

## Preliminary Study of Oil Removal using Hybrid Peel Waste: Musa Balbisiana and Citrus Sinensis

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### ABSTRACT

The use of cheap and eco-friendly adsorbent studied as an alternative substitution of adsorbent for removing of oils from the water. Adsorbents prepared from two different types of fruit peel, banana (*Musa Balbisiana*) peel and orange (*Citrus Sinensis*) peel, which are a domestic waste, successfully used to remove the different density of oil including light, medium and heavy oil. The hybridization of different ratios banana peel (BP) to orange peel (OP) that are 2:1, 1.5:1.5 and 1:2 were used to determine the potential of adsorptivity of lubricant oil (LO) and petrol oil (PO). The chemical modification of fruit peels was carried out using Sodium Hydroxide (NaOH). Treated banana and orange peels used to adsorb the LO and PO. LO and PO were used to be treated with the powders with to presence of distilled water as a solvent. The batch adsorption was done using a magnetic stirrer at 350 rpm for 10 minutes. The results obtained show that the percentage of adsorption for LO using ratio BP to OP at 2:1 is the highest adsorption with percentage removal of 38.120%, while the highest percentage removal for PO is at 32.169% in the ratio BP to OP at 1:2. The adsorption capacity of BP and OP were different with different types of oil. The adsorption capacity for BP was highest in heavy oil like LO, while the orange peel can react effectively with a light oil such as PO due to the different contains of cellulose. The chemical modification of the fruit peels was evaluated by using a Fourier Transform Infrared (FTIR) spectrophotometer in order to determine its functional group. This study demonstrated and proposed that the OP and BP has a good potential as a low cost and eco-green adsorbent for oil removal in wastewater.

**KEYWORDS:** *Musa Balbisiana*, *Citrus Sinensis*, Lubricant Oil, Petrol Oil, Hybridization.

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### INTRODUCTION

Pollution can be described as the presence in or introduced into the environment of a substance which has harmful or poisonous [1]. Some of the pollution include water, soil and environment. Water pollution can be presented as a contaminant of water, which can make it unfit for use. Water pollution usually caused by industrial waste, agricultural and oil spills. According to [2], urbanization is continuously releasing waste and wastewater to the environment and eventually toxic to living organism. This factor can cause water pollution. The water pollution mainly caused by heavy metal, dye and oil released. However, the environmental pollution from oil has been taken seriously since last few decades. This is because the increasing in demand for oil as one of the natural sources for the growth of the country. The phenomenon of oil spill also caused toxicity to marine life due to forming of floating film on water [3].

The oil spilled not only messy, but it also hazardous and eventually will treat the life. The most popular technologies for oil removal include chemical treatment, gravity separation, parallel plate coalescers, gas flotation, cyclone separation, granular media filtration and cartridge filtration [1]. According to [3], the occurrence of oil spill will cause toxicity to marine life due to forming of floating film in water. Besides, massive urbanization is continuously releasing waste and wastewater to the ecosystem and causing pollution to environment and eventually harmfulness to ecosystem [2]. Therefore, they are many methods for removing oil are introduced included gravity separation, dissolved air flotation, chemical coagulation, filtration, membrane process and biological process [1]. All these technologies are very expensive. Hence, a simple tool adsorbent approach which is from fruit peel was used in removing oil from the aqueous solution in this study.

The use of natural organic adsorbents was widely used because of their greater adsorption capacities, most eco-friendly and cost effective [3]. Natural adsorbents are not only biodegradable when disposed, but more efficient than chemical adsorbent as they showed a greater adsorption capacity [4]. Natural sorbent like fruit fibers can be used as oil sorbents due to its hydrophobic properties that can help in oil adsorption [3]. Thus, natural adsorbent can be commercialized for cleaning purpose in oil domestic spill for kitchen, factories and workshops. Because of the factors above, this study was conducted to determine the potential of fruit peels as an adsorbent in removing oil.

In Malaysia, some of the traders or consumers usually do not practice a good healthy standard for the waste that they are produced. The banana peels (BP) waste usually were thrown in improper ways. Banana peels were reported as the agriculture waste that discharged all over the world. Because of that, it causes waste problems although they have some compost and cosmetics potentiality [2]. Banana peels were contained cellulose, lignin and hemicellulose that are insoluble dietary fiber fraction and it also contained pectin as a soluble dietary fiber [5]. These fruit peels have microporous structures, heterogeneous, rough surfaces with crater-like pores that has the ability to absorb oil. This characteristic shows that banana peels have the potential as adsorbent [2].

Orange peel (OP) is also one of the valuable biomass waste. Orange production was almost 18 million tons, which representing approximately 49% of the total fruit production in the world [6]. Besides, according to [7], oranges take up 75% of the total citrus fruits in the world, and China is one of the main producers. In Malaysia, this fruit also is one of the favorable fruits. This peel are usually can find in the fruit stall area or cafe. Orange peels were associated with a low cost and contained many nutrients including vitamin C, A and B, mineral such as calcium, phosphorus and potassium, dietary fiber and many phytochemicals including flavonoids, amino acids, triterpenes, phenolic acids and carotenoid [6]. Besides that, orange peel also contained of cellulose, hemi-cellulose, pectin substances, chlorophyll pigment and other low molecular weight compounds like limonene and so on [7]. These components contained various types of functional group like carboxyl and hydroxyl and that can make orange peel to be potential adsorbent material [8].

The percentages of cellulose contain for the fruit peels are different and it can influence the amount of adsorption. Banana peel contains 83% of cellulose in its fiber and easier to retain the lubricant oil [3]. While cellulose contain in the orange peels is less than in banana peel and it is effectively to react with a light oil such as petrol. Therefore, in this study, the hybridization of banana peel and orange peel as adsorbent will be determined because those peels have special characteristics that can react to various types of oil.

## METHODOLOGY

### Preparation of Biosorbent

Musa Balbisiana (banana) peel and Citrus Sinensis (orange) peel were collected from the fruit stall and café in an area of Bukit Besi. The peels were washed using distilled water to remove all the impurities and were cut into smaller pieces to give a large surface area when treated with sodium hydroxide. The pieces of the peels were dried under sunlight for 24 hours and soaked into 1.0 M of sodium hydroxide (NaOH). The peels were stirred at 350rpm for 24 hours to ensure the completed reaction with sodium hydroxide. These treated peels then were dried in an oven at 70°C for 24 hours before ground to powder adsorbent forms (60 µm).

### Adsorption of Oil

Oil adsorption was investigated using two different types of oil, which is lubricant oil and petrol oil. The biosorbent of banana peel and orange peel was prepared and mixed in three different ratios namely 2:1, 1.5:1.5 and 1:2. Oil solution was prepared by mixed 1.0 ml of oil type into 100 ml distilled water. The different biosorbent ratio was poured into three oil solution separately and stirred about 10 minutes at 350rpm. Solutions were filtrated and dried at 70°C for 2 hours. The precipitates were measured again to determine the percentage adsorption of the fruit peel adsorbent.

### FTIR Analysis

In order to identify the chemical modification of fruit peels, Fourier Transform Infrared (FTIR) spectra were recorded on the FTIR spectroscopy. Sample in the form of powder is compressed into a thin pellet and analysis by scanning using FTIR spectra between 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>.

## FINDINGS AND DISCUSSION

### Adsorption Treatment

The effects of different ratio, types of oil and temperature in removing oil were investigated. The volume of oil used for the treatment were kept constant at 1.0 ml of oil in 150 ml of distilled water (v/v). The percentage of oil removal (Q<sub>e</sub>) was calculated by the formula in equation 1:

$$\text{Removal percentage } Q_e = \frac{(W_i - W_f)}{W_i} \times 100 \tag{1}$$

where  $W_i$  = initial mass of adsorbent and  $W_a$  = final mass of adsorbent.

**Effect of ratio**

The effects of different ratio of adsorbent on the percentage of oil removal for lubricant oil were investigated using orange peel and banana peel (OP:BP) at the ratios of 1:2, 1.5:1.5 and 2:1 as presented in Table 1. It can be observed that adsorbent with the ratio of OP to BP at 1:2 obtained the higher percentage of oil removal (38.120%) as compared to the ratio 1.5:1.5 and 2:1 of adsorbent used at room temperature. Effectively, higher composition of BP favor the removal of lubricant oil from water due to the high content of cellulose in the BP [9]. According to [3], banana can easily retain the heavy oil because their cellulose content is high as compared to an orange peel. With the high percentage of cellulose, efficient adsorption can be achieved with viscous oil such lubricant oil. Besides that, the banana fiber contains high hydrophobicity as well as holds the minimum moisture requires for hydrocarbon biodegradation.

Table 1: The effect of different quantity ratio of adsorbent on removal of lubricant oil [orange:banana](OP:BP)

Ratio	Initial Weight	Final Weight	Qe (%)
1:2	1.5089	2.0841	38.120
1.5:1.5	1.5069	1.8253	21.129
2:1	1.5188	1.8193	19.785

The results for the effects of using different ratio of adsorbent on the percentage of oil removal for petrol oil is depicted in Table 2. It has shown that using adsorbent (OP:BP) with a ratio of 1:2 gave similar results when applied to lubricant oil, but with a slightly lower percentage of oil removal of 32.169% for petrol oil. However, at the ratio of 2:1 (OP:BP) gave the lowest percentage of oil removal for both lubricant and petrol oils. Employing a higher composition of OP was found to be inefficient in oil removal due to the fact that OP contains low cellulose (13.61%) as reported by [10].

Table 2: The effect of different quantity ratio of adsorbent on removal of petrol oil [orange:banana](OP:BP)

Ratio	Initial Weight	Final Weight	Qe (%)
1:2	1.5300	2.0222	32.169
1.5:1.5	1.5103	1.5052	2.3107
2:1	1.5112	1.6365	8.291

**FTIR Analysis**

FTIR spectra of adsorbent with ratio OP to BP before contacted with oil was shown in Figure 1 (a). According to [11] in OP spectra, the broad and intense absorption peaks at around 3420  $\text{cm}^{-1}$  correspond to the O-H stretching vibrations due to inter- and intra-molecular hydrogen bonding of polymeric compounds (macromolecular associations) such as alcohols, phenols and carboxylic acids, as in pectin, cellulose and lignin [11]. The BP also consist of OH stretching, C-H stretching of alkane, C-H and C=O stretching of carboxylic acid or ester, COO- anion stretching, OH bending, C-O stretching of ester or ether and N-H deformation of amines respectively [12]. The alcohol group at wave number at 2400-3400  $\text{cm}^{-1}$  show the O-H group is present in both fruit peel. The alkanes which are C-H also exist in both peels that located at wave 3278.08  $\text{cm}^{-1}$ . Carboxylic acid which is C=O at peak 1700-1732.51  $\text{cm}^{-1}$  also present in both peels adsorbent. Figure 1 (b) showed IR spectra for the hybrid adsorbent after contacted with lubricant oil. The adsorbent after contacted with lubricant oil consist of alcohol group (O-H) at wave number 3332.57  $\text{cm}^{-1}$ , alkanes group (C-H) at wave number 2852.60-2922.06  $\text{cm}^{-1}$ , alkenes group wave number 1637.53  $\text{cm}^{-1}$  and carboxyl group (C=O) at wave number 1700  $\text{cm}^{-1}$ . The IR spectra of hybrid adsorbent after treated with petrol oil (Figure 1 (c)) showed the alcohol group (O-H) increased at wave number 3330.65  $\text{cm}^{-1}$ , alkanes group (C-H) occurs in wave number 2852.99-2953.85  $\text{cm}^{-1}$ , alkenes group increased at wave number 1630.55  $\text{cm}^{-1}$  and Carboxyl group (C=O) occurs at wave number 1700  $\text{cm}^{-1}$ . The ethers (C-O-C) also present at the wave number 1029.29-1202.69  $\text{cm}^{-1}$ .

It shows that the adsorption band of  $-\text{COOCH}_3$  on fruit peel surface hydrolyzed to  $-\text{COO}-$ , thereby increasing the amount of carboxylic acid [11]. The wave number at 3000-3400  $\text{cm}^{-1}$  in all the FTIR results before and after contacted with oil show increasing peak in this range due to the high content of carboxylic acids in these adsorbent. Besides that, the modification of cellulosic fiber also can increase the oil sorption capacity based on changing of hydrophilic characteristic to hydrophobic [3]. The lubricant oil has a high content of alkanes. According to [13],

alkanes liquid is often mixed with oil in an attempt to reduce the heavy viscosity. So, it shows that the acne C=C stretching mode was increased in wave number  $1629.92\text{cm}^{-1}$  in the fruit peels adsorbent when mixed with lubricant oil. Besides that, the best adsorbent for a process of lubricating oil is present of acid properties in the substances [13]. The hybrid adsorbent present carboxylic acid stretching mode at wave number  $2922.44\text{-}2852.71\text{cm}^{-1}$ , so it can give higher adsorption for lubricant oil when react with these adsorbent. Moreover, the present of O-H stretching mode at wave number  $3355.41\text{cm}^{-1}$ , N=O stretching mode at wave number  $1453.34\text{ cm}^{-1}$ , C-O stretching mode at wave  $1017.50\text{ cm}^{-1}$  can give higher adsorption for reaction lubricant oil with BP and OP.

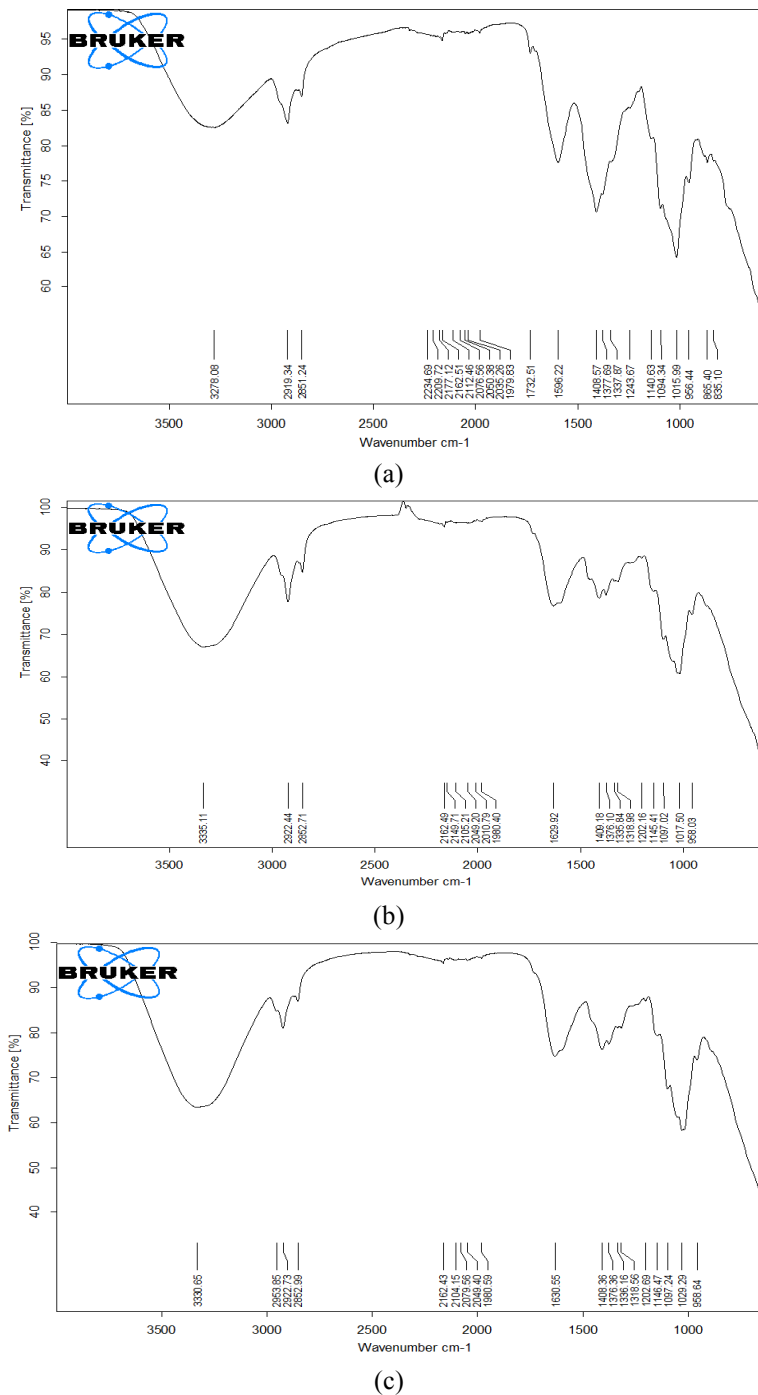


Figure 1: FTIR result for (a) hybrid adsorbent (b) hybrid adsorbent after react onto lubricant oil (c) hybrid adsorbent after react onto petrol oil

According to [14], motor gasoline is the complex mixture of volatile flammable liquid hydrocarbon that contain abundant toluene and benzene and some methyl-tert butyl ether. FTIR result shows that the aromatic group for benzene are present at wave 1411.65-1636.34  $\text{cm}^{-1}$  when fruit peel adsorbent was tested with petrol oil. In addition, FTIR spectra of fruit peels adsorbent shows O-H stretching mode at wave 3339.79  $\text{cm}^{-1}$ , O-H which present the carboxylic acid stretching mode at wave number 2853.47-2954.11  $\text{cm}^{-1}$ , C=O stretching mode at wave number 1636.34 $\text{cm}^{-1}$  and C-O stretching mode at wave number 1098.40  $\text{cm}^{-1}$  when mixed with petrol oil.

### CONCLUSION

The oil adsorption capacity depends on ability of fruit peel to adsorb oil from the solution. Adsorbent with highest cellulose can remove heavy oil more effectively than those with lower contain of cellulose. From the study, the ratio OP to BP at 1:2 gave the higher adsorption in both lubricant oil and petrol oil. It shows that the lubricant oil and petrol oil have the highest percentages of adsorption by the BP. Thus, mean the fruit peels can be a good potential as one of the alternative eco-friendly and cost effective adsorbent in oil waste treatment.

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