

# Fabrication of Carbon Aerogels from Cigarette Butts for the Oil Spills Treatment

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Recently, oil spills have been received numerous concerns all over the world because of its harmful influences for ecosystem and human being. Various techniques are introduced to manage this kind of pollution, including physical adsorption by porous materials. Carbon aerogel is one of those promising materials because of its great potential in extremely fast oil adsorption without any emission of toxic compounds. Cigarette waste is one of the most littered things around the world that can be endanger for the environment. For the first time, carbon aerogels have been successfully fabricated via a simple pyrolysis of eco-friendly cellulose acetate-based aerogels from cigarette butts waste from the tobacco factory. The prepared ultralight carbon aerogels exhibit significantly low density (36.34-50.50 mg/cm<sup>3</sup>) and high porosity (98.39-97.76 %). The aerogel has highly porous structure with irregular shaped pore in range of 10 to 100 μm. Carbon aerogels express good hydrophobicity with water contact angles more than 120°. The oil adsorption capacity of carbon aerogels is up to 14-21 times their own weight within 40 s, which is significantly higher than original cellulose-based aerogels (11-14 times their own weight). The oil adsorption of carbon aerogel follows pseudo-second order kinetics which adsorbs quickly in few seconds and reaches equilibrium in less than 60 min. In conclusion, the carbon aerogels from cigarette butt-derived cellulose acetate exhibit a great potential in the field of oil spills treatment.

## 1. Introduction

Water pollution such as oil and many hazardous organic solvents caused by human activities particularly in the chemical industry can be the serious threat for the marine environment and ecosystem (Li et al., 2016). More severely, these toxic chemicals can be accumulated to a marine food chain and consumed by human being (Barron et al., 2020). Many techniques were deployed to remediate this problem and mainly divided in three categories such as physical methods (booms, skimmers, and sorbents), chemical methods (solidifier, in-situ burning, etc.), and biological methods (Dhaka and Chattopadhyay, 2021).

Among these methods, using sorbent is considered as one of the most effective and optimal ways because of cost efficiency and ready to use (Kim et al., 2022). Aerogel, a type of porous material, lately is rising as a very promising adsorbent because it has diverse advantages, including high porosity, super lightweight, great adsorption capacity (Paulauskiene et al., 2021), outstanding thermal properties, and so forth (Nguyen et al., 2021). Notably, aerogels fabricated from biopolymers or recycled feedstocks are gaining a great attention from both commercial and scientific sentiments (Tran et al., 2022). Carbon-based aerogel can be considered one of the most suitable oil adsorbents since it is genuinely hydrophobic without any modification, high surface area and extremely porous (Lee and Park, 2020). Especially, carbon materials fabricated from biomass or industrial waste can bring many benefits including low-cost process and reducing waste pollution.

According to many research, cigarette butts are one of the most common litters in the world as every year trillions of cigarette are smoked and discarded without being recycled (Torkashvand et al., 2020). The cigarette butts waste can exert ecotoxic impacts by releasing many toxic chemicals such as nicotine, tar, tobacco-specific

nitrosamine that endangers ecosystem (Araújo and Costa, 2019). Cellulose acetate (CA), which is the main component of cigarette butt, is a very potential precursor for not only aerogel fabrication but also for carbonization since CA is one of the most carbon-rich cellulose derivatives. There are many efforts in recycling cigarette filters to give that waste a second life to be useful in human life, which can promote circular economy and sustainable development including synthesizing them to aerogel and transform to carbon materials (Marinello et al., 2020). Boikovych et al introduced a modest fabrication cellulose acetate aerogel recycled from cigarette filters by using sol-gel method with acetone and cold water (Uebe et al., 2021). Yu et al. (2018) utilized pyrolysis to turn cigarette filter into carbon anode in lithium ion battery. Alhokbany et al. (2020) developed carbon aerogel from discarded cigarette butts to use as an absorbent of bisphenol-A.

Even though recycling cigarette butts has been caught a lot of attention recently, there has not been any research on fabricating carbon aerogel from cigarette butts for oil adsorption yet. In the present study, the methodology of synthesizing carbon aerogel by carbonizing the initial cellulose-based aerogel recycled from cigarette filters was reported. The aim of this study is to investigate the oil adsorption ability of carbon aerogel, giving a new solution for oil spill treatment.

## 2. Experiments

### 2.1 Materials and chemicals

CA fibers were removed from the wrapped paper of cigarette filters collected in a local Vietnam tobacco company (Degree of substitution (DS) 2.5). Sodium hydroxide (NaOH) and urea ( $\text{CH}_4\text{N}_2\text{O}$ ) were purchased from Xilong (China). The absolute ethanol was purchased from Chemsol (Vietnam). The alkaline solution was made with deionized water. Commercial 5w30 motor oil was bought from local market.

### 2.2 Methodology

#### 2.2.1 Fabrication of cellulose acetate aerogel (CA-AU aerogel)

NaOH and urea were dissolved in water in a ratio of 7:12:81 by mass to create the alkaline solution. The fibers separated from cigarette filters were blended to reduce the length, then dispersed into NaOH-urea solution in different concentrations of 4, 5, 6 and 7 %w/v, suspiciously stirred in cold temperature and sonicated until it turned into a homogenous mixture. The gelation was continued in freezer at 0 °C for 24 h, then the gel was defrosted at room temperature and absolute ethanol is used to coagulated the gel. The gel was immersed in deionized water for several days for the solvent exchange until reaching neutral pH. To finish, the water in CA-AU aerogels were removed in a freeze-dryer (Toption TPV – 50F).

#### 2.2.3 Fabrication of carbon aerogel by CA-AU aerogel

The resulted aerogel was directly placed in a furnace and performed under a nitrogen atmosphere from room temperature to 300 °C in 60 min with heating rate of 3 °C/min and  $\text{N}_2$  flow of 100 mL/min, then held at 300 °C for 30 min before cooling down to room temperature.

#### 2.2.4 Characterization of aerogels

There are some techniques were applied to characterize the aerogels. The chemical structure of samples was determined through FTIR spectra was examined by FTIR, Frontier, Bruker Tensor 37 in the range from 400 to 4,000  $\text{cm}^{-1}$ . To understand the morphology of the aerogels, scanning electron microscopy (SEM) was performed by FE-SEM S4800 Hitachi and water contact angle (Dataphysics) for hydrophobicity. The density ( $\rho_{\text{aerogel}}$ ) of aerogels was evaluated by its measurement of weight and volume, then the bulk density of aerogel was the density of components in aerogel, in here is carbon ( $\rho_{\text{carbon}} = 2 \text{ g/cm}^3$ ) (Nguyen et al., 2022). The porosity ( $\varphi$ ) of aerogel was estimated by the Eq(1):

$$\varphi = \left( 1 - \frac{\rho_{\text{aerogel}}}{\rho_{\text{carbon}}} \right) \times 100 \% \quad (1)$$

To investigate the oil absorption, 10 g motor oil 5w30 was poured into a beaker containing water. After that, a 0.05 g aerogel sample was placed onto the oil layer and then let it adsorbs the oil. Finally, the immersed aerogel was lifted from beaker, leaved to drain in 5 min, and weighted again at several time in range from 0-150 s. the oil adsorption capacity ( $q_i$ ) of the aerogels is calculated by using Eq(2):

$$q_i = \left( \frac{m_i - m_0}{m_0} \right) \quad (2)$$

where  $q_i$  is the oil adsorption capacity of the aerogel at the series of time (g/g),  $m_i$  (g) and  $m_0$  (g) are the aerogel

weights before and after the oil adsorption test at time  $i$  (s). To study the adsorption kinetics, the kinetic data are calculated by using two common pseudo-first and pseudo-second order models expressed by Eq(3) and Eq(4), respectively (Wang and Guo, 2020).

$$\ln\left(\frac{q_e}{q_e - q_i}\right) = k_1 \cdot t \quad (3)$$

$$\frac{t}{q_i} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where  $q_e$  (g/g) is the oil adsorption capacity at equilibrium time,  $k_1$  and  $k_2$  are the kinetic rate constant of the pseudo-first and pseudo-second order model separately.

### 3. Results and discussion

#### 3.1 Morphology and physical properties of carbon aerogel

SEM images of carbon aerogels are illustrated in Figure 1a - 1d. As can be seen, carbon aerogels have a highly porous structure with irregular range of pore size from 10 to 100  $\mu\text{m}$ . Due to the alkaline treatment, the morphology of CA fibers in Figure 1e is changed into CA-AU aerogel which has the open 3D network structure of irregular shaped pores separated by thin walls as shown in Figure 1f. After carbonization, the carbon aerogels still keep the structure of CA-AU aerogel, but more pores are created than CA-AU aerogel. Because of the pyrolysis, the loss of chemical elements led to the creation of new pores inside the aerogel structure and , pores in CA-AU aerogel can be widened during this process. The differences can be clearly seen between Figure 1a and Figure 1f are the thinner of the wall, smaller pores created and some larger pores in the carbon aerogel compared to the CA-AU aerogel. In general, the resulted aerogel has a light and fragile structure. The more fibers added to the aerogel, the more enhancement of the network which are shown in Figure 1a - 1d, the walls between pores are thicker when there are more cellulose chains in the original CA-AU aerogels. Because of the carbonization, pore size of carbon aerogel had a wide range from extremely small which are less than 10  $\mu\text{m}$  to larger than 100  $\mu\text{m}$ .

The physical properties of carbon aerogel can be discussed about the effects of CA concentration on the density and porosity of aerogels. The synthesized carbon aerogels are determined for their density and porosity with the results displayed in Figure 2a. As can be seen in the illustration, all the aerogels own a high porosity in a range of 97.76-98.39 % and low density in a range of 36.34 - 50.50  $\text{mg}/\text{cm}^3$ . Compared with CA-AU aerogels, the shrinkage of carbon aerogels is significant which in range of 44.64-55.64 %, as shown in Figure 2a. The carbon aerogel witnesses the trend of the decrease of porosity and increase of density when adding more fibers into aerogel because the thicker of the walls inside the structure and the mass increasing of added matter can narrow the pore size and increase the weight of aerogel as can be seen in Figure 1 and calculated by Eq(1).

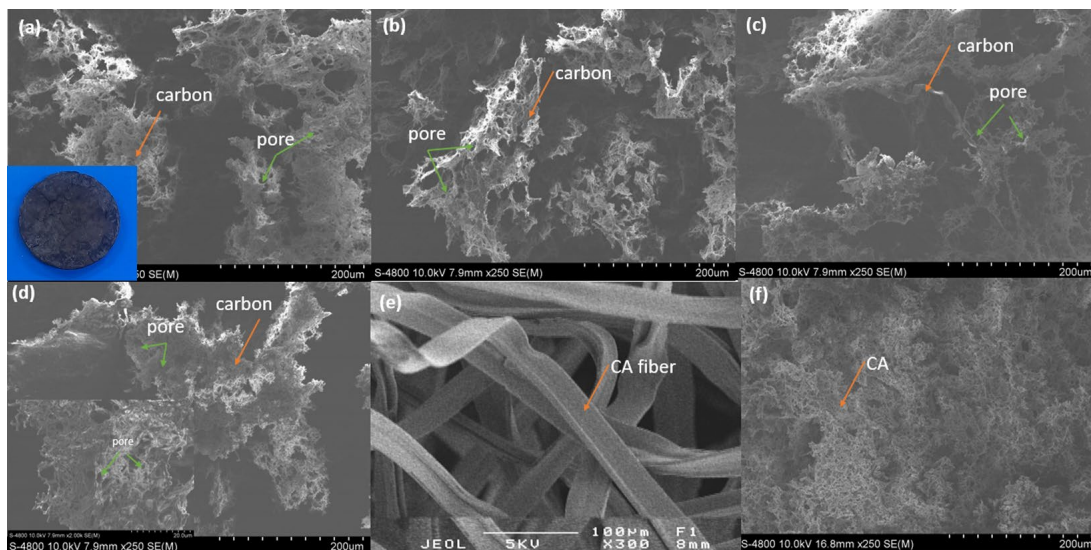


Figure 1: SEM images of carbon aerogel in various concentration of fibers 4 % to 7 % (a-d), (e) CA fibers and (f) CA aerogel in concentration of fibers 4 %w/v

### 3.2 Chemical structure of carbon aerogel

FTIR spectra shows the change of the typical function groups during the fabrication and carbonization is represented in Figure 2c. As can be seen in Figure 2c, all the bands at  $736\text{ cm}^{-1}$ ,  $1,645\text{ cm}^{-1}$ ,  $1,163\text{ cm}^{-1}$  are represented for  $\text{-C=O}$  and  $\text{-C-C-O}$  bonds in carboxylic group of cellulose acetate (Chen et al., 2016). After the sol-gel method, intensities of all bands of carboxylic group are weakened in CA-AU aerogel replacing with an significantly enrichment in intensities of bands that are typical for cellulose molecules at  $3,480\text{ cm}^{-1}$  ( $\text{-OH}$  group) and  $1,028\text{ cm}^{-1}$  ( $\text{-C-O}$  group) (Yang et al., 2008). This is the evidence that NaOH-urea mixture contributes to the change of physical and chemical properties of CA fiber. In term of carbonization, it can be clearly seen that all the remaining bands of CA-AU aerogel are disappear and replace with some characteristic band of carbon including bands at  $1,580\text{ cm}^{-1}$  ( $\text{C=C}$  in aromatic rings),  $1,225\text{ cm}^{-1}$  ( $\text{C-O}$ ) (Nguyen et al., 2022), which is confirmed that the CA-AU aerogel is decomposed and transformed to carbon aerogel through pyrolysis.

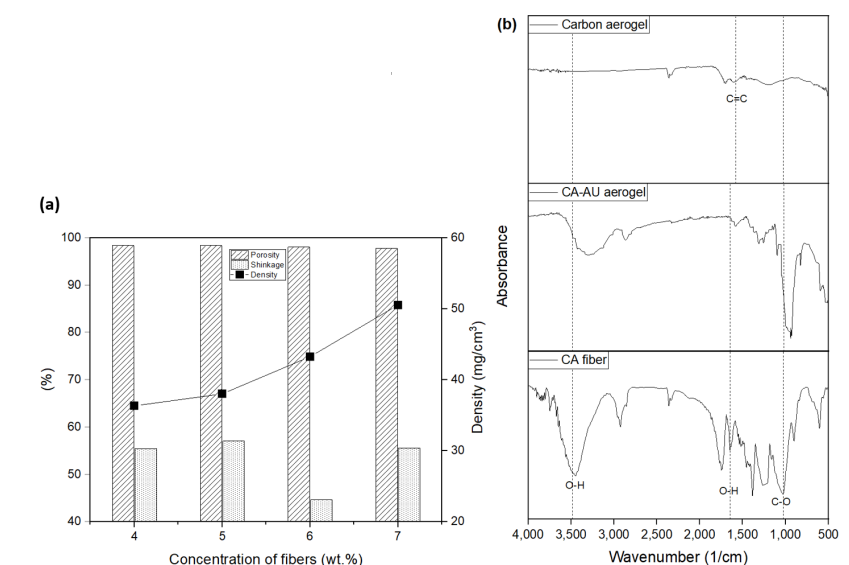


Figure 2: (a) Density, porosity and shrinkage of carbon aerogel, (b) FTIR spectra of carbon aerogel, CA-AU aerogel and CA fiber

### 3.3 Oil adsorption performance of carbon aerogel

Hydrophobicity is a key factor influencing the effectiveness of sorption ability of oil and determined by the water contact angle. The hydrophobicity can enhance the oil-water selectivity, repel the water penetration and lower surface energy (Chen et al., 2022). As shown in Table 1, all the aerogels have the water contact angle in a range of  $126\text{--}136^\circ$ , indicating an excellent oil adsorbent candidate. The increase of fiber concentration can lead the greater water contact angles.

Table 1: Water contact angle and kinetic model parameters of carbon aerogel

CA concentration (% w/v)	4	5	6	7
Water contact angle ( $^\circ$ )	126	128	130	136
Pseudo-first order $k_1$	0.008	0.003	0.009	0.001
$R^2$	0.955	0.861	0.905	0.961
Pseudo-second order $k_2$	0.027	0.061	0.043	0.220
$R^2$	0.9997	0.9997	0.9998	0.9999

The illustration in Figure 3a compares the maximum oil adsorption capacity between CA-AU aerogels and carbon aerogel. As can be discussed, the aerogels after pyrolysis show a significantly better adsorption capacity of  $13.69\text{--}20.92\text{ g/g}$ ; while the aerogels synthesized by alkaline method perform lower oil adsorption capacity of  $11.48\text{--}14.89\text{ g/g}$ . It can be explained by the appearance of more pores inside the network structure of carbon aerogel, and the widening of size from the initial pore of CA-AU aerogel that gives the oil more chance to diffuse into the aerogel due to the capillary force (Smirnova and Gurikov, 2017). In addition, since the water contact of carbon aerogels are high, the oil affinity to surface increases that improve the oil adsorption capability. As same

as other properties, it is obvious that the higher porosity, which is in lower concentration of fiber, the better the oil adsorption capacity in two kinds of aerogel. These results of carbon aerogel and CA-AU aerogel were comparable to the carbon aerogel made from waste newspaper (29-51 g/g) (Han et al., 2016),  $\alpha$ -cellulose (10-25 g/g) (Wang et al., 2014), winter melon (16-50 g/g) (Li et al., 2014), coconut coir (22.71 g/g) (Nguyen et al., 2022), recycled cigarette filter sorbent (17.2 g/g) (Ifelebuegu et al., 2018) and so forth.

The oil sorption of carbon aerogel versus time is shown in Figure 3b. It can be clearly detected from the curves that the aerogels adsorbed the oil very rapidly at the first 10 s and quickly reached equilibrium after approximately 40 s. The study on pseudo-first order and pseudo-second order kinetic model is reported in Figure 4 and Table 1. Figure 4a and 4b show the fitting plots using the pseudo-first model and the pseudo-second model, respectively. According to the calculated results, because the correlation coefficient  $R^2$  values for the pseudo-second order model is much closer to 1 than those of the pseudo-first order, it can be concluded that the oil adsorption behaviour carbon aerogels follow pseudo-second order model more exactly, which indicates the chemisorption where the oil removal is because of the physicochemical interaction between liquid-solid phase. In addition, the kinetic rate constant  $k_2$  is much higher than  $k_1$ , which is more suitable for experimental data, as shown in Figure 4.

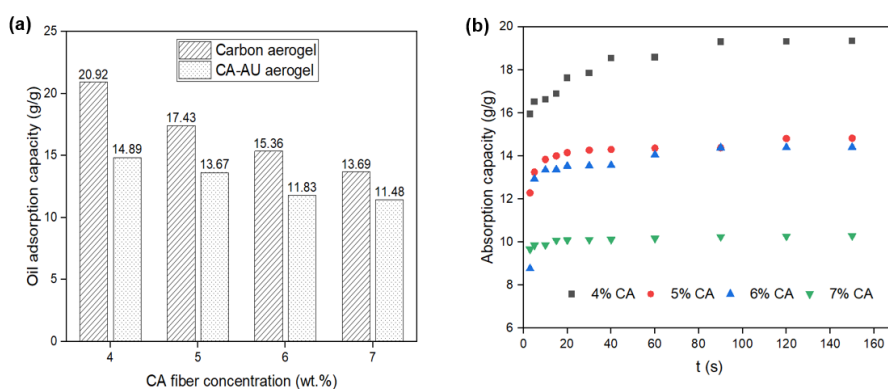


Figure 3: (a) The maximum oil adsorption capacity of CA-AU aerogel and carbon aerogel and (b) adsorption kinetics with different concentration of CA fiber of carbon aerogel

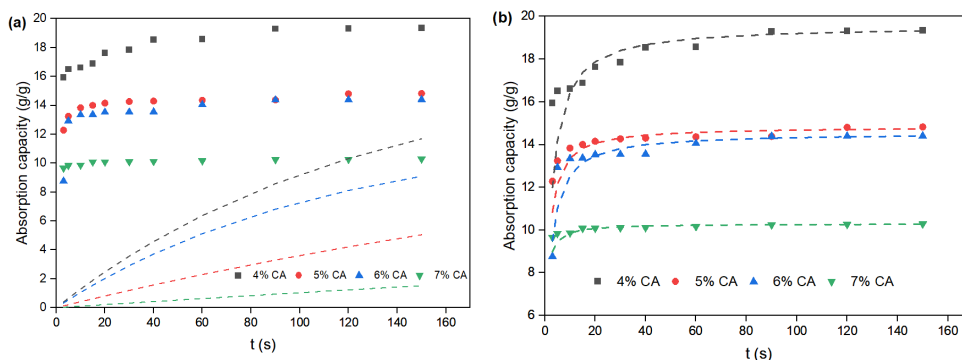


Figure 4: (a) Pseudo-first order and (b) pseudo-second order fitting graphs for oil adsorption of carbon aerogels

#### 4. Conclusion

A simple process to produce carbon aerogel from cigarette filter has been successfully developed by using sol-gel method, freeze-drying and carbonization. The obtained carbon aerogels are lightweight with highly porous network structures as well as a great oil adsorption performance following the pseudo-second order model. This demonstrates that cigarette butt-derived carbon aerogel without any modification of adding hydrophobic agents is a potential alternative for oil adsorbent instead of cellulose aerogel with costly silane coating.

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