A hydrophobic cellulose aerogel from coir fibers waste for oil spill application

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Abstract. In this work, a hydrophobic cellulose aerogel was successfully developed from coir fibers waste. The hydrophobic aerogel was prepared using a simple sol‒gel and freeze‒drying method followed by surface modification using either trimethylchlorosilane (TMCS) or hexamethyldisilazane (HMDS). The operating temperature was varied around the boiling point of the modifying agent ranging from 50‒70°C for TMCS and 110‒130°C for HMDS. The concentration of modification agents was varied from 40‒60 wt.% in n‒Hexane. The best condition in term of its hydrophobicity was obtained at 50% of TMCS with a temperature of 60°C and 40% of HMDS at 120°C. The obtained aerogel has a good hydrophobic characteristic indicated by a high of water contact angle of 100‒150°C. The aerogel also could selectively absorb only oil from the mixture of oil‒water. Therefore, it could be the promising material used to overcome the oil spill issue due to its biodegradability, abundant availability, and low cost.

1. Introduction
In the past decades, oil spill has become one of the most dangerous disasters which threatening the marine ecosystem. Deepwater Horizon in Mexico Bay at 2010 and Pertamina Refinery in Balikpapan waters at 2018 had been a serious disaster that should be considered to be prevented and overcame as soon as possible. Oil spill is not a simple problem because it has a long‒term effect to the marine ecosystem. Hydrocarbons from the spilled oil need many years to be naturally remediated and sedimented in the sea, hence it seriously threats the marine ecosystem. Many methods have been developed to overcome this oil spill disaster such as chemical, mechanical, and biological remediation, utilization of solidifier, skimmer, and dispersant, and in situ burning [1–6]. Unfortunately, those methods were expensive, needed a long period to finish, a kind of complex process, and non‒biodegradable. The effective method is sorption using absorbent with high selectivity to oil instead of water [7]. Therefore, it is highly desirable to synthesize a hydrophobic‒oleophilic material with high porosity and selectivity to oil. The porous material also must be biodegradable due to its application for marine ecosystem, to prevent a damage of the marine environment.

Aerogel is a kind of porous material with excellent properties such as ultralow density, high pore volume, high specific surface area, and strong sorption capability [8,9]. It is easily synthesized from biopolymer with simple chemicals and processes. The most common material used for aerogel synthesis is cellulose [8,10–13] which is abundantly available in nature and biodegradable for long term. Cellulose is easily found in biomass such as coir fiber. Coir fiber is an agricultural waste and abundantly available in tropical countries. It has a high content of cellulose which is about 23–43% and 35–54% of lignin [14]. Hence, coir fiber is a promising material for cellulose aerogel production.
Beside the high sorption capability, cellulose aerogel must have a high selectivity to oil due to its application for oil sorption in marine environment. Many researches have been studied to develop a cellulose aerogel material with hydrophobic property, which were aerogel modification using methyltrimethoxysilane (MTMS) with supercritical drying [15], vapor phase deposition using octyltrichlorosilane [16], and vapor deposition of trimethylcholorosilane (TMCS) [17]. Unfortunately, some chemicals used as the hydrophobic modification agents were expensive and the methods applied were not simple. In attempt to address those issues, this work would study to create a cellulose aerogel from waste material, coir fibers, with hydrophobic modification via a simple method. The basic concept of this idea was to synthesize using an economic material, chemical, and easy process. Therefore, the effect of temperature and concentration of hydrophobic modification agent would be further investigated.

2. Experimental Section

2.1. Materials
Coir fibers were collected from a coconut milling facility in Surabaya, Indonesia. Sodium hydroxide (NaOH), ethanol (C₂H₅OH), trimethylchlorosilane (TMCS), hexamethyldisilazane (HMDS), and n–Hexane (n–C₆H₁₄) were purchased from Merck. Urea (CON₂H₄) was supplied by PT. Petrokimia Gresik, Indonesia. Demineralized water was used for all synthesis and treatment processes. All chemicals were reagent grade and were used as received without further purification.

2.2. Methods
Lignin contained in coir fibers was firstly removed by mechanical milling and sieving in a 120 mesh. The milled coir fibers were then chemically delignified by atmospheric extraction using 20 mL of 6% NaOH per gram coir fibers as the solvent, at temperature of 100°C for 4 h. The obtained pulp was filtrated and washed by demineralized water to remove the sodium–lignin side product. To obtain the aerogel structure, NaOH–urea solution was used as the cellulose crosslinking solution [12,18] with a modification. One gram of pulp was then dispersed in an aqueous solution containing 1 g of NaOH, 4 g of urea, and 10 mL of demineralized water by ultrasonicating for 30 min. The suspension was placed in a refrigerator for 24 h to allow gelation process. After the gel had set, it was thawed at room temperature and immersed in ethanol (98%) for coagulation. After coagulation, solvent exchange was carried out by immersing the gel in demineralized water until free from ethanol. The sample was then frozen at −20°C for 12 h and followed by freeze drying to obtain the desired cellulose aerogel. The surface modification process was initiated by immersing cellulose aerogel in 50% of TMCS or HMDS, which previously dissolved in n–Hexane. The immersion was conducted in a hydrothermal reactor then heated for 8 h. To investigate the effect of temperature, the hydrothermal reactor was heated at various temperatures ranging from 50–70°C for TMCS and 110–130°C for HMDS. The heating temperature was varied around the boiling point of the modifying agents. The concentration of the modifying agents was varied from 40–60%. After modification, the aerogel was dried in an oven at 80°C for 1 h.

2.3. Characterizations
The changes of chemical structures in the cellulose aerogels were investigated using Fourier transform infrared spectroscopy (FTIR; Shimadzu IRTracer–100) over the wavenumber range of 400–4000 cm⁻¹. The morphology of the aerogels was studied by scanning electron microscopy (SEM; FEI Inspect S–50). The specific surface area and pore characteristics were quantitatively determined by N₂ adsorption–desorption instrument (NOVA–e Series Models 25, Quantachrome Instruments). The samples were degassed at 80°C for 5 h prior to the measurements. The specific surface area and pore size distribution were determined by Brunauer–Emmet–Teller (BET) and Barret–Joyner–Halenda (BJH) methods, respectively. The hydrophobicity of the aerogels was investigated by contact angle measurement and immersion in a mixture of oil and water. Contact angle was measured by dropping a
droplet of water on to the surface of cellulose aerogel. The resulted angle between the curvature of water droplet and the aerogel surface was measured using an arc. The immersion test was conducted by preparing lubricant oil and water mixture in a beaker glass then the aerogel was immersed in it. The oil used for the test was lubricant oil with kinematic viscosity of SA 40 API Service SE/CC.

3. Results and Discussions
Figure 1(a) shows the physical appearance of the original cellulose aerogels (CA). It has a light brown colour due to the remaining lignin contained in the pulp after delignification. It also has an ultralight weight which makes it possible to be put on the leaves. The cellulose aerogel which is modified by TMCS has a greyish–black colour as depicted in Figure 1(b). The greyish–black colour might be caused by the presence of hydrochloric acid (HCl) as the side product of the reaction between cellulose and TMCS. HCl could hydrolyse cellulose into simpler compound such as glucose [19], and the presence of lignin which reacted with HCl could result a greyish–black colour. While the aerogel which is modified by HMDS has a similar colour with the original cellulose aerogel, as shown in Figure 1(c).

The change of chemical structures of cellulose aerogel due to surface modification was studied using FTIR spectra, as shown in Figure 2. FTIR spectra of all three aerogels show the presence of intramolecular hydrogen bonding (O–H stretching) at wavenumber of 3331 cm\(^{-1}\) for CA, 3310 cm\(^{-1}\) for CA–TMCS, and 3339 cm\(^{-1}\) for CA–HMDS. The spectra also present the C–H stretching of cellulose at 2891 cm\(^{-1}\) for CA and CA–TMCS, and 2955 cm\(^{-1}\) for CA–HMDS. Both bands correspond to the cellulose compounds [20,21]. The bands at wavenumber of 1660 cm\(^{-1}\) and 1633 cm\(^{-1}\) are attributed to C–N functional group and C=O stretching, respectively. There is also a C=O stretching at a wavenumber of 1428 cm\(^{-1}\), which slightly shifts to the right into wavenumber of 1420 cm\(^{-1}\) after TMCS and HMDS modifications [Figure 2(b–c)]. Those three bands were assumed to be functional group of urea which crosslinked cellulose fibers physically. After hydrophobic modification, Figure
2(b) shows the presence of $\text{CH}_3$ deformation vibration and a vibration of Si–O at wavenumber of 1428 cm$^{-1}$ and 1029 cm$^{-1}$ respectively, which explains that TMCS had modified the cellulose fibers by its alkyl–silane functional group [22]. On the other hand, cellulose aerogel modified by HMDS [Figure 2(c)] shows a different band at wavenumber of 3432 cm$^{-1}$ which corresponds to N–H functional groups, which is the constituent of the HMDS compound. This spectrum also shows the bands of 1428 cm$^{-1}$ and 835 cm$^{-1}$ which attribute to the alkyl band of $\text{CH}_3$ deformation vibration and Si–C functional group, respectively. Both bands indicate the modification of HMDS to the cellulose fibers by its alkyl–silane functional group.

The morphology of the obtained cellulose aerogels was observed by the SEM images as presented in Figure 3. Figure 3(a–c) show the cross–sectional area of the original CA, CA modified by TMCS, and HMDS. They seem to have a similar morphology, which is a three–dimensional porous network consisted of cellulose fibers. The obtained pore is a kind of macropore as the result of interconnected large size fibers. All three aerogels have an average fiber size of 70 µm. On the other hand, the cellulose fiber itself, has a different surface. The fiber of CA [Figure 3(d)] has a cylindrical–like shape with smaller cylindrical line on the surface. While the CA–TMCS fiber [Figure 3(e)] has a cylindrical–like shape with flakes spreading uniformly on the surface of the fiber. Along with that, the fiber of CA–HMDS [Figure 3(f)] also has a cylindrical–like shape with flakes unevenly spreading on the surface. The presence of flakes spreading on the fiber changes the roughness of the surface. The surface of cellulose fibers are rougher after TMCS or HMDS modification compared to the original CA, as depicted in Figure 3(d–f). The increase of roughness would increase the hydrophobicity of the fiber [23]. Unlike the fiber of CA–TMCS, the fiber of CA–HMDS not only has many flakes on the surface, but also has many pores spreading over the fiber. Those pores might increase the surface area and pore volume of the aerogel.

![Figure 3. SEM images of the cross sectional area of (a) CA; (b) CA–TMCS; (c) CA–HMDS; the fiber of (d) CA; (e) CA–TMCS; and (f) CA–HMDS.](image)

Figure 4(a–c) present the adsorption–desorption isotherm profile of CA, CA modified by TMCS, and HMDS. It shows that all three aerogels have a similar type of adsorption–desorption profile, which is type IV. Type IV is indicated by the presence of hysteresis loop which means the presence of
mesoporous materials. It was clearly depicted in the SEM images [Figure 3(a–c)], that all the aerogels have a macroporous structure due to the interconnected network of cellulose fibers, but the adsorption–desorption profile shows that the aerogels also have a mesoporous structure with average pore size of 3.4 nm. It seems that the mesopores were located inside the fiber, which means that the fiber consisted of some long cylindrical pores. Therefore, there are some cylindrical line on the surface of the cellulose fibers as depicted in Figure 3(d–f). The CA has a specific surface area of 69.92 m$^2$/g which increases after modified by TMCS and HMDS up to 190.74 m$^2$/g and 2324.25 m$^2$/g, respectively. The increasing of specific surface area was proportional to the increasing of total pore volume contained in the aerogels. CA has a total pore volume of 0.055 cm$^3$/g which increased up to 0.078 cm$^3$/g for CA–TMCS and 0.939 cm$^3$/g for CA–HMDS. The high pore volume of CA–HMDS corroborated its SEM image [Figure 3(f)] which presented some pores on the fiber surface. Hence, it contributed to the high specific surface area of CA–HMDS compared to the others.

![Figure 4](image)

**Figure 4.** Adsorption–desorption isotherm profile of (a) CA; (b) CA–TMCS; and (c) CA–HMDS. Inset: the pore size distribution of each aerogel.

The hydrophobicity of the cellulose aerogels was represented by the contact angle of water droplet on the aerogel surface. As a comparison, the water contact angle of the original cellulose (CA) aerogel was carried out. CA was immediately absorbed the water droplet when it was firstly dropped in the test, hence no water contact angle data which could be measured. In a contrast, a high of water contact angle was clearly measured as shown in the inset of Figure 5(a–b). Effect of the heating temperature during immersion with TMCS and HMDS to the water contact angle was shown in Figure 5(a–b). For TMCS, the heating temperature was varied around its boiling points which were 50, 60 and 70°C with TMCS concentration was fixed at 50%. Figure 5(a) shows that all the heating temperature gives a water contact angle more than 100° which is hydrophobic characteristic (>90°). It indicated that TMCS has successfully modified the aerogel surface becomes a hydrophobic at all varied temperature. The temperature providing the highest contact angle was obtained at 60°C which is the nearest point to the boiling point of TMCS (57°C). The contact angle obtained using this temperature takes the value
of approximately 148°. It might be caused by the highest composition of TMCS in the vapor phase required for modification to occur. While for the HMDS [Figure 5(b)], the highest water contact angle which was approximately 133°, was obtained at a heating temperature of 120°C which was also near to boiling point of HMDS (125°C). Water contact angle decreases with an increase in heating temperature that may be caused by the low composition of the modifying agents in the vapor phase. Although lower than those of TMCS, Figure 5(b) also shows that HMDS also successfully modify the cellulose aerogel become a hydrophobic at all the varied temperature.

![Figure 5. Effect of temperature to the contact angle of (a) CA‒TMCS and (b) CA‒HMDS. Inset: measurements of water contact angle.](image)

The effects of TMCS and HMDS concentration on the water contact angle on the aerogel surface are presented in Figure 6(a). Effect of concentration was studied at the temperature providing the highest contact angle, which was 60°C for TMCS and 120°C for HMDS. Figure 6(a) shows that either TMCS or HMDS gives a good hydrophobicity with water contact angle above 110° for all the varied concentration. For TMCS, the highest water contact angle, 148°, is obtained at a concentration of 50%. The water contact angle of CA‒TMCS increases at low TMCS concentration, reaches a maximum value, and then decreases again. It suggests that the concentration of TMCS in the vapor phase plays an important role for hydrophobic modification. Thus, the temperature should be adjusted to give highest concentration of modifying agents in the vapor phase. Moreover, the important one was the fact that TMCS could modify cellulose aerogels into hydrophobic materials. For HMDS, the highest water contact angle is obtained at HMDS concentration of 40%, which is 140°. The water contact angle decreases with the increase in HMDS concentration. Similar to the TMCS, the HMDS concentration in the vapor phase plays an important role during cellulose hydrophobic modification. In spite of that, this work presented that both TMCS and HMDS had successfully modify cellulose aerogels into hydrophobic material.

To get better insight into the effect of hydrophobicity on oil absorption, the hydrophobic cellulose aerogel was also used to remove oil from the mixture of oil–water. Figure 6(b) shows the image of modified cellulose aerogel which is immersed in the oil–water mixture. Oil is in the upside part while the water is below it due to the lower density of oil. The hydrophobic cellulose aerogel could absorb the lubricant oil only, without the water. Figure 6(b) also represents that the hydrophobic coating was not only on the surface of the aerogel but also into the interior of the aerogel. The aerogel keeps staying in the oil region (upper side) due to its hydrophobicity, even a pressure was given to sink it into the bottom side. If the cellulose aerogel still had a hydrophilic characteristic, it would go down to the water side and sink at the bottom side. Therefore, Figure 6(b) gave a better illustration that the aerogel is a hydrophobic material and can perfectly separate oil from oil–water mixture. The obtained aerogel also had a good recyclability, in which it could absorb oil in a short time, less than 1 min for
absorbing 10 g oil in 1 g aerogel, then squeezed to remove the absorbed oil and reused for the next absorption. Hence, the hydrophobic aerogel seemed to have a good recyclability and efficiency.

Figure 6. (a) Effect of TMCS and HMDS concentration to the contact angle of CA–TMCS and CA–HMDS; and (b) The immersion of a hydrophobic cellulose aerogel in a mixture of oil–water.

4. Conclusion
In summary, coir fiber waste material was successfully functionalized as a hydrophobic cellulose aerogel. The aerogel was prepared using a simple sol–gel method followed by freeze–drying. The hydrophobic surface modification was carried out using either trimethylchlorosilane (TMCS) or hexamethyldisilazane (HMDS) which was dissolved in n–Hexane and heated in a hydrothermal reactor. The effect of the surface modification agent concentrations and hydrothermal temperature to the performance of the aerogels were systematically investigated. The best condition in term of its hydrophobicity was obtained at 50% of TMCS with a temperature of 60°C and 40% of HMDS at 120°C. The obtained aerogel has a good hydrophobic characteristic indicated by a high of water contact angle of 100–150°C. The aerogel also could selectively absorb oil from the mixture of oil–water with good recyclability and efficiency.

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