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A facile energy-efficient approach to prepare super oil-sorbent thin films

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Abstract

Oil spills on water surface and shoreline have caused significant water pollution, and one of the ways to deal with them is to use oil sorbents. An effective sorbent provides high oil uptake and retention values, high selectivity, super-fast uptake kinetics, and sufficient mechanical strength to ensure practical application under different conditions. In this regard, synthetic sorbents made up of graphene, carbon nanotubes, and polymers in the form of aerogels, thin films, pads, and non-woven fibers have been widely explored. However, none of them addresses all the attributes of an ideal oil sorbent. Aerogels provide extremely high uptake values, but they are so light that it is difficult for the end user to handle them. On the other hand, thin films and non-woven fibers can quickly absorb oil but suffer from low uptake capacity with low retention values. Similarly, commercial oil sorbent pads have sufficient mechanical strength, but low uptake capacity compared to aerogels. Herein, we present a super oil sorbent with a porous structure using a facile energy-efficient approach. The as-prepared sorbent comprises a porous thin film with micropores and macro-cavities, resulting in super-fast uptake kinetics and a high oil uptake value of 85 g/g. Moreover, tensile test results confirm sorbent's effectiveness in spill response. Lastly, our unique design does not involve expensive hydrophobic functionalization and thus utilizes lower embodied energy and generates lower carbon footprints.

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1. Introduction

Water pollution caused by oil spills has been a critical threat to the environment. An estimated 5 million tons of oil and organic liquid are transported annually [1], and shorelines and inland water areas are increasingly polluted by the spillage [2].

One of the effective ways to counter oil spillage is using sorbents, especially when a thin film of oil and organic compounds is floating on top of the water's surface. An effective oil sorbent should be porous, oleophilic, and hydrophobic to achieve satisfactory uptake capacities and oil–water separation. When an oil sorbent is brought in contact with a mixture of oil and water, the non-polar attraction, along with the porous structure, will facilitate the initial passage of oil inside the sorbent. The hydrophobic surface forms a layer of oil around itself, acting as a waterproof barrier [3].

The oil sorption mechanism relies on several factors, including surface roughness, surface attraction towards oil, porous structure, cavities to hold oil, the cohesion of oil molecules, and adhesive forces acting on the surface of sorbent through capillary action. Diersch et al. described capillary action as one of the main driving forces of oil sorption [4]. Further, surface roughness also plays a part as the adhesion between oil and the sorbent's surface increases with surface roughness [5].

On the other hand, the sorbent's thickness determines how quickly the saturation is reached [6–8]. Generally, the thinnest possible sorbent films with sufficient mechanical strength are the fastest to reach oil saturation [9]. However, thin films do not have adequate oil storage capacity. Although they may have high g/g values (i.e., amount of oil absorbed per unit mass of dry sorbent), the actual amount absorbed is hardly significant. Hence, preparing an oil sorbent that addresses all the issues discussed here was hypothesized. It should provide pores and macro cavities to enhance surface roughness for quick oil diffusion.

2. Experimental section

2.1. Materials

Reagents like *p*-xylene ACS reagent was purchased from Sigma Aldrich and was used without further purification, high-density polyethylene (HDPE), and ultra-high-molecular-weight polyethylene (UHMWPE) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Plain glass plate was cut to a size of 5 cm × 5 cm and was fixed on the chuck of the spin coater. The chuck was customized by Ossila. Sodium chloride was purchased from a local market and was sieved to a size of 150 μm to 200 μm.

2.2. Equipment

Spin coater from Ossila was used for spin coating. PerkinElmer DSC 8500 was used for differential scanning calorimetry, Friction/peel tester Lloyd instruments Ltd Bognor Regis, UK was used for tensile strength and modulus calculations. SEM images were captured with *FEI Quanta650FEG*. The optical contact angle was calculated using OCA 35, Dataphysics instruments GmbH – Filderstadt, Germany.

2.3. Methodology

1.275 g of HDPE, 0.225 g of UHMWPE, and 50 ml of *p*-xylene were added and allowed to stir under reflux conditions at 130 °C till a clear solution was achieved (see Fig. 1). Usually, the polymer dissolves in 10–15 min. Then 3 g of sodium chloride as a filler of size 150 μm–200 μm was added into the polymer solution and stirred for 10–15 min or till a homogeneous dispersed solution was achieved. Moreover, the glass substrate was heated at 120 °C and was placed on the customized spin coater chuck. The polymer solution was then poured onto the hot glass surface and the lid of the spin coater was closed to avoid solvent evaporation and exposure. The spin coater was turned on and allowed to spin in three steps. Initially, the spin speed was 500 rpm for 5 s, followed by 1000 rpm for 60 s, and finally 3000 rpm for 60 s. After the completion of spin coating, a white powdered layer was observed. The glass plate was removed from the chuck and placed in a hot air oven at 130 °C for 20 min. Finally, the as-prepared thin film was peeled off using a tweezer. The reaction hotplate stirrer and spin coater were placed side-by-side to avoid solvent exposure to the environment, and the whole setup was kept inside the fume hood. The spin coater drain was connected to a receiver to collect solvent and excess polymer.

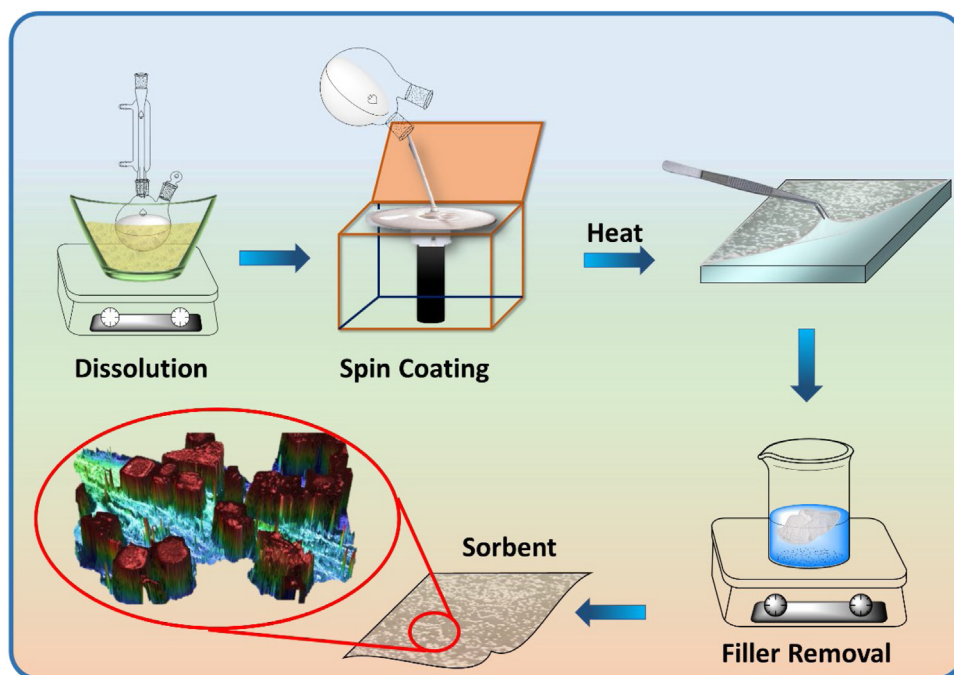


Fig. 1. The process of preparing super-sorbents using spin coating technique.

3. Results and discussion

3.1. Oil sorption

The saturation kinetics of our sorbent were examined to determine how quickly it reaches saturation. Fig. 2 represents the oil uptake kinetics using synthetic oil with density of 0.89 g/cm^3 . The as-prepared sorbent reached its maximum capacity within a minute. Upon removing the oil sorbent film from the oil container, it should be allowed to drain any oil that is loosely connected with the film's surface. Hanging the sorbent in the air and letting it drain under gravitational force is the best way to perform this test. The ASTM F716 and F726 standards suggest reporting the oil uptake capacity after 2 min of dripping. We kept the sorbent hanged for 5 min to reach equilibrium values. The equilibrium uptake was found to be 85 g/g though the value obtained after 0 min of dripping was 140 g/g . As we placed the film in the oil, the porous thin film started absorbing and storing it in the cavities. The small pores were helpful in diffusion as well as absorption.

The high oil uptake capacity is due to the following reason: The presence of micro-pores throughout the surface of film, macro-cavities of size 150 to $200 \mu\text{m}$, roughness of the film surface, thinness of the film, strong capillary action that exerts force to keep oil inside the pores, cohesion between oil molecules that are inside the cavities and on the surface of the film, and adhesion between the oil molecules and the surface of the film.

Fig. 3 depicts a comparison among different oils and organic solvents. Synthetic oil exhibited the highest uptake values, while toluene showed the lowest. The synthetic oil had higher viscosities at room temperature compared to toluene, sunflower oil and paraffin oil. Thus, they flowed slower and showed more adhesion towards sorbent. A higher viscosity generates more resistance to flow, which can be combined with a stronger capillary action to increase uptake capacities.

3.2. SEM and profilometry

The SEM micrograph of the thin film sorbent with open pores ranging from 1 – $10 \mu\text{m}$ and macrocavities is shown in Fig. 4a, while profilometric images of surface roughness and macrocavities are shown in Fig. 4b to d. The

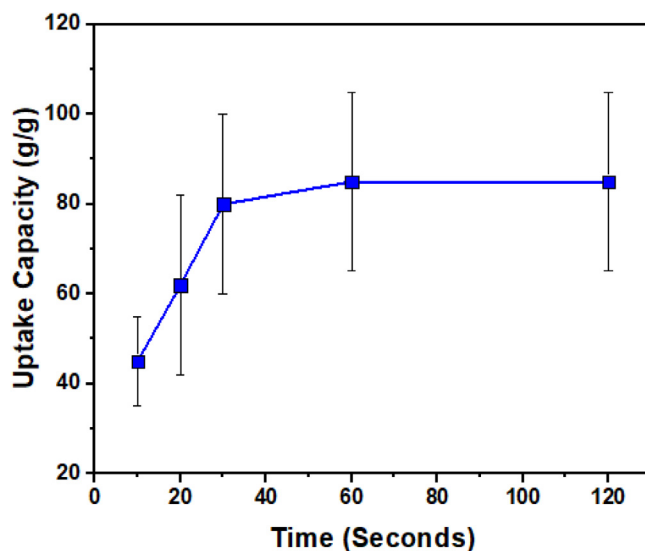


Fig. 2. Oil uptake of super-sorbent at different times using synthetic oil.

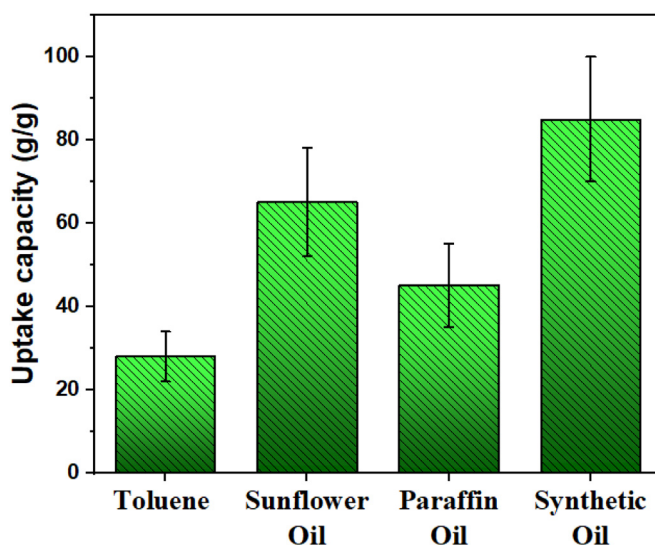


Fig. 3. Uptake capacity of super-sorbent with different types of sorbates.

cavities were created once the filler was removed from the sorbent structure. The size of the cavity depends upon the size of the filler. In our case, we used the particle size of 150 to 200 μm with three-dimensional shape. If the filler is larger than 200 μm , it will settle down to the bottom and comes into direct contact with the solid substrate as it has a much higher density than the polymer. During spin coating, the top and side surfaces of the filler are fully covered with a polymer layer, while the bottom portion is only covered by 20%. As the size of the filler was 200 μm in our case, therefore the size of the cavity's opening was 20% smaller i.e., 160 μm .

3.3. Mechanical properties

Table 1 shows the tensile strength, tensile modulus, and % elongation of the sorbent film. The tensile strength and tensile modulus of our sorbent were found to be 10 MPa and 362 MPa, respectively which reflect the strength

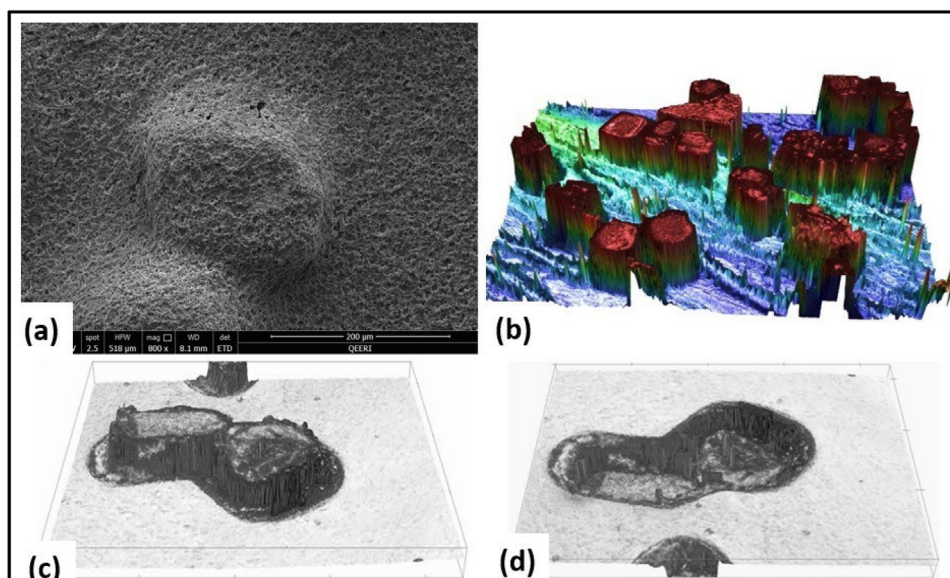


Fig. 4. (a) SEM micrograph showing macrocavities and micropores; (b–d) Profilometry image showing cavity for oil storage.

Table 1. Mechanical properties of as-prepared super-sorbent.

Sample name	Tensile strength (MPa)	Young's modulus (MPa)	Elongation (%)
Super-sorbent	10 ± 2	362 ± 40	36 ± 3
A4 Paper	38 ± 3	4136 ± 35	6 ± 1

and stiffness of the material. The results were compared with commonly available material such as A4 paper to show that the sorbent can be used in all types of practical applications.

3.4. Selectivity test and contact angle

Fig. 5a depicts the oil–water selectivity test. In real-world applications, oil is rarely required to be absorbed separately. It is always connected with water and stays at the surface of the water in the form of a thin or thick film. Hence, the oil–water selectivity test is essential to predict the real-time performance of the sorbent. When an oil sorbent is brought in contact with a mixture of oil and water, the non-polar attraction, along with the porous structure, will facilitate the initial passage of oil inside the sorbent. The hydrophobic surface forms a layer of oil around it, thus acting as a waterproof barrier. The water uptake was found to be 0.6 g/g, and the values did not change with the increase or decrease of the percentage of oil.

Fig. 5b reflects the contact angle of the sorbent film using synthetic oil. The contact angle was measured after 5 s and found to be 17° , which confirmed the oleophilicity of the sorbent.

4. Conclusion

The super-sorbent was synthesized and systematically characterized. The microporous structure with macrocavities facilitated the oil sorption mechanism as revealed by SEM micrographs and profilometry. The equilibrium uptake capacity of the sorbent was 85 g/g; however, it varied depending on the type of oil used. The sorbent had sufficient mechanical strength for practical applications. Combining these attributes with the materials' cost-effectiveness, the as-prepared sorbent meets the requirements of an effective oil sorbent.

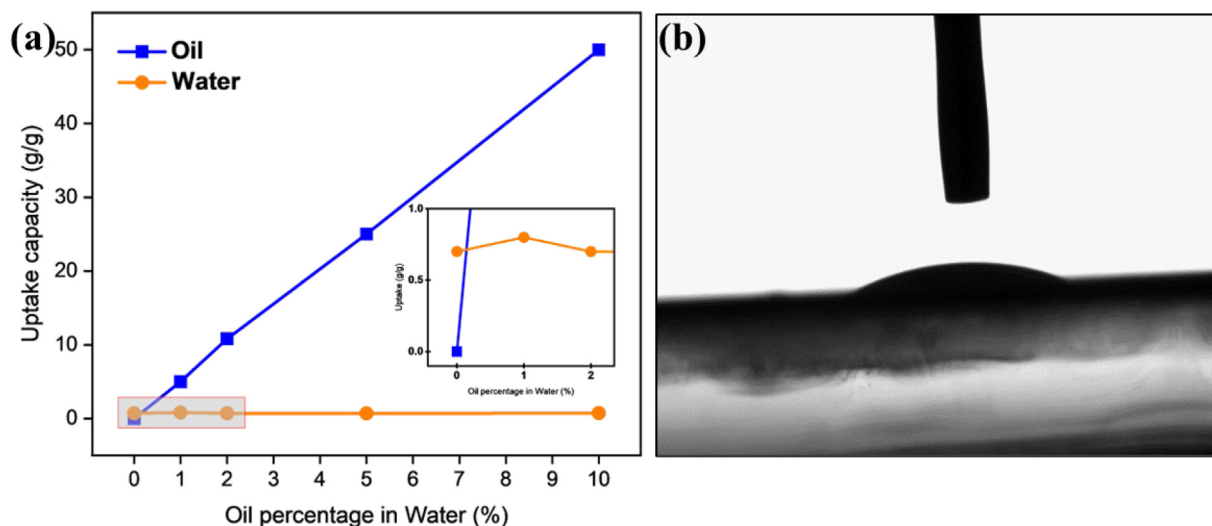


Fig. 5. (a) Selectivity test of oil/water mixtures; (b) Contact angle with synthetic oil.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

- [1] Oliveira LMTM, Saleem J, Bazargan A, Duarte JLda S, McKay G, Meili L. Sorption as a rapidly response for oil spill accidents: A material and mechanistic approach. *J Hazard Mater* 2021;407:124842. <http://dx.doi.org/10.1016/j.jhazmat.2020.124842>.
- [2] Herkenberg W. Method for the removal of oil from oil spills. 1995, US Pat. 5, 451, 325.
- [3] Hoang AT, Nižetić S, Duong XQ, Rowinski L, Nguyen XP. Advanced super-hydrophobic polymer-based porous absorbents for the treatment of oil-polluted water. *Chemosphere* 2021;277:130274. <http://dx.doi.org/10.1016/j.chemosphere.2021.130274>.
- [4] Diersch H-JG, et al. Modeling unsaturated flow in absorbent swelling porous media: Part 1. Theory. *Transp Porous Media* 2010;83(3):437–64. <http://dx.doi.org/10.1007/s11242-009-9454-6>.
- [5] Moreno MC, Brown CA, Bouchon P. Effect of food surface roughness on oil uptake by deep-fat fried products. *J Food Eng* 2010;101(2):179–86. <http://dx.doi.org/10.1016/j.jfoodeng.2010.06.024>.
- [6] Saleem J, Bazargan A, Barford J, McKay G. Application of strong porous polymer sheets for superior oil spill recovery. *Chem Eng Technol* 2015;3:482–8. <http://dx.doi.org/10.1002/ceat.201400068>.
- [7] Saleem J, Ning C, Barford J, McKay G. Combating oil spill problem using plastic waste. *Waste Manage* 2015;44:34–8. <http://dx.doi.org/10.1016/j.wasman.2015.06.003>.
- [8] Saleem J, Bazargan A, Barford J, McKay G. Oil spill remedy using bi-axially oriented polymer films. *WIT Trans Ecol Environ* 2014;182. <http://dx.doi.org/10.2495/WP140131>.
- [9] Saleem J, Bazargan A, Barford J, McKay G. Super-fast oil uptake using porous ultra-high molecular weight polyethylene sheets. *Polym Adv Technol* 2014;25(10). <http://dx.doi.org/10.1002/pat.3376>.