Polycarbonate and activated charcoal-engineered electrospun nanofibers for selective recovery of oil/solvent from oily wastewater

Prakash M. Gore^{1,2} · Pawan Gawali³ · Minoo Naebe² · Xungai Wang² · Balasubramanian Kandasubramanian¹

Received: 16 June 2020 / Accepted: 29 September 2020 / Published online: 7 October 2020
© Springer Nature Switzerland AG 2020

Abstract

Present study reports polycarbonate (PC) nanofibers functionalized with industrial grade activated charcoal for emphatic oil–water separation and recovery of petroleum oils and organic solvents from oily wastewater. The developed PC nanofibers demonstrate hydrophobicity (water contact angle of 133°) and oleophilicity (oil and/or solvent contact angle is equal to 0°), simultaneously. The functionalized PC nanofibers exhibit average permeation flux of 10,834.5 L m⁻² h⁻¹ and 39,886.5 L m⁻² h⁻¹ toward diesel, and n-Hexane solvent, respectively. Developed PC nanofibers demonstrated an excellent oil recovery toward petroleum oil products like petrol, diesel, and engine oil, which was found to be 308%, 872%, and 1738%, respectively, till 10 washing cycles. Thermogravimetric analysis of developed PC nanofibers revealed thermal stability up to 350 °C, thereby demonstrating its applicability in harsh environmental conditions. Functionalization of PC polymer nanofibers with activated charcoal was confirmed using FTIR study. The morphological analysis of charcoal functionalized PC nanofibers revealed a heterogeneous rough patterned textures with a porosity (which facilitate the air-pockets for improved hydrophobicity) manifesting inside the fibers. The pH-based performance (pH range of 2–14) demonstrated that the developed microfibers maintain its hydrophobicity ad service durability under harsh acidic and alkaline mediums (corrosive environments). The PC nanofibers demonstrate simultaneous hydrophobic–oleophilic behavior which is well explained using principal Cassie–Baxter’s theory. The successive results demonstrate that the activated charcoal functionalized PC microfibers could be successfully utilized for practical recovery of oil/organic solvents from oily wastewater, and for the oil-spill cleanups.

Keywords Polycarbonate · Activated charcoal · Nanofibers · Oil recovery · Hydrophobic–oleophilic

1 Introduction

The ever increasing need of petrochemical products and organic solvents in energy, automobiles, and chemical-based industries has accelerated the development of word economies [1, 2]. During transportation of these petroleum products through sea-based routes,

frequently, oil-seepage accidents occur which release nearly 1.7–8.8 MT of oils per year in the oceans [2, 3]. Moreover, discharge of organic solvent contaminated toxic industrial wastewater in an environment is polluting the ground and surface-based water sources, and endangering the health of living species in the ecosystem [4–7]. Lack of light and oxygen, chemical

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s42452-020-03609-x>) contains supplementary material, which is available to authorized users.

✉ Balasubramanian Kandasubramanian, meetkbs@gmail.com | ¹Nano Surface Texturing Lab, Department of Metallurgical and Materials Engineering, Defence Institute of Advanced Technology (DU), Ministry of Defence, Girinagar, Pune 411025, Maharashtra, India. ²Institute for Frontier Materials, Deakin University, Waurn Ponds Campus, Geelong, VC 3216, Australia. ³Department of Polymer and Surface Engineering, Institute of Chemical Technology, Mumbai 400019, Maharashtra, India.

SN Applied Sciences (2020) 2:1786 | <https://doi.org/10.1007/s42452-020-03609-x>

noxiousness, and physical asphyxiation are some of the hazards of the oil-spills and polluted wastewater. There are some conventional methods like gravity-based separation, membrane-based filtration, ultrasonic-based separation, flocculation-coagulation, and adsorption, which have been utilized by the industries and scientific fraternity. However, these conventional techniques possess limitations like poor separation performance over the long period, high operation costs, and the resultant pollution [5, 6, 8]. Recently, scientific community has been exploring new methods based on oil/solvent–water absorption, and separation, which utilize nano-functional materials [2, 5, 8–15]. In this sense, more recently, materials exhibiting simultaneous oleophilicity-hydrophobicity (absorption tendency toward oil/solvents and repulsion toward water) have fascinated the researchers, which demonstrate greater selectivity and separation productivity [2, 10, 12, 16]. Researchers have explored various foam and sponge-based materials, however, considering the reusability, flexibility, and easier surface functionalization, fiber-based materials are strong contenders for oil recovery application, since they facilitate the incorporation of heterogeneous wetting toward various oil/solvents, which can be rendered by its modifications via surface architecture (patterns) and/or surface chemistry [2, 10, 12]. Modification via surface patterns requires multiscaled textures, which helps in imparting of hydrophobicity as it facilitates air-pockets on surface i.e. beneath water droplet, and oleophilicity due to capillary pressure effect. The modification via surface chemistry requires regulation of surface tension between oils (30 mN/m), and organic solvents (18.4 mN/m), and water (72.8 mN/m), thereby allowing only oil/solvent absorption but avoiding water wetting [2, 10, 12, 16]. In present study, the authors have utilized engineering polycarbonate (PC) polymer for oil recovery, as it is mechanically strong (izod impact strength = 600–850 J/m), thermal stability (up to 350 °C), ability to facilitate solution formation, and maintaining its structural rigidity up to its high glass transition temperature (140 °C) [17–22]. The activated charcoal was utilized in conjunction with PC polymer, since it exhibits functionalized surface encompassing functional groups like C=O, CO_3 , O–H, and C–O which facilitates bonding with polymer matrix, and is readily available in commercial market at low cost [23, 24]. Furthermore, the activated charcoal inherently exhibits porous nature, and some polarity imparted by functional groups, which help in facilitating the absorption of various solvents and liquids, due to which it is widely used in water treatment applications [25, 26]. In order to fabricate the nanofibers, the electrospinning technique was utilized as it facilitates formation of nanofibers with control over

diameter, surface morphology, smooth and facile operation [27–30].

Recently, Wang et al. have reported a polylactic acid-based superhydrophobic material for effective oil–water separation [31]. The developed foam exhibited a honeycomb-shaped porous structure, which was fabricated using dioxane and water as a solvent using freeze-drying process (skin-peeling mechanism). The reported porous PLA material exhibited a stable adsorption performance toward petroleum oils, and organic solvents over 10 oil absorption and 10 permeation flux cycles. They claimed that the reported foam exhibited oil absorption capacity of 11–26 times of its original weight, and a permeation flux of $50.9 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$. They claimed that the high performance of the developed PLA material was attributed to its superhydrophobic nature, and porous honeycomb structure generated at the micro-level [31]. In another similar study, Wang et al. have studied the superhydrophobic PLA-based foams prepared via freeze-drying method (skin-peeling) for recovery of the oils from oily wastewater [32]. They claimed that the reported PLA foam exhibited superhydrophobicity (water contact angle of 151°), with highest adsorption capacity of 31.5 g/g and oil–water separation efficiency of 98% till 10 cycles, and continuous performance for more than 15 h under pressure. They noted that the improved oil adsorption performance of the PLA foam was attributed to its swelling properties. They claimed that the 3D interrelated porous configuration of the reported PLA foam most probably facilitated the continuous transportation i.e. entry and exit, of the oil through the foam, thereby improving its recycling performance. They further asserted that the micro- and nano-hybrid type structures (observed in the SEM micrographs) are responsible for imparting the hydrophobic effect into the PLA foam [32]. Zhang et al. [33] reported 3D porous high density polyethylene (HDPE) shaped in bundle forms and prepared by melt extrusion, leaching technique, and skin-peeling, for practical oil recovery. They reported that the prepared porous HDPE bundles exhibited hydrophobic nature (WCA = 139°) which was attributed to the porous nature and villi structures [33]. In another study, Wang et al. reported a polyurethane-based foam which exhibited hydrophobic nature with WCA of 147° , high porosity (higher than 90%), outstanding compressibility (more than 1000 cycles), high oil recovery performance (more than 98%) [34]. They claimed that the porous nature and the porosity distribution in the foam are responsible for the generation of the hydrophobic nature, whereas the inherent elastic nature of the PU facilitated the high compressibility [34].

In this sense, the authors have fabricated nanofibers-based PC polymer functionalized with activated charcoal in weight concentrations of 0.5%, 1%, and 1.5% (wt/wt),

using facile electrospinning method. The developed PC nanofibers hydrophobicity (WCA = 133°), and oleophilic nature (oil and solvent contact angle is 0°), simultaneously. The developed functionalized PC nanofibers exhibit average permeation flux of 10,834.5 L m⁻² h⁻¹ and 39,886.5 L m⁻² h⁻¹ toward diesel, and n-Hexane solvent, respectively. The developed PC nanofibers demonstrated an excellent average oil recovery for petroleum oil products like petrol, diesel, and engine oil, which was found to be 308%, 872%, and 1738%, respectively, till 10 washing cycles. The developed functionalized PC nanofibers were characterized using thermogravimetric analysis, FTIR study, and morphological analysis (FE-SEM micrograph study). The successive results indicate that the developed PC nanofibers could be proficiently utilized for practical recovery of oil/organic solvents from oily wastewater, and for the oil-spill cleanups which frequently occur in oceans during transportation of oils.

2 Experimental section

2.1 Materials

Polycarbonate (grade-Lexan 143 R) was purchased from SABIC Innovative Plastics, India, Pvt Ltd. Activated charcoal in powder form was purchased from Merck Specialties India, Pvt. Ltd. Japan. Dichloromethane (DCM) (purity-99.8%, synthesis grade) and n-Hexane (purity > 99%, synthesis grade) were acquired from Sigma-Aldrich, Pvt Ltd, India. Petrol, engine oil, and diesel were obtained from Hindustan Petroleum Corporation Ltd., India. Deionised water (purity-18.2 MΩ cm) was obtained from Barnstead Nano-Pure Water System (Cole-Parmer, India). All utilized chemicals were of high purity grade and were used without additional treatment. The details of all utilized chemicals are provided in Table 1.

2.2 Electrospinning setup

The standardized uniform solution for electrospinning was formulated by liquifying polycarbonate (PC) in DCM solvent at a loading of 12 wt/wt% in a magnet-based stirrer (stirring speed of 200 rpm, and stirring time of 2 h at room temperature). After 2 h of magnetic stirring, the electrospinning solution was ultrasonicated (sonication time of 05 s, and interval time of 05 s) for 10 min for uniform distribution of the additives. Activated charcoal was added in situ during preparation of the electrospinning solutions, at a concentration of 0.5, 1, and 1.5 wt/wt%, respectively. The PC + AC solutions did not show any agglomeration or suspended particles of the activated charcoal powder, thereby confirming the homogeneous nature of the electrospinning solution. Electrospinning is a distinctive and versatile technique for generation of the nanofibers. The electrospinning experiment was conducted in a horizontal electrospinning instrument (Model Name = ESPIN-Nano, Manufacturer = Physics Equipments, India) (Fig. 1).

During electrospinning operation, solution was taken in a 10 mL volume syringe (Needle diameter of 0.55 mm), the voltage was maintained at 18 kV with a needle to collector plate distance at 15 cm, and feed/flow rate of 1.5 mL/hr. The viscosity of the solution was measured using Brookfield viscometer (Model Name = DV2T Pro,

Fig. 1 Setup assembly for electrospinning operation

Table 1 Details of utilized chemicals (chemical sample table)

Chemical name	CAS number	Chemical formula	Molar mass	Mass fraction
DI water	7732-18-5	H ₂ O	18.02 g/mol	> 0.99
Polycarbonate	25037-45-0	(C ₁₅ H ₁₆ O ₂) _n	254.3 g/mol	> 0.95
Activated charcoal	7440-44-0	C (Hill)	12.01 g/mol	> 0.98
Dichloromethane	75-09-2	CH ₂ Cl ₂	84.93 g/mol	> 0.99
n-Hexane	110-54-3	C ₆ H ₁₄	86.18 g/mol	> 0.99
Petrol	8006-61-9	mixture of hydrocarbons	82.2 g/mol	> 0.98
Diesel	68476-30-2	C ₁₃ -C ₁₈	Not available	> 0.98
Engine oil	Not available	Gasoline fraction	Not available	> 0.95

Maker = Brookfield Engineering Inc., USA) with a spindle no. SC4-21, and a rotational speed of 10 rpm (experiment running time was 60 s). The solution viscosity was found to be 80 cP. The obtained nanofibers were obtained in a non-woven shape, which were consequently dried at a temperature of 140 °C for 2 h, for the confirmation of complete exclusion of the solvent.

3 Characterization study

3.1 FTIR analysis

FTIR analysis was performed on the electrospun nanofibers of pristine polycarbonate (PC), activated charcoal (AC), polycarbonate functionalized with activated charcoal (at various concentrations) to evaluate the actual present functional groups before their utilization in the oil–water separation experiments (Fig. 2). The FT-IR investigation of pristine PC shows characteristic intense peaks at 1768 cm^{-1} associated with carbonyl group which possesses oxygen atoms attached to carbon atom via double bond. Peak at 1506 cm^{-1} is attributed to the stretching of phenol ring, where the resonance frequency of two phenol rings is attained. Peak at 1223 cm^{-1} corresponds to asymmetric O–C–O carbonate stretching, while adjacent peaks at 1187 cm^{-1} , and 1156 cm^{-1} correspond to stretching of C–O present in polycarbonate structure. The last peak at 824 cm^{-1} is attributed to the para-substituted phenol rings present in the back bone of the PC polymer structure [17–22, 35].

FTIR analysis of activated charcoal shows characteristic broad peak in 1500–1600 cm^{-1} , and 1100–1300 cm^{-1} range corresponds to C=O, and C–O stretching, and O–H bending, respectively, thereby indicating the surface

activation of carbon present in activated charcoal [25, 26, 36, 37]. FTIR analysis of polycarbonate functionalized with activated charcoal i.e. 0.5%, 1%, and 1.5% (wt/wt), shows dominating characteristics peaks associated with C=O stretching, and C–O stretching, most probably due to higher quantity of polycarbonate as compared to activated charcoal.

Considering, the characteristic adjacent crowded peaks appearing between 4000 cm^{-1} to 3500 cm^{-1} belonging to activated charcoal reappear with reduced peak intensity in PC + AC(0.5%) PC + AC(1%), and PC + AC(1.5%) electrospun microfibers, thus confirming the molecular interaction between activated charcoal and polycarbonate. Furthermore, the small characteristic peaks of activated charcoal appearing near to 3000 cm^{-1} re-occur with small intensity in PC + AC(0.5%) PC + AC(1%), and PC + AC(1.5%) electrospun microfibers, thereby indicating the interaction between activated charcoal and polycarbonate at molecular level.

In a summary, FTIR study revealed the presence of polar functional groups like C=O, C–O, and O–C–O, which bring polarity onto molecules, thereby repelling the polar groups present in water, which in turn helps in improving the hydrophobicity of nanofibers, and oleophilicity toward oil during oil–water separation experiments [2, 5, 8–15].

3.2 Thermogravimetric analysis (TGA)

Thermal stability of the pristine PC and activated charcoal functionalized PC nanofibers was performed using thermal gravimetric analysis (TGA) instrument (Model—TGA 400, Make—PerkinElmer, USA) as shown in Fig. 3. During TGA experiment nitrogen gas flow rate, heat scanning rate was maintained at 50 mL/min, and 20 °C/min, respectively.

Fig. 2 FTIR analysis of pristine and activated charcoal functionalized PC nanofibers

Fig. 3 TGA analysis of pristine and activated charcoal functionalized PC nanofibers

TGA analysis revealed that the pristine and functionalized PC nanofibers exhibit thermal stability up to 350 °C, and beyond that it undergoes degradation with onset degradation starting at 380 °C.

The nanofibers show average weight loss of 5% till 350 °C, which is attributed to the entrapped solvent molecules which release upon relaxation of PC polymer chains when it crosses its glass transition temperature i.e. 147 °C. The weight loss from zone I to zone II is found to be around 68%, which is in line with the developed literature [17–21, 35]. From zone II to zone III, the pristine PC, PC + AC(0.5%), and PC + AC(1.5%) nanofibers show weight loss of 8%, 3%, and 6%, respectively. The slightly improved heat stability by PC + AC(0.5%) nanofibers is possibly due to the uniform distribution of the charcoal particles, and their heat sustaining ability (melting temperature > 3000 °C) in the PC matrix. At the end of TGA experiment, pristine PC, and PC + AC(0.5%) nanofibers show complete degradation; however, PC + AC(1.5%) nanofibers show residual mass (uncombusted material) of 9.7%, which is attributed to the higher loading of activated charcoal which binded with PC polymer chains, and prevented their complete degradation [17–20, 38]. In a summary, it was observed that the activated charcoal helped in improving the thermal stability of the PC polymer.

3.3 Morphological analysis

The morphological study was performed on the pristine and charcoal functionalized PC nanofibers for determining its microstructural attributes, using a field emission scanning electron microscopy (FE-SEM) (Model Name = JSM-6700F, Maker = Carl Zeiss AG, Germany). The FE-SEM analysis of activated charcoal showed a randomly an oriented flake-type morphology (Fig. 4a), possibly due to its surface activation which helps in keeping the carbon molecules binded together. The morphological analysis of pristine and charcoal functionalized nanofibers showed multi-scaled heterogenous rough surface exhibiting porous morphology, as shown in Fig. 4b–e, where the average pore diameter of the generated pores was found to be 141 ± 64 nm (determined using ImageJ software). The electrospinning operation requires extending of fibers moving from needle tip to collector plate, and simultaneously, the evaporation of solvent takes place during movement of the fibers, which leads to generation of micro-sized pores due to escaping of the solvent molecules. After electrospinning operation, PC nanofibers were dried in an air-oven at a temperature of 140 °C (glass transition temperature of 147 °C) for 2 h to facilitate the relaxation PC polymer chains thereby helping the evaporation of any entrapped solvent molecules operation [17–20, 38]. Thus, in addition to pore generation during electrospinning

operation, the drying treatment also leads to generation of micro-pores during heating at 140 °C [35, 39–41]. Considering the FE-SEM micrographs (Fig. 4), it is observed that the microfiber diameter of Pristine PC (2 ± 1 μm) increased with PC + AC 0.5% (4 ± 1 μm) and PC + AC 1% (7 ± 1 μm) loading of activated charcoal; however, the fiber diameter was found to be decreased (4 ± 1 μm) for 1.5% loading of activated charcoal. The decrease in fiber diameter for 1.5% loading could probably be due to the threshold loading of activated charcoal into the PC matrix.

The activated charcoal molecules exhibit functional groups like C=O, $-\text{CO}_3$, O–H, and C–O which imparts polarity unto it, and the effect of these polar charges probably becomes more pronounced when the activated charcoal molecules try to organize themselves in the polymer during fiber formation (stretching of polymer chains) in electrospinning process [2, 5, 8–15], thereby helping improving the water repellency characteristics. Since the electrospinning process parameters are constant, the activated charcoal molecules at 1.5% loading get probably less space to relax and re-organize during fiber formation, as compared to PC + AC(0.5%), and PC + AC(1%) microfibrers. Thus, the collective effect of these parameters tends in improving the hydrophobic property, and decreasing the fiber diameter in PC + AC(1.5%) microfibrers [2, 5, 8–15].

Considering the FE-SEM micrographs shown in Fig. 4, it is observed that average diameter of the electrospun microfibrers has increased for the loading of activated charcoal at 0.5% and 1%. The FE-SEM micrograph of PC + AC 0.5% microfibrers shows pores possessing larger diameter, but less porosity distribution as compared to PC microfibrers exhibiting 1wt% and 1.5wt% loading. This is attributed to the more relaxation space available for the activated charcoal molecules, which probably leads to less repulsion of polar charges present in the functional groups of the activated charcoal molecules. When the loading of activated charcoal i.e. 1 wt% and 1.5 wt%, increases in the PC microfibrers, then probably the available relaxation space decreases and the effect of polar charges becomes more pronounced in less confined space, thereby decreasing the diameter of the space and limited porosity distribution in the electrospun microfibrers [2, 5, 10, 34, 41]. The porosity distribution histograms of the PC microfibrers for Pure PC, PC + AC(0.5%), PC + AC(1%), and PC + AC(1.5%) have been represented in Fig. 5.

3.4 Surface wettability investigation

In order to claim the utilization of functionalized PC nanofibers for retrieval of petroleum oils from oily wastewater, it requires study on its wetting behavior toward oils, and solvents. The wetting performance of pristine and activated charcoal-engineered PC nanofibers was

Fig. 4 FE-SEM micrographs of **a** activated charcoal, and nanofibers of **b** pristine PC, **c** PC + AC(0.5%), **d** PC + AC(1%), and **e** PC + AC(1.5%)

investigated via sessile drop-based method using contact angle goniometer (Model Name = DSA 25, Kruss GmbH, Germany) for water, petrol, diesel, and engine oil. The static water contact angles of pristine PC, PC + AC(0.5%), PC + AC(1%), and PC + AC(1.5%) nanofibers were found to

be $123^\circ \pm 1^\circ$, $133^\circ \pm 3^\circ$, $129^\circ \pm 0.5^\circ$, and $117^\circ \pm 0.5^\circ$, respectively (Fig. 6a–d). The wetting performance of petroleum oils viz. petrol, diesel, and engine oil, toward PC nanofibers was studied, which showed an instant oil wetting i.e. oleophilic (Fig. 6e).

Fig. 5 Pore size distribution histograms of microfibers for **a** pure PC, **b** PC + AC(0.5%), **c** PC + AC(1%), and **d** PC + AC(1.5%)

The surface patterns of the electrospun PC nanofibers are similar to the surface exhibiting heterogeneity, as it possesses porous nature and rough patterns, simultaneously, which is evident from the morphological analysis of the PC nanofibers (randomly oriented) described in previous section.

The porosity generated in the PC nanofibers helps in the development of air-compartments i.e. pockets, between pores and heterogeneously patterned rough surface textures, thereby holding the water droplet on its surface, and maintaining the hydrophobicity [10, 12, 42, 43]. This phenomenon is well elucidated by the Cassie-Baxter's theory, which interprets the hydrophobicity of heterogeneous rough patterned textures exhibiting porous nature.

The principal equation for Cassie-Baxter's theory is elucidated as follows [44]:

$$\cos \theta_c = f_1 \cos \theta_1 - f_2 \quad (1)$$

where θ_c = contact angle (apparent), f_1 and f_2 = fractions of surface exhibiting, phase 1 and phase 2, correspondingly, θ_1 = phase 1 contact angle.

The improvement in hydrophobicity of PC + AC(0.5%), and PC + AC(1%) nanofibers i.e. 133° and 129°, respectively, as compared to pristine PC nanofibers i.e. 123°, is possibly due to the uniform distribution of the surface activated charcoal in the PC polymer matrix, which exhibits small amount of polarity and inherent porous nature [2, 5, 35, 36, 38]. However, in case of PC + AC(1.5%) nanofibers, the WCA was found to be decreased i.e. 117°, is possibly due to higher loading of activated charcoal which leads to formation of clusters i.e. coalescing of particles, thereby restricting its uniform distribution in the polymer matrix [5, 18].

Fig. 6 Water contact angles (WCA) of nanofibers of **a** pristine PC, **b** PC + AC(0.5%), **c** PC + AC(1%), **d** PC + AC(1.5%), and **e** oil wetting i.e. oleophilic nature, behavior of PC + AC(0.5%) nanofibers

Further, the hydrophobicity of PC nanofibers toward water is attributed to its greater surface tension i.e. 72.8 mN/m, whereas its oleophilic nature toward petroleum oils is attributed to the low surface tension of engine oil, petrol (29 mN/m), and diesel (29.5 mN/m) [2, 8, 10, 12]. Thus, considering the above-described attributed of pristine, and activated charcoal functionalized PC nanofibers, it shows hydrophobic effect toward, while simultaneously maintaining the oleophilic nature toward petroleum oils.

3.5 Oil–water separation analysis

The ability of the developed hydrophobic PC nanofibers for practical recovery of petroleum oils is important for establishing its functioning for oil–water separation.

The practical recovery of petroleum oil from oily wastewater, and the pictorial representation for oil–water separation mechanism owing to the hydrophobic-oleophilic nature of the PC nanofibers has been depicted in Fig. 7a, b. As pronounced in the earlier section, the synergistic influence of the porosity, the air-pockets, and the heterogeneous rough surface on the PC nanofibers for exhibiting the simultaneous hydrophobic-oleophilic nature has been represented in Fig. 7b.

Considering the oil-liking nature of the PC nanofibers, its maximum oil absorption performance of toward diesel, petrol, and engine oil was evaluated for practical oil recovery from oily wastewater. Figure 8a–c reveals that functionalized PC nanofibers maximum oil recovery toward engine oil (average oil absorption was found to be 1738% for PC + AC (1.5%)), whereas, toward diesel, and petrol, it showed average oil recovery of 872% (PC + AC (1.5%)), and 308% (PC + AC (0.5%)), respectively, against the original weight of PC nanofibers (0.15 gms for all samples). The maximum oil recovery toward engine oil, and diesel by PC nanofibers could be attributed to their high density, and high surface tension (> 29.5 mN/m) as compared to petrol [2, 8, 10, 12].

Researchers have developed that during oil recovery, the hydrophobic nature and the active capillary forces produce combined influence on the porous heterogeneous surface of the microfibers, thereby enhancing its instant oil absorption i.e. recovery. Further, the pores manifesting inside the microfibers and cavities i.e. voids, present between the microfibers facilitate the storage space for the absorbed i.e. recovered oils/solvents [2, 5, 9, 10, 12].

The oil recovery of the activated charcoal functionalized PC nanofibers toward petroleum oils was calculated expending following equation:

Fig. 7 **a** Practical oil–water separation using PC nanofibers, and **b** pictographic representation of oil–water separation mechanism

Fig. 8 Oil absorption analysis of PC nanofibers toward **a** petrol, **b** engine oil, **c** diesel, and **d** permeation flux analysis

$$\text{Oil Recovery} = \frac{W_2}{W_1} \times 100 \quad (2)$$

where W_1 = weight of the PC nanofibers (gms), W_2 = weight of the oil recovered by PC nanofibers (gms).

The transportation of the petroleum oils through the PC nanofiber membrane sheet was analyzed by measuring its permeation flux using following equation [10]:

$$Q = \frac{V}{A \cdot t} \quad (3)$$

where Q = permeation flux (L m⁻² h⁻¹), V = volume of the oil/solvent (L), A = active surface area of the membrane sheet (m²), t = time (h).

The permeation flux experiment was performed for diesel (Fig. 8d), petrol, and engine oil; however, the study was found to be feasible only for diesel oil, because the volatile nature of the petrol, and high density of the engine oil did not allow it to pass immediately through the membrane

sheet. In order to briefly check the recovery performance of the PC nanofibers toward organic solvent, the permeation flux investigation was also performed for n-Hexane solvent.

The PC nanofibers showed an average permeation flux of 10,834.5 L m⁻² h⁻¹ and 39,886.5 L m⁻² h⁻¹ toward diesel, and n-Hexane solvent, respectively. The high permeation flux demonstrated by n-Hexane solvent could be assigned to its lower surface tension (18.4 mN/m), which facilitated instant absorption, and immediate transportation through the PC nanofiber membrane sheet [10].

3.6 pH-based chemical stability analysis

The pH-based stability of the developed PC + AC microfibers was performed for determining its chemical resistance performance under corrosive (acidic and alkaline) environments. The pH-based study was performed at various pH levels (pH = 1 to 14) to establish its service robustness. The

Figure 9 pH-based performance of electrospun microfibers under corrosive environments

results shown in Fig. 9 reveal that the electrospun pure PC, PC + AC(0.5%), PC + AC(1%) and PC + AC(1.5%) have maintained average statistical contact angles of 121°, 131°, and 115° over the pH range of 1 to 14 under highly corrosive environments (acidic and alkaline). Thus, the results demonstrate that the developed electrospun microfibers maintain their hydrophobicity and service durability in a wide pH range of corrosive environments [45, 46].

4 Conclusion

Present study demonstrated utilization of polycarbonate (PC) nanofibers engineered with activated charcoal for practical oil recovery from oily wastewater. The developed PC nanofibers demonstrated simultaneous hydrophobicity (WCA of 133°), and oleophilicity (oil/solvent contact angle $\leq 0^\circ$). The developed functionalized PC nanofibers exhibited oil recovery toward petroleum oil products like petrol, diesel, and engine oil, which was found to be 308%, 872%, and 1738%, respectively, till 10 washing cycles. Further, the developed PC nanofibers revealed average permeation flux of $10,834.5 \text{ L m}^{-2} \text{ h}^{-1}$ and $39,886.5 \text{ L m}^{-2} \text{ h}^{-1}$ toward diesel, and n-Hexane solvent, respectively. TGA study of developed PC nanofibers revealed its thermal stability up to 350 °C. The pH-based performance (pH = 2–14) demonstrated that the developed microfibers maintain its hydrophobicity and service durability under harsh acidic and alkaline mediums (corrosive environments). The morphological analysis of the charcoal functionalized PC nanofibers showed heterogeneous rough patterned textures with porosity manifesting inside the fibers. The successive results demonstrate that

the activated charcoal functionalized PC nanofibers could be effectively utilized for practical recovery of oil/organic solvents from oily wastewater, and for the oil-spill cleanups which often occur in the oceans during transportation of the petroleum oils.

Acknowledgements The authors are thankful to Dr. C. P. Ramanarayanan, Vice-Chancellor of DIAT (DU), and Prof. (Dr.) Iain Martin, Vice-Chancellor of Deakin University, for the lab facilities, motivation, and support. First author is thankful to Deakin University for research fellowship, and DIAT (DU) for laboratory support and facilities. The authors are thankful to all group members at DIAT (DU) Pune, ICT Mumbai, and IFM Deakin University, Australia for the technical support during experimental work, and during preparation of the manuscript. The authors are thankful to the anonymous Reviewers and the Editor, for improving the quality of revised manuscript by their valuable suggestions and comments.

Compliance with ethical standards

Conflict of interest The authors do not have any competing financial interests. The authors do not have any financial or non-financial conflicts of interest.

References

1. Fingas M (2014) Handbook of oil spill science and technology. Wiley, New York
2. Gore PM, Dhanshetty M, Kandasubramanian B (2016) Bionic creation of nano-engineered janus fabric for selective oil/organic solvent absorption. RSC Adv. <https://doi.org/10.1039/C6RA24106A>
3. Amir-Heidari P, Arneborg L, Lindgren JF, Lindhe A, Rosén L, Raie M, Axell L, Hassellöv I-M (2019) A state-of-the-art model for spatial and stochastic oil spill risk assessment: a case study of oil spill from a shipwreck. Environ Int 126:309–320. <https://doi.org/10.1016/j.envint.2019.02.037>
4. Selvabalan M, Game M, Kumar CRS, Kandasubramanian B (2019) Toward sustainable performance of reservoir sedimentation in aquatic environment of Kateri lake, Tamil Nadu, India. Int J Environ Sci Technol. <https://doi.org/10.1007/s13762-019-02346-6>
5. Gore PM, Purushothaman A, Naebe M, Wang X, Kandasubramanian B (2019) Nanotechnology for oil-water separation. In: Prasad R, Karchiyappan T (eds) Advanced research in nanosciences for water technology, 1st edn. Springer, New York, pp 299–339
6. Bhalara PD, Punetha D, Balasubramanian K (2014) A review of potential remediation techniques for uranium(VI) ion retrieval from contaminated aqueous environment. J Environ Chem Eng 2:1621–1634. <https://doi.org/10.1016/j.jece.2014.06.007>
7. Gupta P, Lalalikar V, Kundu R, Balasubramanian K (2016) Recent advances in membrane based waste water treatment technology: a review. Energy Environ Focus 5:241–267. <https://doi.org/10.1166/eef.2016.1227>
8. Gore PM, Naebe M, Wang X, Kandasubramanian B (2019) Progress in silk materials for integrated water treatments: Fabrication, modification and applications. Chem Eng J 374:437–470. <https://doi.org/10.1016/j.cej.2019.05.163>
9. Arora R, Balasubramanian K (2014) Hierarchically porous PVDF/nano-SiC foam for distant oil-spill cleanups. RSC Adv 4:53761–53767. <https://doi.org/10.1039/C4RA09245G>

10. Gore PM, Kandasubramanian B (2018) Heterogeneous wettable cotton based superhydrophobic Janus biofabric engineered with PLA/functionalized-organoclay microfibers for efficient oil–water separation. *J Mater Chem A* 6:7457–7479. <https://doi.org/10.1039/C7TA11260B>
11. Mishra P, Balasubramanian K (2014) Nanostructured microporous polymer composite imprinted with superhydrophobic camphor soot, for emphatic oil–water separation. *RSC Adv* 4:53291–53296. <https://doi.org/10.1039/C4RA07410F>
12. Gupta P, Kandasubramanian B (2017) Directional fluid gating by janus membranes with heterogeneous wetting properties for selective oil–water separation. *ACS Appl Mater Interfaces* 9:19102–19113. <https://doi.org/10.1021/acsami.7b03313>
13. Simon S, Balasubramanian K (2018) Facile immobilization of camphor soot on electrospun hydrophobic membrane for oil–water separation. *Mater Focus* 7:295–303. <https://doi.org/10.1166/mat.2018.1511>
14. Simon SM, Chandran A, George G, Sajna MS, Valparambil P, Kumi-Barmiah E, Jose G, Biju PR, Joseph C, Unnikrishnan NV (2018) Development of thick superhydrophilic TiO₂–ZrO₂ transparent coatings realized through the inclusion of poly(methyl methacrylate) and Pluronic-F127. *ACS Omega* 3:14924–14932. <https://doi.org/10.1021/acsomega.8b01940>
15. Thakur K, Rajhans A, Kandasubramanian B (2019) Starch/PVA hydrogels for oil/water separation. *Environ Sci Pollut Res* 26:32013–32028. <https://doi.org/10.1007/s11356-019-06327-z>
16. Gore PM, Naebe M, Wang X, Kandasubramanian B (2019) Silk fibres exhibiting biodegradability & superhydrophobicity for recovery of petroleum oils from oily wastewater. *J Hazard Mater.* <https://doi.org/10.1016/j.jhazmat.2019.121823>
17. Yadav R, Naebe M, Wang X, Kandasubramanian B (2016) Temperature assisted in-situ small angle X-ray scattering analysis of Ph-POSS/PC polymer nanocomposite. *Sci Rep.* <https://doi.org/10.1038/srep29917>
18. Yadav R, Naebe M, Wang X, Kandasubramanian B (2017) Structural and thermal stability of polycarbonate decorated fumed silica nanocomposite via thermomechanical analysis and in-situ temperature assisted SAXS. *Sci Rep.* <https://doi.org/10.1038/s41598-017-08122-7>
19. Katiyar N, Kandasubramanian B (2015) Nano-heat-sink thin film composite of PC/three-dimensional networked nano-fumed silica with exquisite hydrophobicity. *RSC Adv* 5:4376–4384. <https://doi.org/10.1039/C4RA11597J>
20. Katiyar N, Kandasubramanian B (2014) Thermal modelling of hybrid composites of nano cenosphere and polycarbonate for a thermal protection system. *RSC Adv* 4:47529–47535. <https://doi.org/10.1039/C4RA07973F>
21. Yadav R, Naebe M, Wang X, Kandasubramanian B (2019) Thermo-mechanical characteristics of h-BN- and POSS-based bisphenol A polycarbonate nanocomposites. *Polym Plast Technol Mater* 58:1742–1756. <https://doi.org/10.1080/25740881.2018.1563143>
22. Banerjee BS, Balasubramanian K (2015) Nanotexturing of PC/n-HA nanocomposites by innovative and advanced spray system. *RSC Adv* 5:13653–13659. <https://doi.org/10.1039/C4RA15488F>
23. Biniak S, Szymański G, Siedlewski J, Świątkowski A (1997) The characterization of activated carbons with oxygen and nitrogen surface groups. *Carbon* 35:1799–1810. [https://doi.org/10.1016/S0008-6223\(97\)00096-1](https://doi.org/10.1016/S0008-6223(97)00096-1)
24. Mopoung S, Moonsri P, Palas W, Khumpai S (2015) Characterization and properties of activated carbon prepared from tamarind seeds by KOH activation for Fe(III) adsorption from aqueous solution. *Sci World J* 2015:1–9. <https://doi.org/10.1155/2015/415961>
25. Dąbrowski A, Podkościelny P, Hubicki Z, Barczak M (2005) Adsorption of phenolic compounds by activated carbon—a critical review. *Chemosphere* 58:1049–1070. <https://doi.org/10.1016/j.chemosphere.2004.09.067>
26. Shafeeyan MS, Daud WMAW, Houshmand A, Shamiri A (2010) A review on surface modification of activated carbon for carbon dioxide adsorption. *J Anal Appl Pyrol* 89:143–151. <https://doi.org/10.1016/j.jaap.2010.07.006>
27. Rajhans A, Gore PM, Siddique SK, Kandasubramanian B (2019) Ion-imprinted nanofibers of PVDF/1-butyl-3-methylimidazolium tetrafluoroborate for dynamic recovery of europium (III) ions from mimicked effluent. *J Environ Chem Eng* 7:103068. <https://doi.org/10.1016/j.jece.2019.103068>
28. Khurana L, Balasubramanian K (2016) Adsorption potency of imprinted Starch/PVA polymers confined ionic liquid with molecular simulation framework. *J Environ Chem Eng* 4:2147–2154. <https://doi.org/10.1016/j.jece.2016.03.032>
29. Gore PM, Khurana L, Siddique S, Panicker A, Kandasubramanian B (2018) Ion-imprinted electrospun nanofibers of chitosan/1-butyl-3-methylimidazolium tetrafluoroborate for the dynamic expulsion of thorium (IV) ions from mimicked effluents. *Environ Sci Pollut Res* 25:3320–3334. <https://doi.org/10.1007/s11356-017-0618-6>
30. Gore P, Khraisheh M, Kandasubramanian B (2018) Nanofibers of resorcinol–formaldehyde for effective adsorption of As (III) ions from mimicked effluents. *Environ Sci Pollut Res* 25:11729–11745. <https://doi.org/10.1007/s11356-018-1304-z>
31. Wang X, Pan Y, Yuan H, Su M, Shao C, Liu C, Guo Z, Shen C, Liu X (2020) Simple fabrication of superhydrophobic PLA with honeycomb-like structures for high-efficiency oil–water separation. *Chin Chem Lett* 31:365–368. <https://doi.org/10.1016/j.cclet.2019.07.044>
32. Wang X, Pan Y, Liu X, Liu H, Li N, Liu C, Schubert DW, Shen C (2019) Facile fabrication of superhydrophobic and eco-friendly poly(lactic acid) foam for oil–water separation via skin peeling. *ACS Appl Mater Interfaces* 11:14362–14367. <https://doi.org/10.1021/acsami.9b02285>
33. Zhang X, Wang X, Liu X, Lv C, Wang Y, Zheng G, Liu H, Liu C, Guo Z, Shen C (2018) Porous polyethylene bundles with enhanced hydrophobicity and pumping oil–recovery ability via skin-peeling. *ACS Sustain Chem Eng* 6:12580–12585. <https://doi.org/10.1021/acssuschemeng.8b03305>
34. Wang X, Pan Y, Shen C, Liu C, Liu X (2018) Facile thermally impacted water-induced phase separation approach for the fabrication of skin-free thermoplastic polyurethane foam and its recyclable counterpart for oil–water separation. *Macromol Rapid Commun* 39:1800635. <https://doi.org/10.1002/marc.201800635>
35. Malik A, Magisetty R, Kumar V, Shukla A, Kandasubramanian B (2020) Dielectric and conductivity investigation of polycarbonate-copper phthalocyanine electrospun nonwoven fibres for electrical and electronic application. *Polym Plast Technol Mater* 59:154–168. <https://doi.org/10.1080/25740881.2019.1625390>
36. Kristianto H, Arie AA, Susanti RF, Halim M, Lee JK (2016) The effect of activated carbon support surface modification on characteristics of carbon nanospheres prepared by deposition precipitation of Fe-catalyst. *IOP Conf Ser Mater Sci Eng* 162:012034. <https://doi.org/10.1088/1757-899X/162/1/012034>
37. Pradhan BK, Sandle NK (1999) Effect of different oxidizing agent treatments on the surface properties of activated carbons. *Carbon* 37:1323–1332. [https://doi.org/10.1016/S0008-6223\(98\)00328-5](https://doi.org/10.1016/S0008-6223(98)00328-5)
38. Sohrabi M, Ebrahimezhad F (2018) Concentration and duration dependence of a new prototype polycarbonate/activated-carbon fabric individual and environmental radon monitor. *J Inst* 13:P11012–P11012. <https://doi.org/10.1088/1748-0221/13/11/P11012>
39. Yördem OS, Papila M, Menceloğlu YZ (2008) Effects of electrospinning parameters on polyacrylonitrile nanofiber diameter:

- An investigation by response surface methodology. *Mater Des* 29:34–44. <https://doi.org/10.1016/j.matdes.2006.12.013>
40. Shawon J, Sung C (2004) Electrospinning of polycarbonate nanofibers with solvent mixtures THF and DMF. *J Mater Sci* 39:4605–4613. <https://doi.org/10.1023/B:JMSC.0000034155.93428.ea>
41. Liao C-C, Wang C-C, Shih K-C, Chen C-Y (2011) Electrospinning fabrication of partially crystalline bisphenol A polycarbonate nanofibers: Effects on conformation, crystallinity, and mechanical properties. *Eur Polym J* 47:911–924. <https://doi.org/10.1016/j.eurpolymj.2011.01.006>
42. Sahoo BN, Kandasubramanian B (2014) Recent progress in fabrication and characterisation of hierarchical biomimetic superhydrophobic structures. *RSC Adv* 4:22053. <https://doi.org/10.1039/c4ra00506f>
43. Sahoo BN, Balasubramanian K, Sucheendran M (2015) Thermally triggered transition of superhydrophobic characteristics of micro- and nanotextured multiscale rough surfaces. *J Phys Chem C*. <https://doi.org/10.1021/acs.jpcc.5b02917>
44. Cassie ABD, Baxter S (1944) Wettability of porous surfaces. *Trans Faraday Soc* 40:546. <https://doi.org/10.1039/tf9444000546>
45. Li Z, Wang B, Qin X, Wang Y, Liu C, Shao Q, Wang N, Zhang J, Wang Z, Shen C, Guo Z (2018) Superhydrophobic/superoleophilic polycarbonate/carbon nanotubes porous monolith for selective oil adsorption from water. *ACS Sustain Chem Eng* 6:13747–13755. <https://doi.org/10.1021/acssuschemeng.8b01637>
46. Wang Y, Wang B, Wang J, Ren Y, Xuan C, Liu C, Shen C (2018) Superhydrophobic and superoleophilic porous reduced graphene oxide/polycarbonate monoliths for high-efficiency oil/water separation. *J Hazard Mater* 344:849–856. <https://doi.org/10.1016/j.jhazmat.2017.11.040>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.