CARBON FIBER AEROGEL FROM NANO-FIBRILLATED CELLULOSE OF SUGARCANE BAGASSE AND WASTE ENGINE OIL RESIDUE FOR OIL SORPTION

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ABSTRACT: The oil adsorption method is one of the best approaches that can be used to treat an oil spillage on the water surface. Researchers have moved forward in the development of highly efficient and low-cost oil absorbent materials for the oil adsorption process, in addition to having environmentally friendly properties. Following this, combination of two different wastes has been used as raw material to prepare oil sorbent material with such characteristic in this study. Nano-fibrillated cellulose was extracted from sugarcane bagasse and was combined with carbon residue from waste engine oil to produce carbon fiber aerogel (CFA). Different ratio of cellulose to waste engine oil residue, WER (0.5, 1.0, 1.5) at different carbonization temperature (500ºC, 600ºC, 700ºC) was used to develop CFA and the oil sorption capacity was investigated. It was observed that ratio of cellulose to WER of 1.5 and carbonization temperature of 600 ºC achieved the highest oil sorption capacity of 5.47 g/g. The fabricated sample CFA possessed highly fibrous and rough surface structure as observed by FESEM, low density (0.17 g/cm^3) with high carbon content (C-C and C≡C) as confirmed by the FTIR. The results of this study are expected to encourage the use of sustainable waste sources as raw materials for the development of oil sorbent materials.

KEY WORDS: *Sugarcane bagasse, Waste engine oil residue, Porous carbon fiber aerogel, Nano-fibrillated cellulose, Oil sorption*

1. INTRODUCTION

Lately, the demand for petroleum products is increasing rapidly, parallel to the rapid development of the world economy. However, the expanding process of oil exploration and transportation for meeting the high demand of customers has led to the frequent occurrence of large and small oil spills around the world [1]. Without immediate action, oil spillage will heavily impact lives around us which will cause economic losses and threaten the environment. In addition, clean water is vital for our bodies and a resource where we benefit it in our daily life. According to the latest UNICEF & WHO (2015), report on sanitation and drinking water worldwide indicates that over 663 million individuals still lack access to safe

drinking water [2]. Hence, this pollutant source needs to be treated very well from time to time because the water needs to be used daily.

Physical water treatment through physical adsorption by porous materials, is regarded as the most successful and promising strategy to tackle oil spill problem [3]. An excellent oil sorbent material should present the following characteristics: high adsorption capacity, high selectivity, low density, and environmental friendliness. These characteristics are essential to separate oil-water mixtures effectively. Recently, 3D carbon-based aerogel has been investigated as an oil sorbent material. Aerogel, as a kind of porous material with a spatial mesh structure, has attractive characters including multi-level pore structure and high specific surface area [4, 5]. Various synthetic carbon-based aerogels, such as carbon nanotube sponges, graphene and carbon nanofiber, have been established and showed very high adsorption capacity as oil sorbent [2, 6]. However, the method used to synthesis these materials involved high cost and complicated steps. Moreover, they are not environmentally friendly and sustainable [4].

As alternative, researchers have investigated the use of organic waste such as agricultural biomass to produce carbon-fiber aerogel for oil sorption through pyrolysis process. Micro-fibrilated and nano-fibrillated cellulose were extracted from agricultural waste sources such as peanut shell [4] or banana peel [7] which were later converted to carbon fiber aerogel. Similarly, porous carbon material has also been prepared from oil sludge residue [2] however its oil sorbent property has not been studied. The combination of different type of waste sources for the preparation of carbon aerogel is yet to be investigated. Thus, this paper describes the development of carbon fiber aerogel through green approach using nano-fibrillated cellulose extracted from sugarcane bagasse and waster engine oil residue (WER) as oil sorbent material. The physicochemical properties as well as oil sorption capacity of the novel carbon fiber aerogel were studied. The fabricated carbon fiber aerogels found to possess unique characteristics such as being lightweight, hydrophobic, and recyclable.

2. METHODOLOGY

2.1. Pretreatment of waste engine oil carbon residue

Waste engine oil residues (WER) were obtained from Pentas Flora Sdn. Bhd. and were pre-treated before use. The WER were washed few times with ethanol to remove oil residue and were dried overnight in an oven at 80℃. The dried WER were further crushed using mortar and pestle to obtain small size particles. Then, the small size WER was proceeded with sieving process to obtain powdered carbon residue of less than 100 μm.

2.2 Synthesis of RF polymer

Resorcinol formaldehyde (RF) resins were synthesized using resorcinol and 37% formaldehyde solution as precursors. Firstly, 1.2 mL of aqueous ammonia solution (NH_4OH, 25%) was mixed with solution containing 48 mL absolute ethanol (EtOH) and 288 mL of deionized water (DI). After stirring it for more than 1 h, 0.84 mL formaldehyde solution and 1.2 g resorcinol was added to the stirred solution and stirred again for another 24 h at 30 ℃.

Next, the solution being slow centrifuged at 4750 rpm at 30 min and the pellet were air-dried at 100 ℃ for 48 h.

2.3 Synthesis of nano-fibrillated cellulose

The method to prepare the nano-fibrillated cellulose was obtained from Asem et al., [8] with slight modification. Sugarcane bagasse (25 g) was added into the mixture of 500 mL of distilled water and 10 g NaOH in 1L beaker in which, it placed in water bath for 5 h at temperature 80 ºC. Then, the sample is washed and filter with distilled water at least three times using vacuum pump. Next, the sample is bleached with 250 mL of water and 250 mL of hydrogen peroxide. The sample is washed and filtered again with distilled water at least three times using vacuum pump. After that, the sample is then bleached with the mixture of 60 g of NaOH and 500 mL distilled water in 1 L beaker for 1 h at temperature 80ºC. After that, the sample is washed and filtered with distilled water at least three times using vacuum pump. Then, 2.5 g of isolate sample is added into 5 mL of 1% sulfuric acid at temperature 80ºC for 1 h. Next, the sample is washed and filtered many times (at least 10 times) with distilled water using vacuum pump. After that, the sample is mixed with 20 g of NaOH with 400 mL of water for 24 h. Then, treat crude cellulose into 400 mL distilled water, 8g of sodium chlorite and 3 mL acetic acid for 3 h. Lastly the sample is washed and filtered with distilled water at least ten times using vacuum pump.

2.4 Preparation of Carbon Fiber Aerogel (CFA)

Pre-treated WER and nano-fibrillated cellulose (NC) were mixed with cross linker recorsinol formaldehyde (RF) polymer, maleic acid, and polyethyleneimine at different ration. The mixture was blended well in ultrasonic bath sonicator for 30 min. Then, the mixture was poured into the mold before freezing it at -80 ℃ for 24 h. Next, the mold was put in freeze drier machine to remove water from the sample for about 3 d. Next, the sample was subjected to carbonization where the samples were activated using tube furnace with flowing nitrogen gas (N_2) at different temperature in a ceramic boat. The temperature inside the tube furnace was programmed to increase linearly at ~5 ºC/min, dwelling hold at 600 ℃ for 30 min and ramping down ~30 ℃/min to the room temperature. To study the response towards oil adsorption capacity, two parameters were varied which include ratio of NC to WER which is from 0.5 until 1.5 and activation temperature from 500 ℃ until 700 ℃ for carbonisation process.

2.5 Engine oil Sorption Measurement

The CFA aerogel was weighed before being immersed in engine oil (liquid moly) around 15 min to let oil sorption into the sample and then removed for another weight measurement [3]. The process for oil adsorption can be calculated by using Equation 1. To ensure the recyclability of the PCF aerogels, the sorbents were extensively washed with hexane following oil absorption and oven-dried at 80°C.

The process can be calculated by using the following equation:

$$OA = (m_f - m_i)/m_i \quad (1)$$

where,
OA = oil adsorption capacity
m_i = weight before adsorption
m_f = weight after adsorption

2.6 Characterization of PCFA

The CFA was characterized by using Fourier transform infrared (FTIR) spectroscopy to measure the availability of functional group present on the sample and to confirm complete conversion of raw material to carbon aerogel and field emission scanning electron microscope (FESEM) is used to observe the surface microstructure and porosity. The bulk density (ρ) was calculated from the mass and volume measurements. The water contact angle (Θ) on the surface of the aerogel was also measured to support the water sorption test.

3. RESULTS AND DISCUSIONS

3.1 Physicochemical Properties of Carbon Fiber Aerogel (CFA)

3.1.1Physical Properties of CFA

As shown in Fig. 1a, white colored nano-fibrillated cellulose was successfully extracted from sugarcane bagasse. Fig. 1b displaying the nanocellulose fiber-WER (NCFW) composite revealed fair distribution of carbon residue of waste engine oil around the white nanocellulose fiber. After the carbonization process at different carbonization temperature and nanocellulose to WER ratio, carbon fiber aerogel (CFA) cubes were successfully prepared as shown in Fig. 1c.

The physical characteristic of CFA such as weight, density and diameter were measured before oil adsorption tests were performed. Density of the samples were calculated based on the weight and volume of the sample. All measurements of the CFA sample before and after carbonization are tabulated in Table 1. It was observed that the weight, thickness, diameter, and density of the sample was reduced following the carbonization process. The weight of the sample is reduced by half of its initial weight where the weight was reduced from 0.5 g to 0.2 g while the thickness of the sample was reduced from 1.5 cm to 1.13 cm after carbonisation process giving the slight reduction in the density of the sample from 0.15 gcm^{-3} to 0.14 gcm^{-3}. The dimensional changes and mass loss were influenced by carbonization temperature for nano-fibrillated cellulose of sugarcane bagasse. The mass loss was due to removal of water and degradation of small molecules in the NCFW to become carbonaceous material [9]. The density of the obtained CFA sample is higher than the previously reported carbon fiber aerogel from agricultural waste due to integration of the WER with much heavier weight.

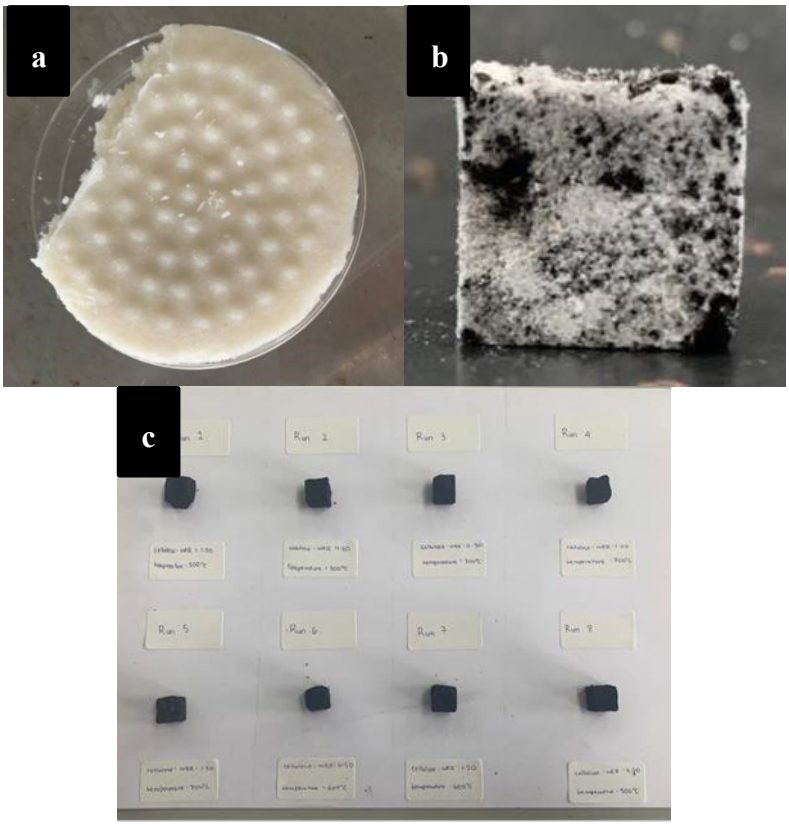

Fig. 1. Nanocellulose prepared from sugarcane bagasse (a), NCFW sample (b) and the CFA sample carbonized at 600 ℃ (CFA-600) (c).

Table 1: Physical properties of NCFW and developed CFA-600

Properties	**Before carbonization process**	**After carbonization process**
Weight (g)	0.50± 0.02	0.20 ± 0.02
Thickness (cm)	1.50 ± 0.03	1.13 ± 0.03
Density (gcm^{-3})	0.15 ± 0.03	0.14 ± 0.006

3.1.2 Microstructure of carbon fiber aerogel

The morphologies of the NCFW and CFA-600 are presented in Fig 2. From Fig. 2a, it was observed that the morphology of NCFW is having rod-like whisker shape with interconnected structure of nano-fibrillated cellulose (diameters < 200 nm) [8, 10]. Meanwhile, WER having random geometry of solid granules and RF polymer in microspherical shape. The RF polymer particles were added into the sample to bridge the nano-fibrillated cellulose to the WER [11]. It was observed that the surfaces of nano-fibrillated carbon fibers in Fig 2b which were converted from the nanocellulose fiber having rough surface structure. Irregular porous structure in between the carbon fiber was also observed in the CFA-600 sample (Fig. 2b) is assumed as able to provide large free space volume for oil uptake. No obvious aggregation of the WER is observed, suggesting that the fabrication method is appropriate in preparing the cabon fiber aerogel. Fig. 3 shows XRD

pattern of the CFA-600. It is observed that sample exhibits a broad hump at around 22°, a signature for amorphous carbon [12] which confirms complete conversion of the nano-fibrillated cellulose to carbon.

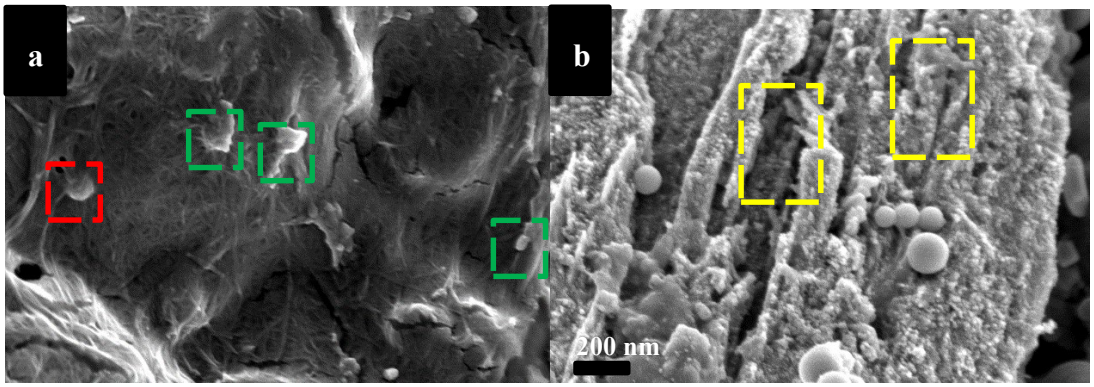

Fig. 2. FESEM images NCFW (a) and CFA-600°C (b) at 30000x magnification. Red box indicates the RF microsphere, green box indicates the WER and yellow box indicate the porous structure.

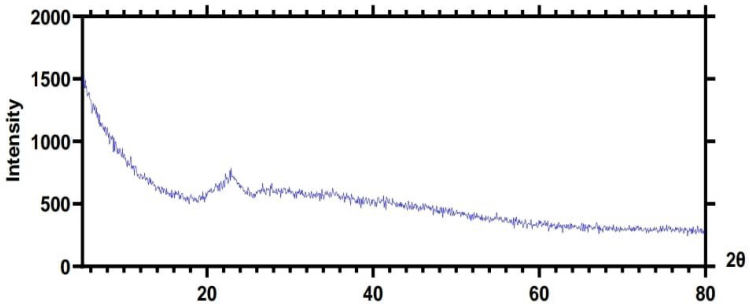

Fig. 3. XRD patterns of the CFA-600.

3.1.3 Surface functional group of carbon fiber aerogel

Fig. 4 shows the FTIR spectra of NCFW, NC, WER and CFA-600 respectively. The characteristic functional groups of NC are present for the NCFW sample but is absent for the CFA-600 i.e. the C-O bond at 1027 cm^{-1}. The transmittance band of CH group is also reduced at wavenumber 3442 cm^{-1}. The characteristic peaks of C−C at 1100 cm^{-1}, C═C at 1580 cm^{-1} and C≡C bonds at 2070 cm^{-1} are observed in the CFA-600, indicating the formation of a full carbon structure after the carbonization process. Wan et al. [13] reported that by exposing the NC at 600°C in N_2, the reduced atmosphere transforms the cellulose to a carbon fiber. Similar functional groups are found in WER, but the peak intensities are much weaker for C-C bond but much higher for C=C bond. The 3518 cm^{-1} bands that shows in the NC and NCFW illustrate that O-H group from nanocellulose fiber (NC), and RF polymer reduced after carbonization. It is reported that the conversion of the cellulose fiber to carbon through pyrolysis process will remove active hydrophilic group [14, 15].

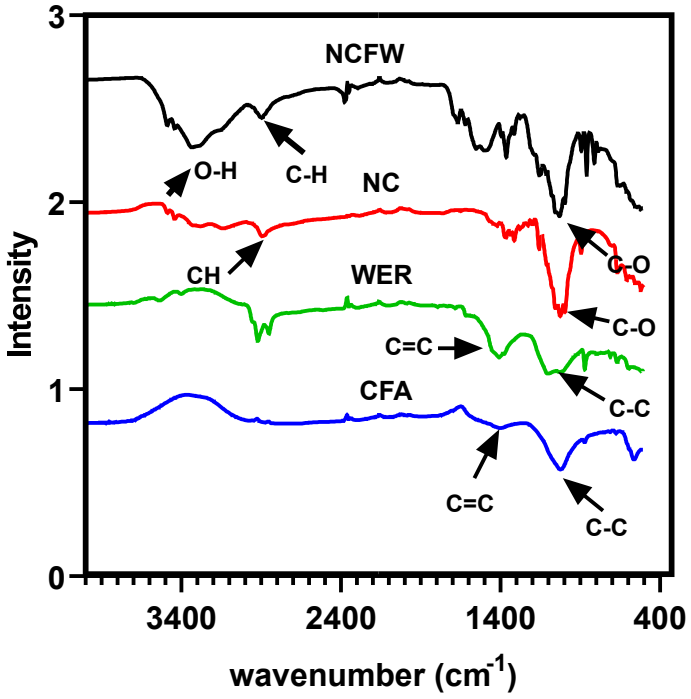

Fig. 4. FTIR spectra NCFW, NC, WER and CFA-600 samples

3.1.4 Water sorption test of carbon fiber aerogel

The study of hydrophobicity of CFA-600 can be performed by analyzing the CFA600 on the water surface. Fig. 5b shows that the CFA-600 sample remains floating on water surface after 24 h at room temperature compared to when it is initially added into the water (Fig 5a) even with slight agitation of the sample in the water. This is probably due to its ultra-lightweight and hydrophobic properties. The contact angle (Θ) of CFA-600 with water was measured as ~101° which support its hydrophobic properties. For selective oil sorption application, the ultra-lightweight and hydrophobic properties of the aerogel is of great importance. This observation suggested that the prepared sample is an ideal candidate as oil sorbent material with could eliminate competition of oil sorption with water.

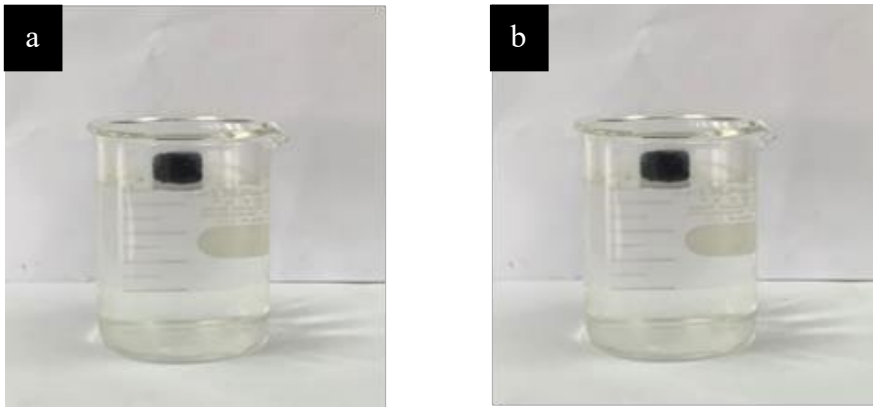

Fig. 5. Water sorption test of CFA-600 sample at initial condition of 0 h (a) and after 24 h (b)

3.2 Oil sorption behavior of CFA

As supported by the FTIR result, the pyrolysis condition of 600°C in an N_2 atmosphere is sufficient to convert the NCFW composite to a full CFA matrix with optimal oil sorption capacity. It is interesting to further investigate the effect of the carbonization temperature on the engine oil sorption behavior of the CFA. As shown in Fig. 6, increasing the temperature from 600°C to 700°C at ratio of the NC to WER 1 slightly decreased the oil loading capacity from 4.66 g/g to 4.40 g/g meanwhile reducing the temperature to 500 ℃ slightly increased oil loading capacity to 5.33 g/g. It is reported that increasing the pyrolysis temperature would increases the surface area of the biochar sample along with lower water content and higher fixed carbon amount [16]. However, greater surface area sometimes is not much desirable because it increases water retention capacity to a greater extent. The absorption capacity varied between the samples could be due to different pore morphologies of the aerogels induced by different carbonization temperature [17]. The loading capacity achieved by this CFA is not as high as the one achieved by the Ieamviteevanich et al., where bacterial nanocellulose were employed to prepare the carbon aerogel at 500℃.

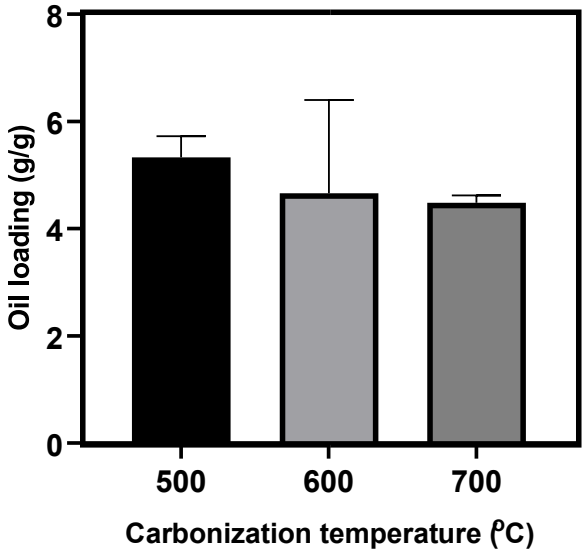

Fig. 6: Oil loading behavior relationship with carbonization temperature of the sample at ratio of cellulose to WER 0.5.

Oil sorption test was also performed for the CFA-600 sample by changing the ratio of the NC to WER from 1 to 0.5 and 1.5. It was observed in Fig. 7a that reducing the ratio of the NC to WER to 0.5 slightly reduced the oil sorption capacity from 4.49 to 3.48 g/g. Meanwhile, further increasing the amount of NC to WER to 1.5 increased the oil sorption capacity to 5.47 g/g. Thus, the result suggested that higher amount of NC compared to WER at carbonisation temperature of 600℃ will help to synthesis CFA with good oil adsorption capacity. Even though previous studies reported that carbon produced from agricultural waste tend to have hydrophilicity behavior [6], adding the hydrophobic WER particles into the 3D aerogel framework could reduce the total surface area of the final sample due to possible aggregation behavior of the WER. Fig. 7b, demonstrated that a

piece of CFA-600 with NC to WER ratio of 1 placed in a beaker filled with fresh engine oil can fully absorbed the oil within less than 2 min.

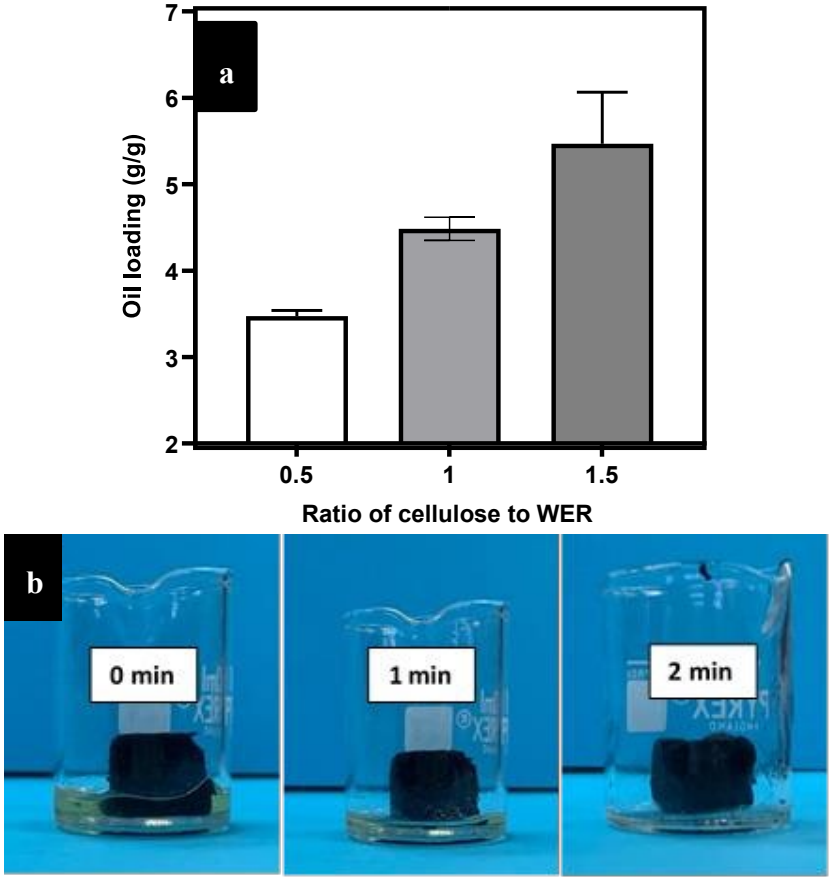

Fig. 7: Oil loading capacity relationship with the ratio of cellulose to WER at 600℃ (a) and the oil sorption behavior of the CFA-600 with time (b)

3.3 Recyclability test of PCFA

CFA-600 sample at ratio of the NC to WER 1.5 is used to do the recyclability test. The oil-absorbed aerogel is washed with hexane before drying at 80 °C to remove the absorbed oil. It is observed that the 3D structure of the sample is still intact after washing and drying and carbonaceous surface of the fibers of the aerogel are preserved. However, the CFA-600 sample capacity to absorb the oil reduced by 80% after the second cycle with 1 g/g oil sorption capacity compared to the first cycle (Fig. 8a). The CFA-600 sample take slightly longer time to absorb the oil compared to the first cycle where 30 min is needed to absorb the engine oil as shown in Fig. 8b. It takes longer time to absorb the oil compared to the first cycle might be due to some of the oils were still trapped in the pores of the sample which suggests that more washing cycles with hexane is needed [18]. Overall, the experiment shows that the sample is capable to be recycled back for adsorption process.

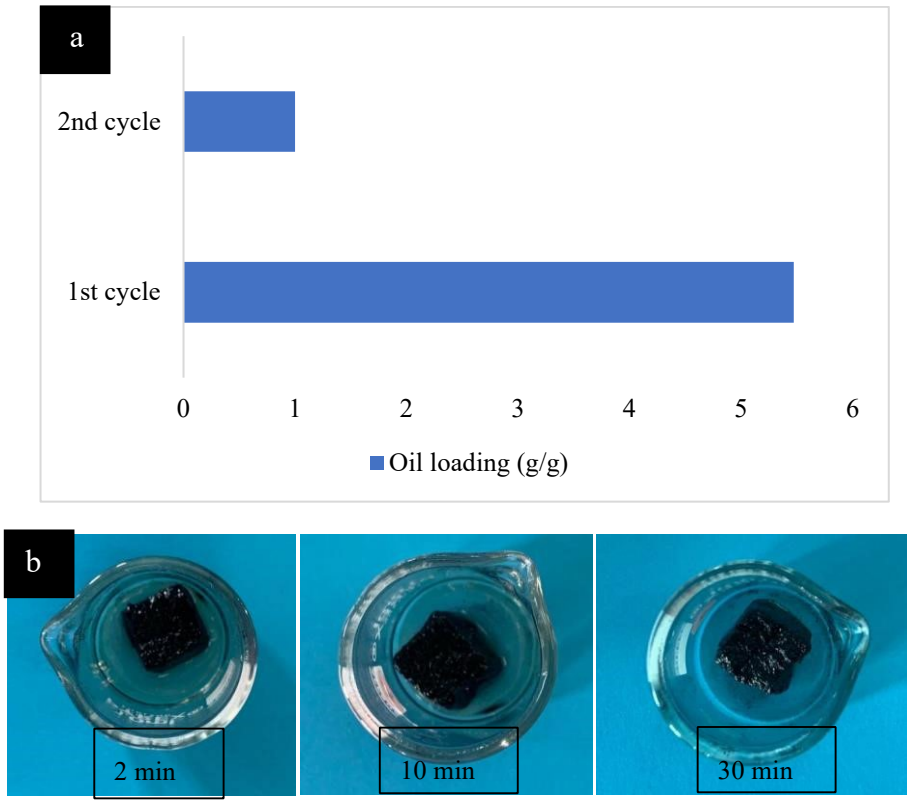

Fig 8. Oil loading capacity of CFA-600 at two different cycles (a) and demonstration of oil sorption behaviour of CFA-600 sample with time during the second cycle (b).

4. CONCLUSION

In summary, 3D carbon nanofiber aerogel (CFA) derived from nano-fibrillated cellulose and WER as oil sorbent material has been successfully developed by carbonization method. The CFA sample consists of porous network of the fibrillated carbon and exhibits ultralighweight and high selectivity towards oil. The CFA has an adsorption capacity of 5.47 g/g achieved at nanocellulose to WER ratio of 1.5 and carbonization temperature of 600 °C. The CFA can be recycled due to its intact structure with proper removal of the absorbed oil after previous oil sorption. The present work demonstrates an exciting prospect from using combination of different waste materials to alleviate oil spills incidents, that will have positive benefits to the environment.

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