I&EC research
Industrial & Engineering Chemistry Research

Article

pubs.acs.org/IECR

Cellulose Aerogel from Paper Waste for Crude Oil Spill Cleaning

Son T. Nguyen,[†] Jingduo Feng,[†] Nhat T. Le,[‡] Ai T. T. Le,[‡] Nguyen Hoang,[‡] Vincent B. C. Tan,[†] and Hai M. Duong*,[†]

[†]Department of Mechanical Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117575

[‡]R&D Center for Petroleum Safety and Environment (CPSE), Vietnam Petroleum Institute (VPI), Ward 27, Binh Thanh District, Hochiminh City, Vietnam

ABSTRACT: Polyprolylene is commonly used for crude oil spill cleaning, but it has low absorption capacity and is nonbiodegradable. In our work, a green, ultralight, and highly porous material was successfully prepared from paper waste cellulose fibers. The material was functionalized with methyltrimethoxysilane (MTMS) to enhance its hydrophobicity and oleophilicity. Water contact angles of 143 and 145° were obtained for the MTMS-coated recycled cellulose aerogel. The aerogel achieved high absorption capacities of 18.4, 18.5, and 20.5 g/g for three different crude oils at 25 °C, respectively. In the investigated temperature range of 10, 25, 40, and 60 °C for the absorption of the tested crude oil on the aerogel, a highest absorption capacity of 24.4 g/g was obtained. It was found that the viscosity of the crude oils is the main factor affecting their absorption onto the aerogel. The strong affinity of the MTMS-coated recycled cellulose aerogel to the oils makes the aerogel a good absorbent for crude oil spill cleaning.

1. INTRODUCTION

Oil spills have been considered as one of the most serious disasters that are threatening the marine ecosystem. Recently, the explosion of a drilling rig in the Gulf of Mexico caused significant environmental damage. Oil spills are usually related to accidents in oil production, storage, and transportation. As long as fossil fuels are needed, oil spills are still a big problem that human beings are facing.[1−7] Therefore, it is essential to solve this environmental problem. There have been many ways for oil spill cleanup classified as chemical, biological, and physical methods. Dispersion, in situ burning, and solidification are considered to be chemical methods which are complicated and expensive. Use of microorganisms in the biological methods is effective but it requires a long time, and the microorganisms are affected by pH, temperature, oxygen content, etc. In physical methods, booms and skimmers are often used, but they cannot remove oil from sea effectively. Among these methods, sorption has been considered to be one of the most effective ways for oil spill cleaning due to its ability of collection and the complete removal of oil from oil spill sites.[6,8−15]

There have been several materials used as absorbents for oil spill cleaning in research and real applications. The oil absorbents can be catergorized as inorganic mineral, synthetic organic, and natual organic materials.[9,10,12,13] Inorganic materials (i.e., vermiculite, exfoliated graphite, diatomite, fly ash, etc.)[16−18] have low oil absorption capacity. Meanwhile, synthetic organic materials (i.e., polypropylene, polyurethane, etc.)[10,12,13] possess high affinity to oil but cause a waste problem after use due to their slow degradation. Natural organic materials from plants and animal residues, such as kapok fiber, sugar cane bagasse, rice husk, coconut husk, cotton, wool, sawdust, chitosan, etc., have been examined for oil absorption.[19−21] However, most of the materials show low oil absorption ability and also absorb water. Therefore, there is a high demand for finding new environmentally friendly absorbents with high oil absorption capacity, good selectiveness, and low cost for oil spill removal.

Aerogels are the world's lowest-density solid materials, composed of up to 99.98% air by volume but also highly porous and extremely rigid, capable of bearing weight many times their own. Aerogels are a diverse class of amazing materials with advanced properties. Transparent superinsulating silica aerogels exhibit the lowest thermal conductivity of any solid known. Ultrastrong, bendable x-aerogels are the lowest-density structural materials.[22−27] Normally aerogels are brittle and fracture under too much force. Overcoming the characteristic stiffness of the aerogels could open up a whole new range of uses such as oil absorption applications. In order to circumvent the stiffness, cellulose is chosen. Cellulose, better known as "plants, mostly", is normally used to make products such as paper and cardboard, but some forms of cellulose can also be quite strong.[28,29] One of the best methods to make aerogel out of cellulose is to freeze-dry it, removing all moisture and leaving nothing but a web of pure, solid fibers.[25,30,31]

The increase of paper comsumption has been creating a huge amount of paper waste which contributes 25−40% of global municipal solid waste.[32] Recycling paper waste will help to preserve forests as well as solve the environmental problem. Recycled cellulose fibers from paper waste are a cheap and abundant resource. A combination between aerogel structure and recycled cellulose fiber will form a new material—named "recycled cellulose aerogel"—which is cost-effective and promising for oil absorption. Although there have been some studies on using cellulosic materials for oil absorption,[4,6,29,33−36] no studies have been carried out on fabricating aerogels from paper waste cellulose fibers and investigating

Received: October 1, 2013
Revised: December 4, 2013
Accepted: December 5, 2013

   dx.doi.org/10.1021/ie4032567 | Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

them as absorbents for crude oil spill cleaning. In our work, a fabrication procedure for making cellulose aerogels from paper-waste cellulose fibers was developed and the materials showed high absorption capacity for different crude oils.

2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. Sodium hydroxide, urea, and ethanol were of analytical grade and purchased from Sigma-Aldrich. All the solutions were made with deionized (DI) water. Recycled cellulose fibers were donated by Insul-Dek Engineering Pte. Ltd. (Singapore). Crude oils were supplied by Petrovietnam Research and Development Center for Petroleum Processing (PVPro).

2.2. Fabrication of Recycled Cellulose Aerogels. Recycled cellulose fibers (2 wt %) were dispersed into a sodium hydroxide/urea solution (1.9 wt %/10 wt %) by sonicating for 6 min. Then the solution was placed in a refrigerator for more than 24 h to allow gelation. After the solution had been frozen, it was then thawed at room temperature, followed by immersion into ethanol (99 vol %) for coagulation. The specimen thickness was controlled around 1 cm with a diameter of 3.8 cm using a beaker as a mold. After coagulation, solvent exchange was carried out by immersing the gel in DI water for 2 days. Freeze-drying was carried out for the sample for 2 days at −98 °C with a ScanVac CoolSafe 95-15 Pro freeze-dryer (Denmark) after prefreezing the sample at −18 °C for 12 h.

2.3. Hydrophobic Coating of Recycled Cellulose Aerogels. The recycled cellulose aerogel was placed in a big glass bottle. A small open glass vial containing methyltrimethoxysilane (MTMS) was added into the glass bottle. Then the glass bottle was capped and heated in an oven at 70 °C for 2 h for the silanation reaction. Thereafter, the coated sample was placed in a vacuum oven to remove the excess coating reagent until the pressure reached 0.03 mbar.

2.4. Morphology Characterization. Morphologies of aerogel samples were investigated using field-emission scanning electron microscopy (FE-SEM). The samples were kept in a dry cabinet prior to FE-SEM. They were then coated with a thin gold layer using sputtering. A Hitachi S4300 scanning electron microscope (Japan) operated at 1/5 kV was used to capture structural images of the aerogels.

2.5. Contact Angle Measurement. The test was carried out for uncoated and coated samples on a VCA Optima goniometer (AST Products Inc., USA) to investigate their water repellency. Water was dispensed, drop by drop, using the syringe control of the machine. This was repeated at different positions of the sample, and an average was taken.

2.6. Crude Oil Absorption Test. Crude oil absorption capabilities of aerogel samples were investigated using a modified ASTM F726-06 test method.[5,10,20,37] Three crude oils used for the absorption tests were Ruby (RB), Te Giac Trang (TGT), and Rang Dong (RD). The specifications of the crude oils are displayed in Table 1. The dry aerogel sample dimensions were 38 mm (diameter) × 11 mm (thickness). The sample was weighed and placed in 300 mL of crude oil for a certain time. Then the wet sample was removed from the liquid using a stainless steel mesh basket and drained for 1 min. The wet sample was weighed, its dimensions were measured, it was squeezed by hand, and it was weighed again. The test was repeated several times.

Table 1. Specifications of Crude Oil Samples

crude oil	density at 25 °C, g/cm^3	viscosity, Pa·s 10 °C	25 °C	40 °C	60 °C
RB	0.8236	42	0.0090	0.0049	0.0027
TGT	0.8264	n/a	0.0088	n/a	n/a
RD	0.8153	n/a	0.0062	n/a	n/a

Crude oil absorption capacity was calculated using the following formula:

$$Q_t = \frac{m_w - m_d}{m_d} \quad (1)$$

where Q_t (g/g) is the crude oil absorption capacity of the aerogel at a certain time t (min), m_w (g) is the weight of the aerogel after absorption, and m_d (g) is the weight of the aerogel before absorption.

The ratio of the sample volume before the absorption test and its original volume (V_n) was calculated as below:

$$V_n = \frac{V_d}{V_i} \quad (2)$$

where V_d (mm^3) is the volume of the sample before the absorption test and V_i (mm^3) is the original volume of the sample.

The squeezed ratio of crude oil (Q_s) was calculated using the formula

$$Q_s = \frac{\text{squeezed amount of oil}}{\text{absorbed amount of oil}} = \frac{m_w - m_s}{m_w - m_d} \quad (3)$$

where m_s (g) is the weight of the aerogel after squeezing.

To evaluate the oil absorption capability of the aerogel in oil/water mixture, 40 mL of deionized (DI) water and 5 mL of RB oil were added to a Petri dish. An MTMS-coated aerogel sample of 0.722 g was used for the absorption test.

3. RESULTS AND DISCUSSION

Figure 1a shows an FE-SEM image and a photograph of the recycled cellulose aerogel. It can be seen that the aerogel possesses a highly porous structure consisting of a network of interconnected uniform cellulose fibers. Contrary to aerogels fabricated from cellulose nanofibers having mesoporous structures,[38] the aerogel formed from recycled cellulose fibers shows a macroporous three-dimensional network, as displayed in Figure 1a, possibly due to the large size of recycled cellulose fibers. However, its low density (0.04 g/cm^3) and high porosity (97.3%) are comparable to those of nanocellulose aerogel (0.03 g/cm^3, 95−98%).[38] These characteristics are essential for a good absorbent.

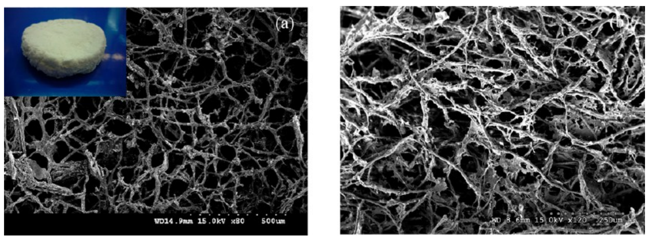

Figure 1. FE-SEM images of the recycled cellulose aerogel (a) before MTMS coating and (b) after MTMS coating. Inset: a photograph of the aerogel.

Hydrophilicity is the nature of cellulose due to its hydroxyl groups. Therefore, a hydrophobic coating was carried out for the recycled cellulose aerogel to make it oleophilic. To achive this, a simple chemical vapor deposition procedure[39] was performed for the aerogel with MTMS at 70 °C, as described in section 2.3. After the silanation reaction between the aerogel and MTMS, the excess MTMS was removed using a vacuum. As presented in Figure 1b, the open porous structure of the material is still preserved after the coating. To determine the effect of the coating on the hydrophobicity of the aerogel, water contact angle measurement was carried out for the uncoated and coated aerogels. The uncoated sample immediately absorbed the water droplets in the test and no measurable contact angle was recorded. By contrast, as shown in Figure 2a,

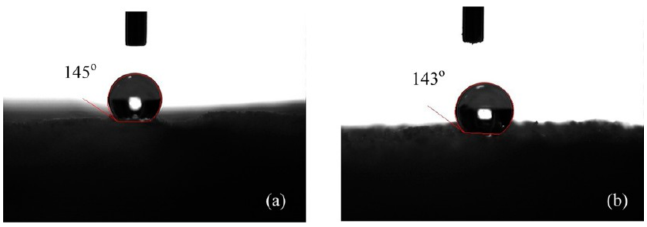

Figure 2. Water contact angle (a) on the external surface of the coated aerogel and (b) on the cut surface of the coated aerogel.

a high contact angle of 145° was found for the aerogel coated with MTMS, indicating the hydrophobicity of the material. To ensure that the internal surfaces of the pores are fully coated with MTMS, the sample was cut into two pieces and a water contact angle of 143° was obtained on the cut surface of the sample (Figure 2b), proving that the whole porous structure is hydrophobic.

To investigate the crude oil absorption behavior of the MTMS-coated aerogel, three different crude oils, RB, TGT, and RD, were used. Figure 3 shows the first minutes of the sorption process. It is seen that the material easily absorbed crude oil and completely immersed into the oil after about 3 min, indicating the high crude oil afinity of the absorbent. The sorption kinetics of the three crude oils on the aerogel are shown in Figure 4. The absorption rates are very high at the first stage and saturation is achieved after about 20 min. The maximum absorption capacities (calculated by eq 1) of RB, TGT, and RD oils on the aerogel (18.4, 18.5, and 20.5 g/g, respectively) are nearly double those obtained with polypropylene fibrous mats which are widely used as absorbents for crude oil spill cleaning.[12,13,40−45] The highest absorption capacity value is found for RD oil, while the aerogel shows similar oil absorption behavior for RB and TGT oils. This is probably due to the fact that RD oil possesses the lowest

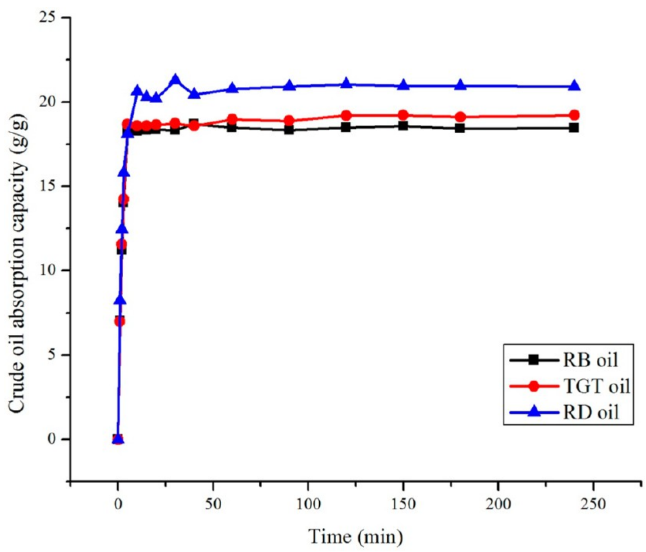

Figure 4. Absorption kinetics of crude oils on the coated aerogel.

viscosity while RB and TGT oils have comparable viscosity values (Table 1).

It is well-known that the absorption process of oils on absorbents is controlled by the capillary effect, van der Waals forces, hydrophobic interaction between the oils and absorbents, pore morphology, and oil viscosity.[9,35,40,42,46,47] In this case, oil viscosity seems to play the main role in the absorption capacity difference among the three crude oils. A lower viscosity facilitates the penetration of the oil into the porous network of the aerogel and, thus, results in a higher oil absorption capacity.[9,35,41]

The effect of temperature on the crude oil absorption capability of the MTMS-coated recycled cellulose aerogel was examined with RB crude oil at 10, 25, 40, and 60 °C. As shown in Figure 5, the oil absorption capacity increases from 13.9 to 18.4 g/g when the temperature is increased from 10 to 25 °C, achieves the highest value of 24.4 g/g at 40 °C, and decreases to 19.9 g/g when the temperature is increased to 60 °C. This can be explained based on the change of oil viscosity with temperature, as displayed in Figure 5 and Table 1. At 10 °C, the oil forms a gel with a high viscosity value of 42 Pa·s. This high viscosity inhibits the diffusion of the oil into the pores of the absorbent and leads to a low absorption capacity. When the testing temperature is increased to 25, 40, and 60 °C, the reduction of the crude oil viscosity from 42 to 0.0090, 0.0049, and 0.0027 Pa·s lets the oil diffuse into the porous matrix of the aerogel faster and more easily. However, the large decrease of the oil viscosity at 60 °C will result in a low adherence of the oil to the pore walls, and as a consequence, more oil is drained out

Figure 3. First minutes of the crude oil absorption process of the coated aerogel.

dx.doi.org/10.1021/ie4032567 | Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

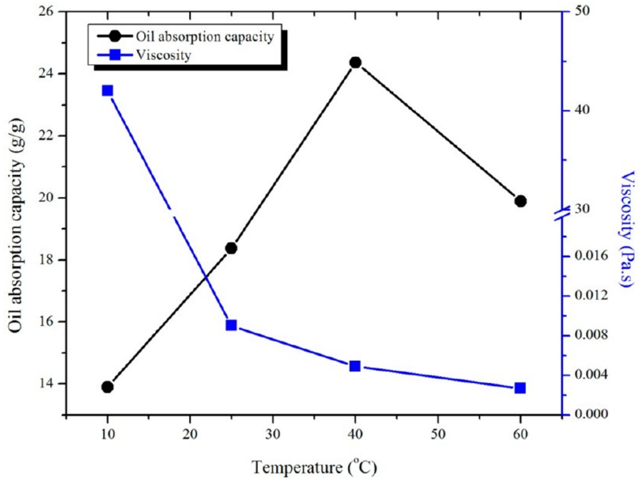

Figure 5. Effect of temperature on crude oil absorption capability of MTMS-coated recycled cellulose aerogel and on viscosity of RB crude oil.

during the drainage step.[9,35,41,48] The maximum oil absorption capacity is achieved at 40 °C, at which the low oil viscosity value facilitates the penetration of the crude oil into the pores and is also high enough for the retention of oil in the structure of the aerogel.

The effect of cycles of sorption on the oil absorption capacity of the aerogel was investigated. Figure 6a,b shows images of the aerogel sample before and after the first oil absorption test cycle. It can be seen that sizes of the sample are nearly unchanged after absorbing oil. This is confirmed by a volume ratio of 1.05 found for the sample. To remove the absorbed oil, a simple squeezing was performed (Figure 6c). Figure 6d,e shows the sample after squeezing and the good flexibility of the sample, respectively. Then the squeezed sample was used for the next absorption test cycle. The oil absorption capacities of the sample after five sorption cycles are displayed in Figure 7a.

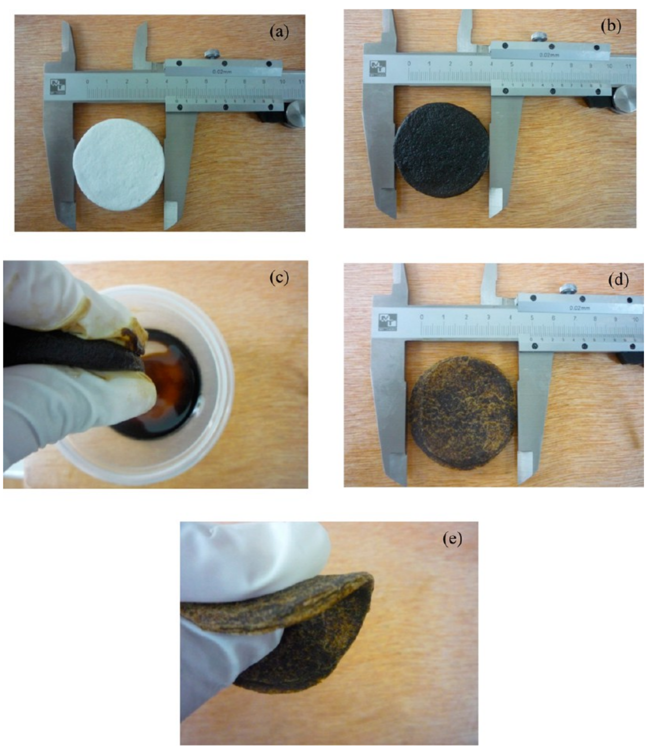

Figure 6. (a) Aerogel sample before first absorption cycle. (b) Aerogel sample after first absorption cycle. (c) Squeezing. (d) Aerogel sample after squeezing. (e) Flexibility of the sample.

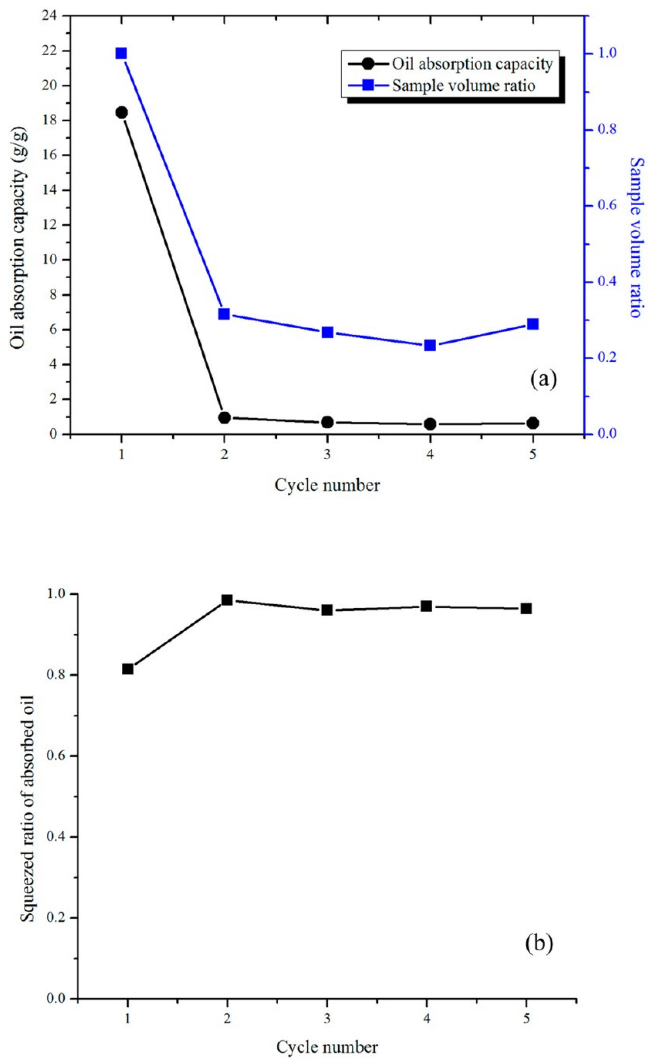

Figure 7. Effect of cycles of sorption on (a) oil absorption capacity and sample volume of the aerogel and (b) squeezed ratio of absorbed oil.

The sample achieved a high absorption capacity of 18.4 g/g in cycle 1. However, the capacity dropped to 0.96, 0.68, 0.59, and 0.63 g/g in cycles 2, 3, 4, and 5, respectively. This phenomenon can be explained based on the change of the sample volume (caculated by eq 2), as shown in Figure 7a. After cycle 1, the sample was squeezed to remove the absorbed oil and the squeezed sample was used for cycle 2. After this squeezing, the ratio of the volume of the squeezed sample and its original volume is 0.32, indicating that the porous structure of the sample has largely collapsed. As a result, the oil absorption capacity of the aerogel sharply decreased to 0.96 g/g in cycle 2. In later cycles, the volume ratio values (0.27, 0.23, and 0.29) are similar to the value after the first cycle, implying that the sample structure has not changed anymore. Regarding the squeezed amount of the absorbed oil (calculated by eq 3), as presented in Figure 7b, 81.5, 98.5, 95.9, 96.9, and 96.4% of the absorbed oil

dx.doi.org/10.1021/ie4032567 | Ind. Eng. Chem. Res. XXXX, XXX, XXX−XXX

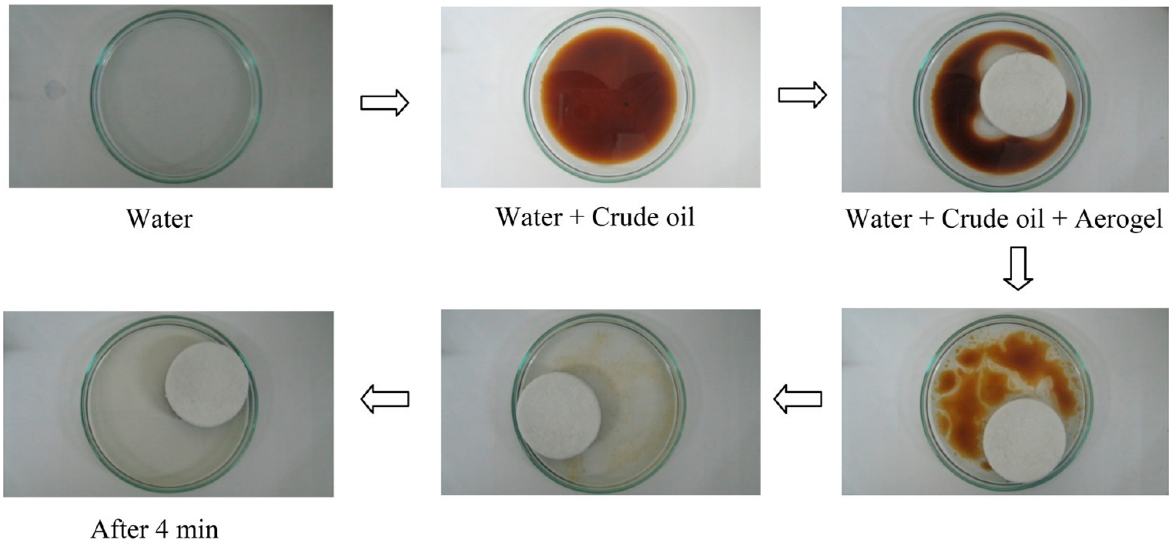

Figure 8. Crude oil absorption test of the coated aerogel with a mixture of RB crude oil and DI water (40 mL of water/5 mL of RB oil).

was released after cycles 1, 2, 3, 4, and 5, respectively, by using the simple squeezing.

Figure 8 shows the crude oil absorption test of the material with a mixture of RB crude oil and DI water (40 mL of water/5 mL of RB oil). The crude oil forms a dark layer on the water surface. It can be observed that the hydrophobic aerogel floats on the mixture and rapidly absorbs the crude oil. After about 4 min, most of the oil (99.4%) was absorbed by the hydrophobic aerogel. The test indicates that the MTMS-coated aerogel is promising for crude oil spill cleaning application.

4. CONCLUSIONS

A low density and highly porous aerogel for crude oil spill cleaning was successfully prepared from paper-waste cellulose fibers with a simple alkaline/urea method. After being coated with MTMS for crude oil absorption purpose, the material showed good hydrophobicity with water contact angles larger than 140°. The MTMS-coated aerogel exhibited high absorption capacities of 18.4, 18.5, and 20.5 g/g for three different crude oils, which are nearly double those values obtained with polypropylene—the common oil absorbent. The aerogel showed the highest absorption capacity of 24.4 g/g for RB crude oil at 40 °C. The high crude oil affinity of the MTMS-coated aerogel indicates that the material is promising for oil spill cleanup. The structural stability of the aerogel would be further improved for higher reusability.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mpedhm@nus.edu.sg. Fax: +65 67791459. Tel.: +65 65161567.

Author Contributions

The article was written through contributions of all authors. Son T. Nguyen and Jingduo Feng contributed equally. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful to the Singapore National Environment Agency—Environment Technology Research Program (7th RFP) (R-265-000-450-490) for financial support for the project. We would like to thank Insul-Dek Engineering Pte. Ltd. (Singapore) for giving us recycled cellulose fibers. We deeply appreciate Prof. Phan Thien Nhan for valuable advice and Dr. Lin Yuan for help in measuring crude oil viscosity.

■ REFERENCES

(1) Zhu, Q.; Chu, Y.; Wang, Z.; Chen, N.; Lin, L.; Liu, F.; Pan, Q. Robust superhydrophobic polyurethane sponge as a highly reusable oil-absorption material. *J. Mater. Chem. A* **2013**, *1*, 5386−5393.

(2) Zhu, K.; Shang, Y. Y.; Sun, P. Z.; Li, Z.; Li, X. M.; Wei, J. Q.; Wang, K. L.; Wu, D. H.; Cao, A. Y.; Zhu, H. W. Oil spill cleanup from sea water by carbon nanotube sponges. *Front. Mater. Sci.* **2013**, *7*, 170−176.

(3) Xiao, N.; Zhou, Y.; Ling, Z.; Qiu, J. Synthesis of a carbon nanofiber/carbon foam composite from coal liquefaction residue for the separation of oil and water. *Carbon* **2013**, *59*, 530−536.

(4) Wang, J.; Zheng, Y.; Kang, Y.; Wang, A. Investigation of oil sorption capability of PBMA/SiO2 coated kapok fiber. *Chem. Eng. J.* **2013**, *223*, 632−637.

(5) Singh, V.; Kendall, R. J.; Hake, K.; Ramkumar, S. Crude oil sorption by raw cotton. *Ind. Eng. Chem. Res.* **2013**, *52*, 6277−6281.

(6) Li, D.; Zhu, F. Z.; Li, J. Y.; Na, P.; Wang, N. Preparation and characterization of cellulose fibers from corn straw as natural oil sorbents. *Ind. Eng. Chem. Res.* **2013**, *52*, 516−524.

(7) Li, H.; Liu, L.; Yang, F. Hydrophobic modification of polyurethane foam for oil spill cleanup. *Mar. Pollut. Bull.* **2012**, *64*, 1648−1653.

(8) Gui, X.; Zeng, Z.; Lin, Z.; Gan, Q.; Xiang, R.; Zhu, Y.; Cao, A.; Tang, Z. Magnetic and highly recyclable macroporous carbon nanotubes for spilled oil sorption and separation. *ACS Appl. Mater. Interfaces* **2013**, *5*, 5845−5850.

(9) Gui, X.; Li, H.; Wang, K.; Wei, J.; Jia, Y.; Li, Z.; Fan, L.; Cao, A.; Zhu, H.; Wu, D. Recyclable carbon nanotube sponges for oil absorption. *Acta Mater.* **2011**, *59*, 4798−4804.

(10) Cojocaru, C.; Macoveanu, M.; Cretescu, I. Peat-based sorbents for the removal of oil spills from water surface: Application of artificial neural network modeling. *Colloids Surf., A* **2011**, *384*, 675−684.

(11) Chu, Y.; Pan, Q. Three-dimensionally macroporous Fe/C nanocomposites as highly selective oil-absorption materials. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2420−2425.

(12) Adebajo, M. O.; Frost, R. L.; Kloprogge, J. T.; Carmody, O.; Kokot, S. Porous Materials for Oil Spill Cleanup: A Review of Synthesis and Absorbing Properties. *J. Porous Mater.* **2003**, *10*, 159−170.

(13) Bayat, A.; Aghamiri, S. F.; Moheb, A.; Vakili-Nezhaad, G. R. Oil spill cleanup from sea water by sorbent materials. *Chem. Eng. Technol.* **2005**, *28*, 1525−1528.

(14) Al-Majed, A. A.; Adebayo, A. R.; Hossain, M. E. A sustainable approach to controlling oil spills. *J. Environ. Manage.* **2012**, *113*, 213−227.

(15) Peng, D.; Lan, Z.; Guo, C.; Yang, C.; Dang, Z. Application of cellulase for the modification of corn stalk: Leading to oil sorption. *Bioresour. Technol.* **2013**, *137*, 414−418.

(16) Bastani, D.; Safekordi, A. A.; Alihosseini, A.; Taghikhani, V. Study of oil sorption by expanded perlite at 298.15 K. *Sep. Purif. Technol.* **2006**, *52*, 295−300.

(17) Karakasi, O. K.; Moutsatsou, A. Surface modification of high calcium fly ash for its application in oil spill clean up. *Fuel* **2010**, *89*, 3966−3970.

(18) Rajakovic, V.; Aleksic, G.; Radetic, M.; Rajakovic, L. Efficiency of oil removal from real wastewater with different sorbent materials. *J. Hazard. Mater.* **2007**, *143*, 494−499.

(19) Wahi, R.; Chuah, L. A.; Choong, T. S. Y.; Ngaini, Z.; Nourouzi, M. M. Oil removal from aqueous state by natural fibrous sorbent: An overview. *Sep. Purif. Technol.* **2013**, *113*, 51−63.

(20) Yuan, X.; Chung, T. C. M. Novel solution to oil spill recovery: Using thermodegradable polyolefin oil superabsorbent polymer (Oil-SAP). *Energy Fuels* **2012**, *26*, 4896−4902.

(21) Deschamps, G.; Caruel, H.; Borredon, M.-E.; Bonnin, C.; Vignoles, C. Oil Removal from Water by Selective Sorption on Hydrophobic Cotton Fibers. 1. Study of Sorption Properties and Comparison with Other Cotton Fiber-Based Sorbents. *Environ. Sci. Technol.* **2003**, *37*, 1013−1015.

(22) Wang, D.; McLaughlin, E.; Pfeffer, R.; Lin, Y. S. Adsorption of oils from pure liquid and oil-water emulsion on hydrophobic silica aerogels. *Sep. Purif. Technol.* **2012**, *99*, 28−35.

(23) Sun, H.; Xu, Z.; Gao, C. Multifunctional, Ultra-Flyweight, Synergistically Assembled Carbon Aerogels. *Adv. Mater.* **2013**, *25*, 2554−2560.

(24) Aulin, C.; Netrval, J.; Wågberg, L.; Lindström, T. Aerogels from nanofibrillated cellulose with tunable oleophobicity. *Soft Matter* **2010**, *6*, 3298−3305.

(25) Pierre, A. C.; Pajonk, G. M. Chemistry of Aerogels and Their Applications. *Chem. Rev.* **2002**, *102*, 4243−4266.

(26) Liu, S.; Yan, Q.; Tao, D.; Yu, T.; Liu, X. Highly flexible magnetic composite aerogels prepared by using cellulose nanofibril networks as templates. *Carbohydr. Polym.* **2012**, *89*, 551−557.

(27) Aerogels.org. Strong and Flexible Aerogels. http://www.aerogel.org/?p=1058. Accessed Nov 28, 2013.

(28) Olsson, R. T.; Azizi Samir, M. A. S.; Salazar Alvarez, G.; Belova, L.; Ström, V.; Berglund, L. A.; Ikkala, O.; Nogués, J.; Gedde, U. W. Making flexible magnetic aerogels and stiff magnetic nanopaper using cellulose nanofibrils as templates. *Nat. Nanotechnol.* **2010**, *5*, 584−588.

(29) Cervin, N. T.; Aulin, C.; Larsson, P. T.; Wågberg, L. Ultra porous nanocellulose aerogels as separation medium for mixtures of oil/water liquids. *Cellulose* **2012**, *19*, 401−410.

(30) Gurav, J. L.; Jung, I.-K.; Park, H.-H.; Kang, E. S.; Nadargi, D. Y. Silica Aerogel: Synthesis and Applications. *J. Nanomater.* **2010**, *2010*, 409310.

(31) Bryning, M. B.; Milkie, D. E.; Islam, M. F.; Hough, L. A.; Kikkawa, J. M.; Yodh, A. G. Carbon Nanotube Aerogels. *Adv. Mater.* **2007**, *19*, 661−664.

(32) Nourbakhsh, A.; Ashori, A. Particleboard made from waste paper treated with maleic anhydride. *Waste Manage. Res.* **2010**, *28*, 51−55.

(33) Korhonen, J. T.; Kettunen, M.; Ras, R. H. A.; Ikkala, O. Hydrophobic nanocellulose aerogels as floating, sustainable, reusable, and recyclable oil absorbents. *ACS Appl. Mater. Interfaces* **2011**, *3*, 1813−1816.

(34) Wang, J.; Zheng, Y.; Wang, A. Effect of kapok fiber treated with various solvents on oil absorbency. *Ind. Crops Prod.* **2012**, *40*, 178−184.

(35) Wang, J.; Zheng, Y.; Wang, A. Coated kapok fiber for removal of spilled oil. *Mar. Pollut. Bull.* **2013**, *69*, 91−96.

(36) Payne, K. C.; Jackson, C. D.; Aizpurua, C. E.; Rojas, O. J.; Hubbe, M. A. Oil spills abatement: Factors affecting oil uptake by cellulosic fibers. *Environ. Sci. Technol.* **2012**, *46*, 7725−7730.

(37) ASTM. ASTM Standard F 726-06: Standard Test Method for Sorbent Performance of Adsorbents. In *2006 Annual Book of ASTM Standards*; American Society for Testing and Materials (ASTM): West Conshohocken, PA, 2006.

(38) Pääkkö, M.; Vapaavuori, J.; Silvennoinen, R.; Kosonen, H.; Ankerfors, M.; Lindström, T.; Berglund, L. A.; Ikkala, O. Long and entangled native cellulose I nanofibers allow flexible aerogels and hierarchically porous templates for functionalities. *Soft Matter* **2008**, *4*, 2492−2499.

(39) Jin, H.; Kettunen, M.; Laiho, A.; Pynnönen, H.; Paltakari, J.; Marmur, A.; Ikkala, O.; Ras, R. H. A. Superhydrophobic and superoleophobic nanocellulose aerogel membranes as bioinspired cargo carriers on water and oil. *Langmuir* **2011**, *27*, 1930−1934.

(40) Choi, H.-M.; Kwon, H.-J. Cotton nonwovens as oil spill cleanup sorbents. *Text. Res. J.* **1993**, *63*, 211−218.

(41) Choi, H. M.; Cloud, R. M. Natural sorbents in oil spill cleanup. *Environ. Sci. Technol.* **1992**, *26*, 772−776.

(42) Lin, J.; Shang, Y.; Ding, B.; Yang, J.; Yu, J.; Al-Deyab, S. S. Nanoporous polystyrene fibers for oil spill cleanup. *Mar. Pollut. Bull.* **2012**, *64*, 347−352.

(43) Wei, Q. F.; Mather, R. R.; Fotheringham, A. F.; Yang, R. D. Evaluation of nonwoven polypropylene oil sorbents in marine oil-spill recovery. *Mar. Pollut. Bull.* **2003**, *46*, 780−783.

(44) Teas, C.; Kalligeros, S.; Zanikos, F.; Stournas, S.; Lois, E.; Anastopoulos, G. Investigation of the effectiveness of absorbent materials in oil spills clean up. *Desalination* **2001**, *140*, 259−264.

(45) Moriwaki, H.; Kitajima, S.; Kurashima, M.; Hagiwara, A.; Haraguchi, K.; Shirai, K.; Kanekatsu, R.; Kiguchi, K. Utilization of silkworm cocoon waste as a sorbent for the removal of oil from water. *J. Hazard. Mater.* **2009**, *165*, 266−270.

(46) Deschamps, G.; Caruel, H.; Borredon, M. E.; Bonnin, C.; Vignoles, C. Oil removal from water by selective sorption on hydrophobic cotton fibers. 1. Study of sorption properties and comparison with other cotton fiber-based sorbents. *Environ. Sci. Technol.* **2003**, *37*, 1013−1015.

(47) Wu, J.; Wang, N.; Wang, L.; Dong, H.; Zhao, Y.; Jiang, L. Electrospun Porous Structure Fibrous Film with High Oil Adsorption Capacity. *ACS Appl. Mater. Interfaces* **2012**, *4*, 3207−3212.

(48) Radetić, M. M.; Jocić, D. M.; Jovancić, P. M.; Petrović, Z. L.; Thomas, H. F. Recycled Wool-Based Nonwoven Material as an Oil Sorbent. *Environ. Sci. Technol.* **2003**, *37*, 1008−1012.