Hydrophobic, superabsorbing aerogels from choline chloride-based deep eutectic solvent pretreated and silylated cellulose nanofibrils for selective oil removal

Ossi Laitinen[a],*, Terhi Suopajärvi[b], Monika Österberg[c] and Henrikki Liimatainen[d]

a,* Corresponding author:

Ossi Laitinen, Postdoctoral Research Fellow, University of Oulu, Fibre and Particle Engineering, P.O. Box 4300, FI-90014 Oulu, Finland, Phone: +358503504960, ossi.laitinen@oulu.fi

b Terhi Suopajärvi, Postdoctoral Research Fellow, University of Oulu, Fibre and Particle Engineering, P.O. Box 4300, FI-90014 Oulu, Finland, terhi.suopajarvi@oulu.fi

c Monika Österberg, Associate Professor, Aalto University, Department of Bioproducts and Biosystems, School of Chemical Engineering, P.O. Box 16300, FI-00076 Aalto, Espoo, Finland, monika.osterberg@aalto.fi

d Henrikki Liimatainen, Associate Professor, University of Oulu, Fibre and Particle Engineering, P.O. Box 4300, FI-90014 Oulu, Finland, henrikki.liimatainen@oulu.fi

Abstract

Superabsorbents are highly appealing materials for use in cleaning up oil and chemical spills. However, the development of a low-cost, highly efficient superabsorbent remains a major challenge. This paper demonstrates a straightforward method of producing a cellulose nanofibril aerogel that is low-cost, ultralight, highly porous, hydrophobic, and reusable superabsorbing cellulose nanofibril aerogel from recycled waste fibers using a simple, environmentally friendly nanofibrillation treatment involving deep eutectic solvent and freeze drying. Nanofibrillation and hydrophobic modification (silylation) of waste cellulose fibers resulted in nanofibril sponges with ultralow density (0.0029 g/cm^3) and high porosity (up to 99.81%) after freeze drying. These sponges exhibited excellent absorption performances for various oils and organic solvents and were reusable. In particular, the nanofibril aerogels showed selectivity in absorbing marine diesel oil from an oil-water mixture and possessed ultra-high absorption capacities of up to 142.9 g/g, much higher than those of the commercial absorbent materials (i.e., polypropylene based material) (8.1–24.6 g/g) that were used as references. The absorbed oil could easily be recovered by means of simple mechanical squeezing. In addition, the nanofibril sponges exhibited excellent reusability, maintaining a high capacity to absorb diesel oil for at least 30 cycles at 71.4–81.0% of capacity compared to a fresh absorbent. The above-mentioned advantages make cellulose nanofibril superabsorbents created from recycled waste cellulose fibers promising material for cleaning oil and chemical spills.

1. Introduction

Due to their significant effects on environmental and ecological systems, oil and chemical pollutants are among the most serious global concerns. For example, it has been estimated that oil tankers released 224,000 tons of oil into the global marine environment from 2000–2011.[1] The potential magnitude of the environmental threat of oil and chemical pollutants can be exemplified by the fact that 1 dm^3 of benzene can effectively render several thousand cubic meters of water unfit for human consumption.[2] Due to its coating properties, unsightliness, and offensive odor, oil-contaminated water has a disastrous effect on aquatic and terrestrial life and threatens human health and the economy, particularly tourism.[3]

Generally, oil and chemical cleanup methods or strategies are classified into several categories: *in-situ* burning, mechanical methods, chemical treatments, bioremediation, and absorption.[4] Of these alternatives, absorption using sorbents is generally considered the optimal technology because of its relatively low cost and high efficiency and because it produces less secondary pollution than many other approaches.[1] Conventional oil and chemical sorbent materials can be grouped into three major classes: inorganic mineral sorbents, synthetic polymer sorbents, and natural organic sorbents.[5] To effectively collect spills from water, the sorbent material should have high sorption capacity and porosity, oil/water selectivity, and a fast sorption rate. In addition, it is clearly beneficial if the sorbent material is low cost, environmentally friendly, and recyclable. Typically, sorbent materials are either highly floatable (i.e., low density) or sinkable (i.e., mineral sorbents).[6]

Inorganic mineral sorbents, also known as sinking sorbents, are dense, fine-grained, natural or processed mineral or inorganic materials that are used to sink floating oil and chemicals. Due to their inherent oleophilicity and hydrophobicity, synthetic-polymer oil sorbents, including

polypropylene fibers,[7] polyurethane foams,[8] and polypropylene nonwoven webs,[9] are the commercial sorbents most commonly used to clean up oil spills. Despite moderate oil-sorption capacities, one major drawback of these sorbents is that they degrade or disintegrate very slowly, so their environmental and ecological effect is greater than that of mineral or natural products.[10,11] In contrast, natural organic sorbents, including kapok, sugarcane bagasse, cotton, rice straw, and wood chips, are ecofriendly alternatives for removing oil and chemicals from wastewater. They have moderate oil-sorption capacity (i.e., 3−50 times their own weight), comparable or sometimes lower density than inorganic and synthetic sorbents, and excellent biodegradability.[6,12] Other advantages include their recyclability, their ability to recover oil and chemicals relatively easily, and their relatively easy disposal compared to other types of conventional sorbents. Despite these advantages, the majority of traditional natural sorbents also have many drawbacks, including poor buoyancy/floatability and poor selectivity of oil or chemical sorption, which is due to the relatively high water uptake of these inherently hydrophilic materials.

Recently, porous and ultra-low density cellulose aerogels[13] (also designated as cellulosic sponges or foams) based on cellulose nanofibrils (CNFs) have aroused considerable research interest due to their renewability, good mechanical properties, low density, high porosity, natural biodegradability, and environmental friendliness, which increase the potential of CNF aerogels for use as oil and chemical sorbents.[13–19] However, due to the presence of abundant hydroxyl groups, native cellulose aerogels display amphiphilicity (i.e., poor selectivity in absorbing oil and hydrophobic compounds),[20–22] and feasible approaches are needed to enhance the hydrophobicity of aerogels. Typically, hydrophobicity is evaluated in terms of wettability by measuring the water contact angle (WCA) on material surfaces. Depending on their WCA value, materials are classified as hydrophilic, hydrophobic, or superhydrophobic. Materials having a WCA of less than 90° are

described as hydrophilic; materials with WCAs of between 90° and 150° are hydrophobic; and those with WCAs of more than 150° are superhydrophobic.[23]

In this study, we report an easy, straightforward method of producing an ultra-low density (0.0029 g/cm^3), highly porous (up to 99.81%), cost-effective, reusable, hydrophobic, superabsorbent CNF aerogel from recycled waste fibers using a simple, environmentally friendly nanofibrillation treatment involving choline chloride – urea – based deep eutectic solvent (DES), freeze drying, and a combination of two silylation agents. To the best of our knowledge, this is the first time recycled waste celluloses and this combination of two types of silylation agents have been used to fabricate superabsorbing, cost-effective, reusable, nanostructured aerogels. Prepared CNF sponges exhibited excellent oil/water selectivity and ultra-high capacity to absorb oil (marine diesel oil, kerosene, gasoline, motor oil, castor oil, and linseed oil) and organic solvents (dimethyl sulfoxide, chloroform, n-hexane, toluene, acetone, and ethanol). In addition, the absorbed oil was readily recovered by means of simple mechanical squeezing, and the superabsorbent aerogel could be reused for at least 30 cycles.

2. Material and Methods

2.1 Materials

Recycled box board and recycled milk-container board were collected directly from board-container collections, and fluting board was supplied by Heinola Fluting (Finland). A dry sheet of industrially bleached birch kraft pulp (*Betula verrucosa*) was used as a reference cellulose raw material. All pulps were first pulped without chemicals using a Kenwood KM020 pulper (UK), which has an operating principle similar to that of the Hobart pulper, at a consistency of 1.5% at approximately 45 °C using a rotor speed of 2 for 10 min and then washed and screened using a Somerville screen (Lorentzen & Wettre; Sweden).

Methyltrimethoxysilane (98%, MTMS) was obtained from Evonik Industries (Germany), and Hexadecyltrimethoxysilane (> 85%, HDTMS) was purchased from Sigma-Aldrich (Germany). Urea (97%) and choline chloride (> 98%) for DES were purchased from Borealis (Austria) and Algry Qu Mica (Spain), respectively. Lightweight marine diesel oil and kerosene were obtained from Neste (Finland), and gasoline (E95) and motor oil (5w40) were purchased from a local gas station. Dimethyl sulfoxide (> 99%, DMSO) was obtained from TCI (Germany). Castor oil, linseed oil, chloroform (> 99%), n-hexane (> 98%), toluene (> 99.9%), acetone (> 99.8%), and ethanol (> 99.9%) were obtained from VWR (Finland). All chemicals were used as received, without further purification. Two different types of commercial oil-absorbing booms were obtained from local rescue services.

2.2 DES pre-treatment and nanofibrillation of cellulose materials

To pre-treat the cellulose pulps (box board, milk-container board, fluting, and birch kraft used as a reference), a DES solution was produced by heating 1620 g of choline chloride and 1223 g of urea in a large beaker (5 dm^3) at 105 °C until the mixture melted, after which it was placed into a water bath at 100 °C under constant stirring for ~5 min to obtain a clear, colorless liquid. Then, 25 g (abs) of cellulose material at a consistency of ~30% was added to the suspension and mixed for 2 h. After that the beaker was removed from the water bath and 1000 cm^3 of deionized water was added to the mixture.[24] Finally, the treated cellulose was washed with water using a Somerville screen (Lorentzen & Wettre; Sweden) until clear wash water was obtained.

Next, 4 batches of each pulp were treated with DES prior to nanofibrillation with a Masuko super masscolloider grinder MKCA6-2J (Japan) to obtain cellulose nanofibrils. For this purpose, the pre-treated, fibrous cellulose materials were diluted with water to a 1.5% consistency. The grinding discs of the Masuko grinder were first carefully brought into close contact, which was

verified by the low friction sound. Then, the treated cellulose was passed twice through the grinder using the zero grinding discs gap, after which the discs were adjusted to negative gap values. The pulps were passed through the grinder a total of 10 times, using negative gap values of -20 μm, -40 μm, -50 μm, -70 μm, and -80 μm. The TEM images of ground pulps indicated that all cellulosic samples were efficiently nanofibrillated and had widths from 2 nm to 80 nm. A detailed characterization of the CNFs obtained has been reported by Suopajärvi et al.[25]

2.3 Fabrication of hydrophobic CNF sponges

The CNF suspensions were diluted with deionized water, homogenized using an Ultra-Turrax system set to 8000 rpm for 30 s, and their pH adjusted to 4 with 0.5 M HCl solution. Various dilutions were used, depending on the sample (Table 2).

The both silane solutions (20 wt-%) for hydrophobization of celluloses were prepared separately by diluting MTMS and HDTMS in ethanol. After dilution, hydrolyzed silane solutions were mixed with a magnetic stirrer for 10 min. Then, 25 wt-% of freshly prepared silane solutions (MTMS and HDTMS, ratio of 50/50%) against cellulose fibril amounts were added by micropipette to the CNF suspensions and stirred with a magnetic stirrer at room temperature for 2 h.

Silylated CNF suspensions (75 cm^3) were introduced into metallic, round molds (77 mm in diameter and 20 mm in height), frozen in liquid nitrogen, and transferred to the vacuum chamber of the freeze-drying device (Scanvac Coolsafe 55-15 Pro; Denmark) for 72 h (cooling chamber temperature was adjusted to -54°C) to obtain hydrophobized CNF sponges (Table 2). The silylation levels of the prepared sponges were determined by X-ray photoelectron spectroscopy (XPS) and are presented in Table 3.

2.4 Density and porosity of CNF sponges and reference polypropylene absorbents

The apparent volumetric mass density of CNF sponges and reference polypropylene materials was calculated using the following formula:

$$\rho = \frac{m}{V} \qquad (1)$$

where m and V are the mass (g) and volume (cm^3) of the materials, respectively.

The porosity (P, %) of the CNF sponges and polypropylene materials was calculated according to eq. (2):

$$P = \frac{V - m/\rho_c}{V} * 100\% \qquad (2)$$

where V (cm^3) is the volume of the materials, m (g) is the mass, and ρ_c is the density of bulk cellulose (1.528 g/cm^3) or polypropylene (0.9075 g/cm^3).

2.5 X-ray photoelectron spectroscopy

The silylation level of the prepared sponges was determined by XPS using Thermo Fisher Scientific ESCALAB 250Xi (UK) (Table 3). A monochromatic Al$K\alpha$ X-ray source operated at 300 W was used with a combination of electron flood gun and ion bombardment for charge compensation. The take-off angle was 45° in relation to the sample surface. Low-resolution survey scans were taken using a 1-eV step and a 150-eV analyzer pass energy, and the high-resolution spectra were taken with a 0.1-eV step and a 20-eV analyzer pass energy. The binding energy (BE) scale was referenced to the C 1s line of aliphatic carbon, set at 284.6 eV. All measurements were made in an ultra-high vacuum pressure chamber (5 x 10^{-9} mbar).

Prior to measurement, a dry sample was pressed on the indium film. Three measurements were made from each of the silane-treated CNF sponges. The first measurement was on top of the

aerogel, the second at the bottom, and the third in the center of the aerogel after it had been sliced into two halves. The untreated reference aerogel was measured only once, in the center.

2.6 Contact angle measurement

The surface wettability of the CNF sponges (Table 3) was evaluated using contact angle measurement. The static contact angles of Milli-Q water droplets on the aerogel surfaces were measured at 22 °C and 10% RH using a CAM 2000 (KSV Instruments Ltd; Helsinki, Finland). Measurements were performed by placing a 6.5-μL drop of Milli-Q water on the aerogel surface using a syringe and capturing images at the rate of 1 frame/sec to be sent directly from the CCD camera to the computer for analysis. Determination of the contact angle was based on analysis of the drop's shape using the full Young-Laplace equation and assuming a spherical drop. The WCAs at 60 s are reported. 5 parallel measurements were made at various positions on each aerogel sample, and the average values and standard deviation were calculated. Typical uncertainties in the experiments were less than 5°.

2.7 Field emissions electron microscopy (FESEM) characterization

To visualize the structure of the various CNF sponges, FESEM analysis was performed using a Zeiss Ultra Plus instrument (Zeiss, Germany). The samples were imaged using low voltage (5 kV) and a working distance of ~5 mm. The CNF sponges were analyzed by simply placing each sample on a sample holder using a carbon pad and coating it with a thin layer of platinum.

2.8 CNF sponges' diesel oil sorption selectivity from oil-water mixtures

A fresh sorbent sample (0.05–0.1 g) was placed on the surface of a solution having a 5-mm layer (i.e., 13.00 g) of marine diesel oil floating on an 80-mm layer of water at room temperature. The

sample was left for 15 min, and then the sorbent was removed and left to drip for 30 s before being weighed. The amount of oil left in the oil-water mixture was determined using gravimetric analysis, as accepted by the United States Environmental Protection Agency (US EPA). In this case, diesel oil extracted using a solvent (i.e., n-hexane) from an oil-in-water sample is the EPA-accepted method (EPA 1664) for oil-in-water analysis. After sorption testing, the residual oil-water mixture was acidified to a pH of 2, and the sample was extracted 3 times using n-hexane. The combined collected extracts were distilled at 85 °C and weighed to determine absorption selectivity in terms of oil-absorption capacity (g/g) and water uptake (g/g). At least 3 measurements were conducted for each sample, and the average value is presented.

2.9 Absorption capacities for various oils and organic solvents

In the absorption test, pre-weighed hydrophobic CNF sponges were placed in various oils (marine diesel oil, kerosene, gasoline, motor oil, castor oil, and linseed oil) and organic solvents (dimethyl sulfoxide, chloroform, n-hexane, toluene, acetone, and ethanol) for 2 min to reach absorption equilibrium and then removed and weighed. All these tests were made at room temperature. The sorption capacity (g/g), defined as the mass of absorbed oil or solvent (g) per unit mass of dry absorbent (g), was used to characterize oil-absorption capacity. At least 3 measurements were conducted for each sample, and the average value is presented.

2.10 Reusability of CNF sponges

Mechanical compression was used to extract the remaining liquid from the sorbent so that reusability could be tested at room temperature. The absorbed marine diesel oil was recovered by simple mechanical squeezing. The squeezed CNF sponges absorbed oil again without any post-treatment, and the oil stored in the sponges was measured again. Oil storage capacity, defined as

the mass of oil (g) per unit mass of the dry sponge (g) and values presented as capacity left compared to fresh absorbents were used to characterize the reusability of the CNF sponges.

3. Results and discussion

3.1 Hydrophobicized CNF aerogels

This study used deep eutectic solvent (DESs) based on choline chloride-urea as a pretreatment method to nanofibrillate waste cellulose materials. Mechanically nanofibrillating (with a Masuko grinder) cellulose pretreated with choline chloride-urea resulted in individual nanofibrils and opaque CNF water suspensions.[24] The method uses green bulk chemicals and can be considered a sustainable route to obtaining CNF without toxic or expensive chemicals or other intensive mechanical and/or chemical modification of the cellulose.[26] The strong shear forces in the Masuko grinder break the hydrogen bonds in the loosened cell walls of the cellulose fibers treated with DES, yielding an opaque, viscous gel.[27]

The waste cellulose materials (box board, milk-container board, and fluting) were compared to virgin, bleached birch cellulose and found to be of sufficient quality and to present no problems during chemical modification or fibrillation. In addition, the price of waste cellulose materials is only 80–100 €/ton, while the price of bleached birch cellulose is about 600–800 €/ton, which makes the costs of recycled board 10-17% of the costs of virgin pulp. In DES-pretreatment used chemicals (urea and choline chloride) are so called bulk chemicals, which are not harmful for the environment and also these chemicals can be recycled back to the process after water evaporation. [28,29] Technical grade of urea costs ~200 €/t and choline chloride 300-400 €/t. The simple recycling of the DES-chemicals reduces significant the price of the chemicals and they affect only slightly to the final price of aerogels (recycling rate can be several times, which based on our unpublished data). However they decreased remarkable the pre-treatment costs of the fibrillation. Fibrillation

to the nano-scale fibrils was done in this research with disc grinder, Masuko super masscolloider grinder, with energy consumption of ~ 6000 kWh/t, without any optimization of the device and using laboratory scale equipment. Silylation process is relative cheap, because silylation agents are effective and not very expensive ~1500 €/t. Claussen et al. (2007) have reported that water is removed by freeze drying about 4.6-1.5 kg per kWh [30]. In the Table 1 are calculated estimated prices, when producing 1kg CNF aerogels. Based on simplified calculations presented here, price of 1kg CNF aerogels are between 3.8-4.4 € depending on raw material source.

Table 1. Simplified price calculation of preparation CNF aerogels.

	Virgin kraft	Recycled board	Price of electricity (€/kWh)	Aerogel from virgin pulp (kg)	Aerogel from recycled board (kg)
Raw material cost (€/t)	700	100		0.70	0.10
Mechanical fibrillation (kWh/t)	6000	6000	0.1	0.60	0.60
MTMS (€/t) *	1500	1500		0.19	0.19
HDTMS (€/t) *	1500	1500		0.19	0.19
Freeze drying (kg per kWh) **	3	3	0.1	2.77	2.77
Price of CNF aerogel (€/kg)				**4.4**	**3.8**

*Price from www.alibaba.com

**Price from Claussen, I. et al. (2007). Atmospheric Freeze Drying A Review.

To achieve the porous structure of the CNF sponges (Table 2) and avoid the need for post-treatment, both silylation agents, MTMS and HDTMS, were added before the freeze-drying process to crosslink CNF aerogels while simultaneously improving their hydrophobicity. It is well-known that MTMS is a crosslinking agent for cellulose.[15,31] HDTMS is a silane containing a long carbon chain that contributes to increased hydrophobicity in aerogels. The reaction medium was adjusted to an acidic pH of 4 to favor condensation of the hydrolyzed MTMS and HDTMS with the cellulose surface. At pH 4, the hydrolysis of alkoxysilanes has been reported as rapid and the

self-condensation limited, which maximizes the concentration of the silanol species available to interact with the cellulosic substrate.[32]

Table 2 shows the densities and porosities of the manufactured CNF sponges as a function of CNF suspension consistency. Decreasing nanofibril consistency from 1.0% to 0.2% caused the density of DES_Cel CNF sponges to decrease from 0.0166 g/cm^3 to 0.0029 g/cm^3 and the porosity to increase from 98.91% to 99.81%. Compared to commercial oil-absorption materials (i.e., polypropylene from commercial oil-absorbing booms) the density of the CNF sponges was up to 28 times less and the porosity more than 8% more (Table 2).

Table 2. Consistency, density, and porosity of CNF aerogels and commercial reference materials.

Material	Abbreviation	Consistency [%]	Density [g/cm³]	Porosity [%]
DES Birch Cellulose	DES_Cel(1.0)	1.0	0.0166	98.91
DES Birch Cellulose	DES_Cel(0.5)	0.5	0.0070	99.54
DES Birch Cellulose	DES_Cel(0.3)	0.3	0.0042	99.72
DES Birch Cellulose	DES_Cel(0.2)	0.2	0.0029	99.81
DES Fluting Board	DES_Flu(0.5)	0.5	0.0079	99.48
DES Fluting Board	DES_Flu(0.3)	0.3	0.0049	99.68
DES Fluting Board	DES_Flu(0.2)	0.2	0.0032	99.79
DES Box Board	DES_Boa(0.5)	0.5	0.0075	99.51
DES Box Board	DES_Boa(0.3)	0.3	0.0045	99.71
DES Box Board	DES_Boa(0.2)	0.2	0.0031	99.79
DES Milk-Container Board	DES_MCB(0.5)	0.5	0.0079	99.48
DES Milk-Container Board	DES_MCB(0.3)	0.3	0.0048	99.69
DES Milk-Container Board	DES_MCB(0.2)	0.2	0.0033	99.78
Ref Boom Polypropylene Material (strip)	Ref (strip)	-	0.0807	91.11
Ref Boom Polypropylene Material (plug)	Ref (plug)	-	0.0521	94.26

Fig. 1 shows the morphologies of the CNF sponges with and without hydrophobic modification. Without silylation, the CNF sponges possessed a continuous three-dimensional (3D) porous structure (Figs. 1a–d) that was formed by randomly entangled nanofibrils. Hydrophobic modification with the aid of a crosslinking agent resulted in formation of a continuous, sheet-like

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coating. However, in all cases, the porous structure was well maintained (Figs. 1e–h). In addition, the waste board celluloses formed a well-structured texture compared to the virgin cellulose aerogel.
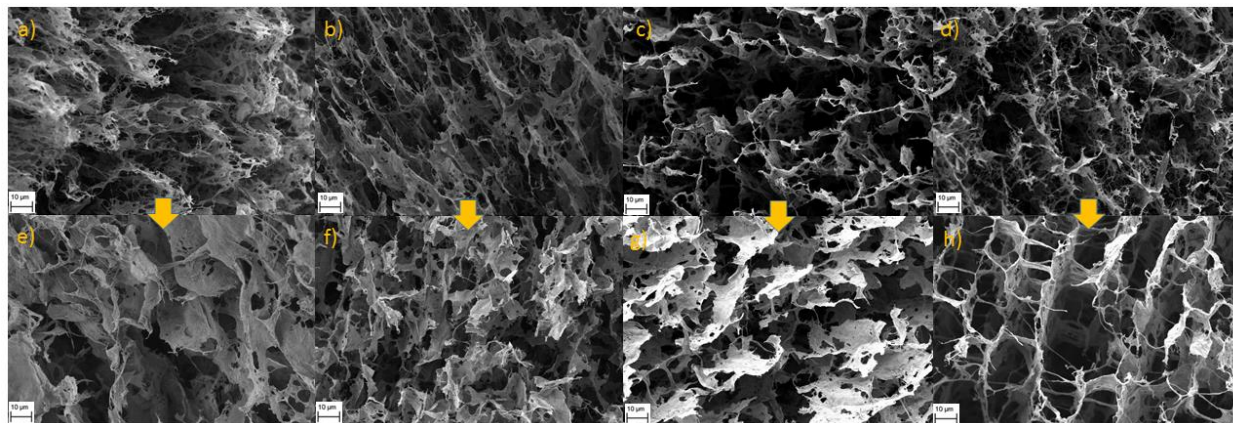

Fig. 1. FESEM images of CNF sponges: (a) unmodified DES_Cel (0.5), (b) unmodified DES_Flu (0.5), (c) unmodified DES_Boa (0.5), (d) unmodified DES_MCB (0.5), (e) modified DES_Cel (0.5), (f) modified DES_Flu (0.5), (g) modified DES_Boa (0.5), and (h) modified DES_MCB (0.5) (scale bar = 10 µm).

Effective oil/water selectivity is essential for oil absorbents.[16] Because of the large number of hydrophilic hydroxyl groups in unsilylated cellulose fibers, freeze-dried CNF sponges cannot be directly used as oil-absorption materials. Hydrophilic aerogels disintegrate rapidly in a water environment because water penetrates the aerogel, destroying the hydrogen bonds between the fibers and causing the aerogel structure to collapse.

The silylation of sponges was confirmed and quantified using X-ray photoelectron spectroscopy (XPS). Without silylation, the surface concentration of silicon in various DES-treated CNF sponges varied from 0.46–0.76 at-%, while, after silylation, a strong peak of silicon was noted, and the surface concentration of silicon in these samples varied from 4.47–6.27 at-% (Table 3). In addition, the present study analyzed the spatial distribution of silicon on the top face, the inner phase, and the bottom phase of the aerogel. The silicon contents were very similar (variation within

0.4%), except for that of DES_MCB (variation of 0.76%), which confirmed successful, homogenous silane treatment of the aerogels (Table 3).

Table 3. Silicon content and WCAs of various CNF aerogels. Consistency of measured aerogels were 0.5%.

Aerogel	Surface concentration of Si on unmodified samples [at-%]*	Surface concentration of Si in silylated samples [at-%]**	WCA [deg]	WCA [std]
DES_Cel	0.47	4.47±0.27	142.9	6.65
DES_Flu	0.74	5.00±0.34	159.0	4.58
DES_Boa	0.74	6.27±0.36	107.2	4.45
DES_MCB	0.46	4.80±0.76	129.4	4.90

* Silicon concentration (atomic weight) of aerogels prepared without silanes according to XPS analysis

** Silicon concentration (atomic weight) of silylated aerogels according to XPS analysis

To indicate the hydrophobicity of silylated CNF sponges, their WCAs were determined. All aerogels were evidently hydrophobic (i.e., WCA > 90°), and DES_Flu could even be characterized as superhydrophobic (i.e., WCA > 150°). Based on visual observations, the water droplets easily rolled off the silylated CNF aerogels when the sliding angle was increased slightly, confirming the hydrophobic nature of all silylated CNF sponges.

3.2 Diesel oil sorption selectivity of CNF sponges in oil-water mixtures

To investigate the selectivity to oil sorption of various CNF sponges, a mixture of marine diesel oil and water was prepared. Fig. 2 shows the oil absorption capacities of various DES-treated hydrophobic CNF sponges. All CNF sponges investigated had similar trends against porosity (i.e., fiber consistency). At the consistency of 0.5%, all materials had nearly the same oil absorption capacity (from 88–97 g/g), while at higher porosities (i.e., < 0.5%), DES_Cel had the highest capacity. Evidently, with increased DES_Cel porosity (i.e., fiber consistency of from 1.0–0.2%),

the absorption capacities for marine diesel oil increased significantly, from 52–143 g/g. Therefore, the CNF sponges with lower density and higher porosity possessed higher oil absorption capacities. Commercial reference materials Ref (strip) and Ref (plug) diesel oil absorption values were 8 g/g and 25 g/g, respectively. Comparing the results obtained for CNF sponges to those for commercial reference materials, CNF sponges had notably higher capacities to absorb diesel from water despite fiber consistency of aerogels.
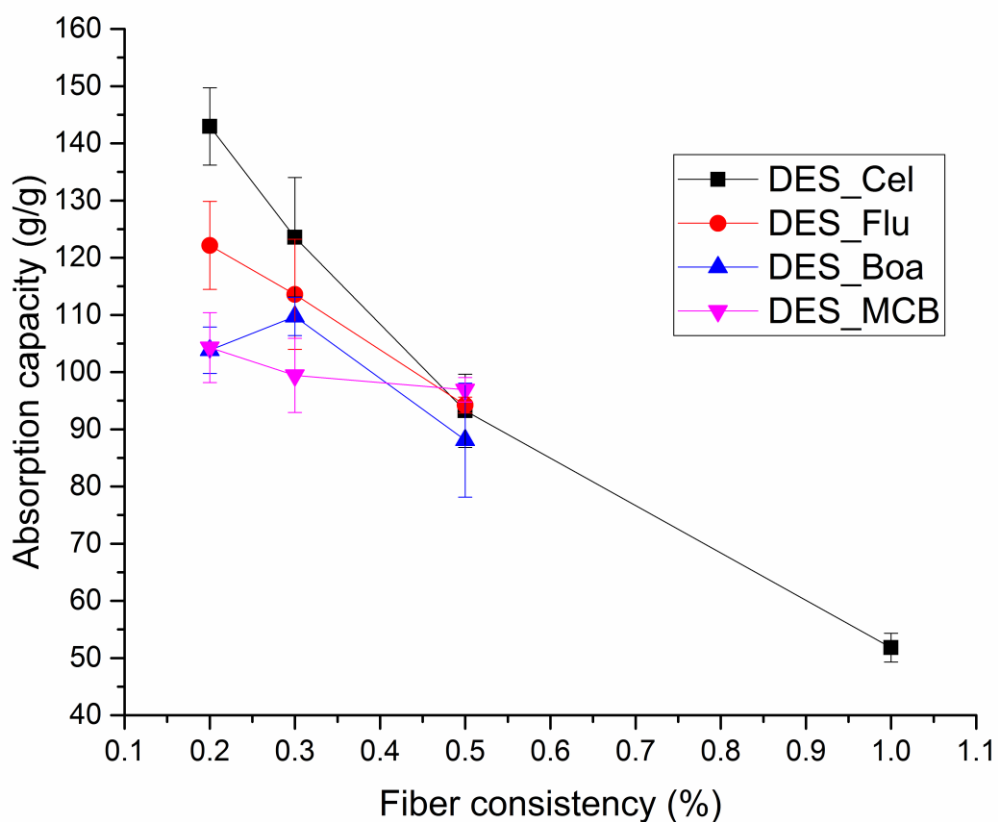
Fig. 2. Oil absorption capacities of various CNF aerogels.

The water uptakes, or water absorption, of various CNF aerogels were also determined, and the results are presented in Fig. 3. In all cases, the water absorption of various CNF sponges was very low (< 6 g/g) compared to marine diesel oil absorption (see Fig. 2), suggesting that the various

DES-treated hydrophobic CNF sponges had excellent selectivity toward diesel oil. Compared to the capacity of DES_Cel (0.3) to absorb water (6 g/g), its capacity to absorb marine diesel oil could be as much as 21 times higher. The water uptake values of commercial reference materials Ref (strip) and Ref (plug) were around 1 g/g, but also diesel oil absorption capacities were lower than that of CNF sponges.

To achieve a very high absorption capacity (>100 g/g), CNF sponges should have the highest possible porosity and clear hydrophobicity. When porosity beyond 99.8% was achieved, problems were encountered because the strength of the CNF sponges was so decreased that handling them was challenging. Another problem was that absorbed oil easily poured out from the aerogel structure after the oil sorption test, meaning that in practice aerogel cannot retain all the oil that it absorbs.
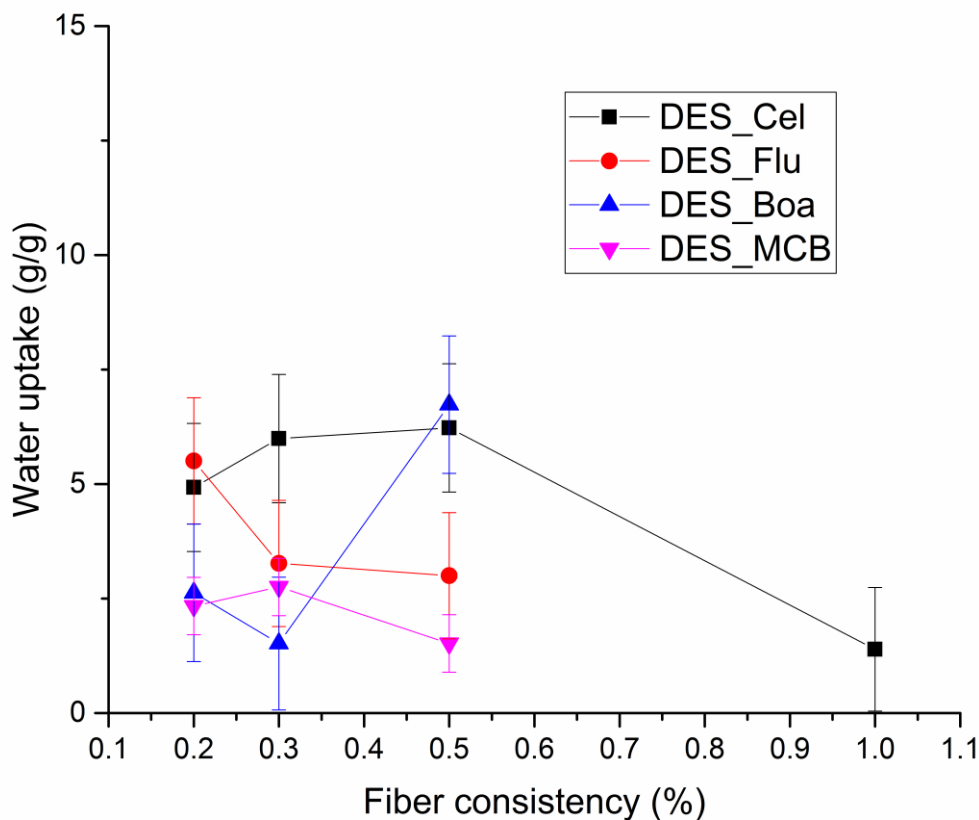
Fig. 3. Water uptakes of various CNF aerogels.

3.3 CNF aerogels' absorption capacities for various oils and solvents

The present study also investigated the capacity of hydrophobic CNF sponges to absorb a wide range of other oils and organic solvents, as shown in Fig. 4. The CNF sponges exhibited excellent oil absorption capacities. For example, DES_Cel (0.3) had a capacity of 124 g/g for marine diesel oil, 90 g/g for kerosene, 92 g/g for gasoline, 120 g/g for motor oil, and 150 g/g for linseed oil.
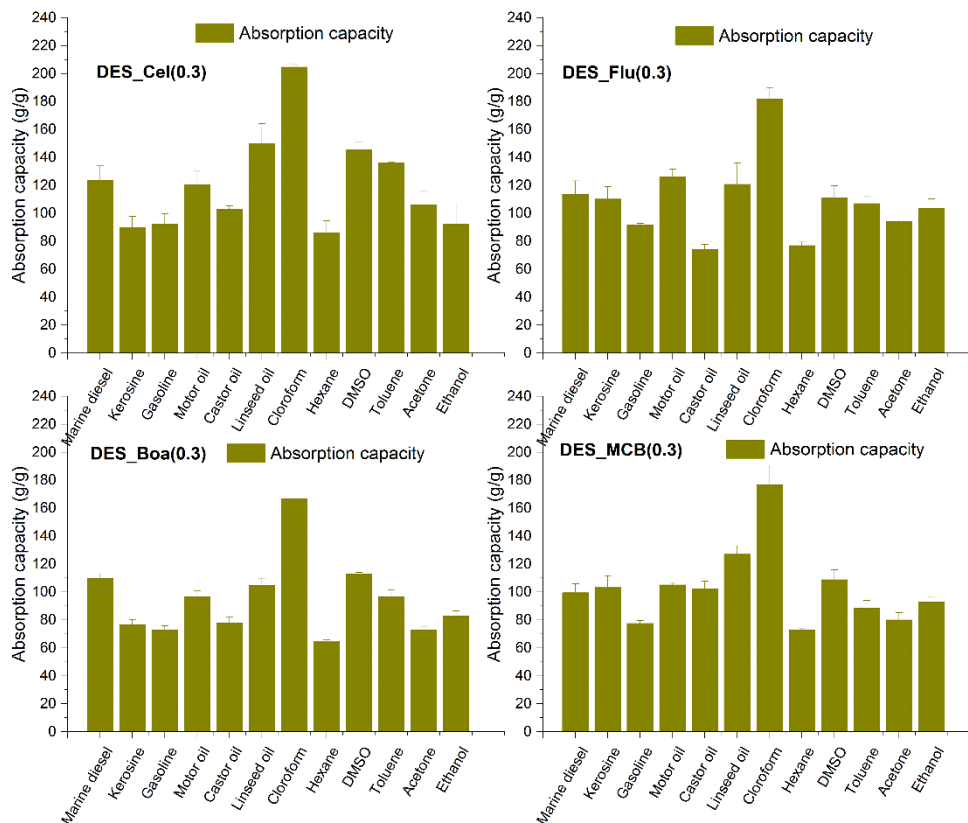
Fig. 4. CNF aerogels' absorption capacities for various oils and solvents.

All CNF sponges also showed ultra-high capacities to absorb a wide range of organic solvents, ranging from 65 g/g for hexane to 205 g/g for chloroform, depending on the density of the liquid (Fig. 5.). These capacities could be attributed to the high porosity (99.72%) and hydrophobicity of the material. Comparing the results obtained for CNF sponges to those for commercial reference absorption materials (Ref (strip) and Ref (plug)), all the CNF sponges created had notably higher capacities to absorb all oils and organic solvents investigated. For instance, the DES_Cel (0.3) sponge had an absorption capacity of 120 g/g for motor oil and 136 g/g for toluene, while the DES_Boa (0.3) sponge had an absorption capacity of 96 g/g for motor oil and 97 g/g for toluene.

In contrast, the Ref (strip) had an adsorption capacity of only 11 g/g for motor oil and 12 g/g for toluene, and the Ref (plug) had values of 40 g/g and 29 g/g for these two liquids, respectively.
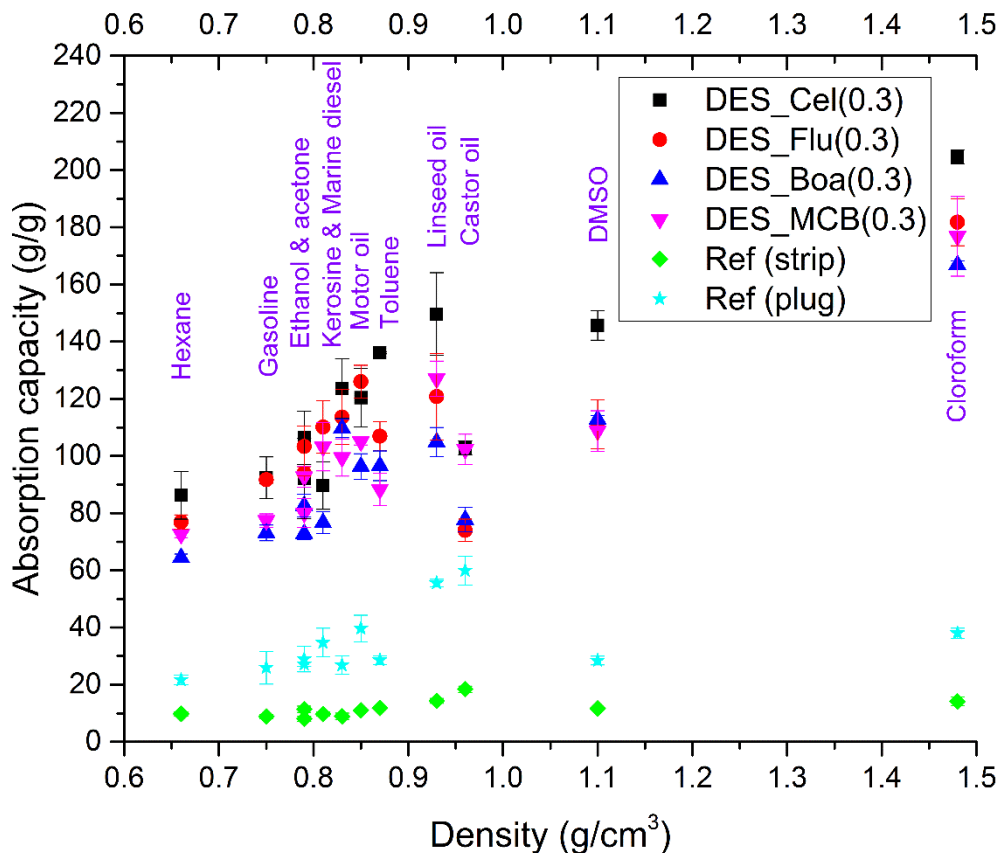

Fig. 5. Absorption capacities of various CNF aerogels and reference materials by the densities of oils and solvents.

3.4 Reusability of CNF aerogels to absorb marine diesel oil

Fig. 6 shows the absorption and reusability performances of the hydrophobic DES_MCB (0.5) sponge in absorbing marine diesel oil. Fig. 6a shows how a water droplet stayed on the cleavage plane of the aerogel, indicating the CNF sponge's hydrophobicity. The sponge could be saturated with marine diesel oil within 30 s (Figs. 6b–d), exhibiting a high absorption efficiency. In addition, the absorbed oil could readily be recovered by simple mechanical squeezing (Figs. 6e and f).

Furthermore, the squeezed sponge could quickly absorb more oil over about 30 s (Fig. 6g) and recovered most of its volume without any post-treatment. Fig. 6h shows the appearance of DES_MCB (0.5) after 30 cycles of mechanical squeezing and reabsorption of diesel oil, demonstrating the sponge's efficiency in recovering oil and its reusability.
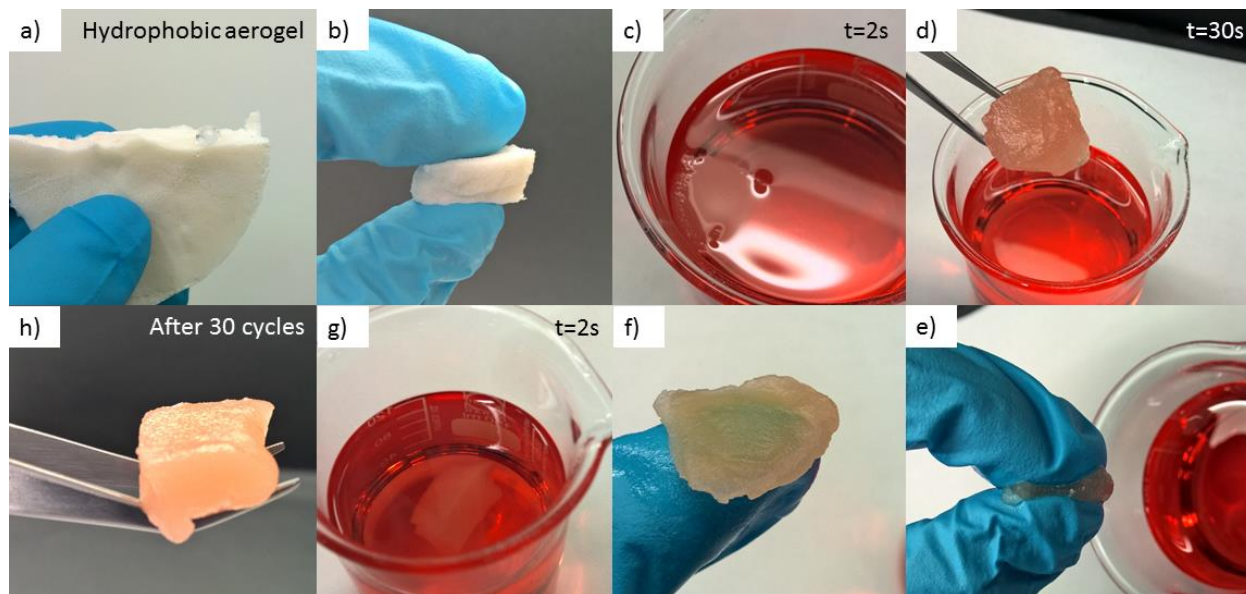

Fig. 6. High efficiency in recovering oil and absorbent reusability of the hydrophobic DES_MCB (0.5) sponge. (a) hydrophobic cellulose aerogel, (b–d) absorbing marine diesel oil, (e–f) squeezing absorbed oil, (g) oil reabsorption, and (h) aerogel after 30 cycles of mechanical squeezing and reabsorption of marine diesel oil.

All DES CNF sponges could be reused, and the absorbed oil could be recovered by simple mechanical squeezing. Fig. 7 shows the oil absorption capacities left after 30 squeezing-and-absorbing cycles. The oil absorption capacities of hydrophobic DES_CEL and DES_Flu sponges decreased from 100% to 80%, indicating high reusability. Although the absorption capacities of DES_Boa and DES_MCB sponges decreased to about 70%, they still had more than two-thirds of

their absorption capacities left after 30 squeezing–absorption cycles. This performance has significant implications for various practical applications.
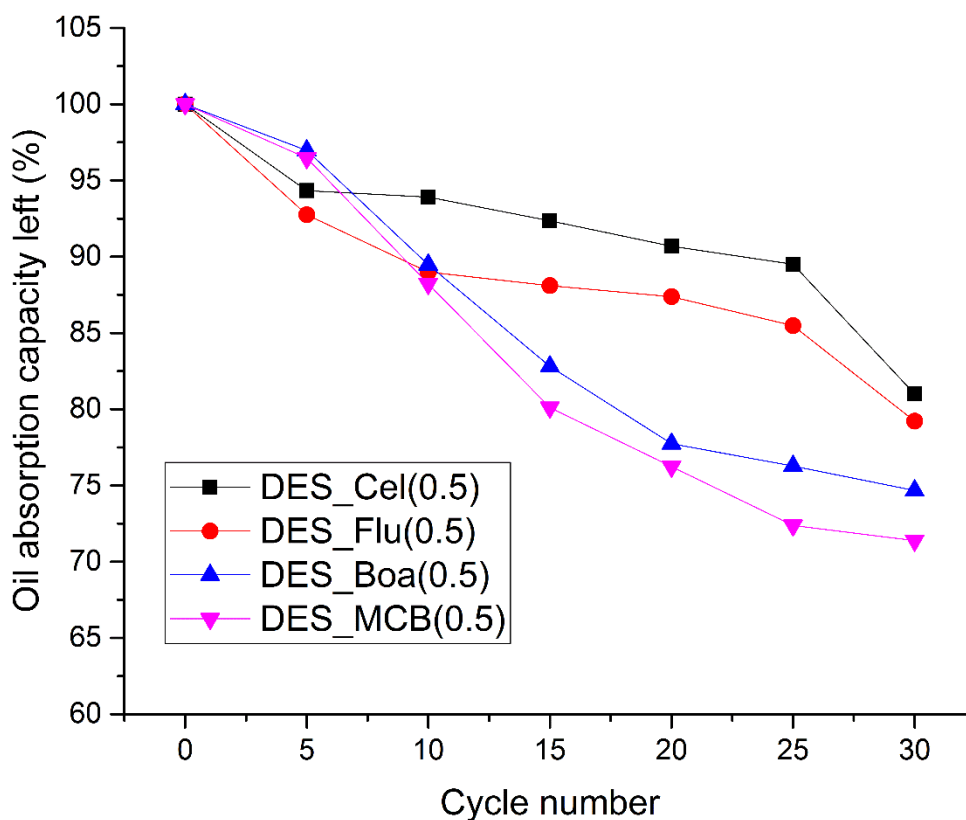

Fig. 7. Reusability of hydrophobic CNF sponges to absorb marine diesel oil.

Compared with other methods of recovering or reusing absorbents, including distillation (heating),[33] rinsing (solvent extraction),[15,34] combustion (burning),[35] and vacuum filtration,[36] squeezing is probably the simplest and most sustainable in terms of use of energy, material, and chemicals. Many of the other methods of recovering oil and reusing absorbents, including distillation, solvent extraction, and burning, are complicated, time consuming, inefficient, and energy intensive. Carbon-fiber aerogels made from raw cotton[37] and waste pulp[38] have previously been mechanically squeezed to recover oil and then reused, but the absorption capacity decreased

dramatically, to less than 55% of its original capacity, after recovery. In the present study, more than 70% of the absorbed diesel oil was efficiently recovered by facile, mechanical squeezing without adding other methods. Furthermore, the sponges could be reused for at least 30 cycles and maintained very high absorption capacities without sustaining significant structural damage. Therefore, CNF sponges derived from waste cellulose using green DES treatment proved to be promising for cleaning oil and chemical spills.

3.5 Comparison of various absorbents

Recently developed various absorbents and their performances are listed in Table 4. Among them, carbon absorbents, either from carbon blocks such as carbon nanotubes (CNTs)[39] and graphene [35,40–42] or directly from carbonized materials such as cotton fibers[37], cellulose fibers[38] and nanobacterial fibers[43], are the representatives of novel superabsorbents, showing ultra-high absorption capacities. Absorbents made from nanocellulose fibers exhibited low density and also high absorption capacity for various oils and organic solvents, arising from the good dispersion and stable suspension of nanocellulose fibers (up to 102 g/g)[15,21,44]. The absorption capacity of nanocellulose fiber-based absorbents was slightly lower than those of carbon materials, but significantly higher than those of other sorbents from synthetic polymers (14-84 g/g)[45,46].

Table 4. Comparison of various superabsorbents developed in recently.

Year	Reference	Cost estimation	Absorbent	Oil recovery method	Absorption capacity (g/g)
2012	39	++	B-doped CNT sponge	Burning	25-125
2012	40	++	N-doped graphene framework	Burning	200-600
2012	35	++	Graphene sponge	Burning	60-160
2012	41	++	Spongy graphene	Distillation	20-86
2013	42	++	RGO foam	Burning	70-122
2013	37	+	Carbon fiber aerogel from raw cotton	Burning or distillation	50-192
2013	38	+	Carbon microbelt aerogel from pulp	Distillation	56-188
2013	43	++	Carbon nanofiber aerogels from BC	Burning	106-312
2014	15	+	Silylated nanocellulose sponge	Solvent extraction	49-102
2014	21	++	Silane-modified nanocellulose aerogel	Distillation	139-356
2014	44	++	PVA/cellulose nanofibril aerogel	-	44-96
2014	33	+	Carbon aerogel from winter melon	Distillation	16-50
2013	45	++	Poly(ODA-co-BA)	Solvent extraction	14-84
2014	46	+	PVF sponge	Squeezing	14-57
2014	36	-	Cotton	Vacuum filtration	20-50
-	Present work	-	CNF aerogel	Squeezing	65-205
Noting: "-" low cost, "+" high cost, "++" very high cost					

In the present work, the marine diesel oil absorption capacity of the hydrophobic CNF aerogel prepared from nanofibrillated cellulose materials were ultra-high (88–143 g/g) and for chloroform up to 205 g/g, being much higher than those previously reported for cellulose fiber-based absorbents, and comparable to those of carbon absorbents, as listed in Table 4. Similar adsorption

capacities have been reached with carbon nanotubes and graphenes[35,39–41], but the cost of carbon nanotubes are at least 100,000-600,000 €/t and price of graphenes can be even higher. Additionally the absorbed marine diesel oil could easily and rapidly be recovered by simply squeezing, and the hydrophobic CNF sponge could be reused extensively without any other post-treatment. The oil recovery method, absorbent recyclability, and cost were much cheaper than most of carbon-based absorbents. Therefore, as an ultralight, cost-effective and highly recyclable superabsorbent, the hydrophobic CNF sponge has been demonstrated to be an interesting alternative to carbon-based absorbents for the removal of oils and organic pollutants.

4. Conclusions

Nanofibrillation, silylation, and freeze-drying were combined to create a porous, hydrophobic, superabsorbent CNF with excellent oil/water selectivity and ultra-high capacity to absorb various oils and organic solvents. Environmentally friendly nanofibrillation treatment involving choline chloride – urea – based deep eutectic solvent (DES), freeze drying, and a combination of two types of silylation agents have been used to fabricate superabsorbing, cost-effective, reusable, nanostructured aerogels. Furthermore, oil was be recovered rapidly, and CNF superabsorbents were reused repeatedly after simple mechanical squeezing. Utilization of renewable resources, low cost raw materials and simple and environmentally friendly manufacturing process make these superabsorbents promising alternatives for cleaning oil and chemical spills.

AUTHOR INFORMATION

Corresponding Author

* Tel.: +358503504960. Fax: not available. E-mail: ossi.laitinen@oulu.fi.

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