HAL
open science

Preparation of magnetic, superhydrophobic/superoleophilic polyurethane sponge: Separation of oil/water mixture and demulsification

Tianlong Yu, Fatima Halouane, Dolci Mathias, Alexandre Barras, Ziwen Wang, Anqi Lv, Shixiang Lu, Wenguo Xu, Dalila Meziane, Nicolas Tiercelin, et al.

To cite this version:

Tianlong Yu, Fatima Halouane, Dolci Mathias, Alexandre Barras, Ziwen Wang, et al.. Preparation of magnetic, superhydrophobic/superoleophilic polyurethane sponge: Separation of oil/water mixture and demulsification. Chemical Engineering Journal, 2020, 384, pp.123339. 10.1016/j.cej.2019.123339 . hal-02963626

HAL Id: hal-02963626

https://hal.science/hal-02963626v1

Submitted on 13 Oct 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Preparation of magnetic, superhydrophobic/superoleophilic polyurethane sponge: Separation of oil/water mixture and demulsification

Tianlong Yu[a,b], Fatima Halouane[b,c], Dolci Mathias[b], Alexandre Barras[b], Ziwen Wang[a], Anqi Lv[a], Shixiang Lu[a], Wenguo Xu[a], Dalila Meziane[c], Nicolas Tiercelin,[b] Sabine Szunerits[b]* and Rabah Boukherroub[b,]*

[a] *School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, PR China*

[b] *Univ. Lille, CNRS, Centrale Lille, ISEN, Univ. Valenciennes, UMR 8520 – IEMN, F-59000 Lille, France*

[c] *Département de Chimie, Faculté des Sciences, Université Mouloud Mammeri, B.P N_17 RP, 15000 Tizi Ouzou, Algeria*

*To whom correspondence should be sent to: rabah.boukherroub@univ-lille.fr (+333 62 53 17 24)

Abstract

Regular problems faced due to chemical leaks and oil spills have caused tremendous threats to lakes and sea water. Therefore, there is an urgent need to develop efficient strategies to remove oil and organic pollutants from water surfaces. The aim of this study is to develop a high performance magnetic, superhydrophobic/superoleophilic three-dimensional porous composite material for efficient and selective adsorption of organic pollutants from water. The composite material was fabricated by simple immersion of a commercially available polyurethane (PU) sponge into a solution of high-density polyethylene (HDPE) containing pre-synthesized magnetic (Fe_3O_4) nanoparticles. The composite material exhibited a water contact of ~155° and an oil contact angle of ~0°. The presence of the Fe_3O_4 particles allowed magnetic-controlled elimination of underwater oil, while the superhydrophobic character of the functionalized PU sponge permitted efficient separation of oil/water mixtures and demulsification of toluene/water emulsions. Moreover, the HDPE coating not only firmly immobilized the magnetic particles, but also contributed to the excellent stability to the composite sponge which withstood acid, base, salts, seawater or temperature variation from -20 ^{o}C to 105 ^{o}C. In addition, the composite material maintained its oil adsorption ability over 10 cycles. The ease of fabrication of the magnetic super wetting 3D material sponge along with its durability and reusability makes it an interesting material with potential for practical applications.

Keywords: *Polyurethane; High-density polyethylene; Magnetic; Superhydrophobic/superoleophilic; Demulsification; Oil/water separation.*

1. Introduction

The increasing number of oil spill incidents throughout the world together with chemical leakage from transportation tanks have put significant threats to coastal environments and oceanic ecosystems. Consequently, the removal of large amounts of oil and organic pollutants from water surfaces has become an important and timely matter to limit severe environmental damage [1]. Traditionally, the clean-up approaches of such leakages are skimming, the addition of chemical dispersants, and using of filtrating medium and various adsorbing materials. The inefficiency and high costs of skimming [2], and addition of toxic chemicals into water using oil dispersants [3] to form oil droplets have made the utilization of filtrating materials and adsorbents the most efficient and promising means to separate the organic phase from the aqueous phase.

Superhydrophobic/superoleophilic materials have proven to be particularly useful for efficient separation of organic pollutants and oil from water and encouraging results have been obtained [4-8]. However, the use of expensive reagents and complicated processes always hampers their wider application. Furthermore, mechanical and chemical instability issues limit their reusability for efficient oil/water separation [9, 10].

Therefore, large efforts have been put into the development of simple methods for the preparation of superwetting materials. In this context, we have recently demonstrated the interest of superhydrophobic polyurethane (PU) sponge, formed through anchoring of polydopamine and *1H,1H,2H,2H*-perfluorodecanethiol modified diamond nanoparticles onto the skeleton of the sponge, as well as perfluorinated modified carbon felts for efficient oil/water separation [11, 12]. Compared to films or meshes, porous three-dimensional structures could adsorb larger volumes of organic pollutants, resulting in considerably increased adsorption capacities. Commercially available hydrophilic PU sponges are thus excellent materials for the formation of superhydrophobic 3D materials, owing to their low weight, high porosity, good elasticity, and low production costs [13-17]. Unlike the pristine PU sponge which

cannot discriminate between water and oil phases, the modified sponges were able to selectively adsorb oil and repel water, resulting in better oil collection.

One issue of superhydrophobic PU sponges is that their superwetting properties prevent them from being easily immersed into solutions. Magnetic superhydrophobic sponges, which can be easily manipulated by an external magnetic field and placed on and into the polluted water zone are viable alternatives, still rarely considered up to now. In this respect, Zhang *et al.* [18] fabricated a superhydrophobic magnetic sponge *via* subsequent immersion in Fe_3O_4/ethanol and stearic acid solution. Liu *et al.* [19] deposited Fe_3O_4 particles onto PU sponge *via* ultrasonication, followed by modification with dopamine and heptadecafluoro-1,1,2,2-tetrahydrodecyltrimethoxysilane to enhance the adhesion and reduce surface energy of coating. To achieve magnetic and super wetting properties, Li *et al.* [20] firstly modified Fe_3O_4 particles with tetraethoxysilane and trimethoxy (1H,1H,2H,2H heptadecafluorodecyl) silane and then drop-casted the modified particles onto the PU sponge.

Our group has recently investigated the potential of high-density polyethylene (HDPE), a cheap and widely-adopted polymer, to impart superhydrophobic properties to various substrates such as zinc [21], glass slide or copper mesh at room temperature [22]. This technique is easy to implement as the full process only requires immersion in or drop casting of a xylene/ethanol solution of HDPE. In this work, we demonstrate that magnetic, superhydrophobic/superoleophilic (MSS) PU sponges can be formed when the process of HDPE functionalization was slightly modified. In a first step, the PU sponge was immersed in a solution of HDPE/magnetic (Fe_3O_4) particles and then heated to 140°C, close to the melting point of HDPE. The HDPE, at this temperature, allowed wrapping the Fe_3O_4 particles onto the backbone of the PU sponge, resulting in a magnetic/hydrophobic sponge. Further modification of the magnetic/hydrophobic PU sample with HDPE solution at 105°C increased the roughness of PU surface and resulted in magnetic sponge along with superhydrophobic/superoleophilic (MSS-PU) properties. The MSS-PU sponge exhibited excellent stability even at elevated

temperatures and in corrosive media, and was capable to separate oil/water mixtures and purify toluene-water emulsions.

2. Experimental

2.1 Synthesis of magnetic Fe_3O_4 nanoparticles

The Fe_3O_4 magnetic nanoparticles (MPs) were prepared following reference [23]. For more details, refer to the **SI**.

2.2. Preparation of magnetic superhydrophobic/superoleophilic PU sponges

The polyurethane (PU) sponge was first cut into 1×1×1 cm^3 cubes and immersed sequentially for 30 min into acetone, ethanol, and water under ultrasonication. Then the clean PU samples were dried in an oven for 6 h at 60 °C.

The HDPE solution was obtained by mixing 200 mg of HDPE with 20 mL of toluene and heating the resulting mixture to 110 °C for 1 h to yield a uniform suspension. The solution was cooled to room temperature and 2 mL of absolute ethanol were added; this stock solution was used for the formation of the magnetic superhydrophobic/superoleophilic PU sponges.

The clean PU sponge (~7 mg) was immersed into 1 mL of a previously prepared HDPE solution (10 mg mL^{-1}) containing magnetic Fe_3O_4 particles (MPs, 2 mg mL^{-1}) (see **SI, Figure S1)** and sonicated for 5 min. The HDPE/MPs loaded sponge was then placed in an oven and heat-treated at 140 °C for 1 h under air atmosphere, resulting in a magnetic/hydrophobic sponge. To reach superhydrophobicity, the hydrophobic sample was additionally modified by drop-casting of HDPE solution (10 mg mL^{-1}), followed by subsequent heating in oven at 105 ^{o}C for 1 h.

2.3 Stability measurements

The chemical stability of the magnetic superhydrophobic/superoleophilic polyurethane (MSS-PU) sponge was assessed through sequential immersion into solutions of different pH and salt concentrations for 6 h. Then the sponge was rinsed with ethanol and dried in the oven at 80 °C for 1 h before water contact angle

measurements were performed.

The thermal stability was evaluated by heating the MSS-PU sponge at different temperatures for 2 h in an oven and then water contact angle measurements were recorded.

2.4 Water/oil separation

The MSS-PU sponge was fixed in a separation funnel, and oil/water mixtures were pored over. For better visualization of the separation process, dichloromethane was dyed with rhodamine B (1 mg mL^{-1}).

2.5 Oil adsorption capacity

The MSS-PU sponge was put in contact with different organic solvents for ~1 min. The adsorption capacity was calculated by weighing the mass of MSS-PU sponge before and after immersion. For studying the constant adsorption capacity, the saturated-loaded MSS-PU sponge was firstly washed extensively with ethanol to remove absorbed organics, then transferred to an oven and dried at 60 ^{o}C for 1 h before the next adsorption-cleaning-drying process.

2.6 Demulsification capacity

Surfactant-free water-in-oil emulsions (W/O) were obtained through mixing water and toluene (1:9 v:v) and sonication (power=60 W) for 1 h to produce a white and milky solution. The obtained emulsion was stable for about 30 min under ambient conditions.

Surfactant-stabilized oil-in-water emulsions (O/W) were obtained by adding Pluronic F-127 (0.1 mg mL^{-1} in water) to toluene/water (1:9, v/v) under stirring at 1000 rpm with magnetic stirring. The emulsion is stable for 24 h.

MSS-PU sponges were immersed in 4 mL of the emulsion and kept until the sponge was completely filled with the solution and the emulsion became colorless. The content of toluene in water was determined by UV-vis measurements, using the absorbance of toluene at 260 nm (calibration curve; see SI, **Figure S5**).

3. Results and discussion

3.1 Fabrication of a magnetic superhydrophobic/superoleophilic polyurethane sponge (MSS-PU)

The formation of a magnetic and superhydrophobic/superoleophilic polyurethane sponge (MSS-PU) was achieved, as illustrated in **Figure 1**. The first step consists of dipping the PU sponge in HDPE/Fe_3O_4 toluene/ethanol solution at room temperature, followed by thermal annealing at 140 °C for 1 h to impart magnetic and hydrophobic properties to the PU sponge. To attain superhydrophobicity, the magnetic/hydrophobic PU sponge was further immersed in the HDPE/ethanol solution at room temperature and subsequently annealed at 105 °C for 1 h.

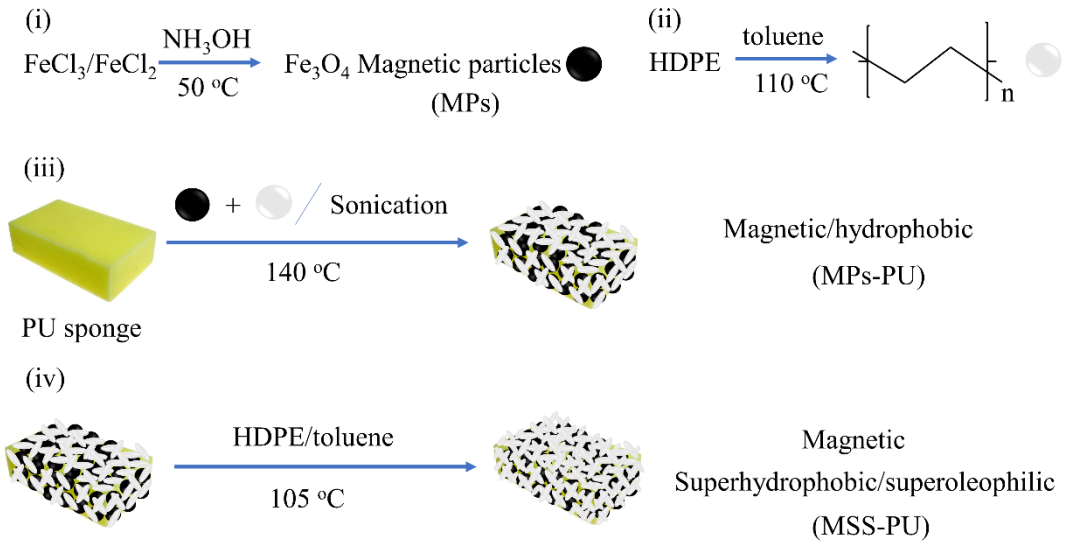


Figure 1: Illustration of the preparation process of a magnetic, superhydrophobic/superoleophilic sponge (MSS-PU): (i) formation of magnetic particles by the co-precipitation reaction of Fe^{2+} and Fe^{3+} salts in alkaline medium; (ii) preparation of HDPE solution in toluene at 110°C, (iii) immersion of the PU sponge into HDPE/MPs solution, followed by annealing at 140 °C for 1 h, (iv) further modification with HDPE/toluene solution and thermal annealing at 105°C for 1 h.

3.1.1. Formation of magnetic Fe_3O_4 nanoparticles (MPs)

First, magnetic Fe_3O_4 particles (MPs) were synthesized by the co-precipitation reaction of Fe^{2+} and Fe^{3+} salts in alkaline medium [23]. The morphology, elemental composition and magnetic properties of the as-prepared MPs were assessed by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and zero-field-cooled (ZFC) magnetization measurements. According to the TEM and HRTEM images (**Figure 2A, B**), the Fe_3O_4 nanoparticles display an average diameter of 10 ± 3 nm and a fringe width of 0.281 nm is deduced.

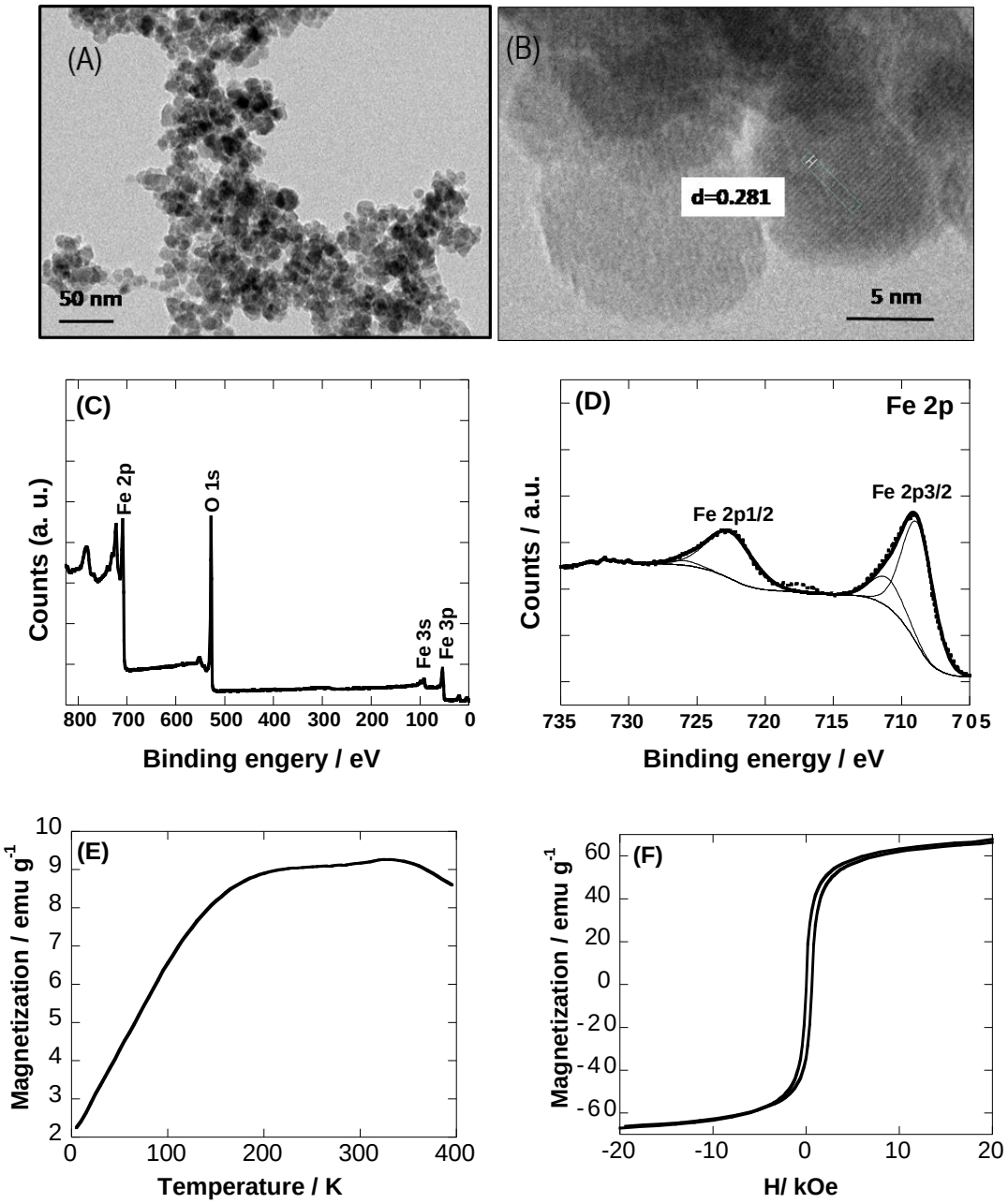


Figure 2: (**A**) Transmission electron microscopy (TEM) and (**B**) high transmission (HR-TEM) images; (**C**) XPS survey spectrum and (**D**) Fe 2p wide scan XPS spectrum; (**E**) Zero-field-cooled (ZFC) magnetization curve at an applied field of 80 Oe; (**F**) hysteresis curves at 250 K of Fe_3O_4 nanoparticles (MPs).

To get more information about the elemental composition and bonding states of the Fe_3O_4 particles, XPS was performed. **Figure 2C** depicts the XPS survey spectrum of the naked magnetic particles. It comprises peaks due to Fe and O, in full accordance with the chemical composition of the particles. An atomic percentage ratio of Fe/O=0.70 is determined, which is between that of Fe_3O_4 (Fe/O=0.75) and Fe_2O_3 (Fe/O=0.66). This is corroborated by the Fe_{2p} high resolution XPS spectrum (**Figure 2D**), which can be deconvoluted into bands at 709.1 eV (Fe 2p3/2) and 722.9 eV (Fe 2p1/2) due to Fe_2O_3 and 711.64 eV (Fe 2p3/2) and 725.9 eV (Fe 2p1/2) ascribed to Fe_3O_4 [24].

The saturation magnetization value of MPs was determined to be ~66 emu g^{-1} at 250 K (**Figure 2E**); this value is lower than that of bulk Fe_3O_4 (~92 emu g^{-1}) at room temperature. This is due to partial oxidation of the particles, but also to the small particle size, large surface-to-volume ratio, and other surface effects [25]. The ZFC magnetization exhibits a maximum above 200 K (**Figure 2F**).

Moreover, the magnetic properties of MPs-PU and MSS-PU were assessed by vibrating sample magnetometer (VSM). Accordingly, all the samples exhibited standard paramagnetic characteristic curves with no hysteresis after removal of the magnetic field. The MPs-PU displayed a saturation magnetization of 5.25 emu g^{-1}. This value decreased to ~2.18 emu g^{-1} for the MSS-PU sponge (**Figure S2**). The decrease in the saturation magnetization during the stepwise surface coating of HDPE polymer onto the PU sponge is expected and is in full accordance with literature data [20, 26]. However, the MSS-PU sponge holds magnetic properties and could be easily manipulated using a magnetic bar. Furthermore, the magnetic properties of the MSS-PU sponge are stable over three months without any apparent decrease of the

saturation magnetization.

3.1.2. Wettability study

The pristine PU sponge was simultaneously functionalized by high-density polyethylene (HDPE) and magnetic nanoparticles (MPs) using a two-step process, consisting of immersion in a solution of HDPE/MPs and heating at 140°C, followed by drop casting of HDPE solution and annealing at 105 °C (**Figure 1**).

Following this procedure, the water contact angle (WCA) of pristine PU sponge increases from 92° to 141° after HDPE/MPs deposition and further to 155° after additional HDPE immersion (**Figure 3A**). The results of optimization are presented in **Figure S1** (see **SI**). Considering these data, a MPs concentration of 2 mg mL^{-1}, a HDPE solution of 10 mg mL^{-1} and three times immersion/heating cycles are necessary to attain superhydrophobicity while maitaining the magnetic properties of the PU sponge. The mass increase (**Figure 3A**) corresponding to each step is determined using equation (1):

$$L = [\frac{m_{loaded} - m_0}{m_0}] \times 100 \qquad (1)$$

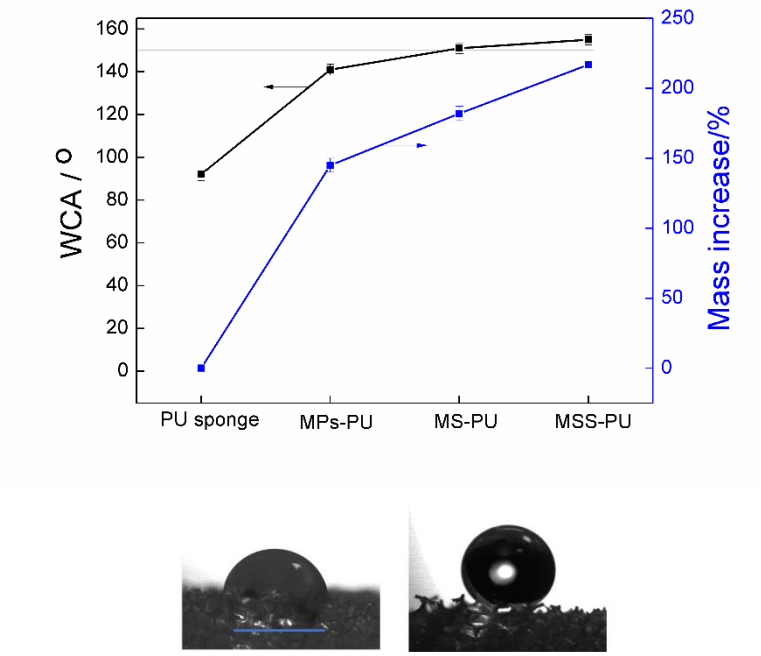
where m_{loaded} is the sponge mass after modification and m_0 is the original sponge mass. The sponge mass increases significantly upon loading with MPs, and the mass of the final MSS-PU sponge is about 2 times the mass of the original PU.

Meanwhile, the ~~surface~~ MSS-PU sponge also exhibits superoleophilic property ~~(**Figure 3B**)~~ with a contact angle of around 0° when a dichloromethane droplet was brought into contact with the MSS-PU surface (**Figure 3B**). Dynamic recording indicated that water droplets are successfully repelled by a horizontally placed MSS-PU sample with a rolling down effect, while a dichloromethane droplet is spontaneously absorbed by the sponge as soon as it contacts its surface (See SI, **video 1**).

In addition, the contact angle and surface energy of the MSS-PU was further

investigated using different test liquids (See **SI**).

(A)



(B)

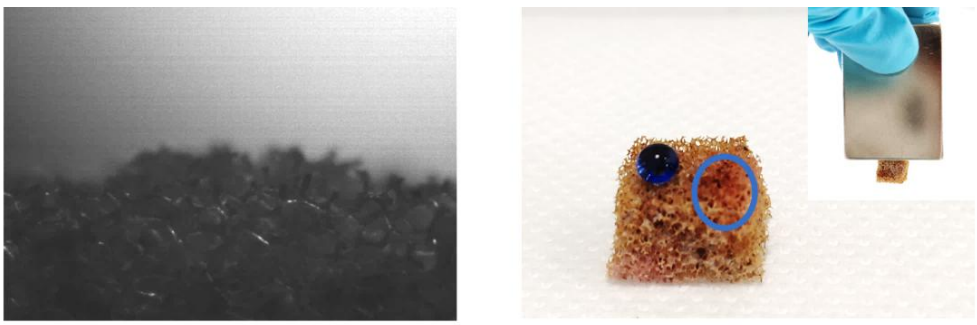


Figure 3: (A) Change in water contact angle (WCA) (black line) and mass increase (blue line) of PU sponge following a three-steps treatment (first modification with magnetic particles/HDPE (MPs-PU), ×1 drop-casted HDPE solution (MS-PU), ×2 drop-casted HDPE solution (MSS-PU)) together with optical images of water contact angle before and after modification, (**B**) (left) Optical image of MSS-PU sponge onto which a droplet of dichloromethane is coated, (right) Illustration of the

superhydrophobic/superoleophilic character of the MSS-PU by dropping methylene blue colored water or dichloromethane droplets onto the sponge (inset: magnetic response of the MSS-PU sample).

3.1.3. Morphological and chemical characterization of the MSS-PU sponge

The superhydrophobic/superoleophilic character of the magnetic MSS-PU is partly linked to its micro-scale morphology. According to the SEM images in **Figure 4**, the pristine PU sponge displays a smooth backbone. After modification with HDPE/MPs (**Figure 4**), the backbone of the PU sponge is covered by numerous irregularly shaped particles of nanoscale dimension. This results in increased surface roughness and consequently in superhydrophobic/superoleophilic property. The pores of the PU sponge are also only partially blocked with the majority remaining open, which is fundamental for a good adsorption process.

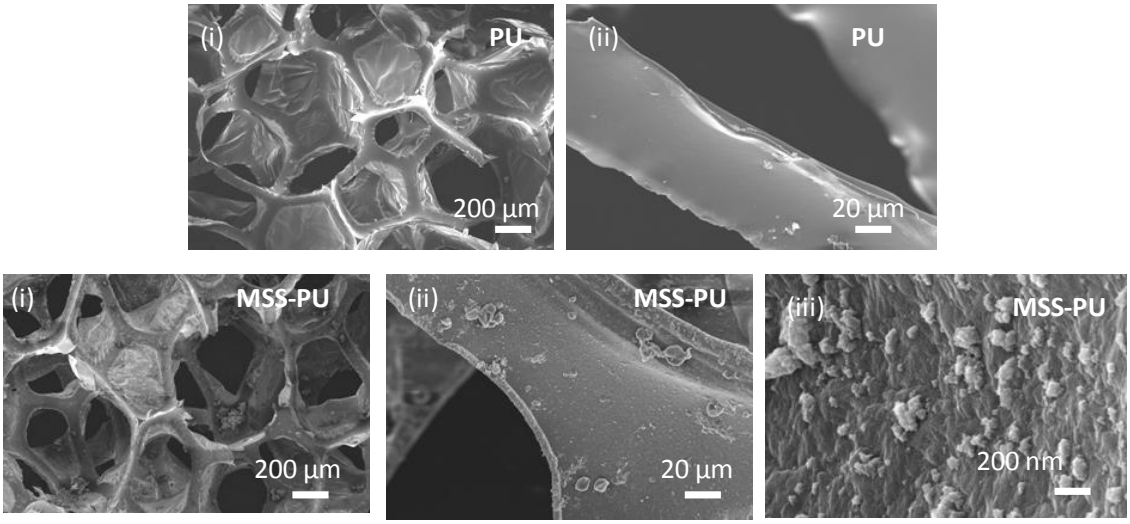


Figure 4: SEM images of bare PU sponge at a magnification of ×50 (i) and ×500 (ii) and of MSS-PU sponge at a magnification of ×50 (i), ×500 (ii), ×50k (iii).

The chemical composition of the MSS-PU sponge was evaluated using EDX analysis. The EDX spectrum in **Figure S4** reveals the presence of C, N, O and Fe elements, which originate from the PU matrix, HDPE coating and Fe_3O_4.

Furthermore, to understand eventual changes in the elemental composition of

MSS-PU, XPS measurements were performed (**Figure 5A**). The XPS survey spectrum of PU sponge displays peaks due to C_{1s} (61.7 at.%) at 284 eV, O_{1s} (34.2 at.%) at 531 eV and N_{1s} (4.1 at.%) at 399 eV. The MSS-PU sponge shows in addition a band of Fe_{2p} (6.13 at.%), suggesting the successful integration of the MPs. The Fe_{2p} core level XPS spectrum is deconvoluted in two main bands at 709.1 eV (Fe 2p3/2) and 722.9 eV (Fe 2p1/2) ascribed to Fe_2O_3 and 711.64 eV (Fe 2p3/2) and 725.9 eV (Fe 2p1/2) ascribed to Fe_3O_4, as observed for the initial MPs (**Figure 5B**). The ratio of Fe_3O_4/Fe_2O_3 is however improved in favor of Fe_3O_4.

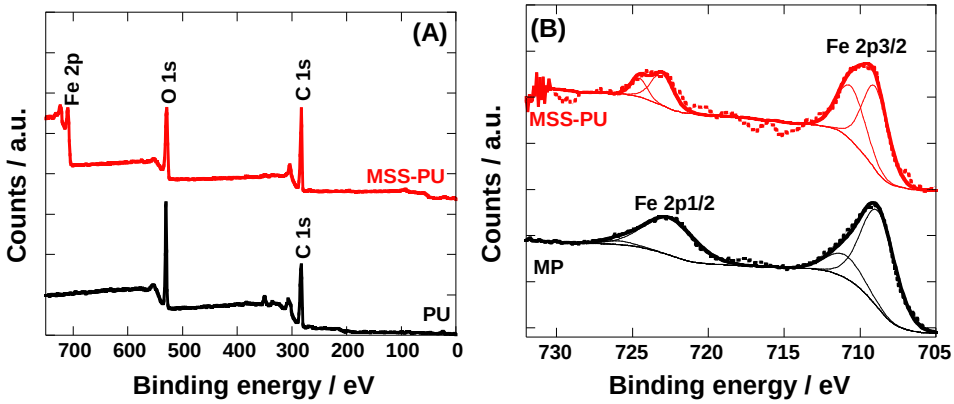


Figure 5: (**A**) XPS survey spectra of pristine PU sponge (black) and MSS-PU sponge (red); (**B**) high resolution XPS spectra of Fe_{2p} of pristine MPs (black) and MSS-PU sponge (red).

3.1.4. Stability of the MSS-PU sponge in acidic, basic and salt solutions

Stability is an essential parameter for evaluating the potential of any adsorbent material for practical application. In reality, there are many circumstances where corrosive media exist. This demands a good resistance of the adsorbent material toward acid, base or salt solutions. **Figure 6** shows that the superhydrophobic character of MSS-PU is not compromised upon immersion into solutions of pH=1-12; thereafter some degradation is observed. The acid-resistance may originate from the HDPE film, a kind of highly stable polymer, coating the magnetic particles onto the sponge skeleton and shields them from acid attack. The sponge is also stable in 3.0% solution of NaCl, K_2SO_4, with a slight degradation in seawater. MSS-PU endures in

addition a wide temperature range from -20 ^{o}C to 105 ^{o}C (**Figure 6B**). When the temperature reaches 125 ^{o}C, close to the melting point of HDPE, the water contact angle sharply decreases to 130°.

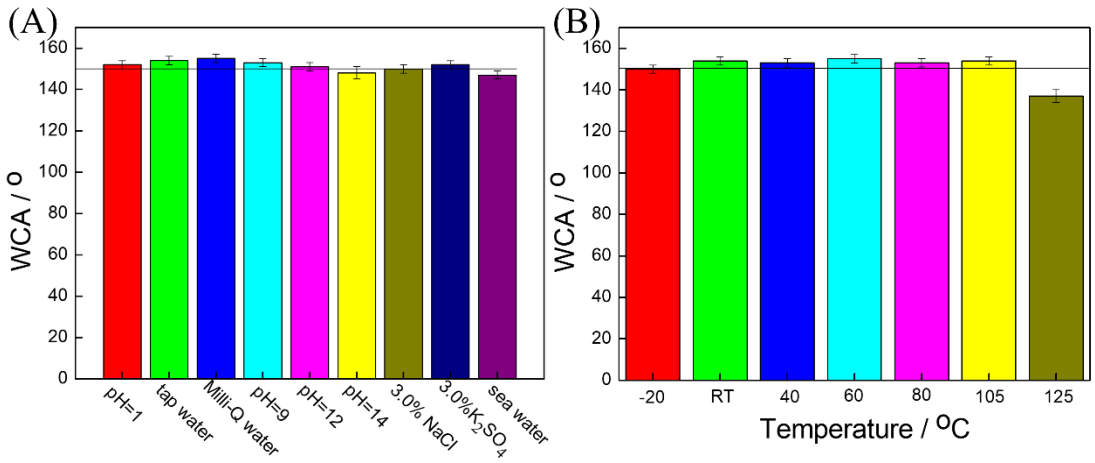


Figure 6: Change of water contact angle of a MSS-PU sponge (**A**) sequentially immersed for 6 h in solutions of different pH and salt concentrations, (**B**) placed at different temperatures for 2 h.

3.2. Separation of oil/water mixtures using the MSS-PU sponge

The ability of the MSS-PU to separate water/oil mixtures, by absorbing the oil component and repelling the water one, is investigated by fixing the MSS-PU sponge in a funnel and using a dichloromethane solution mixed with rhodamine colored water (**Figure 7**). With dichloromethane flowing into the funnel, the MSS-PU sponge is wetted immediately and dichloromethane dips into the bottle below the sponge. During the filtration-like process, bubbles are observed, which arise from the trapped air in the MSS-PU sponge. The whole separation process is seen in **SI** (**video 2**). The MSS-PU sponge works also efficiently as a filter to separate toluene, hexane, chloroform, carbon tetrachloride, and water mixtures (data not shown).

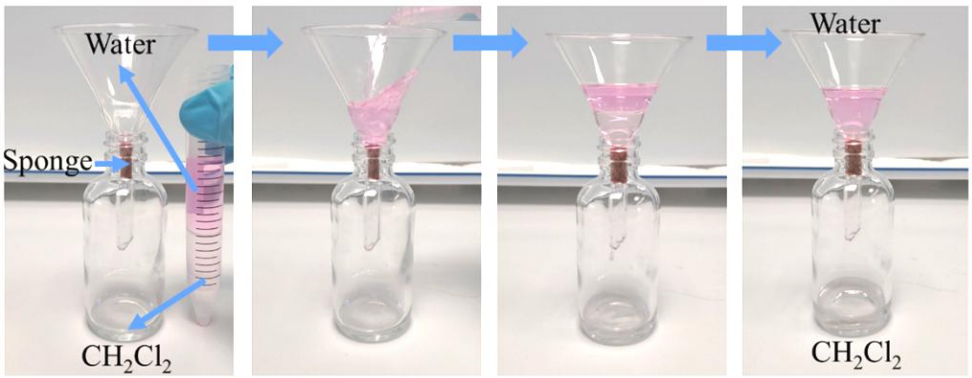


Figure 7: Snapshots of dichloromethane and water (rhodamine B colored) separation using MSS-PU sponge.

3.3. Elimination of oil spills in water with MSS-PU sponge

Oil spills usually lead to severe environmental contamination. While floating oil can be removed with absorbing scavengers, underwater oil is more complicated to eliminate and requires absorbing materials with superhydrophobic/superoleophilic properties. To investigate the capability of the MSS-PU sponge for the elimination of underwater oil droplets, dyed dichloromethane droplet is used as an underwater target (**Figure 8**). Using the magnetic properties of MSS-PU, the sponge could be immersed into the water solution. The formation of bubbles on its interface is due to the superhydrophobic nature of the sponge. A contact with the dyed dichloromethane droplet results in an immediate uptake of the oil (for dynamic recording, see SI, **video 3**).

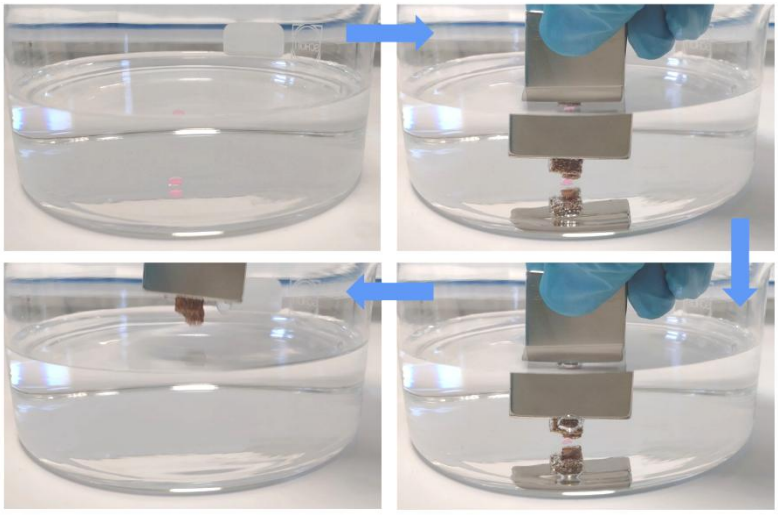


Figure 8: Elimination of rhodamine B dyed underwater dichloromethane droplet by the MSS-PU sponge using a Neodymium magnet bar.

3.4. Oil adsorption capacity of MSS-PU

The adsorption capacity *C* of the MSS-PU sponge for organic solvents is assessed by weighing the sponge before and after immersion and calculated using equation 2:

$$C\ (gg^{-1}) = (m_i - m_o)/m_o \qquad (2)$$

where m_i is the weight of the sponge after oil adsorption (g) and m_o is the weight of the original dry PU sponge (g).

The adsorption capacity is highly related to the porosity of the absorbing material and the inherent physical property of absorbing targets, such as velocity, density and surface tension. The MSS-PU absorbs common organic solvents with adsorption capacities between 15 and 52 gg^{-1}, which corresponds roughly to a half value of bare PU sponge (**Figure 9A**). This reduced adsorption capacity is reasonable and could be attributed to the mass increase *via* surface coating of Fe_3O_4/HDPE onto the PU sponge. However, its current capacity is still comparable to and even better than that of other magnetic sponges and aerogels reported in the literature (**Table 1**).

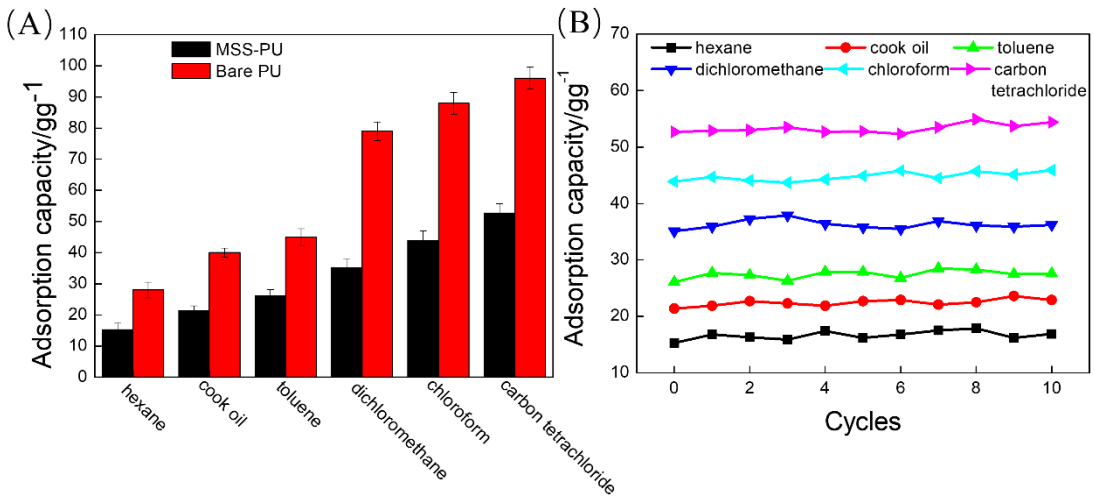


Figure 9: (**A**) Adsorption capacity of the MSS-PU sponge towards organics of different surface tensions ((hexane: 18.4 mNm^{-1}; toluene: 28.8 mNm^{-1};

dichloromethane: 23.1 mNm^{-1}; chloroform: 28.9 mNm^{-1}; carbon tetrachloride: 35.2 mNm^{-1}, T=20 ^{o}C); (**B**) Stability of the MSS-PU sponge as determined by the constant adsorption capacity over 10 washing/drying/immersion cycles.

In detail, the adsorption capacity of different composite materials for hexane and toluene in literature was respectively ~10 and 15 gg^{-1} [28, 31], which is slightly lower than ~15 and 26 gg^{-1} recorded using MSS-PU. However, for carbon tetrachloride, the literature reported a value of 64 gg^{-1} [29], which is higher than our result (52 gg^{-1}). For edible oil, the adsorption capacity of MSS-PU is comparable to the literature values [30, 31]. Overall, the advantage of MSS-PU lies in its facile preparation as well as excellent stability, which is confirmed by an almost constant adsorption capacity over 10 washing/drying/immersion cycles (**Figure 9B**). Taken together, the results obtained in the present study make this absorbent highly competitive to other magnetic composites, and a promising material for practical oil absorption.

Table 1. Adsorption capacity of different magnetic absorbents reported in literature.

Material	**Adsorbed organics**	**Capacity** [k]	**Ref.**
Fe_3O_4/HDPE PU sponge	Toluene, hexane, dichloromethane, chloroform, cook oil, carbon tetrachloride,	15-52	**Present work**
Fe_3O_4-TMHFDS, TEOS /PU sponge	peanut oil, pump oil, and silicone oil	39-46	[20]
Fe_3O_4@HD-silica/HD- polyester sponge	petrol, diesel and crude oil	3-4	[27]
Fe_3O_4-PDMS/MWNTs sponge	Dichloromethane, petroleum ether, hexane, chloroform, tetrahydrofuran, toluene, gasoline	8-20	[28]
Fe_3O_4@TiO_2/polyethylene sponge	Edible oil, lubricating oil, DMF, tetrachloromethane	35-64	[29]
Fe_3O_4@carbon aerogel	Engine oil, chloroethane, and corn oil	10-11	[30]
Fe_3O_4@GO@OTS PU sponge	Lubricating oil, peanut oil, hexadecane, octane, hexane, heptane	9-27	[31]

[k] refers to the times of the weight of adsorbed substances *vs.* the weight of adsorbent.

HDPE: high-density polyethylene, TMHFDS: trimethoxy (1H,1H,2H,2H-heptadecafluorodecyl) silane,

TEOS : tetraethoxysilane, HD: n-hexadecyltriethoxysilane, PDMS: polydimethylsiloxane, MWNTs: multiwalled carbon nanotubes, GO: graphene oxide, OTS: octadecyltrichlorosilane.

3.5. Demulsification capacity of MSS-PU

Emulsions play a key role in industry, but introduce problems such as damage to car engine, deterioration of gasoline or aqueous pollutions [32-35]. Due to the small droplet size, emulsions are difficult to eliminate and/or separate from the rest of the solvents. Absorbents with micro-sized roughness and superhydrophobic/ superoleophilic character have shown to facilitate the demulsification process [36, 37].

To investigate the demulsification ability of the MSS-PU sponge, water is mixed with toluene (W/O mixture) and sonicated until a white and milky solution is formed. The droplets are 5–30 µm in size, as determined under an optical microscope (**Figure 10**). On the other hand, surfactant-stabilized oil-in-water emulsions are obtained by mixing Pluronic F-127 with water/toluene (O/W mixture) under rapid magnetic stirring. The droplets size of this emulsion is comparable to the above one, between 5–20 µm (**Figure 10**). Immersion of the MSS-PU sponge results in a decrease of the toluene content from 10% to 0.18% using UV/Vis analysis (**see SI, Figure S4**), which indicates a removal of 98.2% of toluene. The successful demulsification is also seen in optical image of **Figure 10,** where not droplets are detected.

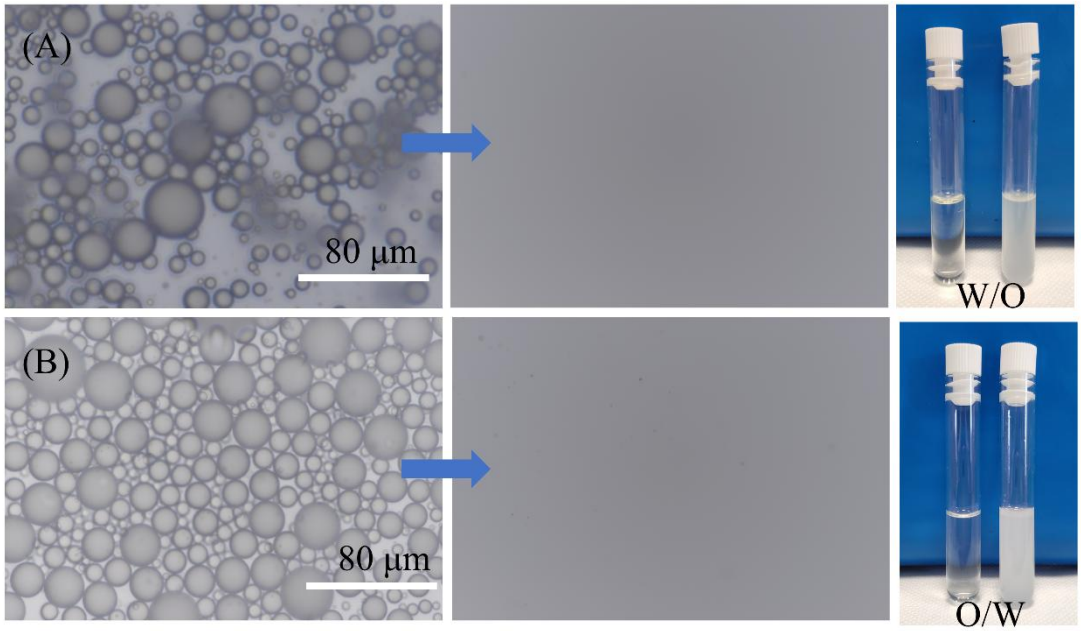


Figure 10: Optical photographs of surfactant-free water/toluene emulsions (W/O) and Pluronic F-127 emulsified toluene/water emulsion (O/W) (a) before and (b) after separation.

Conclusion

A pristine PU sponge was made magnetic through the addition of pre-synthesized Fe_3O_4 particles and superhydrophobic/superoleophilic upon immersion in high-density polyethylene (HDPE). An apparent water contact angle as high as ~155° and oil contact angle of ~0° were recorded on the formed magnetic, superhydrophobic/superoleophilic (MSS-PU) sponge. Owing to the inert property of HDPE, the MSS-PU sponge was able to keep its superhydrophobic/superoleophilic properties under strong acid, base and salt solutions and showed wide temperature stability from -20 ^{o}C to 105 ^{o}C. Various oil/water mixtures could be efficiently separated by MSS-PU *via* a filtration-like process. Moreover, underwater oil could be eliminated by the MSS-PU under magnetic control. The oil absorption capacity was determined to be 15 to 52 gg^{-1} depending on the organic solvent used and no obvious decrease of its value was recorded even after ten immersion/washing/drying cycles. The simplicity of the fabrication method of MSS-PU, together with its outstanding stability, cyclic lifetime and separation capacity makes it of interest for real

applications.

Acknowledgment

R.B., S.S. and T.Y. gratefully acknowledge financial support from the Centre National de Recherche Scientifique (CNRS), the University of Lille and the Hauts-de-France region. T.Y. gratefully thanks the Chinese government for the China Scholarship Council Award. S.L., W.X. and T.Y. gratefully acknowledge the National Natural Science Foundation of China (No. 21271027) for this work.

References

[1] B. Dubansky, A. Whitehead, J.T. Miller, C.D. Rice, F. Galvez, Multitissue molecular, genomic, and developmental effects of the Deepwater Horizon oil spill on resident Gulf killifish (Fundulus grandis), Environ. Sci. Technol. 47 (2013) 5074-5082.

[2] H. Chmiel, M. Kaschek, C. Blöcher, M. Noronha, V. Mavrov, Concepts for the treatment of spent process water in the food and beverage industries, Desalination 152 (2003) 307-314.

[3] E.B. Kujawinski, M.C. Kido Soule, D.L. Valentine, A.K. Boysen, K. Longnecker, M.C. Redmond, Fate of dispersants associated with the Deepwater Horizon oil spill, Environ. Sci. Technol. 45 (2011) 1298-1306.

[4] A.R. Siddiqui, R. Maurya, K. Balani, Superhydrophobic self-floating carbon nanofiber coating for efficient gravity-directed oil/water separation, J. Materials Chem. A 5 (2017) 2936-2946.

[5] Y. Yang, X. Li, X. Zheng, Z. Chen, Q. Zhou, Y. Chen, 3D-Printed Biomimetic Super-Hydrophobic Structure for Microdroplet Manipulation and Oil/Water Separation, Adv. Mater. 30 (2018) 1704912.

[6] C. Zhou, Z. Chen, H. Yang, K. Hou, X. Zeng, Y. Zheng, J. Cheng, Nature-inspired strategy toward superhydrophobic fabrics for versatile oil/water separation, ACS Appl. Mater. Interfaces 9 (2017) 9184-9194.

[7] C. Gao, Z. Sun, K. Li, Y. Chen, Y. Cao, S. Zhang, L. Feng, Integrated oil separation and water purification by a double-layer TiO_2-based mesh, Energy Environ. Sci 6 (2013) 1147-1151.

[8] D.W. Kim, K. Eum, H. Kim, D. Kim, M.D. de Mello, K. Park, M. Tsapatsis, Continuous ZIF-8/reduced graphene oxide nanocoating for ultrafast oil/water separation, Chem. Eng. J. 372 (2019) 509-515.

[9] B. Wang, W. Liang, Z. Guo, W. Liu, Biomimetic super-lyophobic and super-lyophilic materials applied for oil/water separation: a new strategy beyond nature, Chem.Soci. Rev. 44 (2015) 336-361.

[10] C. Cao, J. Cheng, Fabrication of robust surfaces with special wettability on porous copper substrates for various oil/water separations, Chem. Eng. J. 347 (2018) 585-594.

[11] N. Cao, B. Yang, A. Barras, S. Szunerits, R. Boukherroub, Polyurethane sponge functionalized with superhydrophobic nanodiamond particles for efficient oil/water separation, Chem. Eng. J. 307 (2017) 319-325.

[12] Y. Cheng, G. He, A. Barras, Y. Coffinier, S. Lu, W. Xu, S. Szunerits, R. Boukherroub, One-step immersion for fabrication of superhydrophobic/superoleophilic carbon felts with fire resistance: fast separation and removal of oil from water, Chem. Eng. J. 331 (2018) 372-382.

[13] P. Phanthong, P. Reubroycharoen, S. Kongparakul, C. Samart, Z. Wang, X. Hao, A. Abudula, G. Guan, Fabrication and evaluation of nanocellulose sponge for oil/water separation, Carbohydrate Polym.190 (2018) 184-189.

[14] Q. Zhu, Y. Chu, Z. Wang, N. Chen, L. Lin, F. Liu, Q. Pan, Robust superhydrophobic polyurethane sponge as a highly reusable oil-absorption material, J. Mater. Chem.A 1 (2013) 5386-5393.

[15] L. Zhang, H. Li, X. Lai, X. Su, T. Liang, X. Zeng, Thiolated graphene-based superhydrophobic sponges for oil-water separation, Chem. Eng. J. 316 (2017) 736-743.

[16] C. Su, H. Yang, S. Song, B. Lu, R. Chen, A magnetic

superhydrophilic/oleophobic sponge for continuous oil-water separation, Chem. Eng. J. 309 (2017) 366-373.

[17] Z. T. Li, H. T. Wu, W. Y. Chen, F. A. He, D. H. Li, Preparation of magnetic superhydrophobic melamine sponges for effective oil-water separation, Sep. Purif. Technol. 212 (2019) 40-50.

[18] X. Zhang, F. Fu, X. Gao, X. Hou, Magnetically Driven Superhydrophobic Polyurethane Sponge for High Efficiency Oil/Water Mixtures Separation, J. Bionic Eng. 16 (2019) 38-46.

[19] S. Liu, Q. Xu, S.S. Latthe, A.B. Gurav, R. Xing, Superhydrophobic/superoleophilic magnetic polyurethane sponge for oil/water separation, RSC Adv. 5 (2015) 68293-68298.

[20] Z. T. Li, B. Lin, L. W. Jiang, E. C. Lin, J. Chen, S. J. Zhang, Y. W. Tang, F. A. He, D. H. Li, Effective preparation of magnetic superhydrophobic Fe_3O_4/PU sponge for oil-water separation, Appl. Surf. Sci. 427 (2018) 56-64.

[21] S. Lu, H. Gao, Q. Wang, W. Xu, S. Szunerits, R. Boukherroub, Fabrication of stable homogeneous superhydrophobic HDPE/graphene oxide surfaces on zinc substrates, RSC Adv. 6 (2016) 29823-29829.

[22] Y. Cheng, B. Wu, X. Ma, S. Lu, W. Xu, S. Szunerits, R. Boukherroub, Facile preparation of high density polyethylene superhydrophobic/superoleophilic coatings on glass, copper and polyurethane sponge for self-cleaning, corrosion resistance and efficient oil/water separation, J. Colloid Interface Sci. 525 (2018) 76-85.

[23] M. Mazur, A. Barras, V. Kuncser, A. Galatanu, V. Zaitzev, K.V. Turcheniuk, P. Woisel, J. Lyskawa, W. Laure, A. Siriwardena, R. Boukherroub, S. Szunerits, Iron oxide magnetic nanoparticles with versatile surface functions based on dopamine anchors, Nanoscale 5 (2013) 2692-2702.

[24] A. Grosvenor, B. Kobe, M. Biesinger, N. McIntyre, Investigation of multiplet splitting of Fe 2p XPS spectra and bonding in iron compounds, Surf. Interface Anal. 36 (2004) 1564-1574.

[25] A.G. Roca, J.F. Marco, M.d.P. Morales, C.J. Serna, Effect of nature and particle

size on properties of uniform magnetite and maghemite nanoparticles, J. Phys. Chem. C 111 (2007) 18577-18584.

[26] L. Wu, L. Li, B. Li, J. Zhang, A. Wang, Magnetic, durable, and superhydrophobic polyurethane@ Fe_3O_4@ SiO_2@ fluoropolymer sponges for selective oil absorption and oil/water separation, ACS Appl. Mater. Interfaces 7 (2015) 4936-4946.

[27] L. Wu, J. Zhang, B. Li, A. Wang, Magnetically driven super durable superhydrophobic polyester materials for oil/water separation, Polym. Chem. 5 (2014) 2382-2390.

[28] A. Turco, C. Malitesta, G. Barillaro, A. Greco, A. Maffezzoli, E. Mazzotta, A magnetic and highly reusable macroporous superhydrophobic/superoleophilic PDMS/MWNT nanocomposite for oil sorption from water, J. Mater. Chem. A 3 (2015) 17685-17696.

[29] L. Yu, X. Zhou, W. Jiang, Low-cost and superhydrophobic magnetic foam as an absorbent for oil and organic solvent removal, Ind. Eng. Chem. Res. 55 (2016) 9498-9506.

[30] J. Dai, R. Zhang, W. Ge, A. Xie, Z. Chang, S. Tian, Z. Zhou, Y. Yan, 3D macroscopic superhydrophobic magnetic porous carbon aerogel converted from biorenewable popcorn for selective oil-water separation, Mater. Design 139 (2018) 122-131.

[31] C. Liu, J. Yang, Y. Tang, L. Yin, H. Tang, C. Li, Versatile fabrication of the magnetic polymer-based graphene foam and applications for oil–water separation, Colloids Surf. A 468 (2015) 10-16.

[32] W. Zhang, Z. Shi, F. Zhang, X. Liu, J. Jin, L. Jiang, Superhydrophobic and Superoleophilic PVDF Membranes for Effective Separation of Water-in-Oil Emulsions with High Flux, Adv. Mater. 25 (2013) 2071.

[33] A. Ahmad, M. Majid, B. Ooi, Functionalized PSf/SiO_2 nanocomposite membrane for oil-in-water emulsion separation, Desalination 268 (2011) 266-269.

[34] L. Li, B. Li, L. Wu, X. Zhao, J. Zhang, Magnetic, superhydrophobic and durable silicone sponges and their applications in removal of organic pollutants from water,

Chem. Commun. 50 (2014) 7831-7833.

[35] C. F. Wang, S. J. Lin, Robust superhydrophobic/superoleophilic sponge for effective continuous absorption and expulsion of oil pollutants from water, ACS Appl Mater. Interfaces 5 (2013) 8861-8864.

[36] L. Liu, Y. Pan, B. Bhushan, X. Zhao, Mechanochemical robust, magnetic-driven, superhydrophobic 3D porous materials for contaminated oil recovery, J. Colloid Interface Sci. 538 (2019) 25-33.

[37] W. Zhang, Z. Shi, F. Zhang, X. Liu, J. Jin, L. Jiang, Superhydrophobic and superoleophilic PVDF membranes for effective separation of water-in-oil emulsions with high flux, Adv. Mater. 25 (2013) 2071-2076.