Journal of Environmental Management 206 (2018) 872–889

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Review

Surface modification of polymeric foams for oil spills remediation

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ARTICLE INFO

Article history:
Received 17 July 2017
Received in revised form
15 November 2017
Accepted 22 November 2017

Keywords:
Foams
Polyurethane
Melamine
Oil-water separation
Surface functionalization
Continuous oil cleanup

ABSTRACT

In the last decade, a continuous increasing research activity is focused on the surface functionalization of polymeric porous materials for the efficient removal of oil contaminants from water. This work reviews the most significant recent studies on the functionalization of polyurethane and melamine foams, materials commonly reported for oil-water separation applications. After the identification of the key features of the foams required to optimize their oil removal performance, a wide variety of physicochemical treatments are described together with their effect on the oil absorption selectivity and oil absorption capacity, both critical parameters for the application of the foams in the remediation of oil spills. The efficiencies of the different functionalization processes on the same type of foams are compared, determining the main advantages and potentialities of each treatment and remediation procedure.

Contents

1. Introduction

Environmental catastrophes, such as Exxon Valdez in 1989 (Alaska), Prestige in 2002 (Spain), or BP's Deepwater Horizon in 2010 (Gulf of Mexico), bring from time to time to the spotlight the urgent need to control accidental and deliberate releases of oil to open waters. The contamination of water with oil is not limited to these well-known large-scale events since smaller oil spills are much more frequent. For example, about fifteen oil spills are found daily in navigable waters of the United States (Fingas, 2013) as well as hundreds of oil spills have been reported yearly in Nigeria (ENI, 2015; Shell-Oil-Company, 2015). The persistence of the released oil turns these events to a constant threat of utmost importance for the

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https://doi.org/10.1016/j.jenvman.2017.11.060
0301-4797/

environment and the human health (Peacock et al., 2005; Li and Boufadel, 2010; Nyankson et al., 2015). Suitable remediation solutions to this problem should remove large amounts of oil (e.g., BP's Deepwater Horizon released up to 4.9 million barrels of crude oil) (Nyankson et al., 2015) in a relatively fast rate, as the difficulties to recover the spilled oil increase with the time passed from the spill to the recovery attempts (Fingas, 2013). In addition, the type of oil spill, the water and oil temperature, and the weather conditions largely modify the recovery conditions and requirements (Fingas, 2013; Al-Majed et al., 2012), making necessary the development of different remediation solutions, to be used alone or in combination for an appropriate response.

The most common current oil spill-removal options are the utilization of chemical dispersants, the mechanical containment and recovery of the oil spills using booms and skimmers, the oil spills removal using oil absorbents, and the in situ burning of the oil (see Table 1) (Fingas, 2013; Nyankson et al., 2015; ITOPF, 2011, 2012a, 2012b, 2012c; Adebajo et al., 2003; Ventikos et al., 2004). As described in Table 1 these approaches present specific limitations, with their effectiveness and suitability to depend on diverse factors (e.g., oil viscosity, weather conditions, time passed, and surrounding environment), bringing up the necessity to develop new remediation approaches that overpass such drawbacks (Al-Majed et al., 2012).

Among these approaches, only the use of skimmers and oil sorbents can actually remove the oil from the water without releasing residues into the environment. Skimmers provide an efficient oil removal in the initial stages of the oil spill when a homogeneous slick of thick oil is formed, but their efficiency drastically decreases when the spilled oil layer becomes thinner or under harsh marine conditions, leading to recovery rates and efficiencies far from the optimal values (Fingas, 2013; Ventikos et al., 2004). On the other hand, the oil spills remediation efficiency using absorbent booms is usually limited by their low absorption capacity and selectivity, as well as by the presence of waves, currents, or wind. In addition, although the use of skimmers, under appropriate circumstances, allows a continuous removal of the oil, the absorbent booms are commonly non-reusable, being necessary their disposal after one use (Fingas, 2013; Ventikos et al., 2004).

In the last years, the utilization of engineered porous oil sorbents has arisen as an efficient approach for the oil spills remediation, overpassing some of the limitations of the traditional oil absorbents (i.e., low absorption capacity and selectivity) (Nyankson et al., 2015; Adebajo et al., 2003). The oil absorption performance of natural fibers, such as kapok fibers, milkweed, cotton, raw barley straw or bagasse, has been widely studied since these materials are abundant, renewable, and low-cost, and therefore, readily applicable in a larger scale (Husseien et al., 2009; Hussein et al., 2008; Rengasamy et al., 2011; Wang et al., 2012a, 2012b, 2013a; Zhou et al., 2013a; Bayat et al., 2005). Nonetheless, although some of them reach high oil uptake capacities (e.g., about 60 g of oil per gram of sorbent (g/g) in the case of kapok fibers) (Rengasamy et al., 2011), in general, they are highly hygroscopic, and therefore, they absorb water simultaneously with oil, compromising the selectivity of the sorbent (Adebajo et al., 2003).

Alternatively, a great variety of synthetic polymer fibers (Rengasamy et al., 2011; Bayat et al., 2005; Zhu et al., 2011a; Lin et al., 2012; Wu et al., 2012) or sponge-like carbonaceous materials (Hu et al., 2013; Gui et al., 2013, 2010, 2011; Zhao et al., 2011; Moura and Lago, 2009; Liang et al., 2012; Bi et al., 2012; Dong et al., 2012; Kabiri et al., 2014; Hu et al., 2014; Yang et al., 2014; Zhu et al., 2013a; Hashim et al., 2012; Wu et al., 2014a; Li et al., 2013a; Gui et al., 2012; He et al., 2013), such as polystyrene fibers (Zhu et al., 2011a) or carbon nanotubes sponges (Gui et al., 2010), with engineered morphology and porosity have been recently developed in a laboratory scale. These engineered oil sorbents have reached impressive oil absorption capacities (up to 140 g/g) (Zhu et al., 2011a; Gui et al., 2010; Hu et al., 2014) and oil absorption selectivity (Rengasamy et al., 2011; Bayat et al., 2005; Zhu et al., 2011a; Lin et al., 2012; Wu et al., 2012; Hu et al., 2013; Gui et al., 2013, 2010, 2011; Zhao et al., 2011; Moura and Lago, 2009; Liang et al., 2012; Bi et al., 2012; Dong et al., 2012; Kabiri et al., 2014; Hu et al., 2014; Yang et al., 2014; Zhu et al., 2013a; Hashim et al., 2012; Wu et al., 2014a; Li et al., 2013a; Gui et al., 2012; He et al., 2013). Despite the high performances achieved, these materials usually face critical scale-up problematics due to their high production costs and availability. In fact, most of them are mainly composed of high-performance nanomaterials such as carbon nanotubes and graphene, which are still not widely available in the markets at low costs, or require complicated and time-consuming fabrication methods (e.g., electrospun fibers) (Zhu et al., 2011a; Lin et al., 2012; Wu et al., 2012; Hu et al., 2013; Gui et al., 2013, 2010, 2011; Zhao et al., 2011; Moura and Lago, 2009; Liang et al., 2012; Bi et al., 2012; Dong et al., 2012; Kabiri et al., 2014; Hu et al., 2014; Yang et al., 2014; Zhu et al., 2013a; Hashim et al., 2012; Wu et al., 2014a; Li et al., 2013a; Gui et al., 2012; He et al., 2013). For this

Table 1
Summary of the main strategies for the remediation of oil spills in open waters. (Fingas, 2013; Nyankson et al., 2015; ITOPF, 2011, 2012a, 2012b, 2012c; Adebajo et al., 2003; Ventikos et al., 2004).

Technique	When suitable	Advantages	Drawbacks
Chemical dispersants	Floating slicks of oil with low-medium viscosity	Large amounts of oil can be rapidly removed from the water surface, even in rough sea conditions	Ineffective on oils with a viscosity higher than 5000–10,000 cSt. Use not recommended near to shore, coral reefs, and mariculture facilities
Mechanical containment and recovery	Floating, thick, and homogeneous slicks of oil. Best performance with large slicks of freshly spilled oil	In an ideal scenario, this technique allows recovering a significant amount of oil. Moreover, it actually removes the oil from the water (instead of dispersing it)	The required equipment cannot be used in rough weather. Its efficiency decreases with the oil density increase, as well as with the fragmentation of the oil slick
Oil absorbents	Floating slicks of oil, both homogeneous and fragmented. In general, they are most efficiently employed during the final stages of the clean-up	These materials can reach high oil recovery weight ratios (40:1 oil:absorbent). Relatively straightforward to deploy and retrieve. Moreover, they actually remove the oil from the water (instead of dispersing it)	Excessive use should be avoided to minimize subsequent storage, disposal, and secondary contamination problems (due to their non-reusability)
In situ burning	Floating slicks of freshly spilled oil	It rapidly removes large amounts of oil from the water surface	It requires a minimum thickness of oil to sustain a burn. It produces large quantities of toxic smoke, as well as highly viscous residues that may sink to the seabed.