“Super-hydrophobic Materials for Efficient Oil- water Separation”

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Declaration

I, **Archana Bera,** Student of M.Sc. Chemistry in Pure & Applied Science Department, Midnapore City College, Midnapore affiliated to Vidyasagar University, West Bengal hereby declare that semester internship Dissertation entitled **“Super-hydrophobic Materials for Efficient oil-water Separation for Oil-Spillage Application”** is carried out in Indian Oil Corporation Limited, R&D Centre, Faridabad by me under the supervision of **Dr. Amardeep Singh, Research Manager, Analytical Department, Indian Oil Corporation Ltd. R&D Center, Faridabad, Haryana**.
I am certifying that the findings of this project are intellectual property of Indian Oil R&D and will not be used for any conferences and publication without the prior intimation.

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Abstract

In the event of oil spills at sea, conventional industry practices are employed to contain or disperse the oil on the surface. However, enhancing the efficiency of this process necessitates the development of advanced sorbent materials capable of absorbing large quantities of oil. To address this need, we utilized super hydrophobic and super-oleophilic MoS_2@X-coated sponges (X=CNTs or GO), which exhibit exceptional capabilities for separating and absorbing oils and organic solvents from water. Various analytical techniques, including Scanning Electron Microscopy (SEM), Transmission Electron Microscope (TEM), and X-ray Diffraction (XRD), were employed to characterize the properties of the coated sponge materials. The composite materials MoS_2@X displayed an impressive contact angle of up to 149°, indicatingtheir highly super-hydrophobic nature. The MoS_2@X coated sponges (MoS_2@X-coated Y) (Y= carbon, melamine sponge) demonstrated outstanding absorption performance due to its super-hydrophobicity, high porosity, and exceptional stability even in harsh conditions. Compared to carbon electrode and carbon sponge, melamine sponge proved advantageous due to its simplicity and lack of requirement for sophisticated equipment while it was fabricated with MoS_2@X on acid-treated sponges. The process of dipping and drying to create MoS_2@X-coated sponges is straightforward and can be easily scaled up. These findings hold great promise for water remediation and oil recovery efforts.

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Chapter 1: Introduction

1.Introduction

Oil leaks or spills into the aquatic environment are considered a natural disaster and a severe environmental problem for the entire planet. An oil spill is the release of a liquidpetroleumhydrocarboninto the environment due to human activity. Oil spill accidents are of great concern to humans, along with increasing environmental problems in recent years. Oil spill accidents occur due to incidents such as tanker collisions, pipeline leaks, offshore drilling mishaps, or accidents involving oil-carrying vessels. When oil is released into the marine environment, it can have devastating effects on aquatics on life, coastal habitats, and the overall ecological balance. The impact of oil spills is extensive and can include

Environmental contamination Oil spills introduce toxic substances into the marine ecosystem, causing harm to marine organisms such as fish, birds, marine mammals, and plants. The oil can coat the feathers and fur of animals, impairing their ability to fly, swim, or stay insulated, leading to suffocation, hypothermia, and death.

Damage to Ecosystems Coastal habitats, including wetlands, mangroves, and coral reefs, are particularly vulnerable to oil spills. These habitats provide critical breeding grounds, nurseries, and feeding areas for numerous species. Oil can smother and destroy these habitats, disrupting the entire food chain and ecosystem dynamics.

Economic Impact Oil spill have significant economic consequences, particularly in coastal communities dependent on fishing, tourism, and recreation activities. The contamination of fisheries and coastal areas can lead to the loss of livelihoods, reduced tourism revenue, and long-term economic decline.

Thus, removal of oils and organic solvents from water is an important global challenge for energy conservation and environmental protection.[2-4] To mitigate the adverse effects of these incidents, several methods have been investigated, including in-situburning, skimming, bioremediation, chemical dispersion, and adsorption. Among these methods, adsorption has gained significant interest due to its easy implementation, cost-effectiveness and versatile design.[5] An ideal adsorbent material for oil-water separation should possess excellent water repellency, superior adsorption performance, and low materials cost. However, many conventional adsorbent materials, such as vegetable fibers, wool, modified organophilic clay, exfoliated graphite, and cellulose-based materials, exhibited various defects including low oil adsorption efficiency, poor recyclability and high materials cost.[6] These drawbacks limit their practical application in oils removal. Therefore, it is necessary to explore adsorbents with excellent adsorption performance, low cost, and good recyclability.[7]

In order to further increase the adsorption capacity of materials with high adsorption capacity and good selectivity, the introduction of these precursors as additives in the matrix of porous polymers, such as resins, foams, sponges, and aerogels has also attracted interest. Polyurethane (PU) composites with honeycomb structure, PU-clay, PU-carbon, and PUgraphene have recently been investigated for the separation of water-oil systems.[8-11] Few groups have reported superhydrophobic-superoleophilic melamine based sponge material with extensive temperature and fire resistance.[12] However, most of the sponges are having both hydrophobic and hydrophilic character, it can absorb oil and water equally from oilwater mixtures.[13-15] One disadvantage associated with most polymeric sponges is their instability. Therefore, surface modification of sponges is utmost which altered the hydrophilic surface to hydrophobic surface to make it stable.[16] Yang et al. reported Polyurethane Sponge with a Modified Specific Surface for Repeatable Oil-Water Separation.[17] Shuai et al. reported polydimethylsiloxane-TiO_2 coated superdydrophobic polyurethane (PU) sponge.[18]

Recently a number of traditional materials such as CNT, graphene, MoS_2, WO_3, TiO_2, Zeolite etc have been used as a hydrophobic coating/modifying agent to remove and collect spill oil. [18-21] Zhang et al. used a pH responsive poly (2-vinylpyridine) (PVP) and oleophilic hydrophobic polydimethylsiloxane (PDMS) as coating materials onto sponge surfaces for pH responsive wettability. However, these materials have a number of drawbacks such as low absorption capacity, poor selectivity and poor reusability. Therefore, it is urgent to develop absorbent materials with better performance for the efficient removal of oils. Nguyen et al. demonstrated the surface modification of the same type of melamine sponge by dipcoating from ethanolic graphene nanosheet dispersions. MoS_2 materials have recently been reported by Gao et al. to possess unusual wetting behavior, similar to that of graphene. However, MoS_2 composites have been reported the applications of supercapacitors but no studies involving MoS_2 composite materials with both superhydrophobic and superoleophilic properties for the separation and absorption of oil and organic contaminants from water.

We have reported MoS_2@X-coated-Y materials to develop a sustainable oil-water separation system and to increase the number of pores and improve the hydrophobic character of the sponge in order to remove oils and other non-polar organic pollutants from water. The system employs the dip-dry method to create a superhydrophobic and superoleophilic surface on a porous substance, enabling selective separation of water and oil. The goal is to achieve effective separation, oil recovery, and high performance even after multiple uses. Furthermore, it has good flexibility and stability which makes the modified sponges a costeffective multipurpose material that can effectively remove hydrocarbons, especially oil.

Chapter 2: Literature Review

2. Literature review:

Removal of oils and organic solvents from water is an important global challenge for energy conservation and environmental protection.[2-4] To mitigate the adverse effects of these incidents, several methods have been investigated, including in-situburning, skimming, bioremediation, chemical dispersion, and adsorption. Among these methods, adsorption has gained significant interest due to its easy implementation, cost-effectiveness and versatile design.[5] An ideal adsorbent material for oil-water separation should possess excellent water repellency, superior adsorption performance, and low materials cost. However, many conventional adsorbent materials, such as vegetable fibers, wool, modified organophilic clay, exfoliated graphite, and cellulose-based materials, exhibited various defects including low oil adsorption efficiency, poor recyclability and high materials cost.[6] These drawbacks limit their practical application in oils removal. Therefore, it is necessary to explore adsorbents with excellent adsorption performance, low cost, and good recyclability.[7]

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Chapter 3: Aims and Objective

Aims and Objective :

The aim of this thesis is to investigate and develop efficient materials for the separation and remediation of oil spills, with a focus on enhancing the current methods used for containment, recovery, and treatment. In this study, we fabricated a superhydrophobic and underwater super oleophilic protonated melamine sponge for effective separation of water-rich immiscible oil/water mixtures with extremely high separation efficiency. This protonated melamine sponge exhibited excellent antifouling properties and could be used to separate oil/water mixtures continuously for up to 12 h without any increase in the oil content in filtrate. Moreover, our compressed protonated melamine sponge could separate both surfactant-free and -stabilized oil-in-water emulsions with high separation efficiencies. The high performance of this protonated melamine sponge and its efficient, energy- and cost-effective preparation suggest that it has great potential for use in practical applications.

RESEARCH OBJECTIVES

The objective of research work is to develop MoS_2@X-coated-Y materials to develop a sustainable oil-water separation system. The following tasks have been considered to achieve the research objectives:

I. Design and Synthesis of MoS_2@X-coated-Y materials (X = GO, CNTs; =Melamine sponges)
II. Structural characterization of synthesized MoS_2@GO and MoS_2@CNT using various analytical techniques (XRD, SEM, TEM, TGA).
III. Wettability behaviour and absorption studies of MoS_2@X-coated-Y materials

Chapter 4. Experimental and Methods

Experimental Methods

4.1Experimental Section Synthesis of MoS_2@CNTs

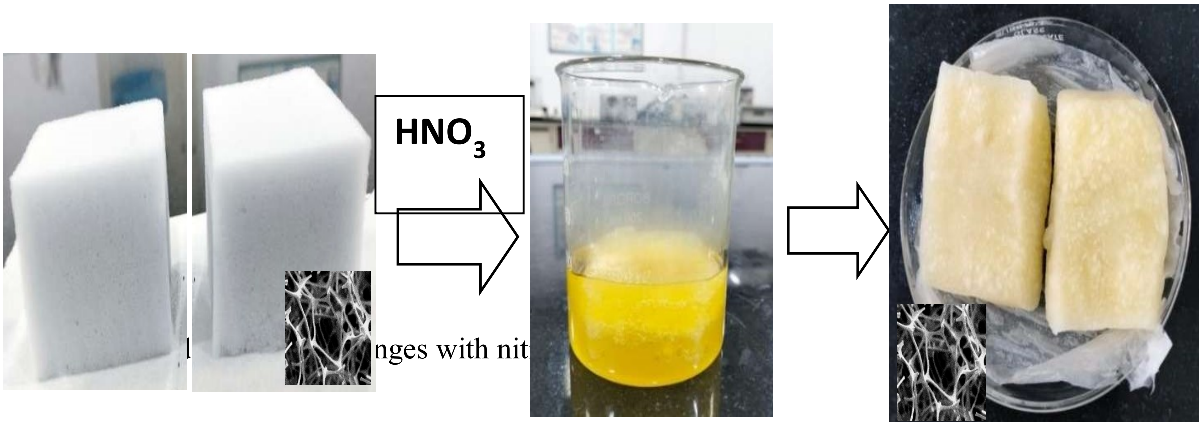
In a typical reaction, 100mg of CNTs were dispersed in 30ml of deionised (DI) water and sonicated for 1hr to break up any agglomerates and ensure uniform distribution of the CNTs. Separately, 100mg of MoS_2 was dispersed in 10ml of DI water, and added drop wise to the CNTs dispersed solution while stirring. Further, the mixture was transferred in stainless Teflon apparatus and kept in oven at 90°C for 12h. The MoS_2@CNTs was then filtered off and dried it.

4.2 Synthesis of MoS_2@GO

In a typical reaction, 100mg of GO were dispersed in 30ml of deionised (DI) water and sonicated for 1hr to break up any agglomerates and ensure uniform distribution of the GO. Separately, 100mg of MoS_2 was dispersed in 10ml of DI water, and added drop wise to the GO dispersed solution while stirring. Further, the mixture was transferred in stainless Teflon apparatus and kept in oven at 90°C for 12h. The MoS_2@GO was then filtered off and dried it.

Scheme 1: Preparation of MoS_2@X(X= CNTs,GO)

At first, sponge was dipped into 10M nitric acid (HNO3) followed by ultrasonication for 1h to modify the surface of the sponge (Y) and improve it adhesion properties. After sonication, the sponge was left to dry in an oven at 70°C. Further MoS2@X was dispersed in methanol solvent and added 5-10drops of diethanolamine into it. Now, the dried sponge (Y) was immersed into the dispersion of MoS2@X and then subjected to ultrasonication for 1h. After sonication, the sponge was left to dry in an oven at 70°C again. This process was repeated thrice with the sponge being dipped and dried after each cycle. After the final drying, the MoS2@X-coated Y materials was ready to use.



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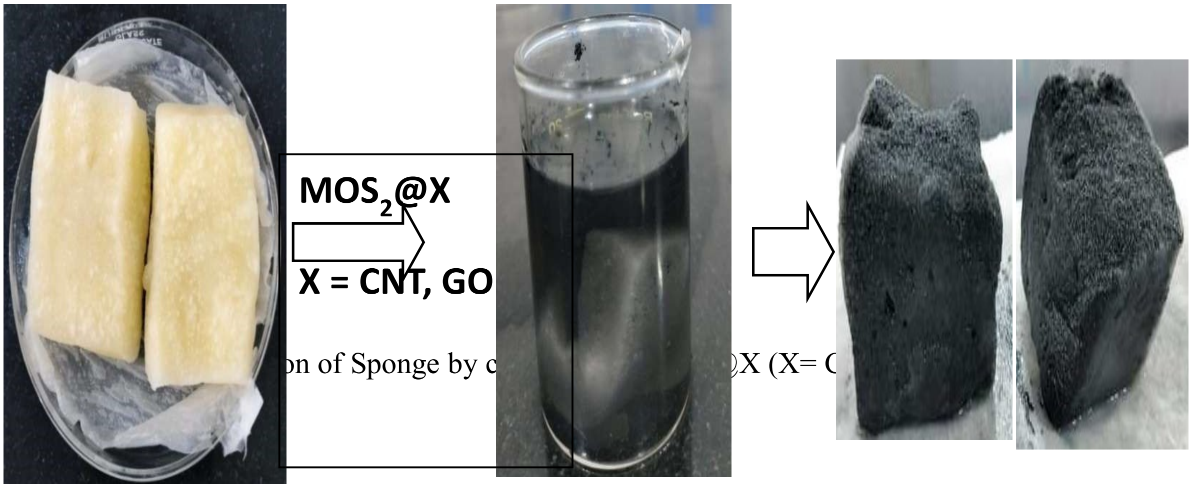

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Characterization:
Powder X-ray diffractometer (XRD) (Rigaku, Japan) was used to study crystal structure. Scanning electron microscope (SEM-JSM-6610LV, JEOL, Japan) and Transmission electron microscope (TEM, JEM 2100, JEOL, Japan) were used to observe microstructures of materials. Energy dispersive X-ray analysis (EDS) were used. Thermo gravimetric analysis (TGA) (Netzsch STA449) was used to examine the thermal stability of materials. Water contact angles were measured using a Rame-hart Model 250 Goniometer at room temperature, and the volume of distilled water droplets was 10 µ L.

Chapter 5: Results & Discussion

Result:

This proposed process for the fabrication of MoS_2@X on varieties of sponges is simple and convenient, and does not require the use of any costly organic solvents or a complicated treatment. Schematic representation of MoS_2@CNTs-coated Y (Y = Carbon Sponge and Melamine Sponge) prepared by dipping and drying process (Scheme 3). The acid treated sponges were dipped in the methanol-solvated MoS_2@X material in the presence of ethanoldiamine and developed novel MoS_2@CNTs-coated Y Materials. This proposed process for the fabrication of MoS_2@X on varieties of sponges is simple and convenient, and does not require the use of any costly organic solvents or a complicated treatment. Schematic representation of MoS_2@CNTs-coated sponges (Carbon cloth, Carbon Sponge and Melamine Sponge) prepared by dipping and trying process are shown in scheme 3. The acid treated sponges were dipped in the methanol-solvated MoS_2@X materials in the presence of ethanoldiamine and dried it. This process was repeated thrice.The MoS_2@X-Coated Y (X = CNTs, GO and Y = carbon cloth, carbon sponge and melamine sponge) were analyzed by various analytical techniques to examine the morphological evolution of the sponge before and after the hydrophobic modification.

SEM analysis

Scanning electron microscopy (SEM) was used to examine the morphological evolution of the sponge before and after the hydrophobic modifications. The sponge before and after coating with the MoS_2@X display exactly the same porous structure which is an inherent interconnected porous structure with macro pores of hundreds of micrometers, thus confirming that the small modification does not damage the original structure of the sponge or block the pores inside it. Fig. 1 shows the SEM images of Pristine MoS_2, CNT and GO.
Flakes and sheets layers are seen in MoS_2 whereas GO indicates layers structure. Pristine CNT reveals tubular morphologies.

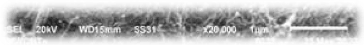

Fig1: SEM images of (a) MoS_2, (b) GO and (c) MWCNTs.

Further, CNTs are seen on the surface of MoS_2 structures in MoS_2@CNTs. However, MoS_2@GO shows mixture of flakes and layer structures. This has further been confirmed by TEM.

Fig. 2: SEM images of (a) MoS_2@CNTs and (b) MoS_2@GO materials.

In continuation of MoS_2@X-coated Y using carbon and melamine sponges, the sponge before and after coating with the MoS_2@X display exactly the same porous structure, which is an inherent porous structure with macro pores of hundreds of micrometers, thus confirming that fabrication with MoS_2@X does not damage the original structure of the sponge or block the pores inside it. These characteristics are beneficial for the rapid uptake of oil, as the openpore network permits the rapid transport of liquid in the sponge. Fig.3 indicates the neat carbon sponge (Fig. 3a) and coating with MoS_2@CNTs (Fig. 3b) and MoS_2@GO (Fig.3c). It is interesting to note that coating of MoS_2@CNTs on sponges was seen to be uniform whereas decoration of sponge with MoS_2@GO was found to be lesser and non-uniform. Further, coatings of MoS_2@CNTs and MoS_2@GO on melamine sponge were spotted as revealed in SEM images Fig. 4(b, c) and Fig.5(b, c). From the result it is confirmed that the appropriate coating is possible by MoS_2@CNTs materials instead MoS_2@GO due to synergistic effect of MoS_2@CNTs.

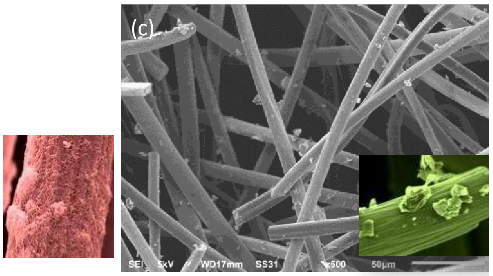

Fig.3: SEM image of (a) neat Carbon Sponge (Y) and (b) MoS_2@CNTs-coated Y and (c) MoS_2@GO-coated Y

Fig.4: SEMimages of (a) neat Melamine Sponge, (b) MoS_2@GO-coated and (c) MoS_2@CNTs coated melamine sponges.

Further, It is clear that the smooth skeletons of the original sponge are covered with MoS_2@X after dip-coating thrice and this highly hydrophobic MoS_2@X in combination with the micro-porous structure of the sponge create a doubly roughened surface, which leads to a composite interface between it, therefore achieving super hydrophobicity.

TEM Analysis

Transmission electron microscopy (TEM) further indicates the internal structure of MoS_2@X. The MoS_2 nanosheet were seen on the surface of MWCNTs whereas layered structures were observed in MoS_2@GO. EDX analysis confirmed the presence of C, Mo, S in the MoS_2@X materials. Elemental mapping confirms the uniformity of Mo and S present in the MoS_2@X matrix (Fig. 5b, f).

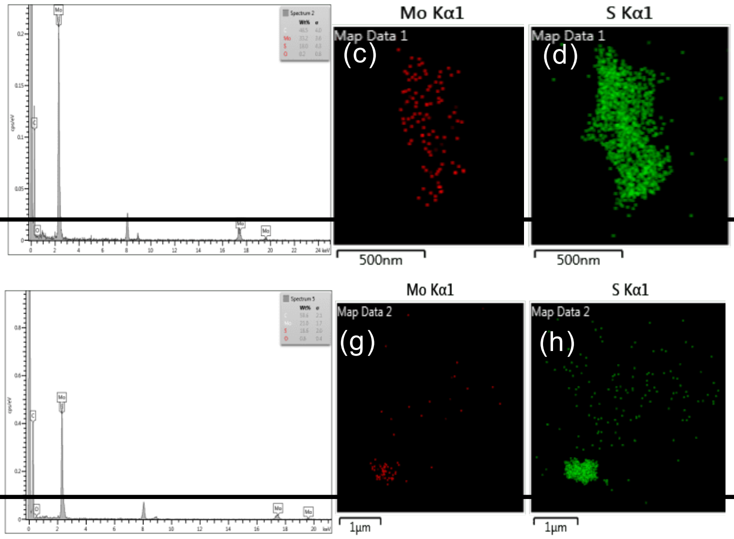

Fig. 5: (a)&(e)TEM images of MoS_2@CNTs and MoS_2@GO, (b)&(f) EDS spectra and (c),(d)&(g),(h) Elemental mapping for Mo and S present in MoS_2@CNTs and MoS_2@GO, respectively.

XRD Analysis

Fig. 6 (a, b) shows the X-ray diffraction (XRD) patterns of the MoS_2@CNT and MoS_2@GO materials. The peaks at 25.2° and 44.6° are indexed to (002) and (100) planes of CNTs in the MoS_2@CNT and MoS_2@GO, respectively due to presence of graphitic carbon. Further, the diffraction peaks appear at 14.2°, 33.5°, 39.8°, 43.1°, 49.1° and 59.3° corresponding to (002), (100), (103), (006), (105) and (110) planes, respectively. Thus, all of the characteristic peaks of MoS_2 are present in both MoS_2@CNT and MoS_2@GO samples. However, graphitic carbon peak was seen very weak in MoS_2@GO but another plane at 44.6° (100) is observed.

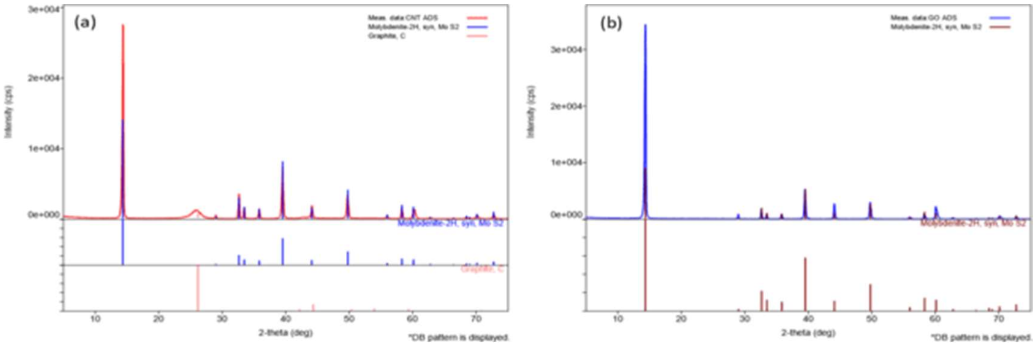

Fig. 6: XRD patternof MoS_2@CNTs and MoS_2@GO.

Thermal Stability

To determine the thermal stability of the MoS_2@CNT and MoS_2@GO materials, thermal gravimetric analysis (TGA) was studied. TGA measurement was employed to evaluate thermal stability of materials in air atmosphere. Fig. 7 (a, b) indicates the TGA curves of MoS_2@CNT and MoS_2@GO above 650ºC. A sharp weight loss after 600°C indicates the decomposition of carbon molecules.

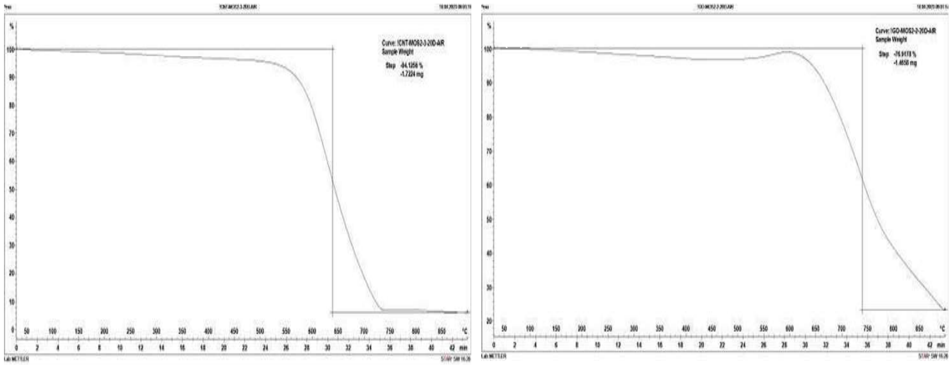

Fig.7: TGA curvesof MoS_2@CNTs and MoS_2@GO.

Water Contact Angles (WCA)

To demonstrate the hydrophobic property of the MoS_2@X, water contact angle (WCA) measurement was performed on the surface of MoS_2@X-coated Y matrix. It was observed that the MoS_2@X-coated Y matrixes are strongly hydrophobic with a WCA of 108°, 124° and 149° (Fig. 8). Thus, superhydrophobic sponges with 10wt% MoS_2@X loading were employed in the following study.

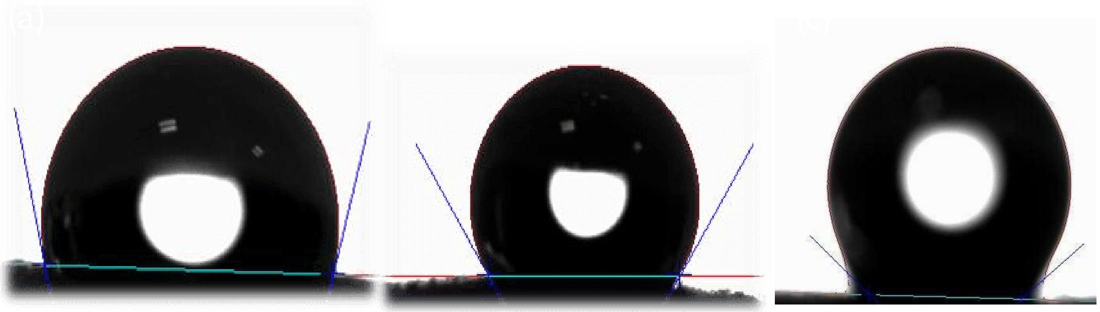

Fig. 8: water Contact angles of (a) MoS_2, (b) MoS_2@GO-coated-Y and (c) MoS_2@CNTscoated-Y and (Y= melamine sponge).

It can be seen that the WCA increases rapidly while incorporating GO and CNT with MoS_2 materials in preparation of MoS_2@X-coated Y. On the loading of CNTs into MoS_2@Xcoated Y matrix, water droplets attained quasi-spherical shapes on the sponge surfaces with CAs of 149°±2°, indicating superhydrophobic behavior of MoS_2@X-coated Y matrix.

Wettability behaviour and absorption studies

Wettability test were performed due it its high porosity, superhydrophobicity and robust stability and checked excellent absorption capacities in diesel oil. To further test the recyclability of MoS_2@X-coated Y for the clean-up of oil, we used typical oil, like- diesel oil to investigate the cyclic absorption and squeezing behavior of the MoS_2@X-coated Y matrix. After absorbing all the oil, the sponges could be squeezed out mechanically to harvest the absorbed oils

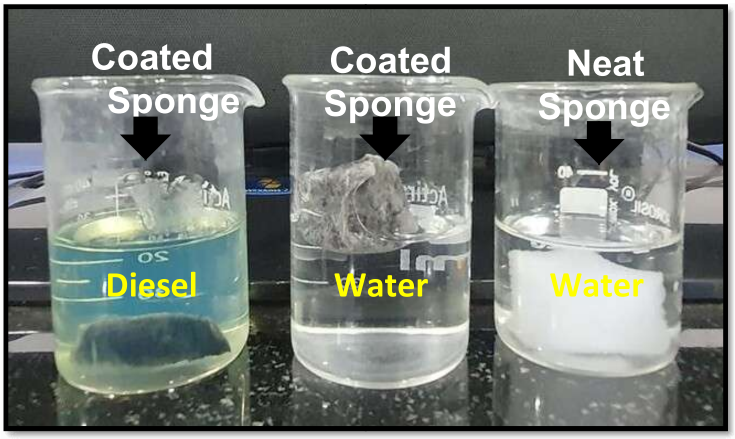

Fig.9: Wettability testing of MoS_2@X using Diesel and water.

As shown in Fig.9, 2x2cm^2 MoS_2@X-coated Y was dropped into diesel and water and seen that the MoS_2@X-coated Y matrix absorbed the oil whereas MoS_2@X-coated Y are seen floating on water. This process was repeated 10 times to check it workability. Such fast absorption kinetics of the MoS_2@X-coated Y is attributed to the combination of its high porosity, capillary action, and super-oleophilic nature.

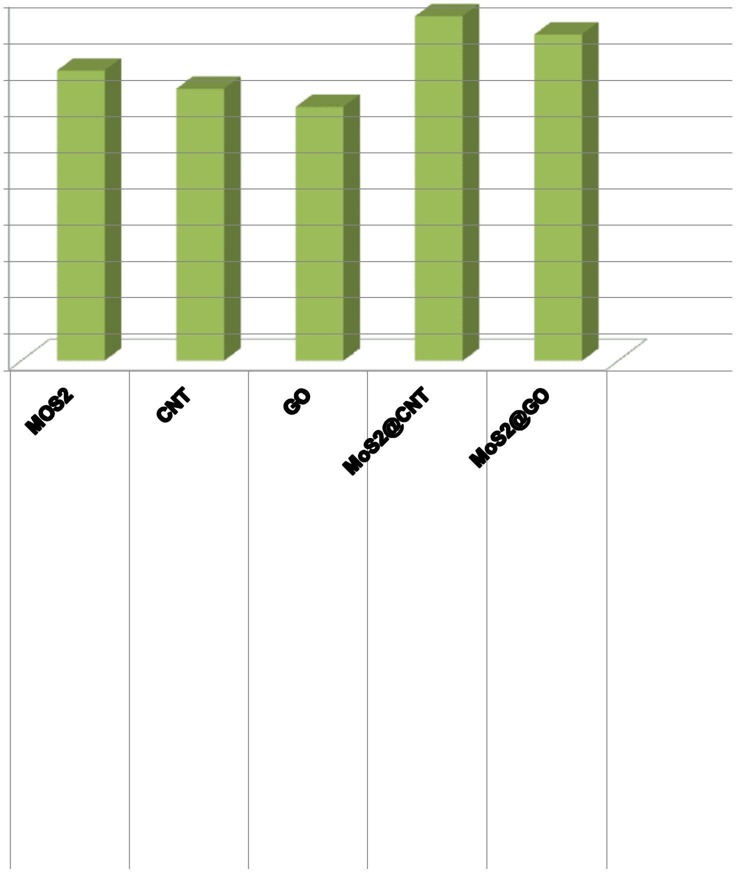

Fig.10: Absorption capacity of MoS_2, CNT, GO, MoS_2@CNTs and MoS_2@GO using melamine sponge were checked in Diesel oil.

Further, absorption capacity of MoS_2, CNT, GO, MoS_2@CNTs and MoS_2@GO MoS_2 was carried out. MoS_2, CNT, and GO individually demonstrate significant absorption capacities, but in the case of composite materials, MoS_2@CNT and MoS_2@GO, show substantially higher absorption capacities compared to the individual materials. MoS_2@CNT composite has the highest absorption capacity among MoS_2@GO and individual materials. This indicates that the combination of MoS_2 and CNT creates highly efficient absorbent materials. The percentage absorption was calculated from the formula where w = Pre-weight, w' = post-weight.

% Absorption =$\frac{Difference\ in\ Wt}{Original\ Wt} \times 100$

Chapter 7: Conclusions

Conclusions

In summary, we have reported a superhydrophobic and superoleophilic MoS_2@X-coated Y for highly efficient separation and absorption of oils from water. This novel MoS_2@X-coated Y matrix exhibits excellent absorption performance including good selectivity, high capacity, and good recyclability, extraordinarily robust stability. Although oil/water separation with MoS_2@X materials is a rapidly growing and promising research field, there are still some challenges to overcome. There is still a lack of understanding of the basic mechanisms of interactions between oil and the surface of the materials used to clean up the oil.

Chapter 8: Future Scope

Future scope:

1. I believe the outcomes will be useful and promising materials for the efficient oil water separation for oil spill. .
2. Moreover, our compressed protonated melamine sponge could separate both surfactant-free and -stabilized oil-in-water emulsions with high separation efficiencies.
3. The high performance of this protonated melamine sponge and its efficient, energy- and cost-effective preparation suggest that it has great potential for use in practical applications.

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