



Morphology, Modification and Characterisation of Electrospun Polymer Nanofiber Adsorbent Material Used in Metal Ion Removal

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Abstract

Among a wide range of technologies available to separate metal ions, adsorption is a major treatment technique for removing or recovering metals from aqueous solutions. Electrospun nanofiber adsorbents have attracted research consideration due to the distinctive properties such as their high surface area, high porosity and high adsorption capacity which makes nanofibers a good choice for selective metal recovery applications. Thus, the modification of electrospun nanofiber adsorbents by functionalisation with suitable ligands for selective metal extraction is a growing area of scientific research aiming to improve the selectivity of the adsorption process. This study reviews and summarises available information related to the different nanofiber modification processes for increasing adsorption efficiency, functionality and selectivity of modified nanofiber adsorbents as well as improving their durability and stability during use. The surface properties of an adsorbent is an essential control factor for its metal ion adsorption efficiency. The various techniques available for characterisation of specific properties of nanofiber adsorbents are also considered. Lastly, the recovery of the metal ions after adsorption by regenerating adsorbent materials and understanding the kinetics of nanofiber adsorption processes is summarised and recommendations made for further studies in order to address existing weaknesses of these materials.

Keywords Adsorption · Electrospinning · Nanofiber · Morphology · Metal ion

Introduction

Water pollution is an environmental problem all over the world due to the discharge of industrial effluents which has become a threat to surface and ground water. Toxic metal pollution from industrial effluents such as tanneries, mining operations, metal plating facilities, and nuclear power plants can have a strong propensity for bioaccumulation in the food chain and a high ecological mobility [1, 2]. The removal

and recovery of toxic metal ions from these sources is of importance, thus a variety of technologies which include ion exchange, adsorption, chemical precipitation, flotation, coagulation–flocculation, filtration, membrane processes, reverse osmosis, and solvent extraction techniques exist [3–5] for the recovery of value or removal of toxic metals from the environment. The easiest, most effective, and cheapest technique among these is adsorption [6, 7].

There are several types of adsorbents in consideration for the adsorption of metals from aqueous solutions but some of these adsorbents are reported to have low selectivity, poor removal and recovery inefficiencies in dilute aqueous solutions containing metal ions. Such effluents often repeatedly fail to meet pollution regulation requirements [8], thus, the need arises for exploring other adsorbents including the unique and unusual properties of nanomaterials, which may have improved metal ion selectivity for recovery or better removal efficiency from low aqueous concentrations. The latest advances in nanotechnology include developing electrospun nanofiber adsorbents with rapid sorption kinetics and enhanced sorption capacity because of the high surface area and active surface sites of the nano adsorbents [9–12].

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Electrospun nanofiber research therefore remains an active area of research in material science mainly due to the potential for novel applications in diverse areas [13, 14].

Nanofibers have high specific surface area and excellent interfiber porosity in comparison with commercial resins or polymers [15–17], therefore nanofibers are becoming useful as commercially and industrially viable materials in various applications. The quantitative scientific and technical information about the nanofiber, electrospinning process and product characterisation are particularly important and recently, electrospinning has gained increased consideration due to its consistent production of fibers in the submicron range and for the versatility in spinning a wide range of polymeric fibers [18]. Diverse functional groups can be attached onto the polymer nanofiber by the application of organic reactions to a solid phase [19, 20] while cross-linked polymeric nanofibers having functional groups capable of binding metal ions also offer potential mechanical advantages such as robust and stable fibers for regeneration and reuse, allowing ease of operation [21]. These properties are important during the separation and removal of target metals from water in the environment and in aqueous solutions [22]. In most applications, it is desirable that the nanofiber adsorbent should be modified efficiently without destruction of its mechanical and adsorptive properties.

Developed nanofiber polymeric supports for the adsorption of various metals find applications for metal recovery in low aqueous concentrations. Polyacrylonitrile (PAN) electrospun nanofibers with Fe(III) and Zr(IV) based metal–organic frameworks (MOFs) were used to treat Pb(II) containing solutions to a drinking water standard of < 10 ppb of permeate Pb(II) concentration [23]. Feng and co-workers prepared electrospun amidoxime polyacrylonitrile/regenerate cellulose (AOPAN/RC) blend nanofibers membranes which exhibited superior adsorption capability for effective and efficient removal of toxic metal ions from water due to the synergistic effect between amidoxime and hydroxyl groups for metal ions chelation/coordination [21]. Electrospun PAN nanofibers synthesised by a two steps chemical grafting method involving chemical modification and hydrolysis with ethylene glycol (EG), ethylenediamine (EDA) or diethylenetriamine (DTA) onto the surface to prepare three novel nanostructured adsorbents that exhibited extremely high adsorption capacities for Zn(II), Cu(II) or Pb(II) from aqueous solutions [24].

This review therefore provides an overview of the synthetic approaches available for modification of the nanofibers and also reviews the nanofiber stability and robustness during and after modification. The review considers the characterisation methods that are suitable to understand nanofiber properties during synthesis and application. Consideration is also given to the regeneration and reuse of modified nanofibers for the recovery of metal ions and

the kinetics of nanofiber adsorption. It is hoped that this review will provide researchers and industry with clarity on the requirements for modification of nanofibers suitable for the recovery of selected metals, as well as for measuring specific nanofiber characteristics using various techniques. It also aims to inform researchers and industry of the current state of art in nanofiber adsorbent development. This review should provide end-users with information to strengthen the transfer of knowledge between research and industrial applications.

Nanofiber and Fabrication Process

Polymer nanofibers are a novel class of materials with diameters in the nanometre range. Fibers having diameters below 200 nm are usually classified as nanofibers and they provide a link between the nanoscale and macro scale world [25]. Polymer nanofibers permit chemical attachment of a higher number of functional groups during surface modifications compared to polymer microfibers and this opens possibilities for better surface functionalisation allowing nanofibers to be utilised as high capacity adsorbents for selected metals [26]. The nanoscale fibers are new functional materials, which have attracted attention due to their special properties such as layer thinness, high surface area per unit mass, cost effectiveness, low basis weight, high porosity, high permeability, flexibility in surface functionalities, and superior directional strength, which differentiate nanofibers from other non-woven fibers [27].

Electrospinning is a technique of electrostatic fiber formation using electrical forces to generate polymer nanofibers ranging from submicron to nanometer sizes from polymer solutions. Electrospinning is an old technology used for the production of polymer fiber, as it was first made known in 1930, but it did not achieve noteworthy engineering and industrial significance due to inconsistent and low molecular orientation, high fiber diameter distribution, low output of the process, and poor mechanical properties of the electrospun fibers [28]. In 1934, Antonin Formhals patented this spinning process which has been further developed into an attractive and established procedure for the preparation of polymeric as well as composite nanofibers today [29].

Nanofiber fabrication technologies have been significantly accelerated to produce nanoscale fibers from a wide range of different polymers. Electrospinning is presently the only procedure among several others such as self-assembly, template synthesis, drawing and phase separation which permits the production of continuous fibers with low nanometre diameters [14]. The important parameters in designing the morphology of electrospun polymeric fibers are spinning solution concentration, the applied voltage, and the solvent properties [30]. Electrospun nanofibers may be collected as

uniaxially aligned arrays, single fibers, nonwoven mats or multi-layered films as a result of changing the electrospinning process and setup [18]. Apart from achieving the control of macroscopic organisation of nanofibers, electrospinning also permits nanofiber structural complexity as well as developing secondary structures of the individual fibers [31].

The electrospinning method brings several advantages over other traditional nanofiber fabrication processes such as the option to fabricate continuous nanofibers from numerous polymers for mass production, increased porosity, and control over morphology. Further advantages of the electrospinning process include its adaptability, technical simplicity [32] and the well-developed commercial up-scale of nanofiber technology for electrospun nanofiber production [33]. A comparison of different nanofiber fabrication methods has been discussed and reviewed elsewhere which demonstrated that the fabrication methods are varied and can utilise thermal, chemical, physical, and electrostatic fabrication techniques [34]. The morphology of the electrospun nanofiber and the fiber diameters can be altered by changing the electrospinning process parameters [18, 27]. Different techniques are applied to fabricate polymeric nanofibers having diverse morphologies [35], and a range of different nanofiber morphologies can be obtained such as aligned nanofibers [36], beaded nanofibers [37], branched fibers [38], core-sheath nanofiber structure [39], nanofibers with ribbon-like morphology [40] and porous nanofibers [15, 41].

Nanofiber Adsorbent and Modification Processes

The surface properties of polymer nanofibers are important for their applications but most polymeric nanofibers are chemically inert and do not perform any function beside filtration. However, the nanofibers' surface can be modified to incorporate specific functional groups or functionality [42]. In numerous applications, the properties that are desired at a polymer surface are often distinct from the bulk properties of the material, and the control of such surface properties can be accomplished by the surface functionalisation using different physical or chemical processes [43]. Passive or non-metabolic adsorption mechanisms includes ionic exchange (displacement of a proton or bound metal cation), adsorption, complexation, electrostatic interaction, van der Waals forces, chelation (covalent or ionic interaction), precipitation, coordination and reduction by reducing functional groups [44].

One of the foremost advantages of nanofiber materials in adsorbent design is their vast versatility for surface modifications [34] after which they subsequently exhibit diverse adsorption behaviour based on the nature of the functional groups on the nanofiber surface [13]. The design of a

nanofiber-supported ligand meant for a targeted metal ion involves two components: the choice of polymer nanofiber as the support and the subsequent functionalisation. The nanofiber support should be physically and chemically stable, with ample porosity to allow access of reagents for the functionalisation reaction and the metal ion's interaction with the ligand. Several functional groups on the nanofiber surface such as amino, carboxyl, ester, hydroxyl, carbonyl-internal, carbonyl-terminal end, phosphate, and sulfhydryl can passively adsorb metal anions and cations from aqueous solutions. Surface functionality engineering of nanofibers is important and will provide new structures for materials science [45].

There is a substantial increase in scientific publications from 1999 to 2019 obtained when a search of the concept “polymer, nanofiber” was made as shown in Fig. 1a, whereas Fig. 1b shows the publications over the same period when the term “polymer nanofiber, metal ion adsorption” was introduced. We found that conducting a Science Direct search which included terms such as “polymer”, “nanofiber”, “metal ion”, and “adsorption” was limiting since this misses many references, whereas “polymer” nanofiber” included most available articles regarding polymer-containing nanofibers. These histograms in Fig. 1a and b are therefore proposed to establish the trends rather than the exact numbers in nanofiber research.

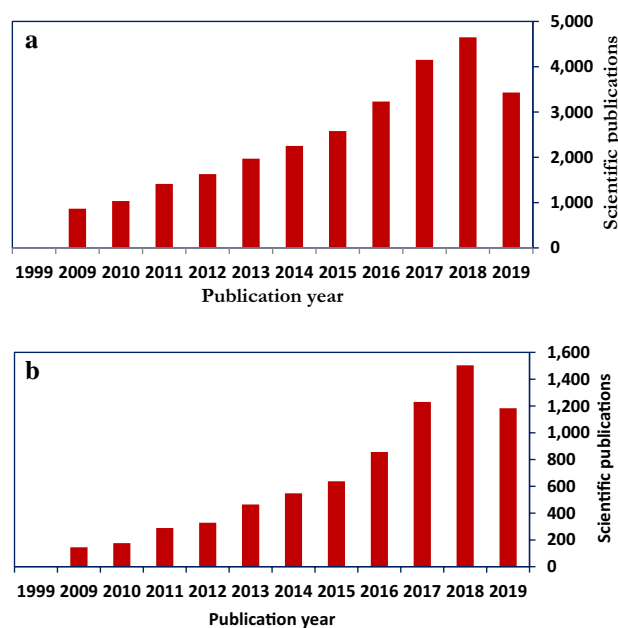


Fig. 1 Annual number of scientific publications (1999–2019) **a** when the terms “polymer nanofiber” was used and **b** when the terms “polymer nanofiber metal ion adsorption” were used as keywords. Data analysis was completed using Science Direct search system on May 13, 2019

The increase in nanofiber fabrication and adsorbent application research may be due to growing interest in the production of different polymeric nanofibers and improvement in analytical tools which allowed the nanofibers produced to be better observed and characterised. Many research studies have reported improved modification strategies but some of them failed to report nanofiber stability, reuse and regeneration. Fibers with ligands are complex and expensive to make and therefore should be highly durable and stable since they will not be commercially viable unless they are highly selective for extraction of metals that have commercial value. The nanofiber adsorbents may not be very useful for low value toxic metals unless there is a specific demand for high purity metal.

The research and development of nanofibers for adsorption is still emerging and it is expected that more approaches will increase the knowledge in this new area especially for the recovery of valuable metals from aqueous solution. Electrospun polymeric nanofiber adsorbents have a vast potential for the deposition and support of selective ligands on their surfaces due to the high inter-fiber connections, high porosity, and high surface area [46]. A variety of new fiber materials have also been developed and have found industrial applications based on their excellent mechanical properties and/or special functions and up to date, a range of natural and synthetic polymers have been electrospun [29] and applied to adsorption of metals. Nanofibers therefore provide an attractive solution to the selective removal of toxic or valuable metals from aqueous and effluent solutions.

Chelating Ligands in Use

To increase adsorption efficiency, surface modifications of semi-natural and synthetic nanofibers by the use of functional groups of sulfonic, carboxylic, amine and amide are being developed [47, 48]. The selected functional ligands are typically chosen based upon their identified or known behaviour under different conditions of extraction. Engineering ligand selectivity into polymeric nanofibers or precursor solutions requires understanding how a targeted analyte could be recognised by a particular ligand. Selectivity is improved using ligands which can chelate or coordinate the targeted metal ion. The selectivity of an adsorbent for metal ions is mainly attributed to the nature of the ligand attached onto the nanofiber matrix. The addition of different complexing agents or changing the environmental characteristics (ionic strength, temperature, pH) can modify the selectivity. Ligands often chemically attached include crown ethers, amines, thiols, imidazoles, Schiff bases, oximes, pyridines, hydroxylamines, and some selected phosphorus ligands [49].

Over several decades, researchers have described the use of pyrazole, pyridine and imidazole ligands in separating cobalt, copper and nickel from some selected base metals

[50, 51]. These ligands generated specific attention because they exhibited high selectivity towards Cu(II), and as soon as the ligands were modified, they became more selective towards Co(II) and Ni(II). Although numerous aromatic bidentate amine ligands were synthesised in the last decades, only a few of the ligands have ever been utilised for adsorption purposes. Okewole et al. [52] investigated the utilisation of an extractant containing imidazole type pyridine ligands which was selective for extraction of nickel(II) while Ndayambaje et al. [53] developed an adsorbent containing imidazole type pyridine ligands which was highly selective for nickel.

Pearce et al. [54] further investigated three pyrazole based pyridine ligands using their capacity for extraction which exhibited selective and effective extraction and removal of copper(II) and nickel(II) metals from diverse metals mixtures. Okewole et al. [55] prepared Merrifield resin by modifying it with 2, 2'-pyridylimidazole, and utilised it for the selective separation and adsorption of nickel from several base metal ions from sulfate synthetic solutions. Several polymer-supported ligands in REEs separations include: EDTA and DTPA [56, 57], 8-hydroxyquinoline (8-HQ) [58], hydroxamic acid [59], tetramethylmalonamide (TMMA) [60], 2,6-diacetylpyridine [61], phosphorus ligands [62], o-vanillinsemicarbazone (OVSC) [63]. Chitosan and cellulose have an intrinsic sorption ability for Nd(III) and the efficient recovery of these metals improved with the grafting of aspartic acid [64] while the grafting of carboxylic acid and amino groups on the surface of cellulose improved La(III) sorption capacity and efficiency [65].

Approaches to Preparing Functional Fibers

The approaches to preparation of functional fibers are essentially via different routes, namely, by pre-electrospinning which is the modification of a functional polymer followed by electrospinning into a nanofiber, or by blending and co-electrospinning the blend using special spinning techniques, or by post-functionalisation i.e., fiber preparation followed by introduction of functional groups [66]. Generally, the modification of any polymer support can be either done chemically (through covalent bonding of the ligand to the matrix) or physically (via sorption of a chelant into the matrix) [67]. The functionalised electrospun nanofibers have a great prospect when functionalised through introduction of metal selective ligands into the fibers. By altering the surface chemistry or by coating techniques, such fibers could then be applied to chelate target metal ions from solution [68]. A selection of the various nanofiber modification studies giving best fitted isotherm and kinetic models and the maximum adsorption capacities for selected metals of some nanofiber adsorbent are provided in Table 1.

Table 1 Nanofiber modification studies with their adsorption isotherms and kinetics model

Adsorbents	Functionalisation	Metal ion	Isotherm models	Kinetic models	Maximum adsorption capacity (mg/g)	References
Keratin/polyamide 6	Blend	Cu(II)	F	Ps2	103.5	[69]
Polyvinyl pyrrolidone	Triethoxysilane	Cr(III)	–	–	97	[70]
PES/PEI	Blend	Pb(II) Cu(II) Cd (II)	L	Ps2	94.34 161.29 357.14	[71]
PVA	TEOS/APTES	Cd(II))	L	DE	327.3	[72]
PAN	Phosphorous	Pb(II)	F	Ps2	176.99	[73]
		Cu(II)	F		131.41	
		Ag(I)	F		237.53	
		Cd (II)	L		37.30	
PEO/Chitosan	Blend	Ni(II)	L	Ps1	357.1	[74]
		Cd(II)		Ps2	248.1	
		Pb(II)			237.2	
		Cu(II)			310.2	
PAN/chitosan	UiO-66-NH ₂ MOF	Pb(II)	R–P	Ps2	441.2	[75]
		Cd(II)			415.6	
		Cr(VI)			372.6	
Chitosan	TiO ₂	Cu(II)	R–P	Ps1	715.7	[76]
		Pb(II)			579.1	
Chitosan	Hydroxyapatite	Pb(II)	L	Ps2	296.7	[77]
		Co(II)			180.2	
		Ni(II)			213.8	
PA6	Mg(OH) ₂	Cr(VI)	F	Ps2	296.4	[78]
PET/PAN	GO/Fe ₃ O ₄	Pb(II)	R–P	Ps2	799.4	[79]
		Cr(VI)			911.9	
Polyethyleneimine	Polydopamine	Cu(II)	L	Ps2	33.59	[80]
Chitosan/PVA/PES	Aminated-Fe ₃ O ₄	Cr(VI)	L	Ps1	509.7	[8]
		Pb(II)			525.8	
PAN	Amidino diethylenediamine	Cu(II)	L	Ps2	150.6	[81]
		Ag(I)			155.5	
		Fe(II)			116.5	
		Pb(II)			60.6	
PAN	Hydrazine	Cu(II)	–	–	114	[82]
		Pb(II)			217	
PAN	SiO ₂ + APTES	Th(IV)	L	Ps2	249.4	[83]
		U(VI)			193.1	
		Cd(II)			69.5	
		Ni(II)			138.7	
PAN	Diethylenetriamine	Cu(II)	L	–	116.52	[84]
PAN	Mercaptopropyl trimethoxysilane	Hg(II)	L	–	57.49	[85]
PAN	Hydroxylamine	Cu(II)	L	–	215.18	[86]
		Fe(II)			221.37	
SF/CA	Blend	Cu(II)	–	–	22.8	[87]
PAN/PANI-nylon	Core–shell	Pb(II)	L	–	960	[88]
		Cd(II)			911.7	

F Freundlich, *L* Langmuir, *RP* Redlich–Peterson, *Ps1* Pseudo-first-order kinetic model, *Ps2* Pseudo-second-order kinetic model, *DE* double-exponential kinetic model, *PAN* polyacrylonitrile, *SF* silk fibroin, *CA* cellulose acetate, *PES/PEI* poly(ether sulfones)/poly(ethyleneimine), *PEO* poly ethylene oxide, *PVA/TEOS/APTES* poly (vinyl alcohol)/tetraethylorthosilicate/aminopropyl triethoxysilane, *GO* graphene oxide, *PET* polyethylene terephthalate, *MOFs* metal–organic frameworks

As shown in Table 1, the metals mostly targeted are those with economic value because the nanofibers adsorbents are costly and not too useful for low value toxic metal removal. The metals include Cu(II), Ag(I) and Ni(II). The ligands often used include different amine compounds such as triethylenetetramine, diethylenetriamine and ethylenediamine and are mostly selective towards Cu(II) ion. The routes of established chemical processes for introduction of functional groups are further discussed below.

Pre-functionalisation and Electrospinning

The abundance of specific functional groups on the surface of polymers can allow different chemical modifications to be carried out in the polymer solution before electrospinning to enable the adsorption of metal ions from aqueous solutions. This modification method may be through monomer-grafting or direct modification, which enables attachment of a diverse range of functional groups or ligands to the polymer backbone [89]. For instance, grafting of monomers onto cellulose is an important modification strategy of cellulose where side chain grafts are covalently attached to a main chain of a polymer backbone to form a branched copolymer. New properties are obtained depending on the monomer grafted onto the cellulose and this grafting can be performed in either an homogeneous or heterogeneous medium [90] and subsequently electrospun into nanofibers. Zhao et al. [91] prepared ethyl-cyanoethyl cellulose from ethyl-cellulose and acrylonitrile. The obtained ethyl-cyanoethyl cellulose was successfully electrospun into porous fibers using tetrahydrofuran (THF) solvent. In 2005, Shukla et al. [92] showed that hydroxypropyl cellulose (derivative of cellulose) could be electrospun utilising two dissimilar solvents at a variety of applied voltages and two different tip-to-collector distances of 10 and 15 cm.

Blending and Co-electrospinning

Another process of surface functionalisation is physical blending and co-electrospinning where the ligands can be incorporated into the bulk nanofiber material in the course of the production or fabrication process. The two most often reported approaches of ligand incorporation into polymer nanofibers are co-axial electrospinning or direct mixing into a polymer solution. It has been made known that the direct mixing technique can allow for greater amounts of molecules to be incorporated resulting in improved activity when compared to other modification approaches [93]. In addition, ligand molecules integrated by this procedure are embedded into the bulk material of the fibers and can enable extended adsorption through the nanofibers. The consequence of the addition of ligands to the electrospinning solution during

electrospinning can lead to viscosity increase, resulting in nanofibers with greater diameters.

This technique for adjusting surface properties through the incorporation of small molecules has a drawback as the molecules are not bonded to the polymer and may migrate to the polymer surface, thus could be removed during washing or regeneration, therefore this approach may not be very effective. Other disadvantages are that the molecules may compromise the nanofiber's bulk physical properties and because they are not strongly bound to the polymeric matrix, they may be detached by leaching, dissolution, evaporation, or wear. Moreover, the processes may also be expensive and difficult [20, 94]. Darko et al. [95] incorporated carbodithioates into polystyrene solution before electrospinning and employed it as a sorbent for adsorptive enrichment of toxic metals. The study observed that the ligand was held in place by the benzene ring of the polymer through hydrogen bonds. The preserved activity of the ligand during use was because the carbodithioates ligands were stable in both basic and acidic conditions. Nevertheless; this method did not produce a nanofiber adsorbent material with the desired properties. Awokoya et al. [96] fabricated imprinted fibers using electrospun nanofiber from a blend of poly (ethyl-enterephthalate)/polyethylenimine solution comprising of molecularly imprinted polymer (MIP) for the removal and extraction of nickel-5,10,15,20-tetraphenylporphine (NTPP) from organic media which effectively and reliably adsorbed NTPP and showed selective adsorption and excellent reusability. Thus, blending of suitable particles into the polymer melt is possible.

Post-functionalisation

The post-functionalisation method is more popular than the two previously discussed methods and offers a significant advantage in that a variety of functional nanofibers can readily be produced from one common precursor polymer by employing suitable, established chemical reactions for introduction of functional groups to the polymer matrix. However, the post functionalisation approach requires fibers with an acceptable mechanical strength as a prerequisite and the resulting fiber can further be subjected to crosslinking to improve the mechanical strength to an adequate extent [66]. The molecular configuration of the polymer nanofiber requiring modification is also essential because suitable functional groups for ligand bonding may already be present, and if not, the functional groups can then be added to the surface by chemical treatments.

Different methods such as plasma treatment [97], or surface graft polymerisation [98] were used to modify the surface of polymers, but for the modification of nanofiber surfaces, rigorous reaction conditions and experimental conditions such as irradiation and plasma treatment should be

avoided since the ultrafine polymeric nanofibers are not as strong as polymer bulk materials and therefore may be easily destroyed. For example, in their work, Ma et al. [99] showed plasma treatment could destroy PET nanofibers severely and therefore, Ce(IV) was used to initiate grafting polymerisation of methacrylic acid (MAA) on PET surfaces and the results showed that the morphology of the PET nanofiber was very well-maintained after the grafting.

Covalent surface bonding as a post-functionalisation approach after electrospinning can be used to chemically bond suitable ligands to exposed functional groups directly on the nanofiber surface. Covalent surface bonding provides greater long term retention and more efficient attachment of ligands [93]. Covalent incorporation of suitable ligands on nanofibers usually involves at least two requirements: exposed functional groups on the fiber surface and covalent bonding of suitable ligands to these functional groups. Amine and carboxyl functional groups are the most frequently used in polymer nanofiber surface modification reactions in literature [100, 101]. Some applications of electrospun nanofibers functionalised with ligands as adsorbent was previously summarised by Pereo et al. [18]. If the desired functional groups cannot be grafted easily or directly to the polymer nanofiber surface then a linker molecule with the desired exposed functional groups can be attached to the fiber surface. For instance, an additional di-amino-poly (ethylene glycol) (di-NH₂-PEG) was used as a linker molecule to add functional amine groups to polyester nanofibers [102].

Fate of Modified Adsorbents

The fate of the nanofiber adsorbent after the modification process should be considered so that the resolution of one problem does not lead to a new problem since the surface property of an adsorbent is an essential control factor for its adsorption efficiency. Care should be taken such that the surface of the modified nanofibers exhibit similar morphologies when compared to the pristine nanofiber mats by showing little signs of degradation or cracks. The fibrous structure of the nanofiber membrane should not be distorted

or over swelled. The nanofibers should be handled properly to ensure that the porous and large surface areas are not compromised during modifications and applications.

The nanofiber stability with the attached ligand should also be confirmed before use so as to be sure that the ligand is not leached during application or regeneration by washing in acid or alkaline solution. Thus, the nanofiber adsorbent can then be reused successfully over several cycles especially during the regeneration of the adsorbent. For instance, in a study by Saeed et al. [103], PAN nanofibers (Fig. 2a) were chemically modified with amidoxime groups. The surface morphology of the PAN-oxime nanofiber mat did not show any serious degradation or cracks and showed a very similar morphology to the pure PAN nanofibers (Fig. 2b).

In another study, the PAN nanofiber surfaces were chemically functionalised by 2-(2'-pyridyl) imidazole (PIM) ligand [53] at different reaction times. The PAN nanofibers direction and shape changed as the surface modification reaction time increased (Fig. 3b–d). The results showed that as the reaction time was increased, the fibers tended to fuse together during the modification reaction. The strands of the fibers were fused extensively after 60 min (Fig. 3c) even though their porosity and flexibility were retained. At 120 min, the fibers were completely deformed and the porosity and mechanical integrity were completely lost and unusable. Therefore prolonged reaction time can cause the modified nanofibers to become more intertwined and the fiber segments conglutinate to each other at touching points leading to loss of their individually fibrous character.

In the study by Da Silva et al. [104], nylon six nanofibers which were initially homogeneous and long, with fiber diameters in the range of 190 to 290 nm, increased in diameter to between 290 and 350 nm with the incorporation of di-(2-ethylhexyl) phosphoric acid (DEHPA) into the nanofibers, together with the appearance of some points of agglomeration. Chitpong and Husson [105] demonstrated the success of polymer grafting when they prepared high-capacity membranes by grafting poly(acrylic acid) (PAA) and poly(itaconic acid) (PIA) to cellulose nanofiber mats but there was an indicated pore constriction due to the thin film coatings by each polymer grafted to the nanofiber

Fig. 2 SEM images of **a** PAN and **b** PAN-oxime (25% conversion) nanofibers which were electrospun from a 15 wt% solution [103]. Reprinted with permission from Elsevier

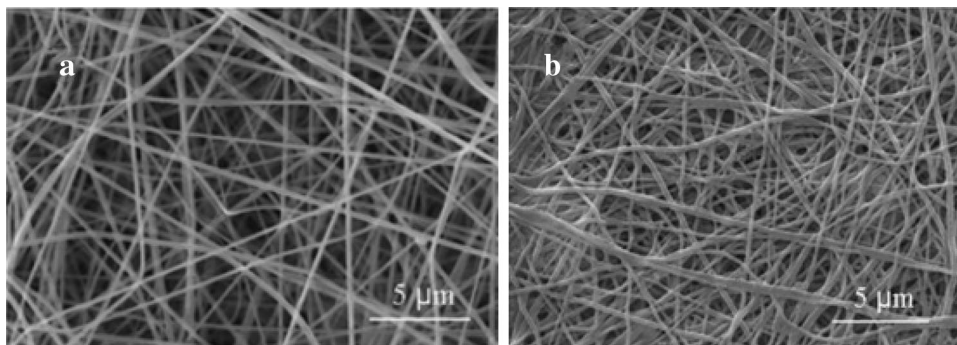
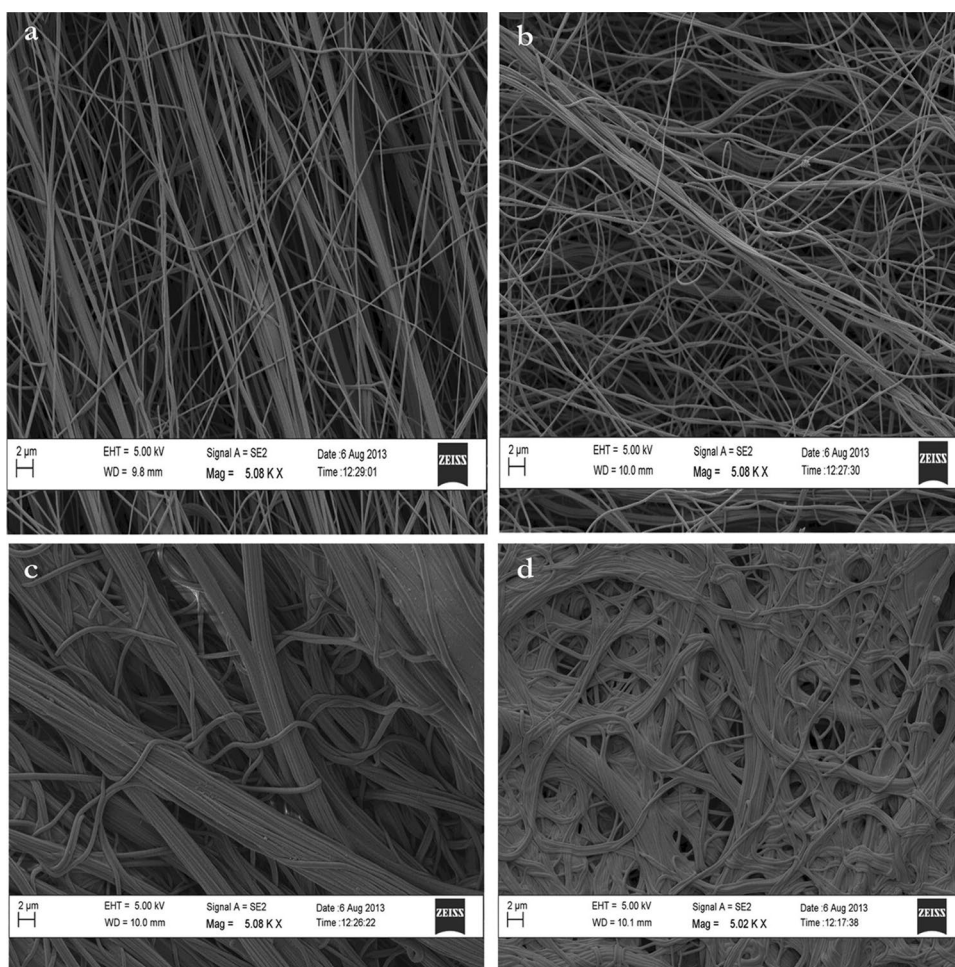


Fig. 3 HRSEM image of **a** unmodified PAN; **b** PAN-pim at 30 min; **c** PAN-pim at 60 min and **d** PAN-pim at 120 min [53]. Reprinted with permission from Elsevier



membranes. The regenerated cellulose (RC) nanofibers after modification with PGMA (in chloroform) showed fibers coated with PAA and PIA but the surfaces of individual nanofibers coated with PIA and PAA thin films partially filled the pore spaces between nanofibers causing an observed decrease in porosity by 15–20%.

Crosslinking of Nanofibers

Crosslinking is used for improving the chemical and/or mechanical properties of nanofibers and the function of the crosslinking reagent is to ensure that all chains are mutually connected by joining the polymer chains together forming an “infinite network” [106]. Cross-linking may be advantageous because it could increase the mechanical properties of the nanofiber membranes and render the nanofibers insoluble in all solvents. But it should be done with care so as not to compromise the high surface area and extensive porosity of the nanofiber mats [107]. Several methods, such as modifying with functional groups [108], radiation crosslinking or

thermal crosslinking [109] have been employed to produce crosslinked polymers.

Some electrospun nanofibers typically lack good structural and mechanical integrity especially when biodegradable or natural polymers form a part of the electrospun mats [110]. Crosslinking such matrices may allow for controlled and sustained nanofiber structure which otherwise would have been influenced by the rapid structural loss or instability of the nanofiber mat. Apart from stabilising the nanofiber structure, crosslinking also controls the thermochemical behaviour of the electrospun structure [110]. Chemical crosslinking, which involves the formation of bonds via chemical reactions between polymer chains, is known to produce stiffer and stronger bonds. Nanofiber chemical crosslinking can be achieved in a number of ways. In one process, known as reactive electrospinning, the crosslinking occurs as the polymer solution is electrospun. The electrospinning solution consists of crosslinker, polymer, and photo-initiator but with the application of UV irradiation, crosslinking starts while the jet is still in-flight. The shortcoming of this process is the viscosity problems that arise when the fibers are crosslinked [111].

Another reported method used to induce crosslinks in electrospun nanofibers is the post-electrospinning crosslinking which can be performed in one of two ways. The fiber mat, after spinning, can be placed in a solution containing the cross linker. This type of solution-based crosslinking works well for microfibers, but fails for some fibers that are in the range of 100 nm because the dissolution of the smaller fibers may occur so quickly that the crosslinks needed to form in the gel simply do not form in time [112]. Nanoscale poly (vinyl alcohol) (PVA) fiber (100–500 nm) aggregates were prepared by Ding et al. [113] using an electrospinning method and crosslinked chemically. They observed that the properly crosslinked PVA fiber aggregates had better mechanical properties and antiwater solubility than the non-crosslinked PVA fiber aggregates. In 2013, Li et al. [114] crosslinked PAN nanofibers before functionalisation of the nanofibers which caused the nanofibers to be thicker without influencing their overall morphology while the fiber surfaces still remained smooth.

The last possibility is that the crosslinker is electrospun with the polymer solution, but crosslinking is only performed later and may be initiated by heating or UV radiation [112]. An example is the crosslinking of PVA/PAA electrospun nanofibers, which after spinning, were placed in an oven at 145 °C for a few minutes to induce an esterification reaction between the acid and hydroxyl groups [115]. The potential of some cross linkers such as glutaraldehyde (GA) and epichlorohydrin (EPI) to have high levels of toxicity, immunogenicity and carcinogenicity to humans and animals should also be considered. This makes it essential to find an environmentally friendly cross-linker and green cross-linking procedure for the fabrication of adsorbents [73]. The solubility of chitosan in acid media is a serious drawback that was overcome by crosslinking [116], where diethylenetriaminepentaacetic acid (DTPA) an environmentally friendly cross-linker was used for the production of the chitosan-DTPA adsorbent [73]. The most commonly reported cross-linkers are glutaric dialdehyde, epichlorohydrin, formaldehyde, nitriloacetic acid, glutaraldehyde, divinyl sulfone, genipin, formaldehyde–urea mixtures, iminodiacetic acid, vinyl ketones, ethylene glycol diglycidyl ether, epoxides and organic diisocyanates [44].

Characterisation Techniques for Electrospun Nanofiber Adsorbents

One of the most common questions that arise during nanofiber adsorption processes includes the stability of the nanofiber adsorbent during and after the modification process as well as during regeneration, therefore the characterisation of the surface chemistry and morphological structure of an adsorbent is essential. The surface properties of the

nanofiber adsorbent can be elucidated using different techniques, including Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray microanalysis (EDX), X-ray diffraction spectroscopy (XRD), and in particular, the studies of the adsorption capacity are essential for full characterisation. The use of only one of these techniques may not support the complete understanding of the mechanisms involved in the modification and adsorption process. Hence, a combination of these analytical techniques is used to ascertain the nature of the morphology, metal binding groups, structure, and nanofiber composition which can be explored and optimised. Specific quantification of nanofiber properties by different analytical techniques are further discussed.

Fourier Transform Infrared (FTIR) Spectroscopy

The Fourier transform infrared (FTIR) spectroscopy technique offers molecular-level information, allowing investigation of the functional groups, bonding types, and molecular conformations [117]. The process is non-destructive to the nanofiber and the measurement is reproducible and involves only a small amount of material with minimum sample preparation but this technique is only capable of providing a qualitative description. Liu et al. [118] confirmed the structural changes between pure PAN nanofibers and 1.4% polyacrylonitrile/ferrous chloride (PAN/FeCl₂) composite nanofibers before and after Cr(VI) adsorption while Wang et al. [119] confirmed that the FTIR spectrum of poly (amic acid)-glycidol-hyperbranched polyethylenimine (PAA-g-HPEI) membrane nanofibers had a new, strong adsorption peak at 3420 cm⁻¹, attributable to the N–H stretching of HPEI terminal amino group. Shariful et al. [120] determined the formation of hydrogen bonding between chitosan and polyethylene oxide (PEO). Their results showed the broad peak of pure chitosan at 3350 cm⁻¹, which corresponded to N–H and hydrogen bonded O–H stretching vibrations. Habiba et al. [121] also used the technique to monitor the deacetylation of chitosan molecules after hydrolysis, where new –NH₂ groups were produced. Ndayambaje et al. [53] used FTIR to confirm the modification of PAN nanofibers with 2-(2'-pyridyl) imidazole for adsorption of nickel (II) and for regeneration experiments to confirm that the amidine linkage between the PIM ligand and the PAN nanofibers remained intact during regeneration cycles with ethylene diamine tetra acetic acid (EDTA) solution.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) in polymer research has been used to get a better understanding of structural

properties in polymers and is utilised by many researchers to observe the morphology of the nanofibers [122]. Besides, SEM is considered to be the most popular of the microscopic techniques due to the general simplicity of image interpretation and the ease of specimen preparation [123]. SEM is considered to be a non-destructive technique, because the X-rays generated by electron interaction do not lead to volume loss of the sample, and so it is possible to analyse the same material repeatedly. SEM interpretation of nanofibers elucidates the topography of the surface features, dimensions of the fibers, and elemental information/metal distribution with an excellent depth of field.

Fayemi et al. [33] observed the morphology and diameter of unfunctionalised and functionalised styrene-based nanofibers using SEM which indicated an increase in the diameter of the sorbent materials after the introduction of ion-exchange groups. In another study of amino-rich hydrothermal carbon-coated electrospun polyacrylonitrile fiber (PAN@NC) adsorbents, the morphologies of PAN and PAN@NC fibers were observed by SEM which showed the pure PAN fibers were continuous and smooth with few beading defects and with an average diameter of 348 nm after loading with hydrothermal carbonaceous materials [124]. Ndayambaje et al. [53] modified PAN nanofibers with 2-(2'-pyridyl) imidazole for adsorption of nickel(II) and SEM observation showed that the fibers lost their structure after excessive crosslinking during modification. Energy-dispersive X-ray spectroscopy (EDS) spectroscopy is routinely coupled with SEM or TEM analysis for elemental characterisation of a sample before and after metal adsorption. The EDS spectra taken before and after metal adsorption can verify the existence of metals on the adsorbent surface. When polyacrylonitrile/ferrous chloride composite nanofibers prepared by electrospinning were used to remove Cr(VI), the EDS analysis of Cr(VI) loaded nanofiber clearly showed that the Cr(VI) was adsorbed onto the composite nanofibers [118].

Transmission Electron Microscopy

Transmission electron microscopy (TEM) is an alternative to SEM for obtaining the fiber diameters of extremely small fibers (< 300 nm). It provides information on the compositional, topographical, crystalline and morphological structures which are widely used for the characterisation of various nanofiber adsorbents. It offers clearer evidence on the internal structure of the nanofiber that can reach sub-atomic resolution. TEM characterisations of the morphologies of PAN and amino-rich hydrothermal carbon-coated electrospun PAN fiber (PAN@NC) fibers revealed the core/shell structure obtained which showed that the carbon materials were coated onto the surfaces of PAN fibers uniformly [124], while TEM images of thiol-functionalised mesoporous poly

(vinyl alcohol) (PVA/SiO₂) composite nanofibers confirmed that the nanofibers obtained after extraction with ethanol/HCl had both porous and rough surfaces [125].

X-ray Diffractometry

X-ray diffractometry provides a non-destructive technique for characterising crystalline materials and gives information on structure, preferred crystal orientation, phase and other structural parameters such as crystallinity, grain size, and crystal defects [126]. Typically the narrower and more intense the peak, the more ordered the nanofiber sample becomes while broad peaks are usually associated with small particle size or a disordered material, lacking regular repeating order. Rathna et al. [127] reported the process of electrospinning where the polymer chains had less than the required time to form an orderly array because of the simultaneous processes of evaporation of solvent and solidification of elongated nanofibers which may inhibit ordering of the subunits and favours their amorphous nature. The formation of hydrogen bonding between chitosan and PEO was determined by XRD to prove the presence of PEO crystals in the PEO nanofiber membrane [120]. The XRD pattern of chitosan/polyvinyl alcohol (PVA)/zeolite nanofibrous composite membrane fabricated via electrospinning and used for adsorption implied that chitosan lost its crystallinity to some extent during modification as shown in Fig. 4 [121].

Figure 4 demonstrates the XRD peaks patterns indicating that some zeolite peaks were changed after incorporation with the nanofibers to prove the interaction between chitosan, PVA, and zeolite. The chitosan peaks around 10°

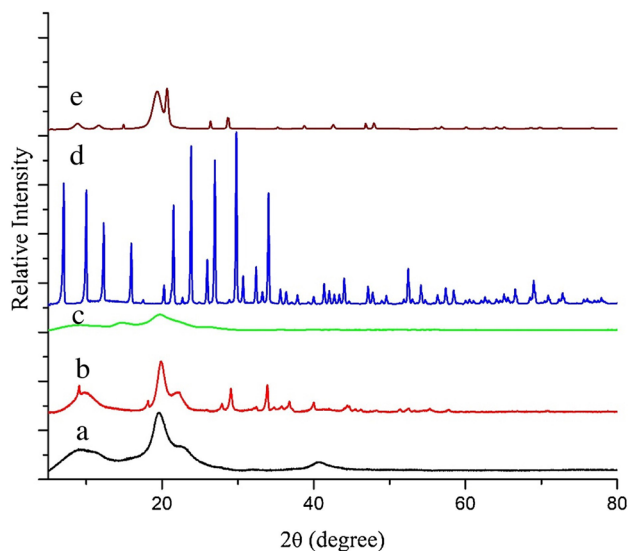


Fig. 4 X-ray diffraction (XRD) spectra of for (a) PVA nanofiber, (b) chitosan (c) chitosan/PVA nanofiber, (d) zeolite and (e) chitosan/PVA/zeolite nanofiber [121] Adapted with permission from Elsevier

and 20° became weak in the composites representing strong interaction between chitosan, PVA, and filler materials, as well as loss of crystallinity.

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is another suitable and sophisticated technique used for surface analysis of adsorbents due to its sensitivity and chemical specificity. This technique is used to determine the empirical formulae, elemental composition, and the oxidation state of the metal bound to the adsorbent and its ligand effects in transition–metal complexes existing within the surface region of the sample [128]. This technique is surface-specific due to the short range of photoelectrons excited from the solid. For each particular element; a certain characteristic binding energy can be associated with each core atomic orbital. In nanofiber adsorption, XPS has been used to scrutinise the surface functional groups, the oxidation state of the bound metal, and the binding sites of the adsorbent during adsorption mechanism studies. XPS was used to further investigate the surface composition of poly (amic acid) (PAA) electrospun nanofiber membranes grafted with hyperbranched polyols. The increased oxygen element content and the increased O/N ratio were attributed to the presence of a large amount of vicinal hydroxyl groups on the membrane surface [119]. In a study by Ju et al. [129], the characteristic peaks of oxygen (O), carbon (C) and fluorine (F) atoms were observed using XPS measurement of PVA-based carbon nanofibers with honeycomb-like carbon porous structure.

Atomic Force Microscopy

Atomic force microscopy (AFM) is one other technique that can be used to determine the fiber diameter even though obtaining an accurate measurement becomes a more difficult process due to tip convolution. However, AFM remains the best instrument for observing the exact descriptions of the fiber surface and any type of surface morphology. For a precise measurement, two fibers crossing each other on the surface are generally chosen [130]. This technique offers a three-dimensional image; therefore, it gives information concerning changes in the surface roughness of a sorbent. AFM was utilised by Neghlani et al. [84] to study the morphology changes of aminated PAN nanofibers before and after copper adsorption which was observed to be completely non-uniform (Fig. 5). The calculated average roughness (S_a) of the surfaces for the APAN nanofibers was 19.2 nm before adsorption which increased to 20.2 nm after the Cu(II) ions were adsorbed.

Koushkbaghi et al. [8], used the roughness information from AFM images of PES/PVA/chitosan before and after crosslinking of nanofibers with moist GTA vapour nanofiber membranes to indicate that the incorporation of aminated- Fe_3O_4 nanoparticles into the PVA/chitosan nanofiber layer was responsible for the increased metal ion sorption and permeability by showing that the average roughness of the dual layered membranes slightly increased due to the loading of A- Fe_3O_4 nanoparticles into the nanofiber membranes.

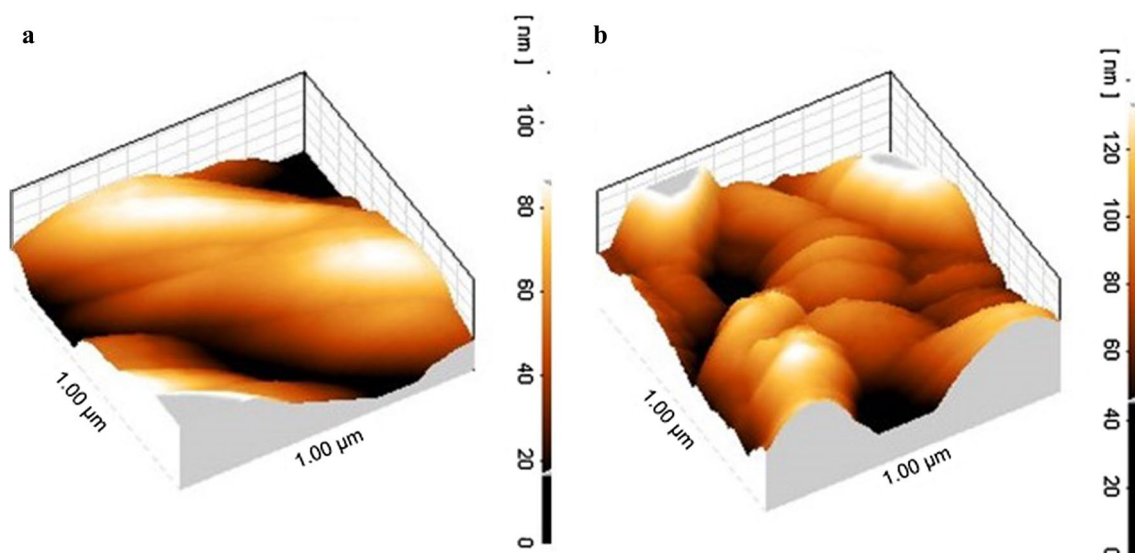


Fig. 5 Tridimensional AFM images of **a** aminated PAN-nF before adsorption and **b** after copper adsorption [84]. Reprinted with permission from Elsevier

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) probes the thermal properties of materials where changes in physical and chemical properties of materials are measured as a function of time (with constant mass loss and/or constant temperature) or as a function of increasing temperature (with constant heating rate) [131]. TGA is generally used to determine selected characteristics of materials that demonstrate either mass loss or mass gain due to oxidation, loss of volatiles (such as moisture) or decomposition. Chaúque et al. [132] modified the surface of electrospun PAN nanofibers with polyethylenediaminetetraacetic acid (EDTA) using ethylenediamine (EDA) as the cross-linker. The TGA thermograms of the nanofibers elucidated the thermal degradation steps. Thermal steps during the preparation of samples may destroy the nanofiber samples since they are heat sensitive, therefore it is important to note the nanofiber thermal profile for any modification procedures in order not to degrade the fibers during functionalisation.

Brunauer, Emmett and Teller

Brunauer, Emmett and Teller (BET) is applied for determining pore volume, surface area, and pore size distribution of the adsorbent using N_2 adsorptions–desorption at cryogenic temperature and under vacuum. The specific surface area and porous feature are crucial parameters that affect adsorption performances of nanofibers. Most nanofibers are organic thus thermally labile and need careful sample preparation before BET measurement to drive off volatiles that could interfere with the BET measurement. The pore size and surface area of functionalised cellulose nanofibers modified with oxolane-2,5-dione were compared to the cellulose fibers using BET with results showing the fiber integrity and porosity were maintained during deacetylation and functionalisation [133]. BET analysis of the surface area of TiO_2 coated chitosan nanofibers did not change significantly when the coated TiO_2 on the surface of chitosan nanofibers was compared with pure chitosan nanofibers [76]. Chen et al. [12] studied the specific surface areas of PAN nanofibers and reported a significant increase from 0.72 to $2.81\text{ m}^2\text{ g}^{-1}$ after grafting branched polyethyleneimine (bPEI), while the pore diameter of PAN nanofibers was mainly distributed between 10 and 80 nm. The pore diameter of aminated polyacrylonitrile nanofibers (APAN) was reduced to the range of 2–30 nm thus APAN nanofibers showed an increased adsorption capacity when compared to other adsorbents [12]. Zhao et al. [124] carried out N_2 adsorption–desorption measurements to determine the specific surface area, pore volume and pore diameter and results showed that the surface area increased from 3.74 to $14.61\text{ m}^2/\text{g}$ (Fig. 6) after the hydrothermal reaction and as the surface area increased,

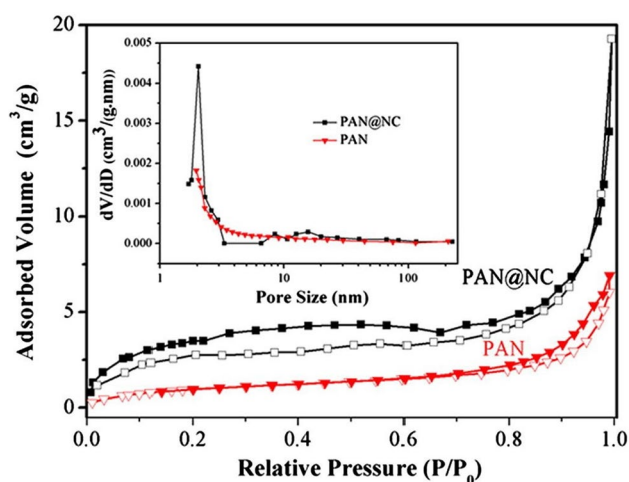


Fig. 6 N_2 adsorption/desorption isotherms for PAN and PAN@NC fibers (the inset shows pore size distribution curves) [124] Reprinted with permission from Elsevier

the pore volume also increase which became beneficial to the adsorption process.

Adsorption Isotherms and Kinetics of Nanofiber Adsorption

Several factors govern the adsorption capacity of nanofibers such as the nature of the metals being extracted, pH of the solution, adsorbent particle size, dosage, agitation, initial metal concentration and temperature. In order to adequately design models for the removal of metals from aqueous media when using nanofiber adsorbents, it is essential to find the kinetic model and best-fit isotherm relating the effect of observable parameters on the overall adsorption rate. This information then makes it possible to estimate the efficiency of the prepared adsorbent for application in suitable industrial adsorption system designs. Adsorption isotherms and the kinetic models are widely used to provide information about the amount of adsorbed ion by a certain adsorbent and about the interaction between the adsorbents and adsorbate [134] while kinetics studies are useful tools for finding the optimal conditions for the full-scale adsorption process [135]. Numerous studies have appeared in which different materials have been investigated for their uptake capacities and kinetics. A selection of these studies giving best fitted isotherm and kinetic models and the maximum adsorption capacities was provided in Table 1 for selected metals of some nanofiber adsorbent.

The mechanism of adsorption between the metals and the nanofiber adsorbent can help to determine the different adsorption behaviour. Adsorption isotherm models are used to describe the relationship between metal ion concentrations

adsorbed at the interface and the amount in bulk [136] and there are several prominent recognised adsorption isotherms such as Dubinin and Radushkevich (D–R), BET, Temkin, Harkins–Jura, Redlich–Peterson, Halsey, Henderson and Smith isotherm equations models [137] which could be used to probe the equilibrium data of nanofiber adsorbent to expose distinct physicochemical properties of the adsorbents which direct the sorption process. Besides these models, the Langmuir and Freundlich models have become the most popular [138]. The Langmuir isotherm assumes that all binding sites have equal affinity for the adsorbate, and when it is applicable, it shows that adsorption occurs through the formation of a monolayer of adsorbed molecules (saturation of the adsorbent) while the Freundlich isotherm describes adsorption onto heterogeneous surfaces that provide adsorption sites of varying affinities. Table 1 depicts the use of nanofiber adsorbents as having higher maximum adsorption capacity especially when compared with typical resins like ion exchange resins 1200H (26.73) and IRN97H (43.29) mg/g for copper adsorption [139], melamine–formaldehyde–diethylenetriaminepentaacetic acid (MF–DTPA) chelating resin with Co: 16.84, Cd: 17.7, Zn: 15.32, and Cu: 14.84 mg/g respectively [140] and IRN77 and SKN1 cation exchange resins for chromium adsorption which was found to be 35.38 and 46.34 mg/g [141].

Kinetic modelling reveals the mechanism of adsorption and potential rate-controlling steps such as mass transport or chemical reaction processes. The most common are the pseudo-first and pseudo-second order kinetic equations. It is worthy to note that the above models include all the adsorption steps (i.e., intra particle diffusion, film diffusion and adsorption); and the reason they are called pseudo models is because they cannot identify the adsorption mechanism [142]. Kinetic models have been used to test experimental data in order to clarify the adsorption process and to probe the mechanism of sorption and possible rate controlling steps such as chemical reaction and mass transport processes. The adsorption process could be governed by diverse types of mechanisms such as mass transfer, pore diffusion, chemical reaction and diffusion control. The kinetics of metal ions sorption is an important parameter for designing sorption systems and is a prerequisite for selecting the optimum operating conditions for full-scale batch metal removal processes. Rapid adsorption kinetics has important practical significance as it will expedite the scale up of the process to smaller reactor volumes ensuring economy and efficiency [143].

Desorption and Regeneration of Nanofiber Adsorbent

Environmental regulations prohibit the release of toxic pollutants from industrial activities to the environment, and the need for conservation of raw materials has led to the

consideration of recycling, extraction, recovery and reuse of metals of value. The choice between recovery of valuable materials from waste and disposal of waste seems to hinge on mainly two factors: economics and technology. The costs are possibly the most essential factor that limit the recycling, recovery and reuse of industrial waste products. In some applications, it may be economic to discard the used adsorbent in which case it may be necessary to describe it as a waste. However, the concentration of metal and nature of the adsorbates will dictate the disposal or recycling and recovery method to be followed. Moreover, better selectivity is needed for recovery of specific elements of value.

Disposal would be preferred when the adsorbent is of low cost or very difficult to regenerate (possibly because adsorbates are held by chemical forces) and the adsorbed products of the adsorptive separation are not of very high value. In the majority of process applications, disposal of the adsorbent as a waste is not an economic option especially in the case of nanofibers and therefore regeneration is carried out either in situ or external to the adsorption vessel to an extent sufficient that the adsorbent can be reused without disrupting the ligand [144]. Regeneration of an adsorbent with simultaneous recovery of the adsorbate can be achieved if, after loading, the process is reversed by shifting the equilibrium point away from the solid phase. This would apply mostly when the adsorption is based on precipitation but if a ligand is holding the metal, it is the metal–ligand bond that needs to be targeted. Typical regenerants used are solvents for organic adsorbates and basic or acidic solutions when the adsorbate metal ion is a weak acid or base, respectively [145].

The regeneration of the modified adsorbent and the stability of any moiety attached to the surface of the nanofiber are very important in adsorption in order to promote their reusability. A major problem in the use of nanofibers adsorbents that is evident from the literature is the ligand stability during reuse. It is therefore important to test the nanofiber adsorbents during regeneration for ligand stability to confirm whether the functional fibers can withstand short term contact with different regenerants. The potential practical application and the process economics depends on stable, reusable fibers. In the adsorption process, the adsorbent materials usually have to be regenerated for reuse after their application and the stability of the grafted chelating moieties on the surface of nanofibers are tested in different media such as acid and basic solutions because pH may have an effect. Desorption studies assist to elucidate the nature of the adsorption process and aid to recover the sorbed metal ions from sorbents. Moreover, it is helpful to be able to regenerate the sorbents so that they can be used repeatedly to adsorb metal ions selectively.

Only a few studies have reported regeneration and ligand stability of the nanofiber adsorbents. However, there are several useful desorption agents currently being explored

for desorption and regeneration of modified nanofibers after adsorption. The desorbing agents could be HCl, HNO₃, NaOH, EDTA, NaCl, H₂SO₄ and H₃PO₄. For instance, desorption efficiency experiments were carried out with 0.05 M EDTA and 0.05 M NaOH solutions for toxic metal ions in a study using poly(ether sulfones)/poly(ethyleneimine) nanofibrous affinity membranes [71]. The regeneration over eight cycles of adsorption–desorption of cadmium ions onto the poly (vinyl alcohol)/tetraethylorthosilicate/aminopropyl triethoxysilane composite nanofiber, was shown by rapidly washing the fibers with 1 mol L⁻¹ HNO₃ [72]. The reusability of the polyvinylpyrrolidone/silica/3-aminopropyl-triethoxysilane nanofiber adsorbent for Cd(II), Pb(II) and Ni(II) was investigated in five adsorption–desorption cycles using 0.5 M HNO₃/0.1 M HCL in equal volume ratio solution [136]. The reusability of polyacrylonitrile nanofibers modified with 2-(2'-pyridyl) imidazole ligand nanofibers was investigated after four successive adsorption regeneration cycles carried out in 10 mL solution of 0.1 M EDTA for 1 h for desorption of nickel [53]. 0.01 M H₃PO₄ aqueous solution was chosen for desorption of La³⁺ ions from the nanofibrous *p*-sulfonatocalix [8] arene membranes [146].

Conclusion and Future Perspectives

The use of functionalised nanofibers offers a technological alternative to classical adsorbents. They show promise for selective recovery of valuable metals from aqueous solution or for water and wastewater treatment. Progress has been made by developing effective binding capacities toward different metal ions. The impetus of nanofiber adsorption development for industrial processes are due to their structural characteristics such as the availability of a wide variety of chemical and morphological modification techniques, good structural stability, high porosity and interconnectivity, high surface area to volume ratio and controllable dimensions of the electrospun nanofiber as well as their rapid kinetics.

The further development of electrospun nanofibers as adsorbents is needed so as to improve the adsorption process. It is vital to examine the morphology of nanofibers after modification. Chemical modifications of nanofibers generally have been found to improve the adsorption capacity of nanofiber adsorbents, possibly due to the formation of new functional groups and the increase in active binding sites after modification which favour higher uptake of specific metals. Part of the challenges therefore faced by nanofiber adsorbent technologies and modification, include aspects such as nanofiber damage, nanofiber structure alteration or degradation, and poor stability which can only be overcome by appropriate functionalisation or crosslinking of the nanofiber adsorbent.

It is also important to note that improvement and research progress in the different modification approaches for preparing modified nanofiber adsorbents remains an emerging field of research that requires further exploitation of innovative methods for developing more efficient, robust and selective adsorbents. The regeneration of the modified adsorbent and the stability of any ligand attached to the surface of the nanofiber are important aspects to consider in adsorption in order to promote their selectivity, reusability, practical application and improve their process economics. A major problem in the use of nanofibers is the ligand stability during reuse, it is therefore important to test the adsorbents during regeneration for stability to confirm that they can withstand short term contact with different regenerants.

The characteristics of nanofiber adsorbents can be clarified using different techniques. The use of any one of these methods alone may not be sufficient to generate information of the properties or mechanisms involved during modification, but a combination of techniques can be used to ascertain the description of metal binding groups, morphology, structure and nanofiber composition which can be optimised and explored. Functional groups like amino, ester, hydroxyl, carboxyl, carbonyl-internal, carbonyl-terminal end, sulfhydryl, and phosphate on the nanofiber surface are used to adsorb metal cations and anions from aqueous solutions, and the nanofiber efficiency can be further quantified by adsorption studies.

Extensive research is presently being devoted to appropriate understanding of the nanofiber ligand stability, nanofiber adsorption isotherms, kinetics, and thermodynamics for developing efficient new nanofiber adsorbents that are highly selective for metals of value and in all cases, it is necessary to determine the best-fit isotherm. A kinetic model relating to the effect of observable parameters on the overall rate is needed to evaluate the efficiency of the prepared nanofiber adsorbent and for developing suitable industrial adsorption systems. There also remain the challenge for future understanding and further research studies on nanofiber adsorbent fabrication and binding kinetics between metal–ligand coordination.

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