Review

Electrospun nanofibers for efficient adsorption of heavy metals from water and wastewater

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Abstract: Heavy metals (HMs) are persistent and toxic environmental pollutants that pose critical risks toward human health and environmental safety. Their efficient elimination from water and wastewater is essential to protect public health, ensure environmental safety, and enhance sustainability. In the recent decade, nanomaterials have been developed extensively for rapid and effective removal of HMs from water and wastewater and to address the certain economical and operational challenges associated with conventional treatment practices, including chemical precipitation, ion exchange, adsorption, and membrane separation. However, the complicated and expensive manufacturing process of nanoparticles and nanotubes, their reduced adsorption capacity due to the aggregation, and challenging recovery from aqueous solutions limited their widespread applications for HM removal practices. Thus, the nanofibers have emerged as promising adsorbents due to their flexible and facile production process, large surface area, and simple recovery. A growing number of chemical modification methods have been devised to promote the nanofibers' adsorption capacity and stability within the aqueous systems. This paper briefly discusses the challenges regarding the effective and economical application of conventional treatment practices for HM removal. It also identifies the practical challenges for widespread applications of nanomaterials such as nanoparticles and nanotubes as HMs adsorbents. This paper focuses on nanofibers as promising HMs adsorbents and reviews the most recent advances in terms of chemical grafting of nanofibers, using the polymers blend, and producing the composite nanofibers to create highly effective and stable HMs adsorbent materials. Furthermore, the parameters that influence the HM removal by electrospun nanofibers and the reusability of adsorbent nanofibers were discussed. Future research needs to address the gap between laboratory investigations and commercial applications of adsorbent

nanofibers for water and wastewater treatment practices are also presented.

Keywords: heavy metals; nanofiber; electrospinning; polymer; adsorption; water; wastewater

Abbreviations: AOPAN/RC: Amidoxime Polyacrylonitrile/Regenerated Cellulose; APTES: Aminopropyl Triethoxysilane; CA: Cellulose Acetate; CNT: Carbon Nanotube; CS: Chitosan; ECNFs: Electrospun Carbon Nanofibers; EDTA: Ethylenediaminetetraacetic acid; FMBO: Fe-Mn Binary Oxide; GO: Graphene Oxide; HMs: Heavy Metals; HAp: Hydroxy Apatite; NPs: Nanoparticles; PAA: Polyacrylic Acid; PAAS: Polyacrylic Acid Sodium; PAN: Polyacrylonitrile; PEI: Polyethyleneimine; PEO: Polyethylene Oxide; PET: Polyethylene Terephthalate; PGMA: Polyglycidyl Methacrylate; PPy: Polypyrrole; PS: Polystyrene; PVA: Polyvinyl Alcohol; PVC: Polyvinyl Chloride; PVDF: Polyvinylidine Fluoride; RO: Reverse Osmosis; TEOS: Tetraethylorthosilicate

1. Introduction

Heavy metals (HMs) are persistent and toxic pollutants even at very low concentrations. They could be naturally present within the environment or be introduced by anthropogenic activities [1–3]. Natural processes such as volcanic activity, soil erosion, and rock weathering could release some levels of Arsenic (As), Cadmium (Cd), Mercury (Hg), Lead (Pb), Copper (Cu), Chromium (Cr), and Zinc (Zn) to the surface or groundwater resources [4–6]. However, most of HMs present in surface waters are originated from storm runoff pollutants, inappropriate wastewater discharge, and chemical spills [7–12]. For instance, excessive and reparative application of HMs containing pesticides and fertilizers and metal-enriched wastewater for crop irrigation could enhance the HMs loadings in agricultural fields runoff [13,14]. High levels of As, Hg, Pb, Zn, Cd, and Cu are also present in wastewater generated by industries such as metal manufacture, paints, pigment, pulp and paper, tannery, distillery, textiles, rubber, steel plant, and mining [7,15,16]. Efficient wastewater treatment practices should be applied to reduce HMs concentrations significantly below the regulatory limits before discharging them to the streams. The HMs release to water resources could endanger the aquatic life and threaten the drinking water safety. Thus, water treatment plants are mandated to reduce HMs concentrations below the regulatory limits. Nonetheless, metallic conveyance used to transport the water in distribution systems and building plumbing materials may release some HMs such as Pb, Zn, Fe, Cu, Ni, and Cr to the tap water [8,17–21]. Table 1 summarizes the sources releasing the HMs to the aquatic environment.

HMs are increasingly recognized as a serious public health concern. To date, numerous studies highlighted the major health issues associated with HMs exposure in drinking water [22–25]. HMs exposure could result in severe health impacts such as liver disease, delay in children's mental development, behavioral disorders, brain and kidney damage, skin, liver, bladder, and lung cancers [24,26–29]. Furthermore, co-exposure to multiple metals in drinking water could intensify the severity of related health impacts [30–32]. HMs release to surface water could adversely impact the aquatic organisms' DNA and enzymatic functions and interfere with their life processes [33,34]. Therefore, efficient removal of HMs from industrial wastewater is crucial to prevent them from polluting the drinking water resources and impacting the aquatic ecosystem. Additionally, recovering the HMs such as Cr, Ni,

Ag, Pb, Cu, and Mn from industrial wastewater promotes metals conservation and environmental sustainability while generating some economic benefits [35–37].

Table 1. The list of major sources releasing HMs to aquatic environments.

Source			Heavy Metals	Ref
Natural Sources	Geological sources		Ni, Pb, As, Se, Cu, Zn, Cd	[38–40]
	Atmospheric deposition		Cd, Pb, Cr, Cu, Ni, Zn	[41,42]
Anthropogenic Sources	Industries	Nuclear plants	Cu, Fe, Cd, Hg	[43]
		Mine tailing	Pb, Zn, Cu, Fe	[44]
		Battery	Cd, Pb, Mn, Zn, Fe	[45,46]
		Steel, Alloy manufacture	Cr, Hg, Pb, Zn, Ni, Cu, As, Cd, Sn	[47,48]
		Textile	Cu, Cr, Ni, Pb, Cd, Zn, As	[49,50]
		Others	Cd, Cr, Cu, Ni, Pb, Zn, Hg, As, Al, Fe, Mn, Se	[51,52]
	Agriculture	Fertilizers	Cu, Cr, Pb, Zn, Cd, As	[53,54]
		Herbicides, Pesticides	Pb, Ni, Cr, As	[55]
	Water distribution systems	Metallic pipe, brass, and fittings corrosion	Pb, Zn, Cu, Ni, Cr, Cd	[56,57] [58–60]
	Storm runoff		Pb, Zn, Cu, Cd	[11,61]
	Chemical spills		Cu, Ni, Pb, Mn, Zn, Hg, Fe, Cu, As, Co	[9,62]

Chemical precipitation, ion exchange, adsorption, and membrane separation are the most common practices applied to remove HMs from water and wastewater [63–67]. Despite their popularity, there are certain drawbacks regarding their economical and efficient operations. Thus, in recent decades nanotechnology has been emerged for various water and wastewater treatment purposes [68–72]. Nanoparticles, nanotubes, nanocomposites, and nanofibers are among the most well-known nanomaterials being used for HM removal from water and wastewater [73–75]. Nanofibers have demonstrated outstanding contaminant removal characteristics due to their high porosity, large surface to volume ratio, fibers' interconnectivity, and small diameters [76–78]. The nanofibers flexible production process beneficially provides the opportunity to prepare products with well-defined composition and structures [79,80]. These superior characteristics resulted in their high selectivity and permeability, low transmembrane pressures, and low maintenance and operating costs for water and wastewater treatment practices. This paper (1) describes the challenges regarding the application of conventional HM removal practices; (2) overviews the most common nanomaterials for HM removal from water; (3) reviews the recent advances in the synthesis of electrospun nanofibers for HM removal purposes; (4) discusses the factors that influence the magnitude of HM adsorption, nanofibers regeneration and reuse, and future research needs to address the gap between laboratory investigations and commercial application of adsorbent nanofibers for HM removal.

2. Conventional treatment practices for HM removal

Chemical precipitation, ion exchange, adsorption, and membrane separation are the most common practices for HM removal from water and wastewater. Through chemical precipitation, a chemical agent is applied to convert the dissolved metal ions to insoluble species that could be removed via settling and filtration [81]. The process efficiency depends on precipitant dosage, pH, contact time, and alkalinity of water or wastewater [81,82]. Chemical precipitation is a low-cost treatment method that involves simple pH adjustment, inexpensive equipment, limited maintenance, and convenient and safe operations. Nonetheless, it has low efficiency, slow kinetics, poor settling properties, and generates a large volume of sludge that requires further treatment [83]. The sludge disposal raises environmental safety concerns regarding the potential long-term ecological impacts [84].

The ion exchange process is an efficient reversible chemical practice where an ion from water or wastewater is exchanged with a similarly charged ion attached to an immobile solid particle [63,85]. The ion exchange resins mostly have a considerable HM removal capacity, high efficiency, and fast kinetics [86]. The magnitude of HM removal by ion-exchange resins is influenced by pH, temperature, initial metal concentration, and contact time [87,88]. Synthetic resins, natural zeolites, and naturally occurring silicate minerals have been widely used to remove HMs from aqueous solutions due to their low cost and high abundance [89–91]. Fouling of resins during the treatment of highly contaminated wastewater is a major disadvantage for this practice [83,86]. Furthermore, applying the ion exchange separation process for treating a large volume of water with a low metal concentration is not economical.

Adsorption is recognized as an effective, economic, and widely used method for HM removal from water and wastewater. Adsorption is a mass transfer process in which HM ions are transferred from an aqueous solution to the solid surface through physical or chemical interactions [83]. Adsorption could be reversible, so the adsorbents can be regenerated through an appropriate desorption process. Adsorption is one of the most preferred treatment practices as several contaminant could be removed simultaneously, without any significant energy consumption [92]. Activated carbon adsorbents are widely used for HM removal, although nowadays, the depleted sources of commercial coal-based activated carbon resulted in raising their cost. During the recent decade, numerous low-cost adsorbents were developed using agricultural wastes and industrial by-products such as lignite, lignin, aragonite shells, natural zeolites, clay, and peat [88,91,93–95]. Biosorption of HMs from water and wastewater is a relatively new and cost-effective practice. The typical biosorbents can be derived from non-living biomass and agricultural wastes, algal or microbial biomass [65,96–98]. Most of adsorbents are in the form of powder or flake, which resulted in their lower surface area to volume ratio and reduced HM removal efficiency. Generally, the adsorption process is simple, effective, and flexible in design, but an additional step of the adsorbent separation process from an aqueous solution is inevitable. Thus, it is desirable to create a continuous structure as an adsorbent to overcome the difficulties associated with the separation of powder adsorbents.

Membrane technologies including low pressure (microfiltration, ultrafiltration) [99,100], high pressure (reverse osmosis, nanofiltration) [101,102], and osmotic pressure driven membranes (forward osmosis) [103] have been widely used for the water treatment. Membranes are operating based on their pore size, pore distribution, surface hydrophilicity, surface charge, and functional groups [104]. The membranes' performance is determined by both selectivity and flux rate. The microfiltration and ultrafiltration membranes operating at low pressure, but their pore sizes are not small enough to

remove the HM ions from water or wastewater [86,104]. Thus, the chemically modified ultrafiltration processes such as micellar enhanced ultrafiltration and polymer enhanced ultrafiltration have been emerged to enhance the HM removal efficiency [105,106]. The membranes performance is influenced by operational conditions, metals and surfactants concentrations, pH, and ionic strength [107]. Nanofiltration is a relatively new technology for the rejection of HMs such as Pb, Ni, Cr, Cu, and As from water or wastewater [108]. This process benefits from the simplicity of operation, low energy consumption, and good HM removal efficiency [86]. Although, the pretreatment is mostly required to reduce the fouling of nanofiltration membranes [109]. Reverse osmosis (RO) is a semi-permeable membrane that acts as a molecular sieve to remove dissolved minerals. Although it can remove both monovalent and multivalent ions, but it works better for multivalent ions [109]. During the RO process, a concentrated by-product solution is generated that should be disposed properly or treated effectively to recover the HMs. Despite the RO's high efficiency, they are expensive membranes to produce and operate. Operating at elevated pressures makes the RO process costly and highly dependent on the operational conditions. Forward osmosis membranes could be used effectively to remove HMs from water. The driving force of this process is the osmotic pressure difference across the semi-permeable membrane. In comparison to pressure driven processes, forward osmosis membranes offer the advantages of no or low operation pressure, low fouling propensity, and easy cleaning [110,111]. Advance technologies are needed to address the economical and operational shortcomings associated with the conventional HM removal practices.

3. Nanomaterials for HM removal

Recent advances in nanotechnology have accelerated production of functionalized nanomaterials for HM removal from water and wastewater [112,113]. Nanomaterials have one, two, or three dimensions in the range of 1–100 nm and offer an elevated surface area, desired surface functional groups, accelerated HMs adsorption kinetics, and enhanced removal efficiencies. The nanoparticles, nano-composites [114], nano-beads [115], nano-fibers [116], and magnetic nano-adsorbents [117] have demonstrated the outstanding HM removal performance. Carbon and graphene based nanomaterials such as carbon nanotubes (CNTs) and graphene oxides (GOs) have demonstrated great performance in Pb, Cd, Cr, Cu, and Ni removal from water and wastewater [71,90,118–124]. The single wall or multiwall carbon nanotubes could be simply functionalized with organic molecules to have superior selectivity and adsorption characteristics. Surface functionalization of CNTs with the ligands such as carboxyl (-COOH), amino ($-NH_2$) and hydroxyl (-OH) has promoted their complexation with the HM ions [125,126]. Nonetheless, the commercial application of CNTs for HM removal is limited due to the CNTs costly production process. Furthermore, CNTs complete separation from wastewater after the adsorption process is problematic. The CNTs' eventual discharge to the environment is raising concerns regarding the generation of secondary pollutants and potential risks toward human health and ecology safety [127]. Limited studies have been conducted to resolve this problem by creating composites with biocompatible materials [128]. Research on CNTs has been mostly restricted to their applications and limited attention has been paid to their toxicological impacts. Graphene oxides and reduced graphene oxides nanoparticles have provided great adsorption capacities for HMs such as Cr, Ni, Pb, and Cu [129]. The oxygen-containing [-OH, -COOH, -COC-, -C=O], sulfur-containing [-C=S, -C-S, -SH], and nitrogen-containing [-NH, -CN, -C=N] functional groups were introduced into the GO-based materials through chemical modification processes to promote

their HM removal efficiencies [123,130]. The evaluated hydrophilicity and agglomeration of these nanoparticles have created some challenges for their effective separation from aqueous phase after the adsorption process [131]. To resolve this recovery issue, advanced methodologies are evolving rapidly to incorporate carbon-based nanomaterials into the other nanostructures such as nanofibers [132].

The great reduction and adsorption capacity of nanoscale zero valent metals (NZVMs) have promoted their applications for HM removal practices [133–136]. For instance, the core-shell structure of zero valent iron nanoparticle combines the reducing power of its metallic core to the oxides/hydroxides shell, which attracts the HMs through electrostatic or surface complexation mechanisms [137]. The nanosized metal oxides such as iron oxides [α-FeOOH, α-Fe$_2$O$_3$, γ-Fe$_2$O$_3$, Fe$_3$O$_4$], zinc oxide [ZnO], titanium oxides [TiO$_2$], aluminum oxides [Al$_2$O$_3$], hydrous manganese oxides [MnO$_2$], and magnesium oxides [MgO] also demonstrated elevated selectivity and HM removal efficiencies compared to the conventional adsorbents [130,138–141]. Evaluation of HMs adsorption characteristics of iron oxide nanoparticles revealed the critical influences of particles size and functionality, solution pH, type and concentration of HM ions, and contact time [142–148]. The instability and aggregation of nanoparticles reduce their HMs adsorption capacities. Moreover, the complex and expensive production process of nanoparticles limits their commercial applications [130]. More investigation is needed to produce the market available nanomaterials. Future research is needed to identify the fate, toxicity, and environmental and human health impacts of nanomaterials.

4. Polymeric nanofibers for HM removal

Challenges associated with the implementation of conventional HM removal practices could be addressed via the application of adsorbent nanofibers. For instance, the nanofibers' large surface to volume ratio, flexibility, interconnectivity, small diameter, and porosity resulted in their elevated HM adsorption capacity and rapid kinetics [149–151]. However, the conventional chemical precipitation approaches are suffering from low efficiency and slow kinetics while generating a significant volume of sludge and created the environmental safety concerns [83,84]. Furthermore, the charming characteristics of nanofibers resulted in nanofibrous adsorbent membranes to have high selectivity and permeability, low transmembrane pressures, low maintenance, and operating costs. Although, the conventional membrane processes are consuming a significant level of energy due to their high transmembrane pressure and are costly to operate. The ion exchange resins are costly to produce and foul rapidly by highly contaminated wastewater [83,86]. However, the nanofibers' large surface area provides numerous surface sites for HM adsorption which facilitates the treatment of highly contaminated wastewater. Nanofibers remove the HMs mostly through adsorption process which is able to remove several contaminant simultaneously, without any significant energy consumption [92]. However, the lower surface area provided by conventional powder or granular adsorbents such as activated carbon resulted in their lower adsorption capacity and slower adsorption rate. Furthermore, the interconnected structure of nanofibrous webs facilitates their efficient recovery following the adsorption process. Although the nanoparticles are also offering a great surface area and adsorption capacity for HM removal, their evaluated hydrophilicity and agglomeration have created significant challenges in their effective recovery from the aqueous phase after the adsorption process [131]. The rapid and effective removal of nanoparticles after the adsorption process is challenging due to their small size. Thus, their discharge to the water resources could generate the secondary pollution problem and raise the recovery costs [152,153]. However, embedding these nanoparticles into other nanostructures such as

nanofibers could resolve this problem [132].

Polymeric nanofibers have shown outstanding performance in contaminant removal from water and wastewater due to their high porosity, large surface to volume ratio, fibers interconnectivity, and small diameters [149–151]. The nanofibers offer the advantages provided by both bulk adsorbents and nanomaterials in terms of facile separation from the aqueous phase and the large numbers of available surface sites due to their elevated surface area. Numerous polymers have been simply electrospun and undergone chemical modifications for enhanced HM removal characteristics. A general comparison of the performance of absorbent nanofibers with other major HM removal practices is shown in Table 2.

Table 2. A comparison of absorbent nanofibers with other major HM removal practices.

Method		Efficiency	Selectivity	Kinetics	Waste Generation	Energy Consumption	Permeate Purity
Chemical Precipitation		Low-Moderate	Low	Slow	High	Low	Low
Ion Exchange		Moderate-High	Moderate	Moderate-Fast	Low	Low	Moderate
Membrane	Microfiltration	None	None	N/A	Low	Moderate	Moderate
	Ultrafiltration	Low	Low		Low	Moderate	Moderate
	Nanofiltration	Moderate	Moderate		Low	Moderate-High	High
	Reverse Osmosis	High	Hight		Low	High	High
Adsorption	Conventional Adsorbents	Moderate	Moderate	Moderate-Fast	Low	Low	Low-Moderate
	Nanoparticle, Nanotube	Moderate-High	Moderate-High	Fast	Low	Low	Low-Moderate
	Nanofibers	Moderate-High	Moderate-High	Fast	Low	Low	Low-Moderate

The nanofibers application for HM removal from water and wastewater has mainly explored as adsorbent materials, and less attention has been paid to their performance as adsorbent membranes. However, the low transmembrane pressure and elevated water flux caused by the high surface area, permeability, tortuosity, and porosity of nanofibrous webs promoted their application for membrane separation processes [154]. The large pore size of regular synthetic nanofibrous webs limits their capability to remove the small size metal ions from the aqueous solutions. Nonetheless, the modified nanofibers could be effectively used to produce the adsorbent membrane which functions as both adsorbent and membrane filters to remove the low concentrations of HMs from water or wastewater. This paper only focuses on recent developments regarding generation of highly adsorbent nanofibers. As demonstrated in Figure 1, HMs are removed by polymeric nanofibers mostly through ion exchange process, electrostatic interaction, and surface complexation. The nanofibers can act as an ion exchange media which their surface ions are exchanged with the cation or anion in aqueous solution [155,156]. The Pb^{2+} removal by cellulose acetate (CA) nanofibers that were impregnated with hydroxyapatite (HAp) was found as an ion exchange process, in which Pb^{2+} ions from the aqueous solution substituted the Ca^{2+} ions present in nanofibers structure (Figure 1a) [78]. The coordination bonding resulted from complexation

between nanofibers surface functional groups (ligands) and metal ions in the aqueous solution could also trigger the HM removal. The electrospun polyacrylonitrile/cellulose acetate (PAN/CA) nanofibers that undergone the hydrolysis and amidoximation processes demonstrated the Fe^{3+}, Cu^{2+}, and Cd^{2+} removal through coordination of these cations with hydroxyl and omidoxime functions present on nanofibers surface (Figure 1b) [157]. The electrostatic interaction between HM species present in aqueous solution with neutral or differently charged functional groups on nanofibers could result in HM removal [158,159]. The modified PAN nanofibers containing amino (-NH$_2$) groups adsorbed the Cr^{6+} oxyanions through electrostatic attraction at low pH values, where the amino groups were more protonated and attracted the Cr^{6+} oxyanions (Figure 1c) [160].
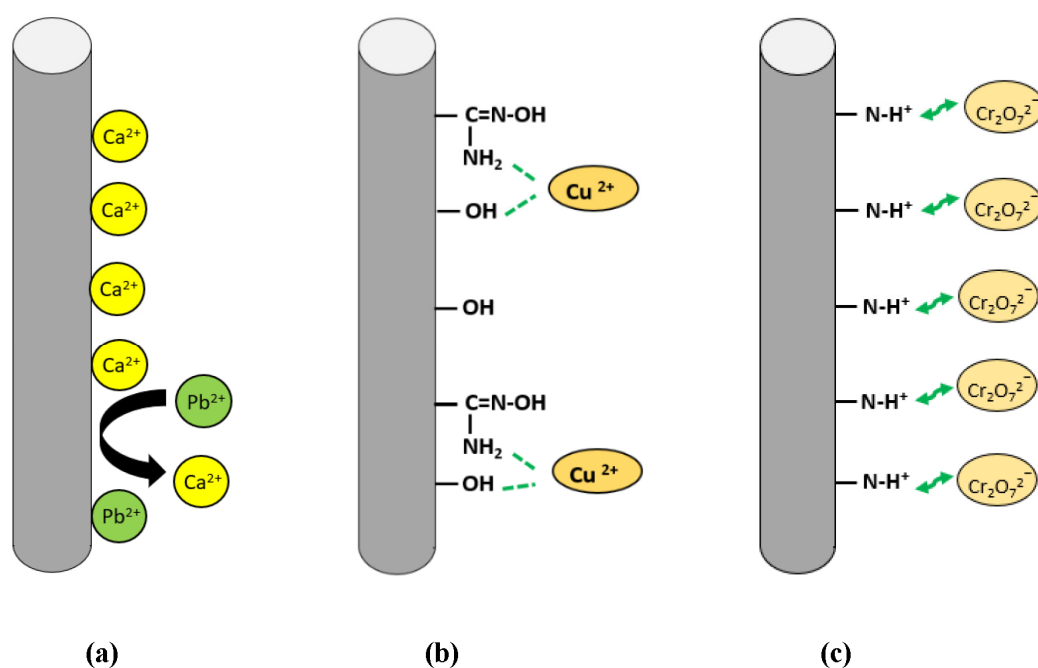

Figure 1. The schematic demonstrating the (a) ion exchange, (b) complexation, and (c) electrostatic interactions responsible for removal of HMs by nanofibers.

4.1. Nanofibers production through electrospinning process

Electrospinning technology is the most commonly applied method to produce continuous polymeric nanofibers with diameters ranging from submicron down to nanometers [151,161]. It is a well-studied method for producing nanofibres from a wide range of natural and synthetic polymers [151]. During the electrospinning process, the polymeric solution is loaded into the syringe having an attached metallic needle; the high voltage is applied to the polymer solution as it is ejected at the desired flow rate. By applying a high voltage into the polymeric solution, an electrostatic force overcomes the surface tension of the polymeric solution at the tip of the needle, and a Taylor cone is formed, which is further elongated into a fluid jet. The charged fluid jet is collected on a grounded device due to the electrical potential difference between the polymeric solution at the tip of the syringe and the grounded collector. The whipping motion of the polymeric jet that takes place between the needle and the plate allows the solvent to evaporate, which results in the collection of a polymeric fiber mesh on the collection plate. The schematic diagram of

the electrospinning process is shown in Figure 2. The polymeric solution concentration significantly influences the fibers diameter and electrospinnability of the solution. One of the advantages of the electrospinning technique is the flexible design of the setup to produce nanofibers with specific compositions and structures. There are few bottlenecks regarding the application of electrospinning technique for large scale commercial manufacture of nanofibers, such as requirements for high voltage and conductive collector, low throughput and mechanical stability of produced nanofibrous layer [162]. Thus, the conventional electrospinning process has been evolved by application of multiple needles or needleless electrospinning to enhance the nanofibers' production rate. Furthermore, the poor mechanical performance of nanofibrous web caused by their highly porous structure and weak bonding at the fibers' junctions may hinder their practical applications as adsorbents. Physical treatments such as post-treatment at elevated temperature through curing, sintering, hot pressing, and heat bonding could be applied to resolve this issue [163].
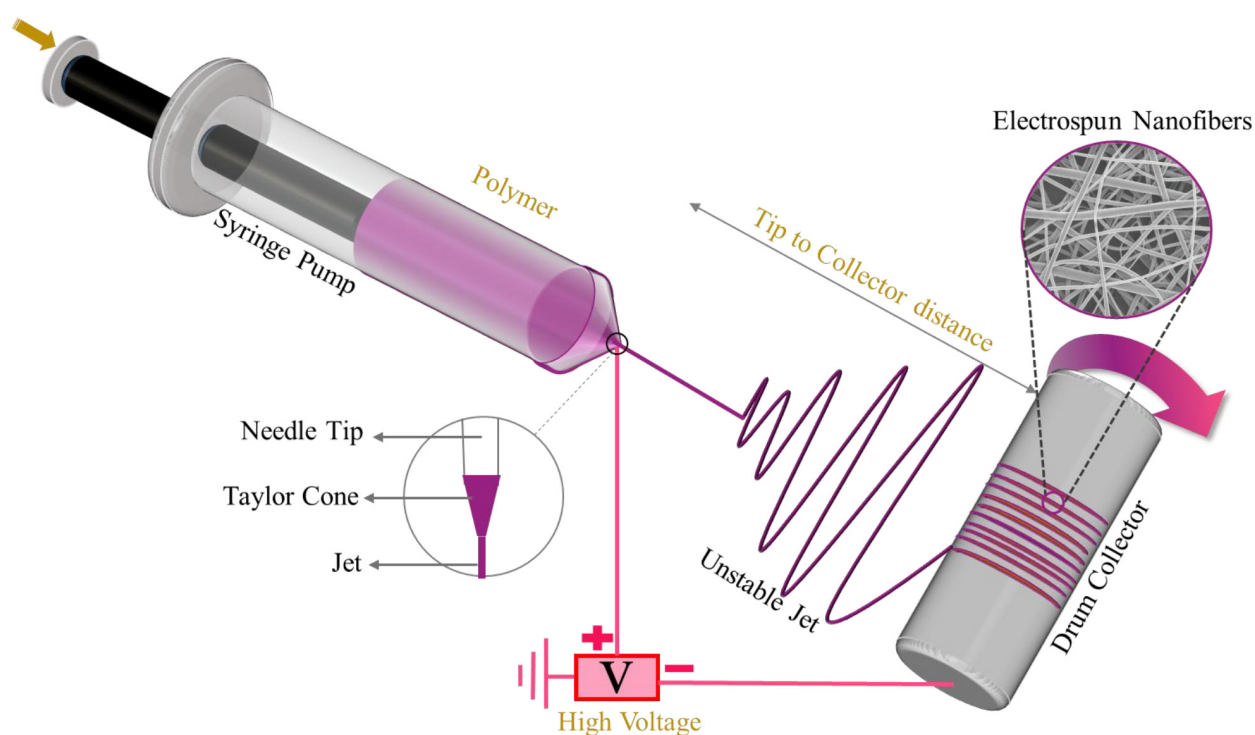

Figure 2. Schematic diagram of the electrospinning setup along with effective parameters.

4.2. HM removal by natural polymeric nanofibers

The nanofibers made by natural polymers (e.g. chitosan, cellulose, wool keratose/silk fibroin) and their derivatives (e.g. cellulose acetate) have been studied for their Cr^{6+}, Co^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} removal characteristics (Table 3) [77,164,165–174]. As shown in Figure 3a, the large numbers of amine ($-NH_2$) functional groups in chitosan (CS) made it a great candidate for HMs adsorption through electrostatic interactions and complexation mechanisms [78,172]. For example, the protonation of amine functions in chitosan structure at low pH values promoted the removal of HM oxyanions such as $Cr_2O_7^{2-}$ through electrostatic interactions. Cellulose (Figure 3b) demonstrated a low adsorption capacity toward HMs in the pure form; thus, certain chelating/metal bonding

functions were introduced, or certain monomers were grafted to its polymer structure [172].
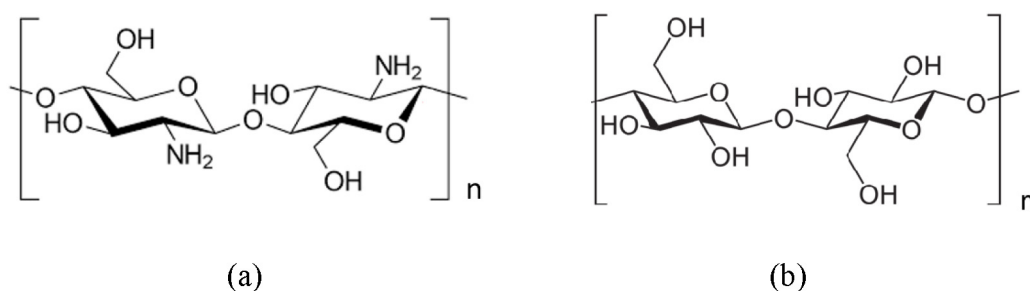

(a)   (b)

Figure 3. The chemical structure of (a) chitosan and (b) cellulose polymers.

Certain drawbacks regarding low permeability, low mechanical strength, slow adsorption kinetics, and low recovery of natural polymeric nanofibers' have limited their widespread applications for HMs adsorption [171,175]. Furthermore, the natural polymers' high viscosity at low concentrations, high intra and inter-chain hydrogen bonding, swelling in aqueous media, and low solubility in organic solvents created some challenges in their electrospinning process [176–178]. To resolve these problems and improve the mechanical properties of produced nanofibers, the natural polymers have been blended with synthetic polymers such as polyethylene oxide (PEO), polyvinyl alcohol (PVA), or Nylon [179–181]. Moreover, the natural polymeric nanofibers were further modified by grafting with oxygen-containing [-COOH, -C=O], nitrogen-containing [-NH$_2$, NH, -CN], and phosphorous-containing [-P-OH, -P=O] functional groups for enhanced HM removal characteristics. For instance, chemical grafting of chitosan nanofibers by poly(glycidyl methacrylate) (PGMA) and polyethyleneimine (PEI) have introduced the amino (-NH$_2$) functions onto its structure and resulted in maximum adsorption capacities of 139.0, 69.3, and 68.3 mg/g for Cr^{6+}, Cu^{2+} and Co^{2+} removal, respectively [182]. The low water stability of chitosan nanofibers has been improved through crosslinking, although this post treatment has reduced the number of its available surface sites for HMs adsorption. To address this issue, the ion imprinting process was applied to compensate the reduced adsorption capacity by creating the recognition site by imprinting the template ions onto the crosslinked structure [183]. The Pb^{2+} and Cd^{2+} imprinted chitosan nanofibers have reached 567.0 mg/g and 341.0 mg/g removal of Pb^{2+} and Cd^{2+}, respectively [168]. The cellulose acetate (CA) nanofibers which were modified with PGMA and grafted with polyacrylic acid (PAA) have generated a high capacity ion exchange membrane for removal of Cd^{2+} from water [184]. Furthermore, the nanoparticles have also been employed to generate the composite nanofibers with natural polymers. The TiO$_2$ entrapped chitosan nanofibers have shown the greater Pb^{2+} and Cu^{2+} adsorption capacities, improved structural stability, and recovery efficiency compared to the TiO$_2$ coated chitosan nanofibers. The increasing TiO$_2$ concentration in TiO$_2$/Chitosan composite nanofibers from 0 to 2 wt.% has improved the Pb^{2+} and Cu^{2+} removal from water. However, increasing the TiO$_2$ content up to 5 wt.% resulted in agglomeration and coagulation of TiO$_2$ nanoparticles, and reduced the Pb^{2+} and Cu^{2+} removal from water [181]. In study conducted by Huang et al. (2018), the large numbers of chitosan/rectorite nanospheres were attached onto the PAN nanofibers and increased their surface roughness. This enhancement of surface roughness is desirable as it increases the specific surface area of nanofiber and finally improving the adsorption

characteristics [185]. Although, the extent of nanoparticle released from composite nanofibers and mechanical stability of natural polymeric nanofibers following the repetitive adsorption/desorption cycles are largely unknown.

Table 3. A summary of studies employed the natural polymeric nanofibers for HM removal.

Polymer	Modification	HMs	Maximum Sorption Capacity (mg/g)	pH	Ref
Chitosan	None	Cr^{6+}	131.6	4.5	[186]
		Pb^{2+}	110.0	7.0	[187]
		Cd^{2+}	364.3	NR	[188]
		Cu^{2+}	485.4	7.0	[189]
		Pb^{2+}	263.1	7.0	[189]
	Grafting with poly (glycidyl methacrylate) and polyethylenimine	Cr^{6+}	139.0	2.0	[190]
		Co^{2+}	68.3	6.0	
		Cu^{2+}	69.3	4.0	
	Crosslinked and imprinted with Pb^{2+} and Cd^{2+}	Pb^{2+}	567.0	6.0	[168]
		Cd^{2+}	341.0	6.0	
	Coated with TiO_2 NPs	Pb^{2+}	475.5	6.0	[181]
		Cu^{2+}	526.5		
	Covered the porous phosphorylated cellulose substrate	Cd^{2+}	591.0	5.5	[171]
	Blended with g-C_3N_4/TiO_2	Cr^{6+}	165.3	2.0	[77]
Cellulose Acetate	Modified with poly(glycidylmethacrylate and grafted with polyacrylic acid	Cd^{2+}	160.0	7.0	[184]
Cellulose	Reaction with Oxalone-2,5-dione	Pb^{2+}	207.2	5.8	[191]
Wool keratose/Silk fibroin	None	Cu^{2+}	2.9	7.0	[173]

Surface chemistry modification of nanofibers could enhance the HMs adsorption capacities, but it may also alter the surface morphology and specific surface area. For example, regeneration of cellulose acetate nanofibers with chloroform curved and slightly fused the nanofibers together. The PAA grafting of cellulose acetate nanofibers filled out space among nanofibers and reduced the web porosity [156]. As shown in Figure 4, the smooth surface of electrospun carbon nanofibers (ECNFs) has become rough, and structural defects were formed in oxidized ECNFs (o-ECNFs), melamine-functionalized ECNFs (melam-ECNFs), and poly(mphenylenediamine)-functionalized ECNFs (PmPDA-ECNFs) [192]. Thus, there are some concerns regarding reduction of nanofibers mechanical performance such as viscoelasticity and strength following the chemical modification processes. Future research is needed to study how chemical functionalization of nanofibers affects

their physical characteristics (e.g. diameter, porosity, and specific surface area) and mechanical performance (e.g. tensile stress and strain).
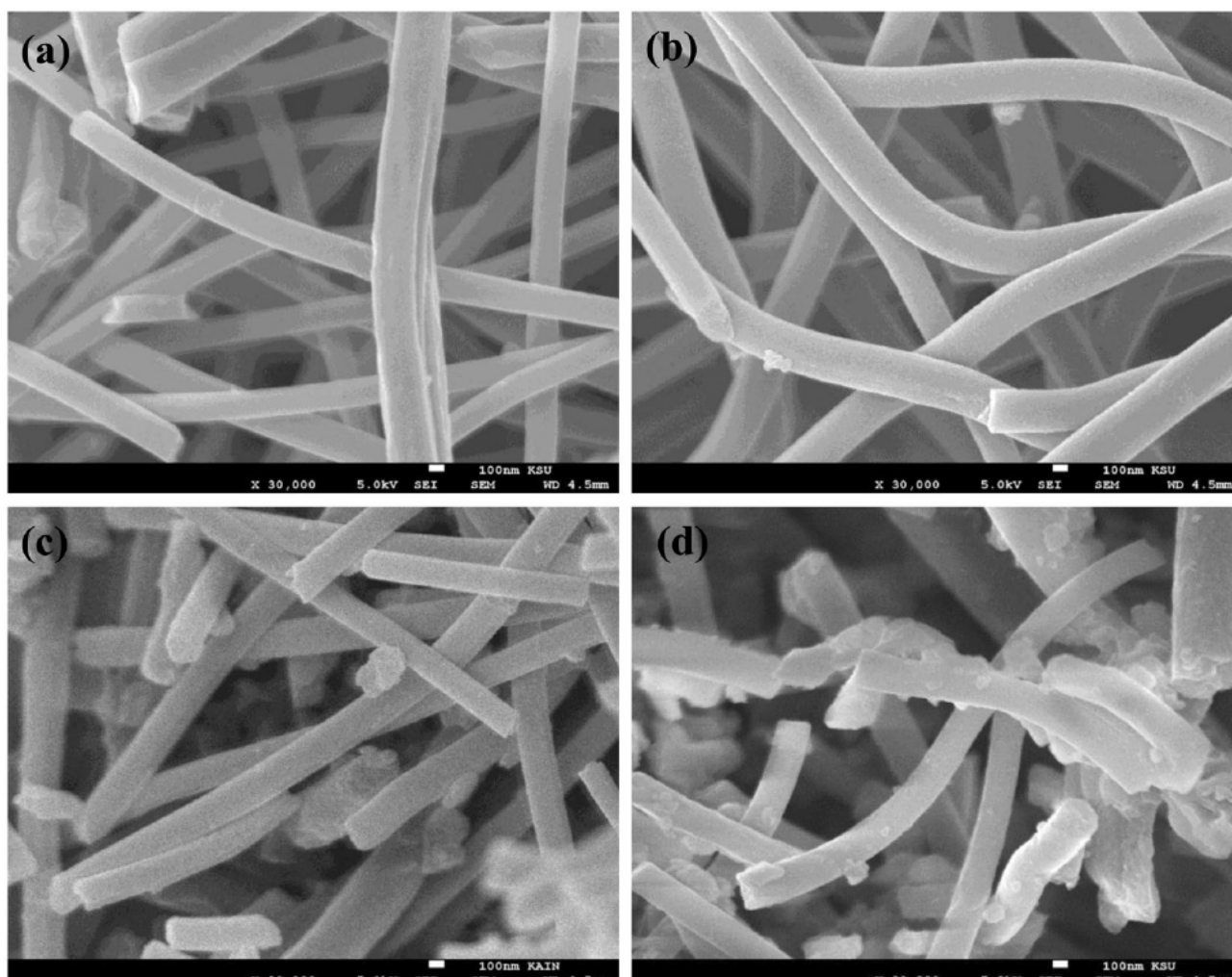

Figure 4. The FESEM images of ECNFs (a), oxidized-ECNFs (b), melam-ECNFs (c), and PmPDA-ECNFs (d), reprint from [192].

4.3. Heavy metals removal by synthetic polymeric nanofibers

Pure synthetic polymeric nanofibers such as PAN and Polyvinyl chloride (PVC) demonstrated very low adsorption capacities as shown in Table 4 [193,194]. Thus, to improve the synthetic polymers' HMs adsorption capacities, the chemical grafting, polymers blending, and composite production processes have been applied.

Table 4. A summary of studies employed the pure or chemically modified synthetic polymeric nanofibers for HM removal.

Nanofibers	Modification	Added Functions	HMs	Maximum Sorption Capacity (mg/g)	pH	Ref
PAN	None	None	Cu^{2+}	31.3	NR	[193]
			Cu^{2+}	51.1	4.0	[194]
	Grafting with branched polyethyleneimine	$-NH_2$	Cu^{2+}	74.7	6.0	[195]
	Hydrolysis & grafting with ethylenediamine, ethyleneglycol, diethylenetriamine	$-N-C=O$ $-N-H$ $-OH$	Cu^{2+} Pb^{2+} Zn^{2+}	283.5 828.0 81.7	6.0	[196]
	Crosslink, amination phosphorylation	$-PO_3H_2$	Cu^{2+} Pb^{2+} Ag^+ Cd^{2+}	62.1 73.3 61.0 7.43	6.0	[197]
	Reaction with hydrazine	$-N-H$	Cu^{2+} Pb^{2+} Cd^{2+}	114.0 217.0 327.1	NR	[198]
	Phosphorylation	$-PO_2$ $-POH$	Cu^{2+} Ni^{2+} Cd^{2+} Ag^+	92.1 68.3 14.8 51.7	6.0	[199]
Polyaryleneether-nitrile	None	None	Cu^{2+}	52.7	NR	[200]
PEI	None	None	Cd^{2+} Pb^{2+} Cu^{2+}	121.9 94.3 70.9	5.0	[201]
PVC	None	None	Cu^{2+} Cd^{2+} Pb^{2+}	5.6 5.3 5.0	7.0	[202]
PET	Amination	$-N-H$	Pb^{2+}	10,350	8.0	[203]

Note: NR: Not Reported.

4.3.1. Chemical grafting

The chemical grafting processes significantly enhanced the HMs adsorption capacities of synthetic polymeric nanofibers by addition of chelating functions or ion exchange groups to their structure. A variety of chemical functions such as carboxyl (-COOH), thiol (-SH), tetrazine ($-C_2H_2N_4$), sulfonic ($-SO_3H$), amino ($-NH_2$), and phosphoric groups ($-PO_4$) could be incorporated into the nanofibers structure to enhance their HMs adsorption capacities. For example, the HMs adsorption characteristics of PAN as a low cost synthetic polymer could be improved by conversion of nitrile functions ($-C\equiv N$) present on PAN nanofibers to the active functions such as carbonyl (-C=O)

or amino ($-NH_2$) [195]. Exclusion of HM ions could be achieved through electrostatic interaction between positively charged metal ions and negatively charged nanofibers or through coordinate bonding between metal ions and nanofibers surface functional groups. Grafting thiol (-SH) functional groups onto SiO_2 nanofibers has increased their adsorption capacity for Cd^{2+} removal from 15.2 mg/g to 25.4 mg/g [204]. Adsorption capacities of Pb^{2+}, Cu^{2+}, and Ag^+ ions have been increased respectively from 49.5 mg/g, 39.7 mg/g and 27.8 g to 98.1 mg/g, 78.0 mg/g and 102.4 mg/g after phosphorylation and amination of crosslinked PAN nanofibers [197]. Plasma-induced graft copolymerization has been applied as a facile and efficient approach to introduce active functions such as carboxyl (-COOH) onto the surface of the nanofibers and enhance the surface hydrophilicity [205]. The plasma treatment of polystyrene (PS) nanofibers in the presence of N_2, mixture of N_2 and H_2, NH_3 gas and N_2 that was followed by acrylamide functionalization resulted in maximum 10 mg/g and 4.9 mg/g adsorption capacities for Cd^{2+} and Ni^{2+} removal from water at pH 5.0 [206]. Despite the significant enhancement in nanofibers HMs adsorption capacity after chemical functionalization, there are some concerns regarding the reduction in their mechanical properties [193].

4.3.2. Polymers blend

An elevated HMs adsorption capacity could be achieved for nanofibers through electrospinning of polymers blend (Table 5). The blended polymeric nanofibers may have significantly different structural, mechanical, and adsorption characteristics from those fibers produced by a single polymer. The poor spinnability and mechanical performance of natural polymers such as cellulose, lignin, algae, and chitosan could be improved through blending with the synthetic polymers such as PAN or polyvinyl alcohol (PVA) [185]. Yarandpour et al. (2018) have blended a water-soluble polymer called dextran with PAA. The produced nanofibers were crosslinked by heat treatment and immersed in polyaniline solution to create the core shell nanofibers. The abundant number of hydroxyl and amine functional groups present in its structure provided lots of resting sites for the HMs cations. Thus, by crosslinking the polymer blend and creating an insoluble structure, an efficient media was produced to remove the HMs. The resulted PAA/dextran-polyaniline core-shell nanofibers revealed the outstanding adsorption capacities of 833.3 mg/g and 1111.1 mg/g for Cu and Pb removal from water [207]. PAN nanofibers have been used as the template for polypyrrole (PPy) to generate the core-shell nanofibers, which demonstrated the maximum adsorption capacity of 44.9 mg/g for Cr^{6+} removal from water at pH 2.0 [208]. The blended PAA/PVA nanofibers have shown the improved mechanical properties, water stability, and water permeability. The superior HMs adsorption characteristics of PAA has been combined with the PVA to create a water stable nanofibrous web after crosslinking at 145°C [209]. The water-soluble polymers need to be cross-linked, even after blending with the synthetic polymers to improve their solvent resistance characteristics.

Table 5. The core-shell and blended polymeric nanofibers for HM removal applications.

Nanofibers		HMs	Sorption Capacity (mg/g)	pH	Ref
Core-shell	PAA/Dextran-PANI	Pb^{2+}	1111.1	7.5	[207]
		Cu^{2+}	833.3	7.5	
	Resorcinol-Formaldehyde/PVA	As^{3+}	11.1	7.0	[210]
	PAN/PPy	Cr^{6+}	44.9	2.0	[208]
Polymer Blends	PVA/CS	Pb^{2+}	266.1	6.0	[170]
		Cd^{2+}	148.8	8.0	
	PAN/Malic Acid	Ni^{2+}	243.2	6.0	[211]
		Cr^{6+}	192.2	4.0	
	PVA/PAA	Pb^{2+}	288.0	5.0	[209]
	CS/Hydroxyapatite	Pb^{2+}	296.7	NP	[212]
		Co^{2+}	180.2		
		Ni^{2+}	213.8		
	Modified CS/PEO	Ni^{2+}	56.0	6.0	[167]
		Cu^{2+}	177.0	5.0	
		Pb^{2+}	142.0	5.0	
	CS/PAAS	Cr^{6+}	78.92	3.0	[213]
	AOPAN/RC	Fe^{3+}	417.2		[214]
		Cu^{2+}	270.7	7.0	
		Cd^{2+}	127.0		
		Cr^{2+}	115.0	3.0	

4.3.3. Composite nanofibers

The superior adsorption characteristics of inorganic nanoparticles such as $FeCl_2$, TiO_2, and Fe_3O_4 could be combined with the high surface area provided by nanofibers through production of composite nanofibers as listed in Table 6. For instance, incorporation of $FeCl_2$ nanoparticles in PAN nanofibers resulted in 110 mg Cr^{6+} removal per g $FeCl_2$, which was significantly greater than adsorption capacity of previously applied nanomaterials such as Fe_3O_4 and Fe_2O_3 for Cr^{6+} removal [215]. Despite, numerous studies reported the elevated HMs adsorption capacities for composite nanofibers, the stability of nanoparticles in nanofibers structure under various operational conditions and after several regeneration cycles has not well studied. Furthermore, the recent literature mainly evaluated the nanofibers reusability in terms of HMs adsorption capacity following few adsorption/desorption cycles and have not quantified the extent of nanoparticle release to the water during these regeneration cycles. Most of prior studies have solely examined the role of nanofibers chemistry on HMs adsorption capacities and have not evaluated the critical influences of nanofibers physical parameters such as diameter and porosity on accessibility and abundance of available surface sites.

Table 6. The composite electrospun nanofibers for HM removal applications.

Composite Nanofibers	HMs	Sorption Capacity (mg/g)	pH	Ref
PAN/Rectorite/CS	Pb^{2+}	29.8	2.0	[216]
		77.4	5.5	
		196.3	6.0	
CS/PVA/Zeolite	Fe^{3+}	4.5		[175]
	Cr^{6+}	4.7	NR	
	Ni^{2+}	5.9		
PVA/TEOS/APTES	Cd^{2+}	141.2	6.0	[217]
CS/PEO/Halloysite/Fe_3O_4	Cr^{6+}	82.2		[218]
	Cd^{2+}	110.4		
	Cu^{2+}	131.4	5.0	
	Pb^{2+}	129.6		
CS/PEO/Iron	As^{3+}	36.1	7.0	[219]
PAA/PVA/MWCNT/ZVI	Cu^{2+}	75.3	4.5	[220]
PVA/SiO_2	Cu^{2+}	489.1	6.0	[221]
PVDF/FMBO	As^{5+}	21.3	7.0	[222]
PAN/ZnO	Pb^{2+}	259.4	5.0	[223]

4.4. Factors influence HMs adsorption by nanofibers

The aqueous solution characteristics (e.g. pH, initial HMs concentration, and abundance of competing ions) and operational conditions (e.g. contact time and temperature) affect the adsorption process. The pH of aqueous solution influences the speciation of HMs as well as surface functionality of adsorbents nanofibers [169]. For instance, the lower pH enhanced the protonation of amine functional groups on chitosan nanofibers, and promoted electrostatic attraction of oxyanions including $HCrO_4^-$ and $Cr_2O_7^{2-}$ and enhances their removal. On the other hand, it increased the electrostatic repulsion with Cu^{2+} ions and reduced their uptake by the nanofibers [169]. The study conducted by Chen et al. (2019) demonstrated a reduction of Cu^{2+} ions uptake by aminated PAN nanofibers as pH decreased from 6.0 to 1.0 [195]. At the lower pH values, a greater numbers of protonated nitrogen ions were present on nanofibers surface; thus their repulsive interaction reduced the Cu^{2+} removal [195]. The protonation of amino groups on PVA composite nanofibers at the lower pH hindered the Cd^{2+} ion adsorption. However increasing the pH from 2.0 to 6.0 promoted the Cd^{2+} adsorption capacity [217]. Increasing the pH from 3.0 to 6.0 resulted in a greater Cu^{2+}, Cd^{2+}, Ni^{2+}, and Ag^{2+} removal by phosphorylated PAN nanofibers, due to the reduction of repelling force of hydrogen ions. However, further increasing the pH to 7.0 reduced the metal uptake due to their competition with OH^- to occupy the available adsorption sites on nanofibers surface [199]. The pH value of zero charge (pH_{ZPC}) was determined as 5.2 for the graphene oxide (GO) and Fe_3O_4 embedded PAN nanofibers (PAN-GO-Fe_3O_4). The fibers' negative charge above this pH, resulted in repulsion of the Cr^{6+} oxyanions and reduced their adsorption capacity. However, an increased positive surface charge of these nanofibers at pH values below the pH_{ZPC}, promoted the Cr^{6+} removal

through a greater electrostatic attraction [224].

Increasing the HMs' initial concentration enhances the adsorption capacity of nanofibers by providing more metal ions to occupy the available surface sites and promoting the probability of collision between HMs ions and nanofibers surface functional groups [195,207,214]. However, saturation of all available adsorption sites will restrain the HMs uptake by nanofibers as initial HMs concentration further increases. The other ions present in the aqueous system could compete with the HMs ions to occupy the available surface sites on fibers. For example, at the lower pH values, the anions such as Cl^-, SO_4^{2-} and NO_3^- are competing with $HCrO_4^-$ and $Cr_2O_7^{2-}$ oxyanions to occupy the protonated amino functional groups present on chitosan nanofibers and thus, they reduce the Cr^{6+} removal by these nanofibers. Although, the presence of common alkaline earth cations such as Na^{2+}, Mg^{2+} and Ca^{2+} have not affected the Cr^{6+} removal by these nanofibers [186]. The Cr^{6+} oxyanions uptake by $PAN/FeCl_3$ nanofibers was reduced up to 95% in the presence of SO_4^{2-} anions [225].

Contact time significantly influences the HMs uptake by nanofibers, HMs are adsorbed rapidly onto the available surface sites and then slowly diffuse into the more interior sites [169]. The presence of large number of vacant adsorptions sites on the nanofibers surface and an elevated initial metal concentration accelerates the immediate adsorption process. However, the accumulation of HMs ions onto the surface of the nanofibers reduces the concentration gradient and slow down the adsorption kinetics over time [207]. Adsorption capacity of Cr^{6+} by PAN/PPy core-shell nanofiber has increased with the contact time until the equilibrium has reached between the Cr^{6+} solution and adsorbents [208]. Increasing the contact time from 10 min to 120 min has increased the Cu^{2+} adsorption by aminated PAN nanofibers from 20.0 to 78.0 mg/g [195]. The kinetics of HMs adsorption by nanofibers has been studied mostly through Pseudo 1st order, Pseudo 2nd order, and intraparticle diffusion models. The Pseudo 1st order reaction kinetic considers the rate of adsorption sites occupation proportional to the number of unoccupied surface sites. However, the Pseudo 2nd order model is applied when the chemical reactions control the rate of HMs adsorption [226]. The intra particle diffusion model evaluates the diffusion mechanism through the sorption process [227]. The kinetics of the adsorption process is influenced by the surface functionality of adsorbent nanofibers and HMs and the rate limiting step caused by electron exchange or sharing processes [78]. The prior studies lack understanding of the kinetics of HMs nucleation and precipitation onto the surface of the nanofibers.

The influence of temperature on HMs adsorption by nanofibers has been studied through linearized Van't Hoff equation (Eq (1)). Th Gibbs free energy change ($\Delta G°$) is calculated by Eq (1), where R is the universal gas constant, T is the absolute temperature (K), and k_c is the adsorption equilibrium constant (Eq (2)). The C_{es} and C_{el} are the solid phase concentration and liquid phase concentration at the equilibrium. The enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) are calculated using Eq (3) from slope and intercept of ln K_c versus 1/T [217]. Obtaining the negative values for the Gibbs free energy change indicates the spontaneous nature of the adsorption process. Positive $\Delta S°$ confirms that randomness at solid-surface interface enhanced at higher temperature [217]. The endothermic nature of the adsorption process could be identified by positive ($\Delta H°$) value. The nature of chemical or physical sorption of HMs onto the nanofibers could be identified using the enthalpy changes [217]. Enthalpy changes between 20.9 kJ/mol to 418.4 kJ/mol indicate chemical adsorption [228].

$$\Delta G^\circ = -RT \ln k_C \qquad (1)$$

$$k_C = \lim_{C_{el} \to 0} \frac{C_{es}}{C_{el}} \qquad (2)$$

$$\ln k_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (3)$$

The Gibbs free energy changes (ΔG°) were calculated as negative values for Cu^{2+} adsorption onto aminated PAN nanofibers, which confirmed the spontaneous nature of this adsorption process. The calculated enthalpies indicated the chemical adsorption [228]. The change of Gibbs free energy and ΔH° were found negative and positive for both Cu^{2+} and Pb^{2+} ions adsorption onto Chitosan/TiO_2 nanofibers for experiments conducted at 298 K to 318 K, which demonstrated a feasible endothermic adsorption process [180]. Increasing the temperature from 298 K to 313 K enhanced Cu^{2+} adsorption by aminated PAN nanofibers and demonstrated an endothermic adsorption process [195]. Investigating the thermodynamic parameters for Cd^{2+} adsorption by PVA composite nanofibers revealed the chemical adsorption process which was more favourable at higher temperature [217].

4.5. Nanofibers regeneration and reuse

The cost-effective usage of nanofibers relies on their ability to be reused. Feasible regeneration approaches are essential to promote the commercial applications of nanofibers. The nanofibers with an elevated regeneration capacity are more economical to be used for large scale water or wastewater treatments. The reusability of nanofibers for HM removal practices is determined by their ability to maintain the adsorption capacity after undergoing multiple regeneration cycles. Each regeneration cycle involves exposure of nanofibers to the alkaline and/or acidic solutions to desorb the HMs. For instance, the HNO_3, HCl, and H_3PO_4 aqueous solutions have been used as stripping agents for the regeneration of nanofibers. At the low pH levels created by these solutions, an excessive number of H^+ ions are present. The smaller size of H^+ ion compared to the HM cation and their greater concentration gradient at the low pH levels results in replacement of adsorbed HM cations by H^+ ion. As an example, the Tannic acid modified PAN nanofibers were regenerated by 0.1 M HCl after adsorption of Cr^{3+} ions. These nanofibers demonstrated a greater than 80% removal efficiency after five regeneration cycles [229]. On the other hand, alkaline solutions such as NaOH have an excessive level of OH^- ions. The OH^- ions could form the complexes with HM cations and dislodge them from the surface of the nanofibers. Investigation of Pb^{2+}, Cu^{2+}, and Zn^{2+} recovery from ion-selective PAN nanofibers using HNO_3, HCl, NaOH, and H_3PO_4 has shown the maximum recoveries using the 0.1 N HNO_3 and 0.5 M H_3PO_4, where a greater than 90% of each metal has been recovered. Although following four regeneration cycles, the Pb^{2+} and Zn^{2+} adsorption capacities have not reduced significantly, but the Cu^{2+} adsorption capacity was reduced from 1.6 mmol/g to 0.35 mmol/g using the HNO_3 as stripping agent. This reduction of removal efficiency could be relevant to the degradation of ethylene glycol functional groups due to the acidity of the stripping solution [230]. Furthermore, the excessive number of OH^- ions present in the highly alkaline solutions could replace the HM oxyanions adsorbed onto the surface of the nanofibers due to their smaller size compared to the HM oxyanions and their greater concentration gradient at elevated pH

values. The electrospun PVA/PEI nanofibers were regenerated with 1.0 M NaOH and did not show any significant reduction in their Cr^{6+} adsorption capacity after four regeneration cycles [231]. The sodium alginate-polyaniline nanofibers were regenerated using 0.5 M NaOH, followed by washing with 2.0 M HCl. After three successive regeneration cycles, a very slight reduction has been found in their Cr^{6+} adsorption capacity, which could be resulted from the loss of nanofibers during the regeneration process [158].

The $NaHCO_3$ could regenerate the nanofibers by replacing the HM cations with Na^+ ions. Moreover, the HCO_3^- ions could result in HM desorption by forming the complexes with them. Ethylenediaminetetraacetic acid (EDTA) is also acting as a stripping agent by binding to the HMs through its four carboxylates and amine functions. The PAA/dextran-polyaniline core shell nanofibers that were regenerated with NaOH, HCl, $NaHCO_3$, and EDTA solutions demonstrated 95.1%, 89.2%, 34.6%, and 40.7% of regeneration efficiency, respectively. The Pb^{2+} and Cu^{2+} adsorption efficiency for these fibers gradually decreased over ten regeneration cycles with NaOH from 95% and 83% to 82% and 70%, respectively [232]. Generally, the nanofibers adsorption capacity cannot fully recover after consecutive use cycles by regeneration process due to the irreversible deformation of the fibers and losing a portion of adsorption sites permanently, or loss of nanofibers during the process [158].

4.6. Limitations for commercial applications

Most of the advances in the production of functional nanofibers for HM removal from water and wastewater are currently at the laboratory exploration stage. There is still a significant gap from these laboratory studies to the commercial applications. The challenges associated with conductance of large-scale electrospinning and chemical modification processes hinder the mass production of functionalized nanofibers for large scale water and wastewater treatment practices [233]. Although, the electrospinning process has already been upscaled and several types of nanofibers are commercially available on the market, but these products are mostly the pure polymeric nanofibers. More effort is needed to mass produce high quality blended or composite nanofibers. Furthermore, the limited stability and reliability of the industrial electrospinning process in the production of uniform and high quality nanofibers should be addressed [234,235]. Low mechanical stability of nanofibers limits their capability to be utilized for large scale water and wastewater treatment practices [236]. Future research is needed to devise advanced technological solutions to promote the mechanical performance of nanofibers. The nanofibers' low mechanical stability also challenges their efficient recovery and reuse. Very limited research is conducted on the reusability of nanofibrous web after undergoing consecutive adsorption/desorption cycles in real wastewater, however, this information is critical prior to the application of nanofibers for large scale industrial processes. No study has been conducted evaluating the long-term degradation and variation of HMs removal characteristics of nanofiber using real wastewater. Many of developed nanofibers are intended to be used for HM removal from industrial wastewater, which might be highly acidic or alkaline. However, the stability of nanofibers under these extreme water chemistry conditions has not been evaluated yet [237]. The compatibility with existing infrastructure, cost, potential environmental and public health consequences are other factors that delayed the industrial implementation of nanofibers for HM removal.

5. Conclusions

Heavy metals are increasingly recognized as serious worldwide human health and environmental safety concern. Their efficient removal from water and wastewater is essential to protect the public health and ecology safety and promote the sustainability. Certain economical and efficiency deficits associated with operation of conventional HM removal practices prompted extensive research on advanced adsorbent nanomaterials. Despite the superior HMs adsorption characteristics of nanoparticles, nanobeads, nanotubes, and nanocomposites, their efficient separation from water or wastewater is challenging and raising concerns regarding creation of secondary pollutants. The electrospun nanofibers have addressed the recovery challenges of nanomaterials by their interconnected fibrous structures. Furthermore, nanofibers' large specific surface area, permeability, porosity, and surface functionalities have made them the great candidates as HMs adsorbents. In recent years, numerous innovative methodologies have been developed to address the low adsorption capacity of low-cost synthetic polymers, challenging electrospinning of natural polymers, and low stability of water soluble polymers. The chemically modified, polymers blended, and composite nanofibers have demonstrated outstanding HMs adsorption characteristics. Aqueous solution characteristics and operational conditions have found to influence the HMs adsorption capacity of nanofibers. Future research is needed to examine the nanofibers' structural stability and the extent of nanoparticle release from composite nanofibers to the water during consecutive regeneration cycles. The quantitative analysis of nanofibers' surface morphology, roughness, diameter, web porosity and thickness are needed to better understand their critical impacts on accessibility and abundance of surface sites for HMs adsorption. The literature is lacking cost analysis of nanofibers application for HM removal from water and wastewater. Future research is needed to evaluate the superiority of nanofibers in comparison to the other conventional practices in terms of economic operations.

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