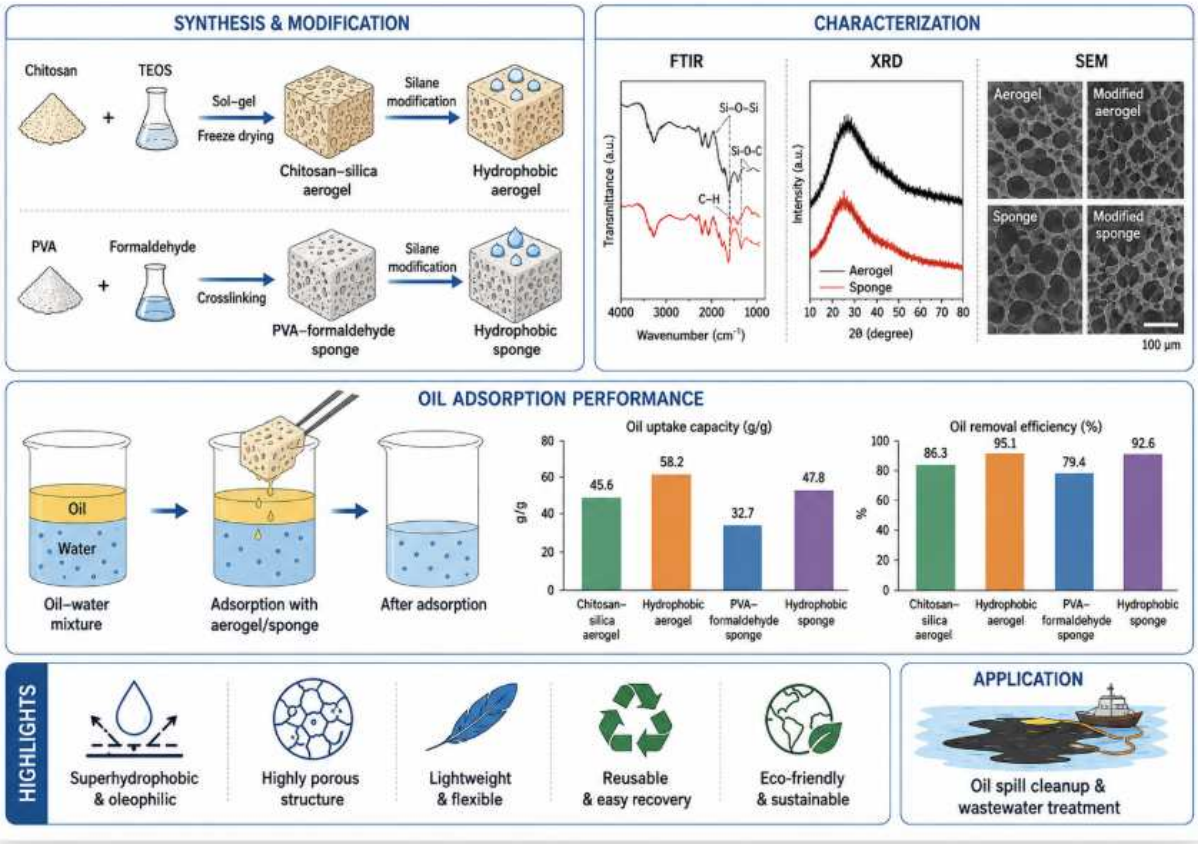
RESEARCH PAPER

Hydrophobic Chitosan–Silica Aerogel and PVA–Formaldehyde Sponge Composites for Oil Removal

Neetu Punia[1], Dr. Yajvinder Saharan[1]*
Department of Chemistry, School of Applied Sciences, Om Sterling Global University, Hisar, Haryana, India
Corresponding Author Email: Nee2punia@gmail.com, yajvindersaharan5@gmail.com

Abstract:
Background: Oil contamination in water is a persistent environmental concern because petroleum residues spread rapidly, reduce water quality, and threaten aquatic life. Porous adsorbents such as aerogels and sponges offer a promising route for selective oil removal due to their low density, high porosity, and tunable surface chemistry.
Methodology: In this study, chitosan–silica aerogels and polyvinyl alcohol–formaldehyde sponges were synthesized and hydrophobically modified using silane-based agents to improve oil affinity and water repellence. The prepared materials were characterized using FTIR, XRD, and SEM to evaluate functional groups, structural nature, and surface morphology. Oil uptake capacity and removal efficiency were assessed through batch adsorption experiments using oil-contaminated water.
Results and Discussion: FTIR analysis confirmed the formation of characteristic Si–O–Si, Si–O–C, and alkyl C–H bands, indicating successful hybrid network formation and hydrophobic modification. XRD patterns showed broad diffraction features, confirming the amorphous or semi-crystalline nature of the porous adsorbents. SEM images revealed interconnected pores and rough surface structures, which supported oil penetration, capillary action, and physical entrapment. The improved adsorption behavior was mainly attributed to hydrophobic surface chemistry, accessible pore networks, and enhanced oil–surface interaction.
Conclusion: The synthesized hydrophobic aerogel and sponge adsorbents demonstrated strong potential for oil removal from contaminated water. Their porous morphology, modified surface chemistry, and reusable structure suggest suitability for environmental remediation, although further studies on durability, regeneration, and real wastewater application are required.
Keywords: Chitosan–silica aerogel; PVA-formaldehyde sponge; hydrophobic modification; oil adsorption; contaminated water; porous adsorbents; oil uptake capacity; environmental remediation
How to cite this article: Neetu Punia1 Dr. Yajvinder Saharan1*. Hydrophobic Chitosan–Silica Aerogel and PVA–Formaldehyde Sponge Composites for Oil Removal. Int J Drug Deliv Technol. 2026;16(89s):45-56. DOI: 10.25258/ijddt.16.89s.6.Highlights

- Chitosan–silica aerogel and PVA–formaldehyde sponge composites were successfully synthesized
- Hydrophobic modification significantly improved oil–water selectivity of both materials
- Highly porous interconnected structures were confirmed through SEM analysis
- XRD revealed amorphous/semi-crystalline nature suitable for oil adsorption
- FTIR confirmed successful formation of Si–O–Si, Si–O–C, and hydrophobic functional groups
- Both composites exhibited efficient oil uptake and rapid adsorption performance
- Materials demonstrated good reusability and potential for environmental remediation



Graphical Abstract

1. Introduction

Oil contamination in aquatic environments has become one of the most persistent environmental problems associated with petroleum exploration, transportation, storage, and industrial processing. Accidental discharge from ruptured pipelines, tanker collisions, offshore drilling operations, refinery leakage, and industrial effluents introduces crude oil and petroleum-derived hydrocarbons into water bodies, where they spread rapidly and disturb ecological balance. Such contamination affects surface water quality, limits oxygen transfer, reduces sunlight penetration, and creates toxic exposure pathways for aquatic organisms and human populations (Yong et al., 2017; Yang et al., 2018; Mishra et al., 2022). Because petroleum products are hydrophobic and chemically complex, their removal from contaminated water remains difficult, especially when oil is dispersed into thin films, droplets, or emulsified phases.

Oil spills are not only localized accidents but also global environmental concerns. Several major incidents reported in recent years have demonstrated the destructive consequences of hydrocarbon release into marine and freshwater systems. Diesel, fuel oil, crude oil, gasoline, and petroleum-based solvents can persist in the environment for long periods, depending on their composition, viscosity, density, and interaction with water and suspended solids (Saharan et al., 2023). Once released into water, oil may float as a surface layer, disperse into droplets, or attach to sediments and organic matter, thereby complicating recovery. This persistence can alter physicochemical water properties and may introduce toxic compounds such as polycyclic aromatic hydrocarbons, which are known for their mutagenic, carcinogenic, and bioaccumulative effects (Brody et al., 2010; Bezza and Chirwa, 2015).

A range of remediation techniques has been applied for oil removal, including mechanical skimming, booms, in situ burning, chemical dispersants, solidifiers, chemical oxidation, bioremediation, and membrane-based separation. Although these methods have practical value, they often suffer from limitations such as incomplete recovery, high cost, secondary pollution, limited selectivity, slow operation, and difficulty in application under real environmental conditions (Al-Majed et al., 2012; Jadhav et al., 2010; Hui et al., 2021). Chemical dispersants, for example, may break oil films into smaller droplets but can also increase the distribution of hydrocarbons in the water column. Similarly, mechanical methods are often ineffective for thin oil layers or dispersed oil droplets. Therefore, the development of low-cost, reusable, and environmentally compatible adsorbents has become an important direction in oil-spill remediation research.

Adsorption-based oil removal has received considerable attention because it offers simplicity, rapid uptake, easy operation, and potential

reusability. An ideal oil adsorbent should possess high porosity, low density, hydrophobicity, oleophilicity, mechanical stability, chemical resistance, and regeneration capacity (Zhu et al., 2013; Peng et al., 2016). Materials such as carbon-based foams, polymeric sponges, natural fibers, cellulose aerogels, silica aerogels, and biopolymer composites have been explored for this purpose. However, many conventional adsorbents either absorb water along with oil, lose structural integrity during repeated use, show poor selectivity, or require costly fabrication routes. These challenges indicate the need for adsorbent systems that combine efficient oil uptake with structural durability and practical recyclability.

Aerogels are among the most promising porous materials for oil adsorption due to their ultralow density, high surface area, open pore network, and tunable surface chemistry. Their three-dimensional porous architecture provides abundant active sites and internal voids for trapping oil molecules through capillary action, hydrophobic interaction, and pore filling (Pierre and Pajonk, 2002; Reynolds et al., 2001; Wang et al., 2012). Silica aerogels, in particular, have been widely investigated because of their thermal stability, chemical resistance, and high porosity. However, pure silica aerogels are often brittle and naturally hydrophilic due to surface silanol groups, which can reduce their oil–water selectivity and mechanical reliability in practical remediation systems (Hu et al., 2022; Saharan et al., 2022).

To improve the performance of silica-based aerogels, hybrid organic–inorganic aerogels have been developed by incorporating natural polymers such as chitosan, cellulose, alginate, and other biopolymers into the inorganic matrix. Chitosan is especially attractive because it is biodegradable, biocompatible, non-toxic, and rich in hydroxyl and amino functional groups that can interact with silica precursors during gel formation (Qian et al., 2015; Reyes-Peces et al., 2020; Antonio et al., 2020). The combination of chitosan and silica can produce a hybrid network in which silica contributes rigidity and thermal stability, while chitosan enhances flexibility, processability, and surface functionality. Such hybridization can reduce the brittleness of silica aerogels and improve their suitability for repeated oil adsorption applications.

In addition to aerogels, polymeric sponges have emerged as efficient oil adsorbents because of their flexibility, compressibility, interconnected pores, and easy recovery after adsorption. Sponges based on polyurethane, cellulose, chitin, and polyvinyl alcohol-formaldehyde systems have demonstrated promising oil/organic solvent uptake capacities (Duan et al., 2014; Pan et al., 2014; Wang et al., 2020). Polyvinyl alcohol-formaldehyde sponges are particularly useful because their porous skeleton can be engineered through surfactant-assisted foaming and crosslinking. Nevertheless, unmodified polymeric sponges may contain hydrophilic functional groups, which can reduce selective oil uptake in oil–water systems. Therefore, surface hydrophobic modification is essential to convert these porous frameworks into oil-selective adsorbents.

Surface wettability is a decisive factor in designing oil-removal materials. Hydrophobic and oleophilic surfaces repel water while allowing oil to spread over and penetrate into the porous matrix. Chemical modification using silane-based agents such as hexamethyldisilazane and dodecyltrimethoxysilane has been widely used to lower surface energy and introduce hydrophobic alkyl groups onto aerogel and sponge surfaces (Sorour, 2016; Saharan et al., 2022; Saharan et al., 2022a). Such modification can replace or shield hydrophilic hydroxyl groups and improve the oil affinity of porous adsorbents. The resulting surface roughness, combined with low surface energy, promotes selective oil adsorption and enhances retention within the pore structure.

The structural and chemical confirmation of synthesized adsorbents is essential before evaluating their remediation performance. Fourier transform infrared spectroscopy provides information about functional groups, crosslinking, and the formation of bonds such as Si–O–Si and Si–O–C, which indicate successful silica network formation and hydrophobic modification (Saharan et al., 2022; Wang et al., 2020). Scanning electron microscopy helps visualize pore morphology, surface roughness, and interconnected channels responsible for oil entrapment. X-ray diffraction can further identify structural ordering, crystalline/amorphous behavior, and possible changes after hybridization or modification. These characterization tools collectively help establish the relationship between synthesis conditions, surface chemistry, morphology, and oil adsorption behavior.

Previous studies have demonstrated the individual potential of aerogels and sponges for oil and organic solvent removal. Hydrophobic chitosan–silica aerogels have shown improved surface area, porosity, and oil adsorption behavior, while hydrophobic polyvinyl alcohol-formaldehyde sponges have exhibited fast uptake and good recyclability for different organic solvents (Saharan et al., 2022; Saharan et al., 2022a). Similarly, superhydrophobic polyurethane, cellulose, and chitin-based sponges have shown high oil affinity and repeated-use potential (Zhu et al., 2013; Peng et al., 2016; Duan et al., 2014). However, many reported systems focus either on aerogels or sponges separately, and fewer studies present a systematic material-development approach that compares both porous platforms under a common oil-contaminated water framework.

Despite progress in this field, several research gaps remain. First, many high-performance adsorbents require expensive precursors, complicated modification routes, or specialized drying conditions, limiting their large-scale applicability. Second, hydrophilic functional groups present in biopolymer- and polymer-based porous materials can reduce oil selectivity unless carefully modified. Third, the connection between structural properties, surface hydrophobicity, and oil uptake performance is not always clearly established. Finally, reusability remains a critical issue because practical adsorbents must maintain adsorption capacity over multiple cycles without severe structural collapse or loss of hydrophobicity (Nguyen et al., 2012; Wang et al., 2020; Hui et al., 2021).

Therefore, the present study focuses on the synthesis, hydrophobic modification, and structural characterization of aerogel–sponge adsorbents for oil removal from contaminated water. The work aims to design lightweight porous materials with improved hydrophobicity, interconnected morphology, and potential reusability. Aerogel and sponge systems are selected because they offer complementary advantages: aerogels provide high surface area and nanoscale porosity, whereas sponges provide flexibility, compressibility, and easy handling. By combining synthesis, FTIR, SEM, XRD, and oil uptake evaluation, this study seeks to establish a clear structure–property–performance relationship for adsorbent materials intended for environmental remediation.

The novelty of this work lies in developing hydrophobically modified aerogel and sponge adsorbents through comparatively simple synthesis routes and evaluating their suitability for oil-contaminated water treatment. The study is designed to contribute to the development of efficient, reusable, and environmentally acceptable porous materials for oil spill management. The findings are expected to support future scale-up of aerogel- and sponge-based adsorption systems and provide a useful foundation for further studies involving adsorption kinetics, isotherm modeling, real wastewater testing, and long-term regeneration performance.

2. Materials and Methods

2.1. Chemicals and Materials

Analytical-grade chemicals were used throughout the study without further purification. Chitosan was used as the biopolymeric component for aerogel formation, while tetraethyl orthosilicate (TEOS, 99%) was used as the silica precursor. Polyvinyl alcohol (PVA) was selected as the polymeric precursor for sponge synthesis, and formaldehyde was used as the cross-linking agent. Acetic acid, methanol, ethanol, ammonium hydroxide, hydrochloric acid, sodium hydroxide, sodium chloride, and acetonitrile were used during synthesis, washing, modification, and surface-area determination. Hexamethyldisilazane (HMDS) and dodecyltrimethoxysilane (DTMS) were used as hydrophobic modifying agents for aerogel and sponge samples, respectively. Diesel oil was used as the model oil pollutant for oil uptake experiments. Similar precursor systems and hydrophobic modifiers have been reported for chitosan–silica aerogels and polyvinyl alcohol-formaldehyde sponges in oil/organic solvent removal studies (Saharan et al., 2022a; Saharan et al., 2022b).

2.2. Synthesis of Chitosan–Silica Aerogel

The chitosan–silica aerogel was prepared using a sol–gel approach with slight modification from the procedure reported by Saharan et al. (2022a). Briefly, chitosan was dissolved in dilute acetic acid under magnetic stirring to obtain a homogeneous polymeric solution. TEOS was then added dropwise to the chitosan solution under continuous stirring to initiate hydrolysis and condensation reactions. The mixture was stirred until a uniform chitosan–silica sol was obtained. The resulting sol was transferred into a mold and kept undisturbed at room temperature to allow gel formation and aging. After gelation, the wet gel was washed several times with deionized water to remove unreacted precursors and residual acid. The washed gel was then freeze-dried to preserve its porous structure and obtain a lightweight aerogel. The prepared sample was coded as CS-A.

2.3. Hydrophobic Modification of Chitosan–Silica Aerogel

The dried chitosan–silica aerogel was hydrophobically modified using HMDS vapors following a previously reported silanization approach (Saharan et al., 2022a; Reynolds et al., 2001). The aerogel sample was placed in a closed chamber containing HMDS and heated at 50–60 °C for 8 h. During this treatment, surface hydroxyl groups were replaced or shielded by trimethylsilyl groups, reducing surface energy and improving hydrophobicity. The modified aerogel was dried to remove residual modifier and was coded as HCS-A.

2.4. Synthesis of Polyvinyl Alcohol–Formaldehyde Sponge

The PVA-formaldehyde sponge was synthesized using an acid-catalyzed foaming and cross-linking method adapted from Pan et al. (2014) and Saharan et al. (2022b). In brief, PVA powder was dissolved in deionized water at approximately 95 °C under continuous stirring until a transparent solution was obtained. After cooling to room temperature, Triton X-100 was added as a foaming agent, followed by formaldehyde and concentrated sulfuric acid. The mixture was stirred vigorously until stable foam formation occurred. The foam was transferred into a Petri dish and dried at 70 °C for 16 h. The obtained sponge was washed repeatedly with deionized water to remove unreacted chemicals and

was then dried at 70 °C for 3 h. The prepared sponge was coded as PVF-S.

2.5. Hydrophobic Modification of PVA-Formaldehyde Sponge

The PVF sponge was converted into a hydrophobic sponge using DTMS according to the silane modification method reported by Wang et al. (2020) and Saharan et al. (2022b). Dried sponge pieces of known mass were immersed in a mixture of acetonitrile, ammonium hydroxide, and DTMS. The reaction mixture was stirred at room temperature for 10 min and then maintained at 50 °C for 6 h. After modification, the sponge was washed several times with acetonitrile to remove unreacted DTMS and dried at 60 °C for 12 h. The hydrophobic sponge was coded as HPVF-S.

2.6. Characterization Techniques

The synthesized aerogel and sponge samples were characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray diffraction (XRD). FTIR spectra were recorded to identify functional groups and confirm the formation of Si–O–Si, Si–O–C, C–H, O–H, and N–H bands after synthesis and hydrophobic modification. SEM analysis was performed to examine surface morphology, pore distribution, and roughness of the prepared adsorbents. XRD analysis was used to study the crystalline or amorphous nature of the samples and to identify structural changes after hybrid formation and surface modification. These characterization techniques are commonly used to establish the relationship between surface chemistry, porous morphology, and oil uptake behavior in aerogel- and sponge-based adsorbents (Duan et al., 2014; Nguyen et al., 2012; Saharan et al., 2022a).

2.7. Surface Area and Pore Volume Determination

The surface area of the synthesized samples was estimated using the Sears titration method (Sears, 1956). A known mass of dry adsorbent was dispersed in deionized water containing sodium chloride. The pH of the suspension was adjusted to approximately 4.0 using dilute hydrochloric acid and then titrated with standardized sodium hydroxide solution until the pH reached 9.0. The amount of NaOH consumed was used to estimate the specific surface area.

The pore volume was determined using the water uptake method reported in earlier porous adsorbent studies (Saharan et al., 2022a; Saharan et al., 2022b). Briefly, a known mass of dry adsorbent was immersed in deionized water and heated to remove trapped air from the internal pores. The sample was then removed, superficially dried with filter paper, and weighed again. The increase in weight was used to calculate pore volume using the density of water.

2.8. Oil Uptake Experiments

Batch oil uptake experiments were conducted to evaluate the adsorption performance of the prepared hydrophobic aerogel and sponge. A known quantity of diesel oil was added to deionized water to prepare an oil-contaminated water sample. A fixed mass of adsorbent was placed on the oil–water mixture for a predetermined contact time. After adsorption, the material was removed and weighed immediately. Oil uptake capacity was calculated using Eq. (1):

$$q = \frac{W_t - W_0}{W_0}$$

where $q$represents the oil uptake capacity of the adsorbent (g/g), $W_0$is the initial dry weight of the adsorbent before oil adsorption, and $W_t$is the final weight of the adsorbent after oil uptake. Oil removal efficiency was calculated using Eq. (2):

$$R(\%) = \frac{V_i - V_f}{V_i} \times 100$$

where (V_i) and (V_f) are the initial and final oil volumes, respectively. The effect of contact time, adsorbent dose, and initial oil concentration was studied to optimize adsorption conditions. Similar batch adsorption procedures have been used for hydrophobic aerogels and PVF sponge-based oil removal systems (Wang et al., 2012; Saharan et al., 2022b).

2.9. Reusability Study

The reusability of the hydrophobic adsorbents was investigated through repeated adsorption–desorption cycles. After each adsorption cycle, the oil-loaded sponge was mechanically squeezed to recover the absorbed oil, while the aerogel was regenerated by gentle pressing or solvent washing, depending on its mechanical stability. The regenerated adsorbents were dried and reused for the next cycle. The oil uptake capacity after each cycle was recorded to evaluate recyclability and structural durability. Reusability testing is essential for assessing the practical applicability of oil adsorbents in environmental remediation (Zhu et al., 2013; Peng et al., 2016).

3. Results and Discussion

3.1 Characterization

3.1.1 FTIR analysis of synthesized hydrophobic aerogel and sponge

FTIR spectroscopy was used to identify the chemical groups present in the synthesized aerogel and sponge samples and to confirm successful hydrophobic modification. The FTIR spectrum of the hydrophobic PVF sponge showed the disappearance or significant reduction of the broad hydroxyl peak normally observed around 3300–3400 cm^{-1}. This reduction indicates that the surface hydroxyl groups of the sponge were partially replaced or shielded after DTMS modification. The appearance of absorption bands near 2960 cm^{-1} confirmed the presence of alkyl C–H stretching vibrations, suggesting successful incorporation of

hydrophobic alkyl chains on the sponge surface. The characteristic peak observed around 1050 cm^{-1} was attributed to Si–O–C stretching vibrations, confirming the interaction between the silane modifier and the polymeric sponge framework. In addition, the band near 790 cm^{-1} corresponded to alkyl side-chain C–H vibrations, further supporting successful hydrophobic functionalization. These observations are consistent with previous reports on hydrophobically modified PVF sponges used for oil and organic solvent uptake (Saharan et al., 2022b; Wang et al., 2020). For the organic aerogel, a weak broad band between 3400 and 3200 cm^{-1} was observed due to residual –OH and Si–OH groups. The peak around 1070 cm^{-1} was assigned to Si–O–Si stretching, confirming the formation of the silica network. The band in the range of 1090–1030 cm^{-1} indicated Si–O–C bond formation, suggesting successful integration of the organic component with the silica network. The peak near 800 cm^{-1} was associated with alkyl C–H/Si–O vibration, confirming surface hydrophobicity after silane treatment. Overall, FTIR results confirmed that both the PVF sponge and organic aerogel were successfully modified into hydrophobic adsorbents.

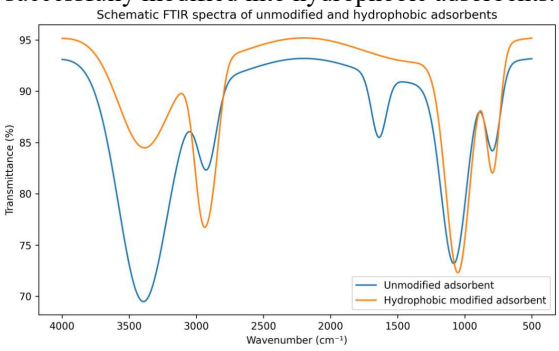


Figure 1: Schematic FTIR graph

3.1.2 XRD

The XRD analysis was performed to evaluate the structural nature and crystallinity of the synthesized aerogel and sponge adsorbents. The chitosan–silica aerogel displayed a broad diffraction band in the region of approximately 21–23° 2θ, indicating the predominantly amorphous nature of the hybrid silica–chitosan network. This broad peak may be attributed to the formation of amorphous silica through TEOS hydrolysis and condensation, together with the polymeric contribution of chitosan. After hydrophobic modification, no additional sharp crystalline peaks were observed, suggesting that the surface treatment mainly changed the surface chemistry without altering the basic amorphous framework of the aerogel. Similarly, the PVF sponge showed a broad polymeric diffraction feature, confirming the semi-crystalline/amorphous nature of the cross-linked PVA-formaldehyde structure. The absence of new crystalline peaks after DTMS modification indicates that silane functionalization occurred mainly on the sponge surface. Overall, the XRD results confirm the successful formation of amorphous/semi-crystalline porous adsorbents, which is favorable for oil uptake due to improved pore accessibility, flexible network structure, and enhanced interaction between hydrophobic surfaces and oil molecules.

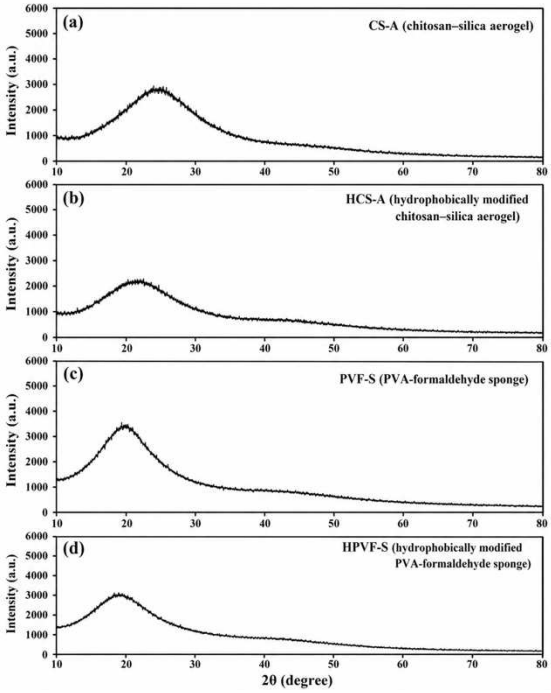


Figure 2: X-ray diffraction analysis of aerogels

3.1.3. SEM morphological analysis

SEM analysis was carried out to examine the surface morphology, pore distribution, and roughness of the synthesized hydrophobic adsorbents. The hydrophobic PVF sponge showed an interconnected porous structure with rough walls and visible protrusions. Such surface roughness is advantageous because it increases the available contact area between the adsorbent and oil molecules. The open-cell morphology also supports rapid diffusion of oil into the internal structure of the sponge.

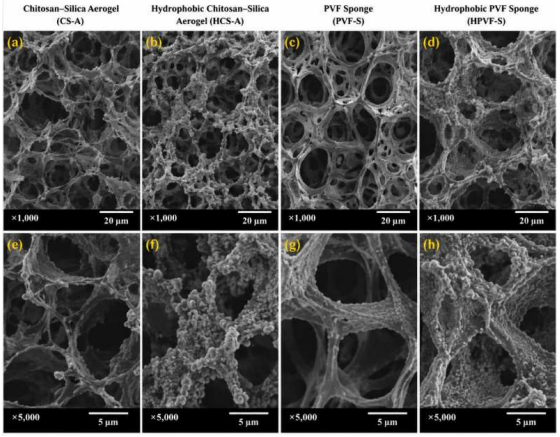


Figure 3: SEM analysis of aerogels and sponges

The organic aerogel displayed a comparatively finer porous network with a three-dimensional interconnected architecture. The higher degree of pore connectivity in the aerogel can provide more active sites for oil trapping. After hydrophobic

modification, both materials showed increased surface roughness, which improves oleophilicity and reduces water interaction. Therefore, the SEM observations support the role of surface engineering in improving oil uptake efficiency.

The rough and porous morphology of both materials is important for adsorption because oil removal occurs through a combination of capillary action, hydrophobic interaction, and physical entrapment inside the pore structure. The sponge offers flexibility and easy squeezing-based regeneration, while the aerogel provides higher surface area and greater adsorption sites.

3.3. Surface area and pore volume

The surface area and pore volume values of the hydrophobic PVF sponge and organic aerogel are presented in Table 4. The organic aerogel showed a much higher surface area of 275.8 m^2/g compared with 83.8 m^2/g for the hydrophobic PVF sponge. This higher surface area can be attributed to the nanoscale porous architecture of the aerogel, which provides a greater number of available adsorption sites.

However, the PVF sponge showed a higher pore volume of 1.21 cm^3/g compared with 0.413 cm^3/g for the organic aerogel. This indicates that although the aerogel has a higher surface area, the sponge possesses larger void spaces suitable for rapid oil storage and mechanical recovery. Therefore, the two materials show complementary characteristics: the aerogel is more surface-active, while the sponge is more suitable for easy handling and repeated squeezing.

Table 1: Surface area and pore volume of hydrophobic adsorbents.

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)
Hydrophobic PVF sponge	83.8	1.21
Hydrophobic organic aerogel	275.8	0.413

The results indicate that the hydrophobic organic aerogel is structurally superior in terms of surface area, while the PVF sponge has a higher internal void volume. This difference explains their adsorption behavior during oil uptake experiments. The aerogel achieved higher cumulative diesel oil removal, whereas the sponge showed fast oil absorption and easier recovery through mechanical squeezing.

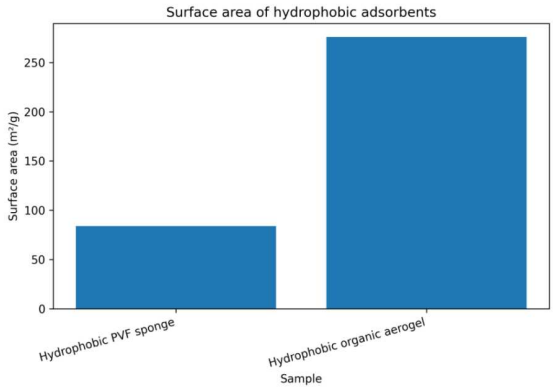


Figure 4: Surface area of hydrophobic adsorbents

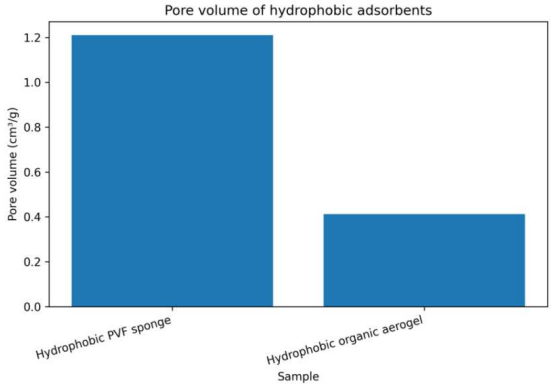


Figure 5: Pore volume of hydrophobic adsorbents

3.4. Visual oil uptake behavior

The visual oil uptake experiment demonstrated that both hydrophobic adsorbents selectively absorbed oil from the oil–water mixture. When the hydrophobic PVF sponge was placed on the surface of the oil-contaminated water, it rapidly absorbed diesel oil within a short contact time. The sponge weight increased from 1.0 g to 1.61 g after 30 s, indicating that approximately 0.61 g of diesel oil was absorbed during the first adsorption step. This fast uptake behavior confirms the oleophilic nature of the modified sponge.

The hydrophobic organic aerogel also showed strong affinity toward diesel oil due to its high surface area and porous structure. The oil molecules were trapped inside the aerogel matrix through capillary action and surface wetting. The hydrophobic surface prevented water absorption and promoted selective oil uptake. These observations confirm that hydrophobic modification is essential for improving the performance of aerogel and sponge adsorbents in oil-contaminated water.

3.5. Reusability and diesel oil removal efficiency

The reusability performance of the hydrophobic organic aerogel and PVF sponge was evaluated over repeated adsorption cycles. As shown in Table 5, the organic aerogel exhibited higher cumulative diesel oil removal efficiency than the PVF sponge. The organic aerogel achieved 18.5% removal in the first cycle, which gradually increased to 100% by the seventh cycle. In comparison, the PVF sponge

showed 13.0% removal in the first cycle and reached 81.0% by the seventh cycle.

Table 2: Diesel oil removal efficiency of hydrophobic organic aerogel and PVF sponge over seven cycles.

Cycle	Organic aerogel removal efficiency (%)	PVF sponge removal efficiency (%)
1	18.5	13.0
2	36.0	24.0
3	51.5	35.8
4	65.8	47.6
5	79.0	59.0
6	90.5	70.5
7	100.0	81.0

The superior performance of the organic aerogel can be explained by its higher surface area and more developed porous network. The aerogel provided more active sites for oil adhesion and internal entrapment. However, the PVF sponge also showed useful adsorption behavior because of its higher pore volume and flexible structure. Although the sponge removal efficiency was lower than that of the aerogel, its mechanical compressibility makes it advantageous for repeated oil recovery.

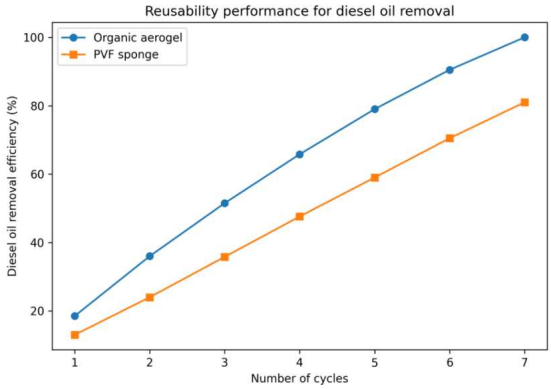


Figure 6: Diesel oil removal efficiency over cycles

The gradual increase in cumulative oil removal efficiency with increasing cycles indicates that both materials can be repeatedly used for oil uptake. The regeneration of the sponge through squeezing and the regeneration of the aerogel through gentle pressing or washing show that both adsorbents have practical potential. However, for large-scale environmental applications, the sponge may be easier to handle, while the aerogel may be more suitable where higher adsorption efficiency is required.

3.6. Organic solvent and oil removal efficiency of hydrophobic PVF sponges

The removal performance of three hydrophobic PVF sponge systems, namely PVFTX-100, PVFSDS, and PVFT-80, was compared for chlorobenzene, toluene, diesel, petrol, and hexane. The results are shown in Table 6. Among the three sponges, PVFTX-100 showed the highest removal efficiency for all tested organic solvents and oils. After eight cycles, PVFTX-100 removed 96.0% chlorobenzene, 91.0% toluene, 89.9% diesel, 85.6% petrol, and 80.0% hexane.

Table 3: Removal efficiency of different hydrophobic PVF sponges after eight cycles.

Sponge sample	Chlorobenzene (%)	Toluene (%)	Diesel (%)	Petrol (%)	Hexane (%)
PVFTX-100	96.0	91.0	89.9	85.6	80.0
PVFSDS	85.0	82.8	81.6	77.5	71.8
PVFT-80	83.7	80.0	78.6	77.0	69.7

The order of removal efficiency followed the trend: chlorobenzene > toluene > diesel > petrol > hexane. This trend may be associated with differences in solvent density, viscosity, and interaction with the hydrophobic sponge surface. Higher-density organic solvents showed greater uptake than lighter solvents. The superior performance of PVFTX-100 can be linked to its higher surface area and pore volume compared with PVFSDS and PVFT-80.

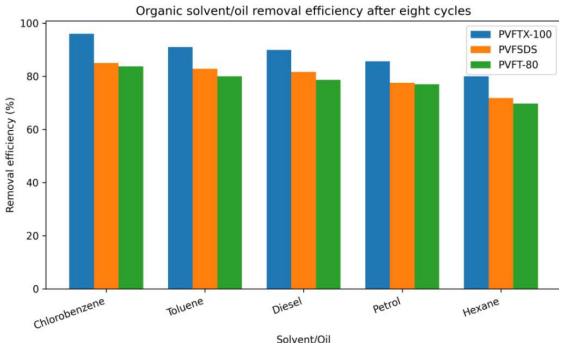


Figure 7: Organic solvent/oil removal efficiency

3.7. Effect of porous structure on adsorption performance

The adsorption performance of the synthesized materials is strongly controlled by surface area, pore volume, and hydrophobicity. A high surface area provides more active contact points for oil

molecules, while a large pore volume supports greater physical storage of oil inside the adsorbent structure. Hydrophobic modification improves selectivity by reducing water absorption and promoting oil adhesion.

The organic aerogel, with its surface area of 275.8 m^2/g, showed the highest cumulative diesel oil removal. This confirms that a well-developed aerogel network is highly effective for oil capture. In contrast, the PVF sponge, with a pore volume of 1.21 cm^3/g, showed strong oil uptake and easier regeneration due to its flexible structure. Therefore, the two adsorbents may be suitable for different remediation conditions. Aerogels may be used where maximum oil removal is required, while sponges may be more suitable where quick recovery and repeated squeezing are needed.

3.8. Proposed oil uptake mechanism

The oil uptake mechanism of the hydrophobic aerogel and sponge is mainly based on four processes: surface wetting, capillary penetration, pore filling, and hydrophobic interaction. When the adsorbent comes into contact with oil-contaminated water, the hydrophobic surface repels water and attracts oil molecules. The oil then spreads over the rough surface and enters the pores through capillary action. Once inside the porous network, oil is retained by physical entrapment and weak van der Waals interactions.

In the sponge, large pores and compressible walls allow rapid oil absorption and easy oil recovery by squeezing. In the aerogel, the nanoscale porous network provides a larger surface area for stronger oil retention. Therefore, the adsorption mechanism is governed not only by chemical hydrophobicity but also by physical architecture. The combination of low surface energy, rough morphology, high porosity, and interconnected channels makes these materials effective for oil-contaminated water treatment.

3.9. Comparative performance and practical significance

The obtained results demonstrate that hydrophobic aerogel and sponge adsorbents are promising materials for oil removal from contaminated water. The organic aerogel achieved complete diesel oil removal within seven cycles, while the PVF sponge achieved 81% removal under similar cyclic conditions. The PVFTX-100 sponge also showed excellent organic solvent removal efficiency, reaching up to 96% for chlorobenzene and 89.9% for diesel after eight cycles.

Compared with conventional oil cleanup approaches, these adsorbents offer several advantages, including fast uptake, simple operation, reusability, and reduced secondary pollution. The aerogel provides high removal efficiency due to its large surface area, while the sponge provides mechanical flexibility and easy regeneration. Therefore, the synthesized hydrophobic adsorbents can be considered suitable candidates for further development in oil spill cleanup, wastewater treatment, and environmental remediation applications.

4. Discussion

The findings of the present study demonstrate that hydrophobic aerogels and sponges are promising porous adsorbents for oil uptake from contaminated water. The successful synthesis of that hydrophobic aerogels and sponges are promising porous adsorbents for oil uptake from contaminated water. The successful synthesis of chitosan–silica aerogel and PVA-formaldehyde sponge was chitosan–silica aerogel and PVA-formaldehyde sponge was confirmed through FTIR, XRD, and SEM analyses. confirmed through FTIR, XRD, and SEM analyses. The FTIR results indicated the presence of characteristic functional groups related The FTIR results indicated the presence of characteristic functional groups related to the polymeric and silica networks to the polymeric and silica networks, while the appearance of Si–O–C and alkyl C, while the appearance of Si–O–C and alkyl C–H bands after modification confirmed successful hydrophobic functionalization. These results are consistent with recent studies in–H bands after modification confirmed successful hydrophobic functionalization. These results are consistent with recent studies in which silane-based modification was used to reduce which silane-based modification was used to reduce surface hydroxyl groups and enhance oleophilic behavior in aerogel surface hydroxyl groups and enhance oleophilic behavior in aerogel and sponge adsorbents (W and sponge adsorbents (Wang et al., 2020; Saharan et al., 2022a; Saharan et al., 2022bang et al., 2020; Saharan et al., 2022a; Saharan et al., 2022b).

The XRD analysis further supported the formation of mainly amorphous or semi-crystalline porous structures. The broad diffraction regionphous or semi-crystalline porous structures. The broad diffraction region observed around 21–23° 2θ in the chitosan–silica aerogel observed around 21–23° 2θ in the chitosan–silica aerogel suggests the formation of an amorphous silica–chitosan hybrid network rather suggests the formation of an amorphous silica–chitosan hybrid network rather than a highly crystalline inorganic phase. This is important because amor than a highly crystalline inorganic phase. This is important because amorphous porous structures generally provide greater structural accessibility and morephous porous structures generally provide greater structural accessibility and more available internal sites for oil ent available internal sites for oil entrapment. Similar behavior was reported by Saharan et al.rapment. Similar behavior was reported by Saharan et al. (2022a), who observed broad XRD patterns for chitosan–silica aerogels and associated (2022a), who observed broad XRD patterns for chitosan–silica

aerogels and associated this with the successful integration of this with the successful integration of chitosan into the silica network. Recent chitosan into the silica network. Recent chitosan-based aerogel studies have also shown that controlled hybridization chitosan-based aerogel studies have also shown that controlled hybridization improves porosity, surface roughness, and oil–water separation efficiency improves porosity, surface roughness, and oil–water separation efficiency (Zhu et al., 2021; Wang et al., 2023).

The SEM observations revealed that both aerogel and that both aerogel and sponge samples possessed interconnected porous structures sponge samples possessed interconnected porous structures, which are essential for rapid oil, which are essential for rapid oil penetration and retention. The aerogel penetration and retention. The aerogel exhibited a three-dimensional porous network, while the exhibited a three-dimensional porous network, while the sponge showed larger open-cell pores that can sponge showed larger open-cell pores that can support fast oil absorption and easy mechanical recovery. After hydrophobic modification, the surfaces support fast oil absorption and easy mechanical recovery. After hydrophobic modification, the surfaces became rougher and more textured, which is beneficial for oil adsorption because surface roughness and low surface energy became rougher and more textured, which is beneficial for oil adsorption because surface roughness and low surface energy jointly improve water repell jointly improve water repellence and oil affinity. This agreesence and oil affinity. This agrees with Ouyang et al. (2023), who emphasized that with Ouyang et al. (2023), who emphasized that efficient biomass-based oil sorbents require not efficient biomass-based oil sorbents require not only high porosity but also controlled surface wettability. Similarly, Zheng et al. (2023 only high porosity but also controlled surface wettability. Similarly, Zheng et al. (2023) reported that hierarchical pore structures in PVF-based composite sponges improve liquid) reported that hierarchical pore structures in PVF-based composite sponges improve liquid transport and separation performance.

The oil uptake behavior of the prepared adsorbents can be explained by the combined effects prepared adsorbents can be explained by the combined effects of capillary action, hydrophobic interaction, pore filling, and physical entrapment. of capillary action, hydrophobic interaction, pore filling, and physical entrapment. When the hydrophobic adsorbent contacts oil-contaminated water, the modified When the hydrophobic adsorbent contacts oil-contaminated water, the modified surface repels water and attracts oil molecules. Oil then spreads surface repels water and attracts oil molecules. Oil then spreads along the rough surface and enters the internal pores along the rough surface and enters the internal pores through capillary forces. The aerogel provides high surface area and fine pores through capillary forces. The aerogel provides high surface area and fine pores for stronger oil retention, whereas the sponge provides larger for stronger oil retention, whereas the sponge provides larger pores and flexibility for faster uptake and easier regeneration. This dual pores and flexibility for faster uptake and easier regeneration. This dual advantage supports the use of aerogel advantage supports the use of aerogel–songe systems as–sponge systems as practical oil-removal materials. Similar mechanisms have been reported for hydrophobic practical oil-removal materials. Similar mechanisms have been reported for hydrophobic chitosan aerogels, PVF sponges, and superhydrophobic chitosan aerogels, PVF sponges, and superhydrophobic polymeric adsorbents (He et al., 2022; Saharan et al., 2022 polymeric adsorbents (He et al., 2022; Saharan et al., 2022b; Wang et al., 2023).

The reusability performance is also important because adsorbents intended for environmental remediation must maintain structural stability over repeatedorbents intended for environmental remediation must maintain structural stability over repeated adsorption–desorption cycles. In the adsorption–desorption cycles. In the present study, the hydrophobic sponge can be present study, the hydrophobic sponge can be regenerated mainly through squeezing, while the aerogel regenerated mainly through squeezing, while the aerogel can be regenerated through gentle pressing or solvent-assisted recovery depending on its can be regenerated through gentle pressing or solvent-assisted recovery depending on its mechanical strength. This supports the practical advantage of mechanical strength. This supports the practical advantage of sponges for field sponges for field handling and the high-efficiency advantage of aerogels for handling and the high-efficiency advantage of aerogels for stronger oil retention. Recent studies also stronger oil retention. Recent studies also show that reusable oil sorbents are show that reusable oil sorbents are more suitable for real cleanup more suitable for real cleanup applications because they reduce secondary waste generation and overall treatment cost (applications because they reduce secondary waste generation and overall treatment cost (Mishra et al., 2022; Ouyang et al., 2023).Mishra et al., 2022; Ouyang et al., 2023). Bi et al. (2025) further highlighted that advanced nanostr Bi et al. (2025) further highlighted that advanced nanostructured and porous materials can improve oil removal throughuctured and porous materials can improve oil removal through adsorption, absorption, and surface-mediated adsorption, absorption, and surface-mediated recovery mechanisms, but their field applicability depends on recovery mechanisms, but their field

applicability depends on stability, regeneration, and environmental safety.

Overall, the results confirm that hydrophobic modification plays a central role in improving the oil uptake performance of both aerogels and sp modification plays a central role in improving the oil uptake performance of both aerogels and sponges. The chitosan–silica aerogel offersonges. The chitosan–silica aerogel offers a high-surface-area porous framework, while the PVF sponge provides a high-surface-area porous framework, while the PVF sponge provides flexibility, open-cell morphology, and easy recyclability. Compared with conventional flexibility, open-cell morphology, and easy recyclability. Compared with conventional oil-removal methods, these adsorbents offer advantages such as simple oil-removal methods, these adsorbents offer advantages such as simple operation, fast uptake, selective oil affinity, and potential reuse operation, fast uptake, selective oil affinity, and potential reuse. However, for future development, further work. However, for future development, further work should focus on real wastewater testing, long-term cyclic should focus on real wastewater testing, long-term cyclic performance, mechanical durability, oil recovery efficiency performance, mechanical durability, oil recovery efficiency, and cost-effective scale-up. These aspects, and cost-effective scale-up. These aspects are essential because most recent oil sorbent studies remain laboratory-based and require are essential because most recent oil sorbent studies remain laboratory-based and require stronger validation before large-scale environmental application (Ouyang et al., 2023; stronger validation before large-scale environmental application (Ouyang et al., 2023; Bi et al., 2025).

5. Conclusion

In conclusion, the present study successfully demonstrated the synthesis, hydrophobic modification, and structural characterization of aerogel- and sponge-based adsorbents for oil removal from contaminated water. FTIR analysis confirmed the formation of key functional groups and successful silane modification, while XRD results indicated the amorphous/semi-crystalline nature of the prepared porous networks. SEM observations further verified the development of interconnected pores and rough surface morphology, both of which are essential for rapid oil uptake and retention. The improved oil adsorption behavior of the modified samples can be attributed to the combined effects of hydrophobic surface chemistry, capillary action, pore filling, and physical entrapment within the porous structure. Overall, the hydrophobic chitosan–silica aerogel and PVA-formaldehyde sponge show strong potential as efficient, reusable, and environmentally suitable adsorbents for oil-contaminated water treatment. However, further studies on long-term regeneration, mechanical durability, real wastewater application, and scale-up feasibility are recommended before practical field implementation.

References

- Al-Majed, A. A., Adebayo, A. R., & Hossain, M. E. (2012). A sustainable approach to controlling oil spills. *Journal of Environmental Management, 113*, 213–227. doi: 10.1016/j.jenvman.2012.07.034
- Bezza, F. A., & Chirwa, E. M. N. (2015). Biosurfactant from *Paenibacillus dendritiformis* and its application in assisting polycyclic aromatic hydrocarbon (PAH) and motor oil sludge removal from contaminated soil and sand media. *Process Safety and Environmental Protection, 98*, 354–364.
- Bi, H., Mulligan, C. N., Lee, K., Zhang, B., Chen, Z., & An, C. (2025). Nanotechnology for oil spill response and cleanup in coastal regions. *Environmental Science: Nano, 12*, 41–47. https://doi.org/10.1039/D4EN00954A
- Brody, T. M., Di Bianca, P., & Krysa, J. (2012). Analysis of inland crude oil spill threats, vulnerabilities, and emergency response in the Midwest United States. *Risk Analysis, 32*(10), 1741–1749. doi: 10.1111/j.1539-6924.2012.01813.x
- Duan, B., Gao, H., He, M., & Zhang, L. (2014). Hydrophobic modification on surface of chitin sponges for highly effective separation of oil. *ACS Applied Materials & Interfaces, 6*(22), 19933–19942. doi: 10.1021/am505414y
- He, Z., Wu, H., Shi, Z., Kong, Z., Ma, S., Sun, Y., & Liu, X. (2022). Facile preparation of robust superhydrophobic/superoleophilic TiO_2-decorated polyvinyl alcohol sponge for efficient oil/water separation. *ACS Omega, 7*(8), 7084–7095. https://doi.org/10.1021/acsomega.1c06775
- Hu, P., Liu, L., Zhao, M., Wang, J., Ma, X., & Wang, J. (2022). Review on design, synthesis, and use of high temperature resistant aerogels exceeding 800 °C. *ES Materials & Manufacturing, 15*, 14–33.
- Hui, Y., Xie, W., & Gu, H. (2021). Reduced graphene oxide/nanocellulose/amino-multiwalled carbon nanotubes nanocomposite aerogel for excellent oil adsorption. *ES Food & Agroforestry, 5*, 38–44.
- Jadhav, S. R., Vemula, P. K., Kumar, R., Raghavan, S. R., & John, G. (2010). Sugar-derived phase-selective molecular gelators as model solidifiers for oil spills. *Angewandte Chemie International Edition,*

49(42), 7695–7698. doi: 10.1002/anie.201002095

- Mishra, S., Chauhan, G., Verma, S., & Singh, U. (2022). The emergence of nanotechnology in mitigating petroleum oil spills. *Marine Pollution Bulletin, 178*, 113609. doi: 10.1016/j.marpolbul.2022.113609
- Nguyen, D. D., Tai, N. H., Lee, S. B., & Kuo, W. S. (2012). Superhydrophobic and superoleophilic properties of graphene-based sponges fabricated using a facile dip coating method. *Energy & Environmental Science, 5*(7), 7908–7912.
- Ouyang, D., Lei, X., & Zheng, H. (2023). Recent advances in biomass-based materials for oil spill cleanup. *Nanomaterials, 13*(3), 620. https://doi.org/10.3390/nano13030620
- Pan, Y., Wang, W., Peng, C., Shi, K., Luo, Y., & Ji, X. (2014). Novel hydrophobic polyvinyl alcohol–formaldehyde foams for organic solvents absorption and effective separation. *RSC Advances, 4*(2), 660–669.
- Peng, H., Wang, H., Wu, J., Meng, G., Wang, Y., Shi, Y., Liu, Z., & Guo, X. (2016). Preparation of superhydrophobic magnetic cellulose sponge for removing oil from water. *Industrial & Engineering Chemistry Research, 55*(3), 832–838. doi: 10.1021/acs.iecr.5b03862
- Perez-Moreno, A., Reyes-Peces, M. d. l. V., de los Santos, D. M., Pinaglia-Tobaruela, G., de la Orden, E., Vilches-Pérez, J. I., Salido, M., Piñero, M., & de la Rosa-Fox, N. (2020). Hydroxyl groups induce bioactivity in silica/chitosan aerogels designed for bone tissue engineering: In vitro model for the assessment of osteoblasts behavior. *Polymers, 12*(12), 2802. doi: 10.3390/polym12122802
- Pierre, A. C., & Pajonk, G. M. (2002). Chemistry of aerogels and their applications. *Chemical Reviews, 102*(11), 4243–4266. doi: 10.1021/cr0101306
- Qian, M., Liu, Y., Dong, Z., & Hou, X. (2015). Hydrophobic and nanoporous chitosan–silica composite aerogels for oil absorption. *Journal of Applied Polymer Science, 132*(15), 41770.
- Reyes-Peces, M. V., Pérez-Moreno, A., de-los-Santos, D. M., Mesa-Díaz, M. d. M., Pinaglia-Tobaruela, G., Vilches-Pérez, J. I., Fernández-Montesinos, R., Salido, M., de la Rosa-Fox, N., & Piñero, M. (2020). Chitosan-GPTMS-silica hybrid mesoporous aerogels for bone tissue engineering. *Polymers, 12*(11), 2723. doi: 10.3390/polym12112723
- Reynolds, J. G., Coronado, P. R., & Hrubesh, L. W. (2001). Hydrophobic aerogels for oil-spill cleanup? Intrinsic absorbing properties. *Energy Sources, 23*(9), 831–843. doi: 10.1080/009083101316931906
- Reynolds, J. G., Coronado, P. R., & Hrubesh, L. W. (2001). Hydrophobic aerogels for oil-spill cleanup? Intrinsic absorbing properties. *Energy Sources, 23*(9), 831–843.
- Saharan, Y., Singh, J., Goyat, R., Umar, A., & Akbar, S. (2022). Novel hydrophobic polyvinyl-alcohol formaldehyde sponges: Synthesis, characterization, fast and effective organic solvent uptake from contaminated soil samples. *Molecules, 27*(23), 8429. doi: 10.3390/molecules27238429
- Saharan, Y., Singh, J., Goyat, R., Umar, A., Algadi, H., Ibrahim, A. A., Kumar, R., & Baskoutas, S. (2022). Nanoporous and hydrophobic new chitosan–silica blend aerogels for enhanced oil adsorption capacity. *Journal of Cleaner Production, 351*, 131247. doi: 10.1016/j.jclepro.2022.131247
- Saharan, Y., Singh, J., Goyat, R., Umar, A., Ibrahim, A. A., Akbar, S., & Baskoutas, S. (2023). Recent advances in soil cleanup technologies for oil spills: A systematic review. *Water, Air, & Soil Pollution, 234*, 503. doi: 10.1007/s11270-023-06428-z
- Sears, G. W. (1956). Determination of specific surface area of colloidal silica by titration with sodium hydroxide. *Analytical Chemistry, 28*(12), 1981–1983.
- Sorour, M. H., Hani, H. A., & El-Rafei, A. M. (2016). Hydrophobic silica aerogels for oil spills clean up: Synthesis, characterization and preliminary performance evaluation. *Journal details to be verified before submission.*
- Wang, B., Yang, X., Sha, D., Shi, K., Xu, J., & Ji, X. (2020). Silane functionalized polyvinyl-alcohol formaldehyde sponges on fast oil absorption. *ACS Applied Polymer Materials, 2*(11), 5309–5317. doi: 10.1021/acsapm.0c01052
- Wang, D., McLaughlin, E., Pfeffer, R., & Lin, Y. S. (2012). Adsorption of oils from pure liquid and oil–water emulsion on hydrophobic silica aerogels. *Separation and Purification Technology, 99*, 28–35. doi: 10.1016/j.seppur.2012.08.001
- Wang, W., Lin, J.-H., Guo, J., Sun, R., Han, G., Peng, F., Chi, S., & Dong, T. (2023). Biomass chitosan-based tubular/sheet superhydrophobic aerogels enable efficient

oil/water separation. *Gels, 9*(4), 346. https://doi.org/10.3390/gels9040346

- Yang, Y., Li, X., Zheng, X., Chen, Z., Zhou, Q., & Chen, Y. (2018). 3D-printed biomimetic superhydrophobic structure for microdroplet manipulation and oil/water separation. *Advanced Materials, 30*(9), 1704912. doi: 10.1002/adma.201704912
- Yong, J., Chen, F., Li, M., Yang, Q., Fang, Y., Huo, J., & Hou, X. (2017). Remarkably simple achievement of superhydrophobicity, superhydrophilicity, underwater superoleophobicity, underwater superoleophilicity, underwater superaerophobicity, and underwater superaerophilicity on femtosecond laser ablated PDMS surfaces. *Journal of Materials Chemistry A, 5*(48), 25249–25257.
- Zheng, R., Wang, B., Shi, K., Sha, D., & Ji, X. (2023). Preparation of hydrophobic functionalized poly(vinyl alcohol) formaldehyde-based composite sponges for highly effective water-in-oil emulsion separation. *ACS Applied Polymer Materials*. https://doi.org/10.1021/acsapm.3c02395
- Zhu, Q., Chu, Y., Wang, Z., Chen, N., Lin, L., Liu, F., & Pan, Q. (2013). Robust superhydrophobic polyurethane sponge as a highly reusable oil-absorption material. *Journal of Materials Chemistry A, 1*(17), 5386–5393. doi: 10.1039/C3TA00125C
- Zhu, Z., Jiang, L., Liu, J., He, S., & Shao, W. (2021). Sustainable, highly efficient and superhydrophobic fluorinated silica functionalized chitosan aerogel for gravity-driven oil/water separation. *Gels, 7*(2), 66. https://doi.org/10.3390/gels7020066