BUKTI KORESPONDENSI JCTM_2023

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Fwd: Manuscript Edianta,et.al. (Review of Ion Imprinted Polymers Nanofiber with Technology Electrospinning: An Advance Materials for Removal of Heavy Metal Ions)

Jaya Edianta <jayaedianta@gmail.com> 15 November 2022 pukul 07.54
Kepada: idha royani unsri <idharoyani@unsri.ac.id>

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Dari: **Jaya Edianta** <jayaedianta@gmail.com>
Date: Kam, 18 Agu 2022 17.40
Subject: Manuscript Edianta,et.al. (Review of Ion Imprinted Polymers Nanofiber with Technology Electrospinning: An Advance Materials for Removal of Heavy Metal Ions)
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To:
Editor-in-Chief
Journal of Chemical Technological and Metallurgy
Dear, Prof.Danalev

I would like to submit the manuscript entitled "Review of Ion Imprinted Polymers Nanofiber with Technology Electrospinning: An Advance Materials for Removal of Heavy Metal Ions" by Jaya Edianta, Octavianus Cakra Satya, Khairul Saleh, Frinsyah Virgo,Fiber Monado and Idha Royani to be considered for publication as Review Article in the Journal of Chemical Technology and Metallurgy.

In general, this article is a literature review of scientific articles on the development of ion imprinted polymers (IIPs) intelligent Nanofiber (NF) materials that utilize electrospinning technology. It discusses initial research in the preparation of IIPs samples, the principles of the synthesis method, the characterization analysis that needs to be conducted and the adsorption research of the IIPs-NF adsorption application.

We believe these findings will be of interest to the readers of your journal.
We declare that this manuscript is original, has not been published before and it is not currently being considered for publication elsewhere.

We know of no conflicts of interest associated with this publication, and there has been no significant financial support for this work that could have influenced its outcome. As first author, I confirm that the manuscript has been read and approved for submission by all the named authors.

We hope you find our manuscript suitable for publication and look forward to hearing from you in due course.

Sincerely,

Jaya Edianta
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Fwd: Manuscript with reference number 22-190 JCTM

Jaya Edianta <jayaedianta@gmail.com> 24 Januari 2023 pukul 21.14
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Dari: **Jaya Edianta** <jayaedianta@gmail.com>
Date: Sel, 24 Jan 2023 09.35
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Journal of Chemical Technological and Metallurgy
Dear, Prof.Danalev

The following is the manuscript (reference numbers: 22-190 JCTM) that we have revised in accordance with the notes that have been provided. We're sure to fix everything. Previously we thank you for the information that has been provided previously.

Sincerely, we will wait for your reply in the near future. Thank you for your attention.

Sincerely,
Edianta

Pada tanggal Rab, 18 Jan 2023 pukul 19.39 Editor-in-Chief <journal@uctm.edu> menulis:

> Dear authors
> You can find the review of your manuscript with a reference number 22-190
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JCTM 22-190 proof

Editor-in-Chief <journal@uctm.edu> 3 Mei 2023 pukul 16.15
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attached is the proof of your paper for final checking. Please, special attention on the text immediately after equations 1 and 2. Symbols do not correspond to the equations.
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idha royani unsri <idharoyani@unsri.ac.id> 7 Mei 2023 pukul 08.07
Kepada: Editor-in-Chief <journal@uctm.edu>

Dear Editor-in-Chief,
Thank you for the information that has been provided. After we have reviewed our article that you have prepared, there are several points that we request and hope to improve:

1. Affiliation for the authors Octavianus Cakra Satya, Khairul Saleh, Frinsyah Virgo, Fiber Monado is **no 2**. Department of Physics, Faculty of Mathematics and Natural Science University of Sriwijaya, South Sumatra, Indonesia, not number 1.
2. Accepted information should probably be changed from Accepted 15 February 2022 to Accepted 15 February **2023**
3. Can we request Table 2. Review of the main components of IIPs. The words "HCL and distilled water" ref 44. Have been corrected to make it tidier.
4. On page 12, after equation 2, we made a mistake about the word "QE". **QE** should be changed to '**qe**'.

We have highlighted some of these important points in the pdf; thank you for your attention.
We hope that some of the important points we mentioned above can be corrected.

Sincerely

Dr. Idha Royani
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paper in JCTM

Editor-in-Chief <journal@uctm.edu> 15 Mei 2023 pukul 14.42
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Dear author,
attached is the paper and it will be published soon on the site. Please send it to your co-authors.
Kind regards
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JOURNAL OF CHEMICAL TECHNOLOGY AND METALLURGY

REVIEW

JCTM 22-190

Review of Ion Imprinted Polymers Nanofiber with Technology Electrospinning: An Advanced Materials for Removal of Heavy Metal Ions

Type of manuscript:

- O Review x
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Review of Ion Imprinted Polymers Nanofiber with Technology Electrospinning: An Advance Materials for Removal of Heavy Metal Ions

Jaya Edianta[1,2], Octavianus Cakra Satya[1], Khairul Saleh[1], Frinsyah Virgo[1], Fiber Monado[1] and Idha Royani*[1,2]

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Abstract: The existence of essential heavy metal ions that pollute the environment has become a substantial concern for countries worldwide due to their ability to damage ecosystems and harm living things. Therefore, research in the field of materials science to eliminate the presence of heavy metal ions that pollute the environment, such as Fe (III), Pb (II), Ni (II), Hg (II), Cd (II), Cr (VI), Ru (III), and AS (III) need to be developed. Ion Imprinted polymers nanofiber (IIPs-NF) is one of the advanced materials with the ability to determine and remove heavy metal ions containing a high degree of selectivity and stability. The use of conjugate electrospinning technology in producing nanofiber (NF) can expand the surface of the material and the recognition sites for target ion elements. This research is a literature review of scientific articles on the development of ion imprinted polymers (IIPs) intelligent NF materials that utilize electrospinning technology. It discusses initial research in the preparation of IIPs samples, the principles of the synthesis method, the characterization analysis that needs to be conducted and the adsorption research of the IIPs-NF adsorption applications. The results showed that modification of the IIPs material with electrospun conjugation can increase the adsorption capacity and have several advantages such as high stability, biocompatibility and a

better regeneration. Therefore, this material has great potential to become an advanced device that plays a role in overcoming harmful metal ions.

***Keywords*:** Adsorption; Nanofibers; electrospinning; heavy metals; Ion imprinted Polymers

Introduction

The existence of essential metal ions that pollute the environment, such as water, soil sediment, food and biological matrices, is a substantial concern for analytical physicists and environmental chemists globally (1,2). Ihsanullah, et.al. in (3) stated that these are usually released from modern industries such as battery factories, mining, metal plating, and pesticide facilities. Some metals, such as mercury (II), copper (II), lead (II) and chromium (III), cadmium (Cd), zinc (Zn), arsenic (As), silver (Ag), chromium (Cr), iron (Fe), and platinum (Pt), are dangerous and tend to damage the ecosystems (4–7)

Several preliminary research succeeded in reducing the presence of hazardous metals using some sophisticated physics analytical instrumentation such as *flame atomic absorption spectroscopy* (FAAS) (8), *atomic fluorescence spectroscopy* (AFS) (9), *inductively coupled plasma optical emission spectrometry* (ICP-OES), *inductively coupled plasma mass spectrometry* (ICP-MS) (10) and *graphite furnace atomic absorption* (GFAAS) (11). However, some of these techniques have specific weaknesses, for example, lengthy processing time, high operational costs and a reasonably complicated instrumentation system. (2). Some other research further stated that analytical instrumentation techniques have a low level of selectivity and cannot specifically identify the target ion element (12). Several research successfully developed a simple and energy-efficient synthesized adsorption materials with fast optimization time to overcome this problem. According to Huang et al. (2018), these are also used for water purification by separating the metal ions. These materials include *aluminium oxide nanopowder* (13), *carbon nanotube filters* (14), *hydroxide* and *jarosite* (15), *chitosan film*

(16), *chelation resin* (17), and silica (18). Generally, these are used to remove metal ions from environmental water samples. The main limitation of this research is the ability of these materials to be less selective with a lower detection limit (19,20). Recent research developments proved that its sensitivity and selectivity, including electrochemical sensors, have been successfully synthesized to detect and eliminate the presence of metal ions, such as imprinted polymer (IIPs) materials (21–23).

Ion imprinted polymers (IIPs) are some type of hollow material with several advantages, such as a simple synthesis method using the comprehensive application and high stability and selectivity values for targets due to the memory effect generated after the printing process (24). According to Fu, et.al. in (25), IIPs are good adsorbents and effective in identifying, monitoring and removing metal ions in aqueous and biological environments. A recent research stated that imprinted polymer ions were successfully synthesized and applied to detect and eliminate some metal ions such as mercury, arsenic (26), lead (27), cadmium (28), chromium (29) and nickel (30). However, some of these research only focused on conventional synthesis processes, which are considered to have specific weaknesses, including slow mass transfer rates and low adsorption capacity (31). Recent research successfully combined modified IIPs with electrospinning techniques to obtain advanced ion imprinted polymers nanofiber (IIPs-NF) materials. Háková, et. al. in (32) reported that electrospinning techniques produce fibre imprinted polymers while maintaining high stability, reloading, mechanical strength, biocompatibility, responsiveness, larger surface area and better adsorption capacity (31,33,34). The use tends to improve the ability of IIPs to absorb and eliminate metal ions (35).

This mini-review focuses on developing IIPs-NF using electrospinning technology compiled based on a systematic and in-depth literature review. Its contents are illustrated in Fig. 1. Several important points were conveyed as the basic preparatory concepts of IIPs materials, development of the fabricated methods using electrospinning tools, and general

knowledge regarding its physical characterization. Incidentally, it is necessary to investigate the application of IIPs-NF for the adsorption of hazardous metals in water and the environment. It is expected that this mini-review provides relevant information about preliminary research and attracts global attention in developing IIPs-NF materials that can potentially eliminate harmful metal ions.

Material Selective IIPs-NF

Polymers produced with moulding technology are applied to thousands of molecules, including biological structures such as metal ions, hormones, proteins, and cells. The ion imprinted ones are used to produce materials that can recognize metal ion structures. Meanwhile, when the active substances are removed, certain voids or moulds are formed, which are highly selective and adsorptive (36,37) IIPs are a multifunctional application of printed materials for selective extraction, separation, and detection of metal ions in environmental media such as water, wastewater, soil, and food samples. Generally, IIPs focus on targeting non-biodegradable heavy metal cations in aquatic habitats, soil and food, such as iron (III), copper (II), cobalt (II), nickel (II), cadmium (II), mercury (II), and lead (II) from industrial manufacturing processes, mineral mining and waste products (6).

Imprinted ion technology is a promising technique in the science of separation and purification of metal ions due to its high selectivity, good stability, simplicity, and low cost (22,38) The synthesis process of the IIPs powder sample was prepared through a mass polymerization procedure involving a mixture of monomers, initiators, crosslinkers, and templates. The resulting polymer mass is ground and sieved to obtain particles of suitable size for various analytical applications (39). The roles and properties of these mixtures that must be met in the preparation of IIPs are shown in Table 1. Some research occasionally involved complex ligands in the polymer matrix. This generally involves trapping technique because certain metals such as Hg (II) and MeHg (II) require ligands to help interact with monomers

(26). Its addition based on the IIPs template tends to interact with several electron-donating heterometals in the recognition process. Ligands play a crucial role in chemical immobilization, do not require a vinyl group, and are represented by monomers. Some examples are 4-VP, 1-vinyl imidazole, acrylamide, and acrylic acid (40).

Fig. 2 shows a schematic representation of the metal ion recognition site using IIPs, and polymeric materials produced after polymerization in the form of a mixture of monomers, active substances, initiators, and crosslinkers chemically bonded to each other in a solvent. The solid material is subjected to either extraction or leaching to eliminate the active substance from the polymer body. This leaves a cavity or template with a similar shape and characteristics to the analyte. In addition, the template in the polymer body serves as a recognition site for the desired or targeted metal ion in the determination and adsorption applications. Table 2 shows some examples of active ingredients, monomers, crosslinkers, initiators and porogrnous solvents used in synthesizing IIPs. The selection is aimed at eliminating the target. In recent years, metal ions based on nitrate chemicals have been successfully used as template-forming active substances in synthesizing IIPs. Functional monomers play an essential role in the site recognition process.Chaipuang, et.al. researched using two functional monomers of IIPs, namely methacrylic acid and Vinyl pyridine to eliminate Cu (III) metal ions. It was further reported that methacrylate acid showed higher specificity for template ions, formed hydrogen bonds with ligand complexes and was more associated with crosslinkers than the vinyl pyridine used as a monomer (43).

The use of sporogenous IIPs solvents is extensive, as shown in Table 2. These are divided into three types, namely non-polar and polar aprotic solvents, including alcohol. However, alcoholic solvents such as methanol or ethanol are often used to synthesize IIPs (40). The polymer extraction process generally involves using an acidic solvent with a lesser pH value, such as HCL (28,44). A common initiator that is frequently used is 2,2-azobisisobutyronitrile

(AIBN). Liu, et. al. stated that increasing the content of the initiator until it reaches an optimum condition triggers a higher concentration of the active centre, thereby accelerating the polymerization rate (45). This affects the molecular weight of the polymer as well as increases the adsorption capacity. Benzoyl peroxide (BPO) initiator is also used to trigger the radical polymerization process in synthesizing IIPs (6).

Further analysis of IIPs using the electrospinning technique involves the addition of a polymer solvent for NF fabrication, as shown in Table 3. This tends to determine the successful synthesis of IIPs-NF and, to a larger extent, polyacrylonitrile (PAN) polymers, which have been widely utilized in the synthesis of both molecular and IIPs-NF(66,69,72). PAN has relatively high Tg properties, low thermal plasticity, and a high crystal melting point (317^{o}C). It also has limited solubility in certain solvents with superior mechanical properties due to the intermolecular forces between polymer chains (73)(74). Crosslinker materials are essential in sample preparation in producing IPs with good adsorption capacity. Hu, et. al. stated that the adsorption capacity of IIPs in metal Chromium (VI) increased with the addition of EGDMA as a crosslinker in the ratio of monomer to its composition (1/4; 1/6; and 1/8) (56). This is in line with the research by Li, et. al. in (68) that the chemical composition of glutaraldehyde as a IIPs-NF crosslinker impacts the stability of lead (II) ion adsorption. Variations in its composition from 0 to 6.7 v/v% showed a higher increase in adsorption. This is because an increase in composition triggers the crosslinking of the chitosan NF, thereby causing it to have a higher level of stability. Moreover, this tends to result in an ideal adsorption capacity of the material. It should be noted that the addition of a crosslinker has an optimum limit because it increases the hydrophobic character and reduces excessive free amino ions, thereby causing the material to experience a decrease in the adsorption capacity (24,75,76)

Electrospinning Technology for the Synthesis of IIPs-NF

Electrospinning is one of the best and most diverse platforms for quality NF fabrication technologies with high compatibility and low costs, such as porous, core-shell, perforated, Janus, nano-nets and sandwiched fibres or membranes. These are used for various applications, including filtration, biomedical, catalysis and adsorption (77). Several preliminary research combined the amazing properties of imprinted polymers and NF to obtain imprinted polymer NF with outstanding qualities such as high reloading, easier target release, responsiveness to stimuli, larger surface area, increased mechanical strength and biocompatibility (31). The application of IIPs advanced materials with electrospinning technology has far more advantages than conventional IIPs synthesis. It tends to maintain the high stability of the IIPs-NF material without any loss of nanoparticles from the fibre bed. The resulting material has a better regeneration rate without loss of binding ability and allows for more selective and efficient target extraction (Háková et al., 2019).

Challenges and Types of Imprinted Polymers Synthesis Methods with Electrospinning Technology

Gonçalves (2020) stated that about three challenges are encountered in producing IIPs-NF with superior quality and properties. This is because it involves a combination of two advanced materials IIPs and NF electrospinning. First, removing active substances in template formation is difficult to achieve and can damage the material. Second, once the pore template has been successfully formed through the extraction process, it is presumed not to have selective properties against the target ion. However, it tends to recognize other complex targets. Third, it is assumed that the IIPs-NF material produced is similar to non-imprinted polymer. This means that its adsorption process has selectivity properties to the target ion. Its adsorption power is slightly different from that of the non-imprinted polymer materials that do not have a site template for recognizing the target ion. However, when these three hurdles are overcome, imprinted polymers NF materials will have great opportunities in intelligent applications such

as determination sensors and adsorption of target substances. In this research, several synthesis methods previously used to successfully produce IIPs-NF with electrospinning technology were also adopted.Patel, et.al. stated that the main approaches are summarized into four major categories, namely molecular imprinting during electrospinning, imprinted polymer layer formation onto electrospinning, solid phase imprinting strategies, and dispersion/conjugation imprinted polymer into/onto electrospun nanofibers. each has its advantages and disadvantages, mainly stemming from the different processing parameters that characterize imprinted polymers and electrospinning (33).

Molecular Imprinting during Electrospinning

This synthesis method involves the preparation of an active substance in an electrospinning solution to produce porous fibres without mixed materials such as crosslinking and functional monomers. Afterwards, the resulting NF material was extracted with an acid solution to produce a porous one that could recognize the target ion, as shown in Fig. 3. (a). Although it looks simple, it is difficult to use this complex method to achieve the desired results due to the inherent distinctive differences between imprinted polymer ion-selective materials and electrospinning technology. In the research carried out by Sharma and Balasubramanian in (66) 8% PAN (w/v) was synthesized with N, N-dimethyl formamide (DMF) solvent mixed with an active substance thorium nitrate and the addition of camphor soot particles. The electrospinning process was carried out afterwards with an HV parameter of 11.5 kV, and the resulting fibres were dried in a vacuum. After which, they were washed with a dilute acid solution to remove Th(VI) ions during the formation of IIPs template. The resulting IIPs-NF has good adsorption capacity and selectivity against Th (VI) radioactive elements. Some other research also reported that the preparation of a precursor solution involves the addition of 8% by weight of PVDF/RTIL polymer in a mixture of DMF solvent and acetone in the ratio of

80:20 (35) and stirred continuously while adding an active substance of Eu (III) metal ion. This synthesis method was successfully used to fabricate the printed surface of NF with Eu^{3+} metal ions leaving voids in the PVDF/RTIL. It is used for selective sensing and recovery of Eu^{3+} ions during sewage treatment. Specifically, after the extraction or removal of the active substance Eu (III), at the end of the synthesis process, EGDMA solvent was added as a crosslinking agent to enhance the characteristics of the imprinted polymer. A similar approach was also adopted for synthesizing IIPs-NF Th (VI) using chitosan/RTIL solution NF. Chitosan amalgamation solution (3%), PVA (8%), thorium nitrate (0.01 wt%) and RTIL (3 wt%) were mixed in a syringe for electrospinning synthesis under a high voltage of 15 kV. The addition of PVA proves that the fibre is able to maintain extensional viscosity, then 2% glutaraldehyde crosslinker is added to complete the IIPs-NF. This differs from previous research because IIPs-NF was extracted at the end of the process using 0.1 M solution of H_2SO_4 (70).

Combining solution/Imprinted polymer Layer Formation onto Electrospinning

This method firstly focuses on synthesizing the electrospinning NF material, after which the resulting fibre is polymerized by adding a mixture of active components to form templates and functional monomers. This is further proceeded with the process of eliminating the active substance either through extraction or leaching. The weakness of this method lies in the polymerization of NF with monomers and active substances, which are difficult to achieve, including the printing of the porous types. Another method involves mixing two solutions, fibre polymer and the IIPs prepolymer, in an electrospinning syringe. Awokoya, et.al. prepared two solutions simultaneously, namely poly(ethylene terephthalate)/polyethyleneimine (PET/PEI) mixed with trifluoroacetic acid (TFA) and dichloromethane (DCM) in the ratio 2:8 (v/v). The fibre polymer solution is mixed with IIPs prepolymer, which already contains crosslinkers and active substances as templates, and then left overnight. The electrospinning process is further fabricated under a high voltage of 15 kV. The resulting IIPs-NF were extracted from a solution

of MeOH and acetic acid (90:10) to eliminate the metal ion Ni(II) from the polymer body. This method successfully created IIPs-NF with better adsorption ability than the non-printing fibre. Based on this, Awokoya concluded that IIPs-NF produced with PET/PEI is suitable for the specific removal of nickel-5,10,15,20-tetraphenyl porphine (NTPP) from fuel oil (64). An illustration of this method is shown in Fig. 3(b).

Solid-Phase Imprinting Strategies

The next method is the incorporation of NF with active substances through the exploitation of template covalent immobilization. This technique is carried out by mixing solvents and fibre polymers in the electrospinning syringe. At the same time, the active substance forming the template is immobilized in the collector, thereby triggering the spinning process. The resulting NF is polymerized directly with the active substance without cross-linking, as shown in Fig. 4. This allows increased accessibility of the binding site during application as well as the elimination of the active substances on NF. The choice of this solid-phase printing method also makes it possible to either maintain or eliminate the presence of the active substance. This technique is more developed due to its molecular applications than the ionic electrospinning imprinting process. However, this is due to the ease of combining the electrospinning method with molecules, eliminating templates and a high chance of reusing the solid phase (33). This method successfully triggered the conjugation of PVP/silica with bovine serum albumin (BSA) or bovine haemoglobin (bHb) as the target substance protein. The resulting NF had fairly good stability with an adjustable porosity level after the solid phase removal. In accordance with the advantages above and conveniences, further development of this method potentially leads to the optimization of IIPs-NF materials in the future.

Dispersion/Conjugation Imprinted Polymer into/onto Electrospun Nanofibers

This is one of the methods commonly adopted by preliminary research for synthesizing molecular-based electrospinning (MIP) and IIPs-NF. It is more advantageous than the previous method because it combines two different materials, IIPs and NF. This technique separates the process parameters of the two material technologies, making them easily adjustable to achieve the desired final architecture with effective recognition performance. The procedure is carried out by synthesizing IIPs and NF separately, as shown in Fig. 5. Incidentally, IIPs are synthesized with a mixture of polymers such as monomers, crosslinkers, and active substances to produce nano or microparticles. On the other hand, solvents and polymers were prepared for the electrospinning process. There are two ways of combining these materials, first (Fig. 5 (a) is combining the resulting nanoparticles dispersed into a polymer solution, followed by an electrospinning process to produce fibrous IIPs-NF. The second method is shown in Fig. 5 (b), which involves the synthesis of electrospinning NF, and then the resulting ones are conjugated with IIPs nanoparticles. This technique utilizes two different advanced materials, IIPs and NF, while maintaining their respective characteristics and synthesis methods.

An example of the use of this method is cited in the research carried out by Rammika, et.al. Rammika et al. (2011), where IIPs particles obtained through precipitation and mini-emulsion polymerization approaches were suspended with 10 m dimethyl formamide (DMF) and 200 mg polysulphone (PSU), and the solution was stirred for three hours. The resulting solution is further electrospinning at a high voltage of 15 kV. The fibre obtained is stored in a desiccator to evaporate the remaining solvent. The adsorption process is carried out at the end using an HCL solution to eliminate Ni (II) metal ions (63). Hassanzadeh et al successfully developed (69)(69)(68)(68)(68)(68)(67)(66)(66)(66)the most recent method of producing NF IIPs for the adsorption of Cr (VI) metal ions by preparing IIPs particles and fibres separately. First, the solid IIPs were synthesized by free radical polymerization; the resulting particles were washed using acetone to separate the unreacted mixture from the reaction. The NaOH solution

eliminates the active substance Cr (VI), thereby forming a template on the particles. On the other hand, the porous NF matrix was prepared by dissolving PAN in a solution with deploy (methyl methacrylate) (PMMA) using an electrospinning device at a voltage of 17 kV. The resulting fibre was further functionalized with the addition of hydroxylamine hydrochloride and sodium carbonate at the end of the process. The PAN functionalized fibre was conjugated with IIPs particles for 12 hours, using a mixture of deionized water and ethanol (1:3 v/v) at 70^{o}C. This method is good at producing IIPs-NF with a maximum adsorption capacity.

Important Parameters of Electrospinning Process for Synthesis of IIPs-NF

Some important attributes that need to be considered in electrospinning tools are the physical parameters affecting the final fibre product obtained under continuous and uniform optimal conditions. Critical variables, such as viscosity and flow rate of polymer solution, and its molecular weight, high voltage, and nozzle-to-collector distance, need to be considered before producing adsorbent fibres (78). In the NF fabrication process, electrospinning applies a high voltage to the polymer solution at the tip of the syringe. At a certain distance between the collector and the syringe, the surface tension of the droplets from the needle breaks due to the flowing electric field, which enables the polymer to move through it to the processed collector (79). The high electrospinning voltage affects the increased spinnability of the polymer solution. A lower voltage affects the surface tension of the smaller polymer solution droplets. The insufficient voltage causes the needle tip to drip, producing bead NF. This is affected by an increase in the flow rate due to minimal and incomplete moisture from the needle fibre jet to the collector. The required flow rate and minimum value tend to be fixed to produce uniform beadles and NF. It should be noted that increasing the flow rate and voltage reduces the charge density, thereby causing the NF to coalesce before being deposited on the collector (80). Table 4 shows several parameter values employed by previous research in synthesizing

NF, later modified into IIPs-NF. These were also used to produce various final fibre diameters with different maximum capacity values for the adsorption target ion.

General Characterization Instrumentation of IIPs-NF

In chemistry and physics, sample characterization is an in-depth research and analysis of polymer properties, including crystal particle size, surface morphology, thermal stability or instability, percentage adsorption of the functional groups, etc. However, characterization instruments that have been used in IIPs technology include scanning electron microscopy (SEM), Fourier transform Infrared spectroscopy (FT-IR), and X-ray diffractometry (XRD) (42). Further analysis of IIPs-NF is distinguished by FAAS and TGA instrumentation. Some initially prepared samples are IIPs which have undergone an extraction process or elimination of the active substance from the pores, as shown in Fig. 6 (a). Non imprinted Polymer (NIP) (Fig. 6 (b)) is a sample synthesized with the same steps and procedures as IIPs, although without the use of template-forming active substances. These were followed by pure fibre polymer or NF, Non-Imprinted Polymers Nanofiber (NIPs-NF), and finally, the IIPs-NF, as shown in Fig.s 6 (c), (d), and (e), respectively. Many samples are based on comparing the diverse characteristics and variations stated in previous research. Each of them was tested and analyzed to determine the target ion's respective properties and selective adsorption ability.

Fourier transform Infrared spectroscopy (FTIR) is a physicochemical characterization tool used to analyze the correspondence between the wave numbers of each sample to determine the chemical bonds. Segundo et al stated that functional group or percentage transmittance are used for the success of the chemical compounds' synthesis process (81). Hassanzadeh et al. (2018) compared the FTIR spectra of $K_2Cr_2O_7$, PANFM, FPANFM, IIPs and PANFM, which functioned as IIPs. The comparison analysis between PANFM and FPANFM showed that PANFM functionalization occurred correctly. All samples were similar to the functional groups formed, indicating the chemical compound's successful performance.

The FTIR IIPs spectrum shows the OeH vibrational band of the silanol group at a wave number of 3460 cm^{-1}. Besides, the low-intensity band at 3118 cm^{-1}, 2955 cm^{-1} and 1479 cm^{-1} is associated with the C–H, CH_3, and CeN strains (imidazole ring). The absorption band at 1728 cm^{-1} was assigned to the carbonyl group of TMSPMA. A comparison of the K2Cr2O7 and IIPs spectra showed no $K_2Cr_2O_7$ index peak, confirming the complete extraction of the Cr (VI) anion from the IIPs structure.

Scanning Electron Microscopy (SEM) characterization instrumentation is essential to determine the surface morphology structure of the polymer material samples (82). Electrospinning fibres synthesized using TFA polymers for solution concentrations of less than 18% emitted from low-viscosity solutions split into droplets due to the lower polymer amount and density required to form a stable beam (67). Meanwhile, beads were observed in solution concentrations between 20 and 24% w/v. These completely disappeared, and finer and more uniform electrospun fibres were formed when the concentration was increased to 26, 28 and 30% w/v. It is believed that the combination of a relatively high viscous solution and the solvent's dielectric constant improves the fibre's morphology. SEM analysis provides information about the estimated number of pores or templates formed after the leaching process by utilizing Matlab Poredize software or image J capabilities. Further applications are X-ray diffractometry (XRD) which confirms the crystallinity structure (83) or IIPs sample crystals after extracting and conjugating electrospun NF. It should be noted that XRD estimates the crystal size through the lattice plane of the resulting sample. This is attributed to the semi-crystalline nature of NF (66).

Further Research on Material Adsorption

Kinetic Study

The kinetic analysis of the adsorption process aims to determine the type of physical or chemical reaction and the number of target ions adsorbed by the IIPs adsorbent, which was adjusted to the varying adsorption time. Quasi-first-order (Equation (1)) and quasi-second-order (Equation (2)) kinetic models were used for fitting to investigate the mechanism of the adsorption rate. Meanwhile, assuming the results are consistent with the first-order quasi-kinetic model, it indicates that the adsorption process is mainly physical. When it is in line with the quasi-second-order kinetics model, this implies the occurrence of chemical reactions in the adsorption process.

$$\log(q_e - q_t) = \log q_e - \left(\frac{kl}{2.303}\right) t \quad \text{..... (1)}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{1}{q_e} \quad \text{..... (2)}$$

In the equation di or QE (mgg^{-1}) is the equilibrium adsorption capacity, qt adsorption capacity at time t (mg/g), Qm (mgg^{-1}) theoretical saturation adsorption capacity, t (min) adsorption time, k1 (min^{-1}) is a quasi-first-order kinetic rate constant, and k_2 ($g(mg\ min)^{-1}$) a quasi-second-order kinetic rate constant (84). Based on the reviews of several research on IIPs-NF, the sorbent tends to fulfil the installation of a second-order pseudo model. This indicates that the IIPs material tends to undergo a chemical adsorption process. The Hg-PBCS sorbent developed by Hajri, et.al. was more effective than the use of Hg (II) ions as an adsorption target compared to the control unprinted sorbent (NI-PBCS) with a maximum capacity of 315 mgg^{-1} that correlated with relatively fast adsorption kinetics, namely the Pseudo-second order (PSO) model (85).

Isotherm Study

The basic physiochemical characteristics related to the adsorption of ions and imprinted polymer molecules was investigated through the research of adsorption isotherms. Operational design and modelling analysis of metal ion concentration in solution as a function of

temperature for an adsorptive system was investigated by mathematical correlation and graphical depiction (70). Furthermore, adsorption isotherm is a graphic notation used to determine the amount of adsorbate on the surface of the adsorbent under pressure at constant temperature (24). It determines the capacity and degree of adsorption, which is stronger or weaker. The adsorption mechanism is described based on thermodynamic assumptions of physicochemical parameters. In accordance with several research, the adsorption data tends to be modelled using differential equations, including the pseudo-second-order rate, the Langmuir, Freundlich, Temkin, and Dubinin – Radushkevich isotherm and three-parameter models, such as the Redlich – Peterson and Sips isotherms using the trial-and-run error method (R). The metal ion uptake IIPS and MIP usually correlate with the Langmuir or Freundlich equations. Langmuir's equation applies to the absorption process on a homogeneous surface. However, Freundlich's equation is valid for adsorption on heterogeneous surfaces. Previous research showed that the Langmuir and Freundlich equations represent different adsorption of heavy metal ions to IIPS and MIP. In most cases, one model best describes the adsorption process (3,70,86). Table 5 shows the development of adsorption study with eletrospun nanofiber.

Thermodynamic Study

It is important to study the thermodynamics of adsorption to monitor the energetic changes during the entire process. Determining the free energies of enthalpy, entropy, and Gibbs is a key to understanding the amount of heat absorbed or released, the energy provided by the system and the randomness at the solid-liquid interface when absorption occurs. Investigating temperature changes in adsorption helps determine whether the process is endothermic or exothermic, spontaneous or non-spontaneous (87). Considering the reviews on studying the thermodynamics of various organic substances adsorption onto various nano-

adsorbents, its parameters were determined from the Gibbs equation. The Gibbs free energy depends on the equilibrium constant in equation (3) is stated as follows:

$$\Delta G^{\circ} = -RT \ln K_c \quad \text{..... (3)}$$

The relationship between Entropy and Enthalpy is stated in equation (4)

$$\ln K_c = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad \text{..... (4)}$$

Where K_C is the equilibrium constant and $K_C = \frac{q_e}{C_e}$, q_e is the adsorption capacity at equilibrium (mg / L), C_e is the equilibrium concentration (mg / L), T T is the temperature, R is the universal gas, ΔH° and ΔS° are standard enthalpy and entropy, respectively. They were also determined from the slope and intercept of the ln Kc versus 1/T plots resulting from the adsorption examination process at different temperatures. Positive enthalpy indicates the endothermic nature of the reaction process, while positive Gibbs free energy refers to the non-spontaneous procedure. All completed adsorption process is categorized into physisorption and chemisorption depending on the Gibbs free energy. The nature of the physisorption process is for $-20 kJ/mol < \Delta G < 0$, and the chemisorption is for $-800\ kJ/mol < \Delta G < -40\ kJ/mol$. The value of enthalpy (ΔH), entropy (ΔS) and Gibbs energy (ΔG) is used to predict the adsorption properties (86).

Conclusion

The presence of harmful heavy metal ions, such as mercury (II), copper (II), lead (II), chromium (III), cadmium, zinc, arsenic (As), silver (Ag), chromium (Cr), iron (Fe) and platinum (Pt), is of enormous concern to chemists and physicists in terms of overcoming its negative effects on the environment and human health. One of the advanced materials developed rapidly is NF material with electrospinning technology. It has excellent properties and characteristics such as mass transfer and good adsorption capacity. To increase the selectivity and sensitivity of NF to metal ions, it is modified with porous materials in the form

of IIPs. IIPs have pores of which the chemical properties and characteristics resemble metal targets due to the leaching process carried out after extraction. This enables the target metal ions to fill every material pore during the adsorption experiment.

Some of the challenges faced in the process of modifying NF and IIPs is the difficulty involved in eliminating active substances in the formation of templates which have the potential to reduce the adsorption ability of the material. This is overcome by adopting several major approaches to the synthesis process using electrospinning technology, such as Molecular Imprinting during Electrospinning, Imprinted polymer Layer Formation onto Electrospinning, Solid-Phase Imprinting Strategies, and Dispersion/Conjugation imprinted polymer into/onto Electrospun Nanofibers. Each method has its advantages and disadvantages, mainly stemming from the different processing parameters that characterize imprinted polymers and electrospinning.

The dispersion or conjugation method is easier to perform. It simply involves the combination of two different materials, IIPs and NF, to achieve the desired final architecture with efficient recognition performance. This method is carried out by synthesizing IIPs and NF separately and conjugating them in the final process. The combination of NF using electrospinning technology with IIPs porous materials maintains high stability values, reloading, responsiveness, large surface area and good adsorption capacity, as well as increased mechanical strength and biocompatibility. Therefore, this material has great potential and needs to be further developed. It commercializes new products for removing heavy metals from water. This research serves as reference material for future analyses in designing and developing IIPs-NF.

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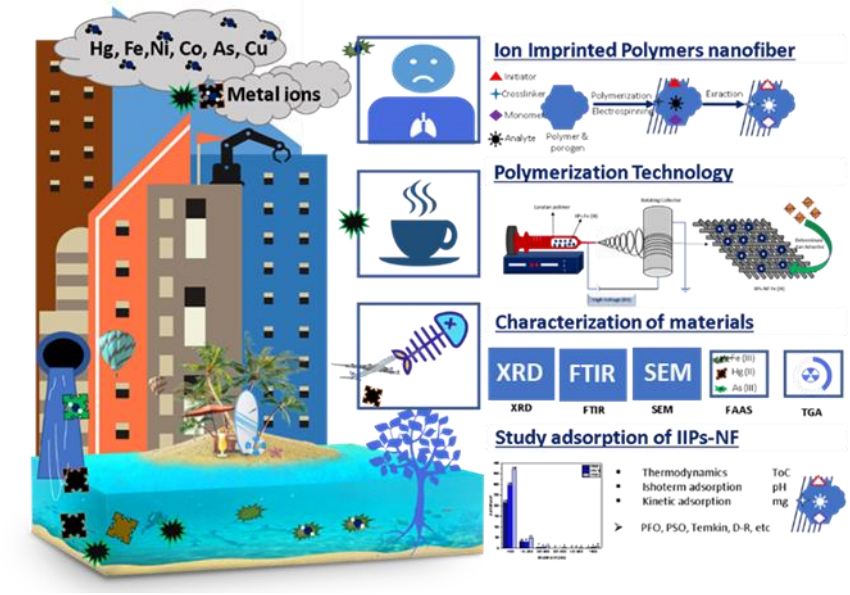

Fig. 1. Mini illustration review of the presence of harmful metal ions in the environment and the adsorption role of advanced IIPs-NF materials

2.

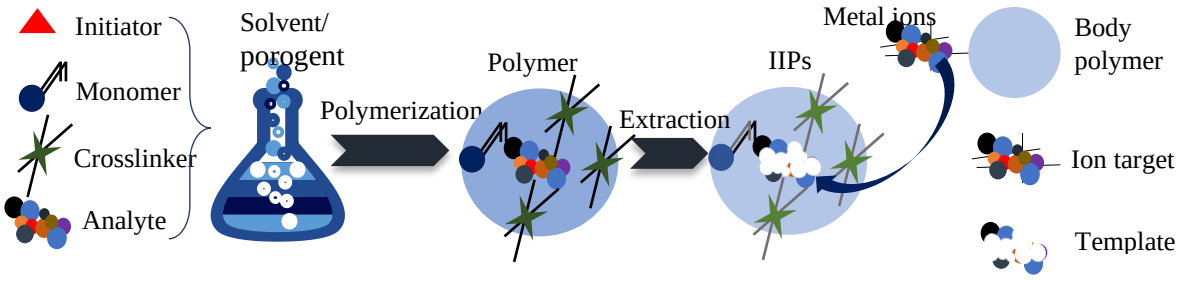

Fig. 2. Schematic synthesis and site recognition of IIPs against metal ion targets in determination applications and adsorption materials

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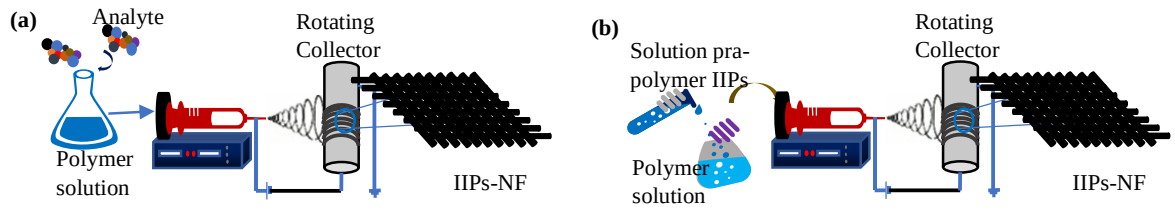

Fig. 3. Illustration of IIPs-NF synthesis method using electrospinning technology (a). Molecular imprinting during electrospinning, (b). Imprinted polymer Layer Formation onto Electrospinning

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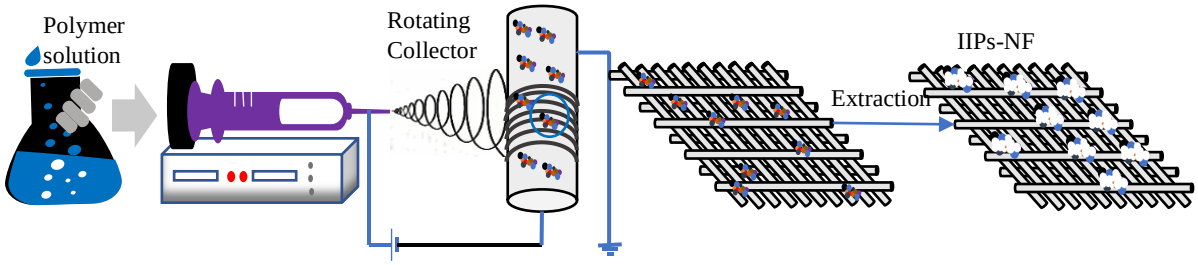

Fig. 4. Illustration of Methods solid-phase imprinting strategies for electrospinning IIPs-NF

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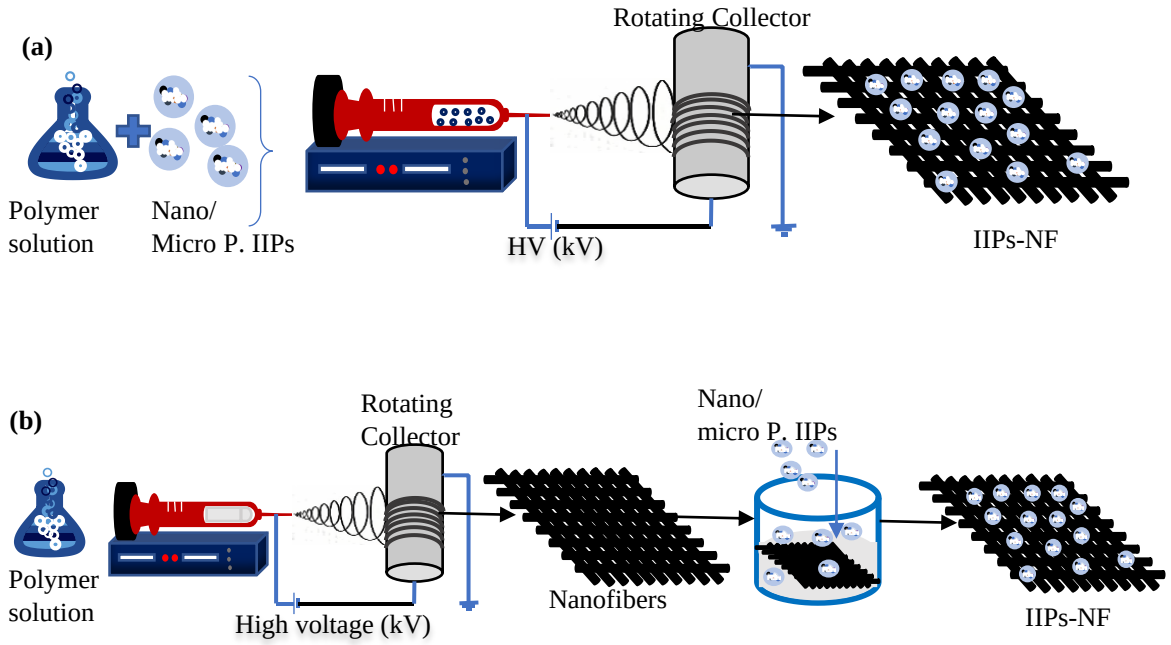

Fig. 5. The main approach of electrospinning technology in producing imprinted polymers NF (a). A polymer solution of NF dispersed with nano/microparticles of IIPs, or (b). Electrospinning NF are conjugated with micro/nanoparticles through chemical reactions

6.

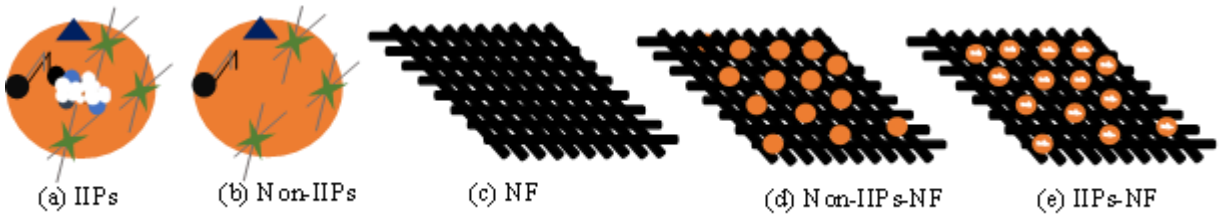

Fig. 6. Illustration of different samples (a) IIPs, (b) Non-IIPs, (c) NF, (d) Non-IIPs-NF, and (e) IIPs-NF

Table 1. The Role and Function of IIPs

Material components	Characteristics, roles, and functions	Ref.
Analyte	Chemically inert, large in number, dissolved during the printing process. It has high stability and chemically bonds with monomers. The active substance is a target ion recognition site in metal determination and absorption applications.	(24)
Monomer of functional	Interacts in solutions with active substances to develop complex or functional networks of hydrogen bonds and reactive substituents that either reacts covalently or noncovalently.	(41)
Crosslinker	Plays a role in the formation of bond chains and polymer features. The main function of the crosslinker is to produce a stable polymer matrix consisting of recognition sites for the analyte.	(36)
Initiator	The initiator is used in lesser quantity than the active substance through the mole ratio of the substance that acts as a radiation source in free radical polymerization	(26)
Solvent	Needs to be able to dissolve the entire mixture of polymerization components which contribute to the expansion of polymer features as well as plays a relevant role in the formation of porous material	(42)

Table 2. Review of the main components of IIPs

Analyte	Monomer	Crosslinker	Initiator	Solvent	Ref.
Fe (III)	Methacrylic Acid	EGDMA	AIBN	Acetonitrile and ethanol	(46)
	Methacrylic Acid	Divinyl Benzene	AIBN	HCL and distilled water	(44)
	BMAOP	EGDMA	AIBN	Acetonitrile	(47)
Pb (II)	Methacrylic Acid	EGDMA	AIBN	Dimethyl formamide	(48)
	Hydroxyethyl methacrylate	Glutaraldehyde	NaHSO3	Distilled water	(27)
	Vinyl pyridine	EGDMA	AIBN	Methanol	(49)
Ni (II)	BDAAT	EGDMA	AIBN	Acrylamide	(45)
	Methacryloyl-L-histidine	Methylene-bis (acrylamide)	Ammonium persulfate	Deionized water	(50)
	Hydroxyphenyl acrylamide	EGDMA	AIBN	CHCl3	(51)
	Methacrylic acid	EGDMA	AIBN	Methanol	(52)
Hg (II)	Vinylanilline	EGDMA	Ammonium persulfate	Glacial acetic acid	(53)
	Methacrylic acid	EGDMA	AIBN	Acrylonitrile	(54)
Co (II)	Dithizone & MAA	Dimethacrylate & EGDMA	AIBN	HCL and CH_3COOH	(55)

Cd (II)	Mercaptopropyl trimethoxysilane	Epichlorohydrin	-	HCL and Ethanol	(28)
Cr (VI)	Vinyl pyridine	EGDMA	ACCN	Methanol and DMF	(29)
	Vinylbenzyltri-methylammonium	EGDMA	-	Dichromic acid	(56)
Au (III)	Polyeugenol	EGDMA	AIBN	HCl, Methanol	(57)
Pd (II)	Aminopropyl triethoxysilane isatin	Silica	AIBN	Anhydrousethyl alcohol	(58)
Eu (III)	Allyl acetoacetate	EGDMA	AIBN	Trifluoroacetic acid	(59)
Ru (III)	Acrylamide	-	TEMED	Ethyl acetate	(60)
As (III)	Methacrylic acid	EGDMA	AIBN	Methanol	(61)
Cu (III)	Methacrylic acid and vinyl pyridine	Pentaerythritol triacrylate	Benzoyl peroxide	Methanol	(43)
Rb (I)	Methacrylic	EGDMA	AIBN	Methanol	(62)

Ethylene glycol dimethacrylate (EGDMA); 1,1`-azobis (cyclohexanecarbonitrile) (ACCN); -Tetramethyle thylenediamine (TEMED); S,S'-bis(α,α'-dimethyl-α''-acetic acid) trithiocarbonate (BDAAT) and 2,2'- azobisisobutyronitrile (AIBN).

Table 3. Further review of the preparation of the main ingredients during the IIPs synthesis process using the electrospinning technique

Analyte	Polymer	Function Monomer	Cross-linker	Initiator	Solvent	Ref

$NiSO_4.6H_2O$ for Ni (II)	DMF and polysulphone	Vinylpyridine	Divinyl benzene	AIBN	nitric acid, hydrochloric acid	(63)
Nickeltetraphenylporphine	Polyethyleimine	Styrene	Divinyl benzene	ACC	Trifluoroacetic acid and acetic acid	(64)
Cadmium chloride for Cd (II)	Chitosan	Dichloromethane	Glutaraldehyde		Hydrochloric acid	(65)
Thorium nitrate for Th (IV)	Polyacrylonitrile (PAN)	Camphor			Dimethyl formamide	(66)
Nickel-tetraphenylporphyrin	polyethyleimine	Styrene	Divinyl benzene	ACC	Trifluoroacetic acid and acetic acid	(67)
lead chloride for Pb (II)	Chitosan	Dichloromethane	Glutaraldehyde		Hydrochloric acid	(68)
chromium (III) chloride for Cr (VI)	Polyacrylonitrile (PAN)	poly (methyl methacrylate)	EGDMA	AIBN	Hydrochloride and dimethylformamide	(69)

Thorium nitrate for Tr (IV)	Chitosan and PVA		Glutaral dehyde	BMIM BF4-	hydrochlori c acid and acetic acid	(70)
Europium nitrate for Eu (II)	Polyvinyli dene fluoride	Ionic liquid (RTIL)	EGDM A		DMF and acetone	(35)
cerium nitrate hexahydrate for Gd (III)	Chitosan	Glacial acetic acid	Glutaral dehyde		Ethanol	(71)

1,1-azobis(cyclohexanecarbonitrile) (ACC); 1-butyl-3- methylimidazolium tetrafluoroborate (BMIMBF4-))

Table 4. Further Research on the Parameters of Using Electrospinning Equipment in Synthesizing IIPs-NF

Materials	IIPs: Polymer	Methode	Parameters of elecrospun				Diameters (nm)	Ref.
			Flowrate (vol/time)	V (kV)	T (h)	D (cm)		
Ni (II)-DMG IIP	1:1 wt%	Bulk polymerization	2 μg·mℓ$^{-1}$	15	6	12	406-854	(63)
NTPP-imprinted composite nanofibers	3:1 wv%	MIP electrospun	20 mL min^{-1}	15	-	13	5.33-9.21	(64)

Nanofiber electrospun Cd (II)	4:0.8 wv%	Imprinted electrospinning	0.6 mL h^{-1}	19	24	9.5	76.1-161.9	(65)
ion imprinted PAN– CS nanofiber	8:8 wv%	Functionalized electrospinning	1 μL min^{-1}	11.5	20	8	~70	(66)
NVMIN For Nickel	14 - 30% w/v	MIT electrospun	-	15	5	13	-	(67)
Chitosan NF MIP	2.4:0.5 wv%	one-step electrospinning imprinted	-	20	24	10	90.3-220	(68)
IIP-functionalized-PANFM	1:3 vv	Imprinted electrospinning	0.7 mL h^{-1}	17	12	15	143–181	(69)
Imprinted chitosan/RTIL nanofiber	3:0.01 wt	Imprinted electrospinning	0.5 mL h^{-1}	15	-	15	40	(70)
ion imprinted PVDF/RTIL	0.01–0.1 wt%	Imprinted electrospinning	0.8 μL min-1	13	1	15	250-700	(35)

Table 5 Review Table of Metal Ion Adsorption Analysis Results Based on IIPs-NF

Adsorbent	Ion metal	Q (mgg^{-1})	Optimal Conditions			Kinetic model	Iso-therm	Reg (time)	Ref.
			m (mg)	t (min)	PH				
Ni(II)-DMG IIP	Ni (II)	-	15	210 s	6	-	-	-	(63)
NTPP-imprinted composite NF		17.54	30	-	7	-	-	11	(64)
NF electrospun	Cd (II)	346.3	-	1440	6	PSO	LF	3	(65)
ion imprinted	Th (IV)	455.5	50	120	7	PSO and	F	4	(66)
PAN– CS NF						D-R			
Chitosan NF MIP	Pb (II)	110.2	-	150	7	PSO	L	3	(68)
IIP-functionalized-PANFM	Cr (VI)	398	100	12	7	PSO	T	3	(69)
Imprinted chitosan/RTIL NF	Th (IV)	325	-	120	7	PSO	L	7	(70)
ion imprinted PVDF/RTIL	Eu (III)	22.37	-	180	7	PSO	F	5	(35)

L: Lang Freundlichmuir model, F: Freundlich, T: Temkin, PSO: pseusosecond-order model, D-R: Dubinin–Radushkevich

SESUDAH REVISI DAN FINAL

REVIEW OF ION IMPRINTED POLYMERS NANOFIBER WITH TECHNOLOGY ELECTROSPINNING: AN ADVANCE MATERIALS FOR REMOVAL OF HEAVY METAL IONS

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ABSTRACT

The existence of essential heavy metal ions that pollute the environment has become a substantial concern for countries worldwide due to their ability to damage ecosystems and harm living things. Therefore, research in the field of materials science to eliminate the presence of heavy metal ions that pollute the environment, such as Fe (III), Pb (II), Ni (II), Hg (II), Cd (II), Cr (VI), Ru (III), and AS (III) need to be developed. Ion Imprinted polymers nanofiber (IIPs-NF) is one of the advanced materials with the ability to determine and remove heavy metal ions containing a high degree of selectivity and stability. The use of conjugate electrospinning technology in producing nanofiber (NF) can expand the surface of the material and the recognition sites for target ion elements. This research is a literature review of scientific articles on the development of ion imprinted polymers (IIPs) intelligent NF materials that utilize electrospinning technology. It discusses initial research in the preparation of IIPs samples, the principles of the synthesis method, the characterization analysis that needs to be conducted and the adsorption research of the IIPs-NF adsorption applications. The results showed that modification of the IIPs material with electrospun conjugation can increase the adsorption

capacity and have several advantages such as high stability, biocompatibility and a better regeneration. Therefore, this material has great potential to become an advanced device that plays a role in overcoming harmful metal ions.

Keywords**:** adsorption; nanofibers; electrospinning; heavy metals; ion imprinted polymers.

INTRODUCTION

The existence of essential metal ions that pollute the environment, such as water, soil sediment, food and biological matrices, is a substantial concern for analytical physicists and environmental chemists globally [1,2]. Ihsanullah, et.al. stated that these are usually released from modern industries such as battery factories, mining, metal plating, and pesticide facilities [3]. Some metals, such as mercury (II), copper (II), lead (II) and chromium (III), cadmium (Cd), zinc (Zn), arsenic (As), silver (Ag), chromium (Cr), iron (Fe), and platinum (Pt), are dangerous and tend to damage the ecosystems [4–7].

Several preliminary research succeeded in reducing the presence of hazardous metals using some sophisticated physics analytical instrumentation such as flame atomic absorption spectroscopy (FAAS) [8], atomic fluorescence spectroscopy (AFS) [9], inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS) [10] and graphite furnace atomic absorption (GFAAS) [11]. However, some of these techniques have specific weaknesses, for example, lengthy processing time, high operational costs and a reasonably complicated instrumentation system. [2]. Some other research further stated that analytical instrumentation techniques have a low level of selectivity and cannot specifically identify the target ion element [12]. Several research successfully developed a simple and energy-efficient synthesized adsorption materials with fast optimization time to overcome this problem. According to Huang et al. (2018), these are also used for water purification by separating the metal ions. These materials include aluminium

oxide nanopowder [13], carbon nanotube filters [14], hydroxide and jarosite [15], chitosan film [16], chelation resin [17], and silica [18]. Generally, these are used to remove metal ions from environmental water samples. The main limitation of this research is the ability of these materials to be less selective with a lower detection limit [19,20]. Recent research developments proved that its sensitivity and selectivity, including electrochemical sensors, have been successfully synthesized to detect and eliminate the presence of metal ions, such as imprinted polymer (IIPs) materials [21–23].

Ion imprinted polymers (IIPs) are some type of hollow material with several advantages, such as a simple synthesis method using the comprehensive application and high stability and selectivity values for targets due to the memory effect generated after the printing process [24]. According to Fu, et.al. in [29], IIPs are good adsorbents and effective in identifying, monitoring and removing metal ions in aqueous and biological environments. A recent research stated that imprinted polymer ions were successfully synthesized and applied to detect and eliminate some metal ions such as mercury, arsenic [27], lead [30], cadmium [31], chromium [32] and nickel [33]. However, some of these research only focused on conventional synthesis processes, which are considered to have specific weaknesses, including slow mass transfer rates and low adsorption capacity [34]. Recent research successfully combined modified IIPs with electrospinning techniques to obtain advanced ion imprinted polymers nanofiber (IIPs-NF) materials. Háková, et. al. in [35] reported that electrospinning techniques produce fibre imprinted polymers while maintaining high stability, reloading, mechanical strength, biocompatibility, responsiveness, larger surface area and better adsorption capacity [34,36,37]. The use tends to improve the ability of IIPs to absorb and eliminate metal ions [38].

This mini-review focuses on developing IIPs-NF using electrospinning technology compiled based on a systematic and in-depth literature review. Its contents are illustrated in Fig. 1. Several important points were conveyed as the basic preparatory concepts of IIPs

materials, development of the fabricated methods using electrospinning tools, and general knowledge regarding its physical characterization. Incidentally, it is necessary to investigate the application of IIPs-NF for the adsorption of hazardous metals in water and the environment. It is expected that this mini-review provides relevant information about preliminary research and attracts global attention in developing IIPs-NF materials that can potentially eliminate harmful metal ions.

MATERIAL SELECTIVE IIPS-NF

Polymers produced with moulding technology are applied to thousands of molecules, including biological structures such as metal ions, hormones, proteins, and cells. The ion imprinted ones are used to produce materials that can recognize metal ion structures. Meanwhile, when the active substances are removed, certain voids or moulds are formed, which are highly selective and adsorptive [26,39] IIPs are a multifunctional application of printed materials for selective extraction, separation, and detection of metal ions in environmental media such as water, wastewater, soil, and food samples. Generally, IIPs focus on targeting non-biodegradable heavy metal cations in aquatic habitats, soil and food, such as iron (III), copper (II), cobalt (II), nickel (II), cadmium (II), mercury (II), and lead (II) from industrial manufacturing processes, mineral mining and waste products [6].

Imprinted ion technology is a promising technique in the science of separation and purification of metal ions due to its high selectivity, good stability, simplicity, and low cost [22,40] The synthesis process of the IIPs powder sample was prepared through a mass polymerization procedure involving a mixture of monomers, initiators, crosslinkers, and templates. The resulting polymer mass is ground and sieved to obtain particles of suitable size for various analytical applications [41]. The roles and properties of these mixtures that must be met in the preparation of IIPs are shown in Table 1. Some research occasionally involved complex ligands in the polymer matrix. This generally involves trapping technique because

certain metals such as Hg (II) and MeHg (II) require ligands to help interact with monomers [27]. Its addition based on the IIPs template tends to interact with several electron-donating heterometals in the recognition process. Ligands play a crucial role in chemical immobilization, do not require a vinyl group, and are represented by monomers. Some examples are 4-VP, 1-vinyl imidazole, acrylamide, and acrylic acid [42].

Fig. 2 shows a schematic representation of the metal ion recognition site using IIPs, and polymeric materials produced after polymerization in the form of a mixture of monomers, active substances, initiators, and crosslinkers chemically bonded to each other in a solvent. The solid material is subjected to either extraction or leaching to eliminate the active substance from the polymer body. This leaves a cavity or template with a similar shape and characteristics to the analyte. In addition, the template in the polymer body serves as a recognition site for the desired or targeted metal ion in the determination and adsorption applications. Table 2 shows some examples of active ingredients, monomers, crosslinkers, initiators and porogrnous solvents used in synthesizing IIPs. The selection is aimed at eliminating the target. In recent years, metal ions based on nitrate chemicals have been successfully used as template-forming active substances in synthesizing IIPs. Functional monomers play an essential role in the site recognition process.Chaipuang, et.al. researched using two functional monomers of IIPs, namely methacrylic acid and Vinyl pyridine to eliminate Cu (III) metal ions. It was further reported that methacrylate acid showed higher specificity for template ions, formed hydrogen bonds with ligand complexes and was more associated with crosslinkers than the vinyl pyridine used as a monomer [43].

The use of sporogenous IIPs solvents is extensive, as shown in Table 2. These are divided into three types, namely non-polar and polar aprotic solvents, including alcohol. However, alcoholic solvents such as methanol or ethanol are often used to synthesize IIPs [42]. The polymer extraction process generally involves using an acidic solvent with a lesser pH value,

such as HCL [31,44]. A common initiator that is frequently used is 2,2-azobisisobutyronitrile (AIBN). Liu, et. al. stated that increasing the content of the initiator until it reaches an optimum condition triggers a higher concentration of the active centre, thereby accelerating the polymerization rate [45]. This affects the molecular weight of the polymer as well as increases the adsorption capacity. Benzoyl peroxide (BPO) initiator is also used to trigger the radical polymerization process in synthesizing IIPs [6].

Further analysis of IIPs using the electrospinning technique involves the addition of a polymer solvent for NF fabrication, as shown in Table 3. This tends to determine the successful synthesis of IIPs-NF and, to a larger extent, polyacrylonitrile (PAN) polymers, which have been widely utilized in the synthesis of both molecular and IIPs-NF[66,69,72]. PAN has relatively high Tg properties, low thermal plasticity, and a high crystal melting point (317^{o}C). It also has limited solubility in certain solvents with superior mechanical properties due to the intermolecular forces between polymer chains [73][74]. Crosslinker materials are essential in sample preparation in producing IPs with good adsorption capacity. Hu, et. al. stated that the adsorption capacity of IIPs in metal Chromium (VI) increased with the addition of EGDMA as a crosslinker in the ratio of monomer to its composition (1/4; 1/6; and 1/8) [56]. This is in line with the research by Li, et. al. in [68] that the chemical composition of glutaraldehyde as a IIPs-NF crosslinker impacts the stability of lead (II) ion adsorption. Variations in its composition from 0 to 6.7 v/v % showed a higher increase in adsorption. This is because an increase in composition triggers the crosslinking of the chitosan NF, thereby causing it to have a higher level of stability. Moreover, this tends to result in an ideal adsorption capacity of the material. It should be noted that the addition of a crosslinker has an optimum limit because it increases the hydrophobic character and reduces excessive free amino ions, thereby causing the material to experience a decrease in the adsorption capacity [24,75,76].

ELECTROSPINNING TECHNOLOGY FOR THE SYNTHESIS OF IIPS-NF

Electrospinning is one of the best and most diverse platforms for quality NF fabrication technologies with high compatibility and low costs, such as porous, core-shell, perforated, Janus, nano-nets and sandwiched fibres or membranes. These are used for various applications, including filtration, biomedical, catalysis and adsorption [77]. Several preliminary research combined the amazing properties of imprinted polymers and NF to obtain imprinted polymer NF with outstanding qualities such as high reloading, easier target release, responsiveness to stimuli, larger surface area, increased mechanical strength and biocompatibility [34]. The application of IIPs advanced materials with electrospinning technology has far more advantages than conventional IIPs synthesis. It tends to maintain the high stability of the IIPs-NF material without any loss of nanoparticles from the fibre bed. The resulting material has a better regeneration rate without loss of binding ability and allows for more selective and efficient target extraction.

CHALLENGES AND TYPES OF IMPRINTED POLYMERS SYNTHESIS METHODS WITH ELECTROSPINNING TECHNOLOGY

Gonçalves (2020) stated that about three challenges are encountered in producing IIPs-NF with superior quality and properties. This is because it involves a combination of two advanced materials IIPs and NF electrospinning. First, removing active substances in template formation is difficult to achieve and can damage the material. Second, once the pore template has been successfully formed through the extraction process, it is presumed not to have selective properties against the target ion. However, it tends to recognize other complex targets. Third, it is assumed that the IIPs-NF material produced is similar to non-imprinted polymer. This means that its adsorption process has selectivity properties to the target ion. Its adsorption power is slightly different from that of the non-imprinted polymer materials that do not have a site template for recognizing the target ion. However, when these three hurdles are overcome, imprinted polymers NF materials will have great opportunities in intelligent applications such

as determination sensors and adsorption of target substances. In this research, several synthesis methods previously used to successfully produce IIPs-NF with electrospinning technology were also adopted.Patel, et.al. stated that the main approaches are summarized into four major categories, namely molecular imprinting during electrospinning, imprinted polymer layer formation onto electrospinning, solid phase imprinting strategies, and dispersion/conjugation imprinted polymer into/onto electrospun nanofibers. each has its advantages and disadvantages, mainly stemming from the different processing parameters that characterize imprinted polymers and electrospinning [36].

MOLECULAR IMPRINTING DURING ELECTROSPINNING

This synthesis method involves the preparation of an active substance in an electrospinning solution to produce porous fibres without mixed materials such as crosslinking and functional monomers. Afterwards, the resulting NF material was extracted with an acid solution to produce a porous one that could recognize the target ion, as shown in Fig. 3. (a). Although it looks simple, it is difficult to use this complex method to achieve the desired results due to the inherent distinctive differences between imprinted polymer ion-selective materials and electrospinning technology. In the research carried out by Sharma and Balasubramanian in [66] 8 % PAN (w/v) was synthesized with N, N-dimethyl formamide (DMF) solvent mixed with an active substance thorium nitrate and the addition of camphor soot particles. The electrospinning process was carried out afterwards with an HV parameter of 11.5 kV, and the resulting fibres were dried in a vacuum. After which, they were washed with a dilute acid solution to remove Th(VI) ions during the formation of IIPs template. The resulting IIPs-NF has good adsorption capacity and selectivity against Th (VI) radioactive elements. Some other research also reported that the preparation of a precursor solution involves the addition of 8 % by weight of PVDF/RTIL polymer in a mixture of DMF solvent and acetone in the ratio of

80:20 [38] and stirred continuously while adding an active substance of Eu (III) metal ion. This synthesis method was successfully used to fabricate the printed surface of NF with Eu^{3+} metal ions leaving voids in the PVDF/RTIL. It is used for selective sensing and recovery of Eu^{3+} ions during sewage treatment. Specifically, after the extraction or removal of the active substance Eu (III), at the end of the synthesis process, EGDMA solvent was added as a crosslinking agent to enhance the characteristics of the imprinted polymer. A similar approach was also adopted for synthesizing IIPs-NF Th (VI) using chitosan/RTIL solution NF. Chitosan amalgamation solution (3 %), PVA (8 %), thorium nitrate (0.01 wt %) and RTIL (3 wt %) were mixed in a syringe for electrospinning synthesis under a high voltage of 15 kV. The addition of PVA proves that the fibre is able to maintain extensional viscosity, then 2 % glutaraldehyde crosslinker is added to complete the IIPs-NF. This differs from previous research because IIPs-NF was extracted at the end of the process using 0.1 M solution of H_2SO_4 [70].

COMBINING SOLUTION/IMPRINTED POLYMER LAYER FORMATION ONTO ELECTROSPINNING

This method firstly focuses on synthesizing the electrospinning NF material, after which the resulting fibre is polymerized by adding a mixture of active components to form templates and functional monomers. This is further proceeded with the process of eliminating the active substance either through extraction or leaching. The weakness of this method lies in the polymerization of NF with monomers and active substances, which are difficult to achieve, including the printing of the porous types. Another method involves mixing two solutions, fibre polymer and the IIPs prepolymer, in an electrospinning syringe. Awokoya, et.al. prepared two solutions simultaneously, namely poly(ethylene terephthalate)/polyethyleneimine (PET/PEI) mixed with trifluoroacetic acid (TFA) and dichloromethane (DCM) in the ratio 2:8 (v/v). The fibre polymer solution is mixed with IIPs prepolymer, which already contains crosslinkers and active substances as templates, and then left overnight. The electrospinning process is further

fabricated under a high voltage of 15 kV. The resulting IIPs-NF were extracted from a solution of MeOH and acetic acid (90:10) to eliminate the metal ion Ni(II) from the polymer body. This method successfully created IIPs-NF with better adsorption ability than the non-printing fibre. Based on this, Awokoya concluded that IIPs-NF produced with PET/PEI is suitable for the specific removal of nickel-5,10,15,20-tetraphenyl porphine (NTPP) from fuel oil [64]. An illustration of this method is shown in Fig. 3(b).

SOLID-PHASE IMPRINTING STRATEGIES

The next method is the incorporation of NF with active substances through the exploitation of template covalent immobilization. This technique is carried out by mixing solvents and fibre polymers in the electrospinning syringe. At the same time, the active substance forming the template is immobilized in the collector, thereby triggering the spinning process. The resulting NF is polymerized directly with the active substance without cross-linking, as shown in Fig. 4. This allows increased accessibility of the binding site during application as well as the elimination of the active substances on NF. The choice of this solid-phase printing method also makes it possible to either maintain or eliminate the presence of the active substance. This technique is more developed due to its molecular applications than the ionic electrospinning imprinting process. However, this is due to the ease of combining the electrospinning method with molecules, eliminating templates and a high chance of reusing the solid phase [36]. This method successfully triggered the conjugation of PVP/silica with bovine serum albumin (BSA) or bovine haemoglobin (bHb) as the target substance protein. The resulting NF had fairly good stability with an adjustable porosity level after the solid phase removal. In accordance with the advantages above and conveniences, further development of this method potentially leads to the optimization of IIPs-NF materials in the future.

DISPERSION/CONJUGATION IMPRINTED POLYMER INTO/ONTO ELECTROSPUN NANOFIBERS

This is one of the methods commonly adopted by preliminary research for synthesizing molecular-based electrospinning (MIP) and IIPs-NF. It is more advantageous than the previous method because it combines two different materials, IIPs and NF. This technique separates the process parameters of the two material technologies, making them easily adjustable to achieve the desired final architecture with effective recognition performance. The procedure is carried out by synthesizing IIPs and NF separately, as shown in Fig. 5. Incidentally, IIPs are synthesized with a mixture of polymers such as monomers, crosslinkers, and active substances to produce nano or microparticles. On the other hand, solvents and polymers were prepared for the electrospinning process. There are two ways of combining these materials, first (Fig. 5 (a) is combining the resulting nanoparticles dispersed into a polymer solution, followed by an electrospinning process to produce fibrous IIPs-NF. The second method is shown in Fig. 5 (b), which involves the synthesis of electrospinning NF, and then the resulting ones are conjugated with IIPs nanoparticles. This technique utilizes two different advanced materials, IIPs and NF, while maintaining their respective characteristics and synthesis methods.

An example of the use of this method is cited in the research carried out by Rammika, et.al. Rammika et al. (2011), where IIPs particles obtained through precipitation and mini-emulsion polymerization approaches were suspended with 10 m dimethyl formamide (DMF) and 200 mg polysulphone (PSU), and the solution was stirred for three hours. The resulting solution is further electrospinning at a high voltage of 15 kV. The fibre obtained is stored in a desiccator to evaporate the remaining solvent. The adsorption process is carried out at the end using an HCL solution to eliminate Ni (II) metal ions [63]. Hassanzadeh et al successfully developed the most recent method of producing NF IIPs for the adsorption of Cr (VI) metal ions by preparing IIPs particles and fibres separately. First, the solid IIPs were synthesized by

free radical polymerization; the resulting particles were washed using acetone to separate the unreacted mixture from the reaction. The NaOH solution eliminates the active substance Cr (VI), thereby forming a template on the particles. On the other hand, the porous NF matrix was prepared by dissolving PAN in a solution with deploy (methyl methacrylate) (PMMA) using an electrospinning device at a voltage of 17 kV. The resulting fibre was further functionalized with the addition of hydroxylamine hydrochloride and sodium carbonate at the end of the process. The PAN functionalized fibre was conjugated with IIPs particles for 12 hours, using a mixture of deionized water and ethanol (1:3 v/v) at 70^{o}C. This method is good at producing IIPs-NF with a maximum adsorption capacity.

IMPORTANT PARAMETERS OF ELECTROSPINNING PROCESS FOR SYNTHESIS OF IIPS-NF

Some important attributes that need to be considered in electrospinning tools are the physical parameters affecting the final fibre product obtained under continuous and uniform optimal conditions. Critical variables, such as viscosity and flow rate of polymer solution, and its molecular weight, high voltage, and nozzle-to-collector distance, need to be considered before producing adsorbent fibres [78]. In the NF fabrication process, electrospinning applies a high voltage to the polymer solution at the tip of the syringe. At a certain distance between the collector and the syringe, the surface tension of the droplets from the needle breaks due to the flowing electric field, which enables the polymer to move through it to the processed collector [79]. The high electrospinning voltage affects the increased spinnability of the polymer solution. A lower voltage affects the surface tension of the smaller polymer solution droplets. The insufficient voltage causes the needle tip to drip, producing bead NF. This is affected by an increase in the flow rate due to minimal and incomplete moisture from the needle fibre jet to the collector. The required flow rate and minimum value tend to be fixed to produce uniform beadles and NF. It should be noted that increasing the flow rate and voltage reduces

the charge density, thereby causing the NF to coalesce before being deposited on the collector [80]. Table 4 shows several parameter values employed by previous research in synthesizing NF, later modified into IIPs-NF. These were also used to produce various final fibre diameters with different maximum capacity values for the adsorption target ion.

GENERAL CHARACTERIZATION INSTRUMENTATION OF IIPS-NF

In chemistry and physics, sample characterization is an in-depth research and analysis of polymer properties, including crystal particle size, surface morphology, thermal stability or instability, percentage adsorption of the functional groups, etc. However, characterization instruments that have been used in IIPs technology include scanning electron microscopy (SEM), Fourier transform Infrared spectroscopy (FT-IR), and X-ray diffractometry (XRD) [28]. Further analysis of IIPs-NF is distinguished by FAAS and TGA instrumentation. Some initially prepared samples are IIPs which have undergone an extraction process or elimination of the active substance from the pores, as shown in Fig. 6 (a). Non imprinted Polymer (NIP) (Fig. 6 (b)) is a sample synthesized with the same steps and procedures as IIPs, although without the use of template-forming active substances. These were followed by pure fibre polymer or NF, Non-Imprinted Polymers Nanofiber (NIPs-NF), and finally, the IIPs-NF, as shown in Fig.s 6 (c), (d), and (e), respectively. Many samples are based on comparing the diverse characteristics and variations stated in previous research. Each of them was tested and analyzed to determine the target ion's respective properties and selective adsorption ability.

Fourier transform Infrared spectroscopy (FTIR) is a physicochemical characterization tool used to analyze the correspondence between the wave numbers of each sample to determine the chemical bonds. Segundo et al stated that functional group or percentage transmittance are used for the success of the chemical compounds' synthesis process [81]. Hassanzadeh et al. compared the FTIR spectra of $K_2Cr_2O_7$, PANFM, FPANFM, IIPs and PANFM, which functioned as IIPs. The comparison analysis between PANFM and FPANFM

showed that PANFM functionalization occurred correctly. All samples were similar to the functional groups formed, indicating the chemical compound's successful performance. The FTIR IIPs spectrum shows the OeH vibrational band of the silanol group at a wave number of 3460 cm^{-1}. Besides, the low-intensity band at 3118 cm^{-1}, 2955 cm^{-1} and 1479 cm^{-1} is associated with the C–H, CH_3, and CeN strains (imidazole ring). The absorption band at 1728 cm^{-1} was assigned to the carbonyl group of TMSPMA. A comparison of the $K_2Cr_2O_7$ and IIPs spectra showed no $K_2Cr_2O_7$ index peak, confirming the complete extraction of the Cr (VI) anion from the IIPs structure [63].

Scanning Electron Microscopy (SEM) characterization instrumentation is essential to determine the surface morphology structure of the polymer material samples [82]. Electrospinning fibres synthesized using TFA polymers for solution concentrations of less than 18 % emitted from low-viscosity solutions split into droplets due to the lower polymer amount and density required to form a stable beam [67]. Meanwhile, beads were observed in solution concentrations between 20 and 24 % w/v. These completely disappeared, and finer and more uniform electrospun fibres were formed when the concentration was increased to 26, 28 and 30 % w/v. It is believed that the combination of a relatively high viscous solution and the solvent's dielectric constant improves the fibre's morphology. SEM analysis provides information about the estimated number of pores or templates formed after the leaching process by utilizing Matlab Poredize software or image J capabilities. Further applications are X-ray diffractometry (XRD) which confirms the crystallinity structure [83] or IIPs sample crystals after extracting and conjugating electrospun NF. It should be noted that XRD estimates the crystal size through the lattice plane of the resulting sample. This is attributed to the semi-crystalline nature of NF [66].

FURTHER RESEARCH ON MATERIAL ADSORPTION

KINETIC STUDY

The kinetic analysis of the adsorption process aims to determine the type of physical or chemical reaction and the number of target ions adsorbed by the IIPs adsorbent, which was adjusted to the varying adsorption time. Quasi-first-order (Equation (1)) and quasi-second-order (Equation (2)) kinetic models were used for fitting to investigate the mechanism of the adsorption rate. Meanwhile, assuming the results are consistent with the first-order quasi-kinetic model, it indicates that the adsorption process is mainly physical. When it is in line with the quasi-second-order kinetics model, this implies the occurrence of chemical reactions in the adsorption process.

$$\log(q_e - q_t) = \log q_e - \left(\frac{kl}{2.303}\right) t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{1}{q_e} \quad (2)$$

In the equation di or QE (mgg^{-1}) is the equilibrium adsorption capacity, qt adsorption capacity at time t (mg/g), Qm (mgg^{-1}) theoretical saturation adsorption capacity, t (min) adsorption time, k1 (min^{-1}) is a quasi-first-order kinetic rate constant, and k_2 ($g(mg\ min)^{-1}$) a quasi-second-order kinetic rate constant [84]. Based on the reviews of several research on IIPs-NF, the sorbent tends to fulfil the installation of a second-order pseudo model. This indicates that the IIPs material tends to undergo a chemical adsorption process. The Hg-PBCS sorbent developed by Hajri, et.al. was more effective than the use of Hg (II) ions as an adsorption target compared to the control unprinted sorbent (NI-PBCS) with a maximum capacity of 315 mgg^{-1} that correlated with relatively fast adsorption kinetics, namely the Pseudo-second order (PSO) model [85].

ISOTHERM STUDY

The basic physiochemical characteristics related to the adsorption of ions and imprinted polymer molecules was investigated through the research of adsorption isotherms. Operational design and modelling analysis of metal ion concentration in solution as a function of

temperature for an adsorptive system was investigated by mathematical correlation and graphical depiction [70]. Furthermore, adsorption isotherm is a graphic notation used to determine the amount of adsorbate on the surface of the adsorbent under pressure at constant temperature [24]. It determines the capacity and degree of adsorption, which is stronger or weaker. The adsorption mechanism is described based on thermodynamic assumptions of physicochemical parameters. In accordance with several research, the adsorption data tends to be modelled using differential equations, including the pseudo-second-order rate, the Langmuir, Freundlich, Temkin, and Dubinin – Radushkevich isotherm and three-parameter models, such as the Redlich – Peterson and Sips isotherms using the trial-and-run error method (R). The metal ion uptake IIPS and MIP usually correlate with the Langmuir or Freundlich equations. Langmuir's equation applies to the absorption process on a homogeneous surface. However, Freundlich's equation is valid for adsorption on heterogeneous surfaces. Previous research showed that the Langmuir and Freundlich equations represent different adsorption of heavy metal ions to IIPS and MIP. In most cases, one model best describes the adsorption process [3,70,86]. Table 5 shows the development of adsorption study with eletrospun nanofiber.

THERMODYNAMIC STUDY

It is important to study the thermodynamics of adsorption to monitor the energetic changes during the entire process. Determining the free energies of enthalpy, entropy, and Gibbs is a key to understanding the amount of heat absorbed or released, the energy provided by the system and the randomness at the solid-liquid interface when absorption occurs. Investigating temperature changes in adsorption helps determine whether the process is endothermic or exothermic, spontaneous or non-spontaneous [87]. Considering the reviews on studying the thermodynamics of various organic substances adsorption onto various nano-

adsorbents, its parameters were determined from the Gibbs equation. The Gibbs free energy depends on the equilibrium constant in equation (3) is stated as follows:

$$\Delta G° = -RT \ln K_c \quad (3)$$

The relationship between Entropy and Enthalpy is stated in equation (4)

$$\ln K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (4)$$

Where K_C is the equilibrium constant and $K_C = \frac{q_e}{C_e}$, q_e is the adsorption capacity at equilibrium (mg / L), C_e is the equilibrium concentration (mg / L), T T is the temperature, R is the universal gas, $\Delta H°$ and $\Delta S°$ are standard enthalpy and entropy, respectively. They were also determined from the slope and intercept of the ln Kc versus 1/T plots resulting from the adsorption examination process at different temperatures. Positive enthalpy indicates the endothermic nature of the reaction process, while positive Gibbs free energy refers to the non-spontaneous procedure. All completed adsorption process is categorized into physisorption and chemisorption depending on the Gibbs free energy. The nature of the physisorption process is for $-20kJ/mol < \Delta G < 0$, and the chemisorption is for $-800\ kJ/mol < \Delta G < -40\ kJ/mol$. The value of enthalpy (ΔH), entropy (ΔS) and Gibbs energy (ΔG) is used to predict the adsorption properties [86].

CONCLUSIONS

The presence of harmful heavy metal ions, such as mercury (II), copper (II), lead (II), chromium (III), cadmium, zinc, arsenic (As), silver (Ag), chromium (Cr), iron (Fe) and platinum (Pt), is of enormous concern to chemists and physicists in terms of overcoming its negative effects on the environment and human health. One of the advanced materials developed rapidly is NF material with electrospinning technology. It has excellent properties and characteristics such as mass transfer and good adsorption capacity. To increase the selectivity and sensitivity of NF to metal ions, it is modified with porous materials in the form

of IIPs. IIPs have pores of which the chemical properties and characteristics resemble metal targets due to the leaching process carried out after extraction. This enables the target metal ions to fill every material pore during the adsorption experiment.

Some of the challenges faced in the process of modifying NF and IIPs is the difficulty involved in eliminating active substances in the formation of templates which have the potential to reduce the adsorption ability of the material. This is overcome by adopting several major approaches to the synthesis process using electrospinning technology, such as Molecular Imprinting during Electrospinning, Imprinted polymer Layer Formation onto Electrospinning, Solid-Phase Imprinting Strategies, and Dispersion/Conjugation imprinted polymer into/onto Electrospun Nanofibers. Each method has its advantages and disadvantages, mainly stemming from the different processing parameters that characterize imprinted polymers and electrospinning.

The dispersion or conjugation method is easier to perform. It simply involves the combination of two different materials, IIPs and NF, to achieve the desired final architecture with efficient recognition performance. This method is carried out by synthesizing IIPs and NF separately and conjugating them in the final process. The combination of NF using electrospinning technology with IIPs porous materials maintains high stability values, reloading, responsiveness, large surface area and good adsorption capacity, as well as increased mechanical strength and biocompatibility. Therefore, this material has great potential and needs to be further developed. It commercializes new products for removing heavy metals from water. This research serves as reference material for future analyses in designing and developing IIPs-NF.

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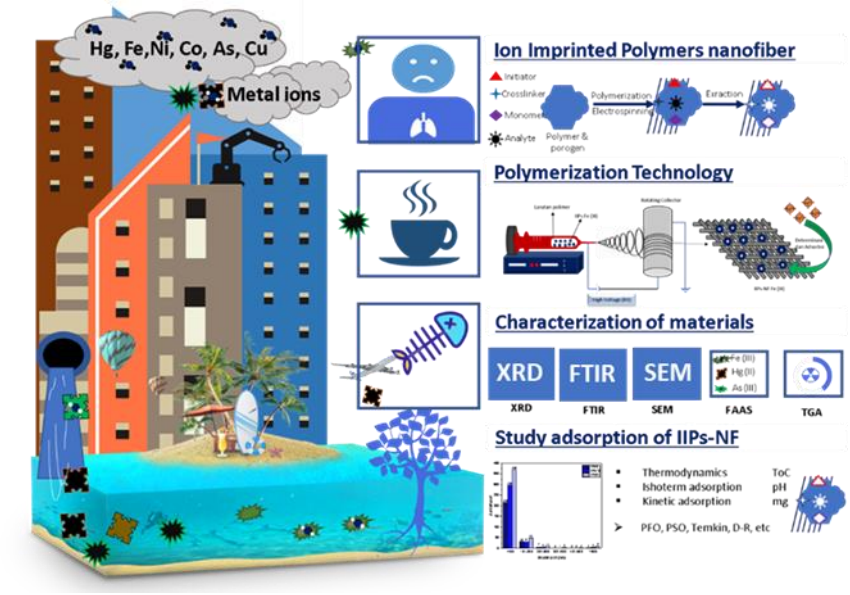

Fig. 1. Mini illustration review of the presence of harmful metal ions in the environment and the adsorption role of advanced IIPs-NF materials

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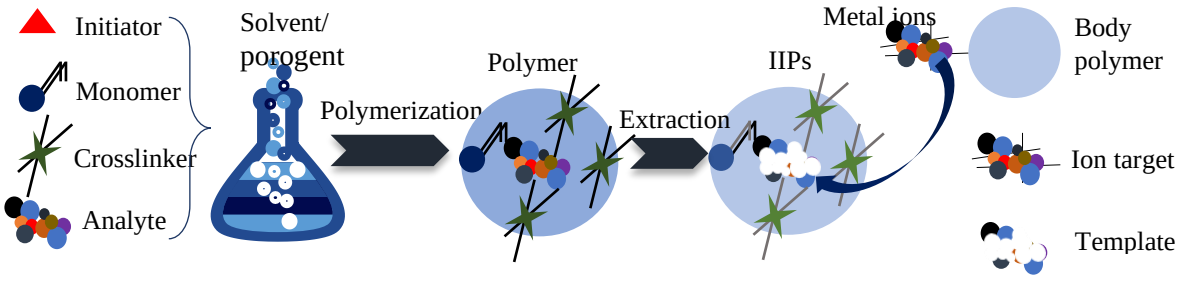

Fig. 2. Schematic synthesis and site recognition of IIPs against metal ion targets in determination applications and adsorption materials

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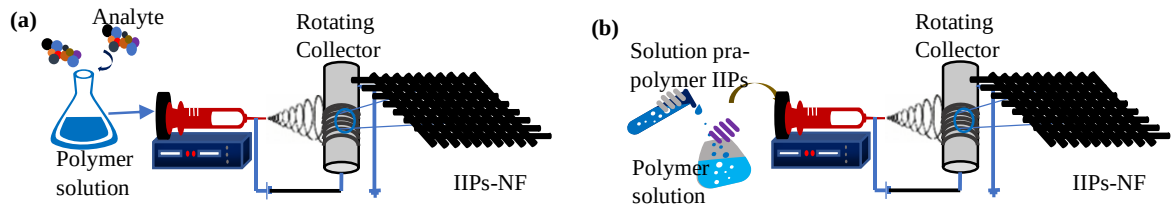

Fig. 3. Illustration of IIPs-NF synthesis method using electrospinning technology (a). Molecular imprinting during electrospinning, (b). Imprinted polymer Layer Formation onto Electrospinning

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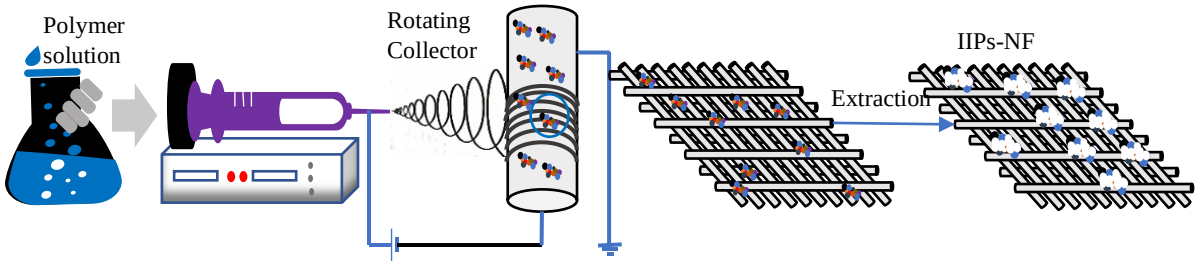

Fig. 4. Illustration of Methods solid-phase imprinting strategies for electrospinning IIPs-NF

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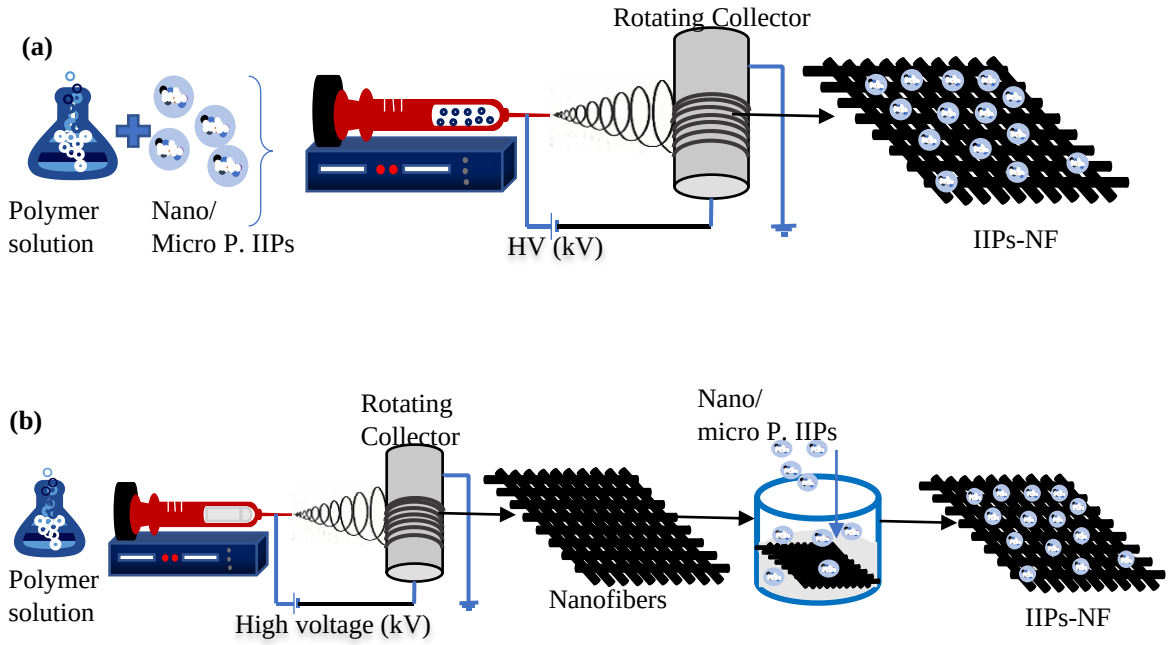

Fig. 5. The main approach of electrospinning technology in producing imprinted polymers NF (a). A polymer solution of NF dispersed with nano/microparticles of IIPs, or (b). Electrospinning NF are conjugated with micro/nanoparticles through chemical reactions

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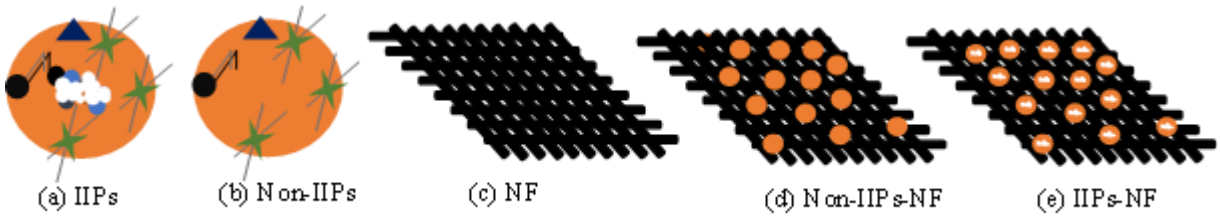

Fig. 6. Illustration of different samples (a) IIPs, (b) Non-IIPs, (c) NF, (d) Non-IIPs-NF, and (e) IIPs-NF

Table 1. The role and function of IIPs.

Material components	Characteristics, roles, and functions	Ref.
Analyte	Chemically inert, large in number, dissolved during the printing process. It has high stability and chemically bonds with monomers. The active substance is a target ion recognition site in metal determination and absorption applications.	[24]
Monomer of functional	Interacts in solutions with active substances to develop complex or functional networks of hydrogen bonds and reactive substituents that either reacts covalently or noncovalently.	[25]
Crosslinker	Plays a role in the formation of bond chains and polymer features. The main function of the crosslinker is to produce a stable polymer matrix consisting of recognition sites for the analyte.	[26]
Initiator	The initiator is used in lesser quantity than the active substance through the mole ratio of the substance that acts as a radiation source in free radical polymerization	[27]
Solvent	Needs to be able to dissolve the entire mixture of polymerization components which contribute to the expansion of polymer features as well as plays a relevant role in the formation of porous material	[28]

Table 2. Review of the main components of IIPs.

Analyte	Monomer	Crosslinker	Initiator	Solvent	Ref.
Fe (III)	Methacrylic Acid	EGDMA	AIBN	Acetonitrile and ethanol	[46]
	Methacrylic Acid	Divinyl Benzene	AIBN	HCL and distilled water	[44]
	BMAOP	EGDMA	AIBN	Acetonitrile	[47]
Pb (II)	Methacrylic Acid	EGDMA	AIBN	Dimethyl formamide	[48]
	Hydroxyethyl methacrylate	Glutaraldehyde	NaHSO3	Distilled water	[30]
	Vinyl pyridine	EGDMA	AIBN	Methanol	[49]
Ni (II)	BDAAT	EGDMA	AIBN	Acrylamide	[45]
	Methacryloyl-L-histidine	Methylene-bis (acrylamide)	Ammonium persulfate	Deionized water	[50]
	Hydroxyphenyl acrylamide	EGDMA	AIBN	CHCl3	[51]
	Methacrylic acid	EGDMA	AIBN	Methanol	[52]
Hg (II)	Vinylanilline	EGDMA	Ammonium persulfate	Glacial acetic acid	[53]
	Methacrylic acid	EGDMA	AIBN	Acrylonitrile	[54]
Co (II)	Dithizone & MAA	Dimethacrylate & EGDMA	AIBN	HCL and CH_3COOH	[55]

Cd (II)	Mercaptopropyl trimethoxysilane	Epichlorohydrin	-	HCL and Ethanol	[31]
Cr (VI)	Vinyl pyridine	EGDMA	ACCN	Methanol and DMF	[32]
	Vinylbenzyltri-methylammonium	EGDMA	-	Dichromic acid	[56]
Au (III)	Polyeugenol	EGDMA	AIBN	HCl, Methanol	[57]
Pd (II)	Aminopropyl triethoxysilane isatin	Silica	AIBN	Anhydrousethyl alcohol	[58]
Eu (III)	Allyl acetoacetate	EGDMA	AIBN	Trifluoroacetic acid	[59]
Ru (III)	Acrylamide	-	TEMED	Ethyl acetate	[60]
As (III)	Methacrylic acid	EGDMA	AIBN	Methanol	[61]
Cu (III)	Methacrylic acid and vinyl pyridine	Pentaerythritol triacrylate	Benzoyl peroxide	Methanol	[43]
Rb (I)	Methacrylic	EGDMA	AIBN	Methanol	[62]

Ethylene glycol dimethacrylate (EGDMA); 1,1`-azobis (cyclohexanecarbonitrile) (ACCN); -Tetramethyle thylenediamine (TEMED); S,S'-bis(α,α'-dimethyl-α''-acetic acid) trithiocarbonate (BDAAT) and 2,2'- azobisisobutyronitrile (AIBN).

Table 3. Further review of the preparation of the main ingredients during the IIPs synthesis process using the electrospinning technique.

Analyte	Polymer	Function Monomer	Cross-linker	Initiator	Solvent	Ref
$NiSO_4.6H_2O$ for Ni (II)	DMF and polysulphone	Vinylpyridine	Divinyl benzene	AIBN	Nitric acid, hydrochloric acid	[63]
Nickeltetraphenylporphine	Polyethyleneimine	Styrene	Divinyl benzene	ACC	Trifluoroacetic acid and acetic acid	[64]
Cadmium chloride for Cd (II)	Chitosan	Dichloromethane	Glutaraldehyde		Hydrochloric acid	[65]
Thorium nitrate for Th (IV)	Polyacrylonitrile (PAN)	Camphor			Dimethyl formamide	[66]
Nickel-tetraphenylporphyrin	polyethyleneimine	Styrene	Divinyl benzene	ACC	Trifluoroacetic acid and acetic acid	[67]
lead chloride for Pb (II)	Chitosan	Dichloromethane	Glutaraldehyde		Hydrochloric acid	[68]

chromium (III) chloride for Cr (VI)	Polyacrylonitrile (PAN)	poly (methyl methacrylate)	EGDMA	AIBN	Hydrochloride and dimethylformamide	[69]
Thorium nitrate for Tr (IV)	Chitosan and PVA	-	Glutaraldehyde	BMIMBF4-	Hydrochloric acid and acetic acid	[70]
Europium nitrate for Eu (II)	Polyvinylidene fluoride	Ionic liquid (RTIL)	EGDMA	-	DMF and acetone	[38]
cerium nitrate hexahydrate for Gd (III)	Chitosan	Glacial acetic acid	Glutaraldehyde	-	Ethanol	[71]

1,1-azobis(cyclohexanecarbonitrile) (ACC); 1-butyl-3- methylimidazolium tetrafluoroborate (BMIMBF4-))

Table 4. Further research on the parameters of using electrospinning equipment in synthesizing IIPs-NF.

Materials	IIPs: Polymer	Methode	Parameters of elecrospun				Diameters (nm)	Ref.
			Flowrate (vol/time)	V (kV)	T (h)	D (cm)		
Ni (II)-DMG IIP	1:1 wt %	Bulk polymerization	2 μg·mℓ$^{-1}$	15	6	12	406-854	[63]

NTPP-imprinted composite nanofibers	3:1 wv %	MIP electrospun	20 mL min^{-1}	15	-	13	5.33-9.21	[64]
Nanofiber electrospun Cd (II)	4:0.8 wv %	Imprinted electrospinning	0.6 mL h^{-1}	19	24	9.5	76.1-161.9	[65]
ion imprinted PAN– CS nanofiber	8:8 wv %	Functionalized electrospinning	1 μL min^{-1}	11.5	20	8	~70	[66]
NVMIN For Nickel	14 – 30 % w/v	MIT electrospun	-	15	5	13	-	[67]
Chitosan NF MIP	2.4:0.5 wv %	one-step electrospinning imprinted	-	20	24	10	90.3-220	[68]
IIP-functionalized-PANFM	1:3 vv	Imprinted electrospinning	0.7 mL h^{-1}	17	12	15	143–181	[69]
Imprinted chitosan/RTIL nanofiber	3:0.01 wt	Imprinted electrospinning	0.5 mL h^{-1}	15	-	15	40	[70]
ion imprinted PVDF/RTIL	0.01–0.1 wt %	Imprinted electrospinning	0.8 μL min-1	13	1	15	250-700	[38]

Table 5. Review table of metal ion adsorption analysis results based on IIPs-NF.

Adsorbent	Ion metal	Q (mgg^{-1})	Optimal Conditions			Kinetic model	Iso-therm	Reg (time)	Ref.
			m (mg)	t (min)	PH				
Ni(II)-DMG IIP	Ni (II)	-	15	210 s	6	-	-	-	[63]
NTPP-imprinted composite NF		17.54	30	-	7	-	-	11	[64]
NF electrospun	Cd (II)	346.3	-	1440	6	PSO	LF	3	[65]
ion imprinted PAN– CS NF	Th (IV)	455.5	50	120	7	PSO and D-R	F	4	[66]
Chitosan NF MIP	Pb (II)	110.2	-	150	7	PSO	L	3	[68]
IIP-functionalized-PANFM	Cr (VI)	398	100	12	7	PSO	T	3	[69]
Imprinted chitosan/RTIL NF	Th (IV)	325	-	120	7	PSO	L	7	[70]
ion imprinted PVDF/RTIL	Eu (III)	22.37	-	180	7	PSO	F	5	[38]

L: Lang Freundlichmuir model, F: Freundlich, T: Temkin, PSO: pseusosecond-order model, D-R: Dubinin–Radushkevich

REVIEW OF ION IMPRINTED POLYMERS NANOFIBER WITH TECHNOLOGY ELECTROSPINNING: AN ADVANCE MATERIALS FOR REMOVAL OF HEAVY METAL IONS

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ABSTRACT

The existence of essential heavy metal ions that pollute the environment has become a substantial concern for countries worldwide due to their ability to damage ecosystems and harm living things. Therefore, research in the field of materials science to eliminate the presence of heavy metal ions that pollute the environment, such as Fe (III), Pb (II), Ni (II), Hg (II), Cd (II), Cr (VI), Ru (III), and As (III) need to be developed. Ion Imprinted polymers nanofiber (IIPs-NF) is one of the advanced materials with the ability to determine and remove heavy metal ions containing a high degree of selectivity and stability. The use of conjugate electrospinning technology in producing nanofiber (NF) can expand the surface of the material and the recognition sites for target ion elements. This research is a literature review of scientific articles on the development of ion imprinted polymers (IIPs) intelligent NF materials that utilize electrospinning technology. It discusses initial research in the preparation of IIPs samples, the principles of the synthesis method, the characterization analysis that needs to be conducted and the adsorption research of the IIPs-NF adsorption applications. The results showed that modification of the IIPs material with electrospun conjugation can increase the adsorption capacity and have several advantages such as high stability, biocompatibility and a better regeneration. Therefore, this material has great potential to become an advanced device that plays a role in overcoming harmful metal ions.

Keywords: adsorption, nanofibers, electrospinning, heavy metals, ion imprinted polymers.

INTRODUCTION

The existence of essential metal ions that pollute the environment, such as water, soil sediment, food and biological matrices, is a substantial concern for analytical physicists and environmental chemists globally [1, 2]. Ihsanullah et al. stated that these are usually released from modern industries such as battery factories, mining, metal plating, and pesticide facilities [3]. Some metals, such as mercury (II), copper (II), lead (II) and chromium (III), cadmium (Cd), zinc (Zn), arsenic (As), silver (Ag), chromium (Cr), iron (Fe), and platinum (Pt), are dangerous and tend to damage the ecosystems [4 - 7].

Several preliminary research succeeded in reducing the presence of hazardous metals using some sophisticated physics analytical instrumentation such as flame atomic absorption spectroscopy (FAAS) [8], atomic fluorescence spectroscopy (AFS) [9], inductively coupled plasma - optical emission spectrometry (ICP-OES), inductively coupled plasma - mass spectrometry (ICP-MS) [10] and graphite furnace atomic absorption (GFAAS) [11]. However, some of these techniques have specific weaknesses, for example, lengthy processing time, high operational costs and a reasonably complicated instrumentation system. [2]. Some other research further stated that analytical instrumentation techniques have a

low level of selectivity and cannot specifically identify the target ion element [12]. Some research successfully developed a simple and energy-efficient synthesized adsorption materials with fast optimization time to overcome this problem. According to Huang et al., these are also used for water purification by separating the metal ions. These materials include aluminium oxide nanopowder [13], carbon nanotube filters [14], hydroxide and jarosite [15], chitosan film [16], chelation resin [17], and silica [18]. Generally, these are used to remove metal ions from environmental water samples. The main limitation of this research is the ability of these materials to be less selective with a lower detection limit [19, 20]. Recent research developments proved that its sensitivity and selectivity, including electrochemical sensors, have been successfully synthesized to detect and eliminate the presence of metal ions, such as imprinted polymer (IIPs) materials [21 - 23].

Ion imprinted polymers (IIPs) are some type of hollow material with several advantages, such as a simple synthesis method using the comprehensive application and high stability and selectivity values for targets due to the memory effect generated after the printing process [24]. According to Fu et al. in [29], IIPs are good adsorbents and effective in identifying, monitoring and removing metal ions in aqueous and biological environments. A recent research stated that imprinted polymer ions were successfully synthesized and applied to detect and eliminate some metal ions such as mercury, arsenic [27], lead [30], cadmium [31], chromium [32] and nickel [33]. However, some of these research only focused on conventional synthesis processes, which are considered to have specific weaknesses, including slow mass transfer rates and low adsorption capacity [34]. Recent research successfully combined modified IIPs with electrospinning techniques to obtain advanced ion imprinted polymers nanofiber (IIPs-NF) materials. Háková et al. in [35] reported that electrospinning techniques produce fibre imprinted polymers while maintaining high stability, reloading, mechanical strength, biocompatibility, responsiveness, larger surface area and better adsorption capacity [34, 36, 37]. The use tends to improve the ability of IIPs to absorb and eliminate metal ions [38].

This mini-review focuses on developing IIPs-NF using electrospinning technology compiled based on a systematic and in-depth literature review. Its contents are illustrated in Fig. 1. Several important points were conveyed as the basic preparatory concepts of IIPs materials, development of the fabricated methods using electrospinning tools, and general knowledge regarding its physical characterization. Incidentally, it is necessary to investigate the application of IIPs-NF for the adsorption of hazardous metals in water and

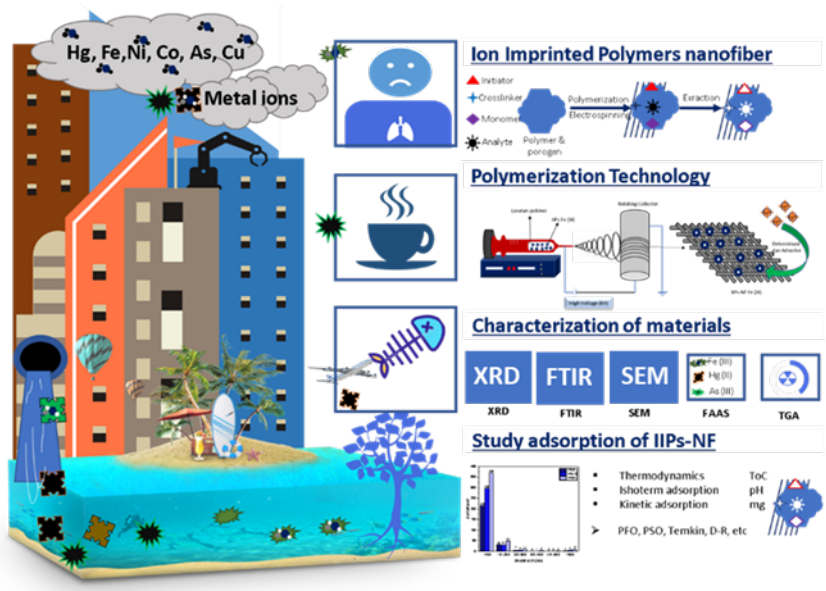

Fig. 1. Mini illustration review of the presence of harmful metal ions in the environment and the adsorption role of advanced IIPs-NF materials.

the environment. It is expected that this mini-review provides relevant information about preliminary research and attracts global attention in developing IIPs-NF materials that can potentially eliminate harmful metal ions.

MATERIAL SELECTIVE IIPS-NF

Polymers produced with moulding technology are applied to thousands of molecules, including biological structures such as metal ions, hormones, proteins and cells. The ion imprinted ones are used to produce materials that can recognize metal ion structures. Meanwhile, when the active substances are removed, certain voids or moulds are formed, which are highly selective and adsorptive [26, 39] IIPs are a multifunctional application of printed materials for selective extraction, separation, and detection of metal ions in environmental media such as water, wastewater, soil, and food samples. Generally, IIPs focus on targeting non-biodegradable heavy metal cations in aquatic habitats, soil and food, such as iron (III), copper (II), cobalt (II), nickel (II), cadmium (II), mercury (II), and lead (II) from industrial manufacturing processes, mineral mining and waste products [6].

Imprinted ion technology is a promising technique in the science of separation and purification of metal ions due to its high selectivity, good stability, simplicity, and low cost [22, 40] The synthesis process of the IIPs powder sample was prepared through a mass polymerization procedure involving a mixture of monomers, initiators, crosslinkers, and templates. The resulting polymer mass is ground and sieved to obtain particles of suitable size for various analytical applications [41]. The roles and properties of these mixtures that must be met in the preparation of IIPs are shown in Table 1. Some research occasionally involved complex ligands in the polymer matrix. This generally involves trapping technique because certain metals such as Hg (II) and MeHg (II) require ligands to help interact with monomers [27]. Its addition based on the IIPs template tends to interact with several electron-donating heterometals in the recognition process. Ligands play a crucial role in chemical immobilization, do not require a vinyl group, and are represented by monomers. Some examples are 4-VP, 1-vinyl imidazole, acrylamide, and acrylic acid [42].

Fig. 2 shows a schematic representation of the metal ion recognition site using IIPs, and polymeric materials produced after polymerization in the form of a mixture of monomers, active substances, initiators, and crosslinkers chemically bonded to each other in a solvent. The solid material is subjected to either extraction or leaching to eliminate the active substance from the polymer body.

Table 1. The role and function of IIPs.

Material components	Characteristics, roles, and functions	Ref.
Analyte	Chemically inert, large in number, dissolved during the printing process. It has high stability and chemically bonds with monomers. The active substance is a target ion recognition site in metal determination and absorption applications.	[24]
Monomer of functional	Interacts in solutions with active substances to develop complex or functional networks of hydrogen bonds and reactive substituents that either reacts covalently or noncovalently.	[25]
Crosslinker	Plays a role in the formation of bond chains and polymer features. The main function of the crosslinker is to produce a stable polymer matrix consisting of recognition sites for the analyte.	[26]
Initiator	The initiator is used in lesser quantity than the active substance through the mole ratio of the substance that acts as a radiation source in free radical polymerization	[27]
Solvent	Needs to be able to dissolve the entire mixture of polymerization components which contribute to the expansion of polymer features as well as plays a relevant role in the formation of porous material	[28]

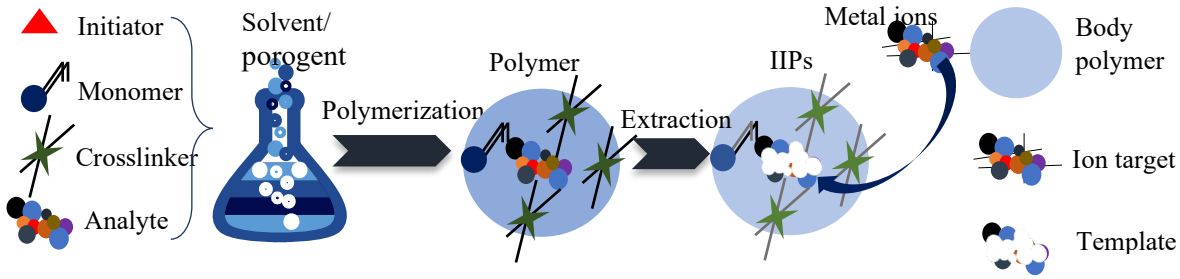

Fig. 2. Schematic synthesis and site recognition of IIPs against metal ion targets in determination applications and adsorption materials.

This leaves a cavity or template with a similar shape and characteristics to the analyte. In addition, the template in the polymer body serves as a recognition site for the desired or targeted metal ion in the determination and adsorption applications. Table 2 shows some examples of active ingredients, monomers, crosslinkers, initiators and porogrnous solvents used in synthesizing IIPs. The selection is aimed at eliminating the target. In recent years, metal ions based on nitrate chemicals have been successfully used as template-forming active substances in synthesizing IIPs. Functional monomers play an essential role in the site recognition process.Chaipuang et al. researched using two functional monomers of IIPs, namely methacrylic acid and vinyl pyridine to eliminate Cu (III) metal ions. It was further reported that methacrylate acid showed higher specificity for template ions, formed hydrogen bonds with ligand complexes and was more associated with crosslinkers than the vinyl pyridine used as a monomer [43].

The use of sporogenous IIPs solvents is extensive, as shown in Table 2. These are divided into three types, namely non-polar and polar aprotic solvents, including alcohol. However, alcoholic solvents such as methanol or ethanol are often used to synthesize IIPs [42]. The polymer extraction process generally involves using an acidic solvent with a lesser pH value, such as HCL [31, 44]. A common initiator that is frequently used is 2,2-azobisisobutyronitrile (AIBN). Liu et al. stated that increasing the content of the initiator until it reaches an optimum condition triggers a higher concentration of the active centre, thereby accelerating the polymerization rate [45]. This affects the molecular mass of the polymer as well as increases the adsorption capacity. Benzoyl peroxide (BPO) initiator is also used to trigger the radical polymerization process in synthesizing IIPs [6].

Further analysis of IIPs using the electrospinning technique involves the addition of a polymer solvent for NF fabrication, as shown in Table 3. This tends to determine the successful synthesis of IIPs-NF and, to a larger extent, polyacrylonitrile (PAN) polymers, which have been widely utilized in the synthesis of both molecular and IIPs-NF[66, 69, 72]. PAN has relatively high Tg properties, low thermal plasticity, and a high crystal melting point (317°C). It also has limited solubility in certain solvents with superior mechanical properties due to the intermolecular forces between polymer chains [73, 74]. Crosslinker materials are essential in sample preparation in producing IPs with good adsorption capacity. Hu et al. stated that the adsorption capacity of IIPs in metal Chromium (VI) increased with the addition of EGDMA as a crosslinker in the ratio of monomer to its composition (1/4; 1/6; and 1/8) [56]. This is in line with the research by Li et al. in [68] that the chemical composition of glutaraldehyde as a IIPs-NF crosslinker impacts the stability of lead (II) ion adsorption. Variations in its composition from 0 to 6.7 v/v % showed a higher increase in adsorption. This is because an increase in composition triggers the crosslinking of the chitosan NF, thereby causing it to have a higher level of stability. Moreover, this tends to result in an ideal adsorption capacity of the material. It should be noted that the addition of a crosslinker has an optimum limit because it increases the hydrophobic character and reduces excessive free amino ions, thereby causing the material to experience a decrease in the adsorption capacity [24, 75, 76].

ELECTROSPINNING TECHNOLOGY FOR THE SYNTHESIS OF IIPS-NF

Electrospinning is one of the best and most diverse platforms for quality NF fabrication technologies with

Table 2. Review of the main components of IIPs.

Analyte	Monomer	Crosslinker	Initiator	Solvent	Ref.
Fe (III)	Methacrylic Acid	EGDMA	AIBN	Acetonitrile and ethanol	[46]
	Methacrylic Acid	Divinyl Benzene	AIBN	HCL and distilled water	[44]
	BMAOP	EGDMA	AIBN	Acetonitrile	[47]
Pb (II)	Methacrylic Acid	EGDMA	AIBN	Dimethyl formamide	[48]
	Hydroxyethyl methacrylate	Glutaraldehyde	NaHSO3	Distilled water	[30]
	Vinyl pyridine	EGDMA	AIBN	Methanol	[49]
Ni (II)	BDAAT	EGDMA	AIBN	Acrylamide	[45]
	Methacryloyl-L- histidine	Methylene-bis (acrylamide)	Ammonium persulfate	Deionized water	[50]
	Hydroxyphenyl acrylamide	EGDMA	AIBN	CHCl3	[51]
	Methacrylic acid	EGDMA	AIBN	Methanol	[52]
Hg (II)	Vinylanilline	EGDMA	Ammonium persulfate	Glacial acetic acid	[53]
	Methacrylic acid	EGDMA	AIBN	Acrylonitrile	[54]
Co (II)	Dithizone & MAA	Dimethacrylate & EGDMA	AIBN	HCL and CH_3COOH	[55]
Cd (II)	Mercaptopropyl trimethoxysilane	Epichlorohydrin	-	HCL and Ethanol	[31]
Cr (VI)	Vinyl pyridine	EGDMA	ACCN	Methanol and DMF	[32]
	Vinylbenzyltri-methylammonium	EGDMA	-	Dichromic acid	[56]
Au (III)	Polyeugenol	EGDMA	AIBN	HCl, Methanol	[57]
Pd (II)	Aminopropyl triethoxysilane isatin	Silica	AIBN	Anhydrousethyl alcohol	[58]
Eu (III)	Allyl acetoacetate	EGDMA	AIBN	Trifluoroacetic acid	[59]
Ru (III)	Acrylamide	-	TEMED	Ethyl acetate	[60]
As (III)	Methacrylic acid	EGDMA	AIBN	Methanol	[61]
Cu (III)	Methacrylic acid and vinyl pyridine	Pentaerythritol triacrylate	Benzoyl peroxide	Methanol	[43]
Rb (I)	Methacrylic	EGDMA	AIBN	Methanol	[62]

Ethylene glycol dimethacrylate (EGDMA); 1,1`-azobis (cyclohexanecarbonitrile) (ACCN); -Tetramethyle thylenediamine (TEMED); S,S'-bis(α,α'-dimethyl-α''-acetic acid) trithiocarbonate (BDAAT) and 2,2'- azobisisobutyronitrile (AIBN).

high compatibility and low costs, such as porous, core-shell, perforated, Janus, nano-nets and sandwiched fibers or membranes. These are used for various applications, including filtration, biomedical, catalysis and adsorption [77]. Several preliminary researches combined the amazing properties of imprinted polymers and NF to obtain imprinted polymer NF with outstanding qualities such as high reloading, easier target release, responsiveness to stimuli, larger surface area, increased mechanical strength and biocompatibility [34]. The application of IIPs advanced materials with electrospinning technology has far more advantages than conventional IIPs synthesis. It tends to maintain the high stability of the IIPs-NF material without any loss of nanoparticles from the fibre bed. The resulting material has a better regeneration rate without loss of binding ability and allows for more selective and efficient target extraction.

Table 3. Further review of the preparation of the main ingredients during the IIPs synthesis process using the electrospinning technique.

Analyte	Polymer	Function Monomer	Cross-linker	Initiator	Solvent	Ref
$NiSO_4.6H_2O$ for Ni (II)	DMF and polysulphone	Vinylpyridine	Divinyl enzene	AIBN	Nitric acid, hydrochloric acid	[63]
Nickeltetraphenylporphine	Polyethylenimine	Styrene	Divinyl benzene	ACC	Trifluoroacetic acid and acetic acid	[64]
Cadmium chloride for Cd (II)	Chitosan	Dichloromethane	Glutaraldehyde		Hydrochloric acid	[65]
Thorium nitrate for Th (IV)	Polyacrylonitrile (PAN)	Camphor			Dimethyl formamide	[66]
Nickel-tetraphenylporphyrin	polyethylenimine	Styrene	Divinyl benzene	ACC	Trifluoroacetic acid and acetic acid	[67]
lead chloride for Pb (II)	Chitosan	Dichloromethane	Glutaraldehyde		Hydrochloric acid	[68]
chromium (III) chloride for Cr (VI)	Polyacrylonitrile (PAN)	poly (methyl methacrylate)	EGDMA	AIBN	Hydrochloride and dimethylformamide	[69]
Thorium nitrate for Tr (IV)	Chitosan and PVA	-	Glutaraldehyde	BMIMBF4-	Hydrochloric acid and acetic acid	[70]
Europium nitrate for Eu (II)	Polyvinylidene fluoride	Ionic liquid (RTIL)	EGDMA	-	DMF and acetone	[38]
cerium nitrate hexahydrate for Gd (III)	Chitosan	Glacial acetic acid	Glutaraldehyde	-	Ethanol	[71]

1,1-azobis(cyclohexanecarbonitrile) (ACC); 1-butyl-3- methylimidazolium tetrafluoroborate (BMIMBF4-))

CHALLENGES AND TYPES OF IMPRINTED POLYMERS SYNTHESIS METHODS WITH ELECTROSPINNING TECHNOLOGY

Gonçalves stated that about three challenges are encountered in producing IIPs-NF with superior quality and properties [37]. This is because it involves a combination of two advanced materials IIPs and NF electrospinning. First, removing active substances in template formation is difficult to achieve and can damage the material. Second, once the pore template has been successfully formed through the extraction process, it is presumed not to have selective properties against the target ion. However, it tends to recognize other complex targets. Third, it is assumed that the IIPs-NF material produced is similar to non-imprinted polymer. This means that its adsorption process has selectivity properties to the target ion. Its adsorption power is slightly different from that of the non-imprinted polymer materials that do not have a site template for recognizing the target ion. However, when these three hurdles are overcome, imprinted polymers NF materials will have great opportunities in intelligent applications such as determination sensors and adsorption of target substances. In this research, several synthesis methods previously used to successfully produce IIPs-NF with electrospinning technology were also adopted. Patel et al. stated that the main approaches are summarized into four major categories, namely molecular imprinting during electrospinning, imprinted polymer layer formation onto electrospinning, solid phase imprinting strategies, and dispersion/conjugation imprinted polymer into/onto electrospun nanofibers. each has its advantages and disadvantages, mainly stemming from the different processing parameters that characterize imprinted polymers and electrospinning [36].

MOLECULAR IMPRINTING DURING ELECTROSPINNING

This synthesis method involves the preparation of an active substance in an electrospinning solution to produce porous fibres without mixed materials such as crosslinking and functional monomers. Afterwards, the resulting NF material was extracted with an acid solution to produce a porous one that could recognize the target ion, as shown in Fig. 3(a). Although it looks simple, it is difficult to use this complex method to achieve the desired results due to the inherent distinctive differences between imprinted polymer ion-selective materials and electrospinning technology. In the research carried out by Sharma and Balasubramanian in [66] 8 % PAN (w/v) was synthesized with N,N-dimethyl formamide (DMF) solvent mixed with an active substance thorium nitrate and the addition of camphor soot particles. The electrospinning process was carried out afterwards with an HV parameter of 11.5 kV, and the resulting fibres were dried in a vacuum. After which, they were washed with a dilute acid solution to remove Th(VI) ions during the formation of IIPs template. The resulting IIPs-NF has good adsorption capacity and selectivity against Th (VI) radioactive elements. Some other research also reported that the preparation of a precursor solution involves the addition of 8 % by weight of PVDF/RTIL polymer in a mixture of DMF solvent and acetone in the ratio of 80:20 [38] and stirred continuously while adding an active substance of Eu (III) metal ion. This synthesis method was successfully used to fabricate the printed surface of NF with Eu^{3+} metal ions leaving voids in the PVDF/RTIL. It is used for selective sensing and recovery of Eu^{3+} ions during sewage treatment. Specifically, after the extraction or removal of the active substance Eu (III), at the end of the synthesis process, EGDMA

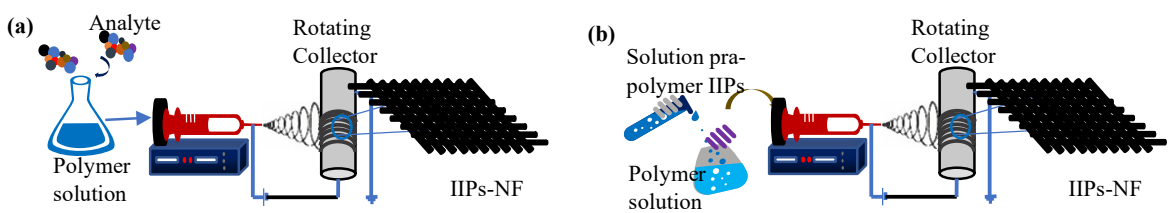

Fig. 3. Illustration of IIPs-NF synthesis method using electrospinning technology (a). Molecular imprinting during electrospinning, (b). Imprinted polymer Layer Formation onto Electrospinning.

solvent was added as a crosslinking agent to enhance the characteristics of the imprinted polymer. A similar approach was also adopted for synthesizing IIPs-NF Th (VI) using chitosan/RTIL solution NF. Chitosan amalgamation solution (3 %), PVA (8 %), thorium nitrate (0.01 wt. %) and RTIL (3 wt. %) were mixed in a syringe for electrospinning synthesis under a high voltage of 15 kV. The addition of PVA proves that the fibre is able to maintain extensional viscosity, then 2 % glutaraldehyde crosslinker is added to complete the IIPs-NF. This differs from previous research because IIPs-NF was extracted at the end of the process using 0.1 M solution of H_2SO_4 [70].

COMBINING SOLUTION/IMPRINTED POLYMER LAYER FORMATION ONTO ELECTROSPINNING

This method firstly focuses on synthesizing the electrospinning NF material, after which the resulting fibre is polymerized by adding a mixture of active components to form templates and functional monomers. This is further preceded with the process of eliminating the active substance either through extraction or leaching. The weakness of this method lies in the polymerization of NF with monomers and active substances, which are difficult to achieve, including the printing of the porous types. Another method involves mixing two solutions, fibre polymer and the IIPs prepolymer, in an electrospinning syringe. Awokoya et al. prepared two solutions simultaneously, namely poly(ethylene terephthalate)/polyethyleneimine (PET/PEI) mixed with trifluoroacetic acid (TFA) and dichloromethane (DCM) in the ratio 2:8 (v/v). The fibre polymer solution is mixed with IIPs prepolymer, which already contains crosslinkers and active substances as templates, and then left overnight. The electrospinning process is further fabricated under a high voltage of 15 kV. The resulting IIPs-NF were extracted from a solution of MeOH and acetic acid (90:10) to eliminate the metal ion Ni(II) from the polymer body. This method successfully created IIPs-NF with better adsorption ability than the non-printing fibre. Based on this, Awokoya concluded that IIPs-NF produced with PET/PEI is suitable for the specific removal of nickel-5, 10, 15, 20-tetraphenyl porphine (NTPP) from fuel oil [64]. An illustration of this method is shown in Fig. 3(b).

SOLID-PHASE IMPRINTING STRATEGIES

The next method is the incorporation of NF with active substances through the exploitation of template covalent immobilization. This technique is carried out by mixing solvents and fibre polymers in the electrospinning syringe. At the same time, the active substance forming the template is immobilized in the collector, thereby triggering the spinning process. The resulting NF is polymerized directly with the active substance without cross-linking, as shown in Fig. 4. This allows increased accessibility of the binding site during application as well as the elimination of the active substances on NF. The choice of this solid-phase printing method also makes it possible to either maintain or eliminate the presence of the active substance. This technique is more developed due to its molecular applications than the ionic electrospinning imprinting process. However, this is due to the ease of combining the electrospinning method with molecules, eliminating templates and a high chance of reusing the solid phase [36]. This method successfully triggered the conjugation of PVP/silica with bovine serum albumin (BSA) or bovine haemoglobin (bHb) as

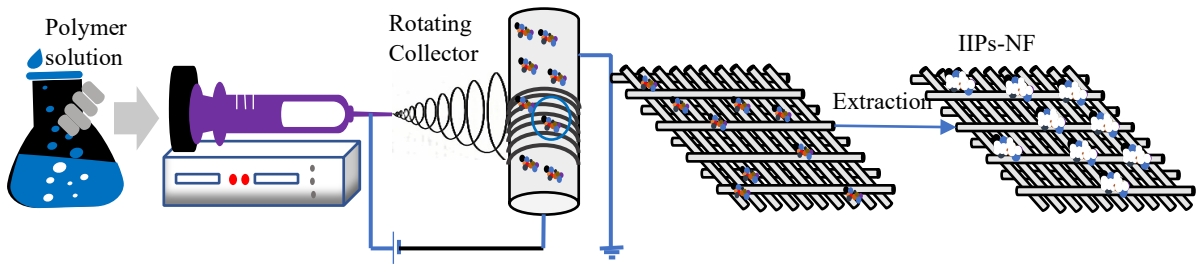

Fig. 4. Illustration of Methods solid-phase imprinting strategies for electrospinning IIPs-NF.

the target substance protein. The resulting NF had fairly good stability with an adjustable porosity level after the solid phase removal. In accordance with the advantages above and conveniences, further development of this method potentially leads to the optimization of IIPs-NF materials in the future.

DISPERSION/CONJUGATION IMPRINTED POLYMER INTO/ONTO ELECTROSPUN NANOFIBERS

This is one of the methods commonly adopted by preliminary research for synthesizing molecular-based electrospinning (MIP) and IIPs-NF. It is more advantageous than the previous method because it combines two different materials, IIPs and NF. This technique separates the process parameters of the two material technologies, making them easily adjustable to achieve the desired final architecture with effective recognition performance. The procedure is carried out by synthesizing IIPs and NF separately, as shown in Fig. 5. Incidentally, IIPs are synthesized with a mixture of polymers such as monomers, crosslinkers, and active substances to produce nano or microparticles. On the other hand, solvents and polymers were prepared for the electrospinning process. There are two ways of combining these materials, first (Fig. 5(a)) is combining the resulting nanoparticles dispersed into a polymer solution, followed by an electrospinning process to produce fibrous IIPs-NF. The second method is shown in Fig. 5(b), which involves the synthesis of electrospinning NF, and then the resulting ones are conjugated with IIPs nanoparticles. This technique utilizes two different advanced materials, IIPs and NF, while maintaining their respective characteristics and synthesis methods.

An example of the use of this method is cited in the research carried out by Rammika et al. (2011), where IIPs particles obtained through precipitation and mini-emulsion polymerization approaches were suspended with 10 m dimethyl formamide (DMF) and 200 mg polysulphone (PSU), and the solution was stirred for three hours. The resulting solution is further electrospinning at a high voltage of 15 kV. The fibre obtained is stored in a desiccator to evaporate the remaining solvent. The adsorption process is carried out at the end using an HCl solution to eliminate Ni (II) metal ions [63]. Hassanzadeh et al. successfully developed the most recent method of producing NF IIPs for the adsorption of Cr (VI) metal ions by preparing

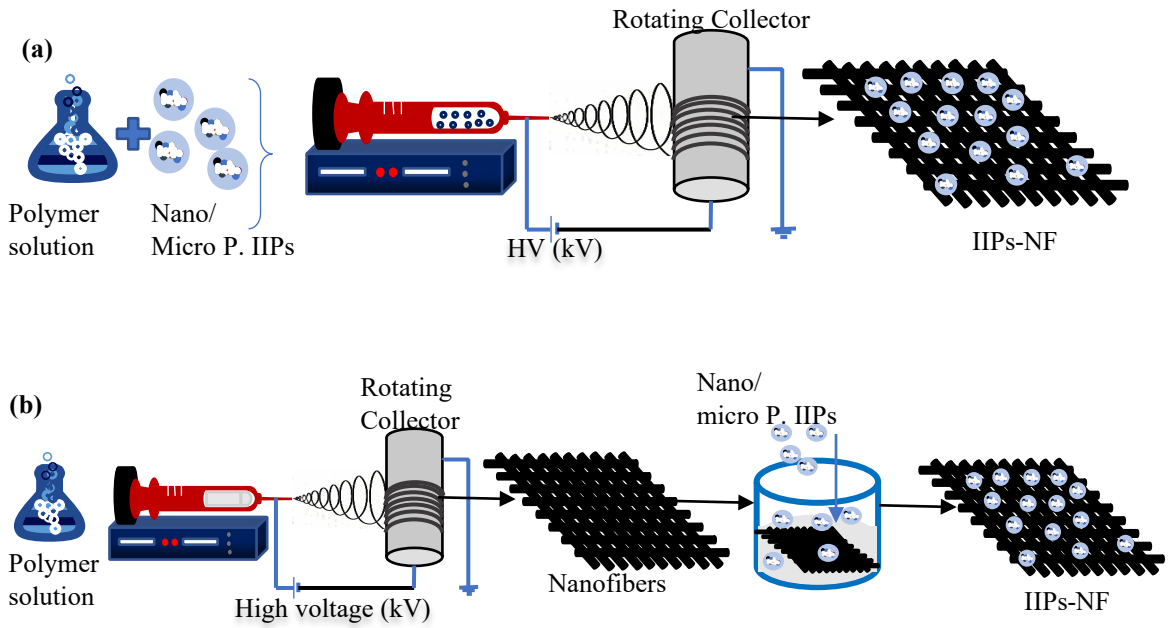

Fig. 5. The main approach of electrospinning technology in producing imprinted polymers NF (a). A polymer solution of NF dispersed with nano/microparticles of IIPs, or (b). Electrospinning NF are conjugated with micro/nanoparticles through chemical reactions.

IIPs particles and fibres separately. First, the solid IIPs were synthesized by free radical polymerization; the resulting particles were washed using acetone to separate the unreacted mixture from the reaction. The NaOH solution eliminates the active substance Cr (VI), thereby forming a template on the particles. On the other hand, the porous NF matrix was prepared by dissolving PAN in a solution with deploy (methylmethacrylate) (PMMA) using an electrospinning device at a voltage of 17 kV. The resulting fibre was further functionalized with the addition of hydroxylamine hydrochloride and sodium carbonate at the end of the process. The PAN functionalized fibre was conjugated with IIPs particles for 12 hours, using a mixture of deionized water and ethanol (1:3 v/v) at 70^{o}C. This method is good at producing IIPs-NF with a maximum adsorption capacity.

IMPORTANT PARAMETERS OF ELECTROSPINNING PROCESS FOR SYNTHESIS OF IIPS-NF

Some important attributes that need to be considered in electrospinning tools are the physical parameters affecting the final fibre product obtained under continuous and uniform optimal conditions. Critical variables, such as viscosity and flow rate of polymer solution, and its molecular mass, high voltage, and nozzle-to-collector distance, need to be considered before producing adsorbent fibers [78]. In the NF fabrication process, electrospinning applies a high voltage to the polymer solution at the tip of the syringe. At a certain distance between the collector and the syringe, the surface tension of the droplets from the needle breaks due to the flowing electric field, which enables the polymer to move through it to the processed collector [79]. The high electrospinning voltage affects the increased spinnability of the polymer solution. A lower voltage affects the surface tension of the smaller polymer solution droplets. The insufficient voltage causes the needle tip to drip, producing bead NF. This is affected by an increase in the flow rate due to minimal and incomplete moisture from the needle fibre jet to the collector. The required flow rate and minimum value tend to be fixed to produce uniform beadles and NF. It should be noted that increasing the flow rate and voltage reduces the charge density, thereby causing the NF to coalesce before being deposited on the collector [80]. Table 4 shows several parameter values employed by previous research in synthesizing NF, later modified into IIPs-NF. These were also used to produce various final fibre diameters with different maximum capacity values for the adsorption target ion.

GENERAL CHARACTERIZATION INSTRUMENTATION OF IIPS-NF

In chemistry and physics, sample characterization is an in-depth research and analysis of polymer properties, including crystal particle size, surface morphology, thermal stability or instability, percentage adsorption of the functional groups, etc. However, characterization instruments that have been used in IIPs technology include scanning electron microscopy (SEM), Fourier transform Infrared spectroscopy (FT-IR), and X-ray diffractometry (XRD) [28]. Further analysis of IIPs-NF is distinguished by FAAS and TGA instrumentation. Some initially prepared samples are IIPs which have undergone an extraction process or elimination of the active substance from the pores, as shown in Fig. 6(a). Non imprinted Polymer (NIP) (Fig. 6(b)) is a sample synthesized with the same steps and procedures as IIPs, although without the use of template-forming active substances. These were followed by pure fibre polymer or NF, Non-Imprinted Polymers Nanofiber (NIPs-NF), and finally, the IIPs-NF, as shown in Figs. 6(c),(d),(e), respectively. Many samples are based on comparing the diverse characteristics and variations stated in previous research. Each of them was tested and analyzed to determine the target ion's respective properties and selective adsorption ability.

Fourier transform Infrared spectroscopy (FT-IR) is a physicochemical characterization tool used to analyze the correspondence between the wave numbers of each sample to determine the chemical bonds. Segundo et al. stated that functional group or percentage transmittance are used for the success of the chemical compounds' synthesis process [81]. Hassanzadeh et al. compared the FT-IR spectra of $K_2Cr_2O_7$, PANFM, FPANFM, IIPs and PANFM, which functioned as IIPs. The comparison analysis between PANFM and FPANFM showed that PANFM functionalization occurred correctly. All samples were similar to the functional groups formed, indicating the chemical compound's successful performance. The FT-IR IIPs spectrum shows the OeH

Table 4. Further research on the parameters of using electrospinning equipment in synthesizing IIPs-NF.

Materials	IIPs: Polymer	Methode	Parameters of elecrospun				Diameters (nm)	Ref.
			Flowrate (vol/time)	V (kV)	T (h)	D (cm)		
Ni (II)-DMG IIP	1:1 wt %	Bulk polymerization	2 μg·mℓ$^{-1}$	15	6	12	406-854	[63]
NTPP-imprinted composite nanofibers	3:1 wv %	MIP electrospun	20 mL min^{-1}	15	-	13	5.33- 9.21	[64]
Nanofiber electrospun Cd (II)	4:0.8 wv %	Imprinted electrospinning	0.6 mL h^{-1}	19	24	9.5	76.1-161.9	[65]
ion imprinted PAN–CS nanofiber	8:8 wv %	Functionalized electrospinning	1 μL min^{-1}	11.5	20	8	~70	[66]
NVMIN For Nickel	14 – 30 % w/v	MIT electrospun	-	15	5	13	-	[67]
Chitosan NF MIP	2.4:0.5 wv %	one-step electrospinning imprinted	-	20	24	10	90.3-220	[68]
IIP-functionalized-PANFM	1:3 vv	Imprinted electrospinning	0.7 mL h^{-1}	17	12	15	143–181	[69]
Imprinted chitosan/ RTIL nanofiber	3:0.01 wt	Imprinted electrospinning	0.5 mL h^{-1}	15	-	15	40	[70]
ion imprinted PVDF/ RTIL	0.01–0.1 wt %	Imprinted electrospinning	0.8 μL min^{-1}	13	1	15	250-700	[38]

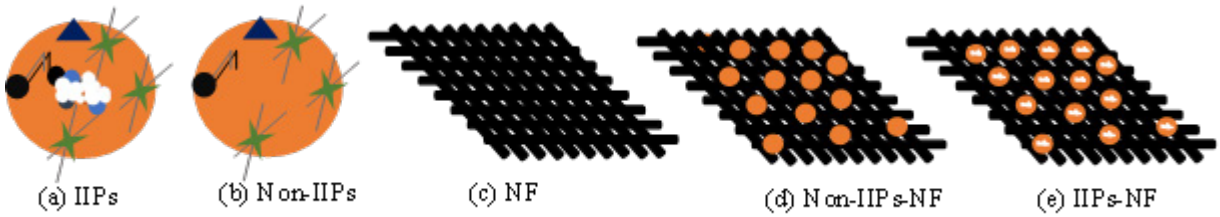

Fig. 6. Illustration of different samples (a) IIPs, (b) Non-IIPs, (c) NF, (d) Non-IIPs-NF, and (e) IIPs-NF.

vibrational band of the silanol group at a wave number of 3460 cm^{-1}. Besides, the low-intensity bands at 3118 cm^{-1}, 2955 cm^{-1} and 1479 cm^{-1} are associated with the C–H, CH_3, and CeN strains (imidazole ring). The absorption band at 1728 cm^{-1} was assigned to the carbonyl group of TMSPMA. A comparison of the $K_2Cr_2O_7$ and IIPs spectra showed no $K_2Cr_2O_7$ index peak, confirming the complete extraction of the Cr (VI) anion from the IIPs structure [63].

Scanning Electron Microscopy (SEM) characterization instrumentation is essential to determine the surface morphology structure of the polymer material samples [82]. Electrospinning fibres synthesized using TFA polymers for solution concentrations of less than 18 % emitted from low-viscosity solutions split into droplets due to the lower polymer amount and density required to form a stable beam [67]. Meanwhile, beads were observed in solution concentrations between 20 % and 24 % w/v. These completely disappeared, and finer and more uniform electrospun fibres were formed when the concentration was increased to 26 %, 28 % and 30 % w/v. It is believed that the combination of a relatively high viscous solution and the solvent's dielectric constant improves the fibre's morphology. SEM analysis provides information about the estimated number of pores or

templates formed after the leaching process by utilizing Matlab Poredize software or image J capabilities. Further applications are X-ray diffractometry (XRD) which confirms the crystallinity structure [83] or IIPs sample crystals after extracting and conjugating electrospun NF. It should be noted that XRD estimates the crystal size through the lattice plane of the resulting sample. This is attributed to the semi-crystalline nature of NF [66].

FURTHER RESEARCH ON MATERIAL ADSORPTION

Kinetic study

The kinetic analysis of the adsorption process aims to determine the type of physical or chemical reaction and the number of target ions adsorbed by the IIPs adsorbent, which was adjusted to the varying adsorption time. Quasi-first-order (Equation (1)) and quasi-second-order (Equation (2)) kinetic models were used for fitting to investigate the mechanism of the adsorption rate. Meanwhile, assuming the results are consistent with the first-order quasi-kinetic model, it indicates that the adsorption process is mainly physical. When it is in line with the quasi-second-order kinetic model, this implies the occurrence of chemical reactions in the adsorption process.

$$\log(q_e - q_t) = \log q_e - \left(\frac{kl}{2.303}\right)t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{1}{q_e} \quad (2)$$

In the equation di or QE (mgg^{-1}) is the equilibrium adsorption capacity, q_t adsorption capacity at time t (mg/g), Qm (mgg^{-1}) theoretical saturation adsorption capacity, t (min) adsorption time, $k1$ (min^{-1}) is a quasi-first-order kinetic rate constant, and k_2 ($g(mg\ min)^{-1}$) a quasi-second-order kinetic rate constant [84]. Based on the reviews of several research on IIPs-NF, the sorbent tends to fulfil the installation of a second-order pseudo model. This indicates that the IIPs material tends to undergo a chemical adsorption process. The Hg-PBCS sorbent developed by Hajri, et.al. was more effective than the use of Hg (II) ions as an adsorption target compared to the control unprinted sorbent (NI-PBCS) with a maximum capacity of 315 mgg^{-1} that correlated with relatively fast adsorption kinetics, namely the pseudo-second order (PSO) model [85].

Isotherm study

The basic physiochemical characteristics related to the adsorption of ions and imprinted polymer molecules was investigated through the research of adsorption isotherms. Operational design and modelling analysis of metal ion concentration in solution as a function of temperature for an adsorptive system was investigated by mathematical correlation and graphical depiction [70]. Furthermore, adsorption isotherm is a graphic notation used to determine the amount of adsorbate on the surface of the adsorbent under pressure at constant temperature [24]. It determines the capacity and degree of adsorption, which is stronger or weaker. The adsorption mechanism is described based on thermodynamic assumptions of physico-chemical parameters. In accordance with several research, the adsorption data tends to be modelled using differential equations, including the pseudo-second-order rate, the Langmuir, Freundlich, Temkin, and Dubinin - Radushkevich isotherm and three-parameter models, such as the Redlich - Peterson and Sips isotherms using the trial-and-run error method (R). The metal ion uptake IIPS and MIP usually correlate with the Langmuir or Freundlich equations. Langmuir's equation applies to the absorption process on a homogeneous surface. However, Freundlich's equation is valid for adsorption on heterogeneous surfaces. Previous research showed that the Langmuir and Freundlich equations represent different adsorption of heavy metal ions to IIPS and MIP. In most cases, one model best describes the adsorption process [3, 70, 86]. Table 5 shows the development of adsorption study with electrospun nanofiber.

Thermodynamic study

It is important to study the thermodynamics of adsorption to monitor the energetic changes during the entire process. Determining the free energies of enthalpy, entropy, and Gibbs is a key to understanding the amount of heat absorbed or released, the energy provided by the system and the randomness at the solid-liquid interface when absorption occurs. Investigating temperature changes in adsorption helps determine whether the process is endothermic or exothermic, spontaneous or non-spontaneous [87]. Considering the reviews on studying the thermodynamics of various organic substances adsorption onto various nano-adsorbents, its

Table 5. Review table of metal ion adsorption analysis results based on IIPs-NF.

Adsorbent	Ion metal	Q (mgg^{-1})	Optimal Conditions			Kinetic model	Iso-therm	Reg (time)	Ref.
			m (mg)	t (min)	PH				
Ni(II)-DMG IIP	Ni (II)	-	15	210 s	6	-	-	-	[63]
NTPP-imprinted composite NF		17.54	30	-	7	-	-	11	[64]
NF electrospun	Cd (II)	346.3	-	1440	6	PSO	LF	3	[65]
ion imprinted PAN– CS NF	Th (IV)	455.5	50	120	7	PSO and D-R	F	4	[66]
Chitosan NF MIP	Pb (II)	110.2	-	150	7	PSO	L	3	[68]
IIP-functionalized-PANFM	Cr (VI)	398	100	12	7	PSO	T	3	[69]
Imprinted chitosan/ RTIL NF	Th (IV)	325	-	120	7	PSO	L	7	[70]
ion imprinted PVDF/ RTIL	Eu (III)	22.37	-	180	7	PSO	F	5	[38]

L: Lang Freundlichmuir model, F: Freundlich, T: Temkin, PSO: pseusosecond-order model, D-R: Dubinin–Radushkevich

parameters were determined from the Gibbs equation. The Gibbs free energy depends on the equilibrium constant in equation (3) is stated as follows:

$$\Delta G^{\circ} = -RT \ln K_c \quad (3)$$

The relationship between Entropy and Enthalpy is stated in equation (4)

$$\ln K_c = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (4)$$

where K_C is the equilibrium constant and $K_C = \frac{q_e}{C_e}$, q_e is the adsorption capacity at equilibrium (mg/L), C_e is the equilibrium concentration (mg/L), T is the temperature, R is the universal gas, ΔH^0 and ΔS^0 are standard enthalpy and entropy, respectively. They were also determined from the slope and intercept of the *ln Kc* versus *1/T* plots resulting from the adsorption examination process at different temperatures. Positive enthalpy indicates the endothermic nature of the reaction process, while positive Gibbs free energy refers to the non-spontaneous procedure. All completed adsorption process is categorized into physisorption and chemisorption depending on the Gibbs free energy. The nature of the physisorption process is for $-20\ kJ/mol < \Delta G < 0$, and the chemisorption is for $-800\ kJ/mol < \Delta G < -40\ kJ/mol$. The value of enthalpy (ΔH), entropy (ΔS) and Gibbs energy (ΔG) is used to predict the adsorption properties [86].

CONCLUSIONS

The presence of harmful heavy metal ions, such as mercury (II), copper (II), lead (II), chromium (III), cadmium, zinc, arsenic (As), silver (Ag), chromium (Cr), iron (Fe) and platinum (Pt), is of enormous concern to chemists and physicists in terms of overcoming its negative effects on the environment and human health. One of the advanced materials developed rapidly is NF material with electrospinning technology. It has excellent properties and characteristics such as mass transfer and good adsorption capacity. To increase the selectivity and sensitivity of NF to metal ions, it is modified with porous materials in the form of IIPs. IIPs have pores of which the chemical properties and characteristics resemble metal targets due to the leaching process carried out after extraction. This enables the target metal ions to fill every material pore during the adsorption experiment.

Some of the challenges faced in the process of modifying NF and IIPs is the difficulty involved in eliminating active substances in the formation of templates which have the potential to reduce the adsorption ability of the material. This is overcome by adopting several major approaches to the synthesis process using electrospinning technology, such as Molecular Imprinting during Electrospinning, Imprinted polymer Layer Formation onto Electrospinning, Solid-Phase Imprinting Strategies, and Dispersion/ Conjugation imprinted polymer into/onto Electrospun

Nanofibers. Each method has its advantages and disadvantages, mainly stemming from the different processing parameters that characterize imprinted polymers and electrospinning.

The dispersion or conjugation method is easier to perform. It simply involves the combination of two different materials, IIPs and NF, to achieve the desired final architecture with efficient recognition performance. This method is carried out by synthesizing IIPs and NF separately and conjugating them in the final process. The combination of NF using electrospinning technology with IIPs porous materials maintains high stability values, reloading, responsiveness, large surface area and good adsorption capacity, as well as increased mechanical strength and biocompatibility. Therefore, this material has great potential and needs to be further developed. It commercializes new products for removing heavy metals from water. This research serves as reference material for future analyses in designing and developing IIPs-NF.

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