J. Phys. D: Appl. Phys. 49 (2016) 145601 (8pp)

Effect of the porous structure of polymer foams on the remediation of oil spills

Javier Pinto, Athanassia Athanassiou and Despina Fragouli

Smart Materials, Istituto Italiano di Tecnologia (IIT), Via Morego 30, 16163 Genova, Italy

E-mail: Sanz.Pinto@iit.it

Received 30 September 2015, revised 4 December 2015 Accepted for publication 7 December 2015 Published 1 March 2016



Abstract

Current approaches for the remediation of oil spills propose the utilization of functionalized polymeric foams as efficient oil absorbents. However, for the majority of the materials employed, the studies are focused on sophisticated surface treatments while the significant role of the morphological parameters of the porous structure of the pristine foams remains unexplored. Herein, we prove that the structural parameters of the pores of the polymeric foams play a fundamental role for the efficient removal of oil from water. The presented experimental and theoretical study shows that pristine polyurethane foams with highly interconnected open porous structures, and pore sizes below 500 μ m are able to reach oil absorption capacities as high as 30 gr of oil per gr of polyurethane. Chemical functionalization of the porous structure does not increase further the oil absorption efficiency but it significantly contributes to the increase of the selectivity of the process. The current findings demonstrate the importance of the right choice of the pristine foams for the fabrication of cost-effective absorbents with high water-oil separation performance.

Keywords: polyurethane foams, pore size, surface properties, absorption capacity, oil spills

S Online supplementary data available from stacks.iop.org/JPhysD/49/145601/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Remediation of oil spills in open waters is a research topic of great importance, due to the catastrophic effects on the marine and aquatic environment [1]. The severity of this problem is reflected not only in the magnitude that these spills can reach, (e.g. up to 210 million gallons of oil were released in the Gulf of Mexico after the explosion of BP's Deepwater Horizon in 2010) but also in their persistence [2, 3] and frequency: currently about 15 oil spills are found daily in navigable waters, just in the United States [4]. Common effective 'water-oil separation' approaches, based on the use of superhydrophobic and superoleophilic filters [5, 6], cannot be applied directly in the remediation of oil spills in open waters, due to the necessity to collect the contaminated water before any filtration process. On the contrary, porous materials that selectively absorb oil do not present such limitation, and they can be applied *in*

situ for the remediation of the oil spills, as well as used on land after the landfall of the oil spills [7, 8]. Hence, several functional materials have been developed able to efficiently absorb the oil, based on natural fibrous or porous materials (e.g. cotton, kapok, milkweed, cork) [9–13], polymeric fibers (e.g. polypropylene, polystyrene) [10, 14–16], carbon nanotubes [17, 18], spongy graphene [19, 20], nanowire membranes [21], or polymeric foams (e.g. polydimethylsiloxane (PDMS), polyurethane (PU)) [22–30].

Suitable absorbent materials for large-scale oil spills remediation should present a high oil absorption capacity and selectivity, and at the same time be low-cost systems. According to these requirements, PU foams are among the most promising materials. In particular, several works have reported increased oil absorption capacity and oil-water selectivity of PU foams by means of the chemical modification of their surface properties [23–30]. However, these studies did not take into account the particular morphology and parameters of the porous structure of the studied PU foams, thus overlooking an important intrinsic factor that may influence the oil absorption performance. Indeed, previous studies on the oil absorption behavior of fiber assemblies, prove that parameters of the porous structure, such as the pore size, define their oil absorption performance [10]. Therefore, the determination of the effect of the porous morphology of the PU foams on their oil absorption performance is of significant importance for the optimal design of an efficient absorbent. Most importantly, defining the influence of the foams' structural parameters is essential for the correct evaluation of the performance of any additional surface treatments, and their actual impact on the oil absorption capacity and efficiency.

Herein, the influence of the structural parameters of PU foams, such as porosity, pore size, and pore connectivity, are studied and related to their capacity and efficiency as oil absorbents. We prove that foams with open porous structures, high connectivity and pore sizes about or below 500 μ m can absorb oil of 40 times the PU volume and can separate water from oil in a few seconds. Such performance is comparable with various surface treated PU foams taken by the recent literature, leading to the conclusion that the chemical modification of the surface of the pores might not be necessary to increase the oil absorption capacity if the appropriate foam is previously selected. Alternatively, surface chemical modification can be used for the enhancement of the oil-water selectivity, and the decrease of the oil saturation time. Therefore we show that the selection of an optimized pristine PU foam offers the opportunity to develop high performance oil absorbent materials, significantly better than current commercial products, avoiding the utilization of complicated and time consuming chemical modifications for the remediation of oil spills.

2. Materials and methods

2.1. Materials

PU foams with porosity 0.975 were a kind offer of Recticel Flexible Foams Inc. PU foams with porosity 0.98 were reused from packaging wastes. Others PU foams were provided by the Cellular Materials Laboratory (CellMat, University of Valladolid (Spain)). Iron nanopowder with hydrophobic carbon shells (particle sizes from 5 to 200 nm with average primary particle size ~30–60 nm) was purchased from PlasmaChem, Germany. Poly(tetrafluoroethylene) (PTFE) submicron particles (mean diameter 1 μ m) were purchased from Sigma–Aldrich. Motor oil (SAE 15W-40, dynamic viscosity = 287.23 mPa·s, surface tension $\gamma_{oil} \approx 31$ mN m⁻², and $\rho_{oil} = 0.8787$ g cm⁻³ at room temperature (RT)) was employed for the oil absorption behavior characterization.

Chemical modification of the foams: The process followed for the chemical modification of the foams is reported elsewhere [23]. In brief, iron nanoparticles were transferred to the PU foam's external and inner surfaces by dip-coating using chloroform as solvent (10 mg ml^{-1}). Then, after drying, PTFE particles were deposited onto the external surfaces of the foam by triboelectric charging.

2.2. Experimental techniques

Characterization of the PU foams: bulk densities of the PU foams ($\rho_f = w_f / v_f$) were calculated by measuring their weights (w_f) and geometric volumes (v_f). Average pore sizes, pore size distribution, and pore morphologies were determined using FIJI/ImageJ [31] from scanning electron microscopy (SEM) micrographs taken from two different perpendicular planes (e.g. *XY* and *YZ*) of the foams using a JEOL Model JSM-6490.

Oil absorption measurements: the determination of the oil absorption capacity was carried out by placing at least two samples of each kind of PU foam on a motor oil surface for 10 min at RT and ambient pressure. Oil absorption process is carried out only by the interactions between the oil and the PU foams, without external forces involved (i.e. the samples were not forced below the surface of the oil or squeezed). The oil absorption capacity is usually defined in the literature as the ratio between the weight of oil absorbed by the foam and the weight of the PU (w_{oil}/w_{PU} , grams of oil absorbed per gram of PU) [30]. Samples were weighed before (w_0) and after (w_1) the oil absorption, and the oil absorption capacity was calculated according to equation (1).

$$w_{\rm oil}/w_{\rm PU} = \frac{(w_1 - w_0)}{w_0} \tag{1}$$

It should be noted that the measured oil absorption capacities represent the amount of oil that the samples can take and retain after being extracted from the oil. Other oils with similar viscosities (e.g. mineral oil (dynamic viscosity = 14 mPa·s at 15 °C), peanuts oil (dynamic viscosity = 70 mPa·s at RT)) were also tested, and the obtained results are similar as the ones reported for the motor oil.

However, this definition of the oil absorption capacity (w_{oil}/w_{PU}) hinders the comparison between different studies and the identification of the parameters taking place during the oil absorption process, because of the influence of the density of the oil and the added weight of the surface treatment employed in each study. These limitations can be overcome by the utilization of the volumetric absorption ratio, denoted as the volume of oil absorbed by the foam divided by the volume of the solid PU phase (v_{oil}/v_{PU}) (equation (2)).

$$v_{\rm oil}/v_{\rm PU} = \frac{\frac{(w_1 - w_0)}{\rho_{\rm oil}}}{\frac{w_0}{\rho_{\rm s}}} = \frac{(w_1 - w_0)}{w_0} \cdot \frac{\rho_{\rm s}}{\rho_{\rm oil}} = w_{\rm oil}/w_{\rm PU} \cdot \frac{\rho_{\rm s}}{\rho_{\rm oil}}$$
(2)

where ρ_s is the bulk density of the solid PU matrix ($\rho_s \approx 1.2 \text{ g} \text{ cm}^{-3}$). Using the volumetric ratio it is possible to precisely compare the performance of treated and non-treated samples, as well as the absorption of different oils, assuming that the oil does not induce swelling of the PU matrix, and that the surface treatments present a negligible influence on the volume of the foam. In such case, the maximum volume of oil that can be adsorbed by the foam will correspond to the volume of the voids inside the foam (i.e. porosity or volume fraction of voids (V_f)). Therefore, it is possible to determine theoretically the maximum oil volumetric absorption ratio (v_{oil}/v_{PU})_{max} using equation (3).



Figure 1. Capillary pressure calculation for an oil-PU foam system ($\gamma_{oil} \approx 31 \text{ mN m}^{-2}$) for pore diameters ranging from 400 to 4000 μ m for different oil contact angles (from 0° to 40°).

$$(v_{\rm oil}/v_{\rm PU})_{\rm max} = \frac{V_{\rm f}}{\rho_{\rm r}} = \frac{1 - \rho_{\rm r}}{\rho_{\rm r}} = \frac{1 - \frac{\rho_{\rm f}}{\rho_{\rm s}}}{\frac{\rho_{\rm f}}{\rho_{\rm r}}}$$
(3)

where $\rho_{\rm r}$ is the relative density of the foam, and $\rho_{\rm f}$ and $\rho_{\rm s}$ are the bulk densities of the foamed and solid PU, respectively. According to equation (3), the maximum oil absorption capacity can be determined solely by the relative density of the pristine foam. Moreover, the oil absorption efficiency (OAE) can be defined as the ratio between the actual volumetric absorption capacity (v_{oil}/v_{PU}) and the theoretical maximum volumetric absorption capacity $(v_{oil}/v_{PU})_{max}$, which is directly related to the percentage of voids filled by the oil and the ability to retain the oil inside the porous structure after being extracted from the oil spill [10]. Increased filling of the porous structure can be achieved when two main conditions are simultaneously fulfilled: the porous structure should be interconnected (as unconnected voids are inaccessible for the oil storage), and there should be a mechanism which drives the oil into the porous structure.

It is known that the oil is driven through the pores, and subsequently retained, in the presence of a capillary pressure (ΔP) [29], which at first approximation will be given by equation (4).

$$\Delta P = \frac{2\gamma_{\rm oil}\cos\theta}{r} \tag{4}$$

where γ_{oil} is the surface tension of the oil, θ is the contact angle between oil and the PU solid surface, and *r* is the radius of the pores. Therefore, it is expected that ΔP increases with the decrease of the size of the pores of the PU as shown in figure 1. Thus, the ability of a PU foam to take the oil and fill as much voids as possible should be determined not only by its surface properties (i.e. oleophilicity, as previous studies suggested), but also by its structural parameters, such as the radius of the pores and also their connectivity.

Oil saturation time: the oil saturation time was defined as the time needed by the samples to sink in the oil during the oil absorption tests.

Reusability: in order to explore the reusability of the foams, after oil absorption they were mechanically squeezed in order to remove the oil, and they were subsequently reused following the process described above. The collected oil after squeezing was weighted in order to determine the amount of oil recovered.

Water absorption measurements: at least two samples of each kind were placed on a distilled water surface for 10 min at RT and ambient pressure. Water absorption process is carried out only by the interactions between the water and the PU foams, without external forces involved (i.e. the samples were not forced below the surface of the water or squeezed). Samples were weighed before (w_0) and after (w_1) the water absorption, and the water absorption capacity $(w_{water}/w_{PU}, grams of water absorbed per gram of PU)$ was determined using equation (1).

3. Results and discussion

3.1. Structural parameters of PU foams

Determination of the structural parameters of the pristine PU foams under study was carried out by SEM microscopy, and representative micrographs of the three different porous structures found are shown in figure 2. All the foams present an open cell structure, with virtually every pore available to store oil; nevertheless, significant differences are found in terms of the degree of connectivity of the pores. In particular, the studied PU foams can be classified in three main categories according to their degree of pore connectivity: open dodecahedral pores with high connectivity (ODHC; figure 2(a)), in which each pore is connected with all the surrounding pores; open dodecahedral pores with medium connectivity (ODMC; figure 2(b), in which each pore is connected with most but not all the surrounding pores; and open dodecahedral pores with low connectivity (ODLC; figure 2(c)), in which each pore is connected with just one or a few of the surrounding pores. For the abovementioned degrees of connectivity, diverse foams with a wide range of pore sizes between 435 and 6692 μ m, and porosities (V_f) between 0.96 and 0.98 were studied, as shown in table S1 of the supplementary information (stacks. iop.org/JPhysD/49/145601/mmedia). As shown in figure 3, the smaller the pore sizes the narrower is the size distribution for all cases, indicating that foams with smaller pore sizes have more homogeneous morphology.

3.2. Oil absorption efficiency (OAE), saturation time, and water absorption

The performance of the abovementioned foams is studied in terms of OAE, oil saturation time, and water absorption as shown in figure 4. Since their surface chemistry is similar, any difference in their performance should be attributed to their porous structure parameters such as pore size and/or pore connectivity. It should be mentioned that the performance of the foams does not depend on the porosity, in the range studied herein ($0.96 \le V_f \le 0.98$), as shown in supplementary information table S1 (stacks.iop.org/JPhysD/49/145601/mmedia).



(a)



Figure 2. Representative SEM micrographs of the studied porous morphologies: (a) open dodecahedral pores with high connectivity (ODHC), (b) open dodecahedral pores with medium connectivity (ODMC), and (c) open dodecahedral pores with low connectivity (ODLC).



Figure 3. Pore size distribution of the studied PU foams.

At the same time, foams with pore sizes higher than 2000 μ m are not able to retain oil inside their pores (OAE < 0.15) due to insufficient ΔP attributed to the large dimensions of the pores. In fact, as already shown in figure 1 the ΔP of the motor oil-PU foams system increases with the decrease of the pore size while for pore sizes higher than 2000 μ m it is more or less stable in the minimum value. Focusing on the foams with pore sizes less than 2000 μ m (figure 4(a)), the strong dependence of the OAE on the pore size and connectivity is evident, demonstrating that these are the key factors for the OAE enhancement. Concerning the pore connectivity, ODHC PU foams reach high OAE values in the range of 0.8–1.1. Although according to the definition of OAE, the maximum value should be 1.0, experimental values slightly higher than 1 are derived due to the presence of oil adhered to the external surface of the foams. This is an additional oil volume not considered within the porosity of the foam. Samples with medium connectivity (ODMC) present a wider range of values, from 0.5 to 1.0. The wider OAE range is probably attributed to the exact amount of the interconnected pores, since when few connections are lost ODMC foams with the appropriate pore size can still reach maximum OAE values, whereas ODMC foams with several connections lost reach intermediate values. Finally, the ODLC foam presents the lowest OAE, of about 0.2. Therefore, the connectivity



Figure 4. (a) Oil absorption efficiency, (b) oil saturation time, and (c) water absorption after 10 min of interaction between the foams and the oil or water, performed on PU foams of diverse pore connectivity, and with pore sizes below 2000 μ m.

degree plays a key role on the oil absorption performance of the PU foams, being their oleophilicity not enough to fill the porous structures in which the oil should follow a tortuous path between adjacent pores. For this reason, high connectivity open pore morphologies are required to ensure maximum OAE performance using pristine PU foams. It should be noted that for samples with specific porosity ($V_{\rm f} = 0.975$) and high pore connectivity (ODHC), there is a clear influence of the pore size on the OAE. In fact, as shown, the average OAE increases with the decrease of the pores size, reaching maximum and reproducible values for pore sizes less than 800 μ m, where the ΔP in each pore is strong enough to completely fill the porous structure of the foam with oil and retain it after extraction. Indeed, as already shown in figure 1, the ΔP increases significantly with the decrease of the pore size, and for samples with mean pore size of 435 μ m, ΔP is four times that of samples with mean pore size of 1741 μ m. This leads to rather constant experimental oil absorption capacity of about 30 gr of oil per each gram of PU, which in volume terms (equation (2)) corresponds to values higher than 40 v/v (table S1 (stacks.iop. org/JPhysD/49/145601/mmedia)). On the contrary, PU foams with pore sizes over 1000 μ m although can also reach OAE values near 1, they present a non-reproducible behavior due to their wider pore size distribution (figure 3) which consequently affects the average OAE.

Another important factor related to the capillary pressure, and therefore to the pore size, is the time required for the samples to be completely saturated by oil, figure 4(b). This is an important parameter since in applications for the remediation of oil spills low saturation times are required in order to minimize the environmental impact. It should be mentioned that samples with low connectivity (ODLC) and most of the samples with medium connectivity (ODMC) are not able to reach the saturation, while the only ODMC sample able to reach saturation requires three times more time to fill its porous structure than the high connectivity samples (ODHC) with similar pore size.

Focusing on the ODHC samples with the best OAE performance (pore sizes below 1000 μ m and OAE = 1, foams retain all the absorbed oil), it is found that the reduction of the pore sizes results in faster oil saturation time, mainly due to the increase of the ΔP as aforementioned (figure 1). In fact, the smaller the pore size the higher the ΔP and therefore the faster is the oil absorption.

On the contrary, for pore sizes higher than 1000 μ m the saturation time decreases with the increase of the size. In this case the higher pore sizes and broader pore size distribution allow to the oil to interact with the foam by two mechanisms: the capillary forces for the smaller pores, and the filling of the voids in the case of the larger pores (OAE < 1, foams



Figure 5. Theoretical maximum oil absorption capacity of PU foams (estimated using equation (3)), presented together with the experimental results of this work and representative results from the literature.

absorb and retain most but not all the oil). Indeed, the oil absorption mechanism for larger pores is exclusively attributed to the filling of the voids as demonstrated using samples with high pore sizes (e.g. PU foams with pore sizes over 2000 μ m). Although the saturation times of these PU foams were all less than 20s, after extraction from the oil these foams were not able to retain the oil due to the absence of any capillary forces (OAE = 0, foams not able to retain the oil).

So far, it has been demonstrated that pristine ODHC PU foams with pore sizes below 952 μ m, are required to achieve high OAE and low oil saturation time, while the optimal performance is attributed to foams with pore sizes of 400–500 μ m. In order, though, to utilize such foams as absorbents in the remediation of oil spills, their oil-water selectivity should also be evaluated. Foams with high selectivity should repel water and at the same time absorb oil, presenting thus certain hydrophobic and oleophilic wetting properties. The water absorption capacity of the ODHC foams which, according to the parameters studied so far, show increased performance compared to the ODMC and ODLC ones, is studied for diverse pore sizes as presented in figure 4(c). It is evident that the pore size reduction causes a linear decrease of the water absorption by the foams, reaching a minimum value of 0.75 gr of water per gr of PU foam for pore sizes of 495 μ m, well below the 30 gr of oil per gr of PU foam that can take the same foam (table S1 (stacks.iop.org/JPhysD/49/145601/ mmedia)). Such effect is attributed to the higher surface roughness of the foams with smaller pore sizes, as well as to the absence of large surface pores where water drops can be stored (since the PU foam surface is highly hydrophobic (WCA about 133°) but not self-cleaning (figure S1, supplementary information (stacks.iop.org/JPhysD/49/145601/ mmedia)). This is a general trend also followed by the other foams utilized in this study, as presented in the supplementary information file (stacks.iop.org/JPhysD/49/145601/ mmedia). Further characterization of the wetting properties of the foams utilizing water contact angle (WCA) measurements cannot be accurately performed due to the non flat foam surface (see supplementary information (stacks.iop. org/JPhysD/49/145601/mmedia)) [27].

3.3. Influence of surface treatments

Therefore, the appropriate selection of the porous structure not only leads to an optimal oil absorption performance, but also to lower water retention, without the utilization of any chemical surface treatment. In fact, as shown in figure 5 the oil absorption capacity of the ODHC ($V_{\rm f} = 0.975$, Pore size = 435 μ m) foam with the optimum experimentally measured performance is 41.8 v/v, which exactly coincides with the maximum theoretical capacity as calculated by equation (3). This is not the case for representative samples of pristine PU foams with different pore connectivity, i.e. ODMC ($V_{\rm f} = 0.975$, Pore size = 694 μ m) and ODLC ($V_{\rm f}$ = 0.98, Pore size = 715 μ m). However, after an appropriate surface treatment following the method reported by Calcagnile *et al* [13] (see Experimental section), the performance of the ODMC and ODLC foams is sufficiently improved, reaching the maximum values in accordance to the theoretical prediction. At the same time, the surface treatment of the ODHC samples does not change the OAE measured previously which, as proven, is the maximum possible obtained according to its structural parameters. Therefore, the surface treatment increases the oil absorption capacity of samples with medium and low connectivity, while the treatment of samples with high connectivity does not change their optimal performance. In the former case, the surface treatment modifies the surface chemistry of the pores by increasing the oleophilicity, which causes an increase in the capillarity pressures of medium and low pore connectivity foams (equation (4)). Therefore, the filling of all the voids and the retaining of the oil inside the porous structure in now permitted, while the OAE is increased to 1 (table S1 (stacks.iop.org/JPhysD/49/145601/mmedia)). Although the treatment does not change the oil absorption capacity of the ODHC foams, it affects the oil saturation time, decreasing to 30 s from 40 s as was recorded for the pristine one. In addition, the water repellency is improved since the treated samples do not absorb water, and therefore the selectivity of oil over water is optimized. This is also the case for the ODMC and ODLC treated foams presenting no water absorption and oil saturation times about 45 and 50 s, respectively. Let us mention again that ODMC and ODLC are not able to reach the oil saturation without treatment.

Comparing these results with different examples from the literature, where high oil absorption performances are reached by means of surface treatments, it can be concluded that, in most cases, although sophisticated methods are followed for the treatments the calculated absorption capacity is less than the maximum absorption capacity defined by the theory (table S1 (stacks.iop.org/JPhysD/49/145601/mmedia) and figure 5). In particular, apart from Calcagnile *et al* and Wang *et al* who reached the maximum absorption capacity after surface treatment of PU foams [23, 24], others obtain lower performances [25, 30]. Other works which reported high absorption ratios (from 15 to 50 w_{oil}/w_{PU} using gasoline) did not provide a detailed characterization of the PU foam that could allow

determination of the OAE, but their results are also in the range predicted by equation (3), confirming that it is not possible to promote the oil absorption capacity of PU foams over this calculated theoretical maximum [26, 28, 29]. Comparing thus with the existing study, it is evident that the choice of the pristine foam is of fundamental importance for the fabrication of functional absorption capacity. If the appropriate material is chosen, the subsequent chemical treatment is only necessary for the increase of the selectivity of oil over water or of the saturation time, but not for the increase of the oil absorption capacity necessary for an efficient performance.

The oil absorption capacity reached by the ODHC pristine PU foams of small pore size, $30 w_{oil}/w_{PU}$, is three times higher than commercially available materials utilized for the remediation of oil spills, such as polypropylene fibers (capacity about $10 w_{oil}/w_{PP}$ [32]). Moreover, the reusability tests carried out show that more than 98% of the absorbed oil can be recovered by mechanical squeezing, and the foam can be subsequently reused preserving its oil absorption capacity. This process can be repeated for more than 10 absorption cycles, leading to an overall oil absorption capacity higher than 300 w_{oil}/w_{PU} . On the contrary, current commercial materials for the remediation of oil spills cannot be reused.

4. Conclusions

This work demonstrates that the appropriate selection of the structural parameters of PU foams leads to absorbent materials with high oil absorption capacities and efficiencies, significantly better than commercially available products, without the need of additional surface treatments. Oil absorption capacities higher than 40 v/v (or 30 w/w) were obtained using pristine PU foams. Open porous structures with high connectivity and pore sizes about or below 500 μ m present the best performance in terms of oil absorption efficiency and oil saturation time. Therefore, this work establishes that the development of reusable PU-based absorbent materials for the remediation of oil spills should be based on a careful selection of the porous structure. On the contrary, surface treatments are just required to enhance the oil-water selectivity of the system, and to decrease the oil saturation times, but not to increase the oil absorption capacity.

Acknowledgments

This study was supported financially by EDISON Spa (Italy). Cellular Materials Laboratory (CellMat, University of Valladolid (Spain)) and Recticel Flexible Foams Inc. are gratefully acknowledged for providing the pristine PU foams characterized in this work.

References

 N. R. C. (NRC) 2005 Oil Spill Dispersants: Efficacy and Effects (Washington, DC: National Academies)

- [2] Li H and Boufadel M C 2010 Long-term persistence of oil from the Exxon Valdez spill in two-layer beaches *Nat. Geosci.* 3 96–9
- [3] Peacock E E, Nelson R K, Solow A R, Warren J D, Baker J L and Reddy C M 2005 The West Falmouth oil spill: ~100 Kg of oil found to persist decades later *Environ. Forensics* 6 273–81
- [4] Fingas M 2013 *The Basics of Oil Spill Cleanup* 3rd edn (Boca Raton, FL: CRC Press)
- [5] Wang S, Li M and Lu Q 2010 Filter paper with selective absorption and separation of liquids that differ in surface tension ACS Appl. Mater. Interfaces 2 677–83
- [6] Feng L, Zhang Z, Mai Z, Ma Y, Liu B, Jiang L and Zhu D 2004 A super-hydrophobic and super-oleophilic coating mesh film for the separation of oil and water *Angew. Chem.* 116 2046–8
- [7] Boufadel M C, Abdollahi-Nasab A, Geng X, Galt J and Torlapati J 2014 simulation of the landfall of the deepwater horizon oil on the shorelines of the gulf of Mexico *Environ*. *Sci. Technol.* 48 9496–505
- [8] Wolfe D A, Hameedi M, Galt J, Watabayashi G, Short J, O'Claire C, Rice S, Michel J, Payne J and Braddock J 1994 The fate of the oil spilled from the Exxon Valdez *Environ*. *Sci. Technol.* 28 560A–8A
- [9] Wang J, Zheng Y and Wang A 2012 Superhydrophobic kapok fiber oil-absorbent: preparation and high oil absorbency *Chem. Eng. J.* 213 1–7
- [10] Rengasamy R S, Das D and Karan C P 2011 Study of oil sorption behavior of filled and structured fiber assemblies made from polypropylene, kapok and milkweed fibers J. Hazardous Mater. 186 526–32
- [11] Wang J, Zheng Y and Wang A 2013 Coated kapok fiber for removal of spilled oil *Mar. Pollut. Bull.* 69 91–6
- [12] Zhou X, Zhang Z, Xu X, Guo F, Zhu X, Men X and Ge B 2013 Robust and durable superhydrophobic cotton fabrics for oil/water separation ACS Appl. Mater. Interfaces 5 7208–14
- [13] Pintor A M, Ferreira C I, Pereira J C, Correia P, Silva S P, Vilar V J, Botelho C M and Boaventura R A 2012 Use of cork powder and granules for the adsorption of pollutants: a review *Water Res.* 46 3152–66
- [14] Wu J, Wang N, Wang L, Dong H, Zhao Y and Jiang L 2012 Electrospun porous structure fibrous film with high oil adsorption capacity ACS Appl. Mater. Interfaces 4 3207–12
- [15] Zhu H, Qiu S, Jiang W, Wu D and Zhang C 2011 Evaluation of electrospun polyvinyl chloride/polystyrene fibers as sorbent materials for oil spill cleanup *Environ. Sci. Technol.* 45 4527–31
- [16] Lin J, Shang Y, Ding B, Yang J, Yu J and Al-Deyab S S 2012 Nanoporous polystyrene fibers for oil spill cleanup *Mar. Pollut. Bull.* 64 347–52
- [17] Wang H, Lin K Y, Jing B, Krylova G, Sigmon G E, McGinn P, Zhu Y and Na C 2013 Removal of oil droplets from contaminated water using magnetic carbon nanotubes *Water Res.* 47 4198–205
- [18] Keshavarz A, Zilouei H, Abdolmaleki A and Asadinezhad A 2015 Enhancing oil removal from water by immobilizing multi-wall carbon nanotubes on the surface of polyurethane foam *J. Environ. Manage.* **157** 279–86
- [19] Bi H, Xie X, Yin K, Zhou Y, Wan S, He L, Xu F, Banhart F, Sun L and Ruoff R S 2012 Spongy graphene as a highly efficient and recyclable sorbent for oils and organic solvents *Adv. Funct. Mater.* 22 4421–5
- [20] He Y, Liu Y, Wu T, Ma J, Wang X, Gong Q, Kong W, Xing F, Liu Y and Gao J 2013 An environmentally friendly method for the fabrication of reduced graphene oxide foam with a super oil absorption capacity *J. Hazardous Mater.* 260 796–805

- [21] Yuan J, Liu X, Akbulut O, Hu J, Suib S L, Kong J and Stellacci F 2008 Superwetting nanowire membranes for selective absorption *Nat. Nanotechnol.* 3 332–6
- [22] Choi S J, Kwon T H, Im H, Moon D I, Baek D J, Seol M L, Duarte J P and Choi Y K 2011 A polydimethylsiloxane (PDMS) sponge for the selective absorption of oil from water ACS Appl. Mater. Interfaces 3 4552–6
- [23] Calcagnile P, Fragouli D, Bayer I S, Anyfantis G C, Martiradonna L, Cozzoli P D, Cingolani R and Athanassiou A 2012 Magnetically driven floating foams for the removal of oil contaminants from water ACS Nano 6 5413–9
- [24] Wang C F and Lin S J 2013 Robust superhydrophobic/ superoleophilic sponge for effective continuous absorption and expulsion of oil pollutants from water ACS Appl. Mater. Interfaces 5 8861–4
- [25] Zhu Q and Pan Q 2014 Mussel-inspired direct immobilization of nanoparticles and application for oil-water separation ACS Nano 8 1402–9

- [26] Shi H, Shi D, Yin L, Yang Z, Luan S, Gao J, Zha J, Yin J and Li R K 2014 Ultrasonication assisted preparation of carbonaceous nanoparticles modified polyurethane foam with good conductivity and high oil absorption properties *Nanoscale* 6 13748–53
- [27] Su C 2009 Highly hydrophobic and oleophilic foam for selective absorption Appl. Surf. Sci. 256 1413–8
- [28] Zhu Q, Pan Q and Liu F 2011 Facile removal and collection of oils from water surfaces through superhydrophobic and superoleophilic sponges J. Phys. Chem. C 115 17464–70
- [29] Zhu Q, Chu Y, Wang Z, Chen N, Lin L, Liu F and Pan Q 2013 Robust superhydrophobic polyurethane sponge as a highly reusable oil-absorption material *J. Mater. Chem.* A 1 5386
- [30] Li H, Liu L and Yang F 2013 Oleophilic polyurethane foams for oil spill cleanup *Proc. Environ. Sci.* 18 528–33
- [31] Abramoff M D, Magalhães P J and Ram S J 2004 Image processing with ImageJ Biophotonics Int. 11 36–42
- [32] Choi H-M 1992 Natural Sorbents in oil spill cleanup Environ. Sci. Technol. 26 772–6