

Electrospun Fibrous Membranes for Efficient Heavy Metal Removal

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ABSTRACT: Heavy metal pollution is a growing environmental problem in recent decades, which requires immediate and urgent action. In this article, we provide an overview of the works published in the last decade concerning the development of electrospinning-based micro- and nano-porous membranes for efficient heavy metal removal. Apart from their super-high surface-to-volume ratio, electrospun nanofibers possess a variety of surface groups which enable their further functionalization and functional nanoparticle incorporation. Compared to typical adsorbents, electrospun fibrous membranes are superior in many ways like higher permeation flux, lower pressure drop, flexible component adjustment, and even multi-target adsorption. Therefore, electrospun-based fibrous membranes hold great potential on the treatment of heavy metal contaminants. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40864.

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INTRODUCTION

During the latest century, heavy metal pollution has become an international issue accompanying with the development of modern industry. Heavy metal wastes are directly or indirectly discharged into the environment increasingly, especially in developing countries. Toxic heavy metals like chromium (Cr), mercury (Hg), arsenic (As), cadmium (Cd), plumbum (Pb), zinc (Zn), and copper (Cu) in contaminated water hold severe threats to human health and agriculture because they are non-degradable and tend to accumulate in the environment. There are hundreds of sources of heavy metal pollutions, including metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries, and so forth.^{1,2} In response to the growing problems, extensive researches and financial resources have been spent on developing cost-effective and efficient technologies to pre-concentrate and eliminate heavy metals and their compounds.^{3–5}

Conventional technologies for the removal of heavy metal ions and compounds from aqueous solutions include ion exchange, chemical precipitation, chemical oxidation/reduction, reverse osmosis, electro dialysis, and ultrafiltration, and so forth.^{6–10} Some of them are quite effective but unfortunately have inherent limitations such as rigorous operating conditions, less efficiency, and production of secondary contaminants.¹¹ Recently, some remarkable works have been done on the utilization of agricultural wastes and industrial byproducts as potential heavy metal biosorb-

ents like saw dust,¹² *Oriza sativa* husk,¹³ rose biomass,¹⁴ and sugarcane bagasse.¹⁵ These biosorption methods are relatively low-cost and high-efficient but meanwhile may bring some problems such as high chemical oxygen demand and biological chemical demand as well as total organic carbon due to soluble organic compounds release,^{16,17} which will exhaust the oxygen reservation in water and threaten the aquatic life. Recent studies suggest that nanosized metal oxides exhibit highly favorable sorption to heavy metals in terms of high capacity and selectivity.^{18–20} However, due to the nature of nanoscale materials, they prone to aggregate and thus decrease or even lose their high capability and selectivity.

Electrospinning is a promising fiber forming technology in generating long polymer fibers with diameters in the range of nanometers to a few microns.^{21–23} Through this facile and low-cost strategy, most polymers can be electrospun to form nanofibers and nanostructured materials with large surface-to-volume ratio (10–40 m²/g) and high porosity (>80%),²⁴ which have found wide applications in energy storage,^{25,26} catalyst,^{27,28} environmental remediation,^{29–31} protective clothing,³² biosensors,³³ drug delivery,^{34–36} and tissue engineering scaffolds.^{37,38} Owing to their potential for further purposeful surface modification and impurity doping, electrospinning-based fibrous membranes can be remolded to meet sorts of requirements. For example, in our previous study we report the preparation of a self-standing membrane of hierarchical SiO₂@ γ -AlOOH (boehmite) core/sheath fibers through the hydrothermal growth of boehmite on the surface of electrospun SiO₂ fibers, which shows excellent removal efficiency for organic dyes and bacteria.³⁹

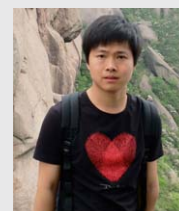
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The present review article compiles an extensive list of adsorbents obtained from electrospinning for the removal of different species of heavy metals from wastewater. Their performance under varying experimental conditions will be evaluated. Post-treatment and reusability will be important indexes. Methods including surface modification of different functional groups, doping of functional nanoparticles in/on fibers, electrospinning-template fabrication of functional inorganic fibrous membranes are the focus.

FUNDAMENTALS

Electrospinning Technology

With a series of patents on electrospinning process issued to Formhals since 1934 where an experimental setup for generating polymer filaments was introduced,⁴⁰ the electrospinning technology is getting increasingly popular in material science. Figure 1 shows a schematic illustration of the basic setup for electrospinning. It consists of three major modules: a high voltage power generator, a syringe pump (syringe included), and a collector. Direct current power supplies are always used as electrospinning power source, though, the alternating current can also be applied. The needle connected to a syringe is used as a spinneret, with the boost of the pump, polymer solution hosted in the syringe can be fed through the spinneret continuously and gently. When a high voltage is applied, an evenly distributed electric field is formed and the liquid surface at the end of the needle is charged. The mutual electrostatic repulsion between polymer chains causes a force directly counterbalancing the surface tension when the voltage increases, under which situation the hemispherical shaped liquid will be distorted to form a conical shape known as the Taylor

cone (Figure 1).⁴¹ Once the intensity of the electric field exceeds the critical value, the balance between electrostatic force and surface tension will be broken. As a result, a jet flow of charged solution is ejected from the tip of the Taylor cone continuously and undergoes stretching and elongation, in which process the solvent will evaporate and the diameter of the jet can be significantly reduced to hundreds of nanometers. Attracted by the negative charged collector, the nanofibers will eventually deposit on the collector in a random manner.⁴²

The basic setup for electrospinning is so simple and efficient that it has found tremendous development during the past decades. A variety of materials such as natural polymers, synthetic

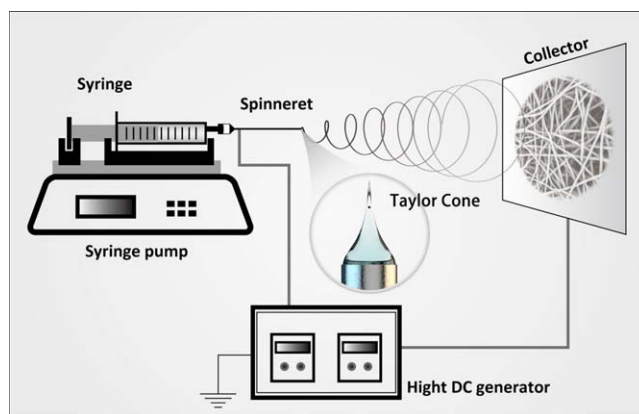


Figure 1. Schematic illustration of basic electrospinning setup. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymers, ceramics, metals, or the mixture of them have been electrospun to produce ultrafine nanofibers with diameter ranging from several nanometers to micrometers, with their sizes, compositions, and morphologies be well-controlled through regulation with the electrospinning parameters.^{43–45} Despite the above merits, electrospinning technique is generally low productive, as the polymer solution must be fed at a low feeding rate to obtain ultrafine fibers. To solve this problem, Chu and coworkers⁴⁶ have designed an array of multiple needles for electrospinning, with the gaps between needles carefully arranged to ensure that the electric field strength is uniform. Moreover, core-shell electrospinning, auxiliary electric fields, rotating tube, rotating disk, needleless electrospinning, patterned electrodes, or magnetic electrospinning were also used to produce nanofibers with different morphologies and structures.^{47–53} The objectives of the above explorations are searching for ideal electrospinning systems to fabricate nanofibers with a controlled alignment, orientation, and special functionalities.

Many parameters can affect the electrospinning process, including (a) the solution properties such as polymer molecular weight, viscosity, conductivity, elasticity, and surface tension; (b) process parameters such as electric potential, flow rate, distance between needle tip and collector, needle inner diameter; and (c) ambient parameters like temperature, humidity, and air velocity in the electrospinning chamber.⁵⁴ For example, the polymer solution for electrospinning should have a concentration high enough to maintain polymer entanglement, but not too high to inhibit deformation caused by the electric field. Improper distance between needle and collector may result in a rough and beaded mat with the porosity also severely decreased. The applied voltage can produce ionized solution and generate elongation and splitting, which would form a uniform fiber structure at a proper level. Whereas, boosting the voltage to an extreme high value would result in an unstable electrospinning.⁵⁵ In a word, electrospinning parameters are quite essential which deserve serious attention.

Removal Mechanism of Heavy Metals

Removal of heavy metal ions and compounds from contaminated metal effluent using electrospun fibrous membranes is basically originated from the interactions between the heavy metal ions and the functional sites on the surface of nanofibers, such as the physical affinity and electrostatic interactions, or chemical chelating and complexation.⁵⁶ That is to say, the functional sites inherent or anchored on the fiber surface are the leading characteristics that determine the heavy metal removal capability of the electrospun membrane.

Moreover, the micro- or nano-porous structure of electrospun fibrous membrane makes it a perfect microfiltration medium. This combination of strong interaction and effective microfiltration property forms the intrinsic quality of an optimal membrane for heavy metal removal. Generally, there are two coupling processes in toxic metal removal: static adsorption which is based on the sorption capacity and adsorption rate of the functional surface, and dynamic adsorption which refers to pressure drop, permeation flux, and working life of the membrane. As most of the works reported on electrospun fibrous

membranes for heavy metal removal are applied in static mode, this review will pay more attention on the adsorbent role of electrospun membranes.

Kinetics of Adsorption

Adsorption Isotherms. Modeling of the adsorption of heavy metals on electrospun fibrous membrane is realized by applying different adsorption isotherms. Three widely used isotherms for wastewater treatment applications will be discussed, that is, Langmuir,⁵⁷ Freundlich,⁵⁸ and Redlich–Peterson isotherms.⁵⁹ The Langmuir isotherm is based on an ideal assumption: the adsorption of a single adsorbate onto a series of equivalent sites on the surface of the sorbent, which means all adsorbing sites are equivalent and each site can hold at most one molecule (monolayer adsorption), and most of all, there are no interactions between the adsorbed molecules. The Langmuir isotherm equation can be expressed as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{k_d}{q_m} \times \left(\frac{1}{c_e} \right), \quad (1)$$

where c_e and q_e , respectively, show the residual metal concentration and the amount of metal adsorbed onto the adsorbent at equilibrium, and k_d is the Langmuir constant of the system. By plotting $1/q_e$ against $1/c_e$ we can get the value of $1/q_m$ (the intercept) and k_d/q_m (the slope), thus the maximum adsorption capacity (q_m) can be calculated.

In real adsorption process, there may be interactions between the adsorbed molecules. Therefore, a molecule adsorbed on one site may somehow make it more difficult for other molecules to be adsorbed on the nearby sites. In this circumstance, Freundlich isotherm equation may give us a better fitting result:

$$\log q_e = \log k_F + \left(\frac{1}{n} \right) \log c_e, \quad (2)$$

where k_F and n are the Freundlich constants of the system, which indicate the adsorption capacity and adsorption intensity of the adsorbents. By plotting $\log q_e$ against $\log c_e$, k_F , and n can be determined.

If the diffusion of the adsorbed metal ions into the porous adsorbent is taken into account, Redlich–Peterson equation below is more suitable to analyze this specific adsorption isotherm.⁶⁰

$$\ln \left(\frac{A C_e}{q_e} - 1 \right) = g \ln c_e + \ln B, \quad (3)$$

where q_e is the adsorbing amount on unite adsorbent, g is the exponent between 0 and 1, c_e is the equilibrium concentration of heavy metal ions, A and B are the Redlich–Peterson isotherm constant of the system.

Adsorption Kinetics. With the purpose to figure out the controlling mechanism of the heavy metal adsorption process, we need to use the two kinetic models, that is, pseudo-first-order and pseudo-second-order equations, to test the experimental data.

Pseudo-first-order equation is one of the most widely used equations for the sorption of adsorbate from a liquid solution. Its linear form can be represented as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}, \quad (4)$$

where k_1 is the rate constant of pseudo-first-order adsorption, q_e and q_t , respectively, represent the adsorption amount of heavy metal ions at equilibrium and time t . By plotting $\log(q_e - q_t)$ against t , a straight line can be obtained if this model is applicable, thus q_e can be further obtained from the intercept in the equation of linear regression.

In addition, the linear form of pseudo-second-order equation based on adsorption equilibrium capacity can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + t \left(\frac{1}{q_e} \right), \quad (5)$$

where k_2 is the rate constant of pseudo-second-order adsorption, q_e and q_t are the adsorption amount of heavy metal ions at equilibrium and time t . By plotting t/q_t against t , a straight line can also be obtained if this model is applicable, thus the rate constant k_2 and equilibrium concentration q_e can be calculated from the slope and intercept.

ADSORPTION OF HEAVY METALS

Functional Polymeric Membrane

Poly(acrylic acid). Poly(acrylic acid) (PAA) is an important polyelectrolyte material, which contains carboxyl groups on the chain and has been widely used as metal ion complexing agent.⁶¹ Xiao et al. has systematically investigated the influence of processing parameters on the morphology and stability of electrospun ultra-fine PAA/PVA (poly(vinyl alcohol)) nanofibers.⁶² They found that water stable PAA/PVA fibers with uniform diameter can be obtained at a high concentration of 25 wt %, followed by thermal treatment at 145°C. The nanofibrous mats were able to quickly remove Cu(II) ions from aqueous environment with the removal percentage approaching 91% within 3 h and excellent selectivity under the co-existence of Ca(II) ions.

Polyethyleneimine. Polyethyleneimine (PEI) shows high affinity for various metal ions, thus can be used as chelating agent for the removal of heavy metal cations in wastewater. In the study of Wang et al.,⁶³ crosslinked PEI nanofibrous affinity membranes were prepared through a special wet-electrospinning process, wherein fiber formation and crosslinking occurred at the same time under a coagulating bath containing crosslinking agent glutaraldehyde. Adsorption experiments showed that this affinity membrane has strong adsorbability for three heavy metal ions of Cd(II), Pb(II), and Cu(II), with the maximum adsorption capacities (from Langmuir isotherm data) of 121.95 mg/g, 94.34 mg/g, and 70.92 mg/g, respectively. The PEI nanofibrous membrane after the first adsorption experiment could be regenerated in EDTA solution, thus the adsorbability could be fully recovered.

Poly(vinyl chloride). Poly(vinyl chloride) fibrous membrane was also prepared through electrospinning.⁶⁴ Owing to the excess chlorine on the fiber surface as negatively adsorption sites, this membrane could be used as adsorbent and separators for heavy metals in groundwater. Static adsorption data showed that the maximum uptakes of Cu(II), Cd(II), and Pb(II) were 5.65 mg/g, 5.35 mg/g, and 5.03 mg/g, respectively.

Proteins. Among the natural materials, keratin proteins could be promising candidates to adsorb heavy metal ions because of the abundant functional amine groups both on the backbone and the side chain.⁶⁵ For instance, electrospun keratose/silk fibroin blend nanofiber was generated via electrospinning with a diameter in the range of 100–1400 nm.⁶⁶ Because of the low molecular weight of keratose, silk fibroin was introduced to improve electrospinnability. It was found that the blend nanofiber with the ratio of 50/50 showed an excellent mechanical property, which was an advantage especially in practical applications. For the heavy metal ion adsorption test, the keratose/silk fibroin blend nanofibrous membrane exhibits much higher adsorption capacity for Cu(II) than that of the ordinary wool fiber. Furthermore, desorption of the adsorbed metal ions could be realized in 1 mM EDTA (ethylene diamine tetraacetic acid) solution with the recycling efficiency kept at 97%.⁶⁷

In another work,⁶⁸ electrospun keratose/polyamide 6 blend nanofiber with an average diameter of 200 nm was fabricated with the keratose acted as a functional site provider. The adsorption process for Cr(VI) could be well described with the Freundlich isotherm, and the maximum adsorption capacity was found to be 55.9 mg/g. The kinetic data well fit the pseudo-second order and the adsorption mechanism for Cr(VI) was explained as an ion-exchange process.

Silk fibroin is mainly composed of amino acetic acid, alanine, serine, and tyrosine. An electrospun silk fibroin nanofibrous membrane comprised of ultra-fine fibers is an excellent adsorbent because of its large amount of functional groups. In a study by Zhou et al.,⁶⁹ silk fibroin/cellulose acetate blend nanofibers with a diameter range of 100–600 nm were prepared by electrospinning, followed by 100% ethanol treatment to improve the anti-felting property. The adsorption ability of this membrane was examined in a Cu(II) solution, which showed that silk fibroin and cellulose acetate had synergetic effect, on the higher affinity for Cu(II) than pure silk fibroin and pure cellulose acetate, with the maximum adsorption amount reached 22.8 mg/g when the cellulose acetate proportion in the blend was 20%.

Chitosan. Chitin is the world's second most abundant natural polysaccharide derived from the significant component in the shells and exoskeletons of crustacean. Chitosan is the derivative of chitin, which is highly stable and difficult to degrade. As the deacetylated form of chitin, there are many amino groups along the chitosan backbone, which can be used to bind metal ions from wastewater.⁷⁰ The adsorption mechanism of heavy metal ions on chitosan might be explained from two different ways. One is chelation and formation of chitosan–ion complex through intra- and inter-chitosan chains. As chitosan can be protonated under acid condition to become positively charged, the other way to adsorb metal ions is by electrostatic interaction.

However, electrospinning of pure chitosan was hindered by its high degree of intra- and inter-chitosan hydrogen bonding and poor solubility in most organic solvents. Researchers found that poly(ethylene oxide) (PEO) can be a good additive to improve the spinnability of chitosan.⁷¹ With the addition of a very low amount of PEO (5% molecular weight fraction), nano-sized chitosan/PEO fibers with fiber diameter of 80 ± 35 nm without

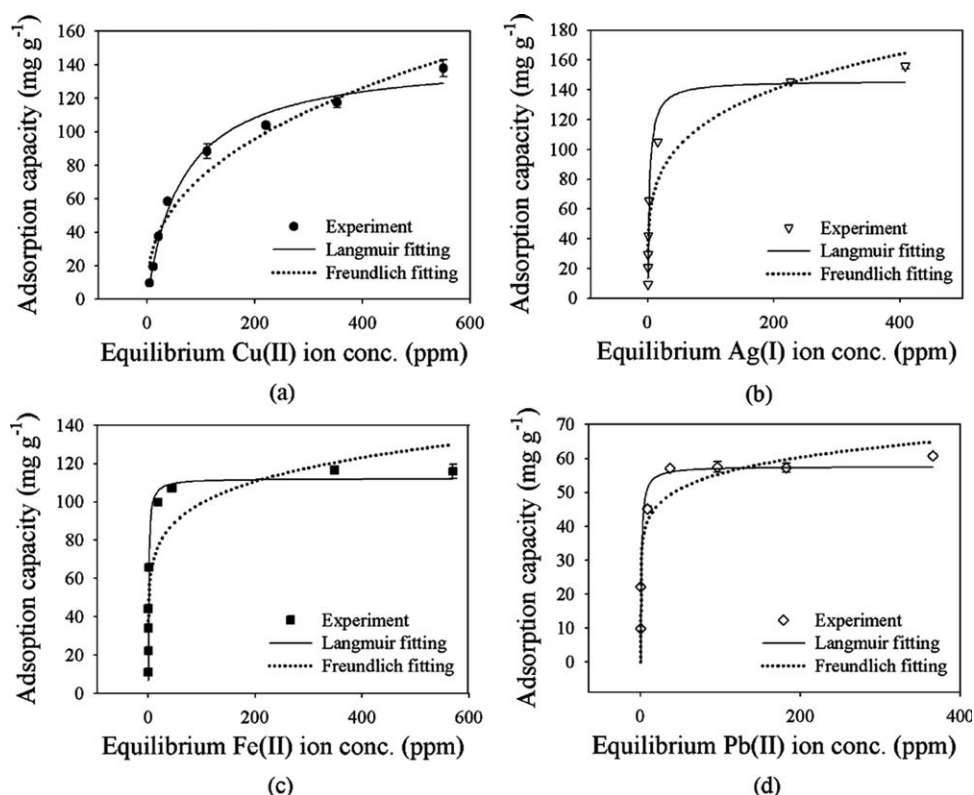


Figure 2. Adsorption isotherms of Cu(II), Ag(I), Fe(II), and Pb(II) ions onto the APAN nanofiber mats ($n = 5$). Experimental conditions: initial ion concentration = 40–1000 ppm, sample dose = 0.1 g/20 mL, initial pH = 4, temperature = 30°C, and contact time = 24 h (reproduced from Ref. 75, with permission from ACS Publications).

bead defects were fabricated by electrospinning. The surface properties of this blend fibrous membrane were characterized by adsorption of Cr(VI) in aqueous solution with the capability found to be 17 mg/g chitosan, which was much higher than that of 93- μm -thick chitosan/PEO blend film. In another work, chitosan was dissolved in trifluoroacetic acid (TFA) followed by electrospinning to generate chitosan nanofibers with a mean diameter of 235 nm.⁷² After neutralization using K_2CO_3 to render the as-spun fibers with water stability, the adsorption ability was evaluated that chitosan nanofibrous membrane had high adsorption affinity for Cu(II) and Pb(II) ions in aqueous solution. Moreover, the adsorption data fitted well with Langmuir isotherm and the equilibrium adsorption capacities for Cu(II) and Pb(II) reached 485.44 mg/g and 263.15 mg/g, respectively. As specific surface area of the adsorbent plays a key role in its performance, decreasing the diameter of electrospun nanofiber is found to be an effective way to improve adsorption efficiency. There was a report about superfine chitosan nanofiber with a mean diameter of 42 nm produced by electrospinning of 0.4 wt % chitosan in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP).⁷³ Because of the super high surface area per unit mass, this membrane can be applied in the continuous removal of Fe(III), Cu(II), Ag(I), and Cd(II). In addition, Cu(II) could be selectively removed in contrast to Cd(II) with a removal percentage of 99%.

Surface-Modified Membranes

Morphology Modification. Surface-to-volume ratio of a fibrous membrane is a major factor that determines the adsorption

capability. This ratio can be adjusted by phase separation during electrospinning process or by post treatment of the membrane. For example, micro-nano structure nanofibrous affinity membranes of polyethersulfone (PES) blended with PEI were fabricated by electrospinning technique followed by solvent etching in crosslinking solution.⁷⁴ In this blended solution of GA (glutaraldehyde), water, and acetone, PEI was not only solvent etched by solvent water but also simultaneously crosslinked by GA. The influence of the component of the crosslinking bath on the morphology of the resulting PES/PEI nanofibers was investigated. A series of static adsorption experiments indicated that the unique micro-nano structure could bring much higher surface area and efficiency for Cu(II) removal from aqueous solution.

Amino Groups. Amine groups are able to bind a variety of metal ions. Electrospun polyacrylonitrile (PAN) nanofibers can be functionalized as amino terminated (APAN) by the reaction with diethylenetriamine (DETA).⁷⁵ The resulted amidino diethylenediamine groups enabled APAN nanofibrous membrane with ability to chelate multiple heavy metal ions, such as Cu(II), Ag(II), Fe(II), and Pb(II). The adsorption of these ions fitted well with the Langmuir isotherm (Figure 2), with the maximum adsorption capacities being 150.6 mg/g, 155.5 mg/g, 116.5 mg/g, and 60.6 mg/g, respectively. Furthermore, heavy metal ions on electrospun APAN fibrous membrane can be desorbed in 2–10 M HCl solution with 90% of them released. In another way, electrospun PAN nanofibers can be amino functionalized

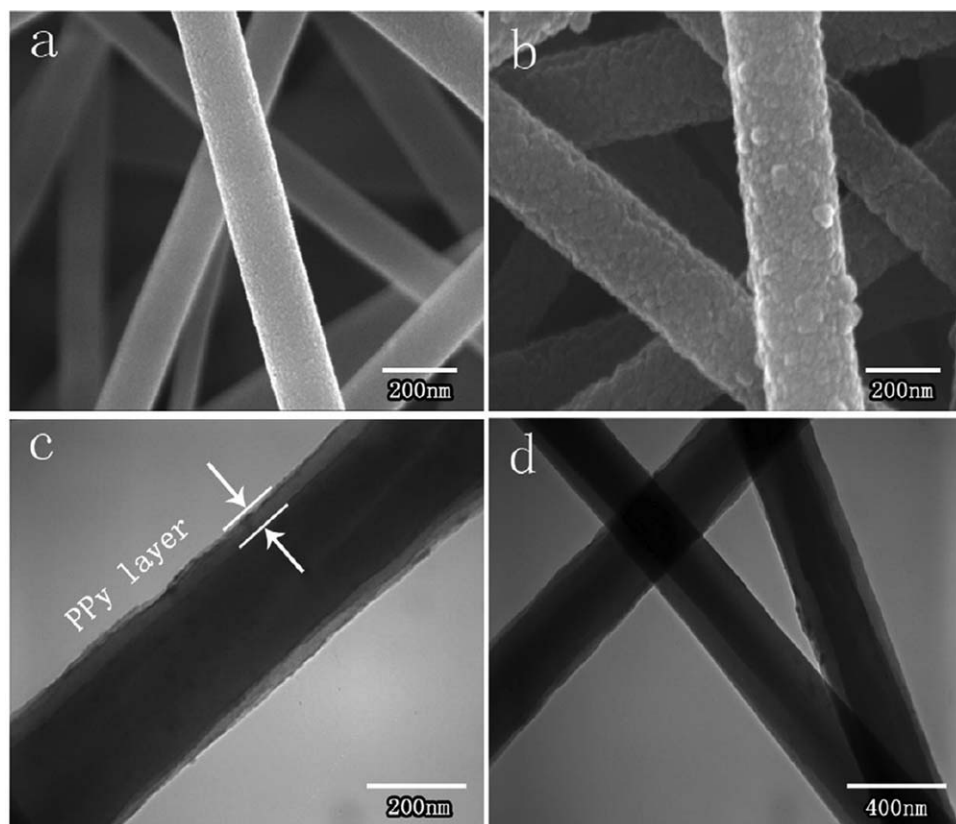


Figure 3. SEM and TEM images of pure PAN and PAN/PPy nanofibers, (a) pure PAN nanofibers; (b) PAN/PPy nanofibers; (c) PAN/PPy nanofibers (large scale); (d) PAN/PPy nanofibers (small scale) (reproduced from Ref. 77, with permission from Elsevier B.V.).

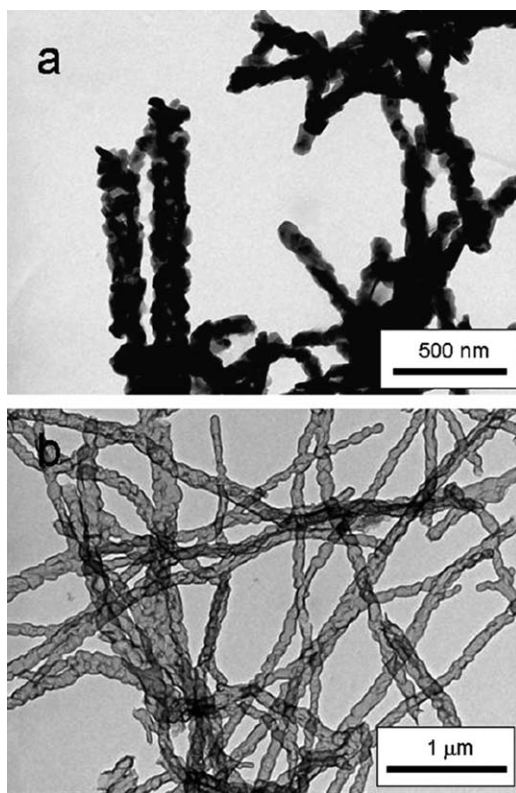


Figure 4. TEM images of (a) V_2O_5 nanofibers and (b) PPy nanotubes (reproduced from Ref. 78, with permission from Elsevier B.V.).

by post treatment like *in situ* polymerization of aniline.⁷⁶ PAN/PANI (polyaniline) composite nanofiber with a core/shell structure can act as a selective adsorbent for Cr(VI) ions, with the adsorption following a pseudo-second-order kinetic model and well fit with the Langmuir isotherm. It is also noticed that PAN/PANI nanofiber mat has a strong ability for reduction of Cr(VI) to non-toxic Cr(III). In addition, the adsorbent can be regenerated by immersing in 0.05 M NaOH solution. In another similar work, electrospun PAN/PPy (polypyrrole) core/shell nanofibers are synthesized via the same chemical oxidative polymerization technique (Figure 3).⁷⁷ This PAN/PPy nanofiber membrane can be used to adsorb Cr(VI) ions through ion exchange and reduction, with the maximum adsorption capacity calculated from the Langmuir isotherm model to be 61.80, 67.11, and 74.91 mg/g at 25, 35, and 45°C, respectively. Desorption results show that the adsorption capacity can remain up to 80% after five times usage.

As known to all, electrospun nanofibers always serve as template for varied deposition and incorporation owing to their tunable composition and nano-scale structure. An interesting work is the fabrication of bamboo-like PPy nanotubes using electrospun V_2O_5 nanofibers as a template.⁷⁸ V_2O_5 nanofibers were first obtained from annealing of electrospun PVP/VO(acac)₂ nanofibers, then PPy was uniformly deposited on the surface of V_2O_5 fiber through a vapor phase polymerization approach. At last V_2O_5 core was removed by 1 M HCl solution to obtain bamboo-like PPy nanotubes for Cr(VI) ion adsorption in

aqueous solution (Figure 4). It is found that the adsorption capacity was much higher than that of traditional PPy nanoparticles.

Other than post treatment, polymer precursors can be functionalized prior to electrospinning. This method possesses an advantage over post treatment because the possible morphology deterioration could be avoided. Polysulfone functionalized with 1-[bis[3-(dimethylamino)-propyl]amino]-2-propanol was electrospun into nanofibers and then used as a novel adsorbent for fast enrichment of heavy metal ions from aquatic environments.⁷⁹ The lowest concentration of metal ions that the functionalized nanofibers could detect was 0.001 mg/L, and the nanofibers could be regenerated and recycled for over five times without significant reduction in adsorption ability. NH₂-functionalized cellulose acetate/silica composite nanofibrous membrane was also prepared by combining sol-gel and electrospinning methods.⁸⁰ Before electrospinning, 3-ureidopropyltriethoxysilan was added to the polymer mixture to functionalize CA (cellulose acetate). The electrospun membranes exhibited high porosity and surface area for the adsorption of Cr(VI) ions from aqueous solution. In addition, a Schiff base ligand, 2-((Z)-(2-aminophenylimino)methyl)-6-methoxyphenol could also serve as a modifier for nylon-6 prior to electrospinning.⁸¹ The as-prepared fibrous membrane composes of nanofibers with average diameter of 80 ± 10 nm and specific surface area of 58 m²/g. The functionalized nanofibers possess strong affinity to heavy metal ions and have been successfully applied to pre-concentrate toxic metals from different aqueous environments.

3-(Triethoxysilyl) propylamine (APTES) can be used as sol-gel active silane coupling reagent with amine functionality. In a previous work,⁸² electrospinning technique was used as a coating method to prepare amine-functionalized solid-phase micro-extraction (SPME) fibers. The sol-gel solution used for coating SPME fibers was prepared by end-functionalization of hydroxyl terminated chains of polydimethylsiloxane (PDMS) with APTES, followed by electrospinning, then the plain silica fiber was uniformly coated by functionalized SPME fibers. This novel sol-gel coating SPME fiber prepared by electrospinning was used for direct mode extraction of dimethylarsinic acid (DMA),

monomethylarsonic acid (MMA), and arsenate (As(V)) from aqueous solutions.

Carboxylate Groups. Cellulose acetate (CA) is usually used in nanofiltration membranes due to its comparatively high modulus, adequate flexural, and tensile strength.⁸³ Grafted with functional carboxylate groups, CA can bind heavy metal ions through surface complexation mechanisms. For example, porous CA nanofibers were first fabricated by electrospinning, and then modified by grafting poly(methacrylic acid) (PMMA) using Ce⁴⁺ initiated polymerization.⁸⁴ The grafted PMMA chain can provide adsorptive carboxylate groups on CA fibers, thus the functionalized CA fibrous membrane inherits the ability to adsorb heavy metal ions. Adsorption results indicate that higher initial pH value leads to higher adsorption capacity and a relatively high selectivity for Hg²⁺. Moreover, regeneration of the adsorbent can be easily realized using saturated EDTA solution. In another circumstance, electrospun CA nanofibers can be deacetylated in NaOH aqueous solution to prepare cellulose nanofibers.⁸⁵ The latter was functionalized through reaction with oxolane-2,5-dione to be surface grafted with carboxylate group and shows great potential for heavy metal remediation. For the evaluation of adsorption ability of functional cellulose membrane, Cd(II) and Pb(II) ions from model wastewater samples were involved in the batch experiment, with the functionalized cellulose nanofibers exhibiting improved sorption compared to the functionalized cellulose bulk fibers.

Among the various fibrous materials, those made of PAN can be easily modified into chelating fibers owing to the presence of nitrile groups (C≡N) which can be readily converted to other chelating groups.^{86–88} For instance, nonwoven PAN nanofibrous membrane was first fabricated by electrospinning, followed by reaction with NaOH ethanolic/aqueous solution to introduce carboxylate groups that is capable of chelating metal ions.⁸⁹ The chelating ability of functionalized PAN fibrous membrane was tested using Cu(II) ions as the model hazardous metal ions, with the adsorption of Cu(II) well fitted with Langmuir isotherm model and the maximum capacity being 31.3 mg/g. Lastly, desorption of the metal ions on PAN fibers was achieved by immersion in 0.1 M HCl aqueous solution for at least 30 min.

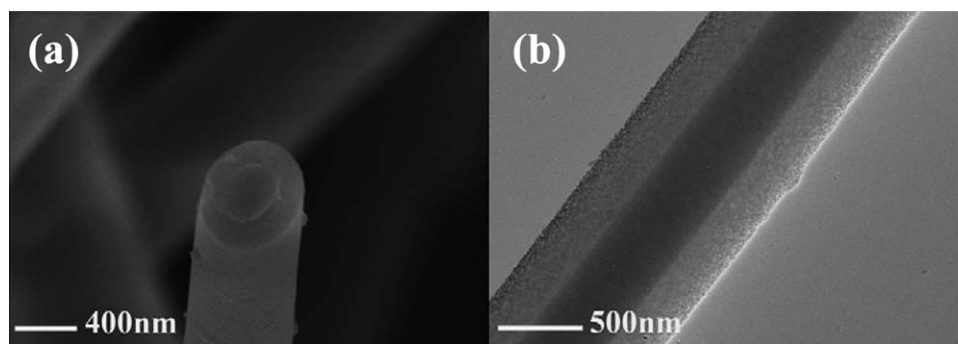


Figure 5. (a) High-magnified SEM images of one single nSiO₂@mSiO₂ fiber observed from the tip; (b) magnified TEM image of one single nSiO₂@mSiO₂ fiber (reproduced from Ref. 97, with permission from Elsevier B.V.). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

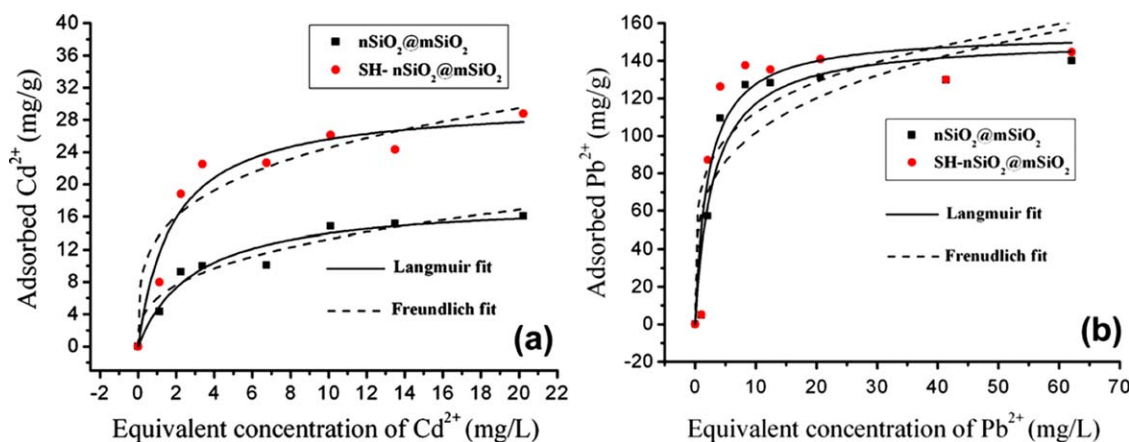


Figure 6. Sorption isotherms and corresponding fits of (a) Cd²⁺ and (b) Pb²⁺ (reproduced from Ref. 97, with permission from Elsevier B.V.). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Sulfonate Groups. Submicron ion-exchange fibers (IEF) of polystyrene (PS) and styrene–isoprene–styrene block copolymer (SIS) blend are prepared by electrospinning technology and further sulfonated with sulfuric acid to produce strong acidic cation ion exchange fibers.⁹⁰ Characterization of structure indicates that there are many sulfonated acid groups introduced onto the benzene wreath of styrene. Ion-exchange capacity (IEC) and Cu(II) ions adsorption tests indicate that the PS/SIS IEF has higher value of IEC and more rapid adsorption rate for Cu(II) than those of the submicron IEF derived from pure PS and the conventional IEF because there are more exposed functional groups for metal ions on PS/SIS IEF surface.

Mercapto Groups. With strong chelating effect for heavy metal ions, mercapto groups were introduced into electrospun PVA/silica nanofibers.⁹¹ PVA/SiO₂ gels were first prepared by adding 3-mercaptopropyltrimethoxysilane (MPTMS) in the mixture, which was then electrospun to generate PVA/SiO₂ fiber membrane and refluxed in ethanol/HCl to remove the template. This mercapto-modified membrane has a great potential for heavy metal ions adsorption. Cu(II) adsorption tests showed that the largest uptake of PVA/SiO₂ mesoporous membrane for Cu(II) was 489.12 mg/g, with the capacity maintained through six recycling processes of adsorption and desorption.

Other Functional Groups. Some researchers also explored other functional groups and combined them with electrospinning technology. Thioamide-group chelating nanofiber membrane was developed for the efficient removal of Au(III) ions from aqueous system.⁹² Electrospun PAN fibers were crosslinked by ethylenediamine, followed by the reaction with Na₂S·9H₂O to introduce thioamide groups. The nanofiber membranes display a high adsorption efficiency for Au(III) ions, which was proposed to be the collaborative effect of chelating and reduction.

Mesoporous PVP/SiO₂ composite nanofibrous membranes functionalized with thioether groups were also fabricated by sol-gel electrospinning.⁹³ The precursor sol was synthesized by one-step co-condensation of tetraethyl orthosilicate (TEOS) and 1,4-bis(triethoxysilyl)propane tetrasulfide (BTESPTS), using triblock copolymer poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (P123) as template. After the addition of PVP

and subsequent electrospinning, thioether functionalized nanofibers were obtained. This composite membrane exhibited highly selective adsorption of Hg²⁺ due to the presence of –S–.

Moreover, electrospun PS nanofibers incorporating pyrazole-1-carbodithioate and imidazole-1-carbodithioate as sorbent for the removal of Cu(II), Ni(II), and Pb(II) were also reported.⁹⁴ This novel composite membrane was proven to be an efficient sorbent for divalent heavy metal ions in aqueous environment. Dithizone is well-known for the determination of various metal ions. Therefore, the S-bonded dithizone was also co-electrospun with PS to fabricate functional fibrous membrane, which was used as a selective sorbent for solid phase extraction of lead (II).⁹⁵

Based on the mechanism that mercury ion can selectively bind to DNA to form thymine (T)-Hg(II)-T base pair, an interesting work was published concerning the preparation of T-grafted electrospun PVA/PEI nanofibers for selective removal of Hg²⁺ with high efficiency.⁹⁶ In this study, thymine groups were first grafted on PEI via conjugating amine groups of PEI and carboxyl groups of thymine-1-acetic acid. The as-formed PEI-T was then mixed with PVA, followed by electrospinning to generate electrospun PVA/PEI-T nanofibers. This functional nanofibrous sorbent displays excellent capability in the specific

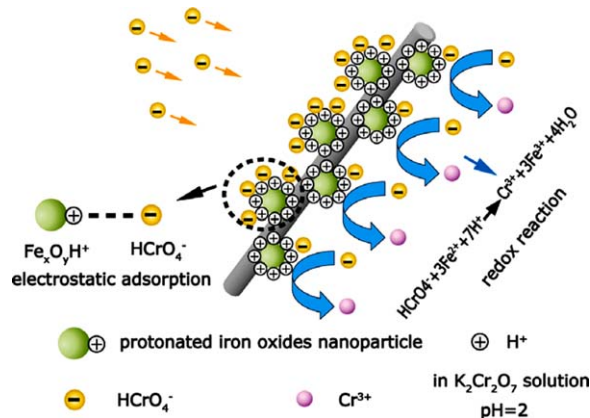


Figure 7. Schematic illustration for Cr(VI) removal mechanism (reproduced from Ref. 105, with permission from Elsevier B.V.). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

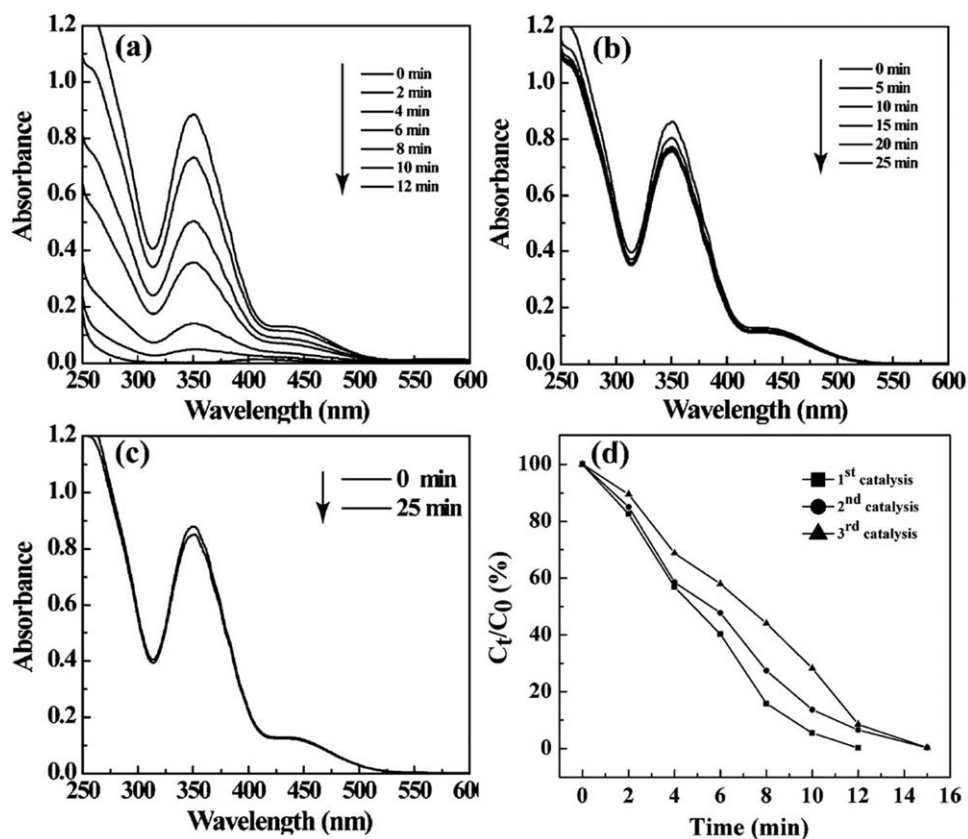


Figure 8. UV–vis spectra of Cr(VI) aqueous solution (a) treated with the Pd NP-immobilized PEI/PVA nanofibrous mat in the presence of formic acid; (b) treated with the PEI/PVA nanofibrous mat without Pd NPs in the presence of formic acid; (c) treated with only formic acid, respectively; (d) remaining fraction of Cr(VI) as a function of reaction time in the presence of the Pd NP-immobilized PEI/PVA nanofibrous mat as the catalyst for the first, second, and third catalytic reaction cycles (reproduced from Ref. 108, with permission from ACS Publications).

adsorption of Hg^{2+} in aqueous solution containing other competitive ions like Cu^{2+} , Zn^{2+} , Ca^{2+} , Cd^{2+} , Mg^{2+} , and so forth.

Electrospinning-Based Inorganic Fibrous Membranes. A novel structure of electrospun SiO_2 nanofibers composed of solid nonporous SiO_2 as core and mesoporous SiO_2 as shell ($n\text{SiO}_2@m\text{SiO}_2$) was developed for the removal of trace heavy metal ions from waste water.⁹⁷ In this investigation, $n\text{SiO}_2$ nanofibers were first generated via electrospinning of TEOS, followed by covering a mesoporous SiO_2 shell based on a modified Stöber method using CTAB (cetyltrimethylammonium bromide) as the directing agent for formation of the mesopores (Figure 5). At last, functional thiol groups were grafted on the $n\text{SiO}_2@m\text{SiO}_2$ fibers using MPTMS as the coupling agent to endow the fibers with chelating property. In this system, the core of nonporous SiO_2 was set to increase the flexibility, and the mesoporous shell was beneficial for increasing the specific surface area. In short, the thiol-functionalized $n\text{SiO}_2@m\text{SiO}_2$ fibrous membrane exhibited impressive performance on the removal of Pb^{2+} and Cd^{2+} from aqueous environment (Figure 6). Iron oxide–alumina mixed nanocomposite fibers also can be synthesized by electrospinning method.⁹⁸ Prior to that, the precursor solution was prepared by impregnating boehmite into polyvinylpyrrolidone (PVP)–iron acetylacetonate solution in a specific ratio. As-prepared electrospun fibers were sintered at

1000°C to convert them into pure oxide form for further adsorption of several heavy metal ions. The maximum sorption capacity from Langmuir equation was found to be 4.98 mg/g for Cu(II), 32.36 mg/g for Ni(II), 23.75 mg/g for Pb(II), and 63.69 mg/g for Hg(II).

Inorganic fibrous webs always tend to be brittle due to the crystallization of the materials. To deal with it, another inorganic component with good mechanical property can be introduced. A mesoporous $\text{TiO}_2/\text{ZrO}_2$ nanofibrous membrane was prepared by electrospinning the mixture of titanium (IV) isopropoxide and zirconium (IV) propoxide in PVE,⁹⁹ and subsequent thermal treatment to remove the organic components. Pluronic P123 was added in the electrospinning precursor to increase the surface area of nanofibers by generating intra-fibrous mesopores. The as-prepared $\text{TiO}_2/\text{ZrO}_2$ nanofibers were further surface modified via phosphonate coupling to graft amine and phosphonate functionalities, which showed excellent adsorption capacity for Cd(II), Pb(II), and Cu(II).

Functional Nanoparticle Incorporated Membranes

In the field of environmental remediation, nanosized materials especially active nanoparticles always play a key role. Iron oxide,¹⁰⁰ alumina hydroxide,¹⁰¹ noble metals,^{102,103} and so forth, have previously been reported to be effective materials for heavy

metal remediation. However, there are some serious drawbacks to restrict their practical applications like aggregation and second contamination. Electrospun fibrous membrane has an inherent ability for metal ion adsorption and filtration due to its large surface area and rich pore structure. The tunable surface functionality also makes it a good substrate and carrier for various active nanoparticles for heavy metal remediation.

The fabrication of boehmite nanoparticles impregnated electrospun fiber membrane has been reported.¹⁰⁴ The former was chosen to increase the surface of the active component. Both hydrophilic nylon and hydrophobic polycaprolactone (PCL) nanofibers were successfully embedded with boehmite, which may be useful for commercial filtration applications. Fe_xO_y incorporated electrospun nylon-6 nanofibers were also synthesized by electrospinning combined with hydrothermal strategy.¹⁰⁵ The amorphous iron oxide nanoparticles on the fiber surface showed excellent performance for the removal of Cr(VI) through electrostatic adsorption and redox reaction (Figure 7). In another study, multiwall carbon nanotubes (MWCNTs) reinforced electrospun PVA/PAA nanofibers were further incorporated with zero-valent iron nanoparticles.¹⁰⁶ The as-prepared material has high capacity and strong sorption of Cu(II) in aqueous solution, which was explained as chemical reduction and surface deposition to form Fe/Cu alloy. Zero-valent iron nanoparticles were also nucleated at the surface of chitosan nanofibers by electrospinning and subsequent liquid phase reduction of FeCl_3 using NaBH_4 .¹⁰⁷ Experimental results showed that this easy-made composite membrane is an excellent sorbent for inorganic arsenic uptake over a wide range of pH values.

Palladium (Pd) is one of the most important noble metal and widely used as catalyst. Electrospun PVA/PEI nanofibers were selected as an effective carrier for Pd nanoparticles by the complexation between PdCl_4^{2-} and amine groups on PEI.¹⁰⁸ After the reduction of NaBH_4 , Pd nanoparticles (NPs) were anchored on PVA/PEI fibers. The catalytic ability of the as-prepared composite fibrous mat was evaluated by reducing the toxic Cr(VI) to non-toxic Cr(III) in the presence of formic acid as reductant. It is found that this catalytic membrane was able to remove Cr(VI) from aqueous solution with an efficiency approaching 99.7% within only 12 min (Figure 8) and an impressive recycling performance.

CONCLUSIONS

Owing to their high porosity, huge specific surface area, flexibility in surface functionalization, and various impurities doping, increasing attention has been focused on electrospinning technology. There is no doubt to say electrospun polymer nanofiber-based materials have exhibited great advantages over other conventional and commercial adsorbents for heavy metal remediation. Even so, there still remain a lot of challenges. First, the difficulty in mass production of high quality nanofibers directly restricts their practical applications. Second, the selection of suitable polymers and modifiers to introduce new functionality to meet specific needs is another critical problem to be solved. And most important of all, the mechanical property of

the electrospun membranes needs dramatic improvements, which can be very essential to their utility.

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