Chapter 6 Electrospun Filters for Organic Pollutants Removal



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Abstract Increasing demand for access to clean and safe water around the globe emphasizes the development of new technologies for removing environmental pollutants. Especially, organic pollutants including dyes, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), pesticides, herbicides, and antibiotics prominently affect environmental health due to their hazardous nature. In the past several decades, advancements in electrospun fibrous membranes have resulted as an efficient filtering platform for removal of various pollutants in water, air, and soil. Electrospun nanofibers are efficient filters complementing their unique feature of accommodating a variety of functional molecules. The choice of material and the effect of experimental condition including pH, contact time, and adsorbent dosage on pollutant removal efficiency have been extensively reviewed previously. Our chapter focuses on recent progress in the developments of the electrospun functional nanofibrous composite membrane for various organic pollutants removal.

6.1 Introduction

The rapid global industrialization and modernization simultaneously have a negative impact on the society in terms of water pollution that continuously threatens the environmental health [1, 2]. Concerns were raised in the recent years for organic pollutants such as dyes, hydrocarbons, pesticides, fertilizers, phenols, plasticizers, biphenyls, detergents, oils, greases, and pharmaceuticals due to their carcinogenic nature and severe toxic impact on aquatic ecosystems [1, 3, 4]. The access to clean water is going to be a serious global challenge in the near future. Therefore, efficient removal of pollutants from water bodies is highly required. Up to date, several

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techniques (biologic, chemical, and physicochemical treatment) have been applied to remove the organic pollutants from wastewater in which the adsorption process is found to be an efficient method because of high adsorption capacity, simple design, ease operation, and scalability [5, 6].

So far, a variety of nanostructured materials were successfully established as adsorbents to remove the various pollutants in the environment [7–9]. In this regard, electrospinning is considered to be an efficient and convenient technique for producing nanofibrous membranes for filter application [10, 11]. These fibers generally possess extraordinary features including high surface area-to-volume ratios and tunable porosities, which make them excellent candidates for sensors, catalysts, and filtration fields [12–16]. Moreover, the fibrous structure promises the possible functionalization and exceptional accommodating features, resulting in superior composite materials that hold a great promise to remove the pollutants [17–19]. At the current scenario, it is sensible to describe the recent progress on the preparation of advanced functional fibrous materials for removal of organic pollutants. In this chapter, we will discuss the various routes to functionalize the electrospun fibrous membrane and their applications for removing potential organic pollutants such as dyes, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), etc., in the environment.

6.2 Electrospun Nanofibrous Filters for Organic Pollutants Removal

6.2.1 Removal of Dye Pollutants

Certainly, dyes are the best-known foremost pollutants of the environment due to their hazardous nature. So far, a variety of techniques were adopted for removal of dyes from water such as adsorption, coagulation, advanced oxidation, and membrane separation [20, 21]. Generally, the tiniest amount of dyes in water can be easily visualized and can be categorized in several ways as represented in Fig. 6.1, which depends on the structure, chromophores, and bonding nature [22]. The dye pollutant in water causes mutagenesis, carcinogenesis, chromosomal fractures, and respiratory toxicity even at lower concentrations.

Adsorption has been widely accepted as a promising technique due to its simplicity, efficiency, and environmental friendliness for removal of various pollutants in water [23–28]. The schematic depiction of removal of dyes using adsorbents is depicted in Fig. 6.2. The term adsorption refers to the accumulation of substances at the interface between two phases. So far, remarkable success has been achieved to design efficient adsorbents including carbon, silica gel, zeolites, clay, and alumina; also further efforts have been initiated to enhance their adaptability in advanced water treatment technologies. In general, it is difficult to recycle the nanoparticles

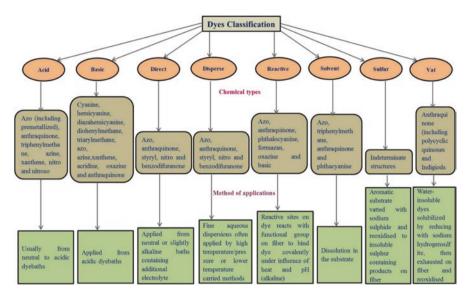


Fig. 6.1 Classification, applications, and method of application of dyes. Reproduced with permission from [22] © 2017 Elsevier

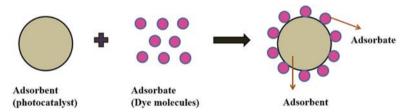


Fig. 6.2 Dye adsorption process using adsorbents. Reproduced with permission from [22] © 2017 Elsevier

after use which may lead to loss of activity and brings about the additional pollutant to the environment.

Therefore, development of new adsorbents combining the advantages of high adsorption efficiency, large surface area, and easy retrieval properties is considered to be of momentous importance in practical applications. As an example, γ -AlOOH (Boehmite) is an aluminum oxyhydroxide possessing plenty of OH groups on the surface resulting in an enhanced interaction with foreign molecules which makes it a suitable candidate for water decontamination. Miao et al. demonstrated the preparation of hierarchical $\text{SiO}_2@\gamma$ -AlOOH (Boehmite) core/sheath fibers through the hydrothermal growth of Boehmite on the surface of electrospun SiO_2 fibers [29]. The schematic representation of the preparation procedure is given in Fig. 6.3.

At first, SiO₂ fibers were produced through the combination of sol-gel and electrospinning approach, followed by the removal of PVA (poly(vinyl alcohol)) via calcination. The high flexibility and thermal stability of electrospun SiO₂ fibers

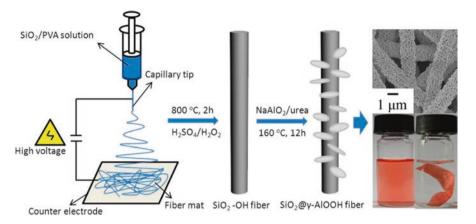


Fig. 6.3 Schematic illustration of the preparation of $SiO_2@\gamma$ -AlOOH (Boehmite) core/sheath fibers and their dye removal performance. Reproduced with permission from [29] © 2012 American Chemical Society

facilitate the construction of hierarchical structure. The obtained open structure offers a much higher contact area between the adsorbent and pollutant in the water, which is considered to be a vital factor in determining the adsorption efficiency. The digital photograph of the SiO₂@γ-AlOOH (Boehmite) core/sheath fibrous membrane before and after adsorption of Congo red solution for over 90 min is depicted in Fig. 6.3.

The porous structured materials gained significant attention in adsorption of pollutants because of their enhanced surface area and pore volumes, resulting in high adsorption capacities [30, 31]. Usually, the adsorption process occurs in three steps: (1) adsorbate species are adsorbed onto the adsorbent surface through several forces such as hydrogen bonding, electrostatic interactions, van der Waals forces, hydrophobic interactions, etc.; (2) pollutants diffuse on the outer surface of the adsorbent and further enter into pores, if present; (3) finally, the pollutants are adsorbed onto the active site of the inner and outer surfaces of the adsorbent.

Figure 6.4a represents the adsorption isotherms of Methyl orange (MO) and Safranin O (SO) onto SiO_2 nanofibers. Figure 6.4b shows the schematic representation of dye adsorption onto SiO_2 nanofibers. The authors reported that mass of dyes adsorbed on the surface of nanofibers determines the adsorption kinetics. This might be due to sharing/exchange of electrons between dye and SiO_2 nanofibers molecules [32].

The results of Langmuir and Freundlich models suggested that the dyes are adsorbed on the SiO_2 nanofibers surface through the weak van der Waals forces. The calculated amounts of dyes were 714 and 958 (mg/g) for MO and SO, respectively. The negatively charged surface of the SiO_2 nanofibers favors the cation exchange of the dye which might be resulted in the high update of cationic dye. The lower adsorption of MO might be resulted from the presence of double bond character of the bridge in the azo group of MO that causes electron delocalization even for the acidic structures which establishes a potential barrier for adsorption. Im et al. dem-

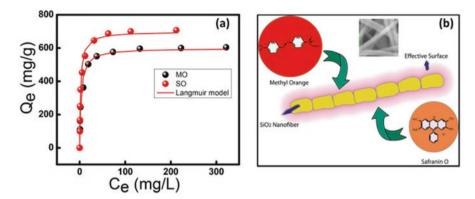


Fig. 6.4 (a) Adsorption isotherms for adsorption of MO and SO dyes onto SiO_2 nanofibers, (b) schematic representation of dyes adsorption onto SiO_2 nanofibers. Reproduced with permission from [32] © 2016 Elsevier

onstrated the graphene-embedded hydrogel nanofibers for detection and removal of aqueous-phase dyes [33].

To date, the outstanding characteristics of graphene have been extensively explored in diverse application. Even though, the agglomeration of graphene layers via $\pi-\pi$ stacking and van der Waals interactions in the aqueous phase limits their enhanced performance. Considering all circumstances, authors introduced graphene into hydrogel fibers to take their benefits of high surface area, porosity, and hydrophilicity. The anchored, water-soluble polymer-based hydrogel architecture on graphene expedites an interaction between the graphene and aqueous-phase dyes. The prepared hydrogel nanofiber structure shows the appropriate mechanical properties enabling aqueous-phase applications, in which embedded graphene can interact more effectively with hydrophilic components. The adsorption capacities were as high as 0.43 and 0.33 mmol g $^{-1}$ s $^{-1}$ for methylene blue (MB) and crystal violet (CV), respectively, even in a 1.5 mL s $^{-1}$ flow system. The adsorption capacities of graphene-embedded hydrogel nanofibers (GHNFs) for four dyes, namely, methylene blue (MB), crystal violet (CV), methyl orange (MO), and disperse red 1 (DR), were examined as a function of time.

In this regard, a piece of GHNF membrane was immersed in an aqueous dye solution and their corresponding ultraviolet (UV)–vis absorption spectra were taken at time intervals of 5 min (Fig. 6.5a–d). The results showed that GHNFs expressed diverse adsorption performances toward the dyes. The substantial decreases in the absorption peak intensities of MB and CV have been noted whereas no remarkable changes were observed for MO and DR. The changes in the dye concentration and adsorbed dye amount are plotted against time (Fig. 6.5e and f, respectively). The dye adsorption performance of GHNFs has been performed, and results showed that the removal efficiency of MB (93%) is slightly higher than that of CV (86%). Remarkably, GHNFs have no obvious effect toward MO (0%) and DR (4%). It is interesting to note that GHNFs exhibit selective adsorption of MB and CV.

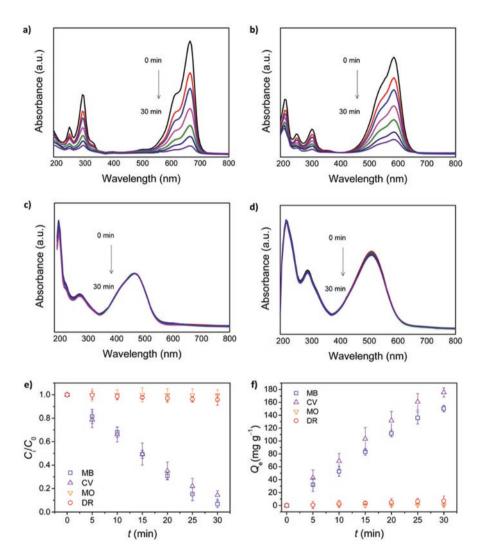
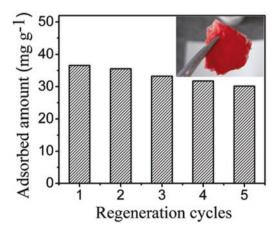


Fig. 6.5 Adsorption of dyes by graphene-embedded hydrogel nanofibers (GHNFs) in aqueous solution (at pH 6.0 and 25 °C in a closed cell). (\mathbf{a} – \mathbf{d}) Time-dependent changes (interval, 5 min) in UV-vis absorption spectra of dye solutions upon addition of GHNFs (0.1 g of GHNFs/50 mL of 1 mM dye solution): (\mathbf{a}) methylene blue (MB), (\mathbf{b}) crystal violet (CV), (\mathbf{c}) methyl orange (MO), and (\mathbf{d}) disperse red 1 (DR) (dissolved in 1/1 (v/v) ethylene glycol/water solution). Plots of the adsorption capacity versus time calculated from (\mathbf{a} – \mathbf{d}): (\mathbf{e}) relative dye concentration change, in which C_0 and C_i denote the initial concentration and the instantaneous concentration at time t, respectively, and (\mathbf{f}) the amount of dye adsorbed at time t, which was normalized by dividing it by the weight of GHNFs. Reproduced with permission from [33] © 2017 American Chemical Society

Alumina has been widely accepted as an excellent candidate for water purification. Even though the adsorption capacities are found to be relatively very high, their scalability is limited in their scattered forms like powder. Maintaining the porous structure of the adsorbent on the solid substrate brings a new way to enhance the adsorption performance. Wang et al. fabricated the mesoporous alumina-based adsorbent called silica/mesoporous alumina core-shell fibrous membranes (denoted as S/M fibrous membrane) in which silica is the core phase and mesoporous alumina is the shell phase [34]. Authors pointed that there are no reports for preparation of electrospun alumina fibers and their being used as adsorbents. Generally, the fragile nature of the alumina fibers cannot retain the membrane form even though they have a large surface area and high chemical and thermal stability. In this work, the authors paid more attention to the porous structure of the fibers and their integrity of the membrane form as well as scalability issues. Overall, the membrane demonstrates high mechanical strength (5.4 MPa) and high specific surface area, which might be attributed to the presence of dense silica core fibers and mesoporous alumina shell. The obtained silica/mesoporous alumina core-shell fibrous membranes exhibit good adsorption performance toward Congo red with an adsorption of 115 mg g⁻¹ within 48 h. The integrality of the fibrous structure and their flexible nature have been well maintained after adsorption of dyes.

The reusable property of the core–shell membrane has been investigated, and results are shown in Fig. 6.6. The observed results showed that the initial adsorption capacity was 36.56 mg g⁻¹, which decreased slightly with increasing cycle times, and the adsorption capacity remained as high as 30.14 mg g⁻¹. The photograph shows the adsorption of Congo red for the fifth cycle, shown as an inset in Fig. 6.6. The stability of alumina shell has been determined by immersing the membrane in aqueous solution for several days, and then the elution of the Al content has been calculated as 0.0433 ppm. Overall, the results showed that the prepared membrane possesses high mechanical strength and good reusable performance in adsorption toward Congo red, as well as the high stability in aqueous solution of the membrane favors its application in the treatment of water.

Fig. 6.6 Relationship between the adsorption capacity and cycle times of the S/M core—shell fibrous membranes calcined at 700 °C. The inset is the optical image of the membranes after the fifth cycle of adsorption toward Congo red. Reproduced with permission from [34] © 2014 Royal Society of Chemistry



It has been already reported that the incorporation of nanoparticles into the polymer matrix significantly enhances the performance of the individual system as well as nanocomposites in diverse field of applications. Electrospinning approach has been accepted as a convenient technique for fabrication of polymer composites in which various nanostructured materials are successfully incorporated/decorated so far. In depth, the approach for making composites via electrospinning also affects the adsorption capabilities. Patel and Hota [35] investigated the adsorption capabilities of three differently prepared electrospun polyacrylonitrile (PAN)/iron oxide composite fibers using Congo red (CR) as model pollutant. In the first method, PAN/iron(III) acetylacetonate composite nanofibers prepared by electrospinning followed by a hydrothermal method for in situ growth of iron oxide nanoparticles on the surface of PAN nanofibers (named as PAN/IO(H) composite nanofibers). In the second method, the electrospun PAN nanofibers were immersed into the iron alkoxide solution followed by a hydrolysis reaction at 80 °C (named as PAN/IO(B)). In the third method, PAN/iron oxide composite nanofibers were prepared by blending the previously prepared iron oxide nanoparticles with the PAN solution followed by an electrospinning technique (PAN/IO(A). The schematic representation for the synthesis of PAN/iron oxide composite nanofibers membranes is shown in Fig. 6.7.

The proposed formation mechanism of iron oxide nanoparticles on the surface of the PAN nanofibers is presented in Fig. 6.8. The adsorption capacity has been studied for PAN/IO(H) and PAN/IO(A) composite nanofibers and can be explained as follows. It is reported that the point of zero charge (PZC) of iron oxide nanoparticles (12–100 nm) is in the range of 7.8–8.8. Therefore, the surface of the nanoparticles is positively charged at neutral pH. The result of which facilitates the electrostatic attraction between the positively charged iron oxide nanoparticles and the negatively charged CR dye molecule. Thus the higher adsorption capacities have been observed for PAN/IO(H) and PAN/IO(A) as compared to that of PAN/IO(B) and un-functionalized PAN nanofibers. Significantly, there is no obvious leaching of iron species into water and thereby this work suggests that the prepared composite fibers may have a possibility to serve as next-generation nanoadsorbents for the removal of CR dye owing to their simple preparation and high adsorption capacity.

As evidence, a molecular filter produced from incorporation of beta-cyclodextrin (β -CD) into polystyrene (PS) fibers through the electrospinning process has shown potential for removing organic compounds, that is, phenolphthalein (PhP). The electrospun nanofibers in this study were prepared from varying the concentration of both polymer PS (15–25% (w/v)) and β -CD (10–50% (w/w)). The filtration studies were conducted on PS and PS/CD fibers by immersing them into a PhP solution, and the change in absorbance of PhP was recorded as a function of time by UV–vis spectrometry. Figure 6.9a–d clearly illustrates that the absorbance of PhP solution decreased significantly over time in the presence of PS/CD fibers, due to the removal of PhP from solution by β -CD. It can be well understood from the experimental results that the distribution of CD at the surface of the fibers is seen in all PS–CD samples (Fig. 6.9e–g) and the distribution behavior will play a large role in determining the efficiency of the fibers as filters. The fact in the removal

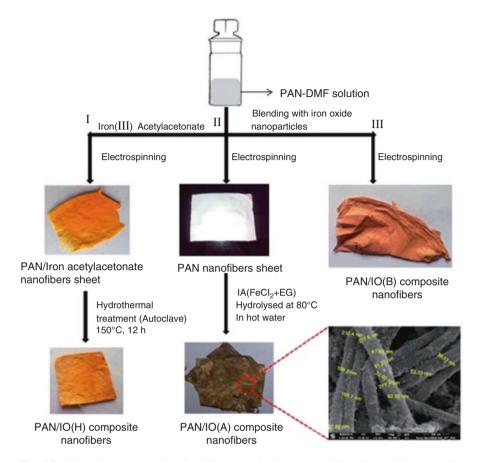


Fig. 6.7 Schematic representation for different synthetic methods of PAN/iron oxide composite nanofibers membranes. Reproduced with permission from [35] © 2016 Royal Society of Chemistry

efficiency solely depends on the distribution of CDs on the nanofibers by forming complexation with target molecules in the CD cavity, and the direct pyrolysis mass spectrometry studies confirmed the same. Hence, the study indicated the potential of using PS/CD fibrous membranes to filter organic molecules in purification/separation processes [36].

Later, Uyar et al. [37] conducted experiments to ensure the size effects and differences in affinity for selective inclusion complex (IC) formation with molecules; three different types of CDs (α -CD, β -CD, and γ -CD) were incorporated into electrospun PS nanofibers. Static time-of-flight secondary ion mass spectrometry (*static*-ToF-SIMS) analysis showed the presence of each type of CD on the PS nanofibers by the detection of both the CD sodium adduct molecular ions (M + Na⁺) and lower-molecular-weight oxygen-containing fragment ions. Further, comparative efficiency of the PS/CD nanofibers/nanoweb for removing phenolphthalein was determined by UV—vis spectrometry, and the kinetics of PhP capture was shown to

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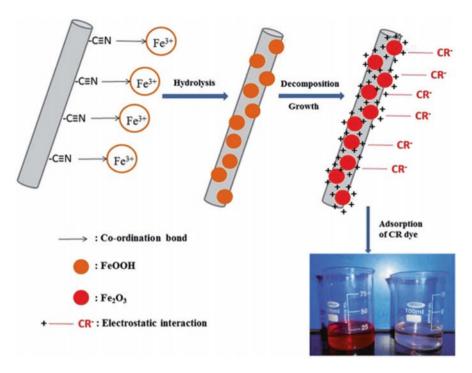


Fig. 6.8 Schematic representation of iron oxide nanoparticles grown on the surface of PAN nanofibers and mechanism of CR dye removal. Reproduced with permission from [35] © 2016 Royal Society of Chemistry

follow the trend PS/α - $CD > PS/\beta$ - $CD > PS/\gamma$ -CD. On the other hand, binding strengths of the PhP for the CD cavities showed the order of β - $CD > \gamma$ - $CD > \alpha$ -CD. The study concluded that the cyclodextrins with different sized cavities can indeed filter organic molecules and can potentially be used for filtration, purification, and/or separation processes [37].

So far, a variety of materials have been proposed and successfully proven to be efficient adsorbents. Consequently, each of them has their own limitations. Considering the toxicity, recent research has focused on the development of costeffective, renewable eco-friendly alternative bio-composites. Bioremediation is believed to be an alternative technology for decontamination of water systems by use of specific microorganisms such as bacteria, fungi, and algae. Usually, the usage of such microorganisms in bioremediation can be performed in two ways either as such or by immobilizing on a surface [38]. The immobilized microorganisms possess advantages over free cells in terms of their potential reusability, lower space and growth medium necessities, and higher resistance to environmental extremes. It is also well proven that the electrospun fibrous mat can act as an efficient platform for immobilization of specific microorganisms [39–42].

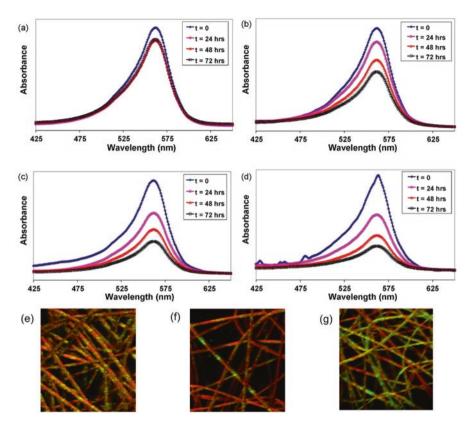


Fig. 6.9 UV–vis spectra of phenolphthalein (PhP) solution as a function of time after dipping the webs of (a) PS25, (b) PS20/CD10, (c) PS15/CD25, and (d) PS10/CD50. ToF-SIMS chemical images of fibers taken using the burst alignment mode. The distribution of CD on the surface of different PS/CD fibers shown by overlays of CD (green) on PS (red) fragment ions image, respectively (software color). (e) PS20/CD10, (f) PS15/CD25, and (g) PS10/CD50. Image area $75 \ \mu m \times 75 \ \mu m$. Reproduced/adapted with permission from [36] © 2009 Elsevier

San et al. demonstrated the three types of bacteria (*Aeromonas eucrenophila*, *Clavibacter michiganensis*, and *Pseudomonas aeruginosa*) immobilized cellulose acetate nanofibrous web (CA-NFW) for decolorization of methylene blue (MB) dye in aqueous medium [43]. The schematic representation of the preparation procedure for making nanofibers, attachment of bacteria cells, and their efficiency toward the decolorization of dye is shown in Fig. 6.10. The maximum dye adsorption capacity of bacteria-immobilized CA-NFWs is evaluated by studying the decolorization time (0–48 h) and different MB dye concentrations (20–500 mg L⁻¹). As a result, it is observed that the effective dye decolorization has been achieved within 24 h and 95% of the dye has been removed effectively. Thus, this work represents that the electrospun porous nanofibrous membranes are very effective solid supports for immobilizing bacterial cells.

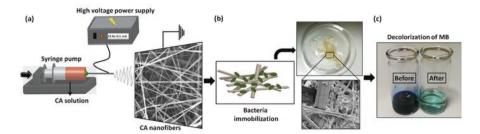


Fig. 6.10 Schematic representation of the electrospinning process for CA nanofibers, immobilization of bacterial cells on CA nanofibrous web, and photograph of the decolarization process. Reproduced with permission from [43] © 2014 Royal Society of Chemistry

Microalgae have been already identified as ideal biosorbents for wastewater treatment due to their specific nature such as ease of growth in simple medium, cheapness, availability, and high binding affinity. Yet, such a biosorbent shows limitations including low resistance to chemicals and heat. To overcome this problem, immobilization of microorganisms has been proposed and investigated as a viable means to achieve decolorization and degradation of dyes.

San Keskin et al. described the microalgae-immobilized polysulfone nanofibrous web (microalgae/PSUNFW) for removal of reactive dyes (Remazol Black 5 (RB5) and Reactive Blue 221 (RB221)) from wastewater [44]. They have selected *Chlamydomonas reinhardtii* as a model organism. The freestanding polysulfone nanofibrous web (PSU-NFW) was produced via electrospinning, and then *C. reinhardtii* was immobilized on their surface.

The SEM image of the electrospun PSU-NFW reveals that the obtained nanofibers are uniform and bead-free as represented in Fig. 6.11a–c. Figure 6.11d–f represents the photos of microalgae cells attached to the surface of PSU-NFW after 3 days and after 10 days from the start of the growth experiments. The green color of the membrane increased as concentration increases with respect to time. The attachment of the microalgae has been studied after 10 days of incubation. The observed results show that *C. reinhardtii* were strongly attached to the PSU-NFW. The decolorization rate for RB5 was calculated as $72.97 \pm 0.3\%$ for microalgae/PSU-NFW, whereas it was $12.36 \pm 0.3\%$ for the pristine PSU-NFW. In the case of RB221 solution, the achieved decolorization rates were 30.2 ± 0.23 and $5.51 \pm 0.4\%$ for microalgae/PSU-NFW and pristine PSU-NFW, respectively.

6.2.2 Removal of Volatile Organic Compounds (VOCs)

Environmental conservation has become a major social concern over few decades to avoid jeopardizing present natural resources. Volatile organic compounds (VOCs) are a large group of carbon-based molecules that easily evaporate at room temperature and considered as one of the major contributors to environmental pollution, emitted by a variety of sources including chemical and petrochemical industries,

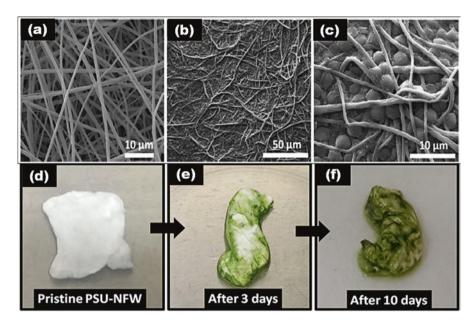


Fig. 6.11 Representative SEM images of (a) pristine PSU-NFW and (b and c) microalgae/PSU-NFW (under different magnifications). Photos ($\mathbf{d}-\mathbf{f}$) of attachment of free microalgae cells on PSU-NFW for 3- and 10-day attachment processes. Reproduced/adapted with permission from [44] © 2015 American Chemical Society

vehicles, ships, aircrafts, etc. [45–49], which undoubtedly has severe adverse effects on human and environmental health. It has been well reported that VOCs are capable of causing headache, nausea, mutagenic and carcinogenic effects [50–52], also has more adverse effect on lungs followed by pulmonary exposure [53]. Therefore, an enormous effort has been put forward to control the pollution arising from VOCs in environment. In this context, various methods have been developed including adsorption, oxidation, biological treatment, distillation, etc., for removal of VOCs from air and water [49, 54–59]. Son very recently discussed different methods adopted for controlling VOCs as illustrated in Fig. 6.12 [49]. However, many complications exist in applying them in actual field due to many influencing factors, thus attempts on identifying new methods and materials continue without hiatus.

As discussed earlier, nanotechnology deals with control of matters at a nanoscale level and production of materials with specific properties and functionalities that have shown potential applications in various sectors. Among the various available techniques for preparation of fibers, electrospinning has been recognized as a simple, versatile, and cost-effective method capable of producing nanofibers from a variety of polymers, inorganic and organic-inorganic compounds. The nanofibers produced through electrospinning have received great attention over the past decade for their application in healthcare to environment due to their specific properties like high surface-to-volume ratio, porous nature, permeability, and fiber diameter [60–66]. The electrospun nanofibers also significantly contributed to controlling VOCs

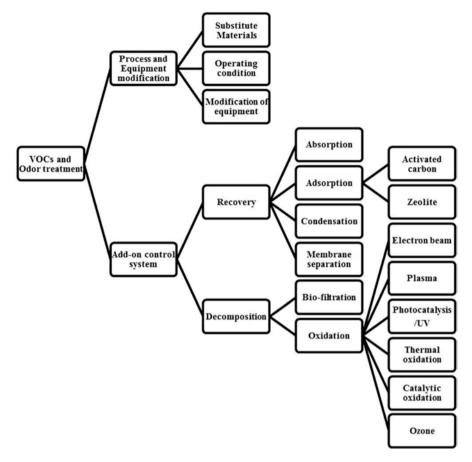


Fig. 6.12 Techniques for treatment of VOCs and odorous compounds. Reproduced with permission from [49] © 2017 Elsevier

pollution in environment using various approaches. This part of this chapter discusses about the different nanofibers intended in removal of VOCs.

A recent study conducted by Chu et al. [67] compared the adsorption/desorption performance of VOCs on electrospun nanofibers prepared from polystyrene (PS) nanofibers, acrylic resin (AR) nanofibers, and polystyrene—acrylic resin (PS—AR) composite nanofibers with activated carbons (ACs), carbon nanotubes (CNTs), and activated carbon fibers (ACFs) against *n*-butanol, toluene, chlorobenzene, anisole, nitrobenzene, dichloromethane, ethyl acetate, benzene, acetone, and *n*-hexane [67]. The surface characteristics of the fibers were investigated by using SEM and TEM; corresponding images are presented in Fig. 6.13. The diameters of the fibers were measured as 300–800 nm for the PS nanofibers, 200–400 nm for the AR nanofibers, and 200–900 nm for the PS—AR nanofibers. A homemade experimental setup has been adapted to conduct the adsorptive experiment using 5 mg of the

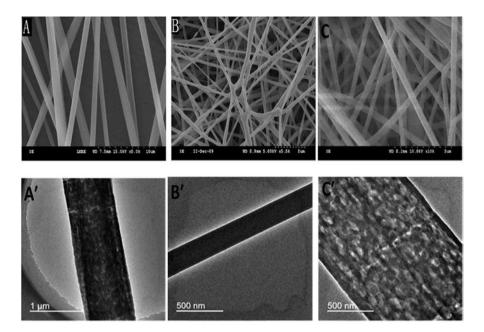


Fig. 6.13 SEM and TEM images of (A, A') PS nanofibers, (B, B') AR nanofibers, and (C, C') PS-AR nanofibers. Reproduced with permission from [67] © 2015 Royal Society of Chemistry

sample followed by gas chromatography measurement. Further, desorption and regenerative performances of the samples were investigated under thermal conditions. The outcome of the study indicated that nanofibers possess selective adsorption property against VOCs based on their composition. The adsorption efficiency of the nanofibers is comparable to that of ACFs and CNTs determined per weight unit. Interestingly, the electrospun nanofibers showed better thermal desorption properties than ACs, CNTs, and ACFs, which emphasize the advantage of the nanofibers over other adsorbents due to gas adsorption/desorption which occurs at the surface of the nanofibers. Overall results of this study found that the electrospun nanofiber could be a potential VOC adsorbent since it holds certain selectivity, short adsorption equilibration time, preferable adsorption/desorption efficiency, reusability, and temperature effect.

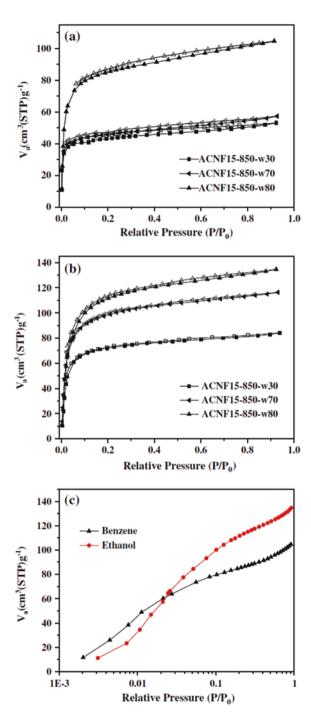
The electrospun polyacrylonitrile (PAN) carbon nanofibers were reported for their applicability as novel alternative adsorbents with commercial ACFs, A–10 for volatile organic compounds (VOCs) removal. The results of isosteric enthalpy of adsorption and adsorption energy distribution tests/equations prove the higher adsorption capacities of PAN carbon nanofibers than the commercial ACFs for benzene removal [68]. In another study, activated carbon nanofibers (ACNFs) produced from electrospinning of polyacrylonitrile solutions demonstrated higher adsorption efficiency of VOCs (benzene and ethanol) than activated carbon fibers (ACFs) in a static vapor adsorption system. The ACNFs were prepared by initially electrospinning 10 wt% PAN solution (ACNF10-800) and 15 wt% solution (ACNF15-800)

followed by stabilizing the electrospun nanofibers by heating the samples to 280 °C at a rate of 1 °C min⁻¹ in air and kept at 280 °C for 2 h, then the fibers were further heated up and carbonized at 800 or 850 °C for 30 min in nitrogen with a flow rate of 212 mL min⁻¹ controlled by the rotameter. Further, the samples were activated by adding 30 vol.% steam-controlled nitrogen gas at the same temperature for 10, 30, and 50 min. The burn-offs were calculated based on the weights of the stabilized electrospun fibers and the resultant samples and denoted as ACNF15-850-w30, 70, and 80. On the contrary, ACFs were prepared from oxidized PAN fibers by carbonization at 850 °C for 30 min and then activated at the same temperature with nitrogen flow containing 50 vol.% steam for 30 min. Outcome of the study indicated that ACNFs fabricated by the method of electrospinning demonstrated higher adsorption capacities for VOCs than ACFs at extremely low relative pressures. Adsorption isotherms of benzene and ethanol were measured at 20 °C using a volumetric adsorption system. The ACNFs demonstrated higher adsorption capacities for VOCs than ACFs at extremely low relative pressures. The physical and chemical properties of ACNFs have significantly improved by varying the activation conditions. The increased burn-off conditions facilitate the enhanced microporosity in the nanofibers which results in better adsorption performance as shown in Fig. 6.14. In addition, surface chemistry has an important effect on the adsorption of polar VOCs. The ACNF with higher oxygen content possesses a higher adsorption capacity for ethanol [69].

Electrospun polyurethane fibers fabricated through the electrospinning method by using polyurethanes based on 4,4-methylenebis(phenylisocyanate) (MDI) and aliphatic isophorone diisocyanate as the hard segments and butanediol and tetramethylene glycol as the soft segments were electrospun from their solutions in N,Ndimethylformamide. The electrospun polyurethane fibers had an average diameter of 2 µm and were found to be smooth and nonporous in nature as illustrated in Fig. 6.15. The fibers were then studied for their adsorbent efficiency against VOCs such as toluene, hexane, and chloroform. The adsorption efficiencies of activated carbon were also studied for comparison. The sorption capacity of the polyurethane fibers was found to be similar to that of activated carbon specifically designed for vapor adsorption, even though the activated carbon possessed a many-fold higher surface area. Additionally, the polyurethane fibers demonstrated a complete reversible adsorption and desorption using a simple purging with nitrogen at room temperature, which was not possible in the case of activated carbon. The fibers possessed a high affinity toward toluene and chloroform, but aliphatic hexane lacked the necessary strong attractive interactions with the polyurethane chains and therefore was less strongly absorbed [70].

Another study reported by Feng et al. [71] revealed the removal of chloroform by using the electrospun poly(vinylidene fluoride) (PVDF) nanofiber membrane in a membrane air-stripping system. Gas-stripping membrane distillation system used in this study is shown schematically in Fig. 6.16. In brief, the results of the study displayed that owing to high surface hydrophobicity and appropriate pore sizes of the electrospun nanofiber the VOC was effectively removed. The overall mass transfer coefficient of chloroform through the nanofiber membrane was found to be

Fig. 6.14 Adsorption/ desorption isotherms of (a) benzene and (b) ethanol on three samples, and (c) adsorption isotherms of benzene and ethanol on ACNF15-850-w80 at 20 °C. Reproduced with permission from [69] © 2013 Springer



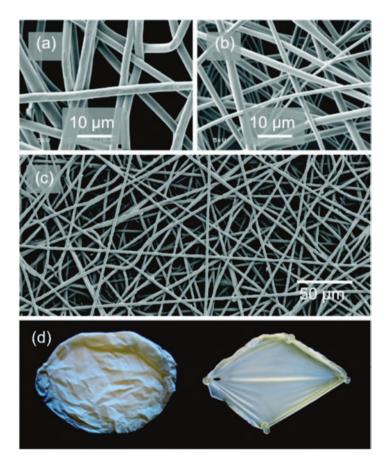


Fig. 6.15 SEM images of (**a**) MDI-based and (**b**) isophorone-based nonwoven fiber mats showing smooth, nonporous fiber surfaces. (**c**) SEM image showing uniformity of MDI-based PU fiber diameter and mat density. (**d**) Strength and elasticity of mats demonstrated by lack of tearing or breaking of stretched fiber mat held in place with push pins. Reproduced with permission from [70] © 2011 American Chemical Society

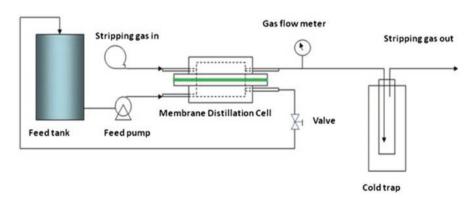


Fig. 6.16 Gas-stripping membrane distillation system. Reproduced with permission from [71] © 2011 Elsevier

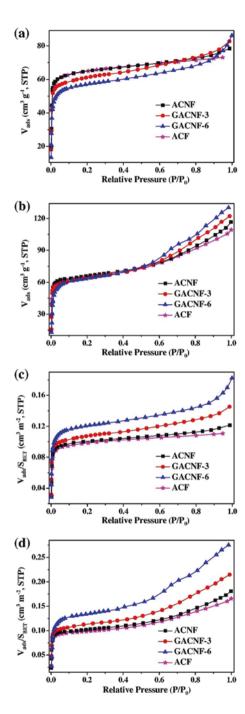
 2.40×10^{-5} m/s, and this value was higher than the values obtained for a membrane air-stripping system based on a hollow fiber module. Notably, activation energy of the overall mass transfer coefficient was found to be nearly equal to that of the Henry constant for chloroform absorption in water. Hence, the study concludes that the use of the electrospun nanofiber contributed to effectively remove the VOC because of their unique properties [71].

Nevertheless, functionalization of nanofibers with various compounds could improve the efficiencies of nanofibers. Hence, several attempts were made to decorate or incorporate different compounds for enhancing the peculiar performances. In the consideration of current discussion, to enhance the surface oxygen content Guo et al. [72] added graphene oxide (GO) sheets at weight percentages (3 and 6 wt.%) into polyacrylonitrile (PAN), further the composite fibers were prepared through the electrospinning process. Pristine carbon nanofibers without addition of GO (ACNF) and conventional PAN-based activated carbon fiber (ACF) were also used for the sake of comparison. The resultant nanofibers were tested for their performances in adsorption of benzene and butanone through vapor adsorption equilibrium isotherms. Interestingly, addition of GO increased mesopores and high surface oxygen content of the nanofibers and exhibited higher adsorption capacities toward both the VOCs as compared to the pristine carbon nanofiber and commercial ACF, as shown in Fig. 6.17. Additionally, surface oxygen content greatly influenced the adsorption behavior of composite nanofibers as butanone, a polar compound, had higher adsorption rate than the nonpolar benzene. The highest benzene and butanone adsorption capacities of the prepared composite nanofibers at 20 °C and with relative pressure of 0.98 reached 83.2 and 130.5 cm³ g⁻¹, respectively. In addition, adsorption capacity ratio isotherms of butanone relative to benzene on the three nanofibers at 20 °C were also calculated against various relative pressures and displayed butanone possessed higher adsorption than benzene. Obviously, VOC adsorption performance of the series of composite nanofibers was significantly improved by the introduction of GO with increasing concentration. In brief, a change of approach in preparing electrospun nanofibers evidently demonstrated the effective adsorption performances against conventional fibers [72].

In another approach aimed for enhancing the removal performance of nanofibers toward pollutants, cyclodextrins (CDs) incorporation has been explored as an ideal strategy. The CDs are cyclic oligosaccharides comprising of 1,4-linked glucopyranoside units with either six, seven, or eight glucose units organized in a cyclic structure, named as α -, β -, and γ -cyclodextrins, respectively. Our group has extensively investigated the influence of filtering and removal capacity of VOCs upon functionalization/incorporation of cyclodextrin (CD) molecules in electrospun nanofibers. As evidence, Uyar et al. [73] reported the preparation of beta-cyclodextrin (β -CD) incorporated poly(methyl methacrylate) (PMMA) nanofibers using electrospinning in order to develop functional nanofibrous webs for organic vapor waste treatment. The systematic characterization studies confirmed distribution of β -CD molecules on the nanofiber surface. In order to investigate the entrapment of aniline, styrene, and toluene by the PMMA nanowebs containing 10%,

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Fig. 6.17 Adsorption equilibrium isotherms of (a) benzene and (b) butanone on various samples at 20 °C. Normalized (c) benzene and (d) butanone adsorption isotherms of various samples with respect to specific surface area at 20 °C. Reproduced with permission from [72] © 2016 Elsevier



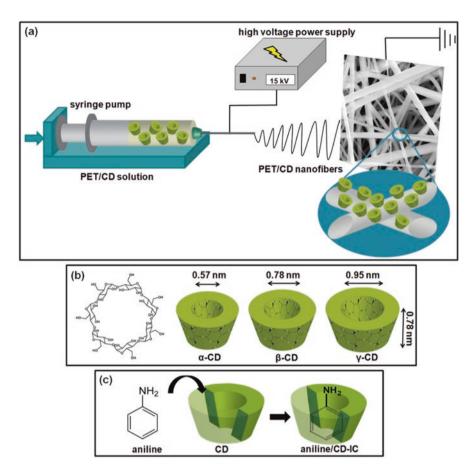


Fig. 6.18 Schematic representations of (a) electrospinning of PET/CD solution, (b) chemical structure of β -CD and approximate dimensions of α -CD, β -CD, γ -CD, and (c) formation of aniline/CD-IC. Reproduced with permission from [74] © 2014 John Wiley and Sons

25%, and 50% β-CD (PMMA/β-CD10, PMMA/β-CD25, and PMMA/β-CD50), the evolution profiles of single-ion pyrograms of the characteristic PMMA- and β-CD-based products were investigated. The pyrolysis mass spectrometry results clearly indicated that the β-CD functionalized nanofibers effectively trap organic waste vapors with respect to increase in exposure period and the amount of CD present in the nanowebs [73].

Kayaci and Uyar [74] incorporated α -CDs, β -CDs, and γ -CDs into polyester (PET) nanofibers by the electrospinning process. Interestingly, bead-free PET/CD nanofibers were obtained from lower polymer concentration owing to the fact that CDs incorporation increased spinnability of electrospun solution. A schematic representation shown in Fig. 6.18 clearly demonstrates the electrospinning process and formation of inclusion complexes with aniline. The entrapment performance of the

PET and PET/CD nanofibrous webs was investigated by using aniline vapor as a model VOC. The amount of aniline entrapped by PET, PET/ α -CD, PET/ β -CD, and PET/ γ -CD nanofibrous webs was calculated by HPLC. The absorption was approximately 1300 ppm aniline by pristine PET nanofibers, whereas PET/ α -CD and PET/ β -CD nanofibrous webs captured approximately 2600 ppm and PET/ γ -CD nanofibrous webs captured approximately 3400 ppm at the end of entrapment test. The findings of the study suggest that CD functionalized electrospun PET nanofibers can be promising filtering materials for air filtration and the removal of VOCs due to very high surface area of nanofibrous webs and surface-associated CD molecules having inclusion complexation capability with VOCs [74].

Another study reported the preparation of functional nylon 6,6 nanofibers incorporating cyclodextrins (CD) with enhanced thermal stability. The nanofibers were prepared by incorporating three types of α -CD, β -CD, and γ -CD at different ratios (25% and 50%, w/w, with respect to nylon 6.6). The resultant membranes without CD were ineffective for entrapment of toluene vapor from the environment, whereas nylon 6,6/CD nanofibrous membranes can effectively entrap toluene vapor from the surrounding by taking advantage of the high surface-to-volume ratio of nanofibers with the added advantage of inclusion complexation capability of CD presenting on the nanofiber surface. Particularly, the nanofibers incorporating 50% of β-CD showed enhanced entrapment performance than α-CD and γ-CD in both concentrations as can be seen from Fig. 6.19a. In brief, it is understood that CD functionalized electrospun nylon 6,6 nanofibers would be very effective for the removal of VOCs from the environment due to their very large surface area along with inclusion complexation capability of surface associated CD on the nanofibers. The modeling studies for formation of an inclusion complex between CD and toluene were also performed by using ab initio techniques and the results confirmed that based on the first principles calculation, the complexation energy of toluene-CD is higher for β -CD compared to α-CD and γ-CD as illustrated in Fig. 6.19b [75].

Celebioglu and Uyar [76] electrospun gamma cyclodextrin (γ -CD) nanofibers from a DMSO–water solvent system without using any carrier polymeric matrix and further investigated the molecular entrapment capability toward aniline and toluene. The γ -CD nanofibers were placed in a desiccator saturated with aniline or toluene vapor and the measurements of organic vapors were performed by 1 H-NMR. The γ -CD powder was treated under the same environment for comparison purpose. The outcome of molecular entrapment experiment indicated that γ -CD nanofibers were quite successful in entrapping of VOCs (aniline and toluene) by inclusion complexation, whereas γ -CD in powder form did not show any entrapment capability. The overall findings suggest that these electrospun CD nanofibers can be used as molecular filters and/or nanofilters for the removal of organic volatile compounds (VOCs) from the environment [76].

Very recently, the molecular entrapment performance of polymer-free nanofibers of hydroxypropyl-beta-cyclodextrin (HP β CD) and hydroxypropyl-gamma-cyclodextrin (HP γ CD) was investigated toward two common VOCs (aniline and benzene). The encapsulation efficiency of CD samples was investigated by varying different factors including CD form (NF and powder), electrospinning solvent (DMF and water), CD

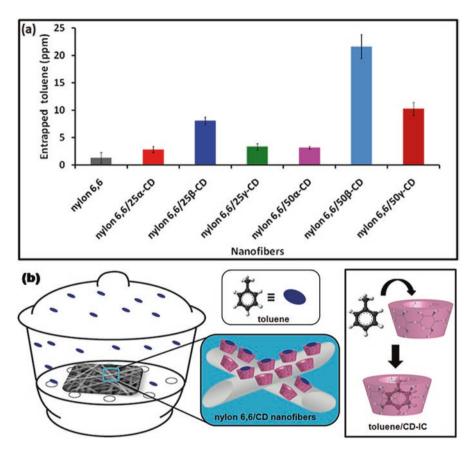


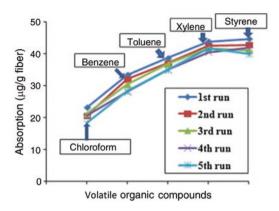
Fig. 6.19 (a) The amount of entrapped toluene (ppm) by the electrospun nanofibers and (b) schematic representation of the formation of toluene/CD-IC. Reproduced/adapted with permission from [75] \odot 2015 John Wiley and Sons

(HPβCD and HPγCD), and VOC (aniline and benzene) types. The observed results recommended that CD NF could entrap a higher amount of VOCs from surroundings than their corresponding powders. Besides, molecular entrapment efficiency of CD NF depended on CD, solvent, and VOC types. Further, the inclusion complexation ability of CD molecules was based on very high surface area and versatile features of CD NF. So evidently, all these reports proved that incorporation of CDs into electrospun nanofibers serves as useful filtering material for the purposes VOCs removal [77].

Likewise, many other attempts have been made to incorporate different compounds into electrospun nanofibers for their enhanced performances in VOCs removal. For instance, commercially available fly ash particles (FAPs) at different concentrations (0, 10, 30, 50, and 70 wt%) were blended with polyurethane (PU) and electrospun to obtain fly ash/polyurethane composite fibrous membrane. The fibers were tested against different VOCs, including chloroform, benzene, toluene, o-xylene, and styrene. The experimental data showed that, among all VOCs, styrene

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Fig. 6.20 Cyclic absorption behavior of different VOCs on a PU composite mat obtained from 30 wt% FAPs containing PU solution. Reproduced with permission from [78] © 2013 Elsevier



was the highly absorbed one, regardless of composition of PU fibers. PU fibers with 30 wt% FAPs showed enhanced VOC absorption capacity, which is 2.52–2.79 times (for five VOCs) higher compared to that of pristine PU fibers. To ensure the practical applicability of the composite fibers in order to their reusability performance, PU fibers containing 30 wt% FAPs have been studied for repeated VOC adsorption experiment. The recyclability results demonstrated that composite fibrous mats have nearly equal absorption efficiency up to five cycles as depicted in Fig. 6.20 [78].

Following the same trend, Loess powder (LP), which is generally used to adsorb the pollutants in water as nanoparticles (NPs), has been incorporated into PU nanofibers at 0, 10, 30, and 50 wt% concentrations. The outcome of adsorption experiments revealed that the PU/LP nanofibers containing 30 wt% LP NPs has highest VOC absorption capacity and follows the trend toluene > benzene > chloroform [79]. In another recent study reported by Ge and Choi [80], polyurethane/rare earth (PU/RE) composite nanofibrous membranes were produced by electrospinning and were intended for the application of removing VOCs from air. The VOC adsorption studies of styrene, xylene, toluene, benzene, and chloroform had shown PU nanofibers containing 50% RE powder highly adsorbed styrene [80].

6.2.3 Removal of Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are other vital environmental pollutants comprising two or more fused benzene rings that are arranged in different configurations and released into environment from natural and anthropogenic sources. The chemical structures of few commonly studied PAHs are given in Fig. 6.21 [81]. PAHs consisting of fewer than four rings are classified as low-molecular-weight compounds, whereas high-molecular-weight compounds consisting of four or more rings are usually colored, crystalline solids at ambient temperature, poorly soluble in water, and highly mobile in the environment because of their physicochemical

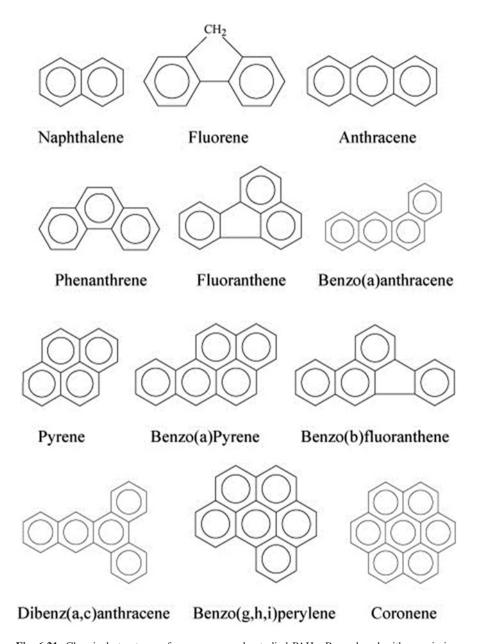


Fig. 6.21 Chemical structures of some commonly studied PAHs. Reproduced with permission from [81] @ 2009 Elsevier

properties and distributed across air, water, and soil [81–83]. Due to their ubiquitous persistence in environment, negative effects of PAHs are well documented for a long time. PAHs cause increased risk of skin, bladder, lung, and gastrointestinal cancers. Moreover, reactive molecules of some PAHs tend to bind with cellular proteins and DNA molecules resulting in cell damage, mutation, malformation development, and cancers. The deleterious effects of PAHs on environment and human health have been reviewed in detail and reported [84–86]. Hence, a variety of methods, including bioremediation, have been exploited to control the PAHs pollution in environment till now and continue to discover for better solution [81, 87, 88]. A variety of nanomaterials, including carbon nanotubes, graphene, and iron nanoparticles, have been reported for their efficiency in significant removal of PAHs [89–91]. In addition, electrospun nanofibers proved for their potency in removing PAHs that will be discussed in the following section.

Electrospun nanofibers of poly(styrene-co-methacrylic acid), poly(styrene-co-pstyrene sulfonate), and polystyrene have been used as solid-phase extraction (SPE) sorbents to extract six aromatic hydrocarbon compounds, including nitrobenzene, 2-naphthol, benzene, n-butyl p-hydroxybenzoate, naphthalene, p-dichlorobenzene in water samples. The high surface-to-volume ratio of PS nanofibers ensured a strong interaction between the nanofiber sorbent and aromatic hydrocarbons and resulted in higher sensitivity, reproducibility, detection limits, and reducing the time. The applicability of the sorbents was also investigated for real-time water samples [92]. A study conducted by Dai et al. [93] used five types of nanofibrous membranes prepared by electrospinning poly(ε-caprolactone) (PCL), poly(DLlactide) (PDLLA), poly(lactide-co-caprolactone) (P(LA/CL)), poly(DL-lactide-coglycolide) (PDLGA), and methoxy polyethylene glycol-poly(lactide-co-glycolide) (MPEG-PLGA) for removal of anthracene (ANT), benz[a]anthracene (BaA), and benzo[a]pyrene (BaP) from aqueous solution. All the sorption processes were mostly achieved within the first 30 min of reaction, and then became more gradual until the equilibrium was reached after 3 h. The sorption rates of the PCL ENFMs for PAHs were relatively faster than others, and their sorption capacity for ANT, BaA, and BaP reached 75.6, 78.3, and 73.5 μg g⁻¹ at 60 min, respectively. The differences in sorption of these three pollutants toward ENFMs are based on the hydrophobic interactions, hydrogen bonding interactions, π – π bonding interaction, and pore-filling factors. A detailed representation of the sorption mechanism is presented in Fig. 6.22 [93].

In order to enhance the adsorption and degradation of PAHs, three different types of electrospun nanofibers poly(D-L-lactide) (PDLLA), poly(D-L-lactide-co-glycolide) (PDLGA), and methoxypolyethylene glycol-poly(lactide-co-glycolide) (MPEG-PLGA) immobilized with laccase (LCEFMs) have been prepared and used for the removal of phenanthrene, fluoranthene, benz[a]anthracene, and benzo[a]pyrene from the soil sample collected at Baisha Shoal (China) in the aqueous solution. The PAH removal studies indicated the degradation efficiencies for the four PAHs were ranked in the order of phenanthrene > fluoranthene > benz[a]anthracene > benzo[a] pyrene. Specifically, the degradation efficiencies of the PAHs by all three LCEFMs

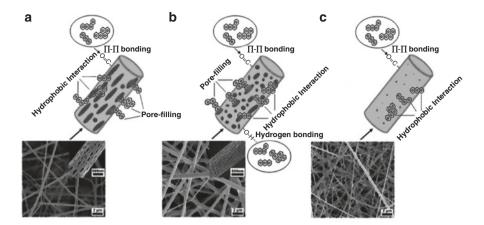


Fig. 6.22 Schematic diagram of the sorption of three PAHs on PDLLA ENFMs (a); MPEG-PLGA ENFMs (b); P(LA/CL), PCL, and PDLGA ENFMs (c). Reproduced with permission from [93] © 2011 Elsevier

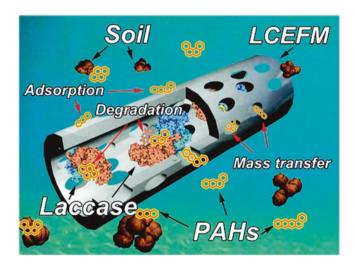


Fig. 6.23 The scheme of the PAH phase transfer and degradation process by laccase-carrying electrospun fibrous membrane. Reproduced with permission from [94] © 2011 American Chemical Society

were much higher than those by free laccase, especially for benzo[a]pyrene, whose degradation efficiency by free laccase was less than 30%, whereas those by the three LCEFMs exceeded 70%. Moreover, the PAHs in aqueous solution was adsorbed on the surface of the LCEFMs and concentrated around the active sites of laccase; thus, the degradation rates of PAHs were significantly enhanced and the corresponding process is explained in Fig. 6.23 [94]. Later, the approach has been adopted to remove the PAHs in contaminated water [95].

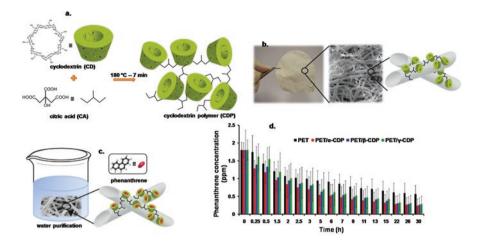


Fig. 6.24 Schematic representations of (a) formation mechanism of CDP and (b) the representative photograph of PET/CDP nanofibrous mat and its SEM image and schematic representation of PET/CDP nanofibers. (c, d) Time-dependent decrease of phenanthrene concentration in the aqueous solution containing nanofibrous mats and phenanthrene complex formation. Reproduced/adapted with permission from [96] © 2013 Elsevier

Considering the beneficial nature of cyclodextrins in capturing environmental pollutants, electrospun polyester (PET) nanofibers with cyclodextrin polymer (CDP) were produced (PET/CDP) with all three α -CD, β -CD, and γ -CD types and investigated for their efficiency in removing the PAH compound phenanthrene from aqueous solution and, further, their efficiency was compared to that of pristine PET nanofibers. The schematic representation of nanofiber preparation, mechanism, and their characteristics is shown in Fig. 6.24. In this study, PET nanofibers were obtained by electrospinning of 22.5% (w/v) PET solution in TFA/DCM (50/50, v/v). The chemical reaction cannot occur between cyclodextrin (CD)/citric acid (CTR) and PET nanofibers directly, since PET, a polymer based on terephthalic acid and ethylene glycol, does not contain free reactive groups.

Therefore, we modified the surface of the electrospun PET nanofibers through the polymerization reaction between CTR and CD. The mechanism of the CDP formation is schematically described in Fig. 6.24a and b. The molecular filtration studies revealed that the concentration of phenanthrene in the aqueous solution decreased within the contact time as depicted in Fig. 6.24c and d. The adsorption of phenanthrene by PET nanofibers for the first 2 h was observed, and then the concentration of phenanthrene slightly decreased over time. On the other hand, the decrease of phenanthrene concentration for PET/CDP mats was more significant. Although less amount of PET/CDP nanofibers was used compared to that of PET nanofibers for filtration test, the removal efficiency of phenanthrene from its aqueous solution was better due to structure of CDP structure that plays a crucial role in molecular capturing of phenanthrene. Therefore, the functionalization approach on electros-

pun nanofibers proved to change the PET/CDP as a molecular filter for water purification through complexation of the phenanthrene with CDP [96].

Cellulose acetate (CA) nanofibers grafted with beta-cyclodextrin (β-CD) prepared by combining electrospinning and "click" reaction have been demonstrated for their efficiency in removing the PAH compound phenanthrene from aqueous solution. In brief, at first, β-CD and electrospun CA nanofibers were modified as azide-β-CD and propargyl-terminated and then "click" reaction was performed between modified CD molecules and CA nanofibers to attain permanent grafting of CDs on nanofibers surface (see Fig. 6.25). The morphological behavior of CA nanofibers before and after the surface modification has been compared by SEM as depicted in Fig. 6.25b. As it is shown in the SEM images, some changes occurred at the morphology of CA nanofibers after each process. The functionalized nanofibers (CA-CD) were capable of removing high amounts of PAH than the CA nanofibers because of the repulsive interactions between the hydrophobic guest and the aqueous environment, and more favorable interactions between hydrophobic guest and apolar CD cavity as depicted in Fig. 6.25c [97].

6.2.4 Removal of Other Organic Pollutants (Antibiotics and Pesticides)

Besides, pollution owing to antibiotics in environment has raised another major concern because of great risk even at trace levels. To date, a variety of technologies (ionexchange, membrane filtration, adsorption, and photocatalytic degradation) have been used to remove antibiotics from aqueous solution [98–100]. There are few studies that reported the removal of antibiotics by using electrospun nanofibers, as an example, novel Fe₃O₄/polyacrylonitrile (PAN) composite nanofibers (NFs) were prepared by a two-step process, namely, electrospinning and solvothermal methods. The composite fibers were evaluated to check their feasibility in antibiotic removal using tetracycline (TC) as the model antibiotic molecule by batch adsorption experiments. The results showed that Fe₃O₄/PAN composite NFs were effective in removing TC with no impactful loss of Fe in the pH regime of environmental interest (5–8) and their adsorption capacity calculated from the Langmuir isotherm model was 257.07 mg g⁻¹ at pH 6. From the experimental analysis, it was proposed that the adsorption of TC on the composite membranes occurs mainly through the cation exchange and complex formation between the Fe atom from the composite NFs and the deprotonated moieties from the TC molecule, as depicted in Fig. 6.26 [101].

Organophosphates (OPs) are a group of organic phosphorous compounds and mostly used as pesticides/insecticides and are of much concern because of their potency to bind with acetylcholinesterase through dermal exposure, resulting in disturbance of nervous impulses and inhibiting nerve cell functions [102]. Various methods to degrade OPs similar to other pollutants were explored, including electrochemical, biodegradation, photolytic, catalytic oxidation, and destructive adsorp-

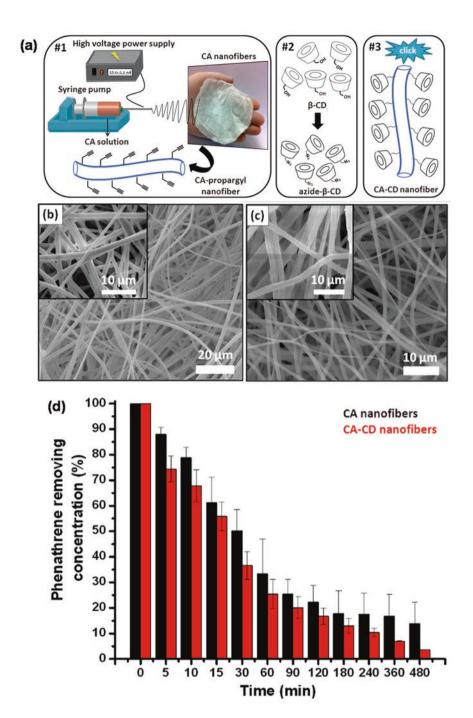


Fig. 6.25 (a) Schematic representation of electrospinning of CA nanofibers and modification of CA-propargyl nanofibers with azide-β-CD by "click" reaction. (b, c) Representative SEM images Fig. 6.25 (continued) of CA-propargyl and CA-CD nanofibers, respectively. The insets show higher magnification images. (d) The time-dependent decrease of phenanthrene concentration in aqueous solution which contains CA and CA-CD nanofibers webs. Reproduced/adapted with permission from [97] © 2014 Elsevier

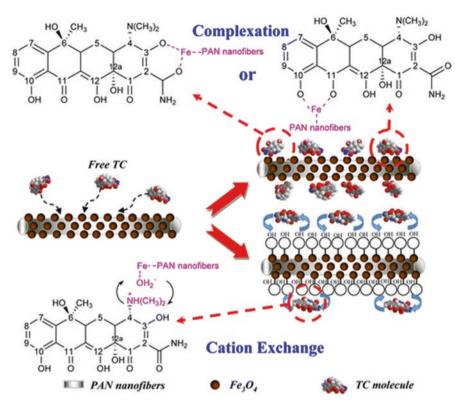


Fig. 6.26 Mechanistic illustration of adsorption of TC on Fe_3O_4/PAN composite NFs. Reproduced with permission from [101] © American Chemical Society

tion. The electrospinning researchers also paid significant attention toward the removal of pesticides. Lange et al. [103] reported the incorporation of Cu-BTC metal-organic framework (MOF-199) into polyacrylonitrile (PAN) nanofibers by the electrospinning process to remove methyl parathion, an OP pesticide in solution. Following 2 h of treatment, the PAN/MOF-199 membranes removed higher (88%) methyl parathion than the unmodified PAN membranes. Based on the outcome of the study, the functionalized nanofibrous membranes were suggested for their potential application in filtration media [103].

6.3 Conclusion and Future Prospects

The electrospun nanofibrous composite membrane has been recognized as an efficient filtering platform that provides competent ways for removing the pollutants from environment. This chapter summarized the recent advancements in the development of electrospun nanofibrous composite membranes as filtering media against

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various organic pollutants. The effective removal of organic pollutants from dyes to PAHs has been discussed comprehensively. However, the toxicity of functional materials and their environmental impact before and after coupling with nanofibers remain unclear and should be investigated systematically. Even though, there are studies focused on the leaching effect of functional nanomaterials from the nanofibers into filtering media, much concern should be paid in protecting functional molecules release from the nanofibrous filters to limit their impacts on environmental health.

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