REVIEW ARTICLE

Recent advancement in development and modification of nanofibrous matrix for the application in sensing and remediation of water pollutants

Dolphee Khurana[1] · Swathi Sadashiva[1] · Bipasa Dey[1] · K. P. Guruprasad[1] · Shyamasunder N. Bhat[2] ·
Bhisham Narayan Singh[1]

Abstract

Electrospun nanofibers have been extensively investigated in recent years for the generation of various advanced sensing technique like high efficiency biosensors, chemosensors, colorimetric sensing strip, and nanofibrillar-based biosorbent for waste water management, remediation and environmental monitoring. The present review article highlights various different types of conventional sensors, their limitations and the further advancement towards development of highly sensitive sensor with faster response time using functionalized nanofibrous matrix. It also explains the various approaches for the generation of nanofibrous matrix through melt blowing, force spinning, template melt extrusion and electrospinning methods and their further modification with suitable probe for the detection and elimination of various water contaminants. This review discussed various nanofibrous matrices that have been modified for the sensing and remediation of heavy metals such as mercury (Hg), lead (Pb), copper (Cu), organic pollutants such as dye, petroleum, phenolic compounds, and microorganisms such as Escherichia coli (*E. coli*), BVDV (bovine viral diarrhoea virus), Staphylococcus aureus (*S. aureus)* and Candida albicans (*C. albicans).* Finally, the various challenges and future perspectives associated with the usage of nanofibrous matrix-based sensors for detection and remediation of water pollutant are discussed.

Keywords Nanofibrous matrix · Biosensors · Water pollutants · Heavy metal sensing and remediation

Introduction

Water is the most irreplaceable liquid that plays an integral role in the survival of life on earth. Water in pure form is necessary for plants, animals, humans, etc. for their survival and utilized by human beings for various purposes such as agriculture, industry, drinking, household, etc. According to WHO (World Health Organization), almost 2 billion people consume microbially contaminated drinking water that can cause diarrhoea, typhoid, cholera, dysentery, and polio, which leads to diarrhoeal death of over 485,000 people per year. Not only microbes but the chemical effluents containing heavy metals like copper (Cu), cadmium(Cd), zinc(Zn), mercury(Hg), arsenic(As), lead(Pb), chromium(Cr), silver(Ag) etc. from the textile, agricultural, and pharmaceutical industry can cause toxicity if consumed, leading to a wide range of health hazards (Some et al. 2021). Heavy metals are one of the most commonly released contaminants in water bodies, since they are non-biodegradable, lead to bioaccumulation and over a period can directly / indirectly affect a wide range of organisms due to biomagnification (Zamora-Ledezma et al. 2021). Other than heavy metals organic compounds such as oil from the mill, oilfield wastewater etc. can also pollute the water. These organic substances may have the potential to react with other substances and leads to formation of very harmful chemicals. For example, it has been reported earlier that when phenolic compounds, chlorine and acetic acid were released in the pond, they reacted with each other to form a herbicide 2,4-D that contaminated the groundwater and caused crop damage upon using as a source for irrigation (He et al. 2022)

✉ Bhisham Narayan Singh
   bhisham.singh@manipal.edu

1   Department of Ageing Research, Manipal School of Life
    Sciences, Manipal Academy of Higher Education, Manipal,
    Karnataka 576104, India

2   Department of Orthopaedic, Kasturba Medical College,
    Manipal Academy of Higher Education, Manipal,
    Karnataka 576104, India

Water quality monitoring helps us to assess the suitability of water for a particular use but the exponential growth of the human population, rapid urbanization, and industrialization leads to a drastic downgrade of the water quality. Early detection and remediation can help in improving the quality of water and further preventing water pollution. There are several types of detectors developed for the monitoring of water quality based on evaluation of changes in pH, conductance, turbidity, dissolved oxygen etc. Previously, used conventional techniques had the disadvantage of frequent data sampling, sample pre-treatment and these majorly comprised of extensive laboratory techniques thus making the conventional technique expensive and time-consuming. The development of biosensors made a difference in allowing the detection of water quality onsite using certain specific biological markers for specific biochemical entities and can be detected using simple electrochemical detection. The conventionally used biosensors for the detection are of four types – optical, thermal, electrochemical, and piezoelectric. The main drawback of these biosensors was that they were unable to create a visual difference to perform naked-eye onsite detection. To circumvent this limitation, nanofibrous biosensors were developed which provided the advantage of naked-eye onsite detection. Though biosensors were an effective tool for the detection of pollutants in water, nanofibers came with a bigger advantage of possessing a high surface area to volume ratio, high porosity, better specificity and sensitivity as well as higher loading capacity which not only helped in sensing water contaminants with a visual difference but also helped in remediation of contaminants (Halicka and Cabaj 2021) (Ejeian et al. 2018) (Odobašić et al. 2019).

The present review highlights the various types of conventional biosensors available for the detection of water contaminants and the advancement of nanofibrous sensing systems for the detection and remediation of water pollutants. The different fabrication techniques for nanofibrous-matrix generation such as melt blowing, force spinning, electrospinning and template melt extrusion have also been highlighted.

Herein we discuss the various nanofibrous matrices that have been developed and modified between the years 2010 and 2021 for the sensing and remediation of heavy metals such as mercury, lead, and copper, organic pollutants such as dye, petroleum, and phenolic compound, microorganisms such as *E. coli*, BVDV (bovine viral diarrhoea virus), *S. aureus* and *C. albicans*. We also summarized the advantages, limitations and efficacy limits associated with the differently functionalised nanofibrous matrices for sensing and remediating different water contaminants. Finally, we put forward the challenges and future scope in the usage of nanofibrous matrices.

Biosensors and their types

Biosensors are devices composed of biological detection elements, a transducer and a display interface. The biological recognition material is immobilised and is connected to a transducer, which converts the biochemical signal into an electrical signal. This electrical signal forms the basis for the detection of an analyte. Figure 1 shows the schematical workflow of biosensors (Odobašić et al. 2019). Detection of water contaminants using biosensors requires the appropriate selection of the biological detection element and transducer based on the action of the contaminant on the targeted subject (Tsopela et al. 2016). In the last few years, biosensors have become important tools in detecting water pollutants because they not only detect the major contaminants but also detect trace levels of contaminant as well and often help in real-time analysis of the contaminant (Ejeian et al. 2018). Moreover, a biosensor can play a potential role in a low-cost portable highly efficient device development for the onsite analysis of contaminants and also overcomes the limitations of conventional technologies in the detection of trace contaminants (Tsopela et al. 2016). Biosensors have been classified into four types based on the transduction mechanism (i) electrochemical, (ii) optical, (iii) piezoelectric and (iv) thermal biosensors (S C I E N C E' S C O M P A S S, n.d.).

Fig. 1 Schematical representation of biosensor and its basic components based on mechanism of analyte detection
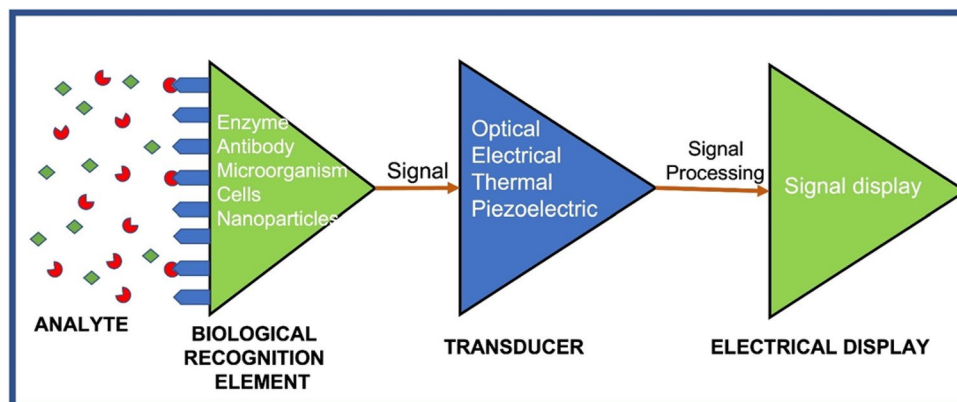
Optical biosensors

Optical biosensor allows direct, real-time and label-free detection of chemical analyte or biological samples (Damborský et al. 2016). In an optical biosensor, the biological detection element reacts with an analyte, which results in changes in input light, and finally detected by the transducer. The amplitude of oscillation in input light will helps in measurement of the analyte's concentration. Also, optical biosensors are free from electromagnetic interference, possess minimal and simple instrumentation and are non-invasive. Optical biosensors can be classified into four types- Absorption-based biosensors, surface plasmon resonance biosensors, Fluorescence-based optical biosensors and Luminescence-based biosensors. In both absorption-based and surface plasmon-based biosensors, the analyte's absorption characteristics as well as its electric or dielectric properties are exploited. Similarly, optical properties such as fluorescence and luminescence of the target molecule are employed in Fluorescence and luminescence-based biosensors respectively (Asal et al. 2018; Bosch et al. 2007; Wijaya et al. 2011).

Structure-switching DNA optical biosensors have been used to detect heavy metal ions such as Hg^{2+} in polluted water. This technique involves a fibre optic sensor with an immobilised DNA probe complementary to the T-rich cDNA labelled with a fluorophore. The cDNA was made to hybridise with the probe, and then Hg^{2+} was introduced over the sensor surface. The Hg^{2+} could bind with the T-T mismatch pairs present in cDNA and lead to the formation of a hairpin loop containing the T-Hg^{2+}-T complex. This structure led to the detachment of fluorescently labelled cDNA and exhibit decreased fluorescence. A quantitative measurement of Hg^{2+} could be done by measuring the changes in fluorescence intensity. The greater the Hg^{2+} concentration in water samples, the more the fluorescence quenching. This technique could be extrapolated for detecting other heavy metal ions such as Ag^+ and Pb^{2+} (Long et al. 2013). Biosensors are generally used for single analyte detection, but array-based enzymatic optical biosensor has been used for multianalyte detection for sensing pH, urea, acetylcholine and heavy metals. Sol–gel matrix designed with FITC-dextran as a sensing probe and urease and acetylcholinesterase used as model enzymes for the detection of pH, urea, acetylcholine and heavy metals like Hg^{2+}, Cu^{2+} and Cd^{2+} in water samples (Tsai and Doong et al. 2005).

Optical biosensors can also be used to detect microorganisms in polluted water samples. The aptamer-based optical biosensor was reported to be used for the detection of the *E-coli O157:H7* strain. Such aptamer-based biosensor involves the mixing of fluorescently labelled *E.coli*

or *E.coli* specific aptamers and the solution was filtered, resulting in free aptamers in the filtrate. These free aptamers were allowed to hybridise with their complementary probe DNA entrapped on the surface of optical fibre. The fluorescence intensity was inversely proportional to the amount of *E.coli* in the sample. This was a very economical, portable and stable system because of the usage of DNA aptamers to detect *E.coli* in water samples (Yildirim et al. 2014).

Electrochemical biosensors

Electrochemical-based biosensors were the first commercialised biosensors that sense the occurrence of a chemical reaction as the analyte react with the biological recognition element. These chemical reactions involve the gain or loss of ions or electrons, which changes the electrical properties, such as the electric current or potential of the analyte solution. The changes in the electric properties is further detected by the transducer and results in producing an electrochemical signal that corresponds to the quantity of an analyte in the sample. Such electrochemical biosensors involve easy sample preparation methods, and detection of an analyte in small sample volumes and are amenable to automation, making them an easy and accessible tool for detecting polluted water samples. These biosensors can be classified into (i) Potentiometric, (ii) Amperometric, (iii) Conductometric biosensors and (iv) Biosensors based on ion-selective field-effect transistors (Belkhamssa et al. 2016). Most of these biosensors rely on chemical reaction-mediated fluctuation in electric potential followed by signal detection and quantification of the analyte. Most of the electrochemical biosensors require minimal effort in sample preparation and direct analysis of the analyte leads to automation of the technique. Belkhamssa et al. 2016 used electrochemical biosensors as a disposable analytical device to detect the presence of alkylphenols in polluted seawater samples. The device consisted of field-effect transistors and a single-walled carbon nanotube and detection is based on immunoreaction between the antibody (anti-alkylphenol) and antigen (4-nonylphenol). The resulting electrical signal will decreases as the amount of analyte in the sample increased because of the formation of immune complexes between antigen and antibody. This system could detect trace alkylphenols as low as five microgram/L in seawater samples (Belkhamssa et al. 2016). Furthermore, Geng et.al 2011 designed an electrochemical biosensor for the detection of *E. coli.* based on specific DNA sequences of the uid A gene which encodes for the enzyme β-D-glucuronidase. The alginic acid-coated cobalt magnetic beads were used to immobilise the NH_2-labelled oligonucleotide DNA probe and helped in the magnetic separation of the hybridised complex of the probe and target sequence. This hybridisation

was detected using daunomycin's current signal and thus used as an indicator of hybridisation. The concentration of hybridised target sequences of *E. coli.* was inversely proportional to the current signal intensity (Geng et al. 2011). Ali et al. 2019 described the same method of detecting Mercury (II) with the help of an optical biosensor as described by Long et al. 2013 but with electrochemical modifications to make it a system that could detect Mercury (II) and Lead (II) ions in water using ssDNA-Aptamer-based electrochemical detection method. The aptamers were labelled at their 5' and 3' ends with ferrocene for Hg^{2+} or methylene blue for Pb^{2+} and thiol groups, respectively. The thiol group plays significant role in aptamer attachment to the screen-printed gold electrode. The binding of heavy metal ions to the aptamer led to its conformational change to a hairpin-like structure and thereby the redox functional groups, i.e., ferrocene or methylene blue, were made closer to the gold electrode and increased the electron charge transfer with subsequent increase in the electrochemical current and could be detected by the transducer. The limit of detection of Hg^{2+} and Pb^{2+} of this system was reported to be as low as 0.1 ppb in water samples and thus such biosensors are widely used for water quality testing (Abu-Ali et al. 2019).

Piezoelectric biosensors

A piezoelectric biosensor device consists of a transducer made up of piezoelectric material and integrated with the biological detection element. It helps in the detection of the analyte based on the characteristic of the piezoelectric material. Such material can undergo deformation when an electric field is applied, or it can also generate an electrical field under the application of mechanical deformation. Measurement of mechanical deformation or induced electric field can be correlated with the amount of analyte present in the sample. Quartz crystal is increasingly used as piezoelectric material because of its accessibility, stability at high temperatures, and is chemically stable in an aqueous solution (Monošík et al. 2012; Pohanka 2017).

Teh et al. 2014 established a piezoelectric method for a pollution-free detection of Pb^{2+} in water samples. In this biosensor, GR5 DNAzyme was incorporated on quartz crystal microbalance with dissipation monitoring (QCM-D) sensor's surface. The substrate with gold nanoparticle attached at its 5' end was allowed to hybridise with the Pb^{2+} specific GR5 DNAzyme. The sensing was based on the principle that the presence of Pb^{2+} would let the DNAzyme to cleave the substrate and finally led to the removal of the substrate from the surface. This resulted in decreasing dissipation factor and increasing frequency signals. This dissipation factor and frequency signals could be measured. The measurement of these signals indicates the amount of Pb^{2+} present in water samples (Teh et al. 2014). Similarly, Serra et al.

2008 showed a method which involves the application of electrochemical quartz crystal microbalance (EQCM) for the biosensing of bacteria in water. Lectins were entrapped on a gold-plated quartz crystal which helped in sensing bacteria through its cell wall glycocalyx constituents. This led to the development of a label-free, real-time monitoring piezoelectric biosensing method based on lectin bacteria binding events (Serra et al. 2008).

Thermal biosensors

Thermal biosensors detect the targeted analyte in present in the samples based on analyte reaction with biological detection element and ultimately leads to a change in temperature. The changes in temperature corresponds to the amount of analyte present in the sample. The transducers in thermal biosensors should be thermistors or thermophiles and should not get degraded with an increase in temperature. Thermal biosensors provide an easy, label-free detection method where there is no interference from the electrochemical and optical properties of the sample (Perumal and Hashim 2014; Wang et al. 2008).

Yao et al. 2014 described the uses of thermal biosensors for quantifying the chemical oxygen demand (COD) of water samples to represents presence of organic pollutants in water. They used a thermal biosensor composed of a flow injection analysis system. The COD measurement was done by determining the heat generated while the different water samples were passed through the flow injection analysis system. After all, the experimental tests are done to check various parameters such as the range of detection and the limit of detection. In comparison with previously available methods, this method proved to be an affordable, eco-friendly, accurate detection system for testing water samples. However, biosensor sensitivity could be enhanced using nanofibrous matrices due to their large surface area to volume ratio and ease to modify surface as per the requirement for analyte-specific detection at a very low level (Yao et al. 2014).

Nanofibrous matrix-based biosensor for detecting water pollutants

The conventional biosensors mentioned above have played a significant role in identification and monitoring of water contamination but there are still many difficulties and drawbacks associated with their uses that need to be resolved. These biosensors feature a very small selection of alternatives for the biological recognition element and thereby limits its application for extremely accurate element detection. With the usage of biosensors, other factors present in the water as pollutants can interfere with the detection of a specific element and ultimately limit the specificity of the biosensor.

Additionally, sample preparation is necessary for biosensors and this makes onsite detection a challenging task. Although biosensors for aqueous systems have made tremendous strides in the last few decades. However, their practical applicability is hampered by the devices' complexity, size, and cost (Baeumner 2003; Bazin et al. 2017; Koedrith et al. 2015; M. Li et al. 2013; Theron et al. 2010). Thereby, the nanofibrous matrix has lately grown significantly in the field of sensing water contaminants since it has the potential to eliminate major drawbacks posed by conventional biosensors. The term "nanofiber" refers to the fibres with a diameter in the nanometre range and usually fabricated using synthetic or natural polymers. A nanofibrous matrix can be generated through the deposition of polymeric fibres in a sheet-like structure. Nanofibers can easily be functionalised for use in biosensing by entrapping or immobilising certain enzymes or nanoparticles over the surfaces. Additionally, the nanoscale architecture of such nanofibrous matrices expands the trapped enzyme's surface area and thereby plays a significant role in enhancing the enzyme's catalytic activity. It also has a very high surface-to-volume ratio, which makes it easier to detect the contaminants with the naked eye due to visible colour changes in the nanofibrous matrix (Nadaf

et al. 2022). Also, the availability of numerous synthetic and natural polymers makes it simple to choose desired polymer to fabricate nanofibers. Nanofibers can simultaneously detect various components and are very sensitive, cost-effective, and specific. Nanofibers are superior to conventional biosensors because they have higher stability, a longer lifespan, and the potential to be reused (Liu et al. 2020). Nanofibers are also becoming more relevant in the remediation of water contaminants due to their excellent adsorption capacity, and customisable pore size by adjusting the polymeric concentration & composition (Y. Li et al. 2021).

Techniques for the fabrication of nanofibrous matrix

Electrospinning

The electrospinning technique is an electrohydrodynamic process that produces a jet of electrified liquid droplets that undergoes stretching and elongation followed by the deposition of nanofibers with an average diameter ranging from 100 to 500 nm. Figure 2a shows various components like power supply (high voltage direct current or alternating current), a syringe pump (capillary with a blunt needle
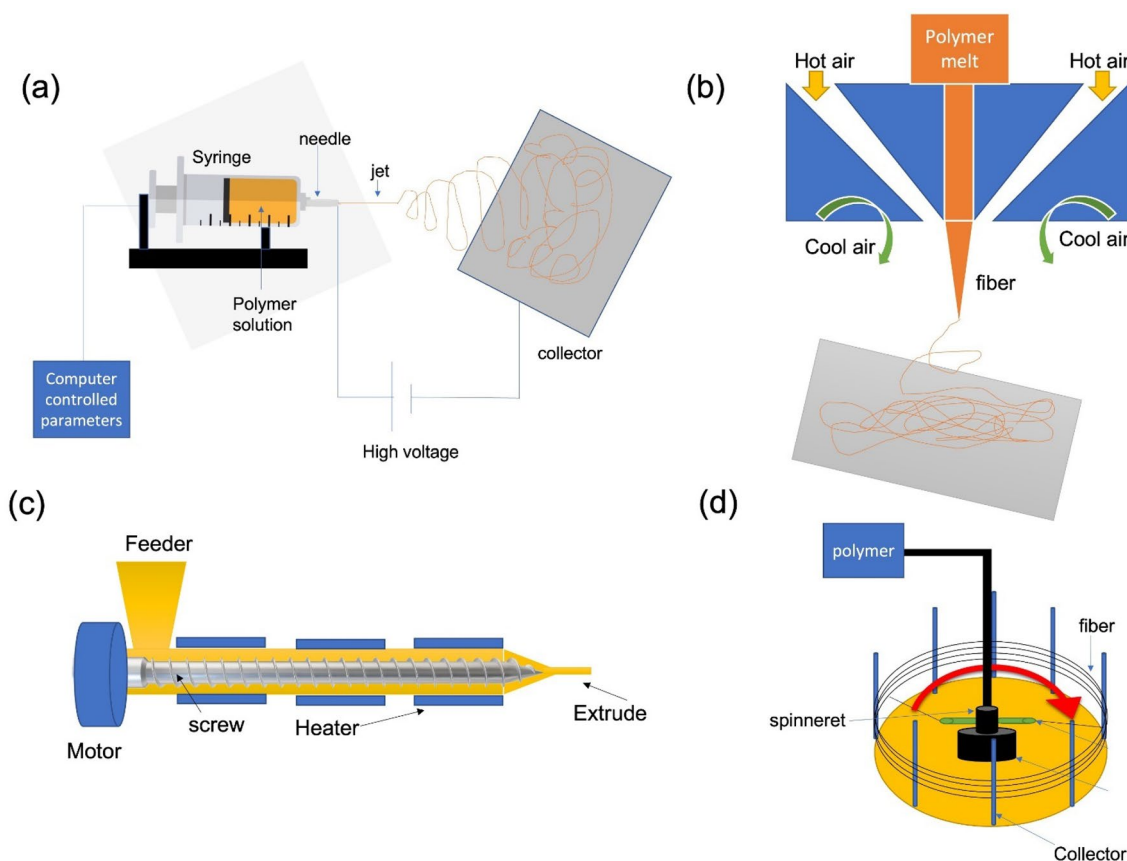

Fig. 2 Different techniques in the fabrication of nanofibers **a** Electrospinning, **b** Melt blowing, **c** Melt extrusion, **d** Force spinning

and spinneret), and a conducting collector (it can be flat, a rotating drum, etc.) associated with electrospinning unit. An electrode is attached to the tip of the syringe to induce free charge in the polymeric solution/melt. The polymer forms a pendant drop at the tip of the capillary under applied electric field and the charged polymeric droplets are forced to move towards the conducting collector with opposite polarity. Upon projection of the polymer, the solvent evaporates and dried polymeric fibres gets collected over the collector. The process can be summarised in 4 steps: -

i)   Taylor cone formation under the influence of applied electric field
ii) The charged jet erupted & gets stretched in the presence of an electric field
iii) Polymeric jet becomes thin and displays bending instability during travelling time from needle tip to the collector (plastic deformation due to high charge density of the jet, resulting in ultra-thin fibres and a whipping motion)
iv) Finally, the solvent evaporates upon contact with the atmosphere and leaves behind the solid fibre on the collector (Xue et al. 2019).

Naturally occurring polymers like silk, cellulose, gelatin etc. have a wide biomedical application and clinical functionality. Biocompatibility and biodegradability make natural polymer as a suitable biomaterial for biosensor development. Synthetic polymers such as Poly D,L-lactic-co-glycolic acid (PLGA), Polyurethane (PU), etc. can be modified and fabricated to provide a wide variety of properties like viscosity, elasticity, strength and controlled rate of degradation. Volatile solvents such as dimethylformamide (DMF), chloroform, dichloromethane etc. can be used for electrospinning. These solvents show characteristics that influence the size, structure, morphology, mechanical properties and thermal properties of the nanofibers. Based on the novel properties of the nanomaterials such as high porosity, ultra-thin structure, and high surface area to volume ratio makes them potential materials for drug delivery, tissue engineering, and water treatment such as ProTura (Parker Ltd) use cellulose nanofiber in the cartridge filtration unit (Bhardwaj & Kundu 2010). Despite the several advantages, electrospinning has low throughput which led to modifications in the approach.

Non-electrospinning method

Melt blowing (Extrusion technology) – This process is most commonly used to fabricate non-woven nanofibers (fibres that adhere to each other physically without any knitting /stitching) with an average fibre diameter in the range of 200–500 nm. Figure 2b shows the physical setup of the

melt blowing process. In the 1950s, Naval Research Laboratory developed nanofibers by environment-friendly single step melt blowing process where the molten polymer was ejected from an orifice die and a drag force was exerted over the polymer by the jet of hot air due to which the polymer gets collected few feet apart on the collector forming self-bonded nanofibers. Various melt blowing parameters such as polymer melt flow rate, airflow speed, temperature, etc. can be optimized to tune the nanofiber diameter/structure. Previously, various nanofibrous matrices were successfully fabricated by this approach using various polymers like polyamides (nylon), polyethylene, poly (butylene terephthalate), etc. (Ellison et al. 2007). Zhang et al.2019 blended PEG (Polyethylene glycol) into PP (Polypropylene) to produce micro-nanofibers by melt blowing approach. Using this approach non-woven micro–nanofibers can be fabricated with large surface area and porosity to fabricate highly efficient filters (Zhang et al. 2019).

Template melt extrusion Template melt extrusion method combines the template wetting and extrusion technology for the production of longer nanofibers. Figure 2c explains the process involved in template melt extrusion based nanofibrous matrices fabrication. In template wetting, anodic aluminium oxide membrane (AAOMs) with nanoscale cylindrical pores is used as templates to prepare nanorods and tubes. At first, the polymer is added to the monomer in the porous template and then the chemically / electrochemically generated nanofiber is separated by etching the template. The only drawback of this method is the production of shorter nanofibers. To overcome this Li et al. 2006 developed a system with 3 components—a feeding polymer, a PTEF seal (polytetrafluoroethylene) and an aluminium membrane. By a hot plate compressor the molten polymer is forced onto the aluminium membrane and it is allowed to cool at room temperature. Then the polymer is isolated by solvent etching of the thin film polymer that connects the polymers inside the hollow cavity of the aluminium membrane. Then the AAOM is removed by NaOH/ethanol and the nanofibers are separated by ultrasonic waves from the bulk feeding film (H. Li et al. 2006).

Force spinning This method was developed by Sarkar et al. 2010 as an alternative method for the fabrication of nanofibers that could overcome the shortcomings of the previous conventional approaches. This approach aimed to have a high throughput rate, increase the choice of materials, and produce economical fibres. This method replaced the uses of an electric field with centrifugal force to generate nanofibers from both conducting and non-conducting materials. Solid materials can be melted and directly spun without the uses of solvent to eliminate the chemical preparation step and prevents material contamination. Figure 2d depicts the

major components of this technique including the spinning system and the collecting system. The polymer fluid/melt is loaded onto the spinning head having multiple nozzles along the sidewalls. Upon rotation of the spinning head to a critical value, the centrifugal force overcomes the surface tension of the fluid and ejects a liquid jet followed by extension of jet by the action of centrifugal, air friction, gravitational and rheological forces. The spinning system can have 2 syringes containing fluid that function simultaneously or have 3 plate spinning heads with one fluid reservoir (Sarkar et al. 2010). Other types of the spinning head can be cylindrical, spheroidal, trapezoidal, etc. The jet then gets deposited as nanofibers on the inner wall of the collector due to the gravitational force. The diameter of the collector controls the structure of the nanofiber. Circular collectors can be used for the batch production, whereas for continuous collection – suction force, air jet and water bath collectors can be used. The polymeric nanofibers that have been generated by this approach include, polyvinyl pyrrolidone, polyethylene oxide, PA-6, polystyrene, etc. (Padron et al. 2013).

Applications of the nanofibrous matrix for the detection and remediation of water contaminants

Nanofibers based non-woven matrices can be used as a direct filter as the interconnected polymeric fibres of nanoscale dimension significantly reduces pore size of the matrices in the micron scale range and thus facilitate filtration of fine contaminants or their aggregates. Furthermore, such nanofibrous matrices can be modified through the functionalisation of nanofibers with chemical compounds or biological molecules with an affinity towards the targeted analyte. He et al. 2022 aimed to separate oil from water using copper nanofibrous mesh functionalised with silver oxide, in which 500 layers of the given mesh showed a promising result in oil–water separation. This shows that nanofibrous matrices can be layered one upon another to obtain multi-layered matrices for remediation (He et al. 2022).

Heavy metals sensing and remediation

Any metallic chemical element that has a relatively high density and is dangerous or toxic at low concentrations is referred to be a heavy metal. Mercury, cadmium, arsenic, chromium, thallium, and lead are a few examples of heavy metals among which mercury and lead are highly hazardous to be used for domestic purposes (Zeitoun and Mehana 2014). Mercury is one of the toxic heavy metals found in water as an abundant water pollutant and mostly wastewater from the industries like chemical manufacturing, fossil fuel combustion and solid waste incineration are the major

source of water pollution. It poses a significant threat to human health even at a low concentration by getting accumulated in organs and tissues. After accumulation, it binds to proteins and enzymes containing sulphur leading to an organ dysfunction and further may lead to complete damage of the nervous system. With the ever-increasing number of industries involving the application of mercury such as chlorine gas, caustic soda and electrical industries the amount of industrial effluent is also being continuously released into water bodies. Thus, leads to gradual increament in the mercury concentration in water bodies. This problem necessitates the usage of efficient detection and remediation methods (Fu et al. 2020). Lead when present in a high amount in the water, pollutes the environment and causes health issues in humans like – high blood pressure, cancer, and neurotoxicity. Also, leads to severe risks in children like slow motor activity, decreased levels of IQ(Intelligence quotient) and developmental disorders. Lead toxicity in agricultural water can also affect the plants by reducing the plant growth rate, exchange of gases, and yield. Hence detection of lead is of great importance to determine its toxicity in the water. Various nanofibrous-based biosensors were reported with superior sensitivity towards various heavy metals and proposed to be suitable for water quality or contaminant detection and remediation (Y. Li et al. 2013).

Nanofibrous biosensor for mercury & lead sensing

The necessity for the detection of heavy metal contamination in water and the prevention of the disease has led to the discovery of various methods to detect heavy metals in polluted water. Figure 3 shows one of the recently formulated detection techniques using cellulose nano fibrillated (CNF) matrix as a substrate used to immobilise luminescent gold nanoparticles (AuNPs) as a sensor unit. CNF is a green substrate because it is produced from natural plant fibre. CNF comprises long (several micrometres) nano-sized (width 5–20 nm) cellulose fibrils. CNF matrix was processed from the spruce by barking, cooking, bleaching and washing procedures. The non-dried fibres obtained were oxidised by subjecting them to 2,2,6,6-tetra- methylpiperidine-1-oxyl radical (TEMPO) and then mechanical disintegration was carried out. These oxidised fibres were isolated into uniform nano-sized CNF suspension. The sensory unit was made from bovine serum albumin to produce ultra-small luminescent gold nanoparticles. A nanofiber matrix with immobilised gold nanoparticles was developed by mixing aqueous gold nanoparticles dispersion into aqueous CNF suspension and then evaporating the water. These gold nanoparticles fluoresced red under exposure of UV light of 365 nm. As mercury reacts with gold nanoparticles, the fluorescence was quenched and shows a "turn off" signal. The sensory detection strategy used in this technique was based

Fig. 3 Diagrammatic representation of the cellulose nanofibrous matrix-functionalised with gold nanoparticle membrane's design and sensing mechanism. Reproduced with permission Fu et al. (2020). Green and transparent cellulose nanofiber substrate-supported luminescent gold nanoparticles: **A** stable and sensitive solid-state sensing membrane for Hg(II) detection. Sensors and Actuators, **B**: Chemical, 319
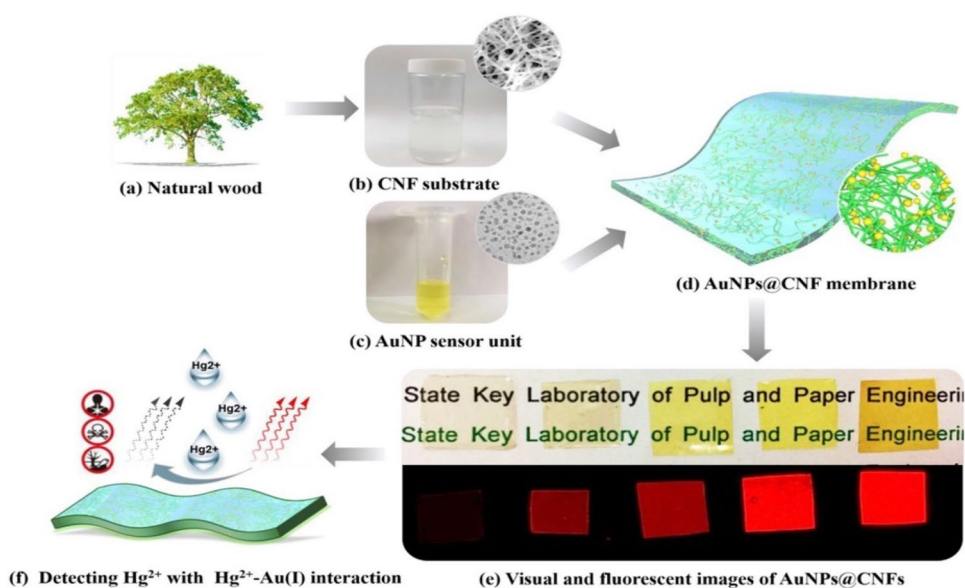
on a high-affinity metallophilic Hg^{2+}–Au(I) interaction mechanism. The quenching can be easily observed with the naked eye, which makes it an easy and portable onsite detection system. This method is very selective and specific for detecting mercury because it shows negative or negligible results for other metals. This technique is stable in an aqueous solution and can be used to detect mercury in aqueous water samples with a limit of detection as low as 1.0 nM. It is anticipated that with certain modifications in the sensory unit, the matrix would be able to detect other metals too, making this technique a pioneering breakthrough in detecting heavy metal toxicity in water bodies (Fu et al. 2020).

Similarly, gold nanoclusters (AuNC) were used by Senthamizhan et al. 2014 as a probe for the colorimetric detection of Hg^{2+}. Herein the gold nanoclusters were incorporated into an electrospun polyvinyl nanofibrous membrane (NFM). The entire system was made water stable through cross-linking with glutaraldehyde vapour to improve its stability in aqueous environment and thus facilitate detection of mercury in water. The gold nanoclusters showed red fluorescence under UV light (366 nm). The contact mode colorimetric response was observed by immersing it in Hg^{2+} solution, which showed fluorescence quenching. Therefore, it was an easy naked-eye detectable method. This method employed selective determination of mercury up to 1 ppb and also reported to be highly stable against time and temperature (Senthamizhan et al. 2014).

Cho et al. 2016 also devised a technique for colorimetric fluorescent detection of mercury using electrospun nanofibrous chemosensors. In this technique, the fluorescent chemosensor was based on rhodamine B derivatives (RhBs), which had high fluorescence quantum yield, high sensitivity and high adsorption coefficient. Since, RhBs was associated with electrospun nanofibers having high surface-to-volume

ratio that facilitate naked-eye detection of contaminant using fluorescent chemosensor. This method involved the grafting of fluorescent sensing probes over the surfaces of electrospun nanofibrous substrates. Grafting has an advantage over other techniques, such as blending, because grafted moieties are not synthesised to have C = C and help in the quick detection of metal ions. The substrate used was made by electrospinning of copolymer poly (2-hydroxyethyl methacrylate-co- N-methylolacrylamide) (poly (HEMA-co-NMA)) using a single capillary spinneret. Poly (HEMA-co-NMA) contained a hydrophilic hydrogel material (HEMA) and consist of a chemically cross-linkable segment (NMA), which was cross-linked later by free radicle copolymerisation for better stability. Then, Hg^{2+} responsive probes with 2-(2-aminoethyl)-3′,6′- bis(diethylamino)spiro[isoindoline-1,9′-xanthen]-3-one (RhBN2) were grafted on the surface of the electrospun matrix for sensing Hg^{2+}. This particular design was found to be stable in an aqueous system. It was also peculiar to only Hg^{2+} and showed orange-red fluorescence at a λ^{PL} of 580 nm when it came in contact with Hg^{2+}. This sensory system showed the lowest and highest limits of detection as 10^{-7}- 10^{-6} M and 10^{-2} -10^{-1} M, respectively. Thereby, it can even detect trace levels of mercury in water. This system shall also be made into an on-and-off system by adding EDTA because it leads to the chelation of Hg^{2+} to EDTA from RhBN2, thus restoring the emission to its original value, and could be cycled at least four times. Furthermore, electrospun non-woven fiber's porous structure could be used to filter heavy metals from water (Cho et al. 2016).

Ma et al. 2016 uses fluorescent nanofibrous membrane (FNFM) carries immobilised fluorescent chemosensor, dithioacetal-modified perylenediimide (DTPDI) on polyacrylonitrile (PAN) nanofibers for the sensing of Hg (II). Electrospinning was done to produce PAN nanofibers from

Table 1 List of the detection limit of different mercury nanofibers

Mercury Nanofibrous biosensor	Mercury ion detection imit	Mercury ion detection limit (μM)
AuNP/CNF	1.0 nM	0.001
AuNC/Polyvinyl NFM	1 ppb	0.004985
RhBN2/poly(HEMA-co-NMA)	0.0000001 M	0.099
DTPDI/PAN	1 ppb	0.004985

DMF solution and then electrospun matrix were treated with sodium hydroxide solution to introduce hydroxyl groups over their surface. At last, the PAN nanofibers were dipped in DTPDI solution to generate FNFM through electrostatic attraction between negatively charged nanofibers and positively charged DTPDI. The developed nanofibrous membrane showed a high surface area to volume ratio and uniform porous structure, thus making it an ultra-sensitive sensor. This system detected mercury by sulphur-mercury affinity reaction in which DTPDI reacted with Hg^{2+} and formed its hydrolysate (AL). This oil-soluble fluorescence dye (AL) could be dissolved in a non-polar solvent such as dichloromethane resulting in its detachment from FNFM, and the solution could be visualised as turning red. UV–vis spectroscopy at 561 nm of the dichloromethane solution could be used in the quantitative analysis of Hg^{2+}. The method was selective, and sensitive to Hg^{2+} (detection limit-1 ppb) which is 0.004985 μM and, at the same time, highly durable (Ma et al.2017). The mercury ion detection limit of various nanofibers discussed above has been listed in Table 1. Upon comparing various nanofibrous biosensor Fig. 4 depicts that AuNP/CNF has the lowest detection limit of 0.001 μM which makes it the most suitable nanofibrous sensor. Whereas, AuNC/Polyvinyl NFM and DTPDI/PAN exhibit detection limit of 0.004985 μM and RhBN2/poly(HEMA-co-NMA) has the highest detection limit of 0.099 μM which makes this sensor a less preferred one.

Li et al. 2013 developed a colorimetric sensor strip using nanofibrous matrices for sensing lead. Such colorimetric sensor strip required a very short time (a few minutes), cost-efficient, need not require skilled personnel to operate and allowed a naked-eye recognition limit of 0.2 μM of lead ions. Figure 9c depicts a method in which immobilized bovine serum albumin (BSA) was attached to the gold nanoparticle to generate BAu (bovine-gold) probe. Polyamide-6 (PA–6)

Fig. 4 Mercury ion detection thresholds for various nanofiber-based biosensors (Fu et al. 2020) (Senthamizhan et al. 2014) (Cho et al. 2016) (Ma et al.2017)
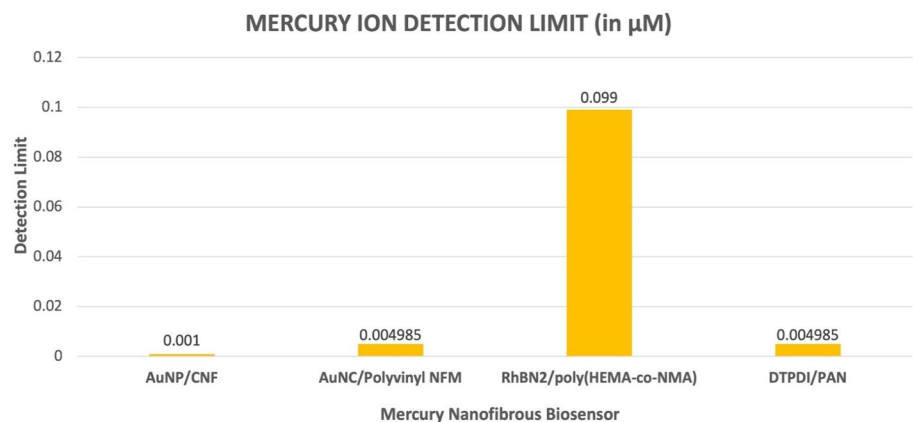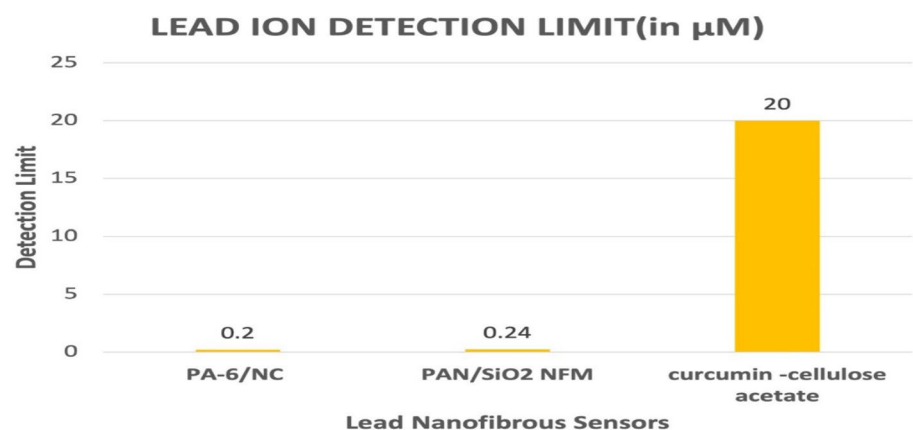

MERCURY ION DETECTION LIMIT (in μM)

Fig. 5 Lead ion detection thresholds for various nanofiber-based biosensors (Y. Li et al. 2013) (Y. Li et al. 2015) (Raj and Shankaran 2016)

LEAD ION DETECTION LIMIT(in μM)

and nitrocellulose (NC) were used to generate nanofiber nano-net structure through dual component alternate distribution multi-jet (DADM) electrospinning. The BAu probes were attached to the nanofiber nets, which gave intense pink colouration and thereafter kept in leaching liquor (glycine NaOH buffer), 2-ME (mercaptoethanol), $Na_2S_2O_3$, and then finally Pb^{2+} was added. After washing, spectrophotometry was done and the colour change was observed both by the naked eye and by diffused reflectance spectrum. Under Field Emission Scanning Electron Microscope images, the PA-6/NC nanofibers were observed to have a porous structure with 2D spider web-like nanonets supported by nanofibers by interlinked ultra-thin nanofibrils. The BAu probe reacts with $S_2O_3{}^{2-}$ and forms $Au(S_2O_3)^{2-}$. These alkanethiols become strong etching agents after the addition of 2-ME and Pb^{2+} due to the formation of the Au–S bond. By a spontaneous redox process, the Pb atoms get deposited on the BSA and accelerate the Au–S formation. Deposition of Pb quenches the pink colour of the probe and results in colour change which helps in simple, rapid and sensitive detection. Figure 6a shows the kinetic sensing response of the sensor was investigated by the UV–vis absorbance spectra of colorimetric strips as a function of time while incubating in leaching liquid containing 1 μM Pb^{2+} ions and Fig. 6b shows the corresponding optical images (Y. Li et al. 2013).

Using similar colorimetric strips with pH paper-like features Pb^{2+} sensing method was developed by Li et al. 2015. The chromic strip was developed by embedding glycine (Gly) and a stimulus-responsive colorimetric polydiacetylene (PDA) on polyacrylonitrile nanofibrous membrane (NFM) containing hydrophobic silicon dioxide nanoparticles
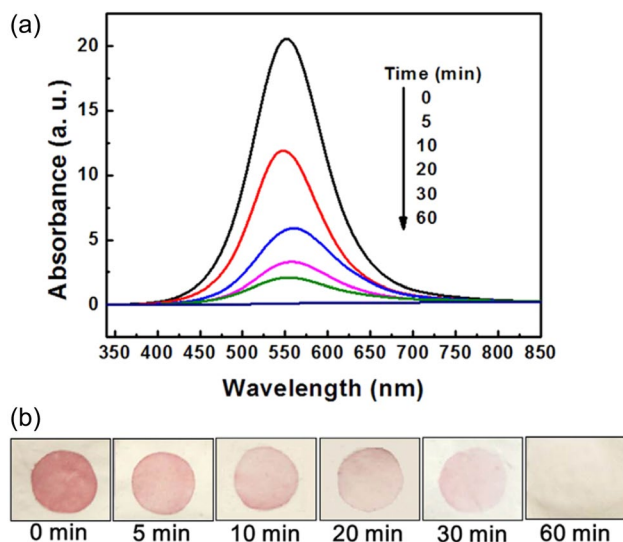
(SiO$_2$ NPs) [PAN/SiO$_2$ NFM]. The presence of Pb^{2+} results in a blue to a red colour change at a naked-eye recognition limit of 0.24 μM. It also showed red fluorescence upon incubation with Pb^{2+}, which was used to detect Pb^{2+} among other ions (Y. Li et al. 2015). Later, a biocompatible cost-efficient colorimetric sensor strip of curcumin-cellulose acetate nanofiber was developed by Raj et al. 2016 with detection limit of 20 μM. Curcumin-cellulose acetate nanofiber was produced by electrospinning undergo a colour change from yellow to orange in the presence of Pb^{2+}. Curcumin was used since it has a high chelating capacity with heavy metal ions and cellulose acetate was used since it has good heavy metal adsorbent properties. It was tested with many metal ions but was found to be only sensitive toward Pb $^{2+}$ (Raj and Shankaran 2016). Ahmadian-Fard-Fini et al. 2020 developed a lead-sensing nanofiber-based sensor based on photoluminescence and magnetic properties. Ball milling was used for the iron nanoparticles (FeNP) preperation, electrospinning was used for constructing cellulose acetate nanofibers, hydrothermal techniques were used for developing photoluminescent carbon dots, and lastly, the sono-chemical technique was used to fabricate nanofiber/iron/carbon dots nanocomposite. Under visible light, the nanofibers appeared brown while under UV irradiation they appeared blue. Carbon dots in water showed the Tyndall effect where longer wavelengths displayed greater transmittance while shorter wavelengths displayed reflection. In the presence of toxic heavy metal ions, a reduction in the photoluminescent intensity of the Carbon dots was observed since the d-orbital of the Pb^{2+} and Hg^{2+} take up electrons from the excited carbon dots, this interaction leads to complex formation resulting in reduced photoluminescent due to the exchange of electrons between the acceptor and the donor molecules. The magnetic property of the nanofiber makes it easy to be collected by employing the magnetic filters despite being in the nano-dimension. Thereby, such magnetic nanofibrous matrices-based biosensors play a significant role in the advancement of biosensing devices for water contaminant detection and remediation (Ahmadian-Fard-Fini et al. 2020). The nanofibers specific for lead ion detection with their limits of detection have been discussed and compared in Table 2 and Fig. 5, respectively. It can be seen in Fig. 5 that PA-6/NC and PAN/SiO$_2$ have an almost similar limit

(a)

(b)

Fig. 6 Time-dependent (**a**) UV–vis absorption spectra and (**b**) Optical images of colorimetric strips incubated in optimum leaching liquid containing 0.2 M Pb^{2+}. Reproduced with permission Li et al. (2013).

Table 2 List of the detection limit of different lead nanofibers

Lead nanofibrous sensor	Lead ion detection limit (μM)
PA-6/NC	0.2
PAN/Sio$_2$ NFM	0.24
Curcumin–Cellulose Acetate	20

for lead ion detection which is 0.2 µM and 0.24 µM, respectively. Thus these two nanofibrous sensors can be considered best for detecting trace levels of lead ions in water than the curcumin-cellulose acetate nanofibrous sensor which has a very high detection limit of 20 µM.

Nanofibrous matrices for heavy metal remediation

Nanofibrous matrices were widely investigated for the generation of suitable and highly efficient techniques for wastewater management and remediation of heavy metals. The technique for remediating mercury from spring water developed by Silva et al. 2020 was composed of dual nano fibrillar-based biosorbent films. The films were produced through vacuum filtration of water suspensions of cellulose nanofibrils (CNF) and lysozyme nanofibrils (LNF). CNF and LNF possess various peptide R-groups, thus making them effective in binding to metal ions which in turn makes them an excellent nanofibrous material for the removal of mercury from polluted waters with a remediation efficiency of 99% at pH 11 or isoelectric point of the protein (Silva et al. 2020). Yaari et al. 2020 also devised a method to remove mercury from polluted water with polymeric carbon nanofiber. In this method, polymeric carbon nanofiber extracted from palm was grafted with poly-trimesoyl chloride and polyethyleneimine, which provided amine functional groups and carbonyl groups for the removal mercury from water. Figure 7 shows the removal efficiency of the nanofiber tested at different pH and temperatures, but the 100% removal efficiency was seen at 298 K between pH of 5 to 7, thus making it a reliable method for the remediation of mercury in polluted water (Al-Yaari et al. 2020).

Similarly (Chen et. 2021) used carboxycellulose nanofiber extracted from the moringa plant, which itself has been shown to have water purification characteristics. carboxycellulose nanofiber contained many carboxylate groups and was produced from the Moringa plant using
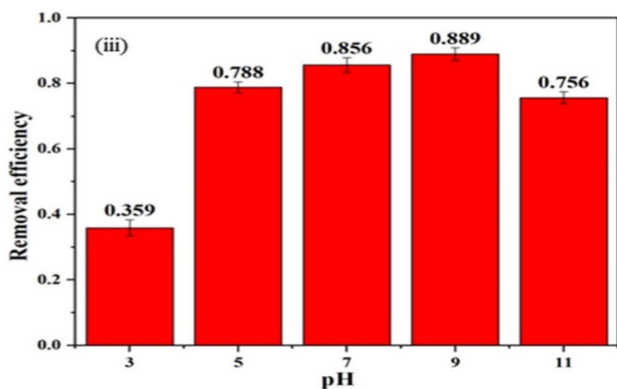

Fig. 7 The effect of pH on the removal efficiency of mercury ion by NOCNF. Reproduced from Al-Yaari et al. (2020)

nitro-oxidation (NOCNF). The large density of carboxylate groups over the fibres plays significant role in the removal of mercury through electrostatic interactions and mineralisation processes. This proved to be a highly efficient method with a removal capacity of 257.07 mg/g of mercury from water at pH 7 (Chen et al. 2021). To further enhance the ion-exchange potential of such nanofibrous devices Juntadech et al. 2021 converted biodegradable electrospun cellulose acetate nanofibers into oxidised regenerated cellulose nanofibers (ORC) for potential use in water treatment by capturing heavy metals such as Pb^{2+} and Cu^{2+} from aqueous solutions. The carboxylate group was introduced via oxidation of the cellulose acetate nanofiber using TEMPO/NaBr/NaOCl. In earlier reports, oxidation of nanofibers was reported to reduce the permeability of aqueous solution but in this study, no such significant changes in permeability rate were observed apart from a slight reduction of 10%. Figure 8d shows that ORC and RC (regenerated cellulose) nanofibers swelled in water as a result of the increased polarity of the carboxylate ion, which results in a potent hydrogen bonding with water molecules. These ORC membranes were seen to have a greater ion-exchange capacity of 200 mg/g of membrane for Pb^{2+} than Cu^{2+} (20 mg/g) based on the hydration stability of the metal and the stability of metal-carboxyl complex (Juntadech et al. 2021).

Malik et al. 2018 developed a PAN (Polyacrylonitrile) loaded with $FeCl_3$ nanofiber using electrospinning for the in-situ production of magnetite on PAN nanofibers. The magnetite particles prevent aggregation/leaching of the nanoparticles during the operational process. In the selective study, Pb^{2+} resulted in higher adsorption over the nanofibers compared to other metals under optimum conditions. In this study, the nanofibers generated displayed reusability capacity up to 3 times due to the high desorption rate of Pb^{2+}. For reuses, nanofiber containing Pb^{2+} need to be centrifuged along with HCL solution and filtered to separate the nanofibers from Pb^{2+}. The large-scale adsorption of Pb^{2+} in this study was related to the high surface area, vacant sites on the surface of the nanofiber and the interfibrous network of the nanofiber (Malik et al. 2018). Hong et al. 2015, performed the extraction of Pb^{2+} from an aqueous solution by the fabrication of highly porous PAN nanofibers using wet electrospinning and then performed amination using DETA (diethylene triamine). This resulted in APAN (aminated PAN) nanofiber with micro/nano structure matrix and hence providing the matrix with a larger surface area. The developed matrix was reported to be 90% efficient in extracting Pb^{2+} even after repeating the extraction and dissociation process 6 times. The binding of the Pb^{2+} ion onto the surface of the APAN nanofiber leads to the formation of hexagonal crystals $Pb_3(CO_3)_2(OH)_2$ which was unique to Pb^{2+} since no such crystal formation was observed in the case of cadmium. The OH^- from the aqueous medium and
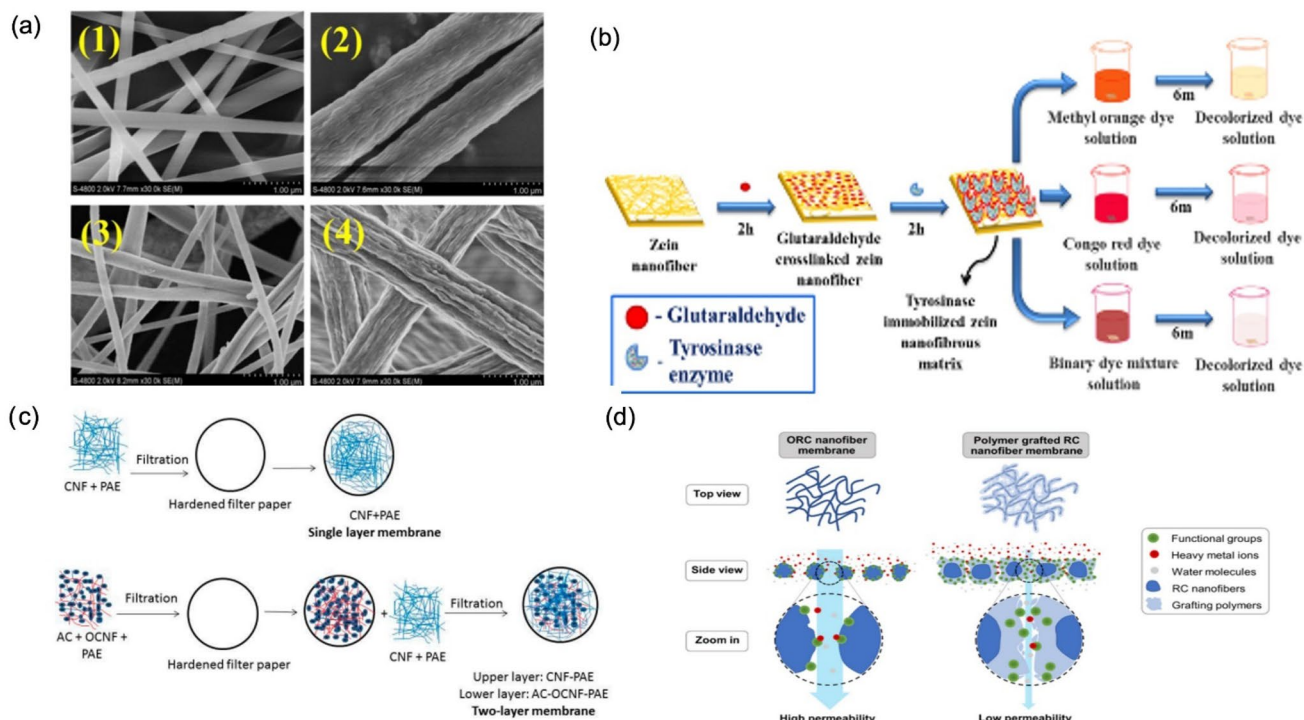
Fig. 8 a SEM images of Nanofiber mats (NFMs):(1)raw PAN NFMs. (2) grooved PAN NFMs. (3) NH2-PAN NFMs. (4) grooved NH2-PAN NFMs. Reproduced with permission Qian et al. (2017). **b** Schematic representation of the fabrication of ZNM-IT and decolourization of methyl orange, Congo red, and their binary dye mixture solution. Reproduced with permission Suryamathi et al. (2021). **c** Fabrication of single-layer cellulose (CNF)and two-layer CNF/AC(activated carbon) membranes on hardened filter paper. Reproduced with permission Hassan et al. (2017). **d** Comparison of direct-flow processes of (ORC) oxidized regenerated cellulose nanofiber membrane and polymer grafted (RC) regenerated cellulose nanofiber membrane. Reproduced with permission Juntadech et al. (2021)

CO_3^{2-} ions from the dissolved CO_2 were considered to have adsorbed over the APAN surface which led to the precipitation of lead carbonate $(Pb_3(CO_3)_2(OH)_2)$ crystals that were extracted and can be used as a potential technique for water treatment (Hong et al. 2015).

Nanofibrous biosensor for detection of organic pollutants

Industries are the major sources of the organic pollutants discharged in water bodies. These organic pollutants include pesticides, petroleum, phenols, chemical dyes, insecticides etc. Zhu et.al. (2020) proposed a sensing technique for nitrophenol developed using polyaniline nanoconical array on carbon nanofiber (PANI-array@CNF). Figure 9b shows the construction process of the PANI-array@CNF. Nitrophenols are one of the important raw materials used in the pesticide, petroleum and dyes industry. They are chemically stable and resistant to microbial degradation and thereby stable in water bodies for years. Accumulated nitrophenols can cause damage to the endocrine system, nervous system, liver and kidney when consumed through water. Thus, it's sensing with an efficient technique becomes a necessity. Aniline monomers were polymerised on the surface of electrospun,

carbonised polyacrylonitrile fibres at low temperatures and the obtained nanofibers exhibit a large surface area to volume ratio, which makes it easier for the electrochemical reduction of nitrophenols. This nanofibrous matrix was further modified with a glassy carbon electrode for an excellent electrochemical response against the electrochemical reduction reaction and this response could be studied using Differential pulse voltammetry. Differential pulse voltammetry gives signals for different concentrations of nitrophenols present in the sample with a limit of detection as low as 1.5 nM of nitrophenol (Zhu et al. 2020).

Pesticides present in water bodies can also pose hazardous threats to the human body even when present at a very low level and causes severe diseases like cancer, reproductive and endocrine system disorders and many more. Detection of pesticides in water samples with electrospun Poly(vinyl) alcohol (PVA) nanofibers placed on a glass substrate and used after coating the fibres with gold nanofilm. These gold-coated fibres have been used as a substrate for surface-enhanced Raman scattering, which helps in the detection of three types of pesticides- deltamethrin, quinalphos and thiacloprid. Raman signals produced using surface-enhanced
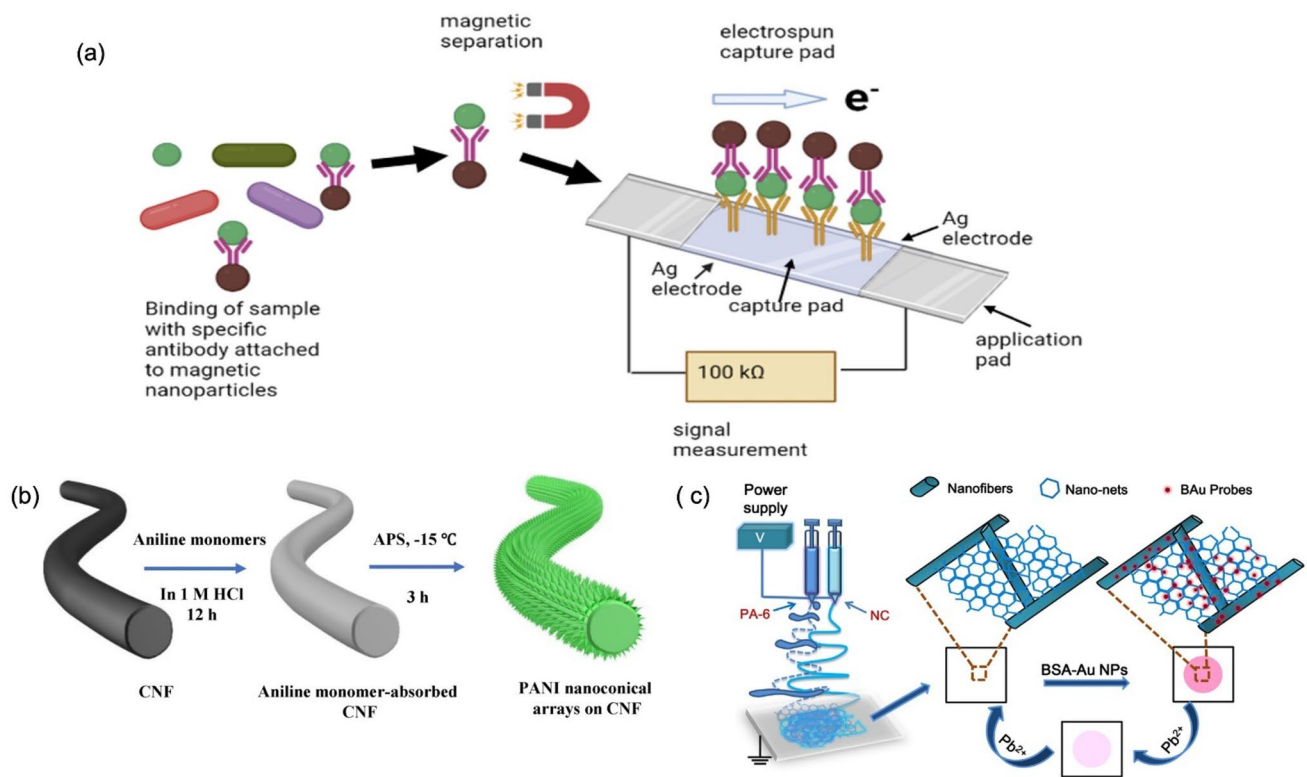
Fig. 9 **a** Schematic representation of the electrospun capture pad specifically separating and detecting the microorganism by antibody-antigen interaction. **b** Schematic illustration of the synthesis pro-cess of PANI-array@CNF. Reproduced with permission Zhu et al. (2020). **c** Fabrication of the BAu probe immobilized PA-6/NC colori-metric strips. Reproduced with permission Li et al. (2013)

Raman scattering were used to detect different concentrations of pesticides (Chamuah et al. 2018).

Vojtěch et al. 2016 established a method for the determination of organochlorinated pesticides namely hexachloro-cyclohexanes and chlorobenzene, which are major pollutants released from the pesticides industry. Polyetherimide nanofibers were produced and fixed on a steel wire solid-phase micro extraction assembly (SPME). These fibres were then tested in a gas chromatograph for the detection of pesticides in water samples. These fibres work as good sorbents in solid-phase microextraction assembly and it is easy to produce thus they can be used as the choice material for SPME (Vojtěch et al. 2016).

Organic pollutant remediation using nanofibrous matrices

The generation of nanofibrous matrices and their modification for organic pollutant remediation is currently being investigated widely across the globe for the development of efficient and sustainable technology for water pollution management. Suryamathi et al. 2021 formulated a method for the degradation of harmful dyes released from different industries such as textiles, printing, leather and pharmaceutical industries. In this technique, a nanofibrous matrix immobilised with tyrosinase was used for the remediation of Azo dyes. Azo dye was reported to be harmful to the living system and can also cause health disorders if used by human beings. Furthermore, Zein based nanofibrous matrix was also used for the immobilisation of tyrosinase enzyme using crosslinker – Glutaraldehyde (ZNM-IT). Tyrosinase enzyme was considered because it plays a significant role in the degradation of azo dyes such as methyl orange, Congo red and as well as a binary mixture of both Congo red and methyl orange. Figure 8b depicts the degradation of these dyes from the samples which resulted in decolourisation of the water sample and this nanofibrous matrix can be reused for 5 cycles without the results being hampered with a removal efficiency of 97% (Suryamathi et al. 2021). Obaid et al. 2015 proposed a method for the separation of petroleum pollutants from water with the help of SiO_2 and Graphene oxide nanoparticle-loaded polysulfone nanofibrous membrane. The SiO_2 nanoparticles were prepared from rice husk by hydrothermal method and graphene oxide nanoparticles were prepared by Hammers' method. These nanoparticles were added to a polysulfone solution and then electrospinning was carried out to manufacture the membrane. These membranes could separate gasoline, kerosene

and hexane from water with daily flux of 100, 115 and 187 m^3/m^2 respectively. Polysulfone membranes exhibited suitable properties like mechanical strength, thermal, aqueous/chemical stability and thus making it a potential membrane for the separation of petroleum contaminants from polluted water (Obaid et al. 2015). The another design developed by Qian et al. 2017 consisted of a grooved polyacrylonitrile nanofiber mat functionalised with an amino group (grooved NH2-PAN NFMs) and aided in removing phenolic pollutants from water. Figure 8(a) shows the SEM images of Nanofiber mats (NFMs) which includes raw PAN NFMs, grooved PAN NFMs and NH2-PAN NFMs. The mat was employed in the removal of six phenolic contaminants (phenol, 3-methoxyphenol, 4-nitrophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol) and three phenolic xenoestrogens (4-tert-octylphenol, 4-nonylphenol and bisphenol A) from water samples. Nanofiber mats provide an extensive surface area and more reaction sites for the phenolic pollutants, thus helping in the remediation of many contaminants with detection ranging from 4 to 60 pg/mL and remediation efficiency between 82.4 and 111.4%. Thus, the nanofibrous matrices with certain modifications through nanoparticle incorporation or functionalization of fibres with suitable enzymes might be beneficial for various organic pollutant remediation (Qian et al. 2017).

Nanofibrous biosensor for detection of microorganism

Including heavy metal and organic industrial effluent contaminants microbial load in water bodies is also one of the crucial challenges in detecting and performing the contaminant remediation before being used for agriculture or other common uses. In a study conducted by Yang et al. 2012, it was observed that 4% of death and 5.7% of global diseases were a result of water contamination with infectious pathogens, poor sanitation and hygiene. According to WHO, it was reported that *E.coli* (*Escherichia coli*) in faecal-contaminated water can result in severe and life-threatening diseases (Yang et al. 2012). Luo et al. 2010 fabricated a portable, economical, biologically functionalized nanofibrous membrane. Figure 9(a) shows the biosensor which was based on immunoassay, immunochromatography, and magnetic separation of the test sample using suitable antibodies over the surface of conducting nanoparticles and then detection by the electrospun nitrocellulose capture pad. The fabricated nanofibers exhibited increased surface area, capillary action, porosity, & superior mass transfer rate that enhanced the biochemical binding effect and sensing potential. The biosensor was reported to detect 61 CFU (colony forming unit) /mL of *E. coli* O157:H7 and 103 CCID (cell culture infectious dose) /mL of BVDV (bovine viral diarrhoea virus) within 8 min. After the study, it was concluded that this method

could be used to detect other microbes as well using specific antibodies. Conventional antibody-antigen interaction-based biosensors are complex and possess certain limitations (Luo et al. 2010). Shaibani et al. 2016 found that the conventional sensing method of using antibody-antigen interactions was not only complex but also had reproducibility issues due to unsuccessful binding or loss of biological activity. To overcome these limitations, they fabricated pH-sensitive PAA/PAV (poly acrylic acid/polyvinyl alcohol) hydrogel nanofibers by electrospinning and annealing for simple, biocompatible, economical detection of E. coli using the LAPS system (Light Addressable Potentiometric Sensor). The detection of E. coli was based on the principle that bacteria ferment sugar and convert it into acidic products which reduce the pH of the environment. This could be further detected by the LAPS system and generate a photocurrent. For selective binding of the E. coli over the hydrogel, the surface of the nanofiber was functionalized with D- mannose using a crosslinker divinyl sulfone. This nanofiber layer was fabricated on the sensor chip of the LAPS system. The hydrogel showed rapid detection within 60 min with a theoretical limit of detection of up to 20 CFU/ml (Shaibani et al. 2016).

Nanofibrous matrices for the remediation of microbial water contaminant:

Hassan et al. 2017 developed an efficient *E. Coli* removal technique from water by fabricating thin film membranes comprising of CNF (cellulose nanofiber) derived from the stalk of palm fruit, AC (activated carbon) and OCNF-TEMPO (2,2,6,6-tetramethyl-1-piperidine oxoammonium salt)-oxidized CNF). Figure 8c explains the fabrication process of single-layer cellulose nanofiber (CNF) as well as two-layer CNF/AC(activated carbon) membranes on hardened filter paper. A double-layered membrane was produced on hardened filter paper – bottom of AC/OCNF and upper side with cross-linked CNF. The use of isopropyl alcohol before drying of the membrane increased its porosity, resulting in increased pure water flux, bacterial suspension flux, and efficient removal of bacteria since the pore size is smaller than the *E. Coli*. The membrane also displayed growth resistance in *E. Coli* and *S. aureus* due to the presence of TEMPO-oxidised CFU (Hassan et al. 2017).

Gupta et al. 2020 fabricated elongated PAZT fibre with a smaller diameter using PMMA (polymethyl methacrylate)/ZnO/TiO_2 and Ag conducting particles by electrospinning. The PAZT fibres displayed dual functions of photocatalysis of dyes and antimicrobial (bactericidal) effect on gram-negative bacteria *E. Coli*. The Ag particles enhance the bactericidal effect of PAZT nanofibers compared to PZT (PMMA/ZnO/TiO_2) fibres by increasing the electron–hole charge separation

time in ZnO and TiO$_2$ which decreases the band gap energy resulting in an antimicrobial effect (Gupta et al. 2020).

Rieger et al. 2016 compared the efficiency of the electrospun cellulose nanofibrous matrix with other membranes and observed that the small fibre diameter and the large porosity exhibit 21 times more *E. Coli* collection over the nanofibrous mats than others. The adsorption coefficient of the nanofibrous mat was estimated to be higher than other membranes at an exposure time sufficient for the microbes to attach to the fibre and attain a quasi-equilibrium state. The study was conducted first for observing the collection efficiency of *E. Coli* but then Gram-negative—Pseudomonas and Gram-positive—Staphylococcus were also removed efficiently proving that the mat is not only specific to one bacterial species. This cellulose nanofiber matrix has wide application for the removal of microbes from wounds, contaminated water or military clothing and many more (Rieger et al. 2016).

Ghosh et al.2010 studied the antimicrobial efficiency of the Ag nanoparticles (15–25 nm) in an agar matrix. The film generated had efficient mechanical stability and was reported to be highly stable for 18 months. The repeated recycling of the film resulted in the depletion of the efficiency due to degraded Ag nanoparticles. The Ag nanoparticles get agglomerated on exposure to microbes and undergo a conformational change in the microbes studied and presumed that the microbial cell membrane /enzyme was damaged. This displayed a potential for microbe purification from the contaminated water (Ghosh et al. 2010).

Current challenges and future scope in detection and remediation of water contaminants

Modification in nanofibers has led to a great advancement in the sensing and remediation of water pollutants even when present at trace levels in the water bodies. The high surface-to-volume ratio and tunable porosity make it a great technique for naked-eye detection and removal of pollutants from water respectively. Though this technology has shown tremendous progress, there are some limitations which need to be tackled. The nanofibers-based biosensor and remediation matrix mentioned in this review have been shown to possess a certain limit of detection, retention capacity, adsorption efficiency and reusability. Some nanofibers show a very good removal efficiency at a certain pH range only and thereby can drastically affect the working of nanofibers if the pH of the water fluctuates. The antibodies used in microbe detection and remediation are mostly specific to only one microbe thus limiting the wide range of detection for other microbes. The limited reusability of nanofibers is also a major drawback because of the damage caused to the functional sensing groups attached to the nanofibers. These

challenges need to be solved by the development of better and robust nanofiber-based biosensors. The key for the waste water monitoring and its purification depends on our ability to detect the contaminants and then successfully remediate them. Over the last few decades, researchers were found that the nanotechnology offers wide range of advantages and provide a potential future for the development highly efficient detection and remediation system to detect and remediate hazardous water pollutants. Most of the nanoscale matrices, membranes, biosensors, nanoparticles etc. developed so far exhibit effective heavy metal detection capacity with the naked eye and can be further enhanced to single sensor with multiple detection ability over a wide range of detection limits for large-scale detection in oceans, river, ponds etc. Along with the advantages of the nanofibrous matrices, they also possess a few shortcomings one of which is the challenge of removal of nano-size particles less than 20 nm and thus to overcome this the production of environment-friendly nanoscale materials should be encouraged. The fabrication of the nanomaterials should be performed under ambient pressure and temperature and the use of hazardous/ toxic solvents should be avoided. After the fabrication of the nanomaterial the characteristic property, level of toxicity associated with health hazards and environmental hazards, reusability, and disposal should be known along with its life-cycle (from generation to degradation) for sustainable and safe development (Puri et al. 2021).

Declarations

Conflict of interest The authors declare no conflict of interest.

Ethical approval Ethical approval is not required for this review. Not Applicable.

Consent to participate Not required for this article.

Consent for publication Not required for this article.

References

Abu-Ali H, Nabok A, Smith TJ (2019) Development of novel and highly specific ssDNA-aptamer-based electrochemical biosensor for rapid detection of mercury (II) and lead (II) ions in water. Chemosensors. https://doi.org/10.3390/chemosensors7020027

Ahmadian-Fard-Fini S, Ghanbari D, Amiri O, Salavati-Niasari M (2020) Electro-spinning of cellulose acetate nanofibers/Fe/carbon dot as photoluminescence sensor for mercury (II) and lead (II) ions. Carbohyd Polym. https://doi.org/10.1016/j.carbpol.2019.115428

Al-Yaari M, Saleh TA, Saber O (2020) Removal of mercury from polluted water by a novel composite of polymer carbon nanofiber: kinetic, isotherm, and thermodynamic studies. RSC Adv 11(1):380–389. https://doi.org/10.1039/d0ra08882j

Asal M, Özen Ö, Şahinler M, Polatoğlu İ (2018) Recent developments in enzyme DNA and immuno-based biosensors. Sensors 18(6):1924. https://doi.org/10.3390/s18061924

Belkhamssa N, da Costa JP, Justino CIL, Santos PSM, Cardoso S, Duarte AC, Rocha-Santos T, Ksibi M (2016) Development of an electrochemical biosensor for alkylphenol detection. Talanta 158:30–34. https://doi.org/10.1016/j.talanta.2016.05.044

Bhardwaj N, Kundu SC (2010) Electrospinning: a fascinating fiber fabrication technique. In Biotechnology Advances 28(3):325–347. https://doi.org/10.1016/j.biotechadv.2010.01.004

Bosch M, Sánchez A, Rojas F, Ojeda C (2007) Recent development in optical fiber biosensors. Sensors 7(6):797–859. https://doi.org/10.3390/s7060797

Chamuah N, Bhuyan N, Das PP, Ojah N, Choudhary AJ, Medhi T, Nath P (2018) Gold-coated electrospun PVA nanofibers as SERS substrate for detection of pesticides. Sens Actuators, B Chem 273:710–717. https://doi.org/10.1016/j.snb.2018.06.079

Chen H, Sharma SK, Sharma PR, Chi K, Fung E, Aubrecht K, Keroletswe N, Chigome S, Hsiao BS (2021) Nitro-oxidized carboxycellulose nanofibers from moringa plant: effective bioadsorbent for mercury removal. Cellulose 28(13):8611–8628. https://doi.org/10.1007/s10570-021-04057-5

Cho CJ, Lu ST, Kuo CC, Liang FC, Chen BY, Chu CC (2016) Pyrene or rhodamine derivative–modified surfaces of electrospun nanofibrous chemosensors for colorimetric and fluorescent determination of Cu2 +, Hg2 +, and pH. React Funct Polym 108:137–147. https://doi.org/10.1016/j.reactfunctpolym.2016.05.019

Damborský P, Švitel J, Katrlík J (2016) Optical biosensors. Essays Biochem 60(1):91–100. https://doi.org/10.1042/EBC20150010

Ejeian F, Etedali P, Mansouri-Tehrani HA, Soozanipour A, Low ZX, Asadnia M, Taheri-Kafrani A, Razmjou A (2018) Biosensors for wastewater monitoring: a review. In Biosensors and Bioelectronics Elsevier Ltd. https://doi.org/10.1016/j.bios.2018.07.019

Ellison CJ, Phatak A, Giles DW, Macosko CW, Bates FS (2007) Melt blown nanofibers: fiber diameter distributions and onset of fiber breakup. Polymer 48(11):3306–3316. https://doi.org/10.1016/j.polymer.2007.04.005

Fu J, Zhu J, Tian Y, He K, Yu H, Chen L, Fang D, Jia D, Xie J, Liu H, Wang J, Tang F, Tao J, Liu J (2020) Green and transparent cellulose nanofiber substrate-supported luminescent gold nanoparticles: a stable and sensitive solid-state sensing membrane for Hg (II) detection. Sens Actuators, B Chem. https://doi.org/10.1016/j.snb.2020.128295

Geng P, Zhang X, Teng Y, Fu Y, Xu L, Xu M, Jin L, Zhang W (2011) A DNA sequence-specific electrochemical biosensor based on alginic acid-coated cobalt magnetic beads for the detection of E. coli. Biosens Bioelectron 26(7):3325–3330. https://doi.org/10.1016/j.bios.2011.01.007

Ghosh S, Kaushik R, Nagalakshmi K, Hoti SL, Menezes GA, Harish BN, Vasan HN (2010) Antimicrobial activity of highly stable silver nanoparticles embedded in agar-agar matrix as a thin film. Carbohyd Res 345(15):2220–2227. https://doi.org/10.1016/j.carres.2010.08.001

Gupta A, Khosla N, Govindasamy V, Saini A, Annapurna K, Dhakate SR (2020) Trimetallic composite nanofibers for antibacterial and photocatalytic dye degradation of mixed dye water. Applied Nanoscience (switzerland) 10(11):4191–4205. https://doi.org/10.1007/s13204-020-01540-6

Halicka K, Cabaj J (2021) Electrospun nanofibers for sensing and biosensing applications—a review. Int J Mol Sci 22(12):6357. https://doi.org/10.3390/ijms22126357

Hassan M, Abou-Zeid R, Hassan E, Berglund L, Aitomäki Y, Oksman K (2017) Membranes based on cellulose nanofibers and activated carbon for removal of Escherichia coli bacteria from water. Polymers. https://doi.org/10.3390/polym9080335

Hong G, Li X, Shen L, Wang M, Wang C, Yu X, Wang X (2015) High recovery of lead ions from aminated polyacrylonitrile nanofibrous affinity membranes with micro/nano structure. J Hazard Mater 295:161–169. https://doi.org/10.1016/j.jhazmat.2015.04.020

Juntadech T, Nantasenamat C, Chitpong N (2021) Oxidized regenerated cellulose nanofiber membranes for capturing heavy metals in aqueous solutions. Cellulose 28(18):11465–11482. https://doi.org/10.1007/s10570-021-04271-1

Li H, Ke Y, Hu Y (2006) Polymer nanofibers prepared by template melt extrusion. J Appl Polym Sci 99(3):1018–1023. https://doi.org/10.1002/app.22597

Li Y, Si Y, Wang X, Ding B, Sun G, Zheng G, Luo W, Yu J (2013) Colorimetric sensor strips for lead (II) assay utilizing nanogold probes immobilized polyamide-6/nitrocellulose nano-fibers/nets. Biosens Bioelectron 48:244–250. https://doi.org/10.1016/j.bios.2013.03.085

Li Y, Wang L, Wen Y, Ding B, Sun G, Ke T, Chen J, Yu J (2015) Constitution of a visual detection system for lead(ii) on polydiacetylene-glycine embedded nanofibrous membranes. J Materials Chem A 3(18):9722–9730. https://doi.org/10.1039/c5ta00608b

Li Y, Zhu J, Cheng H, Li G, Cho H, Jiang M, Gao Q, Zhang X (2021) Developments of advanced electrospinning techniques: a critical review. In Adv Mat Technolo John Wiley Sons Inc. https://doi.org/10.1002/admt.202100410

Liu Y, Hao M, Chen Z, Liu L, Liu Y, Yang W, Ramakrishna S (2020) A review on recent advances in application of electrospun nanofiber materials as biosensors. In Current Opinion Biomedical Engineering Elsevier BV. https://doi.org/10.1016/j.cobme.2020.02.001

Long F, Zhu A, Shi H, Wang H, Liu J (2013) Rapid on-site/in-situ detection of heavy metal ions in environmental water using a structure-switching DNA optical biosensor. Sci Rep. https://doi.org/10.1038/srep02308

Luo Y, Nartker S, Miller H, Hochhalter D, Wiederoder M, Wiederoder S, Setterington E, Drzal LT, Alocilja EC (2010) Surface functionalization of electrospun nanofibers for detecting E.coli O157:H7 and BVDV cells in a direct-charge transfer biosensor. Biosensors

Bioelectronics 26(4):1612–1617. https://doi.org/10.1016/j.bios.2010.08.028

Ma L, Liu K, Yin M, Chang J, Geng Y, Pan K (2017) Fluorescent nanofibrous membrane (FNFM) for the detection of mercuric ion (II) with high sensitivity and selectivity. Sens Actuators, B Chem 238:120–127. https://doi.org/10.1016/j.snb.2016.07.049

Malik H, Qureshi UA, Muqeet M, Mahar RB, Ahmed F, Khatri Z (2018) Removal of lead from aqueous solution using polyacrylonitrile/magnetite nanofibers. Environ Sci Pollut Res 25(4):3557–3564. https://doi.org/10.1007/s11356-017-0706-7

Monošík R, Streďanský M, Šturdík E (2012) Biosensors - classification, characterization and new trends. Acta Chimica Slovaca 5(1):109–120. https://doi.org/10.2478/v10188-012-0017-z

Nadaf A, Gupta A, Hasan N, Fauziya N, Ahmad S, Kesharwani P, Ahmad FJ (2022) Recent update on electrospinning and electrospun nanofibers: current trends and their applications. In RSC Adv Royal Societ Chem. https://doi.org/10.1039/d2ra02864f

Obaid M, Tolba GMK, Motlak M, Fadali OA, Khalil KA, Almajid AA, Kim B, Barakat NAM (2015) Effective polysulfone-amorphous SiO2 NPs electrospun nanofiber membrane for high flux oil/water separation. Chem Eng J 279:631–638. https://doi.org/10.1016/j.cej.2015.05.028

Odobašić A, Šestan I, Begić S (2019) Biosensors for Determination of heavy metals in waters. In Biosensors Environmental Monitoring IntechOpen. https://doi.org/10.5772/intechopen.84139

Padron S, Fuentes A, Caruntu D, Lozano K (2013) Experimental study of nanofiber production through forcespinning. J Applied Physics. https://doi.org/10.1063/14769886

Perumal V, Hashim U (2014) Advances in biosensors: Principle, architecture and applications. J Appl Biomed 12(1):1–15. https://doi.org/10.1016/j.jab.2013.02.001

Pohanka M (2017) The piezoelectric biosensors: principles and applications a review. Inter J Electrochem Sci. https://doi.org/10.20964/2017.01.44

Puri N, Gupta A, Mishra A (2021) Recent advances on nano-adsorbents and nanomembranes for the remediation of water. J Cleaner Production. https://doi.org/10.1016/j.jclepro.2021.129051

Qian L, Li X, Qi F, Li J, Lu L, Xu Q (2017) An amino-functionalized grooved nanofiber mat for solid-phase extraction of phenolic pollutants. Microchim Acta 184(8):2861–2870. https://doi.org/10.1007/s00604-017-2313-1

Raj S, Shankaran DR (2016) Curcumin based biocompatible nanofibers for lead ion detection. Sens Actuators, B Chem 226:318–325. https://doi.org/10.1016/j.snb.2015.12.006

Rieger KA, Thyagarajan R, Hoen ME, Yeung HF, Ford DM, Schiffman JD (2016) Transport of microorganisms into cellulose nanofiber mats. RSC Adv 6(29):24438–24445. https://doi.org/10.1039/c6ra01394e

Sarkar K, Gomez C, Zambrano S, Ramirez M, de Hoyos E, Vasquez H, Lozano K (2010) Electrospinning to Forcespinning™. Mater Today 13(11):12–14. https://doi.org/10.1016/S1369-7021(10)70199-1

S C I E N C E ' S C O M P A S S. (n.d.). www.sciencemag.org

Senthamizhan A, Celebioglu A, Uyar T (2014) Flexible and highly stable electrospun nanofibrous membrane incorporating gold nanoclusters as an efficient probe for visual colorimetric detection of Hg(ii). J Materials Chem A 2(32):12717–12723. https://doi.org/10.1039/c4ta02295e

Serra B, Gamella M, Reviejo AJ, Pingarrón JM (2008) Lectin-modified piezoelectric biosensors for bacteria recognition and quantification. Anal Bioanal Chem 391(5):1853–1860. https://doi.org/10.1007/s00216-008-2141-6

Shaibani PM, Jiang K, Haghighat G, Hassanpourfard M, Etayash H, Naicker S, Thundat T (2016) The detection of Escherichia coli (E. coli) with the pH sensitive hydrogel nanofiber-light addressable

potentiometric sensor (NF-LAPS). Sens Actuators, B Chem 226:176–183. https://doi.org/10.1016/j.snb.2015.11.135

Silva NHCS, Figueira P, Fabre E, Pinto RJB, Pereira ME, Silvestre AJD, Marrucho IM, Vilela C, Freire CSR (2020) Dual nanofibrillar-based bio-sorbent films composed of nanocellulose and lysozyme nanofibrils for mercury removal from spring waters. Carbohyd Polym. https://doi.org/10.1016/j.carbpol.2020.116210

Some S, Mondal R, Mitra D, Jain D, Verma D, Das S (2021) Microbial pollution of water with special reference to coliform bacteria and their nexus with environment. Energy Nexus. https://doi.org/10.1016/j.nexus.2021.100008

Suryamathi M, Viswanathamurthi P, Vennila K, Palvannan T, Bertani R, Sgarbossa P (2021) Tyrosinase immobilized zein Nanofibrous matrix as a green and recyclable material for biodegradation of azo dyes. Fibers and Polymers 22(10):2714–2725. https://doi.org/10.1007/s12221-021-0207-7

Teh HB, Li H, Yau Li SF (2014) Highly sensitive and selective detection of Pb2+ ions using a novel and simple DNAzyme-based quartz crystal microbalance with dissipation biosensor. Analyst 139(20):5170–5175. https://doi.org/10.1039/c4an00922c

Tsai HC, Doong RA (2005) Simultaneous determination of pH, urea, acetylcholine and heavy metals using array-based enzymatic optical biosensor. Biosens Bioelectron 20(9):1796–1804. https://doi.org/10.1016/j.bios.2004.07.008

Tsopela A, Laborde A, Salvagnac L, Ventalon V, Bedel-Pereira E, Séguy I, Temple-Boyer P, Juneau P, Izquierdo R, Launay J (2016) Development of a lab-on-chip electrochemical biosensor for water quality analysis based on microalgal photosynthesis. Biosens Bioelectron 79:568–573. https://doi.org/10.1016/j.bios.2015.12.050

Vojtěch A, Pavel H, Michal K, Martin S (2016) Polyetherimide nanofibres as sorbents for organochlorinated pesticides determination. J Nanomaterials. https://doi.org/10.1155/2016/1390345

Wang Y, Xu H, Zhang J, Li G (2008) Electrochemical sensors for clinic analysis. Sensors 8(4):2043–2081. https://doi.org/10.3390/s8042043

Wijaya E, Lenaerts C, Maricot S, Hastanin J, Habraken S, Vilcot J-P, Boukherroub R, Szunerits S (2011) Surface plasmon resonance-based biosensors: from the development of different SPR structures to novel surface functionalization strategies. Curr Opin Solid State Mater Sci 15(5):208–224. https://doi.org/10.1016/j.cossms.2011.05.001

Xue J, Wu T, Dai Y, Xia Y (2019) Electrospinning and electrospun nanofibers: methods, materials, and applications. In Chem Rev Am Chem Soc. https://doi.org/10.1021/acs.chemrev.8b00593

Yang K, LeJeune J, Alsdorf D, Lu B, Shum CK, Liang S (2012) Global distribution of outbreaks of water-associated infectious diseases. PLoS Negl Trop Dis. https://doi.org/10.1371/journal.pntd.0001483

Yao N, Wang J, Zhou Y (2014) Rapid determination of the chemical oxygen demand of water using a thermal biosensor. Sensors (switzerland) 14(6):9949–9960. https://doi.org/10.3390/s140609949

Yildirim, N., Long, F., Gu, A. Z. (2014). Aptamer based E-coli detection in waste waters by portable optical biosensor system. Proceedings of the IEEE Annual Northeast Bioengineering Conference, NEBEC https://doi.org/10.1109/NEBEC.2014.6972990

Zamora-Ledezma, C., Negrete-Bolagay, D., Figueroa, F., Zamora-Ledezma, E., Ni, M., Alexis, F., & Guerrero, V. H. (2021). Heavy metal water pollution: A fresh look about hazards, novel and conventional remediation methods. In *Environmental Technology and Innovation* Elsevier B.V. https://doi.org/10.1016/j.eti.2021.101504

Zeitoun MM, Mehana ESE (2014) Impact of water pollution with heavy metals on fish health: overview and updates. Global Veterinaria 12(2):219–231. https://doi.org/10.5829/idosi.gv.2014.12.02.82219

Zhang H, Zhen Q, Liu Y, Liu R, Zhang Y (2019) One-step melt blowing process for PP/PEG micro-nanofiber filters with branch

networks. Results in Physics 12:1421–1428. https://doi.org/10.1016/j.rinp.2019.01.012

Zhu G, Tang Q, Huang M, Yang J, Xu R, Liu J (2020) Polyaniline nanoconical array on carbon nanofiber for supersensitive determination of nitrophenol. Sensors Actuators b: Chem. https://doi.org/10.1016/j.snb.2020.128593

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.