

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



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 $\text{OH}\cdot$, whereas electrons react with absorbed O_2 to produce oxygen radicals $\text{O}_2\cdot^-$ and other intermediate forms [9]. The hydroxyl

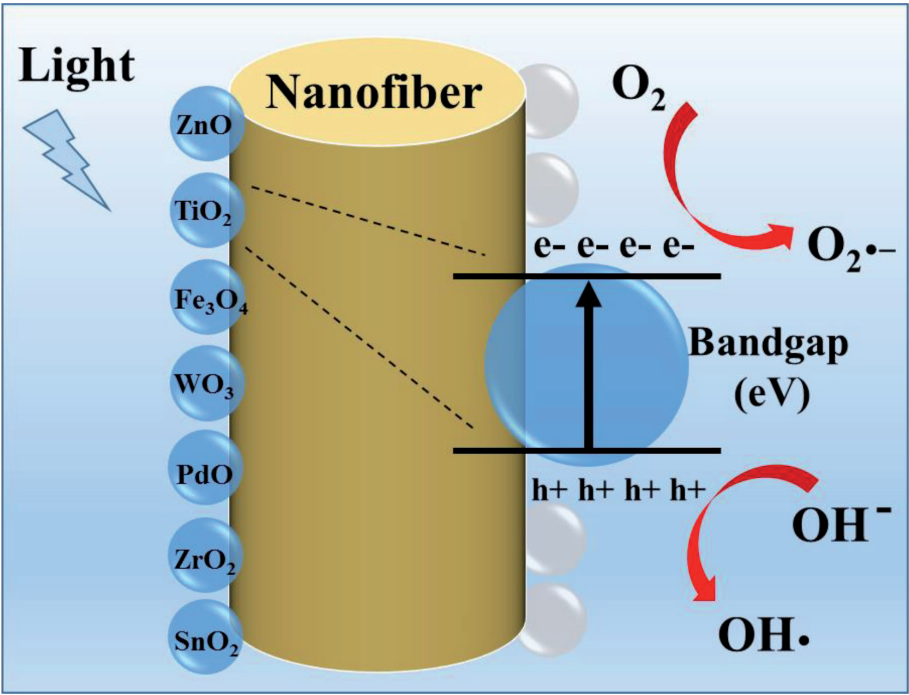


Figure 1. Scheme for photocatalysis of metal oxide nanoparticle-decorated nanofibers under UV or visible light sources.

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

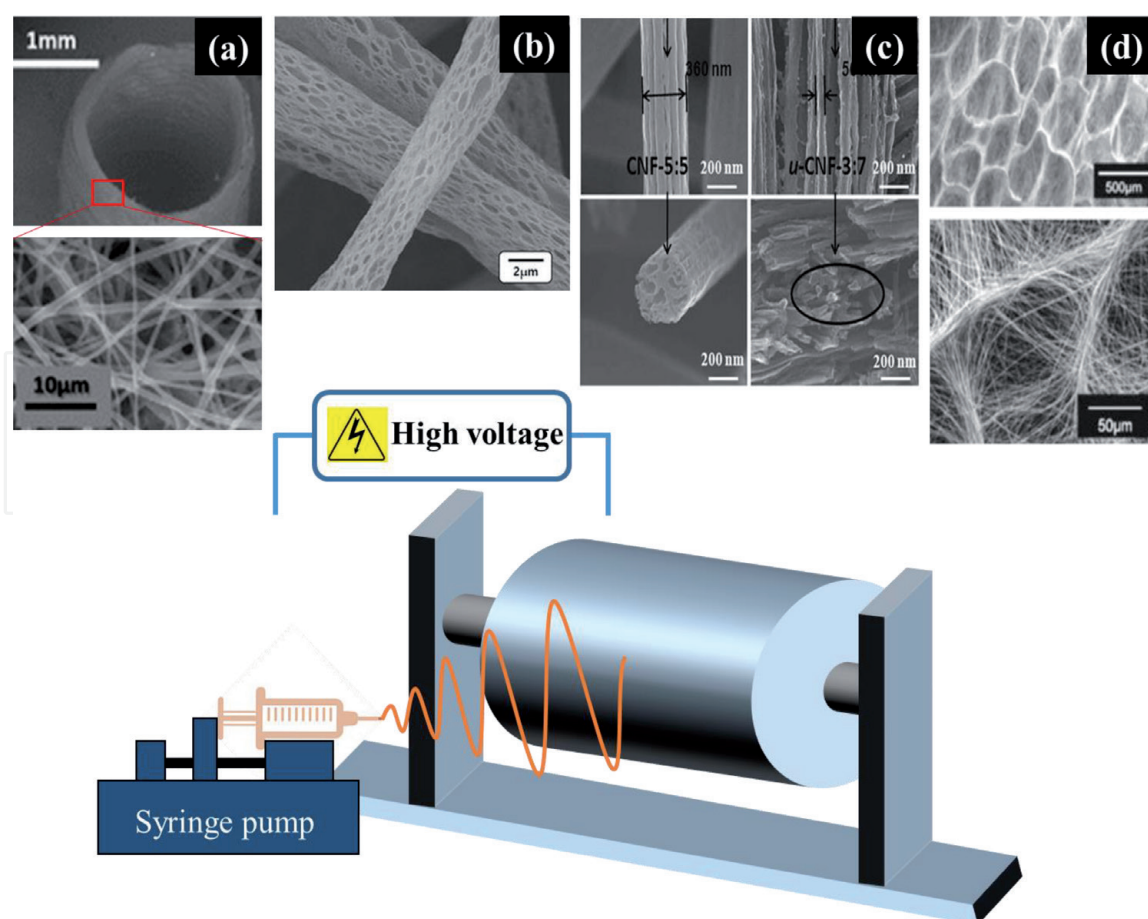


Figure 2. Electrospinning technique to fabricate nanofibers with different morphology (a) poly(ϵ -caprolactone)-poly(l-lactic acid) nanofiber tubes [10], (b) cellulose acetate nanofibers with morphology control [11], (c) porous carbon nanofibers [12], and (d) cellulose acetate nanofibers with honeycomb-like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

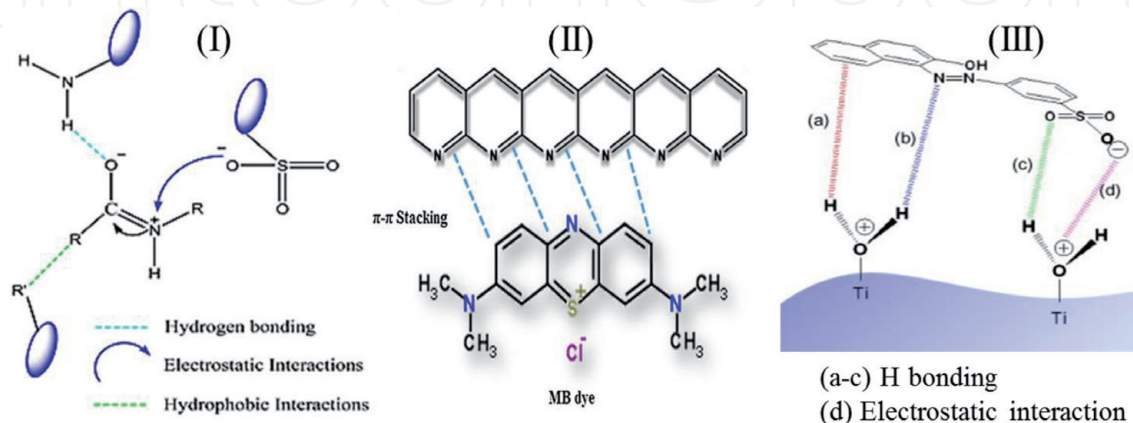


Figure 3. Mechanism of dye affinity: (I) RB5 on zein nanofibers based on hydrogen bonding, electrostatic interactions, and hydrophobic interactions [19], (II) MB on CNFs governed by π - π stacking interactions [20], and (III) orange II on titania aerogel via H bonding and electrostatic forces [5].

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 m²/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 TiO₂ is around neutral values (6–6.8), which is not so much different from those of iron oxides; the PZC values measured for FeO, Fe₃O₄, and Fe₂O₃ were around 6.1–6.5 [28, 29]. The pH_{PZC} of TiO₂ 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, CO₂ 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 ₃ O 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 TiO₂ and SiO₂, 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 TiO₂ composite nanofibers

TiO₂ 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 TiO₂ 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 TiO₂ 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. TiO₂-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 TiO₂ could maintain consistently high photocatalytic activities against RB after five times [48]. Besides, significant efforts have been made to dope and functionalize TiO₂ to trigger the bandgap under the visible light. Qiu et al. presented a novel method of immobilizing Mo/N-codoped TiO₂ 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 ZnFe₂O₄ with a small bandgap of 1.9 eV was successfully integrated into TiO₂ nanofibers by hydrothermal technique; the composite nanofibers promote the photoresponse under a broader region of solar light than TiO₂ [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), Fe₃O₄ (magnetite), α -Fe₂O₃ (hematite), β -Fe₂O₃ (beta phase), γ -Fe₂O₃ (magnetite), and spinel ferrites (MFe₂O₄) have been focused on for the multiple applications including catalysis, sensors, and magnetic data storage. α -Fe₂O₃ presents weak ferromagnetism (saturation magnetization is less than 1 emu g⁻¹) at room temperature in contrast to γ -Fe₂O₃ and Fe₃O₄ (up to 92 emu g⁻¹). Thus, Fe₃O₄ and γ -Fe₂O₃ 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 TiO₂ (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. Bi₂MoO₆, which possesses a small bandgap (2.5–2.8 eV), was prepared by electrospinning; then the solvothermal method was followed to prepare 1D α -Fe₂O₃/Bi₂MoO₆ 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 -Fe₂O₃ and Bi₂MoO₆ composite nanomaterials.

4.4 Other photocatalysts

Different photocatalysts such as WO₃, PdO, ZrO₂, and SnO₂ 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]. WO₃, 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 WO₃ 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. CuCrO₂-decorated SnO₂ 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 SnO₂ [55]. Zr is in the same group IVB of elements as Ti, but ZrO₂ 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 ZrO₂ with other nonmetals, metals, and semiconductors in order to improve light response. The effects of different compositions of TiO₂/ZrO₂ nanofibers were reported in the photocatalytic degradation of MB dye; the nanofibers containing 40 wt% ZrO₂ 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 ₂ O ₄ @TiO ₂ composite nanofibers	MB	Solar light	40 min	> 80	[50]
10.	α-Fe ₂ O ₃ /Bi ₂ MoO 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 nano-composite 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.

IntechOpen

IntechOpen

Author details

Duy-Nam Phan and Ick-Soo Kim*

Division of Frontier Fibers, Nano Fusion Technology Research Group, Institute for Fiber Engineering (IFES), Interdisciplinary Cluster for Cutting Edge Research (ICCER), Shinshu University, Ueda, Nagano, Japan

*Address all correspondence to: kim@shinshu-u.ac.jp

IntechOpen

© 2020 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] Qureshi UA, Khatri Z, Ahmed F, Ibupoto AS, Khatri M, Mahar FK, et al. Highly efficient and robust electrospun nanofibers for selective removal of acid dye. *Journal of Molecular Liquids*. 2017;**244**:478-488
- [2] Gopiraman M, Bang H, Yuan G, Yin C, Song K-H, Lee JS, et al. Noble metal/functionalized cellulose nanofiber composites for catalytic applications. *Carbohydrate Polymers*. 2015;**132**:554-564
- [3] Khatri M, Ahmed F, Shaikh I, Phan D-N, Khan Q, Khatri Z, et al. Dyeing and characterization of regenerated cellulose nanofibers with vat dyes. *Carbohydrate Polymers*. 2017;**174**:443-449
- [4] Phan D-N, Lee H, Choi D, Kang C-Y, Im SS, Kim IS. Fabrication of two polyester nanofiber types containing the biobased monomer isosorbide: Poly (ethylene glycol 1,4-cyclohexane dimethylene isosorbide terephthalate) and poly (1,4-cyclohexane dimethylene isosorbide terephthalate). *Nanomaterials*. 2018;**8**(2):56
- [5] Abramian L, El-Rassy H. Adsorption kinetics and thermodynamics of azo-dye orange II onto highly porous titania aerogel. *Chemical Engineering Journal*. 2009;**150**(2):403-410
- [6] Li LH, Xiao J, Liu P, Yang GW. Super adsorption capability from amorphousization of metal oxide nanoparticles for dye removal. *Scientific Reports*. 2015;**5**(1):9028
- [7] Orozco J, Mercante LA, Pol R, Merkoçi A. Graphene-based Janus micromotors for the dynamic removal of pollutants. *Journal of Materials Chemistry A*. 2016;**4**(9):3371-3378
- [8] Li T, Liu L, Zhang Z, Han Z. Preparation of nanofibrous metal-organic framework filter for rapid adsorption and selective separation of cationic dye from aqueous solution. *Separation and Purification Technology*. 2020;**237**:116360
- [9] Lee H, Kim M, Sohn D, Kim SH, Oh S-G, Im SS, et al. Electrospun tungsten trioxide nanofibers decorated with palladium oxide nanoparticles exhibiting enhanced photocatalytic activity. *RSC Advances*. 2017;**7**(10):6108-6113
- [10] Khatri Z, Nakashima R, Mayakrishnan G, Lee K-H, Park Y-H, Wei K, et al. Preparation and characterization of electrospun poly(ϵ -caprolactone)-poly(l-lactic acid) nanofiber tubes. *Journal of Materials Science*. 2013;**48**(10):3659-3664
- [11] Lee H, Nishino M, Sohn D, Lee JS, Kim IS. Control of the morphology of cellulose acetate nanofibers via electrospinning. *Cellulose*. 2018;**25**(5):2829-2837
- [12] Wei K, Kim K-O, Song K-H, Kang C-Y, Lee JS, Gopiraman M, et al. Nitrogen- and oxygen-containing porous ultrafine carbon nanofiber: A highly flexible electrode material for supercapacitor. *Journal of Materials Science and Technology*. 2017;**33**(5):424-431
- [13] Hamano F, Seki H, Ke M, Gopiraman M, Lim CT, Kim IS. Cellulose acetate nanofiber mat with honeycomb-like surface structure. *Materials Letters*. 2016;**169**:33-36
- [14] Kharaghani D, Tajbakhsh Z, Nam PD, Kim IS. Application of Nanowires for Retinal Regeneration. London: IntechOpen; 2019. DOI: 10.5772/intechopen.90149
- [15] Zhang K, Li Z, Kang W, Deng N, Yan J, Ju J, et al. Preparation and characterization of tree-like cellulose

nanofiber membranes via the electrospinning method. *Carbohydrate Polymers*. 2018;**183**:62-69

[16] Zhu Q, Tang X, Feng S, Zhong Z, Yao J, Yao Z. ZIF-8@SiO₂ composite nanofiber membrane with bioinspired spider web-like structure for efficient air pollution control. *Journal of Membrane Science*. 2019;**581**:252-261

[17] Xing R, Wang W, Jiao T, Ma K, Zhang Q, Hong W, et al. Bioinspired polydopamine sheathed nanofibers containing carboxylate graphene oxide nanosheet for high-efficient dyes scavenger. *ACS Sustainable Chemistry & Engineering*. 2017;**5**(6):4948-4956

[18] Phan D-N, Lee H, Huang B, Mukai Y, Kim I-S. Fabrication of electrospun chitosan/cellulose nanofibers having adsorption property with enhanced mechanical property. *Cellulose*. 2019;**26**(3):1781-1793

[19] Qureshi UA, Khatri Z, Ahmed F, Khatri M, Kim I-S. Electrospun zein nanofiber as a green and recyclable adsorbent for the removal of reactive black 5 from the aqueous phase. *ACS Sustainable Chemistry & Engineering*. 2017;**5**(5):4340-4351

[20] Ibupoto AS, Qureshi UA, Ahmed F, Khatri Z, Khatri M, Maqsood M, et al. Reusable carbon nanofibers for efficient removal of methylene blue from aqueous solution. *Chemical Engineering Research and Design*. 2018;**136**:744-752

[21] Gopakumar DA, Pasquini D, Henrique MA, de Moraes LC, Grohens Y, Thomas S. Meldrum's acid modified cellulose nanofiber-based polyvinylidene fluoride microfiltration membrane for dye water treatment and nanoparticle removal. *ACS Sustainable Chemistry & Engineering*. 2017;**5**(2):2026-2033

[22] Dotto GL, Santos JMN, Tanabe EH, Bertuol DA, Foletto EL, Lima EC,

et al. Chitosan/polyamide nanofibers prepared by Forcespinning® technology: A new adsorbent to remove anionic dyes from aqueous solutions. *Journal of Cleaner Production*. 2017;**144**:120-129

[23] Li Z, Zhou G, Dai H, Yang M, Fu Y, Ying Y, et al. Biomimetic preparation of hybrid membranes with ultra-high loading of pristine metal-organic frameworks grown on silk nanofibers for hazard collection in water. *Journal of Materials Chemistry A*. 2018;**6**(8):3402-3413

[24] Gopiraman M, Kim IS. Preparation, characterization, and applications of electrospun carbon Nanofibers and its composites. In: *Electrospinning and Electrospaying-Techniques and Applications*. London: IntechOpen; 2019. DOI: 10.5772/intechopen.88317

[25] Pant B, Park M, Kim H-Y, Park S-J. Ag-ZnO photocatalyst anchored on carbon nanofibers: Synthesis, characterization, and photocatalytic activities. *Synthetic Metals*. 2016;**220**:533-537

[26] Gusain R, Gupta K, Joshi P, Khatri OP. Adsorptive removal and photocatalytic degradation of organic pollutants using metal oxides and their composites: A comprehensive review. *Advances in Colloid and Interface Science*. 2019;**272**:102009

[27] Malwal D, Gopinath P. Efficient adsorption and antibacterial properties of electrospun CuO-ZnO composite nanofibers for water remediation. *Journal of Hazardous Materials*. 2017;**321**:611-621

[28] Karunanayake AG, Navarathna CM, Gunatilake SR, Crowley M, Anderson R, Mohan D, et al. Fe₃O₄ nanoparticles dispersed on douglas fir biochar for phosphate sorption. *ACS Applied Nano Materials*. 2019;**2**(6):3467-3479

- [29] Zhang C, Li Y, Wang F, Yu Z, Wei J, Yang Z, et al. Performance of magnetic zirconium-iron oxide nanoparticle in the removal of phosphate from aqueous solution. *Applied Surface Science*. 2017;**396**:1783-1792
- [30] Wang H, Huang X, Li W, Gao J, Xue H, Li RKY, et al. TiO₂ nanoparticle decorated carbon nanofibers for removal of organic dyes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2018;**549**:205-211
- [31] Xiao F, Guo X, Li J, Sun H, Zhang H, Wang W. Electrospinning preparation and dye adsorption capacity of TiO₂@ carbon flexible fiber. *Ceramics International*. 2019;**45**(9):11856-11860
- [32] Barhoum A, Pal K, Rahier H, Uludag H, Kim IS, Bechelany M. Nanofibers as new-generation materials: From spinning and nano-spinning fabrication techniques to emerging applications. *Applied Materials Today*. 2019;**17**:1-35
- [33] Habiba U, Siddique TA, Li Lee JJ, Joo TC, Ang BC, Afifi AM. Adsorption study of methyl orange by chitosan/polyvinyl alcohol/zeolite electrospun composite nanofibrous membrane. *Carbohydrate Polymers*. 2018;**191**:79-85
- [34] Lee JLL, Ang BC, Andriyana A, Shariful MI, Amalina MA. Fabrication of PMMA/zeolite nanofibrous membrane through electrospinning and its adsorption behavior. *Journal of Applied Polymer Science*. 2016;**134**(6):44450. DOI: 10.1002/app.44450
- [35] Zhan Y, Guan X, Ren E, Lin S, Lan J. Fabrication of zeolitic imidazolate framework-8 functional polyacrylonitrile nanofibrous mats for dye removal. *Journal of Polymer Research*. 2019;**26**(6):145
- [36] Mercante LA, Facure MHM, Locilento DA, Sanfelice RC, Migliorini FL, Mattoso LHC, et al. Solution blow spun PMMA nanofibers wrapped with reduced graphene oxide as an efficient dye adsorbent. *New Journal of Chemistry*. 2017;**41**(17):9087-9094
- [37] Ma F-f, Zhang D, Huang T, Zhang N, Wang Y. Ultrasonication-assisted deposition of graphene oxide on electrospun poly(vinylidene fluoride) membrane and the adsorption behavior. *Chemical Engineering Journal*. 2019;**358**:1065-1073
- [38] Tran HN, Wang Y-F, You S-J, Chao H-P. Insights into the mechanism of cationic dye adsorption on activated charcoal: The importance of π - π interactions. *Process Safety and Environmental Protection*. 2017;**107**:168-180
- [39] Mahmoodi NM, Oveisi M, Taghizadeh A, Taghizadeh M. Synthesis of pearl necklace-like ZIF-8@chitosan/PVA nanofiber with synergistic effect for recycling aqueous dye removal. *Carbohydrate Polymers*. 2020;**227**:115364
- [40] Jia S, Tang D, Peng J, Sun Z, Yang X. β -Cyclodextrin modified electrospinning fibers with good regeneration for efficient temperature-enhanced adsorption of crystal violet. *Carbohydrate Polymers*. 2019;**208**:486-494
- [41] Zhang J, Yan Z, Ouyang J, Yang H, Chen D. Highly dispersed sepiolite-based organic modified nanofibers for enhanced adsorption of Congo red. *Applied Clay Science*. 2018;**157**:76-85
- [42] Hosseini SA, Vossoughi M, Mahmoodi NM, Sadrzadeh M. Clay-based electrospun nanofibrous membranes for colored wastewater treatment. *Applied Clay Science*. 2019;**168**:77-86
- [43] Ma Y, Qi P, Ju J, Wang Q, Hao L, Wang R, et al. Gelatin/alginate

- composite nanofiber membranes for effective and even adsorption of cationic dyes. *Composites Part B: Engineering*. 2019;**162**:671-677
- [44] Liang Z, Zhao Z, Sun T, Shi W, Cui F. Enhanced adsorption of the cationic dyes in the spherical CuO/meso-silica nano composite and impact of solution chemistry. *Journal of Colloid and Interface Science*. 2017;**485**:192-200
- [45] Yazdi MG, Ivanic M, Mohamed A, Uheida A. Surface modified composite nanofibers for the removal of indigo carmine dye from polluted water. *RSC Advances*. 2018;**8**(43):24588-24598
- [46] Gadisa BT, Appiah-Ntiamoah R, Kim H. In-situ derived hierarchical ZnO/Zn-C nanofiber with high photocatalytic activity and recyclability under solar light. *Applied Surface Science*. 2019;**491**:350-359
- [47] Wang Y, Zheng Y-Z, Lu S, Tao X, Che Y, Chen J-F. Visible-light-responsive TiO₂-coated ZnO:In nanorod array films with enhanced photoelectrochemical and photocatalytic performance. *ACS Applied Materials & Interfaces*. 2015;**7**(11):6093-6101
- [48] Liang Y, Zhou B, Li N, Liu L, Xu Z, Li F, et al. Enhanced dye photocatalysis and recycling abilities of semi-wrapped TiO₂@carbon nanofibers formed via foaming agent driving. *Ceramics International*. 2018;**44**(2):1711-1718
- [49] Qiu J, Liu F, Yue C, Ling C, Li A. A recyclable nanosheet of Mo/N-doped TiO₂ nanorods decorated on carbon nanofibers for organic pollutants degradation under simulated sunlight irradiation. *Chemosphere*. 2019;**215**:280-293
- [50] Al-Meer S, Ghouri ZK, Elsaid K, Easa A, Al-Qahtani MT, Shaheer Akhtar M. Engineering of magnetically separable ZnFe₂O₄@ TiO₂ nanofibers for dye-sensitized solar cells and removal of pollutant from water. *Journal of Alloys and Compounds*. 2017;**723**:477-483
- [51] Wu W, Changzhong J, Roy VAL. Recent progress in magnetic iron oxide–semiconductor composite nanomaterials as promising photocatalysts. *Nanoscale*. 2015;**7**(1):38-58
- [52] Zhao J, Lu Q, Wang Q, Ma Q. α -Fe₂O₃ nanoparticles on Bi₂MoO₆ nanofibers: One-dimensional heterostructures synergistic system with enhanced photocatalytic activity. *Superlattices and Microstructures*. 2016;**91**:148-157
- [53] Wang X, Dou L, Yang L, Yu J, Ding B. Hierarchical structured MnO₂@SiO₂ nanofibrous membranes with superb flexibility and enhanced catalytic performance. *Journal of Hazardous Materials*. 2017;**324**:203-212
- [54] Ma G, Lu J, Meng Q, Lv H, Shui L, Zhang Y, et al. Synergistic effect of Cu-ion and WO₃ nanofibers on the enhanced photocatalytic degradation of Rhodamine B and aniline solution. *Applied Surface Science*. 2018;**451**:306-314
- [55] Dursun S, Kaya IC, Kalem V, Akyildiz H. UV/visible light active CuCrO₂ nanoparticle–SnO₂ nanofiber p–n heterostructured photocatalysts for photocatalytic applications. *Dalton Transactions*. 2018;**47**(41):14662-14678
- [56] Yasin AS, Obaid M, El-Newehy MH, Al-Deyab SS, Barakat NAM. Influence of TixZr(1–x)O₂ nanofibers composition on the photocatalytic activity toward organic pollutants degradation and water splitting. *Ceramics International*. 2015;**41**(9, Part B):11876-11885