Enhanced Capacities of Mixed Fatty Acid-Modified Sawdust Aggregators for Remediation of Crude Oil Spill

Yongsoon Shin, Eric M. Winder, Kee Sung Han, Hongkyung Lee and George T. Bonheyo

ABSTRACT: Mixed fatty acid-modified aggregators have been developed as potential crude oil sorbents. Cheap pine wood flour was first modified with oleic acid (OA) and further modified with a second fatty acid by a leaving group chemistry, where a surface hydroxyl group is first replaced by p-toluenesulfonyl group and a fatty acid forms a covalent bond on sawdust surface through esterification at the elevated temperature (55 °C). Two OA-modified base materials, pine/OA-106 and pine/OA-124, with different OA-coverages were first prepared and the second fatty acids with C3, C6, C8, C10, C12, C14, or C16 alkyl chains were applied to cover the remaining surface hydroxyl groups. The crude oil sorption capacities of the mixed fatty acid-modified aggregators were studied and compared with those of the base materials. The results showed that mixed fatty acid-modified aggregators increased up to 45.6% more crude oil sorption than those of OA-modified base materials. A correlation between surface property and sorption capacity was studied by moisture sorption, Fourier transform infrared spectroscopy, X-ray diffraction, 13C cross polarization and magic angle spinning nuclear magnetic resonance, thermal gravimetric analysis, and scanning electron microscopy. To our knowledge, no report has been published for mixed fatty acid-modified herders or aggregators in the environmental remediation.

INTRODUCTION

Crude oil is one of the most important energy sources for synthetic polymers and chemicals worldwide. However, when this vital resource is accidentally released, it causes significant environmental and ecological problems. From 2007 to 2016, an average of nine spills greater than 50 barrels was reported, and 31% of them were crude oil spills. Effective decontamination and cleanups are necessary for the protection of the environment and human health. Although there are currently many cleanup technologies, such as in situ burning and the use of chemical dispersants and sorbents (such as booms and skimmers), an important technology to mitigate crude oil spills in the Arctic is to apply a chemical herding agent, such as the US Navy (USN) cold water herder formulation (65% sorbitan monolaurate [Span-20] and 35% 2-ethyl butanol) that corrals the oil by reducing the interfacial tension between oil droplets and by pushing inward from the periphery of the spill. The USN herding agents work most effectively when they are applied to undisturbed thin layers of oil slicks (<3 mm) for few hours, and therefore, have limitations when used under realistic marine conditions. The objective is to create an oil slick thickness, >3 mm, which is the minimum thickness that allows the oil to be ignited and burned off. However, chemical herding agents suffer from several limitations, for example, they work best under calm sea conditions, low wind velocity, no ice, and have a limited effectiveness of about an hour upon deployment. Furthermore, the herding agents themselves may be toxic. Effective sorbents for a crude oil spill cleanup should have important characteristics such as oleophilicity, hydrophobicity, oil retention capacity, and biodegradability. Crude oil sorbents can be classified into three basic categories, including inorganic mineral products, organic synthetic products, and organic vegetable products since sorption techniques are one of the most effective approaches for the treatment of crude oil spills. Inorganic sorbents include zeolites, silica, perlite, graphite, vermiculites, sorbent clay, diatomite, glass, wool, sand, and volcanic ash. Materials such as polypropylene and polyurethane are organic synthetic products. Natural organic sorbents include peat moss, wood fiber, cotton fiber, cellulose kapok fiber, kenaf, milkweed floss straw, hay, sawdust, ground corncobs, feathers, and other carbon-based products. However, these sorbent materials also showed limitations especially in the presence of waves and wind. The main drawbacks of plant-derived sorbents are their...
relatively low oil sorption capacity, low hydrophobicity, and poor buoyancy compared to synthetic sorbents, such as polypropylene. Considerable efforts have recently been devoted to the development of superhydrophobic herding materials including 3D aerogel of MOF/r-GO\(^6\text{,}^{10}\) and hydrophobic coating on fabrics.\(^{11,12}\) Once plant-derived sorbents are applied to saturated environments, preferential water sorption is favored over the sorption of crude oil because the sorbents are typically hydrophilic in nature. Agricultural byproducts have well-documented problems with water sorption and a lack of dimensional stability due to their associated hydroxyl functionalities. These groups are abundantly available in all three major chemical components of plant-based materials and are responsible for their hydrophilicity.\(^{13}\) Hydrophobicity (oleophilicity) is one of the major advantages of sorbents that influence the effectiveness of oil sorption in the presence of water. The effectiveness of the sorbents in saturated environments would be enhanced when the density of the hydroxyl functionalities is decreased.\(^{14}\) The hydroxyl functionality of these fibers can be reduced by chemical modification, such as acetylation, acylation, and alkylation.\(^{15}\) To overcome the limitations of available herding agents and sorbents, a next generation material is being sought by agencies charged with planning and overseeing spill response.

We have developed scalable sawdust-based prototype materials with desirable properties: buoyant in sea water, aggregates and maintains a thick oil slick, and supports materials with desirable properties: buoyant in sea water, and effective oil sorption (pine/OA-106 and pine/OA-124), where 106 and 124 means that they were developed by a chemical modification process.

**RESULTS AND DISCUSSION**

Pine wood flour (40–60 mesh) was selected for our work based on our previous work. It showed better exfoliation of cellulose networks than larger pine wood particles (10–20 mesh) or hardwood (maple) so that more OA molecules were infiltrated and reacted on the surface.\(^{6}\) Two base materials (pine/OA-106 and pine/OA-124), where 106 and 124 means that they were modified with C3, C6, C8, C10, C12, C14, C16, or C18 at 55 °C for 8 h. Figure 2a WPG of mixed fatty acid-modified aggregators with second fatty acids. When fatty acids with relatively short alkyl chains (C3, C6, and C8) were applied, their WPG of mixed fatty acid-modified aggregators were very low (0–2.0 wt %). The less hydrophobic character of the shorter alkyl chains was not enough to penetrate into OA surface layers on both pine/OA base materials. However, fatty acids with C10–C14 significantly contributed to WPG of both pine/OA-106 and pine/OA-124. Mixed fatty acid-modified aggregators with C16 fatty acid did not show much enhancement of WPG of both base materials, where large alkyl chains might be too bulky to penetrate into OA layers. The hydrophobic character of mixed fatty acid-modified aggregators was confirmed by a moisture sorption test in K2CO3 at 20 °C, where its relative humidity is 43.2 ± 0.4% (Figure 2b). Unmodified pine sawdust usually sorbs 3–3.5% moisture, and OA modification decreases moisture content down to 0.65–1.10 wt %, depending on the surface coverage. The further modification of the base materials with the second fatty acids significantly decreased their moisture sorption down to ≤0.1 wt %. This result was confirmed by our contact angle measurement. The contact angle of the unmodified pine sawdust was 106.0°. However, the substantial enhancement of the hydrophobic character of the surface of the OA- and mixed fatty acid-modified aggregators was clearly proven by increase in θ with the polar water: 133.07 (pine/OA-106), 133.78 (pine/OA-124), 134.69 (pine/OA-106-C10), 139.51 (pine/OA-106-C12), 136.98 (pine/OA-124-C10), and 135.06 (pine/OA-124-C12) (see Supporting Information Figure S1).

X-ray diffraction (XRD) patterns of unmodified, OA-modified, and mixed fatty acid-modified aggregators were collected, as shown in Figure 3. The main diffraction peaks of unmodified pine sawdust show a typical cellulose I crystalline structure at 2θ = 15.0, 16.2, 22.3, and 35.0, which are assigned to the diffraction planes of 110, 101, 002, and 040, respectively. Peaks with significantly reduced intensity (or complete disappearance) in three diffraction planes, 101, 10i, and 040, were observed in the pattern of the modified aggregators, which indicated that the structure of the cellulose was transformed to an amorphous structure after modification. (002) peak was maintained, but it showed a progressive broadening and exfoliation upon addition of the second fatty acid (Figure 3c). A d-spacing of unmodified pine sawdust used in this study was 3.98 Å. It was significantly increased (4.23 Å) when modified with OA. When further modified with second fatty acids, it increased up to 4.58 Å in pine/OA-124-C12,

---

**Table 1. Base Materials Modified with OA for Mixed Fatty Acid-Modified Aggregators in This Work**

| Base materials | Modification condition and WPG |
|----------------|--------------------------------|
| pine/OA-106    | T (°C) | reaction time (h) | WPG (%) |
| pine/OA-124    | 55     | 6               | 106.21  |
|                 | 55     | 8               | 124.34  |

---

modified with C3, C6, C8, C10, C12, C14, C16, or C18 at 55 °C for 8 h. Figure 2a WPG of mixed fatty acid-modified aggregators with second fatty acids. When fatty acids with relatively short alkyl chains (C3, C6, and C8) were applied, their WPG of mixed fatty acid-modified aggregators were very low (0–2.0 wt %). The less hydrophobic character of the shorter alkyl chains was not enough to penetrate into OA surface layers on both pine/OA base materials. However, fatty acids with C10–C14 significantly contributed to WPG of both pine/OA-106 and pine/OA-124. Mixed fatty acid-modified aggregators with C16 fatty acid did not show much enhancement of WPG of both base materials, where large alkyl chains might be too bulky to penetrate into OA layers. The hydrophobic character of mixed fatty acid-modified aggregators was confirmed by a moisture sorption test in K2CO3 at 20 °C, where its relative humidity is 43.2 ± 0.4% (Figure 2b). Unmodified pine sawdust usually sorbs 3–3.5% moisture, and OA modification decreases moisture content down to 0.65–1.10 wt %, depending on the surface coverage. The further modification of the base materials with the second fatty acids significantly decreased their moisture sorption down to ≤0.1 wt %. This result was confirmed by our contact angle measurement. The contact angle of the unmodified pine sawdust was 106.0°. However, the substantial enhancement of the hydrophobic character of the surface of the OA- and mixed fatty acid-modified aggregators was clearly proven by increase in θ with the polar water: 133.07 (pine/OA-106), 133.78 (pine/OA-124), 134.69 (pine/OA-106-C10), 139.51 (pine/OA-106-C12), 136.98 (pine/OA-124-C10), and 135.06 (pine/OA-124-C12) (see Supporting Information Figure S1).

X-ray diffraction (XRD) patterns of unmodified, OA-modified, and mixed fatty acid-modified aggregators were collected, as shown in Figure 3. The main diffraction peaks of unmodified pine sawdust show a typical cellulose I crystalline structure at 2θ = 15.0, 16.2, 22.3, and 35.0, which are assigned to the diffraction planes of 110, 101, 002, and 040, respectively. Peaks with significantly reduced intensity (or complete disappearance) in three diffraction planes, 101, 10i, and 040, were observed in the pattern of the modified aggregators, which indicated that the structure of the cellulose was transformed to an amorphous structure after modification. (002) peak was maintained, but it showed a progressive broadening and exfoliation upon addition of the second fatty acid (Figure 3c). A d-spacing of unmodified pine sawdust used in this study was 3.98 Å. It was significantly increased (4.23 Å) when modified with OA. When further modified with second fatty acids, it increased up to 4.58 Å in pine/OA-124-C12,

---

**Figure 1.** Illustration of hydrophobic modification of cellulose networks in sawdust.

---

properties, and crude oil capacities of the mixed fatty acid-modified aggregators were systematically evaluated. These aggregators exhibited enhanced sorption capacities relative to unmodified or oleic acid-modified aggregators for crude oil.
indicating that the substitution of hydroxyl groups by OA and second fatty acids breaks inter- and intramolecular hydrogen bonds of cellulose and decreases the degree of crystallinity. The crystallinity index determined in this study was 51.16% for the unmodified sawdust, 6.61% for OA-modified aggregators, and undetectable (0%) for the mixed fatty acid-modified aggregators. A major portion of cellulose is in a crystalline form due to intra- and intermolecular hydrogen bonding of hydroxyl groups. However, modification of the cellulose material often results in a decrease in crystallinity. The substitution of an alkyl group for a hydroxyl group reduces the density of hydrogen bonding because an alkyl group offers a more bulky branch (i.e., a decreased ability to form hydrogen bonding) than a hydroxyl group. Therefore, the fatty acid-modified aggregators will possess more desirable properties for crude oil sorption in an aqueous environment.

Figure 2. (a) WPG measurement and (b) moisture sorption results of mixed fatty acid-modified aggregators.

Figure 3. XRD traces of mixed fatty acid-modified sawdust aggregators: (a) pine/OA-106-modified, (b) pine/OA-124-modified sawdust aggregators, (c) change in d-spacing of (002) peak.
Appearance of new resonances in the spectra of modified sawdust indicates carbonyl groups in lignin. The peaks of fatty acids, hemicellulose, and lignin were assigned according to the literature and previous records. In the pine/OA base materials, a new resonance was observed that the single band in the unmodified pine sawdust was changed to double absorptive bands in all modified aggregators. The decrease in the intensity of the broad band around 3400 cm$^{-1}$, assigned to the cellulose O–H vibration, is additional proof of the successful esterification of sawdust powders. The minimal intensity of O–H vibration peaks of mixed fatty acid-modified aggregators with C10 or C12 was observed. A typical example of $^{13}$C cross-polarization magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectrum of unmodified sawdust is shown in Figure 5. The peaks are not well resolved due to the composite of cellulose, hemicellulose, and lignin. The resonance at 172.98 ppm indicates carbonyl groups in lignin. The peaks of fatty acids were assigned according to the literature and previous records. In the pine/OA base materials, a new resonance at 129.5 ppm is associated with unsaturated carbons of OA. The peak shifting (to 171.95 ppm) and increasing intensity in the carbonyl region was observed with OA- and mixed fatty acid modification due to esterification with fatty acids. Appearance of new resonances in the spectra of modified aggregators, typical of aliphatic hydrocarbons (14–40 ppm), gave additional evidence of the occurrence of the esterification reaction. The total relative intensity of these peaks is well correlated to the WPG of mixed fatty acid-modified aggregators (Figure 2a), as illustrated in Figure 5b,d, even though it is only suggestive. The direct comparison of relative area of crystalline and amorphous C4 (cellulose) peaks around 88 and 84 ppm for all spectra was not possible due to the modification of sawdust, rather than pure cellulose fibers.

Thermal gravimetric (TG) measurements were performed to evaluate the thermal properties of mixed fatty acid-modified aggregators by comparing the temperatures of the first derivative of the weight-loss curves. Thermal gravimetric analysis (TGA) and DTG (first differential TG) curves of all of the aggregators including unmodified pine sawdust are shown in Figure 6. The data of weight loss at 150 °C, initial decomposition temperature $T_d$ and decomposition temperature at maximum degradation rates, $T_{d1}$ and $T_{d2}$, for two sets of mixed fatty acid-modified aggregators are shown (Tables S1 and S2). The unmodified pine sawdust shows a single weight-loss step with a maximum at about 328 °C, where the decompositions of hemicellulose and cellulose were not separated in a 10 °C/min heating rate. The broad peak between 350 and 550 °C in DTG of unmodified sawdust is attributed to the decomposition of lignin. It was observed that mixed fatty acid-modified aggregators showed very similar thermal stability to those of OA-modified base materials due to their similar molecular structures, where the modification of sawdust with mixed fatty acids dramatically changed the thermal stability. Mixed fatty acid-modified aggregators started to decompose at temperatures (~160 °C), which were substantially lower than that of unmodified sawdust (>208 °C), and mixed fatty acid-modified aggregators with C10–C14 showed the lowest thermal stability, as seen from changes in $T_d$, $T_{d1}$ and $T_{d2}$ in Tables S1 and S2. This behavior is attributed to the further decrease in crystallinity associated with substitution of cellulose hydroxyls with second fatty acids. The thermograms of mixed fatty acid-modified aggregators showed two main separate degradation steps, with maximum degradation temperatures around 220 °C ($T_{d1}$) and 270 °C ($T_{d2}$), where $T_{d1}$ was assigned to the cellulose fraction the aggregators and $T_{d2}$ was attributed to the fatty acid fraction. It was also observed that the weight loss in initial temperature (150 °C) decreased with the second fatty acid substitution. This is attributed to less moisture content for the aggregators with the second fatty acid substitution. The second C10 and C12 substitution of pine/OA-106 and pine/OA-124 showed...
least moisture content, which is consistent with the moisture sorption data discussed earlier.

Scanning electron microscopic (SEM) images have been taken to investigate morphological changes of mixed fatty acid-modified aggregators after the second modification of OA-modified base materials. Figure 7 shows the cell structures parallel to the longitudinal directions of the surface of unmodified, OA-modified, and mixed fatty acid-modified aggregators. It was observed that the main structure was maintained, but individual cellulose fibers were separated after OA modification and even more separated after mixed fatty acid modification. This indicates that each individual cellulose fiber is exfoliated by infiltration of fatty acids into the cellular network in pyridine.

Figure 8a shows sorption capacity of mixed fatty acid-modified aggregators including OA-modified base materials. A modified sorption technique has been used to measure maximum crude oil sorption capacity because it is not easy to test crude oil-sorbed aggregators in seawater. Unmodified pine sawdust showed a high capacity of about 4.0 g crude oil per g pine sawdust. However, it showed ≤2.0 g of crude oil sorption in the presence of seawater but also minimal

Figure 5. $^{13}$C solid-state NMR spectra of unmodified, OA-modified, and mixed fatty acid-modified aggregators: (a, b) pine/OA-106, (c, d) pine/OA-124.
Figure 6. TGA and DTG plots of mixed fatty acid-modified aggregators: (a, b) pine/OA-106-modified and (c, d) pine/OA-124-modified aggregators.

Figure 7. SEM images of (a) untreated pine sawdust, (b) pine/OA-106, (c) pine/OA-106-C10, (d) pine/OA-106-C12, (e) pine/OA-124, (f) pine/OA-124-C10, and (g) pine/OA-124-C12. A scale bar in images indicates 100 μm.
buoyancy retention in wavy sea water. Oil sorption capacity of mixed fatty acid-modified aggregators was proportional to alkyl chain length of second fatty acids and showed maximum sorption capacities when the base aggregators were further modified with C12. The maximum capacity, 6.42 g/g, is 45.6% enhanced capacity relative to that of the base aggregator (pine/OA-106). Aggregators modified with longer alkyl chains (C14 and C16) showed decreased capacities. This crude oil sorption pattern is very consistent with moisture sorption, XRD, FT-IR, and 13C CP/MAS NMR data. When the best aggregator, pine/OA-106-C12, was recycled through multiple cycles (washed crude oil with dichloromethane and vacuum-dried), it showed pretty consistent sorption toward crude oil with 2.0–5.1% deviation (Figure 8b).

■ CONCLUSIONS

A cheap byproduct of sawmills, pine sawdust, has been modified with mixed fatty acids and deployed as a sorbent for crude oil spill treatment. The mixed fatty acid-modified aggregators showed hydrophobic, oleophilic, and excellent buoyancy in sea water, and their sorption capacities were substantially enhanced relative to those of OA-modified aggregators. Systematic characterization of mixed fatty acid-modified aggregators with moisture sorption, transformation of crystalline structure into amorphous structure and exfoliation of cellulose d-spacing (XRD), an increase of carbonyl and alkyl group, and a decrease of hydroxyl group (FT-IR, 13C CP/MAS NMR), and an initial decomposition and initial weight loss (TGA) is well aligned with final crude oil sorption data. These easy and inexpensive preparation, excellent buoyancy, biodegrability, and low water retention make the aggregators a very promising alternative for crude oil spill treatment.

■ METHODS

Chemicals and Materials. All chemicals were purchased from Sigma-Aldrich (St. Louis, MO) and used without further purification. Pine sawdust materials (40–60 mesh; 250–400 μm) were purchased from Marth Wood Shaving Supply Inc. (Marathon, WI). Before the reaction, all sawdust samples were vacuum-dried at 60 °C for 2–3 days to prevent the contamination of pyridine with water and the aggregation of the leaving group (p-toluenesulfonyl (p-Ts)) on sawdust samples.

Preparation of Mixed Fatty Acid-Modified Aggregators. Prior to the esterification reaction of sawdust with oleic acid, 3.48 g of p-TsCl was dissolved in 30 mL of pyridine, then 1.0 g of sawdust was added. The reaction flask was placed in a silicon oil bath (55–58 °C), and 5.0 g of oleic acid was slowly added to the mixture with vigorous stirring for 6, 8, or 10 h. Once reaction was completed, the newly synthesized aggregator was cooled, filtered, and ethanol-washed, followed by the Soxhlet extraction with ethanol. The final product was vacuum-dried at 60 °C overnight and ready for further modification with different fatty acids. The two base materials (pine/OA-106 and pine/OA-124) are further modified with C3, C6, C8, C10, C12, C14, C16, and C18 fatty acids using the same process (55 °C for 8 h).

Characterization. Synthesized aggregators were weighed to determine the WPG, [(weight gain/original weight) × 100]. After storing dry samples in saturated aqueous K2CO3 solution (43.2 ± 0.4 relative humidity (RH) at 20 °C) overnight, moisture sorption values were obtained. Formulation to calculate moisture sorption (%) was [increased weight/dry sample weight] × 100. XRD patterns of unmodified and modified aggregators were obtained by a desktop X-ray diffractometer (Rigaku, The Woodlands, TX) using Cu Kα (1.54059 Å) radiation with the X-ray generator operating at 20 kV and 30 mA. Data were collected for a 2θ range of 5.0–40.0° at an angular resolution of 0.01°/s. The crystallinity index (Ic) was determined using eq 1

\[
I_c = \frac{I_{(002)} - I_{(am)}}{I_{(002)}} \times 100 \tag{1}
\]

where \(I_{(002)}\) is the counter reading for the peak intensity at a 2θ angle close to 22° and \(I_{(am)}\) is the amorphous counter reading at a 2θ angle at approximately 18°. FT-IR spectra were recorded over a range from 400–4000 cm⁻¹ with a resolution of 2.0 cm⁻¹, using a Thermo Nicolet Nexus 670 FT-IR spectrometer (Thermo Scientific, Waltham, MA). 13C CP/MAS NMR spectra for a series of aggregators were performed at 11.4 T using a 600 MHz solid-state NMR spectrometer (Agilent) equipped with a 4 mm HFXY MAS probe. All 13C CP/MAS NMR spectra were obtained using a vender-supplied sequence (tancpx in VNMRJ, Agilent) with a 3 s recycle delay and 2 ms contact time at a 15 kHz spinning rate and at ambient temperature (~25 °C). The 2H NMR 90° pulse length was 5 μs. The 13C NMR chemical shift was externally calibrated with hexamethylbenzene (HMB) of 17.3 ppm relative to tetramethylsilane of 0 ppm. TGA was carried out by a NETZSCH STA 449 F1 analyzer equipped with an
alumina cell. Samples were heated at a constant rate of 10 °C/min from 25.0 to 700 °C, with an air flow of 50 mL/min and nitrogen (protecting gas) flow of 15 mL/min. The initial thermal decomposition temperature (T_d) was recorded when sample heating resulted in weight loss (≤0.5%). Materials were prepared for contact angle measurements by first affixing Scotch double-sided tape to a microscope slide and then pouring the sample material in excess on the tape. Material was then brushed with a gloved finger to remove any nonbond material. This slide was then placed on the stage of a ramé-hart 900-U1 automated goniometer. The goniometer was operated using DROImage Advanced v2.7.03 software to apply a 15 μL drop of 18 MΩ purified water to the sample surface. The drop was imaged with backlighting (adjusted to reduce impact of sample surface roughness) using a Basler GenICam. Each sample’s contact angle was determined as an average of 6 distinct 15 μL drops, with each drop being measured 40 times (8 measurements; 5 frames averaged per measurement). Sample imaging was performed using an AmScope MU1000 10 MP camera fixed to an AmScope T340B-LED trinocular compound microscope. The microscope stage at 10X magnification was calibrated using a NIST-certified micrometer, and sample images obtained using the AmScope v3.7.5849 software.

Sorption Test of Crude Oil. The American Society for Testing and Materials (ASTM) methods for oil sorption capacity measurements (F716-09 and F726-12) were considered suitable for testing the wood flour aggregators because the product stuck to the test vessel once it was coated with the added crude oil, leading inconsistencies in mass measurement. The sorption capacity of aggregator samples was tested with crude oil (West Texas Intermediate). Aggregator was weighed and the product stuck to the test vessel once it was coated with the oil that was sorbed by aggregator was assessed, and sorbed oil aggregator until it was saturated then weighed. The amount of oil sorbed by aggregator was calculated, and sorption measurements of crude oil were carried out in triplicate for each type of aggregator to get average and standard deviation values.

ASSOCIATED CONTENT

 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02293.

Water contact angle measurement and TGA/DTA data (Table) of aggregators (PDF)

AUTHOR INFORMATION

*E-mail: yongsoon.shin@pnl.gov.

ORCID

Yongsoon Shin: 0000-0001-7132-2670
Kee Sung Han: 0000-0002-3535-1818
Hongkyung Lee: 0000-0002-7732-2089

Present Address

G.T.B.: Chemical & Biological Signature Science, Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99352, United States and Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164, United States

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Y.S. prepared all samples and characterized them by XRD, FT-IR, and TGA, E.M.W. and G.B. tested crude oil sorption, K.S.H. conducted SSNMR, and H.L. recorded SEM.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by Laboratory Directed Research and Development (LDRD) of Pacific Northwest National Laboratory (PNNL). The NMR measurements were performed at the Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by the DOE’s Office of Biological and Environmental Research and located at PNNL. PNNL is operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC05-76RL01830.

REFERENCES

(1) Teas, C.; Kalligeros, S.; Zanikos, F.; Stournas, S.; Lois, E.; Anastopolous, G. Investigation of the effectiveness of absorbent materials in oil spill cleanup. Desalination 2001, 140, 259–264.
(2) Bureau of Safety and Environmental Enforcement (BSEE). Annual Report 2016, January, 2017; pp. 35–36.
(3) Mitsch, W. J. The 2010 oil spill in the Gulf of Mexico: What would Mother Nature do? Ecol. Eng. 2010, 36, 1607–1610.
(4) Ross, S. L. Environmental Research, Final Report on “Research Using Oil Herding Agents for Rapid Response In Situ Burning of Oil Slicks on Open Water.” Report to US Department of the Interior, Bureau of Safety and Environmental Enforcement (BSEE), Oil Spill Response Research (OSRR) Program, Feb 28, 2012.
(5) Adelaja, M. O.; Frost, R. L.; Klopogge, 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.
(6) She, D.; Sun, R. C.; Jones, G. L. Chemical Modification of Straw as Novel Materials for Industries. Cereal Straw as a Resource for Sustainable Biomaterials and Biofuels, Chemistry, Extractives, Lignins, Hemicelluloses and Cellulose; Sun, R. C., Ed.; Elsevier, 2010; pp 209–217.
(7) Annunziato, T. R.; Sydenstricker, T. H. D.; Amico, S. C. Experimental investigation of various vegetable fibers as sorbent materials for oil spills. Mar. Pollut. Bull. 2005, 50, 1340–1346.
(8) Bayat, A.; Aghamiri, S. F.; Mohab, A.; Vakili-Nezhad, G. R. Oil spill cleanup from seawater by sorbent materials. Chem. Eng. Technol. 2005, 28, 1525–1528.
(9) Ge, M.; Cao, C.; Huang, J.; Zhang, X.; Tang, Y.; Zhou, X.; Zhang, K.; Chen, Z.; Lai, Y. Rational design of materials interface at nanoscale towards intelligent oil–water separation. Nanoscale Horiz. 2018, 3, 235–260 and references therein.
(10) Mao, J.; Ge, M.; Huang, J.; Lai, Y.; Lin, C.; Zhang, K.; Meng, K.; Tang, Y. Constructing multifunctional MOF@rGO hydro-/aerogels by the self-assembly process for customized water remediation. J. Mater. Chem. A 2017, 5, 11873–11881.
(11) Cao, C.; Ge, M.; Huang, J.; Li, S.; Deng, S.; Zhang, S.; Chen, Z.; Zhang, K.; Al-Deyab, S. S.; Lai, Y. Robust fluorine-free superhydrophobic PDMS–ormosil@fabrics for highly effective self-cleaning and efficient oil–water separation. J. Mater. Chem. A 2016, 4, 12179–12187.
(12) Gao, S.; Dong, X.; Huang, J.; Li, S.; Li, Y.; Chen, Z.; Lai, Y. Rational construction of highly transparent superhydrophobic coatings based on a non-particle, fluorine-free and water-rich system for versatile oil-water separation. Chem. Eng. J. 2018, 333, 621–629.
(13) Nwadiogbu, J. O.; Okoye, P. A. C.; Ajiwe, V. I. E.; Nnaji, J. N. J. Hydrophobic treatment of corn cob by acetylation: kinetic and thermodynamic studies. J. Environ. Chem. Eng. 2014, 2, 1699–1705.
(14) Bodirlau, R.; Teaca, C. A. Fourier transform infrared spectroscopy and thermal analysis of lignocellulosic fillers treated with organic anhydride. Rom. J. Phys. 2009, 54, 93–104.
(15) Sun, X. F.; Sun, R. C.; Sun, J. X. Acetylation of sugarcane bagasse using NBS as a catalyst under mild reaction conditions for the production of oil sorption-active materials. Bioresource Technol. 2004, 95, 343–350.
(16) Ali, N.; Eliyas, M.; Al-Sarawi, H.; Radwan, S. S. Hydrocarbon-utilizing microorganisms naturally associated with sawdust. Chemosphere 2011, 83, 1268–1272.
(17) Kosaka, P. M.; Kawano, Y.; Salvadori, M. C.; Petri, D. F. S. Characterization of ultrathin films of cellulose esters. Cellulose 2005, 12, 351–359.
(18) Yang, Z.; Xu, S.; Ma, S.; Wang, S. Characterization and acetylation behavior of bamboo pulp. Wood Sci. Technol. 2008, 42, 621–629.
(19) Yui, T.; Taki, N.; Sugiyama, J.; Hayashi, S. Exhaustive crystal structure search and crystal modeling of β-chitin. Int. J. Biol. Macromol. 2007, 40, 336–343.
(20) Wang, L.-Q.; Shin, Y.; Samuels, W. D.; Exarhos, G. J.; Moudrakovski, I. L.; Terskikh, V. V.; Ripmeester, J. A. Magnetic resonance studies of hierarchically ordered replicas of wood cellular structures prepared by surfactant-mediated mineralization. J. Phys. Chem. B 2003, 107, 13793–13802.
(21) Haw, J. F.; Maciel, G. F.; Schroeder, H. A. Carbon 13 nuclear magnetic resonance spectrometric study of wood and wood pulping with cross polarization and magic angle spinning. Anal. Chem. 1984, 56, 1323–1329.
(22) Vane, C. H.; Martin, S. C.; Snape, C. E.; Abbott, G. D. Degradation of lignin in wheat straw during growth of the oyster mushroom (pleurotus ostreatus) using off-line thermochemolysis with tetramethylammonium hydroxide and solid-state 13C NMR. J. Agric. Food Chem. 2001, 49, 2709–2716.
(23) Jandura, P.; Kokta, B. V.; Riedl, B. J. Fibrous long-chain organic acid cellulose esters and their characterization by diffuse reflectance FT-IR spectroscopy, solid-state CP/MAS 13C-NMR, and X-ray diffraction. Appl. Polym. Sci. 2000, 78, 1354–1365.
(24) http://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi.
(25) Ushanov, P.; Johansson, L.-S.; Maunu, S. L.; Laine, J. Heterogeneous modification of various celluloses with fatty acids. Cellulose 2011, 18, 393–404.
(26) Maunu, S. L. NMR studies of wood and wood products. Prog. Nucl. Magn. Reson. Spectrosc. 2002, 40, 151–174.
(27) ASTM F716-09, Standard Test Methods for Sorbent Performance of Absorbsents, ASTM International, West Conshohocken, PA, 2009, and ASTM F726-12, Standard Test Method for Sorbent Performance of Adsorbents; ASTM International: West Conshohocken, PA, 2012.