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FACILE SYNTHESIS OF SUPER HYDROPHOBIC MATERIAL FOR SELECTIVE REMOVAL OF SPILLED-OIL FROM WATER SURFACES

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Abstract

The present work reports the preparation of super hydrophobic and oleophilic sorbent powder for the selective removal of spilled-oil from oil-polluted water surface. The sorbent powder was prepared by the surface modification of commercially available pure barium sulfate (BS) with palmitic acid via a simple one-step synthetic approach. The powder was observed to exhibit super hydrophobic character with a static water contact angle value of 152±2°. The powder also possesses sufficient buoyancy and exhibits high selectivity towards oil, vital for a sorbent for use in oil spill clean-ups. The oil sorption capacity of the sorbent material was also investigated.

Keywords: Superhydrophobic; sorbent; spilled-oil; contact angle; oil sorption capacity.

INTRODUCTION

With the rapid economic growth all around, the demand of energy from petroleum hydrocarbons is also significantly increased. The rapid transportation of oil through sea routes, diverse oil utilization processes and improper storage of oil has increased the risk of oil spills. The oil released during leakage from oil storage tanks, loading and unloading operations, ruptures of pipelines, etc results in the occurrence of catastrophic oil spill. Oil spill incidents not only results in loss of the precious oil, but also cause serious coastal and aquatic pollution, destruction of aquatic life, water toxicity, and catastrophic effect on fishing and tourism. To reduce the disaster caused by an oil spill, several remediation techniques are adopted like bioremediation, skimming, in-situ burning, using chemicals like dispersants, solidifiers, and sorbents. Among these techniques, the use of sorbents for oil spill clean-ups has drawn great attention due to their simplicity and efficiency[1]. An efficient sorbent should possess hydrophobic and oleophilic nature, high rate of uptake, high selectivity, sufficient buoyancy, cost effectiveness, and less-toxicity.

Various sorbent materials such as rice straw[2], cotton-fibres[3], aerogels[4], clay[5], exfoliated graphite[6], polypropylene fiber[7], non woven wool[8], rubber[9], vermiculite, perlite[10], etc has already been reported for sorbing and removing the spilled-oil from contaminated water during oil remediation process where they are commonly used in the form of bulk sorbents, sorbent pads, sorbent sheets, sorbent rolls, sorbent pillows, sorbent booms, etc. However, these sorbents have their own merits and demerits. For instance, sorbents prepared from natural products such as rice straw[2] and cotton-fibres[3] faces the problem of less selectivity and buoyancy. Sorbents prepared from synthetic polymeric materials such as polypropylene[7] and butyl rubber[9] possess high selectivity with hydrophobic and oleophilic character, but their major disadvantage is their slow degradability and high cost. Hence, attention has been given to prepare sorbents from widely available, non toxic inorganic mineral products such as clay[5], vermiculite, perlite[10], etc via simple synthetic approach. However, inorganic mineral products such as vermiculite, perlite faces the drawback of insufficient buoyancy. Hence, the aim of the present study is to search an appropriate inorganic material for fabricating a superhydrophobic and oleophilic sorbent material for selective and efficient removal of spilled-oil from contaminated water surface.

In the present study, commercially available pure barium sulfate powder has been taken as the starting material and palmitic acid was used as the surface modifying agent to prepare an efficient sorbent powder via a simple one-step synthetic approach. Barium sulfate (BS), obtained from mineral 'barite', is a nontoxic inorganic compound and widely used as drilling fluids, pigments, paper brightener, radiocontrast agent, etc, while palmitic acid is the most common fatty acid (saturated) found in the living creatures. The wettability (i.e. the hydrophobic and oleophilic character) of the prepared sorbent was tested through contact angle measurements. The selectivity, buoyancy and oil sorption capacity of the sorbent material was also tested through various laboratory experiments.

EXPERIMENTAL

Preparation of sorbent

The superhydrophobic and oleophilic sorbent powder was prepared by heating an aqueous mixture of BS (Merck, India) and palmitic acid (Loba Chemie, India) at 70 °C for 1 h under continuous stirring. The water was evaporated from the mixture by heating at 50 °C for 12 h and the dried superhydrophobic barium sulfate (SBS) sorbent powder was collected.

Characterization

X-ray diffraction (XRD) analyses were performed using Cu-Kα radiation over 2θ range of 15-60° at a scan rate of 3° min^{-1}, with a sampling interval of 0.05 at 40 mA and 40 kV, using Bruker AXS Diffractometer D8 Powder XRD. Fourier transform infrared (FT-IR) spectroscopic analyses were performed using Thermo Scientific Nicolet 6700 FT-IR instrument within the scan range

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4000–400 cm^{-1}. Scanning electron microscopic (SEM) analyses were performed using ZEISS EVO 60 Scanning Electron Microscope (Germany) at a magnification of 50 KX.

Contact angle measurements

Contact angle measurements of the powder samples (i.e. BS and SBS) were performed with crude oil (collected from M/S Haldia Refinery, India) and water at 25 °C using Ramé-Hart Automated Goniometer, model 290-G. For the measurements, the samples were pressed on a glass slide to form a smooth surface on which the liquid drops were placed.

Oil sorption capacity studies

A fixed amount of SBS sorbent powder (0.05 g) was added to crude oil-water mixture (concentration of oil was varied from 0.002 to 0.02 w/w of water) and left un-disturbed for 10 min. After sorbing the oil, the powder was removed and the un-sorbed oil was separated from water. Oil sorption capacity (q, in g/g) of the prepared SBS powder was calculated using equation (1).

$q = (w_i - w_f)/m$ (1)

where, w_i is the initial weight of oil (in g), w_f is the final weight of oil (in g), and m is the mass of sorbent.

RESULTS AND DISCUSSION

The crystalline phase identification of BS and SBS by XRD analysis shows that both the samples exhibits similar XRD pattern (Figure 1). The absence of any peaks attributing to palmitic acid molecules in the XRD pattern of SBS indicates the proper dispersion and surface coating of palmitic acid on BS without leaving any residue of the fatty acid. Moreover, the XRD pattern for SBS is slightly shifted to higher 2θ values as compared to the pattern for BS. This shift in the XRD pattern can also be ascribed to the surface coating of BS with palmitic acid. Further, the intensity of d_{210} and d_{301} diffraction peaks in SBS was found to be slightly higher as compared to BS, which may be due to the growth of the crystal along [210] and [301] directions respectively, due to the surface coating by palmitic acid.

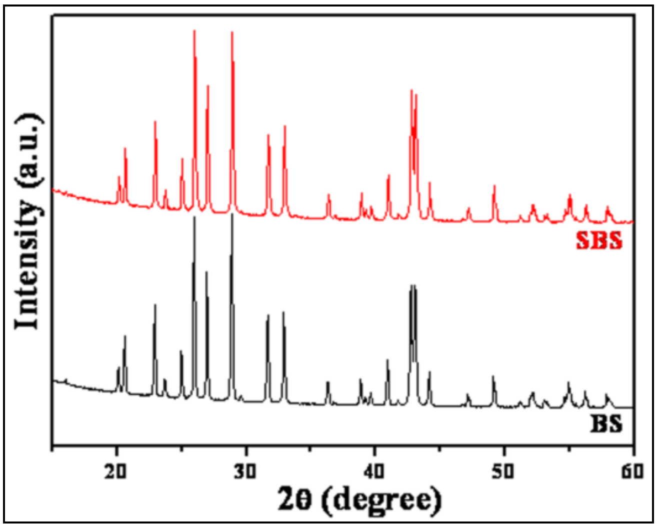

Figure 1: XRD patterns for BS and SBS

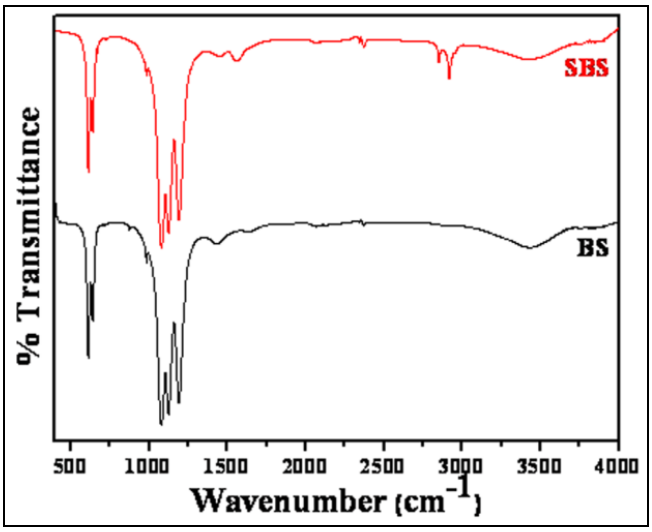

Figure 2: FT-IR spectra for BS and SBS.

Functional group analysis of the samples (i.e. BS and SBS) by FT-IR reveals two peaks at 2915 and 2848 cm^{-1} in the FT-IR spectrum of SBS (Figure 2), which corresponds to the aliphatic C-H stretching of palmitic acid, while the peak at 1560 cm^{-1} can be assigned to C-H bending vibration, thereby substantiating the presence of palmitic acid in SBS powder. The common peaks in the two samples (i.e. BS and SBS) centered at 1189–1077 and 983 cm^{-1} can be assigned to asymmetric stretching mode of the S-O bond (υ_3 and υ_1 respectively) in barium sulfate. Other common peaks in the region 638–610 cm^{-1} can be attributed to the out of plane bending mode of S-O bond in barium sulfate.

Morphological analysis by SEM shows that both BS and SBS particles have elliptical shape (Figure 3). The size of BS particles was found to be in the range of 185–420 nm (Figure 3a) which increases to 210–500 nm following the treatment with palmitic acid in SBS (Figure 3b).

The wettability of the two samples (i.e. BS and SBS) towards water and oil (crude oil) was tested through contact angle measurements. On placing the water drop on BS (Figure 4a), the liquid quickly penetrates into the sample (Figure 4b) indicating the wettable and hydrophilic nature of BS. However, the water drop is sustained on SBS even after 60 min (Figure 4c) revealing the non-wettable behavior of SBS towards water. The static water contact angle on SBS was observed to be 152±2°, indicating the superhydrophobic character of the sample.

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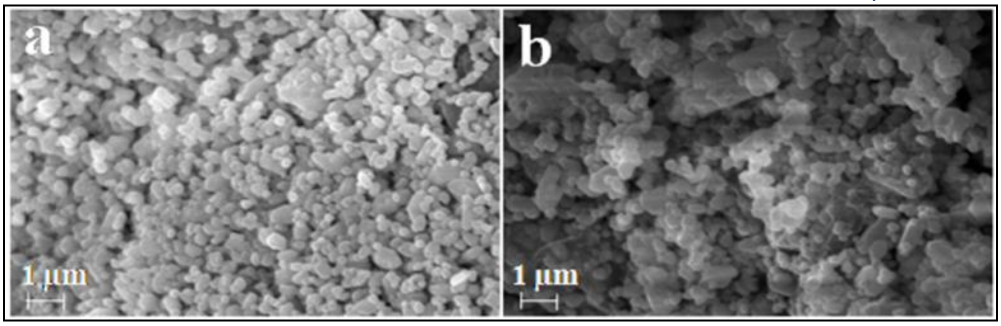

Figure 3: SEM image for BS (a) and SBS (b)

The superhydrophobic and non-wettable behavior of the SBS powder might have arised due to the presence of palmitic acid molecules on the surface with a probable orientation of the long hydrophobic tail of the fatty acid outwards and hydrophilic head inwards, interacting with the Ba^{2+} groups through electrostatic interactions. On the other hand, the static contact angle with crude oil could not be measured for SBS due to rapid uptake of the oil by the powder. The maximum contact angle for crude oil on SBS was measured to be 6 ± 1°, substantiating its oleophilic character.

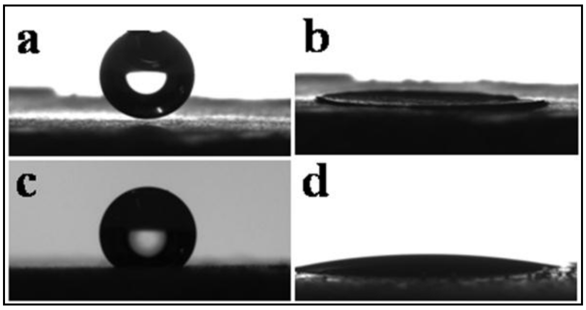

Figure 4: Contact angle measurements: water drop before addition on BS (a), after addition on BS (b), water drop on SBS (c), crude oil drop on SBS (d).

The qualitative demonstration in Figure 5 indicates the buoyant and selective nature of SBS sorbent powder. It was observed that on adding the powder to crude oil-water mixture, it floats on the water surface and selectively sorbs the oil forming a semi-solid lump (Figure 5b) which can then be easily removed from the water surface via scooping technique.

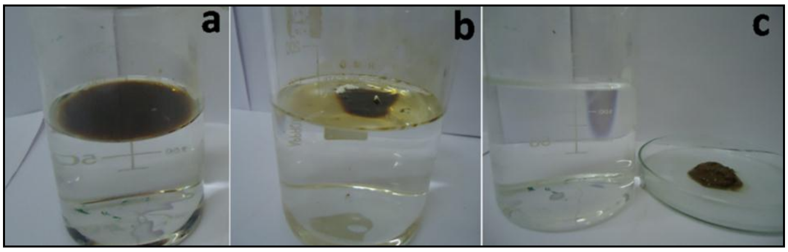

Figure 5: Qualitative demonstration for testing the buoyancy and selectivity of SBS: crude oil-water mixture (a), SBS added to the crude oil-water mixture (b), separated clear water and oil-sorbed SBS (c).

The variation in oil sorption capacity (q) of SBS sorbent powder with varying ratio of crude oil-water mixture, calculated using equation 1, is shown in Figure 6. It was observed that the q value initially increases with increase in the amount of oil in the mixtures, reaches a maximum value and then decreases. The decrease in the q value is due to the increase in the amount of the oil in a confined region containing a fixed amount of sorbent powder which results in non-availability of active oleophilic sites on the sorbent surface towards the excess amount of oil in the confined area. The maximum q value of SBS for crude oil was found to be 0.68 g/g.

CONCLUSIONS

Superhydrophobic and oleophilic barium sulfate sorbent powder (SBS) was successfully prepared via a simple synthetic approach for the selective removal of spilled-oil from oil-polluted water surface. Contact angle measurements confirmed the superhydrophobic (static water contact angle 152±2°) and oleophilic (maximum crude oil contact angle 6±1°) character of the material. The sorbent powder was found to exhibit sufficient selectivity and buoyancy. The oil sorption capacity of the powder was found to 0.68 g/g. The sorbent powder can directly be used on the affected site or can be applied as sorbent boom, pads, and pillows. Owing to the ease and simplicity of the fabrication method, this sorbent powder can be commercially prepared for

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selective and efficient oil removal from oil contaminated waters either in alone or along with main stream technologies to protect the aquatic environment from water toxicity.

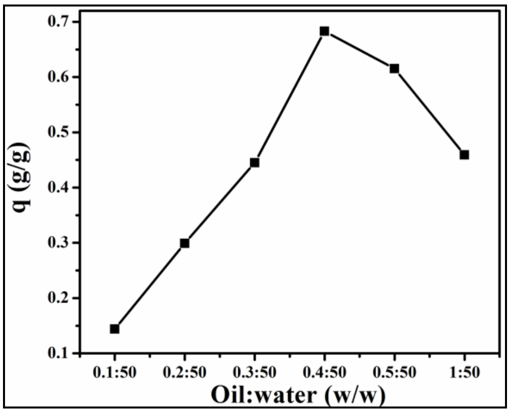

Figure 6: Oil sorption capacity (q, g/g) of SBS towards crude oil

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FUTURE SCOPE OF THE WORK

The prepared sorbent powder can be tested for land oil spill clean-ups. The preparation method can be repeated with other fatty acids e.g. stearic & oleic acid and the changes in the properties can be investigated.

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