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Chapter

Composite Nanofibers: Recent Progress in Adsorptive Removal and Photocatalytic Degradation of Dyes

Duy-Nam Phan and Ick-Soo Kim

Abstract

This chapter intends to review the state of the art of a new nanomaterial generation based on electrospun composite nanofibers for dye removal from wastewater. Natural polymer-based nanofibers, nanofibers with unique morphology, and carbon nanofibers were comprehensively reviewed as capable carriers for a broad spectrum of functional materials such as metal oxides, zeolite, graphene and graphene oxide (GO), and metal-organic frameworks (MOFs) in the application of dye removal. The various nanostructures, adsorption capacity, advantages, and drawbacks were discussed along with mechanistic actions in the adsorption process and photocatalytic performance that emphasize current research development, opportunities, and challenges. The chapter covers multiple intriguing topics with in-depth discussion and is a valuable reference for researchers who are working on nanomaterials and the treatment of colored waters.

Keywords: composite nanofibers, electrospinning, dyes, adsorption, photocatalytic degradation

1. Introduction

The activities of textile, printing, leather, paint, and paper industries are discharging millions of gallons of wastewater every day, contaminating water bodies and terrestrial lands. The impacts on the environment are irretrievable and gravely dangerous. The organic dyes in effluents and discharges used for fabrics and colored materials are persistent in water and pose long-term effects on human health, fish, and aquatic organisms. Many synthetic dyes are considered toxic, carcinogenic, and mutagenic; even a small amount infiltrates the human body. Direct contact with dyestuffs can lead to skin allergy and neurological, reproductive, and endocrine diseases [1].

Nanofibers with high surface area to volume ratio, excellent flexibility, porous structure, reusability, nontoxicity, environmental stability, and low cost are suitable supporting materials for loading functional materials or being modified with different chemical groups in water treatment application. With enhanced surface area and pore volume, the nanofibers as a filtering media deliver high contact between adsorbent and aqueous media, resulting in improved adsorption

capacity with the convenience of recovery and recycling. By engineering various functional groups (carboxylate, amino, acid, and hydroxyl groups) or the integration of adsorbents, including metal oxides, graphene, graphene oxide (GO), and metal-organic frameworks (MOFs) in the nanofibers, the separation capacity can be greatly improved [2–4].

Among various systems, which have been developed for the removal of dyes in wastewater, namely, adsorption, ion exchange, membrane filtration, and coagulation, adsorption is the most effective and versatile strategy to remove dyes at high concentrations with high removal percentage. The adsorption process involves several stages: (i) dissolving dyes into the solution, (ii) the external diffusion of dyes to the surroundings of the adsorbents, (iii) internal or intra-particle diffusion which fills nanoparticle pores with dye molecules, and (iv) adsorption or desorption on the interior sites. If the amounts of dye uptake are correlated with the square root of time in a linear relation, the adsorption process is significantly influenced by intra-particle diffusion because step (iv) usually happens rapidly [5].

Most dyes are water-soluble and can be classified as cationic, anionic, and nonionic; the names are derived from the charging states when being dissolved into an aqueous medium. Depending on the chemical structures of dyes, the approaches and adsorption conditions can vary accordingly, which include material selection, adsorption or photocatalytic degradation, pH, time, and temperature. A spectrum of organic and inorganic materials such as transitional metal oxide, graphene and GO, carbon nanotubes, zeolites, and MOFs have been used for treating colored waters. These materials are suited for separating dyes from wastewater owing to abundance, low cost, ease of being employed, adsorptive selectivity, and biocompatibility [6–8].

The photocatalysis process has emerged as a newly developed technique for wastewater remediation. Photocatalysts with a particular bandgap can be activated by different light sources to generate electron-hole pairs, which either recombine or migrate to the surface and initiate photocatalytic reactions. After that, the holes oxidize H_2O to produce hydroxyl radical OH•, whereas electrons react with absorbed O_2 to produce oxygen radicals O_2• and other intermediate forms [9]. The hydroxyl

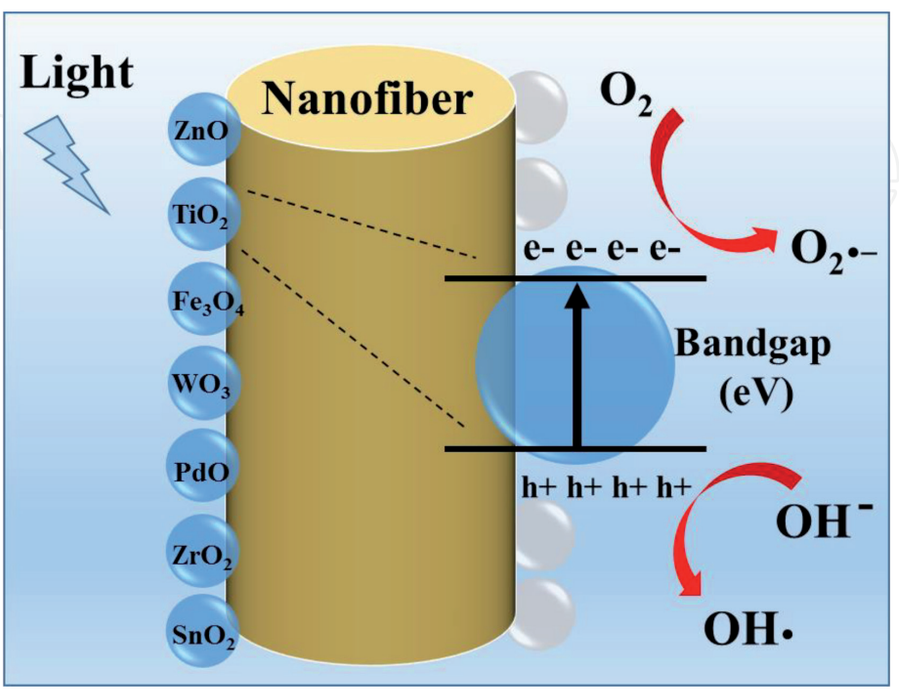


Figure 1.
Scheme for photocatalysis of metal oxide nanoparticle-decorated nanofibers under UV or visible light sources.

radicals and oxygen radicals then attack dye molecules to convert pollutants or contaminants into nontoxic forms or completely decompose them to CO_2 and H_2O (**Figure 1**). The criteria for useful photocatalysts are the capability to absorb the solar spectrum at the visible range, excellent performance, and long-term stability.

2. Electrospinning technique, natural polymer-based nanofibers, and carbon nanofibers (CNFs)

2.1 Electrospinning technique as the fabrication method

Electrospinning is one of the several well-developed techniques to fabricate fibers at micro- or nanoscale (**Figure 2**). The electrospinning with versatility allows excellent controls over the fiber diameters, nanostructures, and morphology to enhance catalytic, mechanical, electrical, biomedical, optical, and adsorptive properties. With a wide selection of polymers and the facilities for additive incorporation, the electrospinning process can manufacture nanofibers into different fascinating structures for varied applications [14]. With recent advancements in the electrospinning technique, fascinating nanostructures could be obtained with inspiration from objects in nature and can be applied in improving pollutant removal. The tree-like structure is composed of trunk fibers and branch fibers. The trunk fibers with the support role can improve the mechanical property, and the thin branches play the role of connection, decrease the pore size of the membranes, and increase the surface area [15]. The spider web-like structure was

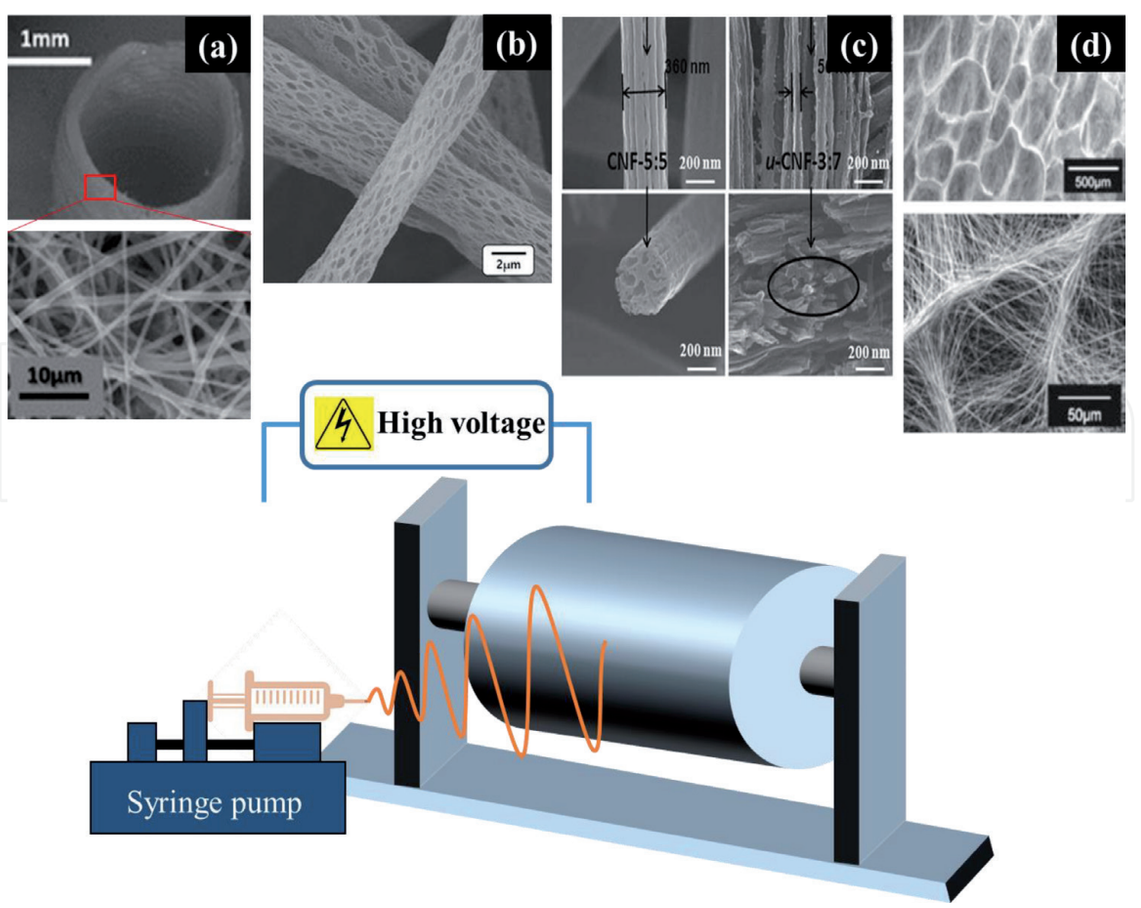


Figure 2.
Electrospinning technique to fabricate nanofibers with different morphology (a) poly(ε-caprolactone)-poly (l-lactic acid) nanofiber tubes [10], (b) cellulose acetate nanofibers with morphology control [11], (c) porous carbon nanofibers [12], and (d) cellulose acetate nanofibers with honeycomb-like surface structure [13].

fabricated by growing zeolitic imidazolate framework-8 (ZIF-8) nanocrystals on the nanofibers. The nanofibers showed high removal efficiency for incense smoke, formaldehyde, and PM particles, which was attributed to the improved surface area and electrostatic interaction between ZIF-8 and particles [16]. Hierarchical bioinspired composite nanofibers comprised of PVA, PAA, GO-COOH, and polydopamine demonstrated the eco-friendly and controllable fabricating process with efficient adsorption capacity for dye removal [17]. The excellent adsorption was due to the strong electrostatic field of carbonyl group modified GO and the unique structure of polydopamine. The membrane exhibited excellent reusability with the potentially large-scale application.

2.2 Electrospinning bio-based polymers for water treatment

Due to concerns about sustainability and environment, bio-based polymers such as cellulose, chitosan, zein, collagen, silk, hyaluronic, alginate, and DNA have been used significantly to fabricate nanofibrous composite membranes [18]. The applications of these polymers in water filtration at the commercialization scale have seen the increase over the past few years due to the beneficial properties of biocompatibility, biodegradability, safety, and nontoxicity. One of the unique features of bio-based polymer is the possession of various functional groups, which can be utilized for pollutant collection (**Figure 3I**). The dye adsorption mechanisms onto polymers can be of chemisorption or physisorption. The former is often related to strong bonding (such as covalent or ionic bonding) or chemical reactions and is irreversible. The latter is a reversible process, thus more preferable. The physisorption is governed by van der Waals forces, hydrogen bonding, hydrophobic interaction, and electrostatic attraction.

Gopakumar and coworkers modified cellulose nanofibers by esterification with Meldrum's acid, which endowed the nanofibers with the affinity toward positively charged dyes [21]; the mechanisms of adsorption were suggested as electrostatic forces between carboxylate groups and the dye molecules. Chitosan/polyamide nanofibers were reported to have excellent adsorption capacity toward anionic dyes, 456.9 mg/g for Reactive Black 5 (RB5) and 502.4 mg/g for Ponceau 4R (P4R), primarily due to the affinity of amino and hydroxyl groups in the chemical structure [22]. With the increase of the ratios of chitosan/polyamide, the adsorption capacities improved, which was assigned to the fact that more reactive sites are present in chitosan than polyamide. Li et al. reported an efficient and facile route to cover electrospun silk nanofibers with MOFs for high removal efficiency toward

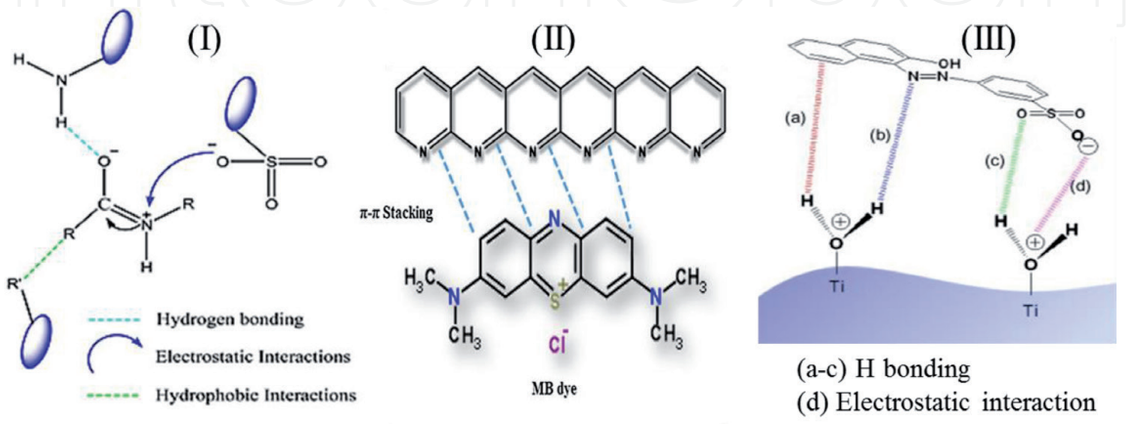


Figure 3.
Mechanism of dye affinity: (I) RB5 on zein nanofibers based on hydrogen bonding, electrostatic interactions, and hydrophobic interactions [19], (II) MB on CNFs governed by π-π stacking interactions [20], and (III) orange II on titania aerogel via H bonding and electrostatic forces [5].

rhodamine B (RB) and malachite green (MG) [23]. The authors successfully loaded the composite nanofibers with high contents of MOFs, and more importantly, the 3D structure of MOFs was well retained within the silk nanofibrous membrane.

2.3 Carbon nanofibers as supporting materials

Carbon nanofibers with unique and tunable morphology have been used in catalytic, environmental, and energy applications [24]. Polyacrylonitrile (PAN) nanofibers have been used extensively as an efficient precursor for CNF fabrication. CNFs have been employed as an efficient carrier for the loading of catalytic and bioactive materials. A broad spectrum of metal oxide nanoparticles has been immobilized in/onto CNFs for dye removal applications. The main approaches to decorate CNFs with active materials include electrodeposition, chemical synthesis, and dry synthesis. Interestingly, the CNFs also present adsorption capacity (**Figure 3II**), due to the binding between aromatic rings of CNFs and adsorbate based on π-π stacking interaction [20]. The high conductive and chemically inert properties of CNFs enhance its application in dye degradation via photocatalysis and promote reusability. The dye molecules have high chances to be attracted to CNFs, having a π-conjugative structure, before being decomposed by photocatalysts loaded on the surface of the nanofibers [25].

3. Adsorptive removal by inorganic absorbents incorporated into nanofibers

3.1 Metal oxide

Transitional metal oxide nanoparticles, including copper oxide, zinc oxide, iron oxide, titanium dioxide, and mixed metal oxide nanocomposites, have been investigated in the dye uptake or dye removal efficiency. Metal oxides have remarkable physical and chemical characteristics, which have been proven useful for water purification. The electrostatic attraction, hydrophobic interactions, and hydrogen linkages between the surface of metal oxides and dye molecules were supposed to dominate the adsorption, controlling the kinetics and isotherm of adsorbent-adsorbate interactions [26].

Li et al. reported that the maximum adsorptions for Fe, Co, and Ni oxides were found to be at neutral pH and the rise of temperature has a positive impact on the capacity of dye removal. The BET surface areas of these composite nanoparticles were reported to be between 97.26 and 273.5 m^2/g [6]. The plausible explanation for the best adsorption capacity at the neutral region is the corrosive destruction of metal oxide nanostructure at high or low pH. At acidic pH, the leaching of metal happens because of the reaction between metal oxides and H^+. At alkaline pH, the hydroxyl groups attach to the active sites on the metal oxides, which are positively charged, reducing the available number of sites and thereby the attraction between adsorbent surface and dye molecules. Malwal and coworkers reported that the pH_{PZC} values of CuO and ZnO nanoparticles were around 9.4 and 9.5, which means at pH lower than pH_{PZC}, the surface of CuO and ZnO becomes positively charged. The electrostatic attraction is the primary mechanism of anionic dye affinity [27]. Similarly, the pH_{PZC} of MgO is 12.4, and the anionic dye adsorption is driven by electrostatic forces. The pH_{PZC} of TiO_2 is around neutral values (6–6.8), which is not so much different from those of iron oxides; the PZC values measured for FeO, Fe_3O_4, and Fe_2O_3 were around 6.1–6.5 [28, 29]. The pH_{PZC} of TiO_2 and iron oxides is in the neutral range, making them efficient adsorbents for both cationic and anionic dyes in a wide range of pH mediums.

The mobilization of metal oxides into carbon nanofibers by several methods has been described in the literature to improve the adsorption performance. The traditional one is to disperse precursors of metal oxides in the PAN polymer solution before electrospinning and carbonization. Nevertheless, the metal oxide nanoparticles are usually located inside the CNFs, which resulted in low adsorption efficiency. Besides, the agglomeration is also of concern because it is detrimental to dye removal efficiency and mechanical properties of the CNFs. The ultrasonic decoration of CNFs with TiO_2 was a straightforward technique to achieve uniform distribution of nanoparticles and yield higher efficiency of dye uptake [30]. TiO_2@carbon composite nanofibers can be prepared by electrospinning technology, followed by a hydrothermal method to acquire the nanoarray structure [31]. The high adsorption performance was explained as the decoration of TiO_2 nanoarray induced the specific surface area enlargement, the tunable wettability from hydrophobicity to the hydrophilicity of the carbon nanofibers, and considerable negative Zeta potential value. Furthermore, the addition of $TiCl_4$ in the electrospinning solution increased the macroscopic flexibility and the adsorption performance of CNF from 9.92 to 24.77% for methylene blue (MB), respectively.

3.2 Zeolite

Zeolite, an aluminosilicate framework obtained from nature, can be chosen as a suitable filler material in the polymeric nanofibrous matrix due to its porous structure and exchangeable cation feature [32]. Its 3D structure with negatively charged lattice, high specific surface area, and competitive price makes zeolite an appealing choice for dye adsorption. The adsorptive sites in zeolites can be controlled by adjusting the ratio between silicon and aluminum. With its strong adsorption capacity for waste products and toxins, zeolite has been reported to show affinity toward methyl orange (MO) [33, 34], MB, and MG [35], with high adsorption capacity and reusability feature. The adsorption mechanisms are complicated, including porous structure, charged surfaces, heterogeneity, and other imperfections. Lee et al. reported that PMMA/zeolite nanofibers exhibit high removal efficiency up to 93% for MO at 30 mg L^{-1}. The isotherm adsorption results were fitted well with the Langmuir model, which indicated that the dye molecules were adsorbed onto the homogeneous surface and monolayer adsorption existed during the process [34].

3.3 Graphene and graphene oxide

Recently, graphene and GO have been studied extensively in the field of catalysis and adsorption as a result of their massive surface area, delocalized π network, and inertness to be used in a wide pH range. Graphene has features of chemical stability, low toxicity, and hydrophobicity. The oxidation of graphene provides an excellent hydrophilic surface; at the same time, it compromises the π electron structure, resulting in poorer attraction to aromatic hazards [36]. The reduction of GO, which forms rGO, is a process to recover the adsorption capacity for GO by giving it back the π-delocalized electron structure and hydrophobic property. Graphene-based materials tend to aggregate due to strong van der Waals and π-π interactions; thus, incorporating them into polymeric nanofibers is a way to overcome the aggregation [7]. Composite GO/PVDF nanofibrous membrane was prepared by ultrasonic treatment for the use of organic dye removal. The facial treatment technique, with the support of ultrasonication, was implemented. The adsorption capacity is mainly dependent on GO contents of the composite membranes, and the

pseudo-second-order model showed a better fit [37]. The mechanism of adsorption was suggested for π-π stacking interaction between delocalized π electrons in graphene and aromatic rings of dyes [38].

3.4 Metal-organic frameworks

MOF is an excellent porous media with a multitude of applications in biomedical engineering, photocatalysis, CO_2 separation, and dye removal. With the properties of chemical and physical stability, effective surface area, excellent adsorption capacity, and nontoxicity, it has been widely used as an essential material for environmental remediation [39]. However, its poor processability hinders the fabrication into filtration devices. Many researchers have successfully applied MOF-based composite nanofibers for contaminant removal from wastewater. Li et al. reported co-electrospun anionic MOF nanofibrous membranes, which displayed synergistic action of PAN and bio-MOF-1 in the adsorption process for MB [8]. The resulting filter could sustain a constantly high adsorption capacity because of the stable nanofibrous structure and no leaching effects. Desorption was conducted in a saturated Na^+ solution based on the ion exchange equilibrium. The ion exchange process happened to settle the dynamic equilibrium between ions of different species. The high adsorption performance of MOF embedded in the polymeric nanofibers could be explained as the diffusion of dye molecules to the surface and internal channels of MOF, which is governed by a multilayered adsorption process associated with the transportation of Gaussian energy into a heterogeneous structure [39].

3.5 Recent novel adsorbents for dye uptake

The surface functions of electrospun composite nanofibers are crucial for dye removing applications, which depend partly on the chemical groups of the used polymers and can be modified by chemical grafting or loaded absorbents. Novel p(NIPAM-co-MAA)/β-CD nanofibers were fabricated by electrospinning and thermal crosslinking for the application of crystal violet (CV) removal. The porous structure obtained from high-temperature treatment caused a hydrophobic surface, which facilitated the dye removal. The high adsorption capacity was attributed to electrostatic attraction, host-guest interaction of β-cyclodextrin, and hydrophobic forces [40]. Zhang and coauthors synthesized acid-activated sepiolite fibers grafted with amino groups for the adsorption of Congo red (CR) [41]. The Weber and Morris model fitting suggested that the adsorption happened through two stages, which included the initial period involving the external mass transfer and the final stage governed by intra-particle diffusion.

Recently, clay minerals have been intensively studied for the fabrication of clay-polymer composite nanofibers owing to the benefits of low cost, nontoxicity, and good adsorption [42]. Montmorillonite/chitosan/PVA nanofibers were utilized for Basic Blue (BB41) separation. The complex formation between amine groups and cationic dyes governed the adsorption and gave an explanation to the maximum adsorption capacity of the composite material at a pH of 7. At acidic pH, the active sites were occupied by hydrogen ions. Natural calcium alginate with biocompatibility and nontoxicity shows promises in colored water treatment due to possessing carboxyl groups, which can attract cationic dye molecules. Gelatin with amino groups also presents high adsorption performance against dyestuffs. The combination of two materials in the form of composite nanofibers showed good adsorption capacity with improved reusability and regeneration compared to using only calcium alginate nanofibers [43].

No.	Adsorbent	Dye	Adsorption capacity, mg g^{-1}	Reference
1.	PVDF/GO nanofibers	MB	621.1	[37]
2.	MOF/PAN nanofibers	MB	20.68	[8]
3.	PVA/PAA/GO-COOH@PDA	MB	26.45	[17]
4.	Gelatin/alginate composite nanofibers	MB	1937	[43]
5.	Zeolitic imidazolate framework-8 functional polyacrylonitrile nanofibers	MB MG	36.92 1531.94	[35]
6.	ZIF-8@CS/PVA-ENF	MG	1000	[39]
7.	MOFs grew on silk nanofibers	RB MG	19 840.2	[23]
8.	CuO-ZnO composite nanofibers	CR	126.4	[27]
9.	NH_2 grafted acid-activated sepiolite fibers	CR	539.71	[41]
10.	Meldrum's acid cellulose nanofibers-based PVDF nanofibers	CV	3.984	[21]
11.	β-Cyclodextrin modified p(NIPAM-co-MAA) nanofibers	CV	1253.78	[40]
12.	Chitosan/polyvinyl alcohol/zeolite electrospun nanofibers	MO	153	[33]
13.	PMMA/zeolite nanofibers	MO	95.33	[34]
14.	Chitosan/polyamide nanofibers	RB5 P4R	456.9 502.4	[22]
15.	APAN/Fe_3O_4–MPA composites nanofiber	Indigo carmine	154.5	[45]

Table 1.
Comparison of different composite nanofibers for the adsorptive removal of dyes.

Owing to the mesoporous structure and the possibility of functionalization, meso-silica has drawn significant interest in the field of dye adsorption. The surface of meso-silica modified with carboxylic acid groups showed affinity toward cationic dyes but presented almost no adsorption for anionic and neutral dyes. The inorganic modification of meso-silica with CuO enhanced the adsorption effects on the cationic dye, which was related to electrostatic forces between CuO and dye molecules [44]. Adsorption capacities of different composite nanofibers for various dyes are listed in **Table 1**.

4. Photocatalytic degradation of dyes using composite nanofibers

4.1 ZnO-loaded nanofibers

The photodegradation is a light-induced process following the contact of contaminants to the photocatalysts, and its efficiency is substantially governed by the adsorption capacity of photocatalysts. Therefore, the adsorption of pollutants into metal oxides is the prerequisite for efficient photodecomposition, which hints that it is necessary to increase the surface area of adsorbents to give more binding sites and restrict the aggregation. Reducing the sizes of metal oxide to nanoscale and loading them onto the surfaces of nanofibers is a well-studied route to improve

the photocatalysis. Among different metal oxide semiconductors, ZnO, an n-type semiconductor in the undoped form, has proven to be an immense potential as a photocatalyst owing to its low cost, environmentally benign character, and high quantum efficiency. ZnO structures with the merit of controllable growth into nanoparticles, spindles, nanorods, and flower-like structures, show promises in photocatalytic dye decomposition. However, the nature of the powder form of ZnO makes the recycling and recovery process an arduous task; the issue can be addressed by immobilizing ZnO to nanofibrous membranes. The processes involving electrospinning and heat treatment were straightforward and delivered an outstanding performance [25, 27]. Besides, due to the wide bandgap of 3.37 eV, the photocatalytic activity of ZnO can only be triggered by UV light. Doping with metals, nonmetals, or other semiconductors can affect the ZnO bandgap, resulting in altered photocatalytic performance. Carbon-doped ZnO nanofibers lowered the bandgap energy of ZnO, which enabled the generation of oxygen and hydroxyl radicals to decompose MB under solar light excitation [46]. The stability of ZnO in mediums with different pH is also a hindrance to commercial purposes. Coating with inert oxides, such as TiO_2 and SiO_2, could show higher photostability and better photolysis due to the passivation of lattice oxygen [47]. In this case, the coating demonstrated remarkably enhanced stability in alkaline and acidic environments as a protective layer.

4.2 TiO_2 composite nanofibers

TiO_2 is one of the most studied semiconductor materials due to many advantages, including the cost-effectiveness, photocatalytic activity, biocompatibility, nontoxicity, and high stability. It has different forms, such as rutile, brookite, and anatase. The bandgaps of TiO_2 are 3.03 and 3.2 eV for rutile and anatase, respectively, and they can be activated by photons in the near UV range ($\lambda < 387$ nm). The technique of decorating TiO_2 onto nanofibers was a well-applied one to deliver the photocatalytic degradation of organic pollutants and mitigate its drawbacks as spontaneous aggregation and the problem of recovery and recycling. TiO_2-embedded CNFs have gained lots of attention in the application of dye elimination by photocatalysis. Liang et al. demonstrated that the CNFs semi-wrapped with TiO_2 could maintain consistently high photocatalytic activities against RB after five times [48]. Besides, significant efforts have been made to dope and functionalize TiO_2 to trigger the bandgap under the visible light. Qiu et al. presented a novel method of immobilizing Mo/N-codoped TiO_2 nanorods onto carbon nanofibers via two facile steps. The composite nanofibers demonstrated superb photocatalytic activity against MB, which suggested that the doping elements exhibited positive effects on dye degradation. H^+ was believed to be the main active species in the photodecomposition confirmed by trapping active species experiments [49]. The doping with other semiconductors has also demonstrated the enhancement in photocatalytic efficiency. Magnetic $ZnFe_2O_4$ with a small bandgap of 1.9 eV was successfully integrated into TiO_2 nanofibers by hydrothermal technique; the composite nanofibers promote the photoresponse under a broader region of solar light than TiO_2 [50].

4.3 Iron-based nanofibrous photocatalysts

Ion-based materials with the unique characteristic of strong magnetic response, leading to unprecedented sorption capacity and photocatalytic activities, have shown great promises in water treatment. The sizes and shapes present significant

influences over the magnetic properties of iron oxide nanoparticles due to the changes in magnetic anisotropy. Among magnetic materials, FeO (wustite), Fe_3O_4 (magnetite), α-Fe_2O_3 (hematite), β-Fe_2O_3 (beta phase), γ-Fe_2O_3 (magnetite), and spinel ferrites (MFe_2O_4) have been focused on for the multiple applications including catalysis, sensors, and magnetic data storage. α-Fe_2O_3 presents weak ferromagnetism (saturation magnetization is less than 1 emu g^{-1}) at room temperature in contrast to γ-Fe_2O_3 and Fe_3O_4 (up to 92 emu g^{-1}). Thus, Fe_3O_4 and γ-Fe_2O_3 have been employed extensively to regenerate photocatalysts owing to good magnetic separation [51]. The convenience of separation by using an external magnetic field helps replace the tedious task of filtration and centrifugation for photocatalyst recovery. One prominent advantage of iron oxides is the relative narrow bandgap for the use of visible light activity, which is between 1.9 and 2.5 eV. In comparison to anatase TiO_2 (3.03–3.2 eV), which can only harvest light at a wavelength of 387 nm or below in the UV region, iron oxide-based photocatalysts prove to be superior in visible light range. The use of heterogeneous photocatalysts can accelerate the photocatalytic performance of iron oxides as a result of the enhanced visible light activation, better separation of electron-hole pair, and interfacial charge transfer. Bi_2MoO_6, which possesses a small bandgap (2.5–2.8 eV), was prepared by electrospinning; then the solvothermal method was followed to prepare 1D α-Fe_2O_3/Bi_2MoO_6 composite nanofibers [52]. The composite was demonstrated to exhibit enhanced photocatalysis in MB and RB degradation under sunlight irradiation because of the charge separation character of heterogeneous α-Fe_2O_3 and Bi_2MoO_6 composite nanomaterials.

4.4 Other photocatalysts

Different photocatalysts such as WO_3, PdO, ZrO_2, and SnO_2 have exhibited distinctive photocatalytic effects against organic dye molecules with various advantageous features such as cost-effectiveness, environmental compatibility, wide applied pH ranges, and flexible nanostructure [26, 53]. WO_3, with its bandgap varied from 2.4 to 2.8 eV, an n-type semiconductor photocatalyst, is considered as a potential photocatalyst; however, due to the fast recombination of electron and hole pairs, the photocatalytic activities of WO_3 were relatively weak. To intercept the recombination as a result of the short diffusion length of charge carriers and enhance the photocatalysis, Ma et al. introduced the grafting of Cu species by impregnation method for interfacial charge transfer effect applied in RB degradation under visible light irradiation [54]. The p- and n-type heterostructured semiconductors show better charge transfer in accordance with Fermi level equilibrium. The redistribution of charges between n-type and p-type produces inner electric fields, which facilitate the transportation of charge carriers and restrict the recombination, thus enhancing the photocatalysis. $CuCrO_2$-decorated SnO_2 composite nanofibers were synthesized by electrospinning, followed by a drop-casting method. The composite nanofibers displayed 41% better rate of constant value in comparison with pure SnO_2 [55]. Zr is in the same group IVB of elements as Ti, but ZrO_2 can only absorb 4% of solar light because of the high energy bandgap and low specific area. Lots of efforts have been made to dope ZrO_2 with other nonmetals, metals, and semiconductors in order to improve light response. The effects of different compositions of TiO_2/ZrO_2 nanofibers were reported in the photocatalytic degradation of MB dye; the nanofibers containing 40 wt% ZrO_2 displayed the best performance under visible light [56]. **Table 2** lists the photocatalytic degradation of varied metal oxide-based composite nanofibers.

No.	Photocatalyst	Dye	Light source	Time (h)	Degradation efficiency, %	Reference
1.	C-doped ZnO nanofiber	MB	Simulated solar light	0.5	> 95	[46]
2.	PdO/WO_3 NFs	MB	Visible light	24	86.4	[9]
3.	Ag-ZnO photocatalyst anchored on carbon nanofibers	MB	UV Visible light	1 2	95 95	[25]
4.	Mo/N-doped TiO_2 nanorods@CNFs	MB	Visible light	3	79.8	[49]
5	$CuCrO_2$-decorated SnO_2 composite nanofibers	MB	UV/visible light	1.5	97	[55]
6.	TiO_2/ZrO_2 composite nanofibers	MB	Visible light	3	82.7	[56]
7.	TiO_2-decorated carbon nanofibers	MB	UV	3	97.4	[30]
8.	TiO_2@carbon flexible fiber	MB	UV	18	76.06	[31]
9.	$ZnFe_2O_4$@ TiO_2 composite nanofibers	MB	Solar light	40 min	> 80	[50]
10.	α-Fe_2O_3/Bi_2MoO_6 composite nanofibers	MB RB	Sunlight	4	94.8 66.8	[52]
11.	Semi-wrapped TiO_2@carbon nanofibers	RB	UV	1	98.2	[48]
12.	WO_3/Cu (II) nanofibers	RB	Visible light	3	85	[54]

Table 2.
Comparison of different photocatalytic materials incorporated into electrospun nanofibers for dye degradation.

5. Conclusion

Electrospun composite nanofibers are advantageous in adsorbing and degrading dyestuffs with better results than using sole absorbents and promote the convenient regeneration. Many transitional metal oxides have shown efficient dye removal effects by both adsorption and photocatalytic degradation. Zeolite, graphene, GO, and MOFs have also demonstrated the high capability for dye adsorption. The mechanisms were driven by physisorption, chemisorption, and so on, which have been discussed thoroughly in this chapter. Future research should be concentrated on combining different adsorbents in the nanofibrous membranes to overcome drawbacks of each adsorbent and create hybrid nanocomposite materials with novelty and super adsorption performance. Lots of advancements are still needed to overcome the remaining issues of recyclability, secondary pollutants, and the viability in the industrial scale for the application in real dye effluents.

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