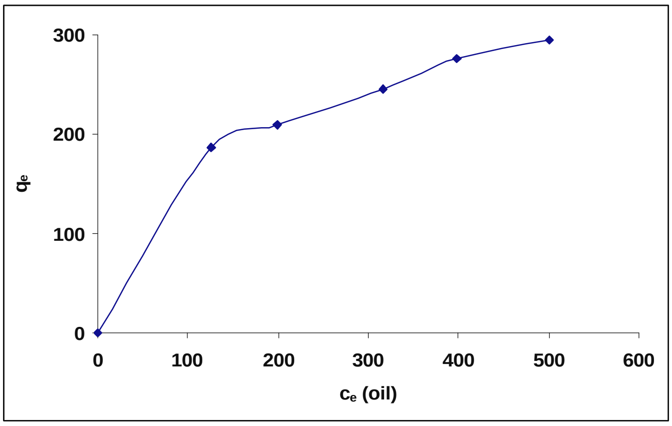

Figure 6: Equilibrium adsorption of residual oil on synthetic rubber powder at 27°C (room temperature) with 30 grams of synthetic rubber powder dosage, a mixing rate of 150 rpm, a mixing time of 3 hr and pH 7.

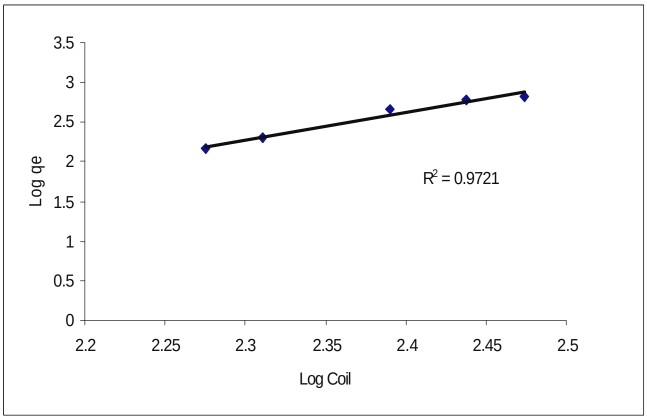

Figure 7: The Freundlich isotherm for adsorption using synthetic rubber powder at 27°C (room temperature) with 30 grams of synthetic rubber powder dosage, a mixing rate of 150 rpm, a mixing time of 3 hr and pH 7.

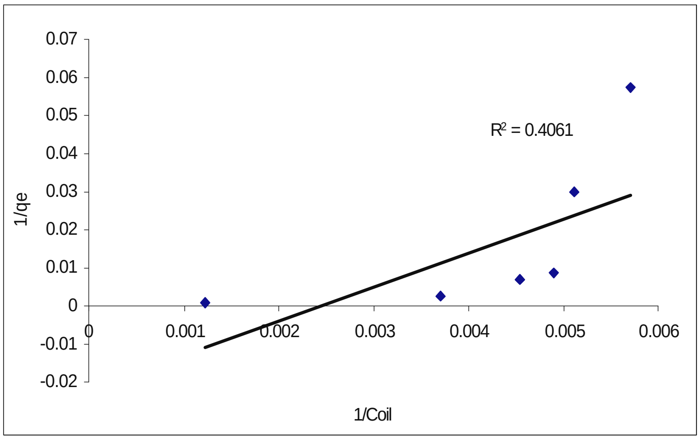

Figure 8: The Langmuir isotherm for adsorption using synthetic rubber powder at 27°C (room temperature) with 30 grams of synthetic rubber powder dosage, a mixing rate of 150 rpm, a mixing time of 3 hr and pH 7.

CONCLUSIONS

The addition of rubber latex powder as an absorbent to a sample of POME reduces the residual oil content of the effluent. It was found that about an 88% reduction in residual oil was obtained using 30 grams of synthetic rubber powder for 100ml of POME, at a mixing rate of 150 rpm for 3 hr at pH 7. The process of adsorption on rubber powder fit the Freundlich isotherm equilibrium adsorption model.

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