



Fabrication of Cellulose Acetate/PTFE-Based Polymer Adsorbent for Oil Spillage

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Abstract

Oil spill is a pollution and environmental problem which occurs due to liquid petroleum hydrocarbon released into the environment and required expensive materials to clean up. Not only this will have an impact on animals and plants, but it also has an impact on the environment. The use of adsorbents is a mechanical recovery method which does not have side effect to the environment. This study aims to fabricate the aerogel from cellulose acetate and polytetrafluoroethylene and evaluate the aerogel capability and suitability for oil spillage. Three (3) polymers of cellulose acetate and polytetrafluoroethylene adsorbents were prepared with each of the sample have different polymer ratio and were used as adsorbents in this study. All the adsorbents were prepared by mixing the solution of cellulose acetate and PTFE together with specified ratio before distilled water were added to form the aerogel. Once dried, the polymers were characterised using ATR-FTIR. The FTIR spectrum for the sample A shows a broad peak at 2948 cm^{-1} and 3480 cm^{-1} which attributed to C-H aromatic vibrations and O-H stretching respectively. The characteristic of PTFE were located at 1218 cm^{-1} and 1149 cm^{-1} which associated with C-F symmetric and asymmetric stretching respectively. For sample B, the characteristic of cellulose acetate had been located at broad peak at 2970 cm^{-1} (C-H aromatic) and 3458 cm^{-1} (O-H stretching). The C-F symmetric and asymmetric stretching had been located at 1218 cm^{-1} and 1158 cm^{-1} respectively. For sample C, the characteristic of cellulose acetate had been located at 2970 cm^{-1} (C-H aromatic) and 3458 cm^{-1} (O-H stretching). The C-F symmetric and asymmetric stretching had been located at 1208 cm^{-1} and 1148 cm^{-1} respectively. To study the efficiency of the polymers as adsorbents, oil recovery rate, sorption capacity and reusability were conducted by using the Petrol RON95 oil in the aerogel sample. Sample A (1:1, cellulose acetate and PTFE) had the sorption capacity of 1.2142 g/g while sample B (2:1, cellulose acetate and PTFE) had the sorption capacity of 1.5328 g/g. Sample C (1:2, cellulose acetate and PTFE) had the sorption capacity of 0.6261 g/g. The oil recovery rate for sample A, sample B and sample C were 13.0%, 29.5% and 10.4% respectively. The efficiency of reusing the aerogel had decrease for all 3 samples after 4 cycles had been done. Sample A had decrease on efficiency of 23.2%, sample B had decrease on efficiency of 20% and sample C had massively decrease on efficiency of 99.2%. Based on the result on capability of sorbents, the sorption capacity and oil recovery rate were higher when the ratio of cellulose acetate is higher than PTFE due to cellulose acetate is a polymer where the solubility is strongly dependent on the degree of substitution. Higher value of degree of substitution will result in insolubility on water.

Keywords: Aerogel, PTFE, cellulose acetate, oil spillage

1. Introduction

An oil spill is a pollution event that occurs when a liquid petroleum hydrocarbon is released into the environment, particularly the marine ecosystem, as a result of human activities. Oil spills are an environmental problem that necessitates the employment of expensive materials to clean up [1]. More than a hundred million gallons of crude oil are estimated to be leaked into the maritime environment each year [2]. Oil spills permeate the structure of birds' plumage and animals' fur, diminishing their

insulating properties and making them more susceptible to temperature variations and less buoyant in water. Many factors contribute to oil spills including the release of crude oil from drilling rigs and wells, tanker and big ship leaks that use heavy oil, and the spillage of refined petroleum products [1].

Controlling the spread of oil after a spill and improving its physical recovery can preserve animals and plants. Therefore, sorbents have been utilised in several oil spill recovery schemes, including retrieving oil traces from the ocean surface, basic treatment methods for small leaks, passive treatment strategy and reinforcement to other containment strategies, such as booms [2]. Sorption materials with the properties of biodegradable, strong and reusable are more appealing as it is simple to execute and produces no by-products. An example of this sorbent material is aerogel. This is due to aerogels being solid networks with filigree pores that are filled with air [3].

One of the potential aerogels that might help to overcome this problem is the combination of cellulose acetate and polytetrafluoroethylene. Since prehistoric times, cellulose has been the most plentiful resource and is the most abundant organic substance. Cellulose has the chemical formula of $(C_6H_{10}O_5)_n$ and is a linear homopolysaccharide comprised of D-glucopyranose units connected by β -1,4 glycosidic linkages [4]. Due to the cellulose properties, its amphiphilic has zero-tolerance of oil-water specificity and will need to undergo a hydrophobized process. A study suggested cellulose acetylation to cellulose acetate. Next, polytetrafluoroethylene is being chosen due to its moderate properties, easy handling and processing, and low cost. These approaches are human-friendly due to non-hazardous solvents.

This study will focus on the sorbents that can be used efficiently in the treatment of oil spillage by monitoring the capability of cellulose acetate and polytetrafluoroethylene-based polymer. An alternative approach using the fabrication of polymer is proposed as one of the methods. The hydrophobization of the cellulose and polytetrafluoroethylene aerogel with a silane chemical transform them into an oil sorbent [3]. The proposed method demonstrates that the procedure is simple and easily recycled after usage due to the non-crosslinked for the aerogel [5]. The performance of cellulose acetate and polytetrafluoroethylene content on aerogel oil sorption, oil recovery rate, and reusability will be discovered.

2. Literature review

2.1. Cellulose

Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$ and the most abundant natural polysaccharide. [6], studies found that due to its cheap cost, sustainability, biocompatibility, and biodegradability, cellulose is regarded as the primary raw material for the energy and chemical industries in the future. It has also become a significant driving force for the sustainable growth of human civilization. The formation of intermolecular hydrogen bonds results in the formation of a fibrous structure and semi-crystalline accumulation, which confers to cellulose a high degree of strength and flexibility [7]. Additionally, because the main hydroxyl groups on cellulose are easily changed chemically, cellulose has a wide range of applications. It has found widespread application in tissue engineering applications such as biological scaffolds, skin tissue healing, and artificial blood vessels [8].

2.2. Cellulose Acetate

Cellulose acetate is of special interest among the numerous cellulose derivatives due to its desired physical qualities such as exceptional optical clarity, biodegradability, and high durability [9]. Due to its water resistance, it is a potentially useful material for food packaging applications. Cellulose acetate is also commonly used as a filler in cigarettes and as a photographic film basis. Additionally, because of its low cost, it may be employed in a wide variety of applications, including membrane technology, medication release, textiles and associated materials, separating membranes, UV protectors, medical implants, the optoelectronic field, and the oil field.

2.3. Polytetrafluoroethylene

Polytetrafluoroethylene, or PTFE for short, is a fluoropolymer of tetrafluoroethylene that has a wide range of uses. At room temperature, polytetrafluoroethylene is a fluorocarbon solid, as it is a high-

molecular-weight polymer composed entirely of carbon and fluorine. PTFE is hydrophobic, meaning that neither water nor compounds containing water wet it, but fluorocarbons exhibit reduced London dispersion forces due to fluorine's strong electronegativity. At normal temperature, PTFE is a white solid. According to [10], polytetrafluoroethylene (PTFE) is commonly referred to as "The King of Plastics" or Teflon due to its outstanding chemical stability and long-term corrosion resistance. Due to its superior corrosion resistance, heat resistance, and electrical insulating properties, polytetrafluoroethylene (PTFE) is widely used in aerospace, mechanical engineering, and biomedicine, among other industries [11]. Polytetrafluoroethylene is exceptionally resistant to abrasion, making it suitable for use in hazardous areas.

2.4. Mechanical Recovery

The use of sorbents is a relatively popular form of the mechanical recovery approach. The recovery process is based on the oil's adherence to the revolving oleophilic skimmer surface [12]. While natural materials have been extensively used to separate oil from water surfaces, limitations such as low absorption capacity, non-recyclability, low selectivity, and sinking after sorption have restricted their practical utilisation. As a result, it is necessary to develop and produce innovative synthetic sorbents with high absorbency. In practical applications, a good sorbent should exhibit the following characteristics: high absorption capacity, hydrophobicity, ability to float both before and after the sorption process, reusability, and cheap cost [13].

3. Results and Discussion

3.1. Chemical Reagent

All of the chemicals used were analytical grade (AR) reagent with highest purity. It is including cellulose acetate, polytetrafluoroethylene, acetone and petrol RON95. All of the chemicals were obtained from R&M chemicals, Sigma Aldrich and Petronas.

3.2. Fabrication of Aerogel

A solution of cellulose acetate was prepared by dissolving 4.4 g of cellulose acetate into 110 mL of acetone to make it 4 w/v %. A solution of PTFE (4 w/v %) was prepared by dissolving 4.4 g of PTFE into 110 mL of acetone. The prepared solutions were stirred until it fully dissolve. Then, sample A (1:1, cellulose acetate and PTFE) was prepared by pouring 25 mL of the prepared solution of cellulose acetate into the 250 mL beaker and 25 mL of the prepared solutions of PTFE also was added into it. Next, distilled water was added into the beaker until it fully precipitate. This process was needed for the complete precipitation of the prepared solution [5]. The procedure was repeated for sample B (2:1, cellulose acetate and PTFE) and sample C (1:2, cellulose acetate and PTFE). Later, all of the samples was filtered and transferred to 50 mL containers. The samples were dried in an oven for 6 hours at 100 °C.

3.3. Fabrication of Aerogel

3.2.1 Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy

ATR-FTIR spectroscopy used to determine the functional group presence in the polymer. No sample preparation to be done as the sample can be directly introduced to the instrument. The aerogel sample was directly placed on the ATR crystal and it was pressed until force gauge around 80-100. The wavelength in the spectrum was set around 650-4000 cm⁻¹.

3.2.2 Thermogravimetric Analyzer

Thermogravimetric analyser (TGA) used to determine the thermal stability of the polymer. The temperature for heating the sample was set in the range of 30-740°C. The sample was introduced to an inert condition using nitrogen gas with a heating rate of 10°C/min.

3.3. Capability of Aerogel in Oil

3.3.1 Testing on Sorption Capacity

The samples of cellulose acetate-PTFE polymer were weighed and the immersed into 30mL of oil which is Petrol RON95 for 5 minutes for an equilibrium process to occur. After that, the samples were taken out and drained for 1 minutes before weighed the aerogel. The maximum sorption capacity of the product was calculated using Equation 1.1 below:

$$Q_t = \frac{m_w - m_d}{m_d} \quad (1.1)$$

where Q_t = the sorption capacity at the relevant time ($g\ g^{-1}$)
 m_d = the dry weight of the aerogel before sorption (g)
 m_w = the weight of the aerogel after sorption (g)

3.3.2 Testing on Oil Recovery Rate

The value of adsorbed aerogel was used for this mechanical treatment. The aerogel will be squeezed over the beaker fir 30 seconds. After aqueezing, the aerogel was weighed and the rate of oil recovery was estimated by Equation (1.2).

$$Q_s = \frac{\text{squeezed amount of oil}}{\text{absorbed amount of oil}} = \frac{m_w - m_s}{m_w - m_d} \times 100\% \quad (1.2)$$

Where Q_s = The oil recovery rate (%)
 m_d = The dry weight of the aerogel before sorption (g)
 m_w = The weight of the aerogel after sorption (g)
 m_s = The weight of the aerogel after squeezing (g).

3.3.2 Testing on Oil Recovery Rate

The reusability of aerogels was determined by compressing the aerogel following each usage [3]. The aerogel was reweighted after the first squeeze and placed in the beaker that filled with oil again. After 1 minute, the aerogel was taken out and allowed to drain for 1 minute before weight again. The steps were repeated until 4 cycles and the maximum sorption capacity were measured.

4. Results and Discussion

4.1. Fabrication of Aerogel

Cellulose acetate-PTFE aerogel was fabricated by mixing the two precursors in acetone at different ratios of cellulose acetate and PTFE. This aerogel had mainly absorbed oil, and water to a lesser extent. It depends on which has first contact with the aerogel, if the aerogel had first contact with the oil, it absorbs mainly oil. This behavior of the aerogel had made it impossible for the contact angle measurement to be determine as the liquid seeps into the surface. For sample A which has the ratio of 1:1 between cellulose acetate and PTFE, the quantity produced is 1.5382 g (76% yield). Sample B which has a ratio of 2:1 between cellulose acetate and PTFE produced 1.5994 g (53% yield) of aerogel. While for the sample C (1:2, cellulose acetate and PTFE), the weight is 1.4853 g (49% yield). Sample B was the highest due to the amount of cellulose acetate that is being added larger than PTFE. This is because cellulose acetate was easier to dissolve in acetone compared to PTFE.

4.2. Characterization of Aerogel

4.2.1 ATR-FTIR Analysis

ATR-FTIR was used to characterize the aerogel based on their functional groups and to identify the compound in the aerogel. Based on Figure 1(a) for sample A, the appearance of C=O of cellulose acetate was identified at strong peak ($1737.73\ \text{cm}^{-1}$) and the CH_3 was shown at peak $1369.68\ \text{cm}^{-1}$. In addition, a broad peak at $2948.07\ \text{cm}^{-1}$ and $3480.81\ \text{cm}^{-1}$ which attributed to the C-H aromatic vibrations and O-H stretching respectively. The sharp peak of C-O stretching was seen at $1037.72\ \text{cm}^{-1}$. The appearance of PTFE was identified as the strong peak at $1218.19\ \text{cm}^{-1}$ and $1149.45\ \text{cm}^{-1}$ represent the C-F symmetric and asymmetric stretching respectively.

Figure 1(b) shows the IR spectrum for sample B, the appearance of cellulose acetate was seen at peak 1739.07 cm^{-1} and 1368.42 cm^{-1} that indicate the C=O and CH_3 respectively. Next, the C-H aromatic vibrations and O-H stretching was identified at broad peak 2970.67 cm^{-1} and 3458.26 cm^{-1} respectively. The C-O stretching was identified at sharp peak 1036.31 cm^{-1} . The functional group for the PTFE in the aerogel was seen at 1218.09 cm^{-1} and 1158.33 cm^{-1} as it represents the C-F symmetric and asymmetric stretching respectively.

Figure 1(c) shows the spectrum for sample C, C=O and CH_3 of cellulose acetate was identified at 1739.83 cm^{-1} and 1368.70 cm^{-1} respectively. Other than that, the C-H aromatic vibrations was seen at 2970.44 cm^{-1} and O-H stretching was seen at broad peak 3458.11 cm^{-1} . The C-O stretching also was seen at sharp peak 1047.75 cm^{-1} . The appearance of PTFE was identified at 1208.46 cm^{-1} and 1148.17 cm^{-1} as both of it represent the C-F symmetric and asymmetric stretching respectively. Figure 1 shows the ATR-FTIR spectra for the three samples.

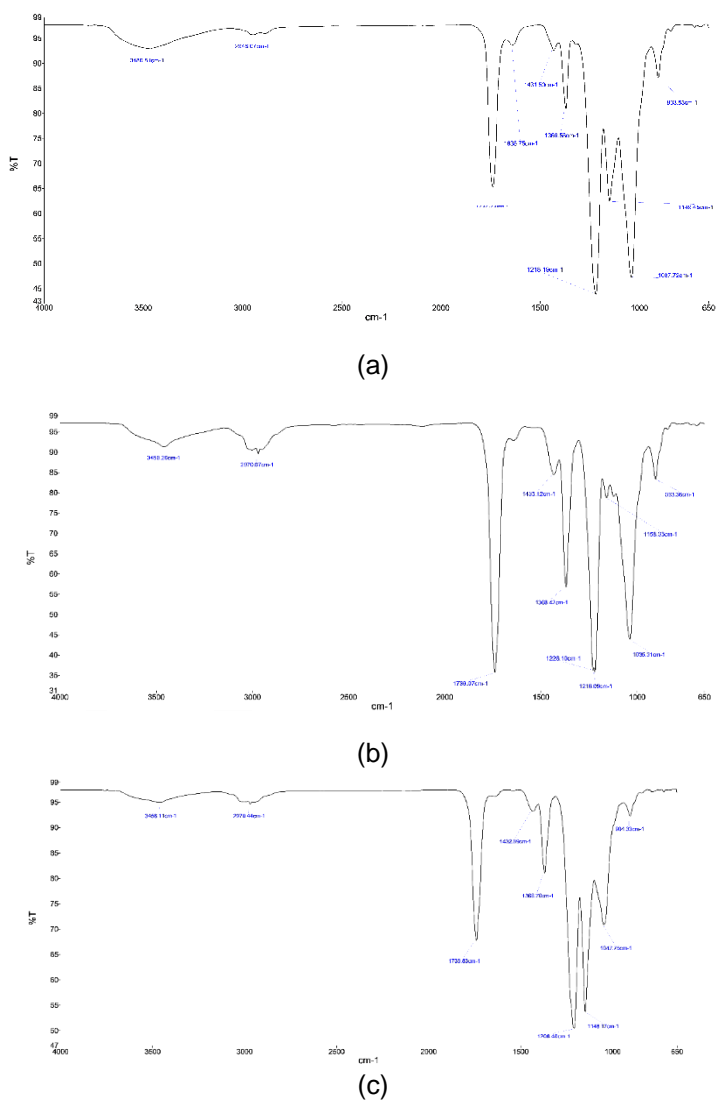


Figure 1. IR spectra for (a) sample A, (b) sample B and (c) sample C

4.2.2. Thermal Analysis using Thermal Gravimetric Analysis (TGA)

TGA was used in the characterization of aerogel to determine the thermal stability of the three samples of aerogel. Based on the Figure 2(a), sample A started with the loss of water molecules with a total of mass of 2% due to the curve began with a decrease in temperature in the region I. In the region II, the sample undergoes mass loss which was 48% due to the pyrolysis of polymer. Region III showed the

sample had loss of mass of 47% due to the decomposition of polymer. From the DTG curve, the highest peak was at the 370°C that indicates the T_{max} .

Figure 2(b) which shows the TGA curve for sample B, the curve began with a decrease in temperature in the region I due to the loss of water molecules with a total mass of 2%. Next, the sample had loss of mass of 83% due to the pyrolysis of polymer from the sample at region II. In the region III, the sample undergoes polymer decomposition and total mass loss was 12%. From the DTG curve, the maximum peak to indicate the T_{max} was at 375°C.

From Figure 2(c), the TGA curve for sample C began with a decrease in temperature due to loss of water molecules with a total mass of 3%. Next, the sample undergoes pyrolysis of polymer with a total of mass loss of 45% from the sample. In the region III, sample undergoes polymer decomposition and total mass of loss was 38%. At the DTG curve, the maximum peak to indicate the T_{max} was at 380°C. When comparing all of the data from TGA and DTG for all three samples, sample C which has highest and maximum peak value of T_{max} . This means it had the lowest percentage of weight loss and highest thermal stability. Figure 2 shows the TGA and DTG curves for all of the samples.

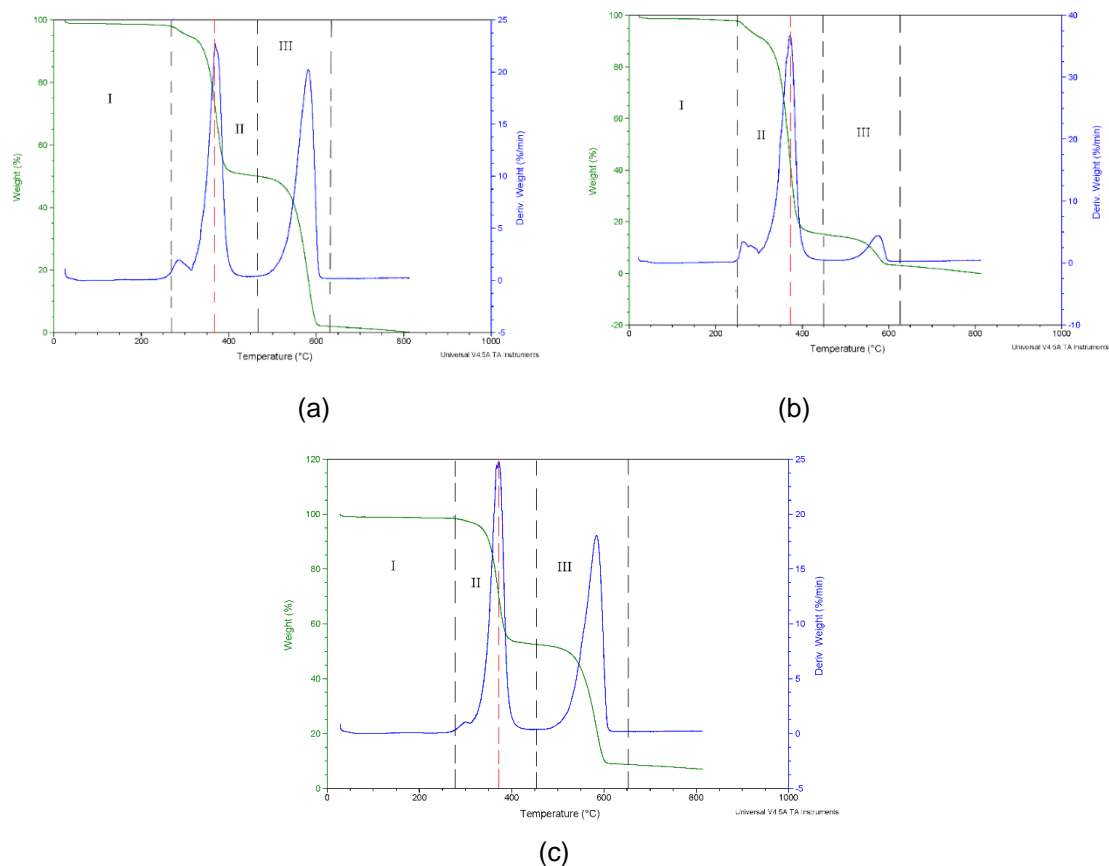


Figure 2. TGA and DTG curves for (a) sample A, (b) sample B and (c) sample C

4.3. Capability of Aerogel

For the sorption capacity, petrol RON95 obtained from nearby petrol station to mimic the oil spillage phenomenon. This fuel consists of many hydrocarbons including butane, isopentane and pentane. All three samples were immersed into the fuel. Based on the Figure 3(a), the oil sorption capacity for sample B is the highest compared to the other two samples (up to 1.5328 g g^{-1}). For the sample A, it had sorption capacity of 1.2142 g g^{-1} which was higher than sample C that had 0.6261 g g^{-1} of sorption capacity. The reason why all three samples had lower value of sorption capacity is due to the petrol RON95 is volatile and can easily evaporate in the room temperature. Therefore, the aerogel need to compete for the adsorption of oil. Figure 3 shows the sorption capacity and oil recovery rate for all three samples.

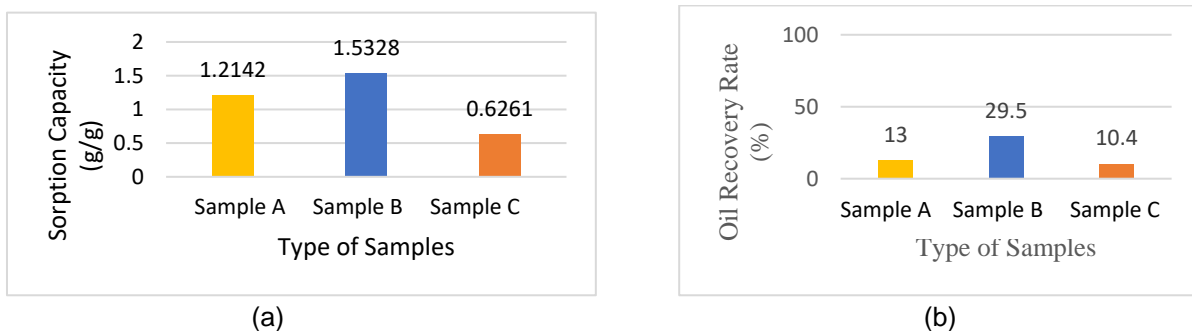
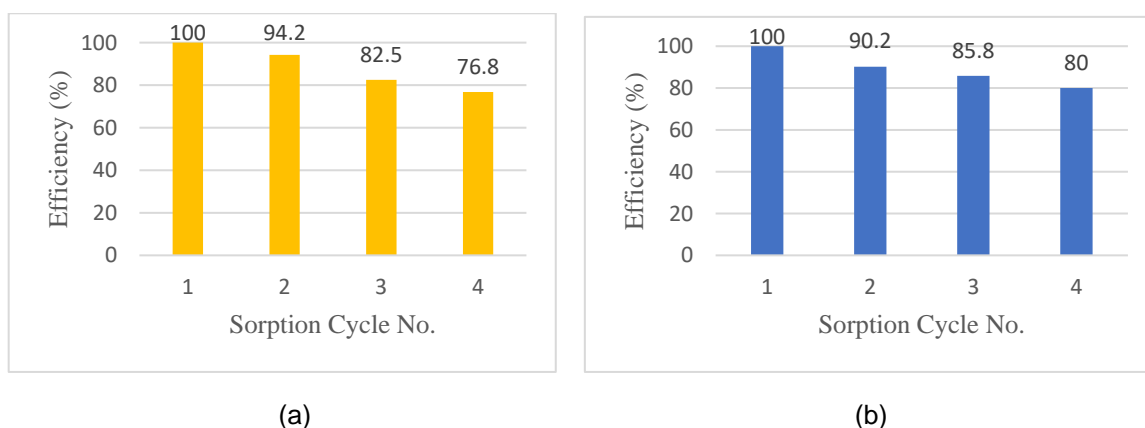


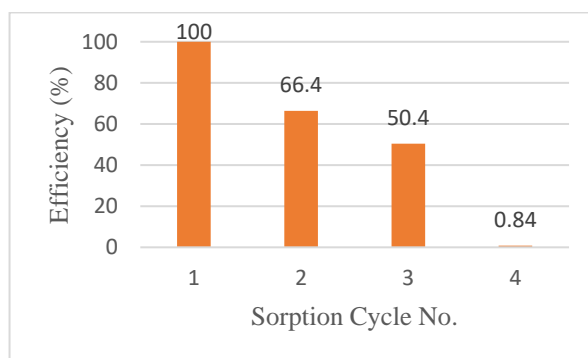
Figure 3. (a) Sorption capacity and (b) oil recovery rate for all three samples

Next, from the Figure 3(b), sample B had the highest value of oil recovery rate after squeezing compared to the other two samples which was 29.5%. Sample C had the lowest value of oil recovery rate (up to 10.4%) and sample A had oil recovery rate of 13%. From these data, the oil recovery rate is decrease when the value of cellulose acetate in the sample decrease. The recovered oil is devoid of apparent contaminants from the sample and can be used again without restriction.

For the reusability of the samples, the efficiency of reusing the sample is presumed to be 100 percent for the first time it was used and it was set as the reference point each time the sample was used again. Based on the Figure 4, all three samples had a decrease on the efficiency of reusing the sample in oil sorption. In the sorption cycle 2, sample A had a decrease of 5.8% of the efficiency while sample B and sample C had a decrease of 9.8% and 33.6% of efficiency respectively. For the sorption cycle 3, sample A had a decrease on the efficiency which was 17.5%. Sample B and sample C, both had a decrease of 14.2% and 49.6% respectively. For the sorption cycle 4, sample A had a decrease of 23.2% on the efficiency of reusability. Sample B had a decrease of 20% while sample C had a massive decrease on the efficiency of reusability which was 99.16%. From these findings, the samples are particularly vulnerable to mechanical treatment and have been degraded following the first cycle of reuse. This can be seen as the sample C cannot be further used for sorption cycle 5 as the efficiency had been massively drop.

All testing was done to measure whether the aerogel is considered as a reliable adsorbent for the oil clean up. In this project, the testing was done in the fume hood. All of the samples were immersed in the oil for 5 minutes before it was weighed. After that, it was compressed to measure the oil recovery rate and weighed again. Next, the samples were immersed again to measure the efficiency on reusing the aerogel. Figure 4 shows the efficiency of reusing the sample for oil sorption.





(c)

Figure 4. Efficiency of reusing (a) sample A, (b) sample B and (c) sample C

Conclusion

The aerogel for all three samples were successfully fabricated without the need of expensive organic solvents and cross-linkers through the characterization using ATR-FTIR and TGA analysis. All samples exhibit a strong absorption peak at 1739.07 cm^{-1} assigned to C=O stretching, a broad band occur at 3458.11 cm^{-1} assigned to O-H peak and C-F peak from PTFE observed at 1208.46 cm^{-1} and 1148.17 cm^{-1} . Next, the aerogel had been tested to measure the capability of sorption, oil recovery rate and the efficiency of reusability. The finding shows that the samples which made of cellulose acetate and PTFE had shown similar properties as a hydrophobized sorbent. When the aerogel was tested in the oil, the aerogel itself does adsorb the oil. Thus, the capability of aerogel had successfully been tested. Other than that, the recovery oil from the aerogel sample does not contain any visible impurities and therefore, it can be used again freely. But the efficiency to reuse the aerogel again is not effective as the first usage. This is because according to the data, the capability of aerogel to adsorb oil had decreased significantly. The finding shows that sample B has the best performance compared the other two samples due to the composition of cellulose acetate is higher and it is a better adsorbent than PTFE.

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