Agri JOURNAL WORLD
www.journalworlds.com
AGRI JOURNAL WORLD
VOLUME 4 ISSUE 2 FEBRUARY, 2024

ELECTROSPUN NANOFIBERS: NEW GENERATION MATERIALS FOR PESTICIDE DELIVERY AND DETECTION

Riya Kundu, Neethu Narayanan, V. S. Rana, N. A Shakil and Parshant Kaushik*

Division of Agricultural Chemicals, ICAR-Indian Agricultural Research Institute, New Delhi-110012

*Corresponding author email: parshantagrico@gmail.com

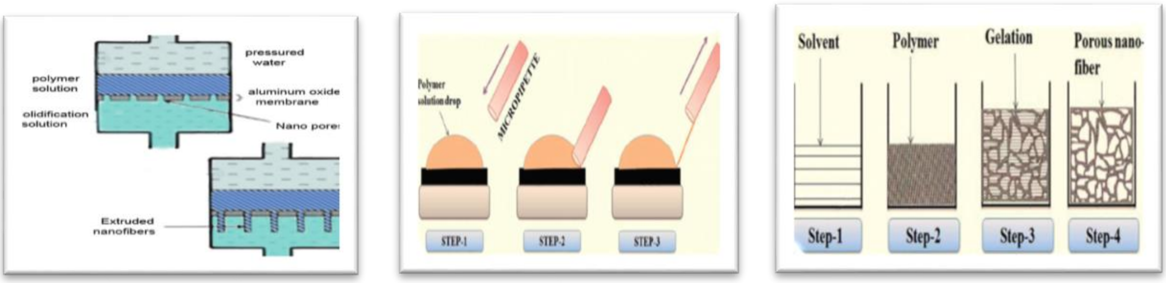
ABSTRACT

Electrospinning, or E-spin, is a unique technique generating nanofibers from polymers and metal oxides through a needle propelled by a peristaltic pump and high-power supply. Electrostatic interactions result in fiber formation, with applications spanning filtration, tissue engineering, wound healing, and energy storage. Electrospun nanofibers function as cost-effective electrocatalysts for simultaneous oxygen and hydrogen generation. In agriculture, they facilitate smart pesticide delivery and rapid detection. A novel nano/micro-structured pesticide detection card, integrating electrospinning and hydrophilic modification, enhances pesticide detection and broadens applications. Eco-friendly electrospinning of cellulose diacetate nanofibers on seeds addresses environmental concerns, exemplifying the versatility of this method in developing effective pesticide delivery systems and detection devices.

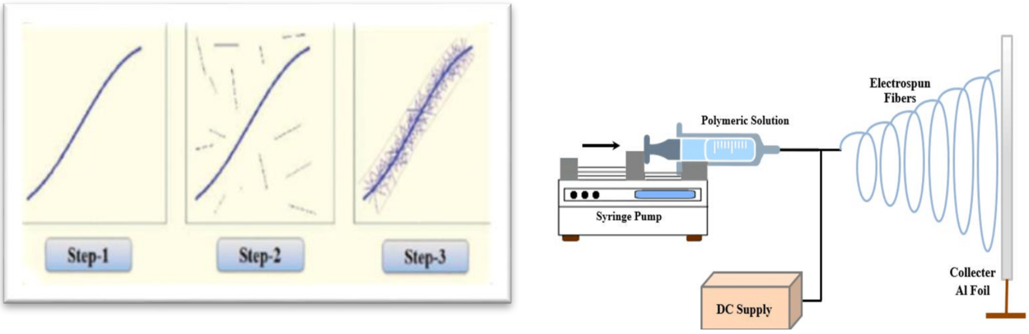
INTRODUCTION

Nanotechnology is highly integrated with our society and will have a greater impact in the coming decades as compared to other technologies. It involves manipulating matter at the atomic scale, where a nanometer represents one billionth of a meter (10^{-9}). By combining the prefix "nano" and "technology," it encompasses the study of tools, machines, and techniques used to understand and control materials at the nanoscale. Essentially, nanotechnology involves the exploration and application of knowledge at the atomic and molecular levels to address challenges and perform specific functions. Nanotechnology finds diverse applications across agriculture, sensors, manufacturing, medicine, defence, electronics and energy. In the agricultural sector, it is employed in development of biosensors, nano pesticides, antimicrobial nanoparticles, agricultural diagnostics, quality control of products and the exploration of plant physiology.

Various methods are available for synthesis of nanofibers (Fig. 1), including template synthesis, phase separation, self-assembly and electrospinning. In template synthesis, a metal oxide template with nanoscale-diameter pores undergoes water pressure application on one side, leading to the extrusion of polymer through a porous membrane. Upon contact with a solidifying solution, nanofibers are formed. Drawing involves introducing a micropipette to a polymer droplet, and pulling a single-strand nanofiber is formed. Phase separation entails preparing a homogeneous polymer solution that tends to separate into polymer-rich and polymer-lean phases, forming a matrix and pores, respectively, after gelation. Self-assembly arranges small molecules concentrically, allowing bond formation and extension in the plain normal to give the longitudinal axis of the nanofiber. Electrospinning, the simplest and most cost-effective method, involves spinning polymeric solutions or melts in a high DC electric field at elevated temperatures, producing high-surface-area submicron and nanosized fibers with exceptional physical properties. These fibers, known as electrospun nanofibers, are obtained from the majority of synthetic and naturally occurring polymers dissolved in suitable solvents.



(A) Template synthesis (B) Drawing (C) Phase separation



(D) Self –assembly (E) Electrospinning

Fig. 1: Different methods for synthesis of nanofibers

HISTORICAL BACKGROUND OF ELECTROSPINNING TECHNIQUE

The electrospray technique, which originated in the late 1890s, underwent a transformation into electrospinning around the year 1900. To provide a detailed historical overview of this innovative method, a comprehensive timeline of electrospinning development is presented in Table 1. It is noteworthy that research publications post-2010 predominantly focus on the applications of electrospun fibers in various fields, leveraging functionalized polymers, fibers incorporating nanoparticles, and composite nanofibers with metal oxides.

Table 1: Timeline of electrospinning development

S. No.	Year	Nature of advancement
1	1900,1902	Cooley and Moeton patented the process of E-spin
2	1914	Jet ejection at the tip of the metal capillary by John Zeleny
3	1934	Formhals patented the invention of E-spin instruement
4	1936	Patent for air- blast fibers formation from melt rather than solution by Norton
5	1938,1940	Others patents by Formhals
6	1950-1959	Factory production of nanofibers as filter for gas mask application
7	1960	Jet formation study and E- spin fibers as filtration material
8	1964	Formation of Taylor cone
9	1971	Apparatus to spin acrylic micrfibers by Baumgarten
10	1995	Doshi Reneker reported the fibers diameter decrease with increase in distance from collector to needle tip and Taylor cone
11	1996-2001	Publication related to working parameters such as, solution, ambient and instruemental parameters
12	2001-2005	Synthesis and characterisation of E- spin nanofibers
13	2006- till date	During these period most of the papers were put forward on the applications of E-spun nanofibers as sensors, tissue engineering materials, protection against chemical warfare stimulants, filters, scaffolds, batteries and catalyst

WORKING, INSTRUMENTATION AND OPERATIONAL PARAMETERS

WORKING:

The fundamental principle underlying fiber-forming technology is rooted in the "electrostatic attraction" of charges. In this process, a syringe contains a polymer solution with its inherent surface tension, and the solution is charged externally by applying high voltage from a power supply at the needle tip. A collector with opposite charges is positioned at a distance (around 10 cm) to gather the discharged fibers. When subjected to high voltage (10–30 kV), the solution within the syringe is ejected, overcoming surface tension and forming a cone-shaped structure known as a "Taylor cone" where drops are ejected from the tip. The jet extends under the influence of the electrical field, allowing solvent evaporation, resulting in the formation of solidified polymer fibers forming an interconnected web on the collector.

INSTRUMENTATION

The E-spin instrument comprises three main components: the primary influencer is the high voltage power supply, followed by the syringe and needle assembly (collectively known as the spinneret in the needleless type), and the collector. They are categorized based on orientation into horizontal and vertical types (Fig.2). In the horizontal configuration, the effective force involves the charged force generated by applied voltage and the opposite attractive force in the collector, which pulls the fibers. Conversely, in the vertical configuration, two forces draw the fibers – the collector charge and the gravitational pull – resulting in narrower fibers with a minimum diameter. Depending on the number of nozzles, such as single nozzle E-spin, easily soluble solutions can be spun into fibers. Multi-nozzle configurations offer an advantage over single nozzles due to increased fiber production. Based on the nature and number of axial units, such as mono-axial, co-axial, and multi-axial E-spin, monoaxial types have only one syringe and needle, co-axial types involve two syringes and a single needle, with solutions of different polymers/precursors that are likely immiscible.

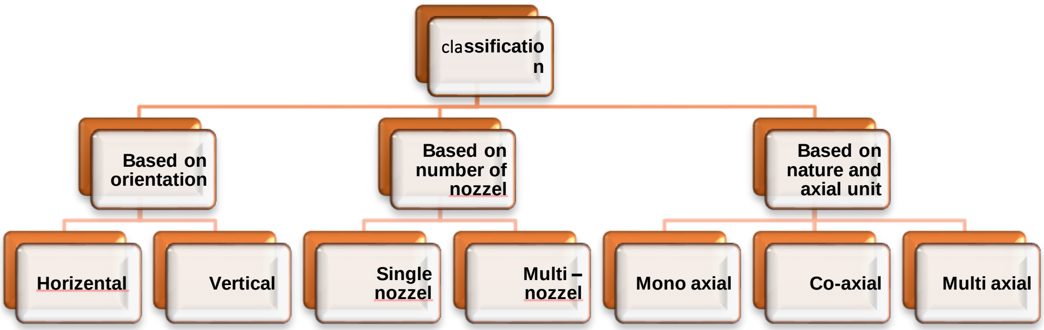


Fig.2: Different types of E-spin instruments

OPERATIONAL PARAMETERS

Solution parameters encompass factors such as concentration, molecular weight, viscosity, surface tension and conductivity/surface charge density. Processing parameters involve applied voltage, feed rate/flow rate, type of collector and tip-to-collector distance. Ambient parameters include humidity and temperature (Fig. 3).

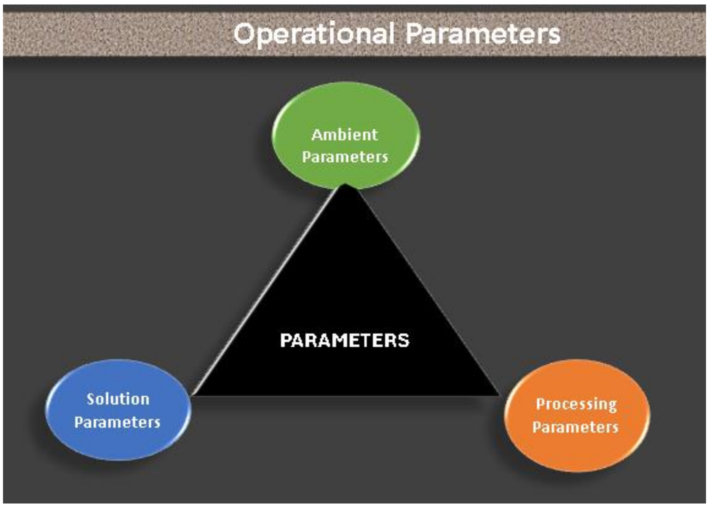


Fig. 3: Different operational parameters for E-spinning

CHARACTERISATION OF ELECTROSPUN NANOFIBERS

Characterizing electrospun fibers poses a considerable challenge due to the rarity of obtaining single fibers. The characterization of these fibers falls into two main categories: physical and chemical. Physical characterization focuses on the structure, morphology, and internal nanofiber structure, which collectively determine the physical and mechanical properties. Geometrical characterization involves parameters like diameter and size distribution, orientation, as well as morphology, encompassing surface roughness and cross-section. Key techniques for classifying fiber structure and morphology include scanning electron microscopy (SEM), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), and atomic force microscopy (AFM). SEM is primarily employed to determine fiber diameter and morphology but requires a conductive sample. However, SEM faces limitations in resolution at extreme magnifications. In contrast, TEM is effective for determining the diameters of extremely small fibers (less than 300 nm). AFM is another useful technique for detecting fiber diameter and providing a detailed examination of morphology and surface characteristics. Additional techniques, such as X-ray diffraction (wide-angle (WAXS) and small-angle (SAXS)) and differential scanning calorimetry (DSC), are considered to assess the degree of crystallinity in the fibers. Surface chemistry is further elucidated using X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR). While this chapter primarily focuses on the physical characterization of electrospun fibers, surface chemical properties can also be explored through molecular structure characterization using Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR).

APPLICATION OF ELECTROSPUN NANOFIBERS

E-spun nanofibers are characterised with large surface area to volume ratio, a beneficial property for application as scaffolds, sensors, filters, membranes, batteries, protective clothing, wound dressing and catalyst (Fig. 4). In the early stages, applications in biomedical and tissue engineering field enlightened research on nanofibers. Over the years, applications were also extended to many fields based on the surface and chemical properties of nanofibers. Few applications of NFs prepared by E-spin technique.

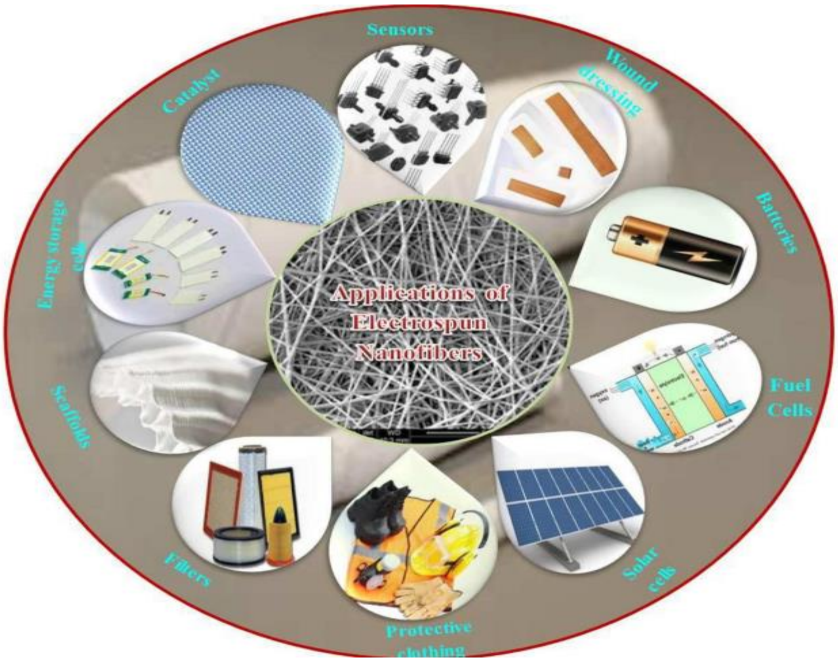


Fig. 4: Various applications of E-spun nanofiers

APPLICATION IN AGRICULTURE

a) SMART DELIVERY OF PESTICIDE BIOCONTROL AGENTS, PHEROMONES

Gao et. al., 2021 employed electrospun nanofibers to develop Thiram/hydroxypropyl-β-cyclodextrin inclusion complex (thiram/HPβCD-ICNF), a fast-dissolving drug delivery system. The thiram/HPβCD-IC-NF exhibited a fiber diameter ranging from 30 to 650 nm, with an average diameter of 270 ± 133 nm. SEM images depicted the electrospinning of thiram and HPβCD into consistent nanofibers without bead formations. The thiram/HPβCD-IC-NF (EC_{50} =0.403 ± 0.007 μg/mL) showed higher antifungal activity as compared to untreated thiram (EC_{50}=0.532 ± 0.013 μg/mL) against *Gibberella sp.*

Electrospinning with cellulose diacetate polymer (CDA) emerges as an efficient method for seed coating, facilitating the localized delivery of active ingredients. Electrospun cellulose diacetate (CDA) nanofibers incorporated with abamectin (Abm) and fluopyram (Flp) were used for coatings soyabean seeds. The SEM analysis showed that diameters for nanofibers incorporated with Abm and Flp, were 242 nm and 129 nm respectively. The release studies of abamectin and fluopyram from nanofibers revealed a slow and sustained release. There was no adverse effect on seed germination irrespective of coating thickness and uniformity. Functional performance, tested using fluopyram-loaded nanofibers in an *in vitro* fungal assay against the plant pathogen *Alternaria lineariae*, consistently inhibits fungal growth. The sustained release profile taken together with moisture stability suggests that nanofibrous seed coatings have a strong potential as an alternative platform to control plant pathogens such as nematodes and fungi (Barbara et. al, 2019).

Trimedlure, a pheromone of Medfly *Ceratitis capitata*, was incorporated in various electrospun nanofibres *viz.* ethyl cellulose, PCL, polyethylene glycol (PEG)-PCL and polyvinyl acetate–polyvinyl pyrrolidone (PVP) in the concentration range of 0.02–10% w/v. The field evaluation studies showed that the insect trapping was significantly higher in case of encapsulated pheromones (Bisotto-de-Oliveira et al. 2014)

b) DETECTION OF PESTICIDE RESIDUE

Feng et al, 2021 used novel electrospun fibers for development of nano/micro-structured pesticide detection card. The rapid detection card has reduced the detectable concentrations for carbofuran, malathion, and trichlorfon by 5-fold, 2-fold, and 1.5-fold respectively, as compared to the national standard values. This detection card has good storage stability and a low minimum detectable concentration, rapid detection, easy to operate as compared to the conventional detection techniques.

c) DNA EXTRACTION IN AGRICULTURE RESEARCH STUDIES

The traditional DNA extraction techniques used in agricultural research are time-consuming and tedious. The electro spun magnetic nanofibers helps in easy separation of magnetic DNA from other biomolecules (Nam et al, 2009). The electro spun nanofibers having positively charged membrane were used in extraction of DNA which is negatively charged biomolecule due to its phosphate groups. These electrospun nanofibres can be reused for DNA extraction, the extraction capacity was found 46% even after five cycles (Demirci et. al, 2014).

d) PREPARATION OF PROTECTIVE CLOTHING FOR FARM WORKERS

Electro spun nanofibrous membranes have shown immense potential for smart protective clothing. The new generation electrospun nanofibrous membranes based protective fabrics not only absorb or block toxic chemical but also detoxify them to reduce the risk of secondary contamination. The high specific surface areas of electrospun nanofibrous membranes help in attachment of functional compounds resulting in detoxification. Liquid pesticide entry was significantly reduced by fabrics laminated with electrospun polypropylene fiber layers which also have better water vapor permeability (Lee et al. 2006). Paraoxon, an organophosphate pesticide can easily be decomposed by protective clothing made of electrospun fibers having reactive species, (3-carboxy-4-iodosobenzyl) oxy-ˇ-cyclodextrin (Ramaseshan et al, 2006). The electrospun zinc titanate nanofibers were found reactive sorbents for detoxifying nerve and mustard agent simulant (Ramaseshan et al 2007).

CHALLENGES

The electro spun techniques has following disadvantages:

- *Requires large solvent:* Large amount of solvent requirement, solution electrospinning is predominately use for fabricating nanofibers which resulting in both economic and environmental concern.
- *Clogging of nozzle:* It is major challenge that limit e-spin technology for industrial production.
- *Reproducibility:* It is still difficult to produce uniform fiber reproducibly and at mass production level, while ensuring the desired size, morphology, structure and other properties.

FUTURE PERSPECTIVES

Optimization of simulation models regarding the electrospinning process by taking into consideration all the properties of a liquid for electrospinning and all the processing parameters to better elucidate the phenomenology of the electrified jets. There is a critical need to develop methods based on “green “solvents or even solvent-free systems. Further, it still remains a challenging task to generate nanofibers with diameters below 10 nm by electrospinning no matter which method is used. In this regard, computational modeling should offer insightful guidance for effectively downsizing the diameter of electrospun fibers.

REFERENCES

Bisotto-de-Oliveira, R., De Jorge, B. C., Roggia, I., Sant'Ana, J., & Pereira, C. N. (2014). Nanofibers as a vehicle for the synthetic attactant trimedlure to be used for ceratitis capitata wied:(Díptera, tethritidae) capture. *Journal of Research Updates in Polymer Science*, *3*(1), 40.

Chaudhary, K., & Kandasubramanian, B. (2022). Self-healing nanofibers for engineering applications. *Industrial & Engineering Chemistry Research*, *61*(11), 3789-3816.

Demirci, S., Celebioglu, A., & Uyar, T. (2014). Surface modification of electrospun cellulose acetate nanofibers via RAFT polymerization for DNA adsorption. *Carbohydrate polymers*, *113*, 200-207.

Fang, J., Niu, H., Lin, T., & Wang, X. (2008). Applications of electrospun nanofibers. *Chinese science bulletin*, *53*, 2265-2286.

Farias, B. V., Pirzada, T., Mathew, R., Sit, T. L., Opperman, C., & Khan, S. A. (2019). Electrospun polymer nanofibers as seed coatings for crop protection. *ACS Sustainable Chemistry & Engineering*, *7*(24), 19848-19856.

Feng, K., Zhai, M. Y., Wei, Y. S., Zong, M. H., Wu, H., & Han, S. Y. (2021). Fabrication of nano/micro-structured electrospun detection card for the detection of pesticide residues. *Foods*, *10*(4), 889.

Gao, S., Liu, Y., Jiang, J., Li, X., Ye, F., Fu, Y., & Zhao, L. (2021). Thiram/hydroxypropyl-β-cyclodextrin inclusion complex electrospun nanofibers for a fast-dissolving water-based drug delivery system. *Colloids and Surfaces B: Biointerfaces*, *201*, 111625.

Lee, S., & Kay Obendorf, S. (2006). Developing protective textile materials as barriers to liquid penetration using melt-electrospinning. *Journal of Applied Polymer Science*, *102*(4), 3430-3437.

Nam, J. H., Joo, Y. H., Lee, J. H., Chang, J. H., Cho, J. H., Chun, M. P., & Kim, B. I. (2009). Preparation of NiZn-ferrite nanofibers by electrospinning for DNA separation. *Journal of Magnetism and Magnetic Materials*, *321*(10), 1389-1392.

Noruzi, M. (2016). Electrospun nanofibres in agriculture and the food industry: a review. *Journal of the Science of Food and Agriculture*, *96*(14), 4663-4678.

Ramaseshan, R., & Ramakrishna, S. (2007). Zinc titanate nanofibers for the detoxification of chemical warfare simulants. *Journal of the American Ceramic Society*, *90*(6), 1836-1842.

Ramaseshan, R., Sundarrajan, S., Liu, Y., Barhate, R. S., Lala, N. L., & Ramakrishna, S. (2006). Functionalized polymer nanofibre membranes for protection from chemical warfare stimulants. *Nanotechnology*, *17*(12), 2947.

Raza, A., Li, Y., Sheng, J., Yu, J., & Ding, B. (2014). Protective clothing based on electrospun nanofibrous membranes. *Electrospun nanofibers for energy and environmental applications*, 355-369.

Thenmozhi, S., Dharmaraj, N., Kadirvelu, K., & Kim, H. Y. (2017). Electrospun nanofibers: New generation materials for advanced applications. *Materials Science and Engineering: B*, *217*, 36-48.

Zhao, Y., Zhang, J., Li, K., Ao, Z., Wang, C., Liu, H., ... & Wang, G. (2016). Electrospun cobalt embedded porous nitrogen doped carbon nanofibers as an efficient catalyst for water splitting. *Journal of Materials Chemistry A*, *4*(33), 12818-12824.

How to Cite:

Kundu, R., Narayanan, N. Rana, V. S., Shakil, A. N. and Kaushik, P. (2024). Electrospun nanofibers: new generation materials for pesticide delivery and detection. Leaves and Dew Publication, New Delhi 110059. *Agri Journal World*, 4(2):7-16.

*********XXXXX**********