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PII: S1385-8947(16)31762-4
DOI: <http://dx.doi.org/10.1016/j.cej.2016.12.010>
Reference: CEJ 16175

To appear in: *Chemical Engineering Journal*

Received Date: 15 October 2016
Revised Date: 1 December 2016
Accepted Date: 2 December 2016

Please cite this article as: J. Wu, A. Kyoungjin An, J. Guo, E-J. Lee, M. Usman Farid, S. Jeong, CNTs reinforced super-hydrophobic-oleophilic electrospun polystyrene oil sorbent for enhanced sorption capacity and reusability, *Chemical Engineering Journal* (2016), doi: <http://dx.doi.org/10.1016/j.cej.2016.12.010>

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CNTs reinforced super-hydrophobic-oleophilic electrospun polystyrene oil sorbent for enhanced sorption capacity and reusability

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ABSTRACT

To meet the challenges of global oil spills and oil-water contamination, the development of a low-cost and reusable sorbents with good hydrophobicity and oleophilic nature is crucial. In this study, functionalized carbon nanotubes (CNTs) were wrapped in polystyrene (PS) polymer (PS-CNTs) and electrospun to create an effective and rigid sorbent for oil. Covalent modification and fluorination of CNTs improved their dispersibility and interfacial interaction with the polymer, resulting in a well-aligned CNTs configuration inside the porous fiber structure. Interestingly, the oil sorption process using PS-CNTs was observed to have two phases. First, the oil swiftly entered the membrane pores formed by interconnected nanofibers due to oleophilic properties of the micro-sized void. In the second phase, the

oil not only moved to nano interior spaces of the fibers by capillary forces but also adsorbed on the surface of fibers where the latter was retained due to Van der Waals force. The sorption process fits well with the intra particle diffusion model. Maximum oil sorption capacity of the PS-CNTs sorbent for sunflower oil, peanut oil, and motor oils were 116, 123, and 112 g/g, respectively, which was 65% higher than that of the PS sorbent without CNTs. Overall, a significant increase in the porosity, surface area, water contact angle, and oleophilic nature was observed for the PS-CNTs composite sorbents. Not only did the PS-CNTs sorbents exhibited a promising oil sorption capacity but also showed potential for reusability, which is an important factor to be considered in determining the overall performance of the sorbent and its environmental impacts.

Keywords: Carbon nanotube; Electrospinning; Oil sorption; Polystyrene; Reusability; Sorbents

1. Introduction

In recent decades, due to rapid industrial development and urban area expansion, the demand for oil as both a fuel source and a commodity has increased greatly [1]. In addition to this unprecedented upsurge of oil demand, oil-water contamination due to industrial oily wastewater discharge and recurrent oil spill incidents has become a major environmental issue worldwide [2]. Hence, efficient treatment for oil-contaminated water is of great importance and interest for many researchers. Consequently, a widespread attention has been paid to developing innovative strategies to reduce the adverse impacts of oily wastewater on human health and natural resources. Various technologies have been developed and employed over the years to treat oil-contaminated water, including in-situ burning, mechanical treatment (using booms or skimmers), chemical treatment (using chemical dispersants), biological treatment, membrane filtration and sorption [3]. All the aforementioned methods are capable of efficiently removing oil from water, however, some of these technologies such as filtration and mechanical

treatment are energy and/or operationally intensive while others are accompanied by environmental concerns, e.g. smoke from in-situ burning and potential toxicity of chemical dispersants [4,5].

Compared to other conventional methods, sorption is by far the most promising technique for oil cleanup due to its high removal efficiency, low cost, and minimal environmental impacts [6]. An ideal sorbent for oil cleanup is considered to have certain properties including high hydrophobicity and oleophilicity (a strong affinity for oils rather than water), high sorption capacity and uptake rate, recoverability of the sorbed oil, and low-cost and ready availability [7]. Generally, sorbents used in oil cleanup processes are divided into three categories: inorganic mineral products such as silica aerogels [8]; organic natural products such as cotton and rice husk [9]; and synthetic organic products such as polytetrafluoroethylene (PTFE), polypropylene (PP) and polyurethane (PU) sorbents [10]. Of these, organic synthetic fibers are given priority for oil-water separation because of their low cost, high hydrophobic and oleophilic properties, and applicability on a large scale. However, the oil sorption capacity of most polymeric fibers is still very low, i.e. few gram of oil per gram of sorbent, which restricts their practical applications.

Recently, many researchers have reported electrospun polystyrene (PS) sorbents with porous fibers to exhibit high oil sorption capacity [11]. Electrospinning is an easy and versatile method for fabricating nanofibers with large surface areas, high porosities, and controllable pores and thicknesses [12–14]. The poor mechanical properties of PS sorbents make them more prone to damage during transportation or post-treatment processes. Therefore, various materials have been introduced to modify the mechanical strength of PS sorbents, including polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), iron oxide (Fe_3O_4), but the incorporation of these materials decreases the oil sorption capacity of the resulting sorbents [15].

Several studies have been conducted to investigate the application of carbon nanotubes (CNTs) in oil-water purification and reported its superior oil sorption capacity [16,17]. As a new member of the carbon family, CNTs have gained increasing recognition in various fields. Regarding sorption studies, CNTs has shown excellent potential for oil-water separation due to their low density, hydrophobic and oleophilic nature, high porosity, large specific surface area, and ease of functionalization [18]. By taking advantage of PS polymer and CNTs' properties, this study fabricated a superhydrophobic PS-CNTs composite sorbent using electrospinning technique to investigate their oil sorption capacity. Four different types of oils (sunflower oil, peanut oil, motor oil 5W-30, and OW-40) representing the major oil pollution in the environment were selected to observe the sorption characteristics of the PS-CNTs sorbents. Furthermore, the effects of different PS and CNTs concentrations on the characteristics of electrospun PS and PS-CNTs sorbents, including specific surface area, pore size and distribution, and wettability were intensively investigated. Sorption kinetic models were used to understand the mechanism of oil sorption onto the PS-CNTs sorbent. Recycle test of the PS-CNTs sorbent was further carried out to evaluate the reusability of the PS-CNTs sorbent.

2. Materials and methods

2.1. Materials

Polystyrene (PS, $M_w = 192,000$ g/mol) and N, N-Dimethylformamide (DMF, ACS reagent, $\geq 99.8\%$) were purchased from Sigma Aldrich and were used as received. The pristine multiwall carbon nanotubes (MWCNTs, internal diameter = about 5–30 nm; length = about 10 μm ; BET surface area = 155 ± 5 m^2/g ; purity = $> 90\%$ and bulk density = $0.04\text{--}0.08$ g/cm^3) were purchased from Carbon Nano-material Technology Co., Ltd., Korea. The 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FTES) used to functionalize CNTs in this study was purchased from Sigma Aldrich. Sunflower oil sample was obtained

from Waitrose sunflower oil, peanut oil sample was obtained from Knife supreme peanut oil, and motor oil samples (OW-40 and 5W-30) were obtained from Mobil 1TM. The viscosity and density of different oil types are given in **Table 1**.

2.2. CNTs functionalization

The homogeneous dispersion and interfacial compatibility of CNTs with the polymer matrix without their agglomeration or exfoliation is the major factor affecting the fabrication of polymer-CNTs composites (i.e. PS-CNTs sorbent). Thus, to enable strong interfacial bonds with the polymer and to endow functional properties, MWCNTs were covalently functionalized using nitric acid (HNO₃, 65%) and FTES in two subsequent steps. In the first step, a predetermined quantity of pristine MWCNTs (2 g) was dispersed in 400 mL of HNO₃ and the dispersion was refluxed under magnetic stirring for 18 h. The oxidized CNTs were added to 50 mL toluene and sonicated for 1h to achieve uniform dispersion of the CNTs for further treatment by FTES. In the second step, FTES solution was added dropwise to the CNTs/toluene solution prepared in the first step, and the mixture was continually stirred for 18h. Later, the resultant highly oxidized CNTs were oven-dried at 120°C for 3h and heated up to 180°C for 30 min to completely remove any unreacted FTES. The procedure of CNTs functionalization is briefly described in **Fig. 1**.

2.3. Fabrication of 3D hydrophobic/oleophilic PS-CNT sorbent by electrospinning

Four different concentrations (15, 20, 25 and 30 wt%) of PS polymer were dissolved in DMF by stirring overnight to prepare precursor polymer solutions and were referred as PS15, PS20, PS25 and PS30 sorbents, respectively. To fabricate PS-CNTs composites by electrospinning, 20-wt% PS precursor solution was mixed with three different concentrations (1, 2 and 3 wt%) of CNTs solutions and were

referred as PS-CNT1, PS-CNT2, and PS-CNT3 sorbents, respectively. The resultant solution was sonicated for 1.5h for well dispersion of CNTs in the polymer solution before the electrospinning process. The sonication process resulted in the wrapping of PS polymer around CNTs to form super molecular complexes. It is a typical example of non-covalent bonding of CNTs (**Fig. 1**), where the polymer wrapping process is achieved through the van der Waals interactions and p-p stacking between CNTs and polymer chains containing aromatic rings [19].

The electrospinning apparatus (ESR200RD, NanoNc Co., Ltd, Korea) consisting of a DC high-voltage supplier, a syringe pump, and a rotating drum collector was used to fabricate PS and PS-CNTs sorbents. The PS-CNTs solution (6mL) was pumped into a 10 mL syringe with a stainless steel needle (diameter = 0.51 mm). The electrospinning was carried out at the flow rate of 1 mL/h under applied voltage of 13-15 kV over a fix tip-to-collector distance of 15 cm ($E = 0.87\text{-}1.00$ kV/cm). A stainless steel plate covered with a sheet of aluminum foil was used as the collector. The electrospun PS and PS-CNTs sorbents were detached from the aluminum foil and placed in the oven at 60 °C overnight to evaporate residual solvent. The electrospinning process was conducted at room temperature with 50-60% relative humidity. A schematic diagram of electrospinning process is presented in **Fig. 2**.

2.4. Sorbent characterization

Morphology and surface structure of the PS and PS-CNTs electrospun sorbents were observed using scanning electron microscope (SEM EVO MA10, Zeiss, Germany) and field emission scanning electron microscope (FE-SEM, QUANTA FEG 450, FEI, US) with different resolutions at 10 keV. Fiber diameter distributions were measured with the SEM images using ImageJ software. Brunauer-Emmett-Teller (BET) surface area was determined by nitrogen sorption using a surface area analyzer (Nova 3200e, US). Wettability of the PS and PS-CNTs sorbents was determined by static water-contact-angle

measurement using Drop Shape Analyzer (FM 4000, Kruss, Germany). Mean flow pore diameter (MFP) of sorbents was measured using porometer (Porolux 1000, Porometer N V. Germany), based on the capillary flow porometry (CFP). Pore (inner) volume was determined based on the weight difference between the dry and wetted sorbent samples, using 1-butanol (ACS, Reagent, $\geq 99.4\%$, Sigma Aldrich) as a solvent. The viscosity of oils was measured at ambient temperature using digital viscometer (ND-9SB, Shanghai weiling scientific instrument Co. Ltd, China). In addition, the oil density was calculated using the values of volume and weight obtained from pouring designated volume of oil into the mess cylinder and subsequent measurement the weight.

2.5. Sorption studies

2.5.1. Maximum oil sorption capacity

Pure oil medium was prepared to investigate the maximum oil sorption capacity of the sorbents. For the sorption experiment, sorbent was immersed into pure oil medium for 90 minutes and then retrieved via tweezers to remove excess oil in the air before weighing to evaluate the maximum oil absorption capacity of different PS and PS-CNTs sorbents. The oil sorption capacity was calculated based on the following equation (Eq. 1) [15]:

$$Q_{max} = \frac{m_1 - m_0}{m_0} \quad (1)$$

where Q_{max} represents the maximum oil sorption capacity of the sorbent (g/g), m_0 (g) is the mass of dry sorbent before oil sorption test, and m_1 (g) is the mass of wet sorbent after sorption for 90 minutes. All sorption tests were conducted at a room temperature and in triplicate to ensure the repeatability of the results. Sorption tests were conducted using four different types of oil with different concentrations of PS and PS-CNTs sorbents.

2.5.2. Sorption kinetics

An oil-water mixture was prepared by adding 10g of oil into 150mL of pure water. The oil layer was immediately formed upper the layer of water due to its lower density. A specific amount of electrospun sorbent was placed into the beaker to test the uptake oil from oil-water mixture. The sorbent stayed in the oil layer because of its high hydrophobic and oleophilic nature. Three sorption kinetic models, including *pseudo* first-order model, *pseudo* second-order model, and intra particle diffusion model were used to investigate the oil sorption mechanism and uptake rate.

Pseudo first-order model was described by the equation as follow [20]:

$$\frac{dq_t}{dt} = k_1 (q_1 - q_t) \quad (2)$$

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (3)$$

where, q_e is the amount of oil sorbed at equilibrium stage, g/g; q_t is the amount of oil sorbent at time t , g/g; and k_1 is the rate coefficient of *Pseudo* first-order sorption, 1/min.

Pseudo second-order model was based on the equilibrium adsorption capacity. The equation can be described as follows [21,22]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where, q_t is the amount of oil sorbed at t time, g/g; q_e is the amount of oil sorbed at equilibrium stage, g/g; and k_2 is the rate coefficient of *Pseudo* second-order sorption, g/g min.

The intra particle diffusion model was more appropriate to present the sorption mechanism. One adsorption can be divided into multiple linear equations. The equation is as below [21,23]:

$$q_t = k_i t^{0.5} \quad (6)$$

where, q_t is the amount of oil sorbed at t time, g/g; and k_i is the intra particle constant, g/g min^{0.5}.

The straight equations were fitted based on the experimental data, and the r^2 was calculated in order to find the model fitness.

2.6. Desorption and reusability test

In order to measure the reusability of the PS and PS-CNTs sorbents, their desorption abilities were investigated. The sorbents with oil were compressed between two plates. Afterwards, the sorbents were rinsed with alcohol and pure water to remove the residual oil and dried in an oven at 60 °C for 10 min. The dried sorbents were then reused for oil sorption, and the sorption/desorption cycles continued unless the sorbent was damaged.

3. Results and discussion

3.1 Electrospun PS sorbent

Electrospinning produce PS fibers, either in the form of beads and beads on strings or pure fibers depending on polymer concentration and operating conditions of electrospinning process. The formation of beads and beads on strings in electrospinning process is attributed to lower polymer concentration, higher surface tension and lower viscosity of the polymer solution [24,25]. **Fig. 3a** and **b** represent the surface morphologies of the PS15 and PS20 electrospun sorbents, respectively, exhibiting bead-on-string structures. Lower polymer concentrations led to the insufficient entanglement of polymer chains, resulting in the polymer solution breaking down into droplets (not fibers) during electrospinning process [26]. On the other hand, as depicted in **Fig. 3c** and **d**, the spherical bead structure disappeared in the PS25 and PS30 sorbents by sufficient entanglements of high concentration polymer. The topographical surface structure of PS electrospun sorbent is generated due to phase separation during the

solvent evaporation and fiber solidification in the electrospinning process [27,28]. In addition, the evaporation of solvent is accelerated at a lower concentration of polymer solution, while the surface of fiber became smoother by increasing PS concentration due to the more stable interfacial condition. As shown in **Fig. 3**, fiber diameter also increased with an increase in polymer concentration, which was attributed to inadequate elongation and stretching of ejected jets with larger viscosity.

Mean pore size in the PS sorbents increased with increasing the PS concentration. The largest mean pore size was observed in the PS30 sorbents ($16.43 \pm 1.51 \mu\text{m}$) with thicker fibers (**Fig. 3d**), whereas the wettability (in terms of water contact angle) of the sorbents slightly decreased from 128° to 118° as the polymer concentration increased from PS15 to PS30. The decline in water contact angle was attributed to the increase in mean pore size (**Table 2**) and the decrease in beads, leading to reduced roughness on the surface of sorbent (**Fig. 3**) [29]. However, the PS electrospun sorbents fabricated in this study were cotton-like fibers, exhibiting weaker mechanical strength (**Table 2**). Particularly, PS15 was unable to be detached from the foil, preserving its original form. This phenomenon was probably due to the higher humidity in the electrospinning surroundings, generating a skin layer covering on the surface of fibers before it reaches the collector [30]. The skin layer reduced the fiber-fiber bonding, thus, demonstrating poor fiber adhesion.

3.2 Electrospun PS-CNTs sorbent

Since it is well-known that the fibers with smaller diameter and high porosity yield large specific surface area [31], therefore, the 20 wt% concentration of PS solution (PS20) was selected to fabricate the PS-CNTs composite sorbents. Three different concentrations of CNTs (1, 2, and 3%) were incorporated into PS solution to produce PS-CNTs sorbents. **Fig. 4** displays the effect of CNTs on the morphologies of PS fibers. It was observed that the beading phenomenon in the PS sorbents was significantly reduced in the PS-CNTs sorbent with the incorporation of CNTs in the PS polymer, predominantly due to the increase

in electrical conductivity of the PS solutions. Furthermore, the increase of electrical conductivity of the polymer solution decreased the mean pore size by allowing a better elongation and stretching of fibers during the electrospinning process. Generally, the morphology of CNTs incorporated polymeric fibers is dependent on both the electrical conductivity of solution and the dispersion of CNTs in the solution. The poor dispersion of CNTs in polymer solution induces the increase in viscosity of the polymer solution. Although 3 wt% CNTs possesses the highest electrical conductivity, thicker fibers were observed in the PS-CNT3 sorbent (**Fig. 4c**). In addition, the mean pore size was not correlated with the increase of CNTs concentration in the solution. These findings indicate that the CNTs were not well dispersed in PS/DMF system, resulting in CNTs aggregation and making fibers and pore size in the PS-CNT3 sorbent larger than that in the PS-CNT2. Overall significant increases in the porosity and water contact angle were observed for the PS-CNTs composite sorbents compared to PS sorbent that in turn played an important role in oil sorption (**Table 2**).

Moreover, the functionalized CNTs were well aligned in the PS fiber as observed in **Fig. 5**. First, PS polymer leads to the wrapping around the CNTs to form super-molecular complexes through the van der Waals interactions and p-p stacking between well dispersed CNTs and aromatic polymer chains. Subsequently, during the electrospinning, the improved CNTs-polymer bonding stabilized the well-dispersed functionalized CNTs in the polymer dope solution, which hindered secondary agglomeration while the fibers were being formed. Interestingly, during the fabrication of PS sorbents, the nano-pores and voids were generated on both the surface of fibers and inside the fibers as shown in **Fig. 6**, which is substantial for the sorption of oil.

3.3 Sorption capacity of electrospun PS and PS-CNTs sorbents.

Five types of fabricated sorbents (PS20, PS25, PS30, PS-CNT1, and PS-CNT2) were selected to investigate their oil sorption capacity. **Fig. 7** represents the hydrophobicity and oleophilicity of the PS

and PS-CNTs sorbents. It can be seen that the PS-CNTs sorbents exhibited high water repelling and oil sorption capability as compared to PS sorbents.

To determine maximum oil sorption capacity, sorbents were immersed into pure oil system without water. The mechanism of oil uptake using pure oil medium is different from the oil/water system, but this method can achieve the maximum amount of oil sorbed by the sorbents without the effect of water.

Fig. 8 demonstrates the maximum oil sorption capacity of different sorbents for different types of oil. Higher oil sorption was achieved with the PS-CNTs composite sorbents than the PS sorbents, which was attributed to their modified properties such as higher specific surface area and smaller fiber diameter. In the case of the PS sorbents, the oil sorption capacity decreased with an increasing PS concentration, which is due to reduced surface area (**Table 3**). On the contrary, the amount of oil sorption for all four oils increased by increasing the CNTs concentration from 1 to 2 wt% (**Fig. 8**). The oil sorption capacity of the PS-CNTs sorbents was able to reach up to 111.45-122.82 g/g while for PS sorbents the oil sorption could only reach up to around 70.90-83.19 g/g, which was three to four times greater than maximum oil sorption capacity of commercially available PP and PVDF sorbents [8,11,15,32,33]. This implies that the PS-CNT sorbent has excellent oil selectivity in the cleanup of oil from water to preserve the environment from oil spill.

3.4 Investigation of oil sorption behavior via kinetic model

Synthetic oily wastewater was prepared and used to evaluate the oil sorption capacity and uptake rate of two different sorbents. The oil used in this study was immiscible with water; thus, two layers (oil and water) were formed immediately after adding the oil into the water. Both the PS and PS-CNTs sorbents exhibiting adequate buoyancy were able to stay in the oil layer, which in turn accelerated the oil uptake rate (**Fig. 9**).

As can be seen from **Fig. 10**, after 90 min of oil sorption, all of the sorbents reached the stationary stage.

In comparison with the PS-CNTs composite sorbents, PS sorbents reached the equilibrium stage in a shorter time. The PS sorbents required almost 30 min to reach the equilibrium stage while the PS-CNTs sorbents took more than 60 min to reach the equilibrium.

The mechanism for synthetic polymeric sorbents to oil sorption was uncertain, therefore, the mechanism of oil uptake is an important factor to understand. Herein, little swelling was observed in our sorbents, which indicates that absorption was not the main process involved in oil sorption using the PS sorbents. The van der Waals forces in the void between fibers and oil played a significant role in oil sorption, indicating that the oil sorption mechanism was mainly based on the physical sorption process. In order to analyze the oil sorption mechanism onto PS and PS-CNTs sorbents, three sorption kinetic models (*Pseudo* first-order model, *Pseudo* second-order model and intra particle diffusion model) were applied to fit with the experimental data and the model was assessed on the basis of linear correlation coefficient, R squared (R^2) values. The results revealed that the calculated equilibrium sorption capacity (q_e) was fitted both in both *Pseudo* first- and second-order models. However, as can be seen that in **Table S1**, *Pseudo* second-order model ($R^2 = 0.9605$ - 0.9998) showed a better fit with experimental data than *Pseudo* first-order model ($R^2 = 0.7646$ - 0.9675). In particular, *Pseudo* first-order model didn't fit well in the initial stages of oil sorption. Hence, *Pseudo* second-order kinetic model was probably the main mechanism involved in the whole oil sorption process. However, *Pseudo* first- and second- model equations are only based on the oil sorption capacity that only reflects the “behavior” of the whole oil sorption process, so the rate-limiting step involved in the oil sorption process cannot be determined. Furthermore, intra particle diffusion model was applied to determine the mass transfer mechanism based on multi-linear regression equations, indicating that two or more stages were involved in the sorption mechanism. **Fig. 11** shows the intra particle diffusion model of the oil sorption and it was evidently observed that the oil sorption process could be divided into two phases for all sorbents. Moreover, none

of the linear equation passed through the origin, which explained that the oil sorption rate was affected by multiple parameters including oil density, surface tension, viscosity, surface area, porosity and oleophilicity. Intra particle diffusion parameters of oil adsorption summarized in Table S2 showed a good fit with experimental data in both phase I and II. The nano-pores and voids generated on the surface and inside the fibers during the fabrication of sorbents provided larger porosity as well as surface area and inter channels that played an important role in the sorption of oils.

It was revealed that during the overall oil sorption process, the oil entered initially to the micro-sized space structured by interconnected nanofibers due to oleophilic properties of prepared sorbents. Later, the oil migrated to the nano-pores on the surface of fibers by capillary forces and filled into the voids between the polymers and CNTs. In addition, the oil was sorbed on the surface of fibers, which was attributed to the Van der Waals forces between the molecules. These findings indicated that the oil was quickly sorbed in the first phase, however after filling the micro-sized voids, surface sorption including second-layer sorption [34], and internal space sorption of fibers was predominantly controlling the oil sorption rate in the second phase. Hence, the higher sorption rate and high amount of oil sorbed by the PS-CNTs sorbents were associated with the higher pore density, large surface area, and hydrophobic and oleophilic nature.

3.5 Sorbent reusability and environmental aspects

Although the PS-CNTs sorbents showed promising oil sorption capacities, the reusability of the sorbents is another important factor that needs to be considered to reflect the overall performance of the sorbent and to reduce its environmental impacts. As aforementioned, PS sorbents exhibited weaker mechanical strength due to the nanopores on the surface of the cotton like fibers, thus, considering the weaker mechanical strength, PS sorbents were not tested for their reusability after the sorption test. However, as

the incorporation of CNTs strengthens the PS sorbents' mechanical strength, their reusability was tested after the sorption tests. Results revealed that PS-CNTs sorbents were not destroyed even after three consecutive sorption/desorption cycles. Although a slight decrease in the oil removal rate was observed after several times of compression and extraction of the sorbent to recover the sorbed oil (**Fig. 12**). Even after three consecutive sorption/desorption cycles, the removal rate was around 80%, indicating the effectiveness and reusability of the PS-CNTs composite sorbent.

The use of inexpensive sorbent materials and their reusability, excellent oil selectivity, and easy fabrication endow this PS-CNT sorbent with three-fold environmental benefits. They are environmental protection by removal of oil from water, lower environmental impact by reducing sorbent waste through reuse of sorbents, and resource minimization from using less materials that last longer through the faster sorption in the first phase and the long-lasting desorption in the second phase. Also, unlike most CNTs incorporated membranes fabricated in previous studies in which CNTs are positioned on membrane surfaces or inside pores, this fabrication method embeds and anchors CNTs inside the electrospun PS nanofibers. Therefore, this anchored CNTs renders greater benefit from its addition as well as preventing potential toxic reactions that may occur when CNTs are exposed to the environment.

4. Conclusion

This study bridges the gap between experimental and theoretical sorption tests by determining the optimal composite ratio for PS-CNTs sorbent and illuminating the role of CNTs in the composite sorbent. A well-aligned PS-CNTs sorbent, which is super-hydrophobic-oleophilic, was fabricated by simple electrospinning. The PS-CNTs composite sorbent exhibited a significant increase in the porosity, surface area, and water contact angle, as well as oleophilic nature, which plays an important role in oil sorption. Moreover, its excellent removal efficiency even after several cycles of the oil sorption test

presented a significant potential for reusability. In sum, this sorbent could be a cost-effective, convenient, and highly efficient oil sorption material for oil spill cleanup at large production scales.

ACKNOWLEDGMENT

This research was financially supported by the Research Grants Council of Hong Kong for Early Career Scheme (Project number: 9048074).

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Table 1 Physical properties of tested four types of oil.

Oils	Density (g/cm ³)	Viscosity (mPa.s) at ambient temperature
Sunflower oil	0.92±0.02	52
Peanut oil	0.91±0.01	65
Motor oil (OW-40)	0.86±0.03	97
Motor oil (5W-30)	0.86±0.03	116

Table 2 Characteristics of electrospun PS and PS-CNTs sorbents.

Sorbents	Pore size (μm)	Porosity (%)	Water contact angle ($^{\circ}$)
PS15	2.19 ± 0.42	- *	- *
PS20	5.61 ± 0.38	98.06 ± 0.20	127.43 ± 0.06
PS25	6.59 ± 0.12	97.57 ± 0.19	123.63 ± 0.25
PS30	16.43 ± 1.51	97.59 ± 0.18	118.53 ± 0.32
PS-CNT1 ⁽¹⁾	4.23 ± 0.08	98.75 ± 0.02	132.98 ± 0.12
PS-CNT2 ⁽¹⁾	3.71 ± 0.28	98.54 ± 0.17	139.13 ± 0.06
PS-CNT3 ⁽¹⁾	4.41 ± 0.12	98.13 ± 0.09	143.76 ± 0.25

Note: * indicates that PS15 sorbent was hard to detach from the aluminum foil so that the data could not be calculated.

(1) PS-CNTs indicates that CNTs weight percentage (wt%) to 20 % polymer (PS).

Table 3 Brunauer-Emmett-Teller (BET) surface area of electrospun PS and PS-CNTs.

Sorbents	Surface area (m ² /g)
PS20	26.43
PS25	24.88
PS30	23.63
PS-CNT1	39.38
PS-CNT2	43.23

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Highlights

- CNTs composite polystyrene (PS) (PS-CNTs) was fabricated by electrospinning.
- An oleophilic nature of PS sorbent is enhanced with CNTs composite.
- Sorption in PS-CNTs sorbent is fitted well with an intra particle diffusion model.
- A super-hydrophobic-oleophilic PS-CNTs sorbent shows a reusable potential.
- PS-CNTs sorbent can be a high efficiency sorption material for oil spill cleanup.