In the last few years oil spillage has become one of the most serious environmental and ecological issues. So there is an urgent need of development of material for collection and separation of organic pollutant from water surfaces. There is a problem in time consumption, cost, environmental and eco-system friendliness with the presently used techniques. The most effective and convenient way to clean and collect oil from oil spillage is the use of sorbents. Highly selective absorption can be realized on a sponge by construction of beffitted surface (chemical and physical) modification.

In this study, we report the first instance of fabrication of polymeric light weight economic sponge based superhydrophobic and superoleophilic highly efficient oil/water separator by facile one pot radiation assisted grafting of acrylate, which is environmental friendly, inexpensive and highly scalable process. We demonstrate here the capability of developed material to separate oil-water from layered (immiscible) as well as emulsified (with and without surfactant) oil/water mixtures.

The quantity of grafting is measured gravimetrically. We have prepared four compositions and four different yields (18wt%, 25wt%, 29wt% and 34wt% grafting) are obtained. For 25wt%, 29wt% and 34wt% grafting, contact angles (CA) of water do not differ much (CA around 153°) and for 18wt% grafting the contact angle of water is around 140°. That's why we have chosen here 25wt% grafted sponge for further studies and discussions.

A water CA of 153°±2° and oil CA of less than 1° obtained in this case, are showing both superhydrophobic and superoleophilic properties of a grafted sponge (Fig. 1A,B). Pure sponge shows moderate hydrophobicity and oleophilicity with a water contact angle of 95° ± 2° and oil contact angle 70 ± 3° respectively (Fig. 1E, F) confirming the nonselectivity towards oil/water. On the grafted sponge, the water drops appear almost like complete spheres but the oil drop is absorbed by the surface instantaneously (Fig. 1C, D).

Optical images of water drop and oil drop on unmodified sponge support the observations from CA measurements (Fig. 1E-H).

SEM images (Fig. 2C-F) indicate the formation of rough surface consisting of micron, submicron and nano size hemisphere or bumps (ups and downs), which are constructed by grafting of acrylate molecule on the sponge surface. SEM images of pure sponge show smooth surface of sponge (Fig. 2A-B). The decrease of surface energy and physical (rough topography) modification of the surface is responsible for super selectivity.

To test oil uptake capacities of modified sponge, we have taken seven different kinds of oils. The oil uptake capacities of modified sponge from immiscible (layered) oil/water mixtures are tested. Due to its porous structure, the absorption capacity is found to be from 30 to 60 times of absorbent's weight (g/g) depending on the oil.

In Fig. 3 (i-v), images of oil removal from layered oil/water mixture by modified sponge and its collection are represented.

To investigate the emulsified oil/water separation efficiency of our modified sponge, a series of surfactant free and surfactant stabilized oil/water emulsions with a droplet size ranges from micron to nano range, are prepared. Modified sponges are immersed into the emulsions. It is noticed that droplets of surfactant free and surfactant stabilized emulsions are demulsified and oils are absorbed by the sponge leaving waters behind in 10 min and 35-40 min respectively (Fig. 4A-C and 4D-E).

This is unprecedented in literature that submicron and nanoscale emulsions are also separated with micron size emulsions. Submicron and nano size emulsions are reportedly difficult to separate by membranes.

In order to recover the absorbed oil and reuse sponge, oil loaded sponge is squeezed and the sponge is reused for next absorption-collection cycle. After using the sponge for 100 cycles the sponge is found to show almost no change in mechanical properties and contact angle. We have already tested 153mmx153mmx2mm sheet, which can be extended up to couple of feet.

In conclusion, for the first time, we are able to fabricate a sponge based superhydrophobic and superoleophilic absorbent material for oil/water separation from layered oil/water mixture as well as emulsified oil/water mixture with wide range of droplets (surfactant free and surfactant stabilized), by a rapid, clean, scalable and economic route, gamma assisted low surface energy molecule grafting. The material is mechanically flexible, extensively reusable and economic. Thus, our material is promising for numerous applications, such as oil spill cleaning from water, purification of crude oil, fuel and emulsified waste water produced in industry and daily life.
Fig. 1: A-H) Images of contact angles (A-B, E-F) and beading (C-D, G-H) of liquid water (A,C,E,G) and oil (B,D,F,H) droplets on both the pure-PU sponge (E-H) and DMA-grafted PU Sponge (A-D).

Fig. 2: SEM images: A-B) unmodified sponge with different magnifications. C-F) modified sponge with different magnifications showing rough surface consisting of micron, submicron and nano size hemisphere or bumps (ups and downs).

Fig. 3: Diagrammatic representation of successive steps (i-v) of separating oil/water mixture and recollection of oil from it.

Fig. 4: A-C) Photographs of emulsions without surfactant: before and after separation. D-F) with surfactant: before and after separation.

References


