Superswelling Hybrid Sponge from Water Glass for Selective Absorption of Crude Oil and Organic Solvents

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ABSTRACT: A lightweight super hydrophilic hybrid sponge is designed and demonstrated out of water glass and an organic polymer, which has a macroporous flaky nature and is superflexible with an apparent density of 0.069 g cc−1, ∼97% porosity, and 3000% water uptake. The octadecyltrimethoxy silane-modified hybrid sponge exhibits selective absorption of oil and organic solvents in open water. An absorption capacity in the range 12−23 g g−1 for the test liquids light crude oil, engine oil, paraffin oil, chloroform, kerosene, and hexane is revealed. Absorption capacity by a weight basis was directly proportional to the density and inversely proportional to the viscosity of test liquids. Trials under both stagnant and turbulent conditions verify selective uptake of oil from sea water. Complete regeneration of the absorbent was possible for ten cycles for the test liquids. The work provides design of an affordable water clean-up material alternative to commonly used polyurethane sponges.

1. INTRODUCTION

Oil and its derivatives, during drilling, transportation, and storage, pose subsequent risk of spillage, which is an environmental catastrophe. The depth at which the oil spills, either deep water or surface spillage, prevents the evaporation of many volatile organic components, triggering the rise in concentration beyond the solubility in sea water.1,2 This calls for the deployment of oil removal techniques either solely or in combination for an effective response.3 Taking out a considerable amount of oil at a relatively faster rate will be the suitable remediation. The use of universal absorbents is not suitable for application-specific studies that require super-hydrophobic and superoleophilic properties. Chemical dispersants,4,5 mechanical containments,6 oil absorbents,7,9,10 and in situ burning are seemingly the best followed strategies at present. Sugar-based gelators have freshly been stated to absorb crude oil effectively.12,13 Recently, membranes have been used for the separation of water from oil in water emulsions.14−16 The effectiveness of the employed methods hinges on several parameters like the viscosity of the oils, weather conditions, temperature, time passed, and so on. Skimmers and oil absorbents are actually in the limelight as they could remove oil without leaving any residue. As the spilled oil layer becomes thinner, a decrease in the efficiency of skimmers is noticed.6 When natural fibers are used, being hygroscopic, a compromise in the selectivity of the absorbent is evident.7,10 Materials that are highly compressible, soft, and porous with excellent capacity for the absorption of solvents are generally labeled sponges.19 Spongy materials serve in different fields of science and engineering as filter aids, absorbent/absorbent materials, drug delivery vehicles, impervious surface cleaning materials, and so on. The leading application is in the field of oil absorption.20,1,2 A sponge substrate offers good oleophilicity, elasticity, and high porosity and is made out of water-soluble polymers.21 Poly(vinyl alcohol) is contemplated as the most attractive polymer for making three-dimensional matrices as it possesses excellent properties like biocompatibility.
mechanical strength, flexibility, biodegradability, cheapness, lower toxicity, and a good degree of hydrophilicity. The PVA formaldehyde sponges with a macroporous structure have been successfully used for oil absorption studies in the past. PVA reacts with formaldehyde in pairs and hence leaves lots of isolated surface −OH groups, which are available for surface modification. Proper surface engineering aids the use of these sponges in oil absorption studies. This situation gives scope for the design and development of a wide variety of synthetic materials. An ideal oil absorbent should be superhydrophobic and superoleophilic, should possess high selectivity in oil–water separation, and also could be regenerated. By selective pruning of the flaws in the mentioned materials, better performance is obtained for different engineered sorbents.

Recently, much emphasis is given to the study of porous silica worldwide. Inorganic silica materials and polymeric macroscopic networks as such possess lower oil absorption capacities (<2 g g⁻¹) due to their abundant surface −OH groups. They as such absorb water that is several times their preliminary mass. Absorbents with hydrophobic surface coverage based on different raw materials like aerogels, foams, sponges, carbon nanotubes, and so on have been noticeably excellent due to their super-hydrophobic and superoleophilic properties, faster kinetics, recovery, and reusability. Studies reveal that the surface functionalization of commercially available sponges with their three-dimensional macroscopic nature and open-cell structure may well produce high-performance oleophilic absorbents that are easy to handle. The common functionalities include stearoyl chloride, styrene(divinyl benzene), silanes like polydimethoxysilane (PDMS), octadecylsilane (OTS), methyltrimethoxysilane (MTMS), aminopropyltrimethoxysilane (APTMS), 1H,1H,2H,2H-perfluoroctyltriethoxysilane (HFOTES), and still more. Silanes, which are a homologous series of inorganic compounds depending on their surface functional groups, could offer a varied range of hydrophobicities on functionalization.

In this work, we have designed an innovative lightweight, super-swellable water glass sponge absorbent out of inorganic sodium silicate in which the macroporous structural stability is provided by organic poly(vinyl alcohol) through simple cross-linking and polymerization. Water glass is a very cheap and available material and is rarely explored for absorption applications. The hybrid material clubbing the property of both inorganic porous silica and organic polymers could be superior to the conventional absorbents. The hybrid material is effectively surface-modified with silanes to deliver hydrophobic sponges for the absorption of lower-, medium-, and high-density/viscosity oils. The absorbent is tested under stringent conditions for evaluating the absorption, regeneration, and reusability competencies.

2. RESULTS AND DISCUSSION

Water glass-based hybrid sponges were successfully synthesized as per the procedure outlined. PVA is an extremely lathering organic polymer, and it along with the surfactant PEG is able to form a white creamy foam base that is prepared to incorporate the inorganic silica. The organic part delivered the necessary strength for the otherwise crumbled material that could be produced from sodium silicate alone. Figure 1 exhibits the synthesis scheme for the preparation of an IOHS, and the material was seen to be floating in nature with numerous dangling surface hydroxyl groups.

Figure 1. Synthesis scheme for inorganic–organic hybrid sponges (IOHS).

Figure 2 displays the physical properties of the IOHS. The fashioned absorbent material was superflexible with a spongy nature and was superhydrophilic. The superflexible and spongy nature is due to the flexible film-forming property of PVA. The inorganic counterpart added superhydrophilicity to the absorbent with the plentiful hydroxyl groups from sodium silicate. Since silica sol is capable of undergoing gelation in the presence of acid at appropriate pH via hydrolysis and condensation, the siloxane bonds formed via addition of silica sol to the already lathered solution hemmed in an interconnected network with the hydroxyl groups of partly cross-linked PVA, resulting in fine-looking hybrid sponges with multifunctional properties. The synthesized sponges hereafter entitled inorganic–organic hybrid sponges (IOHSs) have an apparent density of 0.069 g cc⁻¹ with ~97% porosity. The thermal conductivity of the sample is recorded to be 0.041 W/m K, which is very low, conveying that the heat transfer through the material is poor, which is supported by its macroporous nature. In materials like aerogels, sponges, foams, and so on, the molecules are not tightly packed, and hence heat cannot find a way to propagate through the void-filled networks. The water absorption capacity of the material is tested over 20 cycles to study the superhydrophilic property exhibited, and the absorbent was capable of absorbing water approximately 30 times its own weight even after repeated squeezing. A video showing the superswellable nature of the sponge is provided in Movie S1 of the Supporting Information. The photographic images of the hybrid sponge support its lightweight nature due to its lower density.

To make use of the material for solvent and oil absorption, the surface has to be tailored to meet the definite requirements of a superhydrophobic and superoleophilic nature. Different silanes are capable of forming surface siloxane bonds with the hydroxyl groups, and hence the larger the number of surface hydroxyl groups, the more the moieties that will be available for functionalization. The hydrophobic and oleophilic nature of silanes depends upon their linker or alkyl chain length and the terminal −R groups. The degree of hydrophobicity can be understood from the water contact angle measurements of the sponge samples.

2.1. Water Contact Angle (WCA) Measurements. The WCA measurements of the samples are pictured in Figure 3. For the PVA–formaldehyde sponge, the contact angle was 73
± 1° owing to its hydrophilic nature. The unmodified IOHS was superhydrophilic with a contact angle of <1°, which is imparted by the additional surface −OH groups from sodium silicate. When the surface is functionalized with silanes, the contact angle improved, showing a hydrophobic nature. This enhancement in the hydrophobic and oleophilic nature is established by the presence of abundant surface −OH groups from both PVA and sodium silicate that were available for the alkyl chains of silane to react, thereby imparting the water repellence property. The measured contact angle values were 108 ± 1, 115 ± 0.8, and 124 ± 1° for IOHSV, IOHSE, and IOHSO samples, respectively. Since OTMS has a long alkyl chain or linker length, the number of surface hydrophobic groups will be more and hence better hydrophobicity for the IOHSO sponge. IOHSE falls second due to its numerous surface methyl groups followed by the IOHSV absorbent. The adhesive force between the water droplet and the sample surface decreases in the order 144 < 93.05 < 49.75 < 41.57 < 31.74 mJ m⁻² for the IOHS, PVA sponge, IOHSV, IOHSE, and IOHSO, respectively. This shows that with an increase in

Figure 2. Physical properties of IOHS, showing the water uptake graph over 20 cycles of study, density, porosity, thermal conductivity, superflexible nature, and the digital photographic images of hybrid sponges.

Figure 3. Contact angle measurements for (a) PVA sponge, (b) IOHS, (c) IOHSV, (d) IOHSE, and (e) IOHSO.
hydrophobicity, the water molecules find it difficult to get attached to the substrate surface.

### 2.2. Surface Morphology Analysis

The SEM micrographs of the samples are presented in Figure 4. The PVA sponge (Figure 4a,b) has a three-dimensional highly networked macroporous arrangement. For the IOHS, the whole morphology is transformed into a flaky porous structure as is visible in Figure 4c,d, showing the reaction of the polymer with sodium silicate. Figure 4e–g shows the structures for hydrophobic IOHSO, IOHSE, and IOHSV sponges, respectively. For IOHSO, the morphology is with numerous struts and convolutions, which is due to the hanging of long organic chain groups from the surface. Due to the shorter alkyl chain length, IOHSE and IOHSV show a more sheet-like surface. The more convoluted surface of IOHSO may be the reason for its higher contact angle.

The elemental mapping and EDAX spectrum of the samples are revealed in Figure 5. The EDAX spectra reveals the presence of the elements carbon (red), oxygen (green), silicon (yellow), and sodium (white). From the elemental mapping, we can comprehend an increase in the organic content of the sample, and it is reflected in the concentration of carbon in the images. Also, the addition of silanes led to an increased density of elemental Si in the maps.

### 2.3. FTIR Analysis

The ATR-IR spectra of the samples studied are represented in Figure 6. For the pure PVA sponge, in the region 1000 to 1400 cm\(^{-1}\), five bands were observed at 1380, 1330, 1240, 1135, and 1085 cm\(^{-1}\), which are probably associated with the motions of the substituent groups CH\(_2\), C–O–C, and so on in the material, the last band arising from the stretching of the C–O bond. The assignments of the bands at around 3400, 2925 and 2827, and 1466 cm\(^{-1}\) is for the O–H stretching, C–H stretching, and C–H bending vibrations, respectively.\(^{47,48}\) The peak at 785 cm\(^{-1}\) is from the C–C bond.\(^{49}\) The peak at 1646 cm\(^{-1}\) is related to the O–H bending vibration of physically absorbed water.\(^{50}\) The characteristic peaks for silica were detected at 443, 802, and 1100 cm\(^{-1}\) equivalent to O–Si–O, Si–OH, and Si–O–Si bonds, which implies the condensation of silicon alkoxide.\(^{39,42,50}\) The high-intensity silica peaks for IOHSO confirm that the silane content is high in this sample compared to those in others. Also, intense peaks were observed for C–H stretching vibrations, which are attributed to the long alkyl chains.

### 2.4. Wide-Angle XRD (WAXD) Analysis

Figure 7 shows the wide-angle XRD pattern of the samples studied. For the pure PVA sponge, the fundamental peak of PVA is observed at 2\(\theta\) = 19.6\(^\circ\).\(^{51}\) The broad peak detected at 2\(\theta\) = 23\(^\circ\) for the IOHS is from amorphous silica.\(^{40}\) The silane-modified samples reflect a broad peak between 15 and 25\(^\circ\), which is attributed to the overlapping of peaks from both PVA and silica. The PVA peak decreases when silica is introduced in the material, which
is indicative of the cross-linking reaction between PVA and sodium silicate. The high-intensity peak observed for IOHSO signifies that the silica content is larger in the IOHSO sample followed by IOHSE and IOHSV in that order.

2.5. Thermogravimetric Analysis. The TG analysis of the samples studied is represented in Figure 8. The pure PVA sponge shows complete decomposition due to its pure organic nature. At 150 °C, all the samples show weight loss due to dehydration. The second-stage weight loss for the IOHS is from the decomposition of organic groups from PVA, and the weight loss for IOHSE and IOHSV is due to loss of organics from PVA and the respective silane used for surface modification. IOHSO exhibits a three-stage weight loss. The initial one is due to loss of moisture, the second weight loss is attributed to the ligand organic moiety decomposition, and the final weight loss is due to the loss of alkyl chains, which is supported by the two sharp exothermic peaks at around 250 and 300 °C in the DTA curve. Depending upon the length of the alkyl chain of the silanes modified, the weight loss percentage also increases, attributable to the increase in the number of organic moieties present. After a temperature of 350 °C, the weight loss is high due to the oxidation of Si–R groups to Si–OH. This is also confirmed by the DTA peak of the samples. The weight loss percentage increases in the order 51.2, 72.1, and 79.8 for IOHSE, IOHSV, and IOHSO, respectively, which is in proportion to the organic content present in the samples.

2.6. Analysis for Performance Properties. 2.6.1. Dynamic Degradation Studies. The dynamic degradation studies are directed to determine the buoyancy and hydrophobic and oleophilic properties of the sample. If greater than 10% of the sorbent is observed to sink in the water column or if the column is contaminated with loose sorbent particles, then the absorbent is considered to be a failure and not recommended for use in open waterways.

From the buoyancy studies shown in Figure 9a, it is noticed that after shaking for 15 min, the water column is not tainted by any loose absorbent particles, indicative of the fact that the absorbents are fit for use in open waterways.

The water absorbency ratio of the sample is calculated from the succeeding equation

\[
\text{water absorbency} = \frac{S_W}{S_O}
\]

where \(S_O\) is the initial dry absorbent weight and \(S_W\) is the net water absorbed, which is calculated as \(S_{WT} - S_O\) where \(S_{WT}\) is the weight of absorbent samples at the end of the water test.
Figure 9b shows the plot for the water absorbency ratio by weight. The high uptake ratio for IOHSV is the indication that the material has free surface −OH groups even after the silane treatment. After 15 min, the percentages of water absorbed for the samples IOHSO, IOHSE, and IOHSV are 9.75, 15.06, and 17.53%, respectively, which points to the fact that the sample IOHSO passes the buoyancy test whereas IOHSE and IOHSV are reflected as a failure since >10% water uptake is recorded.

The oleophilic nature of the samples is clearly evident from Figure 10. There is no existence of an oil sheen on the water surface after study, pertaining to the oleophilic nature of the absorbent after the absorption time period.

From the dynamic degradation studies, it is marked that the sample IOHSO possesses all the properties of buoyancy, hydrophobicity, and oleophilicity whereas the samples IOHSE and IOHSV are oleophilic but, in unison, the water absorbency is relatively more, which makes them unfit for use in open water bodies.

2.6.2. Oil Absorption Studies. The oil absorption studies are conducted for all the three hydrophobic sponges IOHSV, IOHSE, and IOHSO. Oil absorbency is defined as the ratio of oil absorbed to the dry absorbent weight as calculated from the equation below:

\[
\text{oil absorbency} = \frac{S_S}{S_O}
\]

where \(S_O\) is the initial dry absorbent weight and \(S_S\) is the net oil absorbed, which is calculated as \(S_S = S_T - S_O\) where \(S_T\) is the weight of absorbent samples at the end of the oil test.

The results for the oil absorption studies conducted for a period of 15 min for different hydrophobic samples are shown in Figure 11.

For IOHSV, the absorption capacity is very low for all the test liquids. TMES and OTMS silane-functionalized samples exhibited better absorption capacities for the six test liquids. IOHSO displayed comparatively higher absorption potential, which is due to the long-order alkyl chains of the silane. The improved absorption capacity can be explained based on the alkyl chain length and number of surface hydrolyzable groups present in the silanes.

The three hydrolyzable methoxy groups of VTMS react with three −OH groups of silica to form siloxane bonds with the end chain −CH=CH2 and methanol as a byproduct (Figure 13a). The extent of reaction rests on the large availability of surface hydroxyl groups from sodium silicate and unreacted −OH groups from PVA. The reaction of OTMS with silica is conversely similar, with the end chain being very long, that is, −CH2−(CH2)16−CH3. Here also, the byproduct is methanol (Figure 13b). In both these cases, one mole of silane can react...
with three hydroxyl groups. In the case of TMES, one mole of silane is capable of reacting with only one hydroxyl group. Thus, more silane is required for proper surface coverage in TMES as compared to OTMS and VTMS. However, the surface is crowded with more methyl groups that may help in improving the hydrophobicity of the functionalized absorbent material. Also, the byproduct is ethanol, which has lower toxicity.

The enhancement in hydrophobicity can be identified from the contact angle measurements. With an increase in the alkyl chain length, the water contact angle will be improved, and also, aligned long alkyl chains ($n \geq 12$) can repel the water from the surface because of their low surface energies.\textsuperscript{42} Due to the short alkyl chain length of TMES and VTMS, their contact angle is lower in comparison with the sample IOHSO, which is functionalized with OTMS. For IOHSV, an ordered range of surface coverage was not achieved, which is reflected in the lower contact angle value of $108 \pm 1^\circ$. In addition to the linker length, the presence of $-R$ groups in silane also adds to the hydrophobic nature of the absorbent. The existence of surface methyl groups imparted hydrophobicity to IOHSE (Figure 12).
Here, each silane molecule is endowed with three methyl groups, the end result being an absorbent surface swarming with $-\text{CH}_3$ groups, and hence a higher contact angle could be expected. Nevertheless, due to the steric hindrance, the surface coverage was not of a well-organized nature, which may have led to a lower contact angle of $115 \pm 0.8^\circ$. For OTMS, owing to the presence of its C18 chain, a long-range order with well-aligned surface coverage was possible, and hence an improved contact angle of $124 \pm 1^\circ$. The FTIR spectra reflect the existence of a large number of carbon groups with high-intensity $-\text{CH}$ stretching vibrations. The intensities of silica peaks were also high in IOHSO followed by IOHSE and IOHSV. This adds to the theory that OTMS silane was better capable of adhering to the superhydrophilic absorbent surface than the two other silanes. It is further supported by the diffraction intensity peaks in WAXD analysis. Here also, the silica content is larger for IOHSO followed by IOHSE and IOHSV. The absorbent sponges with high organic content are observed to have higher weight loss by thermogravimetric analysis. Consequently, among the silane-functionalized hybrid absorbents, weight loss is more for IOHSO followed by IOHSE and IOHSV. The results are in agreement with the SEM morphology, which shows a more sheet-like surface for IOHSV and IOHSE but a highly convoluted ordered surface morphology for IOHSO.

The lower contact angle of IOHSV is the reason for its higher water uptake. High water absorption means a less oleophilic nature, and the same is reflected in the oil absorption studies with the six chosen test liquids. Among the three hydrophobic sorbents, IOHSV possessed the lowest absorption capacities for all the test liquids. IOHSE shows better oil and solvent uptake compared to IOHSV, which is due to the existence of abundant surface methyl groups. For both IOHSO and IOHSE, the oil absorption capacities were more or less the same. However, due to the slow increase in the water absorption nature of IOHSE, when it comes to a mixture of water and oil, the selectivity of the absorbent will be at stake. For OTMS-modified sponges, the water uptake is much less, and also the absorption capacity recorded was very good due to their long-range order of alkyl chains and improved contact angle. In IOHSE, the linker or alkyl chain length determines the hydrophobicity, whereas in IOHSE, the surface methyl groups play a crucial role in imparting a hydrophobic nature. The oil absorption studies show that as the density of the test liquid increases, an increase in absorption capacity is observed since higher density means larger mass and hence an increase in weight. Of all the test liquids, chloroform has a higher density of 1.49 g cm$^{-3}$ and it is a low-viscosity liquid with 0.53 cP. Due to its lower viscosity, it can easily penetrate through the pores of the absorbent. Also, the higher density of the liquid is reflected in the absorption capacity values. From the studies, it is evident that the density and absorption capacity are directly proportional, whereas the viscosity and absorption capacity maintain an inverse proportionality relation. Light crude oil from a petroleum fraction was also selected for the study. The density of the crude was measured and found to be 0.64 g cc$^{-1}$ with a viscosity of 8.04 cP. The absorption capacity for crude oil increases in the order IOHSE < IOHSO < IOHSV with values 12.11, 15.04, and 18.55 g g$^{-1}$, respectively.

For the use of the hybrid sponge under practical conditions, seawater from Vizhinjam local beach was collected, and the water absorption was recorded. Figure 14a shows the hydrophobic sponges before and after absorption, and the water uptake is plotted in Figure 14b. Here, the uptake capacity increases in the order IOHSO < IOHSE < IOHSV with percentages of water absorption of 8.72, 10.63, and 13.73%, respectively, for a time interval of 15 min. It is observed that in sea water, the uptake for IOHSE and IOHSV is less compared than that of ordinary water and also fails to keep up with the ASTM standards.

Since of all the three hybrid sponges IOHSV, IOHSE, and IOHSO, the maximum expectations are met by IOHSO, IOHSO sponge is studied for its regeneration ability in hexane media, and the results are presented in Figure 15. It can be emphasized that hexane serves as an excellent solvent for regeneration of the absorbent material, and in a ten-cycle study conducted with viscous engine oil, the absorption capacity remained essentially the same. The absorption capacity of IOHSO for Castrol 4T engine oil with 6600 cP viscosity is 16.38 g g$^{-1}$.

Then again, under real environmental conditions, the water is not stagnant. Hence, the absorption of engine oil under turbulent conditions were tested, and the results are presented...
in Figure 16, which shows the digital photographs illustrating the progress of absorption of engine oil under stagnant and turbulent conditions. The sponge was found to be a success under both conditions.

The repeated absorption and squeezing of a low-viscosity test liquid (kerosene) by the IOHSO absorbent sponge is provided in Supporting Information, Movie S2. A study was also conducted to identify the absorption of high-density liquids in water. Chloroform was chosen as the test liquid, which has a density of 1.49 g cm$^{-3}$, which is higher than that of water (1 g cm$^{-3}$). The hybrid absorbent sponge was capable of effortlessly removing the chloroform completely from water (Figure 17), and a video illustrating this is provided in Supporting Information, Movie S3.

For light crude oil, complete regeneration of the absorbent was not possible due to the presence of other impurities like asphalts, sulfur, and so on. However, the absorption capacity over repeated cycles was found to be more or less the same. An additional study was conducted to understand if the IOHSO absorbent was capable of selective absorption of crude oil from sea water. As evidenced by Figure 18, the absorbent sponge could take up crude oil selectively from sea water.

3. CONCLUSIONS

Water glass-based hybrid sponge absorbents with superhydrophilicity were successfully synthesized, which possessed multifunctional properties like low density, superflexibility, very low thermal conductivity, and excellent water absorption capability. The material of interest was specifically focused on organic solvent and crude oil absorption and was surface silane-functionalized for studying the absorption. The tailoring from superhydrophilic to hydrophobic was confirmed from contact angle measurements. It was recorded that the long alkyl chain length of silane and the surface functional groups could bring about oleophilic and hydrophobic qualities of the absorbent sponge. The absorption capacity increases with an increase in density and decreases with an increase in viscosity of the test liquids. The absorbent material surface-functionalized with long-alkyl-chain silane has the potential to be used in both open waterways and a sea water environment, which makes the absorbent a prospective candidate. However, studies on scaling up the absorbent to meet practical situations and complete regeneration of the sponge after crude oil absorption require further attention.

4. EXPERIMENTAL SECTION

4.1. Chemicals and Materials. All the chemicals used in this work were of reagent grade and used without any further treatment. Sodium silicate with 7.5–8.5% Na$_2$O and SiO$_2$ 25.5–28.5% SiO$_2$ purchased from Merck (Germany) was used as the inorganic silica source. Octadecyltrimethoxysilane (OTMS) and vinyl trimethoxysilane (VTMS) were procured from Sigma Aldrich (USA). Trimethylethoxysilane (TMES) from Fluka was used. Poly(vinyl alcohol) (PVA; 86–89% hydrolyzed) was purchased from Alfa Aesar. Hydrochloric acid (HCl), poly(ethylene glycol) (PEG), and formaldehyde were procured from Merck, India. 20W-40 4T engine oil from Castrol India Ltd. (Mumbai), crude oil from Kochi Refinery Ltd., paraffin oil and other organic solvents (hexane and toluene) from Fisher Scientific India, and kerosene purchased from the local market were used as adsorbates.

4.2. Inorganic–Organic Hybrid Sponge (IOHS) Synthesis. The synthesis procedure for the preparation of a stable IOHS, which was standardized after numerous attempts by trial and error, is detailed as follows: The IOHS was prepared by cross-linking and polymerization of the precursors 10 wt %
PVA solution, PEG, silica sol, 37% formaldehyde, and 50% HCl. The volume ratio of silica sol to PVA solution is maintained as 1:0.4. Initially, the PVA solution was vigorously agitated with PEG to form a smooth foam followed by the addition of a previously prepared silica sol (sodium silicate was dissolved in distilled water and made up to 25% homogeneous solution at pH 4), formaldehyde, and HCl in succession. The whole process is carried out at 80 °C. When the solution became viscous, it was immediately transferred to a mold and kept intact for 4 days after which the synthesized sponge is squeezed and washed with surplus water until the pH of the supernatant turned neutral. The sponge is squeezed to remove all the water, kept in hexane for solvent exchange of the residual water trapped in the inside pores, and dried under ambient conditions. For comparison purposes, the PVA–formaldehyde sponge without any silica was also prepared.

4.2. Preparation of Hydrophobic Sponges. Three silanes, octadecyltrimethoxysilane (OTMS), vinyl trimethoxysilane (VTMS), and trimethylsilylthoxyxilane (TMES), were studied for imparting hydrophobicity to the samples. The prepared IOHS after solvent exchange with hexane is placed as such in a mould and allowed to cure for 24 h. The samples were denoted as IOHSO, IOHSV, and IOHSE for OTMS-, VTMS-, and TMES-modified hydrophobic sponges, respectively.

4.3. Characterization of Hybrid Sponges. The thermal conductivity of the absorbent material is found using the instrument KD2 Pro (Decagon Devices, Inc.). The micro-morphological features of the samples were investigated using scanning electron microscopes (SEM) Zeiss EVO 18 cryo SEM and JOEL JSM-5600LV. A XEUS SAXS/WAXS system was used to perform wide-angle XRD (WAXD) analysis with a Genix microsource from Xenocs operated at 50 kV and 0.6 mA (λCu = 0.154 nm). The 2D patterns were processed using Fit2D software. The water contact angle was observed using a Kruss drop shape analyzer at ambient temperature using water as the probe liquid (~3 μL). Fourier transform infrared (FTIR) analysis in attenuated total reflectance (ATR) mode was used to study the functional group characteristic of the samples under dynamic conditions. The thermal stability of the samples was determined by thermogravimetric analysis using TG apparatus (Perkin Elmer 6000, the Netherlands).

Porosity of the hydrophobic sponge was calculated from the apparent and bulk density values based on the eq 4

\[
\text{porosity(\%)} = \left(1 - \frac{\rho_{\text{IOHS}}}{\rho_s}\right) \times 100
\]

where \(\rho_{\text{IOHS}}\) is the apparent density of the hydrophilic/hydrophobic sponge and \(\rho_s\) is the bulk density of the sample.

The apparent density of the sample was calculated by measuring the dimensions of the sample using a Vernier caliper and mass using a weighing balance. The bulk density of sodium silicate is taken to be 2.4 g cm\(^{-3}\).

The adhesive force between the water droplet and the hybrid sponges was calculated using the Young–Dupre equation

\[
W_{SL} = Y_L (1 + \cos \theta)
\]

where \(W_{SL}\) is the work of adhesion, \(Y_L\) is the liquid surface tension, and \(\theta\) is the contact angle made by the liquid droplet with the sample surface.

4.4. Procedures for Absorption Studies. Six types of test liquids—hexane, kerosene, chloroform, paraffin oil, engine oil, and crude oil—were selected to identify the oil absorption efficiency of macroporous sponges. The polar volatile organic compounds are represented by hexane and chloroform; lower-viscosity oils like gasoline, diesel, and so on are represented by kerosene; and paraffin oil and engine oil represents highly viscous oils. Oils can be classified as light, medium, heavy, and weathered depending on the viscosity and density values as shown in Table 1. The physical properties of the test liquids selected are listed in Table 2.

| oil type | viscosity range (cP) | density range (g cm\(^{-3}\)) |
|----------|----------------------|-----------------------------|
| light    | 1–10                 | 0.820–0.870                 |
| medium   | 200–400              | 0.860–0.930                 |
| heavy    | 1500–2500            | 0.930–1.000                 |
| weathered| 8000–10000           | 0.930–1.000                 |

4.4.1. Dynamic Degradation Test. The method examines the parameters buoyancy, hydrophobicity, and oleophilicity of the samples under dynamic conditions. Typically, a known weight of the sample is placed in a sealed jar half-filled with water and mechanically rotated for 15 min, and the contents are allowed to be static for 2 min. If greater than 10% of the sample is found to be submerged or the water column is observed to be contaminated with the sorbent particles, then the adsorbent is not recommended for use in open water. The sample is removed to determine the water pick-up ratio. In the next stage, 4 mL of oil is added to the surface of the test jar, and the same procedure is repeated, this time to notice any oil sheen on the water surface.

4.4.2. Oil Absorption—Short Test (15 min). The pick-up ratio of the absorbent for the test liquids under stagnant conditions is determined through this procedure. The weight of the hybrid sponge is noted and placed in a test cell filled with the oil. After 15 min, the samples are withdrawn and allowed to drain for 30 s (for highly viscous liquids, 2 min is allowed for draining). The final weight is noted, and the tests are run in triplicate.
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01655.

Superswelling nature of synthesized sponge absorbent (MPG)

Repeated uptake of kerosene from water by IOHSO absorbent sponge (MPG)

Selective uptake of chloroform from water by the absorbent (MPG).

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NOTES

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