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Morphological variations of micro-nanofibrous sorbents prepared by electrospinning and their effects on the sorption of crude oil

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ABSTRACT

Crude oil spills have both a high environmental and economic impact, ensuring that its removal is an international concern. To aid in its removal, sorbents make of pure and recycled polystyrene (PS) polymers in the form of microfibers have been utilized in this regards. With an electrospinning (ES) technique used to make the fibrous sorbents. These sorbents have both a high surface area and a high degree of hydrophobicity. The effects of varying the electrospinning parameters, on the affinity of the fibrous sorbents prepared thereafter toward oil spills in artificial polluted seawater media was investigated. Such parameters include the polymer type, solvent type, applied voltage, feeding rate, spinning distance, degree of relative humidity and the internal diameter of the spinning nozzles. Results showed a strong correlation between fiber characteristics and their affinity toward the sorption of oil spills. A step-by-step optimization of the electrospinning parameters was shown to enhance the performance of the fibrous sorbents toward the treatment of crude oil spills.

1. Introduction

Oil spills are considered one of the most globally-recognized environmental problems due to its grave impact on all types of habitats. Oil spills take place on land as well as in aqueous media [1]. Crude oil released to the marine environment undergoes a wide variety of weathering processes by which oil is diluted and its effect decreases with time. However, its impact sustains for a longer period of time [1]. Various methods have been explored for the removal of oil spills [2–7]. Among these methods, absorption is a well know approach where sorbents from natural or man-made origins are used to collect oil spills. Natural sorbents such as straw [8], saw dust [9] corncob [10], rice [11], coconut husk [12], cotton [13], wood [14], wool [15], kenaf [16], kapok [17] and seed fibers [18], were investigated. However, it has been shown that most of them have poor buoyancy, relatively low oil absorption capacity, low hydrophobicity, and high affinity toward water absorption [8]. These disadvantages drew the attention of environmental scientists toward the use of synthetic hydrophobic alternatives. Polymers such as polypropylene [19], polyurethane foams [20], and polystyrene [21] were investigated. These synthetic sorbents have excellent hydrophobic and oleophilic properties [22], and could be further treated to enhance their hydrophobic characteristics [22], so that their affinity toward crude oil spills could be increased. An additional parameter for the enhancement of sorption affinity is the surface area of the sorbent material, where the higher the surface area of the sorbent, the higher its affinity toward higher extents of oil sorption. Therefore, fibrous sorbents with fiber diameters in the range of sub-micron to nanometer size, are highly considered to be potential sorbents for the removal of oil spills.

Various methods were explored for the fabrication of higher surface area fibrous sorbents [23–28]. Among these methods, electrospinning appears as a well-recognized technique for making continuous polymeric fibers with diameters of controlled size distribution in the micro-to-nanometer scale. The process offers the ability to control the size and size distribution of the produced fibers via optimization of the process parameters, which include applied voltage, feeding rate, spinning distance and atmosphere and diameter of the spinneret. Electrospinning of polystyrene, as a potential hydrophobic polymer, was carried out by many researchers for different applications [29–34]. Polystyrene/poly (vinyl chloride) nanofibrous sorbents made by Zhu et al. were tested for their affinity toward non-crude oil spills, and showed its superiority over the commercially available polypropylene

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non-woven fabric [35]. These mixed polymer sorbents showed sorption capacities of 38–146 g/g toward motor, peanut, and diesel oils. These are non-crude oils and are known for their lower viscosities and different compositions than crude oil. However, Zhu et al. claimed the superiority of these sorbents where their sorption capacities were 5 times higher than the commercially available polypropylene sorbent. Moreover, it was shown by Lin et al. that the presence of surface porosity on the polystyrene microfibers helped in improving their affinity toward the removal of motor, bean and sunflower seed oils. Maximum sorption capacities of these oils were in the range of 20–110 g/g, which were claimed to be 3–4 times higher than those of commercialized polypropylene fibers [21].

In the current study, the main objectives were to investigate the use of fibrous sorbents made of pure and recycled polystyrene in the removal of crude oil spills, and to study the feasibility of retrieving the collected crude oil. The effect of varying the electrospinning conditions on the characteristics of the polystyrene fibrous mats produced thereafter, and their consequent performance as potential sorbents for the collection of crude oil spills from simulated sea water media, will therefore be thoroughly investigated.

2. Materials and methods

The starting materials included two types of polystyrene PSI (M_w = 100,000 Da) and PSII (M_w = 350,000 Da). These were purchased from Avocado Research Chemicals Ltd., and Sigma–Aldrich Companies. In addition, a recycled polystyrene (PSCIII; M_w = 225,000 Da as measured by GPC) derived from foamy polystyrene materials, was also used. Solvents included *N*,*N*-dimethylformamide (DMF) (>99.8%); purchased from Fluka, and tetrahydrofuran (THF) (>99.8%) that was purchased from LiChrosolv. All Polymers were characterized for their phase purity using infrared spectroscopy before being used in the production of fibrous sorbents. The crude oil investigated in the current study was obtained from TOTAL; which is a French oil company operating in the production of crude oil in UAE. According to the company, the TOTAL crude oil samples used in this study had a density of 0.867 g/cm^3, and a viscosity of 7.0 cP measured at 50 rpm.

Homogeneous solutions of each polymer containing 20, 30, and 40 w/v% were prepared by dissolving the corresponding amounts of the polymer beads in DMF, THF or their combinations. Polymer microfibers were made using an electrospinning technique where 5 cc of each of the polymer solutions were injected using an automatic syringe pump and a high voltage was applied using a Gama High Voltage Research power supply. Fibers were collected on a static grounded metallic collector. The effects of varying the molecular weight of the starting polymer, type and composition of solvent (DMF, THF and their combinations), applied voltage (up to 30 kV), feeding rate (up to 10 ml/hr), spinning distance (up to 20 cm), relative humidity (up to 100%) and needle gauge (up to 29G) on the characteristics of the fibrous sorbents prepared thereof were studied. Electrospun PS microfibers were characterized for their composition using infrared spectroscopy and morphology using a scanning electron microscope (Cambridge Instrument SEM

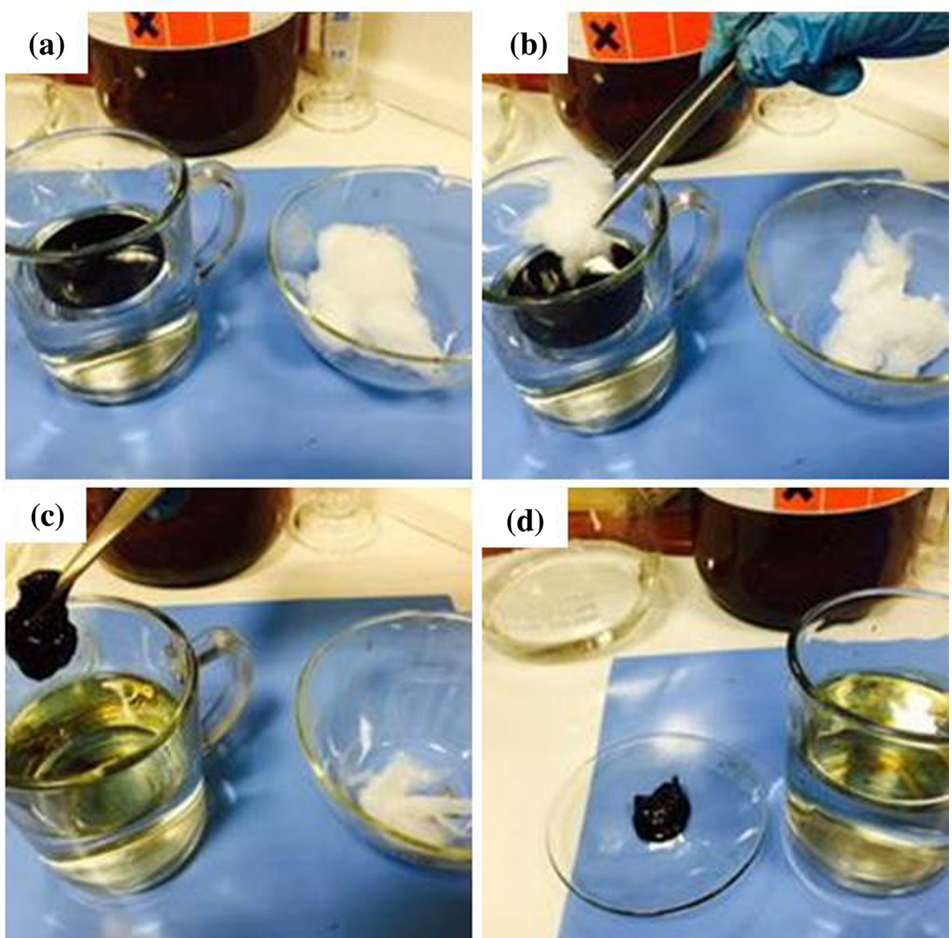

Fig. 1. Step-by-step illustration of the use of fibrous sorbent in the removal of crude oil spills from simulated sea water media.