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Free-standing polypropylene porous thin films using energy efficient coating technique

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Abstract

Amongst various techniques to prepare thin films, spin coating takes less time to make thin films, is less energy-intensive, is easier to use, and provides reproducible results quickly. It is observed that such a user-friendly and quick process has hardly been explored to prepare polyolefin-based free-standing porous or nonporous thin films. Herein, we report a free-standing thin film of at least 5 μm made from polypropylene using the spin coating technique. Our methodology utilizes lower embodied energy and generates lower carbon footprints than the conventional melt extrusion technique. The thin films prepared from the spin coating technique was investigated with DSC, XRD, SEM, XPS, etc., which suggested the heated thin films showed more crystallinity and strength compared to unheated thin films. The SEM images revealed a fibrous structure with a pore size range from 1–10 μm . The tensile strength and modulus of the as-prepared thin films were found to be 7 MPa and 583 MPa, respectively. Also, enthalpy change of 84 J/g and relative crystallinity of 41% were obtained. The as-prepared thin film can be used in various applications with minor modifications, such as in coating layers on the solid surface, porous sorbent, and filtration membrane.

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Keywords: Spin coating; Thin film; Polymeric film; Polymer coating; Free-standing film; Embodied energy; Carbon footprint

1. Introduction

A free-standing thin film is defined as a film that does not adhere to a support such as a substrate or a wall surface to maintain a film structure. It should be used independently without the support of any substrate or without forming a complex with the support. To prepare a homogeneous free-standing thin film with internal porous structure, spin coating and melt extrusion are the preferred and sought-after techniques.

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Nomenclature

PP	Polypropylene
Film 1	PP thin film at low initial speed (400 rpm) before heating
Film 2	PP thin film at high initial speed (1000 rpm) before heating
Film 3	PP thin film at high initial speed (1000 rpm) after heating at 160 °C

Thin films are widely used for various applications, including integrated circuits, micro-electromechanical systems [1,2], air filters [3,4], desalination [5,6], sensors [7–9], and filtration [10,11]. Amongst various techniques to prepare thin films, spin coating takes less time to make thin films, is less energy-intensive, is easier to use, and provides reproducible results quickly. It deals mainly with soluble polymers at ambient temperature. The thickness of the film ranges from a few nanometres to several micrometres. The possible reasons could be as follows: In the thin film coating technique, polymers used are dissolved in a good solvent at ambient temperature; thus, the solution remains in a soluble state, which is a requirement of coating. These polymers can be coated on the material of interest, or they can be coated on the solid substrate. After coating, they can be peeled off using an aqueous or non-aqueous soluble sacrificial layer or without the use of a sacrificial layer. On the other hand, polyolefins, such as polypropylene, a semi-crystalline polymer, cannot be dissolved in any solvent at ambient temperature. Secondly, it is only used for coating a layer on the substrate. The coated layer is not intended to be removed from the substrate. Thirdly, spin-coated polypropylene films do not have sufficient strength to be considered a free-standing thin film, i.e., these films could not maintain their integrity without a supporting layer or a substrate.

Melt extrusion involves polyolefins such as polyethylene and polypropylene. These polymers are crystalline (50 to 70%) in nature and insoluble in any solvent at ambient temperature. Melt extrusion comprises mixing the polymer with a pore-forming agent to prepare a dispersion and extracting the pore-forming agent before or after stretching to form a porous thin film. It is sometimes coupled with thermally induced phase separation to create pores. Whether porous thin films are made using dispersion or phase separation techniques, stretching remains the common step in the formation of porous thin films [12–16].

Spin coating, on the other hand, deals with the polymers that are soluble at ambient temperature so that the polymer solution can be easily coated on the substrate. Spin-coated films are uniform, and their thickness can be achieved in the range of a few nanometres to several micrometres. The technique is easier to use with reproducible results and much quicker than the melt extrusion technique [17–19]. It is observed that such a user-friendly and quick process has hardly been explored to prepare polyolefins-based freestanding porous thin films. The possible reasons could be as follows: In the thin film coating technique, polymers used are dissolved in a good solvent at ambient temperature; thus, the solution remains in a soluble state, which is a requirement of coating. These polymers can be coated on the material of interest, or they can be coated on the solid substrate. After coating, they can be peeled off using an aqueous or non-aqueous soluble sacrificial layer or without the use of a sacrificial layer. On the contrary, polyolefins cannot be dissolved in any solvent at ambient temperature. Secondly, they are only used for coating a layer on the substrate. The coated layer is not intended to be removed from the substrate; thus, free-standing thin film cannot be made. Thirdly, spin-coated polypropylene films do not have sufficient strength to be considered a free-standing thin film, i.e., these films could not maintain their integrity without a supporting layer or a substrate.

Hence, it is an objective of the present study to provide a free-standing thin film and porous thin film using polypropylene through the coating technique. The as-prepared thin film can be used in various applications with minor modifications, such as in coating layers on the solid surface, as a porous sorbent, as a filtration membrane, etc.

2. Experimental section

2.1. Materials and equipment

Reagents like *o*-xylene and PP were purchased from Sigma Aldrich and were used without further purification. Plain glass plates were cut to a size of 5 cm × 5 cm. The chuck and spin coater were from Ossila. PerkinElmer

DSC 8500 was used for DSC. Friction/peel tester Lloyd instruments Ltd Bognor Regis, UK was used for tensile strength and modulus calculations. XRD was carried out on Malvern Panalytical Empyrean XRD diffractometer. SEM images were captured with FEI Quanta650FEG. XPS was measured using Thermo Fischer Escalab 250XI platform. A monochromated X-ray source (Al K α : 1486.6 eV) was used.

2.2. Methodology

Polypropylene (PP) was dissolved in *o*-xylene at 130 °C, and the resultant solution was poured on a plain and clean glass surface at room temperature connected to a spin coater chuck. The spin coater was turned on and programmed to spin in two stages to give a thin film. The first stage includes a rotational speed of 400 rpm or 1000 rpm for 60 s, followed by the second stage with a speed of 3000 rpm for 60 s. The excess polymer and solvent were collected through a drain. After the spin coating, the thin films were heated in an oven at 160 °C for 20 min. The thin films were peeled off from the glass substrate using a tweezer. The PP thin film preparation setup is shown in Fig. 1.

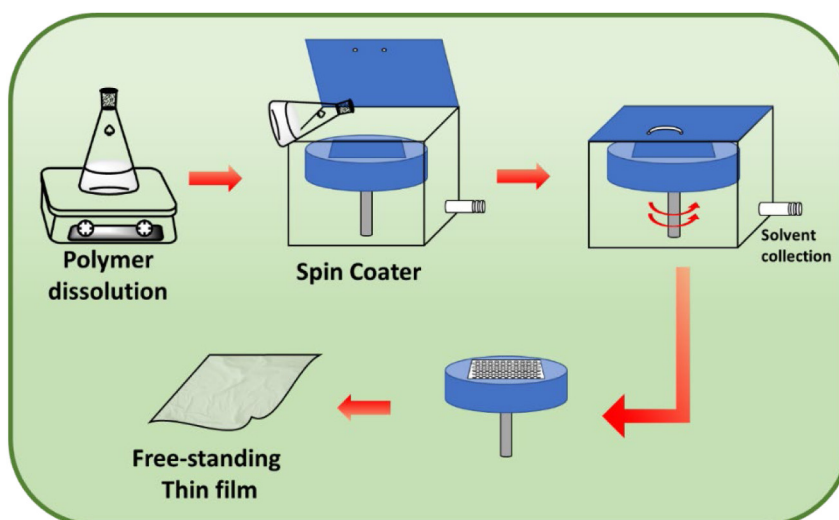


Fig. 1. Preparation of PP thin film using spin coating technique.

Preparation of thin film: 3 g of PP was taken in a round-bottomed flask. 50 ml of *p*-xylene was added to the round-bottomed flask and allowed to stir. The reaction mixture was heated to 130 °C till a clear solution was achieved. Usually, the polymer is dissolved in 15–30 min. The round-bottomed flask was connected to a reflux condenser to avoid solvent loss. After attaining a uniform clear solution, it was poured on a clean glass surface and placed on the customized spin coater chuck. The lid of the spin coater was closed to avoid solvent evaporation and exposure. After the completion of spin coating, a thin film was formed with no solvent in it. The glass substrate with a thin film was detached from the chuck to achieve thin films. It is to note that the hotplate magnetic stirrer and spin coater are placed side-by-side to avoid solvent exposure to the environment, and the whole setup was kept inside the fume hood. The spin coater drain was connected to a receiver to collect solvent and excess polymer.

Film 1 is referred to as thin films that were not heated after the spin coating process and were initially spun at low speed (400 rpm). **Film 2** is referred to as thin films that were not heated after the spin coating process and were initially spun at high speed (1000 rpm). **Film 3** is referred to as thin films that were heated after the spin coating process and were initially spun at high speed (1000 rpm). This heating was done in a hot air oven for 20 min keeping the temperature at 160 °C. In all the three cases the second step comprises spinning at 3000 rpm for 120 s.

3. Results and discussions

3.1. Visible light images of PP thin films

We have successfully prepared uniform polypropylene free-standing porous thin films with a thickness ranging from 2 μm to 6 μm . Although a few research articles reported the preparation of thin film using polyolefin with spin coating technique, the films were not isolated after coating. Thus, they could not be considered as a free-standing thin films as these films could not maintain their integrity without a supporting layer [17,18,20].

We achieved this feat through the following experimentation. The PP was dissolved in an organic solvent by refluxing for 15–30 min and then poured onto the solid substrate, followed by spin-coating. It was observed that after spin coating, the as-prepared thin film comprised loosely connected chains. It may be due to the space created by the removal of the organic solvent, thus generating more voids resulting in a weak structure. Thus, we heated the thin film to 160 $^{\circ}\text{C}$. We observed various changes in heated and unheated thin films, which are discussed here.

After spin coating, we tried to isolate **Film 1** from the substrate without heating. We observed the thin film was difficult to separate by peeling off with a tweezer or submerging the substrate in acetone and ethanol. The thin film was brittle and was chipped easily because of its low strength, which is attributed to weak intermolecular interactions between the polymer chains, and its high amorphous nature. Further, we prepared a thin **Film 2** at a high initial speed of 1000 rpm, which aligned and stretched the polymer chains resulting in translucent thin films with little strength. To overcome the weak intermolecular forces and reduce the amorphous character, we heated the polymer thin film for 20 min at 160 $^{\circ}\text{C}$ in a hot air oven, resulting in **Film 3**. To our observations, the thin film (**Film 1**) before heating at low speed was opaque and fragile, and the thickness of the thin film was more (see Fig. 2a). Before heating at high speed, the thin film (**Film 2**) was translucent, and the thickness of the thin film was slightly less compared to **Film 1** (see Fig. 2b). Upon heating, the polymer chains become soft and reduce the gap between the polymer chains, resulting in a thin film (**Film 3**) with sufficient strength, and it becomes transparent, as shown in Fig. 2c.

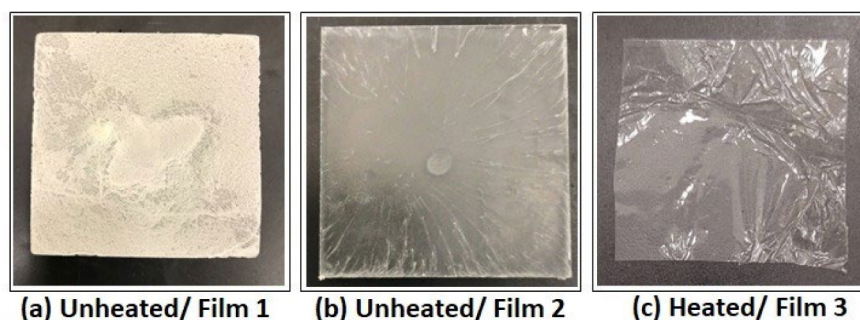


Fig. 2. Polymer thin films; (a) unheated thin film at low initial speed, (b) unheated thin film at high initial speed, (c) heated thin film at high initial speed.

3.2. DSC

Further, differential scanning calorimetry was carried out for **Films 2 and 3**. DSC characterization helps in measuring the heat flow concerning temperature. From the enthalpy results, the amount of crystallinity of polymers was calculated. We investigated the thin **Films 2 and 3** for enthalpy measurements. We observed that thin **Film 2** showed an enthalpy of 72.0 J/g. On the other hand, thin **Film 3** showed an enthalpy of 83.9 J/g combined. The unheated film showed less enthalpy than heated films, which was reflected in the crystallinity calculations reported in Table 1. The standard enthalpy change for pure polypropylene crystal was 205 J/g, as reported in the literature [21]. DSC results confirmed the increase of crystallinity by 6% after heating, as shown in Fig. 3 and Table 1. The increase in crystallinity advocates that the polymer chains are packed condensed.

Moreover, the melting temperature of PP in **Film 2** was found to be 164.3 $^{\circ}\text{C}$, whereas the melting temperature of PP in **Film 3** was found to be 165.5 $^{\circ}\text{C}$. This low temperature of the unheated sample represents the polymer chains are relatively more amorphous and distributed less evenly with more space between the polymer chains, thus,

Table 1. Percentage of crystallization calculated using enthalpy.

S.No.	Polymer	Enthalpy (J/g)	Crystallinity (%)
1.	PP ^a	205	100
2.	Film 2 (PP unheated)	72.0	35.1
3.	Film 3 (PP heated)	83.9	40.9

^a100% crystallized theoretical values collected from the literature.

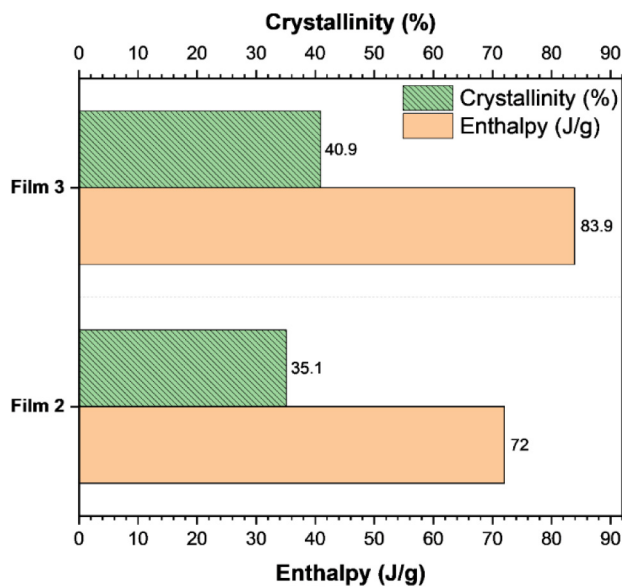


Fig. 3. Enthalpy and crystallinity percentages of unheated **Film 2** and heated **Film 3**.

they absorb less heat to melt. On the other hand, the escalation in melting temperature of the thin **Film 3** attributes the polymer chains in the thin film to be relatively more crystalline, compact, and dense, thus absorbing more heat or energy to melt. Fig. 4 shows the differential scanning calorimetry for the PP thin films.

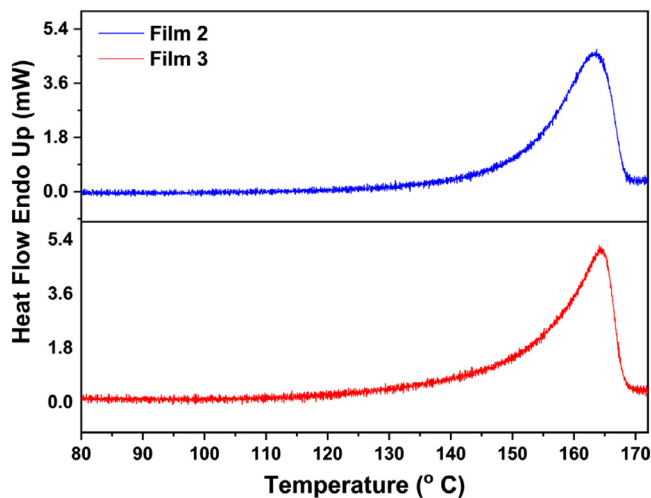


Fig. 4. DSC spectra of **Films 2** and **3**.

3.3. Tensile strength and modulus

Tensile strength and modulus were calculated for polymer thin **Films 2** and **3** and were compared with A4 paper. The tensile strength for nonheated unpeeled films were not determined as they could not be peeled off. However, the 5 μm thin polymer film showed relatively excellent results compared to A4 paper of 94 μm thickness. Thus, the heated thin film showed high modulus and strength. The results are presented in [Table 2](#).

Table 2. Tensile strength and modulus of polymer thin film.

Sample name	Tensile strength (MPa)	Young's modulus (MPa)	Elongation (%)
PP (Film 2)	Not determined	Not determined	Not determined
PP (Film 3)	7 ± 2	583 ± 23	8 ± 1
A4 Paper	38 ± 3	4136 ± 36	9 ± 1

3.4. XRD

The XRD was performed to calculate degree of crystallinity as shown in [Fig. 5](#). When an amorphous material is subjected to X-ray diffraction, the peaks are obtained with less intensity and broader peaks. A sharp peak determines more crystallinity. When the thin film is heated to a higher temperature, the polymer chains become soft and realigned; thus, enhancing the crystallinity. We observed sharp peaks in the heated thin **Film 3** compared to the unheated thin **Film 2**. The increase in peak intensity is attributed to an increase in crystallinity due to the enhancement in the dispersion or Vander Waal forces.

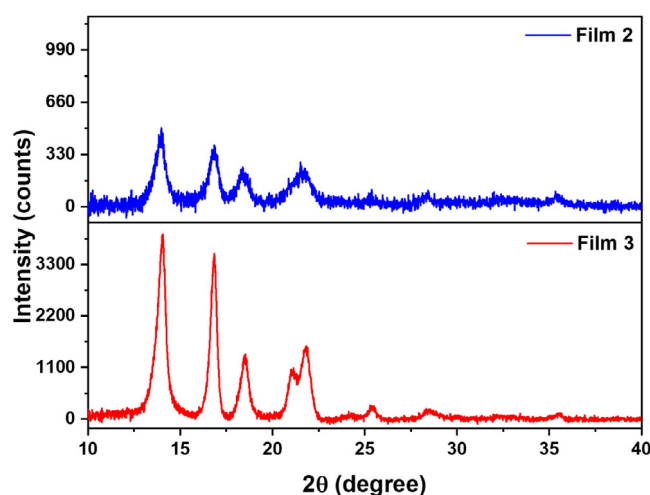


Fig. 5. XRD spectra of **Film 2** (unheated) and **Film 3** (heated).

In short, the two adjacent polymer chains were loosely connected with weak intermolecular interactions before the heating and thus could not be peeled off, and when the glass substrate was heated to 160 $^{\circ}\text{C}$, the polymer chains realigned closely, and the crystallinity of the polymer was enhanced to give sufficient strength to the film.

3.5. SEM

The scanning electron microscopy images of the PP films before (**Film 2**) and after heat (**Film 3**) are shown in [Fig. 6](#). It reveals that the fibrous polymer strands that are not heated ([Fig. 6a](#)) possess high porosity. However, they are extremely delicate to handle and can easily break when separated from the substrate. When heated optimally to 160 $^{\circ}\text{C}$ for 10 min ([Fig. 6b](#)), the polymer chains become soft, reducing the space between the polymer fibres. Further, we heated the PP thin film to 165 $^{\circ}\text{C}$ for 5 min ([Fig. 6c](#)) to its melting point temperature, where we observed

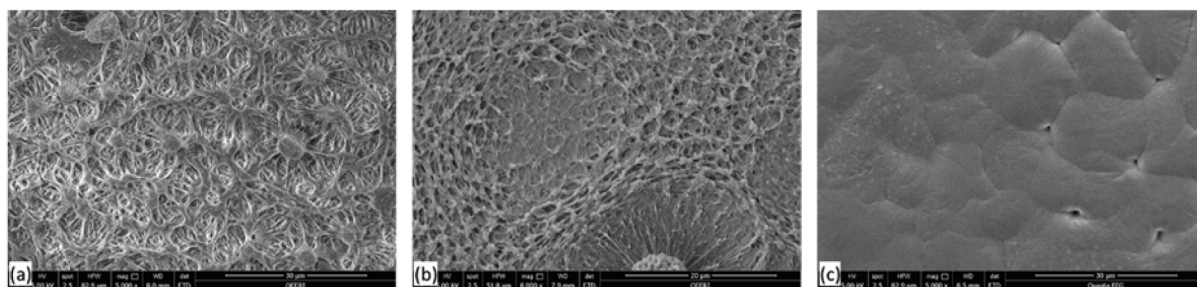


Fig. 6. SEM images of polymer thin films: (a) **Film 2**, (b) **Film 3**, and (c) after overheating.

that the polymer fibres melted to a maximum extent, closing the majority of the pore, but the tensile strength for this film is the highest compared to an unheated thin **Film 2** and the heated thin **Film 3** at 160 °C. Thus, for optimum pores with optimum strength, the heating should be carried out in a controlled manner. These figures also show that fibrous polymer strands were realigned, increasing the crystallinity by enhancing dispersion forces and intermolecular forces, resulting in a free-standing porous thin film. The microporous structure, as shown in **Film 3**, has a pore size range from 1–10 μm .

3.6. XPS

The XPS was performed to investigate the presence of the solvent molecules in the thin films and the chemical composition of the polymeric surfaces. Xylene, a non-polar aromatic solvent, was used to dissolve PP to prepare thin films. The observation of a peak at 292 eV binding peak represents the presence of xylene. Usually, the residual solvent will show $\pi - \pi^*$ interactions of C=C of the aromatic peak and is strongly observed at 292 eV [20], but in our case, we did not find any peak at 292 eV either in **Film 2** or **Film 3** as shown in Fig. 7. It indicates that the xylene was completely removed from the thin films after spin coating. We also observed a small peak (less than two atomic wt.%) of oxygen at ~ 532 eV in **Film 2**, which may be attributed to the partial oxidation of the polymer during the heating process.

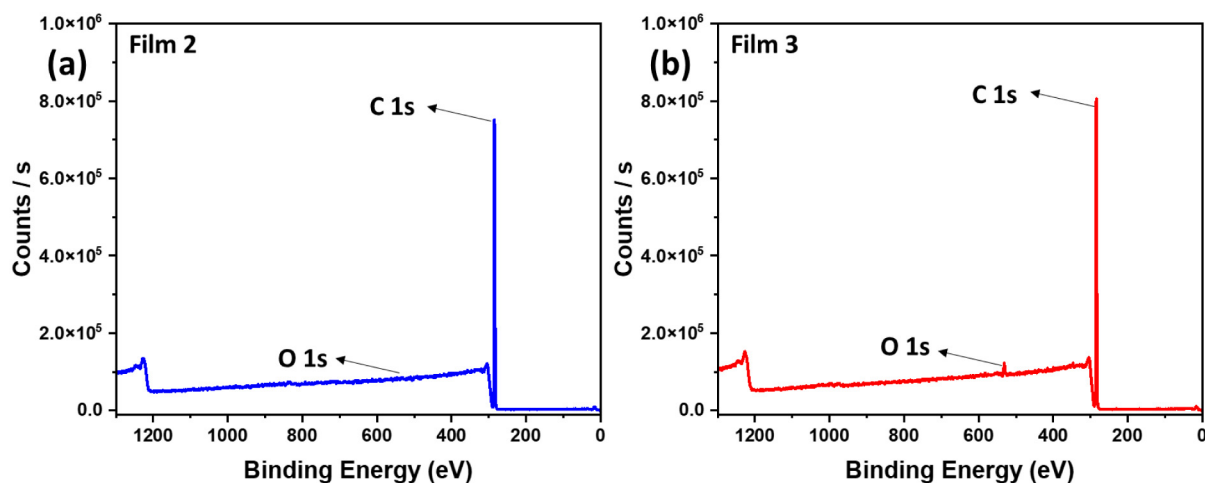


Fig. 7. XPS survey spectra of (a) **Film 2** (b) **Film 3**.

4. Conclusion

We have successfully demonstrated the preparation of free-standing thin films with sufficient strength. The as-prepared thin films were subjected to heating to obtain sufficient strength. The unheated and heated thin films

were investigated for XRD, DSC, SEM, XPS, which proved that the heating of the thin film enhanced strength. SEM images revealed a fibrous structure with a pore size range from 1–10 μm . The relative % crystallinity, tensile strength and modulus of the as-prepared thin films were found to be 41%, 7 MPa and 583 MPa, respectively. The as-prepared thin film can be used in various applications with minor modifications, such as in coating layers on the solid surface, porous sorbent, and filtration membrane.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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