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Chemical modification of hygroscopic magnesium carbonate into superhydrophobic and oleophilic sorbent suitable for removal of oil spill in water

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ABSTRACT

The wettability of hygroscopic magnesium carbonate has been modified to develop a superhydrophobic and oleophilic sorbent for oil spill clean-ups *via* a simple chemical process using palmitic acid. The prepared material was characterized using X-ray diffraction, Fourier transform infra-red spectroscopy, and scanning electron microscopy. Wettability test infers that the sorbent has a static water contact angle of $154 \pm 1^{\circ}$, thereby indicating its superhydrophobic character. The sorbent was capable of scavenging oil for about three times its weight, as determined from oil sorption studies, carried out using the sorbent on model oil-water mixture. Interestingly, the chemically modified sorbent has high selectivity, buoyancy, and rate of uptake of oil. Further, the reusability studies confirm the repeatable usage of the sorbent and its efficacy in oil spill remediation.

1. Introduction

Wettability is an important character of a solid surface that determines its application in environmental, industrial and biological fields [1]. Hence, enormous research work is being carried out to fabricate wettable and non-wettable materials with extraordinary properties for various applications. Surface that exhibits a high degree of water repellence and has a water contact angle value greater than 150° is commonly regarded as superhydrophobic surface. Some of the naturally occurring superhydrophobic surfaces are lotus leaf, paddy leaves, taro leaves, water strider's leg, and butterfly's wings [2]. The hydrophobicity of a surface can be dramatically enhanced by introducing hierarchical micro/nano structures or surface roughness [3], as possessed by Cassie–Baxter type materials [4]. Such a modification offers superhydrophobic property to the material, possess high contact angle values along with the surface composed of solid microstructures having low surface energy and air-filled voids.

Superhydrophobic surfaces are widely used as photoresponsive materials, self-cleaning surfaces, in targeted drug delivery tools, anti-sticking coating [5], for biochemical separation [2], for oil–water separation in waste-water treatments, and for oil spill remediation. Among different applications, usage of superhydrophobic materials in oil spill clean-ups has drawn great attention as the oil spill is a serious issue, and its ill-effects are of long-term effect, creating environmental nuisance. The oil spill incidents not only result in loss of the valuable oil, but also cause pollution to coastal and marine eco-systems, including harmful effects on fishing and tourism. Till date, several artificial superhydrophobic materials have been developed by different scientific groups for oil-water separation such as films [6], meshes [7], and membranes [8] that are used as filters, but the major drawback lies in their recovery process involving the collection of polluted water first, followed by filtration. Although, numerous materials have been fabricated to defeat this drawback, but the use of superhydrophobic sorbents for oil spill removal has gained great attention. It is mainly due to ease of their fabrication and direct application on the site of oil spill. An efficient sorbent should have superhydrophobic and oleophilic character with sufficient buoyancy, selectivity and significant rate of uptake. In addition, it should be reusable, cost effective, non toxic, and biodegradable [9]. Various materials used to fabricate sorbent materials were categorized into synthetic polymers, natural products and inorganic materials. Synthetic polymeric materials such as polyurethane [10], polypropylene [11], butyl rubber [12], etc. have been exploited to develop varieties of sorbent materials, but they face the problem of slow degradability and high cost. Though

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the natural materials like cotton [13], rice straw [14], rubber [15], wool [16], and bagasse [17,18] show good biodegradation, their selectivity is unexpectedly less. Different inorganic products such as vermiculite [19], clay [20], perlite [21,22], graphite [23], zeolite [24], etc. have also been used. Although, they possess good selectivity and biodegradability, they involve multistep synthetic approaches. Superhydrophobic materials like magnetic composite [25], silica nanowires [26] and zinc oxide surface [27] were already reported. However, their modifications involve multi-step synthetic methodologies, which are laborious. In the present study, magnesium carbonate and palmitic acid are used as the substrate and modifying agent, respectively to fabricate a superhydrophobic-oleophilic sorbent powder through a simple synthetic approach.

Palmitic acid (hexadecanoic acid, $CH_3(CH_2)_{14}CO_2H$) is the most common fatty acid found in nature, and the non-toxic and hygroscopic magnesium carbonate is obtained from minerals- magnesite, hydromagnesite, dypingite, etc. Although, individual magnesium carbonate and magnesium carbonate modified with aswanly clay [28] and dodecyl benzene sulfonic acid [29] were already been tested as sorbents, but they have limited oil sorption efficiencies. The use of palmitic acid as the surface modifying agent on hygroscopic magnesium carbonate was explored in the study, which gives a promising improvement in the superhydrophobic character. Hence, the modified material is employed for the oil sorption studies using model oil–water mixtures.

Here, the characterization studies on the prepared sorbent were carried out using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM). The hydrophobic and oleophilic nature of the material was analyzed using contact angle measurements using water and different types of oils. The oil sorption capacity and reusability of the prepared sorbent were determined through various laboratory experiments, and the results are discussed.

2. Experimental

2.1. Chemicals

Magnesium carbonate (magnesium carbonate hydroxide hydrate) and potassium hydroxide were purchased from Merck Specialties Private Limited. Palmitic acid was procured from Loba Chemie, Mumbai. Crude oil was kindly provided by M/S Haldia Refinery, Haldia, India. Diesel oil, engine oil, and kerosene oil were purchased from Indian Oil Fuel Station in Kharagpur (W.B., India). All the chemicals were used as such without any modifications.

2.2. Preparation of sorbent

In the preparation process of superhydrophobic magnesium carbonate sorbent powder, 5 g of magnesium carbonate hydroxide hydrate (MC) was dispersed in water in a beaker by sonication and then heated at 80 °C. Exactly, 0.75 g palmitic acid (PA) was dissolved in hot water containing few drops of potassium hydroxide in a beaker, and then it was added to the dispersion of magnesium carbonate. The resultant mixture was stirred for 60 min at the same temperature (i.e. 80 °C). Finally, the mixture was heated in a hot air oven for 12 h to evaporate the water molecules. The dried white mass was gently crushed to get the modified magnesium carbonate (MMC) sorbent powder.

2.3. Oil sorption studies

The oil sorption ability of the prepared MMC powder was determined quantitatively in batch method, in which different sets of experiments were conducted for crude oil, diesel oil and kerosene oil. Varying amount of MMC powder was added to 1:20 oil–water mixture (w/w) from where it selectively sorbs oil from the water surface. The oil–water mixtures were prepared by adding 2.5 g of oil to 50 g of water, followed by mechanical mixing. The oil, being lighter than water, forms a layer on the water surface. For the oil sorption studies, the powder was initially poured into the oil-water mixture, mixed and left for 5 min at room temperature (26 °C) for complete sorption of oil. The powder sorbs the oil and floats on the water surface from where it was removed by scooping method and remaining oil in the mixture was separated from the water using a separating funnel and weighed. The oil sorption capacity (q, in g/g) was calculated using Eq. (1) [30].

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

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 (in g). All the experiments were performed in triplicate and the error in q values are estimated as ±0.001–0.003 g/g.

2.4. Reusability tests

Reusability of the prepared MMC sorbent powder was studied by washing the crude oil sorbed powders with tetrahydrofuran (THF), since most fractions of crude oil are soluble in THF [31]. Three cycles of the sorption process were performed. In brief, the oil sorbed MMC powder was collected from the crude oil–water mixture (1:20 w/w) by scooping and then washed two times with THF to remove the oil. The washed powder was dried at 50 °C for 8 h, while the crude oil was recovered from THF-crude oil mixture using a rotary evaporator. The dried powder (named as MMC-R1) was again tested for its reusability by repeating the above procedure two more times. The powders obtained after second and third reusability tests were termed as MMC-R2 and MMC-R3, respectively. All the three samples, viz. MMC-R1, MMC-R2, and MMC-R3 were characterized by FT-IR to determine the presence of PA coating and further tested by contact angle measurements to determine their wettability. The oil sorption capacities of the reused samples were calculated using Eq. (1).

A set of control studies was conducted to check the stability of palmitic acid coating on the sorbent under specific conditions (i.e. temperature similar to sea water 30 ± 1 ° C and pH of 8.1). The resultant solution was analyzed using HPLC-PDA detector (Dionex).

2.5. Characterization techniques

XRD was employed to determine the crystalline phase of MC and MMC by using Cu-Kα radiation over 2θ range of 10°-100° 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. The functional group analysis of MC and MMC were performed using Fourier transform infrared spectroscopy (FT-IR) within the scan range 4000–400 cm^{-1}, using Thermo Scientific Nicolet 6700 FT-IR instrument. The morphologies of MC and MMC particles were analyzed using Scanning Electron Microscope (model Zeiss Evo 60). The BET surface areas of MC and MMC were measured through nitrogen adsorption-desorption isotherms obtained from Quantachrome Autosorb Automated Gas Sorption System at 77 K. The surface area was calculated using Brunauer–Emmett–Teller (BET) method and the pore volumes were estimated from the amount adsorbed at a relative pressure of ~0.99. The wettability of MC and MMC powder were determined by contact angle measurements using Ramé-Hart Automated Goniometer, model 290-G, with contact angle images being taken at every 0.5 s interval after applying the droplets.